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Application of Thermoeconomics to Assess and Improve the Efficiency of Bioenergy Production Plants and Land-To-Tank Cycles

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Tesis Doctoral

APPLICATION OF THERMOECONOMICS TO ASSESS AND IMPROVE THE EFFICIENCY OF BIOENERGY PRODUCTION PLANTS AND LAND-TO-TANK CYCLES

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Application of Thermoeconomics to Assess and Improve the Efficiency of Bioenergy Production Plants and Land-To-Tank Cycles

Emilio Font de Mora Rullán

Directed by:
Antonio Valero Capilla, Ph.D.
César Torres Cuadra, Ph.D.

To my beloved wife

There are in fact two things, science and opinion;
the former begets knowledge, the latter ignorance

Hippocrates
Greek physician (460 BC - 377 BC)

Biofuels are neither a panacea nor a pariah but like all technologies
they represent both opportunities and challenges

Achim Steiner
United Nations Under-Secretary General and
Executive Director of the UN Environment Programme

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Abstract

The humankind is facing a two-sided climate and energy dilemma. Both issues are strongly related to the consumption of oil. In order to solve this problem Nations are putting forward policy instruments to reduce the consumption of fossil fuels, among them the promotion of the production and consumption of renewable energies.

This is of special importance in the transport sector where the dependence from fossil fuels is more significant. The transport sector is dependent on oil in around 98% in the EU and is the only economic sector which emissions are set to increase in the future.

Bioenergy is the most used renewable energy source nowadays and its role in the future is set to increase. In the EU, bioenergy currently provides more than 2/3 of the renewable energy, and it is expected to account more than half of the EU's renewable energy in 2020 and about 11 % of the total EU energy consumption.

However, unlike other renewable energy sources, generating net greenhouse gas savings from bioenergy depends on the production processes. Inefficient bioenergy processes may produce more greenhouse gases than the fossil fuel counterpart that bioenergy pretends to substitute. The efficiency of bioenergy processes both at the plant scale and the life cycle needs to be optimized in order to ensure that the greenhouse gas emissions are minimized.

Biodiesel, as a natural substitute to diesel fuel, is one of the most important transport fuels especially in Europe. However, inefficient processes can lead to the consumption of high quantities of fossil fuel and the emission of high quantities of greenhouse gases. This is especially the case of biodiesel produced from energy crops.

Ensuring the sustainability of biofuels for transport is a mandatory requisite for the EU Member States. The EU Renewable Energy Sources Directive focuses on the reduction of greenhouse gas emissions and the protection of high biodiversity and carbon stock lands. An amendment to the policy framework proposes an increase in the greenhouse gas emission levels to 60% compared to fossil fuels. If this framework is finally adopted, biodiesel from certain energy crops could be excluded from use in the EU if the production processes are not improved, according to the European Commission assessment. On the other hand the current framework does not consider the consumption of non-renewable resources.

This PhD presents a methodology based on thermoeconomics to analyse the additional improvements that can be introduced in order to maintain the biodiesel sector in Europe. Thermoeconomics input-output analysis integrates Second Law and economic input-output analysis together with material flows and life cycle analysis to provide a rigorous evaluation procedure for energy saving, sustainability and renewability of bioenergy process. Using exergy as quantitative and qualitative measure, it provides the tools to analyze the detailed processes to identify inefficiencies and propose solutions like process integration, substitution, components' efficiency improvements and flows recirculation. This is applied to a specific transesterification plant and to the land-to-tank cycles of rapeseed, sunflower, palm, soybean and used cooking oil based biodiesels.

Three concepts are defined: the renewability ratio that measures the portion of renewable exergy used respect the total exergy consumption; the exergy rate of investment (ExROI) that evaluates the amount of biodiesel exergy obtained for each unit of non-renewable resources and the exergoecologic factor that evaluates the ratio between the exergy and exergoecologic cost, and evaluate the capability of improvement of the direct processes of the land-to-tank cycles. In addition it presents a sensitivity assessment method to enable understanding the effect on the results of the introduction of changes in the process.

This PhD shows that biodiesel life cycles can be improved by introducing several changes in the process, up to obtaining ExROI values of around 25 and achieving renewability ratios of around 98%; i.e. for one unit of non-renewable sources invested in the process more than 25 units of biodiesel are obtained and only 2% of the exergy costs are of non-renewable origin. With this, biodiesel can be around five times more sustainable than fossil diesel, from the viewpoint of non-renewable resources consumption.

It also demonstrates that with such measures, biodiesel can drive to higher greenhouse gas emission reductions than the proposed threshold and even to cycles that reduce the $CO_{2\text{-eq}}$ in more than 100% compared to diesel fuel. All of this with socio-economic benefits and reduction of direct land use changes.

Although the proposed methodology does not help to assess other impacts that bioenergy may have, such as indirect land use changes, food availability and increased pressure on available arable land, these aspects are discussed trying to provide a neutral vision on such controversial issues.

Resumen

La humanidad se encuentra en una doble encrucijada energética y climática. Ambos aspectos están íntimamente relacionados con el consumo de petróleo. Para solucionar el problema diferentes países están implementando políticas de reducción del consumo de combustibles fósiles, entre ellas la producción y consumo de energías renovables.

El problema se ve acentuado en el sector del transporte, dependiente de los combustibles fósiles en mayor medida. El transporte depende del petróleo aproximadamente en un 98% en la Unión Europea y es el único sector económico cuyas previsiones estiman un continuo incremento en las emisiones de gas de efecto invernadero.

La bioenergía es la fuente de energía renovable más utilizada en la actualidad y su relevancia en el futuro se prevé aún mayor. La bioenergía actualmente constituye más de dos tercios de la energía renovable de la Unión Europea y se espera que en 2020 acapare el 50% del consumo renovable y alrededor del 11% del consumo total de energía de los Estados miembros.

Sin embargo, a diferencia de otras fuentes de energía, generar ahorros netos de gases de efecto invernadero con la bioenergía depende del proceso de producción. Procesos ineficientes pueden producir más gases de efecto invernadero que el combustible fósil que pretenden sustituir. La eficiencia en los procesos de producción, tanto a nivel de planta como en el ciclo de vida, necesita ser optimizada para reducir las emisiones al máximo.

El biodiesel, sustituto natural del diesel fósil, es uno de los combustibles alternativos para el transporte más importantes, especialmente en Europa. No obstante, procesos ineficientes pueden conllevar el consumo de grandes cantidades de combustibles fósiles y emisiones elevadas de gases de efecto invernadero. Este puede ser el caso, especialmente, del biodiesel producido a partir de cultivos energéticos.

Asegurar la sostenibilidad de los biocarburantes es un requisito obligatorio para los Estados miembros de la UE. La Directiva europea de energías renovables centra la sostenibilidad en la reducción de las emisiones de gases de efecto invernadero y en la protección de la biodiversidad y las tierras de alto stock en carbono. Una enmienda a la Directiva propuesta por la Comisión Europea plantea incrementar el nivel obligatorio de reducción de emisiones al 60% comparado con los combustibles fósiles. Si esta enmienda se aprueba, el biodiesel de ciertos cultivos energéticos podría verse excluido en la UE si los procesos de producción no mejoran, tal como refleja la evaluación de impacto realizada por la Comisión Europea. Por otra parte, el marco legislativo actual no tiene en cuenta el consumo de recursos no renovables.

La presente tesis doctoral presenta una metodología basada en la termoeconomía para analizar posibles mejoras adicionales a introducir en los procesos de producción, para mantener el sector del biodiesel en Europa. El análisis input-output termoeconómico integra el segundo principio de la termodinámica con el análisis input-output económico, así como el análisis de flujos de materia y de ciclo de vida para proporcionar un procedimiento de evaluación riguroso enfocado en el ahorro energético, la sostenibilidad y la renovabilidad de procesos bioenergéticos. Mediante el uso de exergía como medida cuantitativa y cualitativa, este procedimiento constituye una herramienta útil para analizar en detalle los procesos de producción, identificar ineficiencias y proponer soluciones tales como la integración de procesos, la sustitución de materiales, la mejora de la eficiencia de componentes y la recirculación de flujos. Esta tesis doctoral aplica dicha metodología a una planta de transesterificacion de biodiesel y al ciclo de vida del biodiesel producido a partir de colza, girasol, palma, soja y aceites usados.

En la tesis doctoral se definen tres conceptos: el ratio de renovabilidad, que mide la proporción de exergía renovable usada en el proceso con respecto al consumo de exergía total; la tasa de retorno exergético (Exergy return on investment, ExROI) que evalúa la cantidad de exergía contenida en el biodiesel por unidad de recursos no renovables consumidos, y el factor exergoecológico, que mide el ratio entre el coste exergético directo y el coste exergoecológico y permite evaluar la capacidad de mejora de los procesos directos en los ciclos de producción. Además, se presenta una metodología de análisis de sensibilidad para permitir comprender el efecto en los resultados de la introducción de cambios en el proceso.

Esta tesis doctoral muestra que el ciclo de vida del biodiesel puede ser mejorado mediante la introducción de cambios en el proceso, de forma que se obtienen valores de ExROI de alrededor del 25 y ratios de renovabilidad de cerca del 98%, es decir, por cada unidad de exergía no renovable consumida en el proceso se obtienen 25 unidades de biodiesel y tan sólo un 2% de los costes exergéticos son de origen no renovable. Con esto, el biodiesel puede ser cinco veces más sostenible que el diésel fósil, desde el punto de vista del consumo de recursos no renovables.

La tesis también demuestra que con la aplicación de dichas medidas, el biodiesel puede reducir las emisiones de gases de efecto invernadero más allá del límite del 60% propuesto en la enmienda de la Directiva y que puede incluso reducir las emisiones por encima del 100% comparado con el diésel fósil. Todo ello con beneficios socio-económicos y reducción de cambios directos en el uso de tierras.

Aunque la metodología propuesta no sirve para evaluar otros impactos potenciales de la bioenergía, tales como los cambios indirectos en el uso de tierras, la disponibilidad de alimentos para consumo humano y el impacto en el uso de tierras arables, estos aspectos son también analizados, intentando aportar una visión ecuánime en estos temas tan controvertidos.

Contents

Chapter 1

Starting point, objectives and scope

The aim of this introductory chapter is to provide an overview of the reasons for producing this Ph.D. and to point out the main objectives and scope of the study.

This work is focused on the application of thermoeconomics to bioenergy production in two different frameworks. The first one applies the exergy cost theory to an actual production plant in a detailed scale to calculate the exergy cost and propose solutions for its reduction. The second framework analyses the land-to-tank production chain in order to calculate the ExROI, exergy return on investment, to evaluate its "resource sustainability" and propose improvements to the production cycle so that less non-renewable resources are used.

Before starting with the calculations, it is first necessary to introduce shortly the methodologies and approaches to be used, i.e. thermoeconomics, Material Flow Analysis and Life Cycle Assessment. Also it is important to explain why the calculations are focused on bioenergy and which bioenergy sources have been selected.

This overview will give the perfect frame to set the specific questions that this PhD aims to answer.

1.1 A brief review of thermoeconomics

The First Law of thermodynamics states that energy and matter can be neither created nor destroyed. The Second Law introduces a new variability: the quality of energy. It states that the energy and materials can only be transformed by the consumption of quality. The level of quality deterioration is measured through the property entropy. Entropy will always increase or in ideal cases will be maintained.

The combination of both laws is gathered in the concept of exergy. It indicates that the important question is not really the existent amount of mass or energy, but the quality of that mass or energy, or in other words its exergy content. Unlike mass or energy, exergy is not a conserved property. It is an extensive property with the same unit as energy. In all physical transformations of matter or energy, it is always exergy that is lost.

The Second Law tells that all the production processes are irreversible and nothing can be done without the expenditure of natural resources. The amount of natural resources needed to produce something is its thermodynamic cost. As most of the analysts agree [118, 180], exergy is the most adequate thermodynamic property with cost because it accounts for energy quality. If we can measure this thermodynamic cost by identifying, locating, and quantifying the causes of inefficiencies of real processes, we are giving an objective basis to economics through the concept of *exergy cost*.

According to Valero [237], the search for the cost formation process is where physics connects best with economics. Thermoeconomics, can be defined, in its widest possible sense, as a general theory of useful natural resources saving, connecting physics and economics by means of the Second Law of thermodynamics. It combines economics and thermodynamics by applying the concept of cost (originally a economic property) to exergy (a thermodynamic property). Concepts such as thermodynamic cost, purpose, causation, resources, efficiency, structure and cost formation process are the bases of thermoeconomics.

Meanwhile, the exergy balance only takes account for the degradation of exergy in a process:

$$\text{Exergy Input} - \text{Exergy Output} = \text{Irreversibilities} > 0$$

If we introduce the concept of efficiency, that is older than thermodynamics, and measures the quality of a process:

$$\text{Efficiency} = \text{Product}/\text{Resource}$$

we are also bringing the idea of purpose of the process, and an implicit classification of the flows crossing the boundary of the system: the flows that are the production objective, the resources required to carry out the production (also known as Fuel) and those that are residual. This information is not implicit in the Second Law and is the most important conceptual leap separating and at the same time uniting physics with economics. The following equation:

$$\text{Resources (F)} - \text{Products (P)} = \text{Residues (R)} + \text{Irreversibilities (I)} > 0$$

is of utmost importance because it places *purpose* in the heart of thermodynamics. The desire to produce a certain product is external to the system, and must be defined beforehand. Once this has been done, the design of the system and its functional structure will fit the aim of using available resources (capital, raw material, man power…). Every definition of efficiency demands a comparison of the product obtained with the resources needed to obtain it. Its inverse value is the unit consumption:

$$\text{Unit Consumption} = \text{Resources}/\text{Product}$$

This expression is also a definition of the unit average cost when resources refer to the overall plant instead of individual processes. This concept is the key of thermoeconomics. A logical chain of concepts can be established, see fig. 1.1, which allows connecting physics with economics.

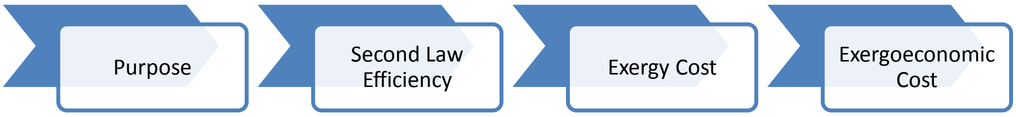

Figure 1.1: Logical chain of thermoeconomic concepts

Thermoeconomics assesses the cost of consumed resources and system irreversibilities in terms of the overall production process. They help to point out how resources may be used more effectively in order to save them. Money costs, or thermoeconomic costs, express the economic effect of inefficiencies and are used to improve the cost effectiveness of production processes. Assessing the cost of the flow streams and processes in a plant helps to understand the process of cost formation, from the input resources to the final products.

Thermoeconomics, as stated by Bejan, Tsatsaronis and Moran [17], can solve problems related to complex energy systems that could not be solved by using conventional energy analyses. Among other applications thermoeconomics are used for:

- Rational prices assessment of plant products based on physical criteria.
- Optimization of specific process unit variables to minimize the final product cost, i.e. global and local optimization.
- Detection of inefficiencies and calculation of their economic effects in operating plants, i.e. plant operation thermoeconomic diagnosis.
- Evaluation of various design alternatives or operation decisions and profitability maximization.

The word *thermoeconomics* was coined in the sixties by Tribus, Evans and El-Sayed [67, 228], when they allocated costs of water and energy streams in desalination plants using exergy (named at that time *availability*). Early contributors to Thermoeconomics include Gaggioli, Weppfer [117] and Reistad [199]. Interest and research regarding thermoeconomic analysis became more prevalent in the eighties, with the work of Tsatsaronis and Winhold [231], Frangopoulos [114], von Spakovsky and Evans [249], Szargut [181] and Valero et al. [239, 241, 242], amongst others.

At the beginning of the nineties, a group of concerned specialists in thermoeconomics decided to compare their methodologies by solving a predefined and simple problem of optimization CGAM [240]. The aim was to show the different methodologies and to compare results. Detailed information about thermoeconomic methodologies can be seen in refs. [66, 159, 243].

In the same direction, in the year 2001 another project called TADEUS [238], aimed to applying procedures from different research groups in thermoeconomic analysis to the diagnosis of the energy system malfunction and inefficiencies. The objective of this new effort was to establish the common concepts and nomenclature, and compare the results and highlight the main characteristics of each approach.

During the last years, methodologies based on thermoeconomic principles are being developed to analyse ecological problems. A forerunner of this application was Szargut [216]. This author proposed the concept of *thermoecological cost* which is the cumulative consumption of non-renewable exergy needed for the fabrication of a given product [218], it should be noted that thermoecological cost includes also environmental impact of emitted harmful substances. Szargut has also proposed a pro-ecological tax based on the consumption of non-renewable resources [220]. Frangopoulos proposes the term *environomics* in order to imply the systematic consideration of thermodynamic, economic and environmental aspects for the analysis and optimization of energy systems [115]. Tsatsaronis et al. have developed the *exergoenvironmental analysis*, which is “the combination of an exergy analysis with a comprehensive environmental assessment method when the principles of exergoeconomic analysis are employed”; this method consists of three steps: (i) exergy analysis of the energy conversion system, (ii) life cycle assessment of each relevant system component and all relevant input streams to the system and (iii) assignation of environmental impact to the product exergy streams of the components and calculation of exergoenvironmental variables [171]. Sciubba [207] proposed the *extended exergy accounting*, which is a framework based on exergy analysis that includes also non-energetic quantities such as labour, capital, and environmental impact. Valero and co-workers apply exergy cost to “Ecological Modeling” and “Industrial Symbiosis” [227, 244].

As Valero and Torres [243] noted, the exergy content of a product is not the most important data in an energy analysis; what is crucial is the amount of exergy that has been consumed for its production, i.e. the exergy consumption or *exergy cost*. This last statement is the core idea that sets the basis of this Ph.D., which is developed in the next chapters.

1.2 Material and Energy Flow Analysis

The methodology of thermoeconomics explained above is based on the Material and Energy Flow Analysis (MFA). MFA, as defined by the UNIDO, is a quantitative procedure for determining the flow of materials and energy of a closed production process [233]. It is based on the First Law of thermodynamics, where the inputs (raw materials, energy sources, e.g. electricity, natural gas) equal the outputs (final products, co-products, by-products, wastes and emissions). For this it is necessary to have clearly established boundaries of the analysed system.

One of the most accepted definitions of flow analysis is provided by the German commission of inquiry "Schutz des Menschen und der Umwelt" –Protection of human life and the environment– of the Deutsche Bundestag, in 1993 [233]:

> *A material flow analysis is a systematic reconstruction of the way a chemical element, a compound or a material takes through the natural and/or the economic cycle. A material flow analysis is generally based on the principle of physical balance.*

The aim of a flow analysis is to identify where the consumption of inputs occur and where/which outputs are produced. The final objective is improving the efficiency of the process by reducing the consumption of inputs while at the same time maximising the production of the desired products and reducing the formation of wastes and emissions. It is normally economically or environmentally driven. A MFA analysis helps to [233]:

- Trace the flow of raw materials and energy sources through the process;
- Retrace waste and emissions to the point where they are generated, identifying as well the volumes and causes;
- Edit data in a decision-oriented way, creating the basis for forecasting of future developments;
- Identify weaknesses in the production process;
- Set priorities for appropriate measures aimed at minimizing waste and emissions.

MFA works with mass or energy units where the (material and energy) analysis are carried out independently. It is the basis for the application of several methodologies to assess production processes such as Input/Output analysis and Life Cycle Assessment.

Thermoeconomics uses as a basis the MFA analysis but besides measuring quantities (in terms of consumption and production), also takes into account the quality of the flows by means of using the exergy concept [226, 237]. Exergy is an adequate magnitude because it expresses the thermodynamic separation of the intensive properties characterising a flow (P, T, μ) with respect those of the environment.

In this work, the MFA analysis is applied to a production plant on the one hand, and to an entire land-to-tank cycle. Once the quantities and intensive properties are known, the exergy is calculated and the Fuel-Product model defined in the previous paragraph is implemented.

1.3 Life Cycle Assessment

Life Cycle Assessment or Analysis (LCA) is a methodology normally used for assessing the potential environmental impacts of goods and services (products). It is a material and energy flow analysis applied to the full life of the analysed product. As the European Platform on Life Cycle Assessment states, LCA helps to quantify the environmental pressures, the environmental benefits, the trade-offs and areas for achieving improvements taking into account the full life-cycle of the product [75]. This methodology was initially conceived in the context of biological systems, but nowadays is widely used in industrial production as an effective instrument of analysis and has been also introduced in legal frameworks as a mandatory mechanism for environmental production assessment, for example in relation to greenhouse gas emissions [125].

There are two ISO standards for the application of LCA: ISO 14040:2006 Principles and Framework and 14044:2006 Requirements and Guidelines [8]. The latter replaced the former standards 14041, 14042 and 14043 . Both standards cover LCA studies and life cycle inventory (LCI) studies, but ISO 14040 does not describe the technique in detail, nor does it specify methodologies for the individual phases of the LCA. Despite establishing general principles, these ISO standards are defined in a quite vague language which make difficult to certificate that a LCA is made according to them. This is why in its Communication on Integrated Product Policy [76], the European Commission concluded that Life Cycle Assessments provide the best framework for assessing the potential environmental impacts but there is still a need for more consistent data and consensus LCA methodologies.

The selection of the life cycle boundaries is very important, thus depending on the processes included in the analyses the values obtained can vary significantly. In this work, the life cycle of a product is understood to comprehend the production of the raw materials needed to produce the product and the processes to produce the product. The manufacture of machinery and equipment and the treatment of residues produced in the process can also be considered, but have not been accounted in this PhD.

The boundaries selection is based on the life cycle considerations used by the European Commission to establish the sustainability criteria for biofuels for transport and bio-liquids in the Directive 2009/28/EC [99] on the promotion of the use of energy from renewable sources and Directive 2009/30/EC [100] amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions. These sustainability criteria are explained in following paragraphs.

Another crucial matter in LCA is how to deal with the valuable products obtained along the cycle. The impacts of the cycle are shared between all the products obtained being them the desired product (for which the production chain has been designed) and the co-products and sub-products. The way the impacts are distributed between the different products can have a significant influence in the values obtained in a LCA.

There are two classic options to distribute impacts to co-products and sub-products: the substitution method and the allocation method. In the substitution method the impact of co-products and sub-products is considered to be the one that is obtained by avoiding the production of these products elsewhere in the society. This method is based in a causality principle: by producing this co-product we are reducing the impact in the environment caused by another production process that will no longer be needed. The impact of the desired product in the LCA is reduced proportionately to the impact avoided.

This method has a major drawback in that there are no established rules on the selection of the production process that is avoided. The method does not say in which sector the impacts are reduced. Therefore the process may be subjectively chosen to benefit or jeopardise the results. For example, in the life cycle of biodiesel production one sub-product is protein meal obtained at the oil extraction process. If this meal is considered to be used for energy purposes rather than for animal feed it may achieve higher greenhouse gas savings, according to Marelli et al. [167]. This unclear framework provides investor uncertainty.

In the allocation method, the impacts are distributed by means of a proportionality principle. This is that the impacts are proportionately distributed taking into account a selected property shared by all the products. With this, the product with a highest value in this selected property will be held responsible for the largest environmental impact in a chain. The main drawback of this method relies in the selection of the property. Most LCA are based on the economic values of the products, others are based on the mass or energy content. None of these options is strictly rational but the allocation method presents some advantages compared to substitution [167]; mainly that the use of the co-products once they exit the boundaries of the system is irrelevant, thus avoiding undesired incentives. In addition, it allows estimating the impact in the sector under analysis and, finally, brings certainty for investors.

The economic value allocation is not fully convenient because these values are subjective, vary in time and depend on the location. The mass allocation procedure presents the advantage to be relatively constant with time, the mass ratio between product and by-product being rarely variable, unless a technological improvement occurs. However, in many cases, mass of by-products can be tremendously above the one of the main product giving misleading results [38].

The energy value allocation is considered by most authors as the most adequate one. While it does not vary in time, it gives values that are closer to those obtained by substitution [167] (when in substitution the same process is selected). The energy value selected normally is the lower heating value (LHV) [77]. According to Marelli et al., [167] the LHV is defined in the Renewable Energy Sources Directive [99] as heat from burning the dry part of the material not including the energy in steam in the exhaust and subtracting the energy to evaporate the water in the material.

With this definition, the allocation of impacts using the energy value may have negative consequences. Firstly, the lower heat value of wet material decreases and therefore the wet by-products get less allocation than dry ones. Secondly, following the European Commission practical implementation guidelines [77], since heat does not have a lower heating value no emissions can be allocated to it on that basis. In third place, LHV cannot be obtained when dealing with non combustible materials. And finally, this definition does not take into account the quality of the energy.

The allocation of impacts using exergy instead of energy avoids these negative consequences. The selection of the allocation method with exergy values as selected property is considered the most objective and neutral methodology. It avoids the subjective choices of the substitution method while providing the advantages of the exergy concept as explained before. This is one of the most important values of this Ph.D.

The use of exergy in the frame of LCA is considered by many authors as a powerful instrument to assess the sustainability of industrial processes. Here some relevant examples are cited. Ayres et al. [14] in 1996 extended the applications of exergy analysis to present the results in Life Cycle Analysis, as an integrated analytical framework. Ayres [12] identified advantages for LCA when using exergy: by using exergy as a common measure of inputs and outputs, the exergetic efficiency can be immediately estimated, allowing the comparison of 'apples' with 'oranges'.

Cornelissen [50] in his PhD thesis defined the ELCA, Exergetic Life Cycle Analysis as a combination of the life cycle approach with exergy analysis. In [51], Cornelissen and Heirs show that the ELCA analysis is a more appropriate instrument to quantify the environmental problem of the depletion of natural resources. ELCA can be used to determine the consumption of natural resources as well as to calculate the depletion of natural resources, introducing the idea of renewable and non–renewable resources. In the same line but with another purpose, Koltun [153] states that the exergy analysis approach based on full LCA is a useful metrics to evaluate mitigation of greenhouse gas (GHG) emissions associated with industrial eco–materials and technologies. Hau and Bakshi [132] use as a basis the exergy analysis and the LCA to evaluate the contribution of ecosystems leading to the creation of the concept Ecological Cumulative Exergy Consumption (ECEC). Finally, Torres et al. [227] connect thermoeconomic analysis with LCA in a methodology closely related to the input/output analysis, showing the capabilities of thermoeconomics in the analysis of environmental systems. They demonstrate that thermoeconomics can become a useful tool for identifying the ways for improving the energy resources cost and the efficiency of macroeconomic systems.

The life cycle calculations in this Ph.D. are mainly based on the life cycles of the JEC Well-to-Wheels Programme established by the Joint Research Centre of the European Commission [148]. The JEC Programme is a collaboration scheme between the European Commission's JRC Institute for the Environment, EUCAR (the European Council for Automotive R&D) and CONCAWE (the oil companies' European association for environment, health and safety in refining and distribution).

Some authors have criticised these data by stating that they are partially based on old data, provably conservative, as stated by Hamelinck [129]. However, these are the data that were used to establish the typical and default greenhouse gas emission values for the biofuel and bioliquids life cycles considered in the above mentioned sustainability criteria (Annex V of the Renewable Energy Directive [99]). Given the political importance of these data it has been decided to use them as a basis.

The European Commission is expected to issue an update of the values of Annex V since 31 December 2012, as required in article 19 of the Renewable Energy Directive [99]. However, this Communication is being delayed. The update will include data for pathways not included in Annex V and may include corrections to the values when considered necessary, although it is not expected that the changes introduced will lead to dramatic changes in the life cycles.

Other Life Cycle Analysis that have also been taken into account are the analysis of alternative fuels for transport commissioned by the Spanish Ministry of Education, Science and Environment [160] and the assessment applied to first generation biofuels consumed in France, commissioned by the Department of Bioresources, Directorate of Renewable Energies, Energy Networks and Markets, of the French Government [3].

1.4 Reasons for focusing on bioenergy

Currently, humankind is facing two major problems related to fossil energy sources, first of all, climate change and, secondly, energy dependence from few unstable countries. Both problems have great implications to the global economy either currently and in the decades to come.

As far as energy dependence is concerned, practically all developed and underdeveloped nations of all Continents depend on few countries that concentrate the bulk of oil and gas supplies.

Despite the growth of non-fossil energy (such as nuclear and renewable energy sources) considered as non-emitting, the share of fossil fuels within the world energy supply is relatively unchanged over the past 39 years. In 2010, fossil sources accounted for 81% of the global total primary energy supply, according to the IEA [140].

More specifically in the European Union (EU-27) the dependence of fossil energy supplies from third countries is in a rate of 54%, according to data released by Eurostat in 2013 [102]. This dependence is increasing year after year. Thus, while energy consumption in 2006 was 1,825 million tonnes of oil equivalent (toe), which was stable compared with 2005, energy production decreased by 2.3% to 871 million toe. As a result, from one year to another, net imports increased by 2.4% in 2006 and the energy dependence rate rose to 54%. In the case of Spain, although from 2005 to 2006 there was a small decrease of gross inland energy consumption of -0.5% and also net imports decreased by -0.1% the energy dependence rate was 81.4%, i.e. of the total 143.9 million toes consumed, up to 123.8 million toes came from abroad. Only Cyprus, Malta, Luxembourg and Ireland were more energetically dependent than Spain.

As far as climate change is concerned, global warming is being growing regarded as one of the greatest environmental, social and economic threats facing the planet. Socio-economically speaking, according to the Stern report [215], not fighting climate change can drive our World to great risks of major disruption to economic and social activity, later in this century and in the next, on a scale similar to those associated with the great wars and the economic depression of the first half of the 20th century.

On the environmental side, the Intergovernmental Panel on Climate Change (IPCC) affirms that observational evidence from all continents and most oceans shows that many natural systems are being affected by regional climate changes, particularly temperature increases [191]. Those effects will affect physical and biological systems causing the extinction of hundred of animal and plant species due to growing disorders of seasons and extreme heat events among other factors.

The Fourth Assessment Report of the IPCC [213] concludes that with current climate change mitigation policies and related sustainable development practices, global greenhouse gas (GHG) emissions will continue to grow over the next few decades. This could be concluded by observing that although in the last decades some countries have put policies in place to reduce GHG gases which have been effective in reducing them in those countries to a certain degree, worldwide emissions have increased by 50% from 1990 to 2010, see fig. 1.2. CO_2 atmospheric concentrations have risen from pre-industrial levels of 280 ppm to 380 ppm in 2005. CO_2 is the most important greenhouse gas, being responsible for about two-thirds of the greenhouse effect. In a business as usual outlook it is expected that CO_2 emissions will increase in 54% between 2004 and 2030, according to the IEA. The IPCC finds that to stabilise the GHG concentration in the 455 to 499 ppm $CO_{2\text{-eq}}$ range, where global temperatures will not increase more than 2 °C compared to the pre-industrial era, being this increase considered not to cause any harm to the global environment [74], global emissions need to be reduced 50 to 85% by 2050.

In order to fight the two aforementioned problems, policy makers are taking into consideration all the technological possibilities available: energy efficiency, renewable energy sources, fossil fuels with carbon capture and storage, nuclear energy, ...

In the EU, the Member States have endorsed an integrated approach to climate and energy policy introducing a series of demanding targets to be met by 2020: a reduction in EU greenhouse gas emissions of at least 20% below 1990 levels; a 20% of EU energy consumption to come from

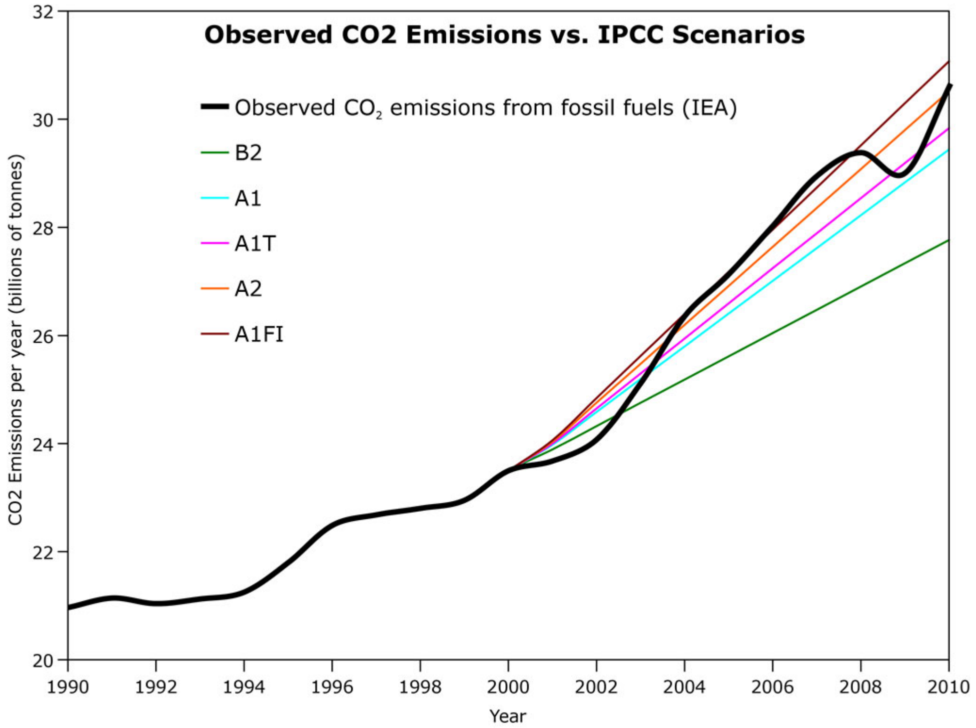

Figure 1.2: Variation of GHG emissions from 1990 to 2010. Source: IPCC

renewable resources; and a 20% reduction in primary energy use compared with projected levels, to be achieved by improving energy efficiency.

As far as renewable energies are concerned, the EU has put into force the Directive 2009/28/EC [99] on the promotion of the use of energy from renewable sources (the before mentioned Renewable Energy Directive). This Directive establishes mandatory targets to be achieved by 2020 for a 20% overall share of renewable energy in the EU and a 10% share for renewable energy in the transport sector. Among all the possible renewable energy sources, sustainable bioenergy has an important role to play.

Bioenergy is a renewable energy made available from materials derived from biological sources. These so-called bio-resources have stored sunlight in the form of chemical energy. As a fuel it may include wood, wood waste, agricultural residues and wastes, such as straw and manure, energy crops such as soy, rape or sugar cane, the organic part of urban wastes, and many other by-products from a variety of agricultural, forestry and industrial processes. These bio-resources can be used to produce electricity, heat and transport fuels depending on the production process followed. Because vegetable species absorb CO_2 during growth and increase the storage of soil organic carbon, sustainable bioenergy reduces greenhouse gas emissions relative to petroleum-derived fuels.

Bioenergy is the dominant renewable energy source, amounting to 10% (1,200 Mtoe) of global primary energy supply. In the future, the IPCC estimates that the use of sustainable bioenergy will triple towards 2050. The IEA has pictured a scenario where bioenergy is considered as a necessary technology to significantly reduce CO_2 emissions in 2050 [137].

As shown in fig. 1.3, in an optimistic technology scenario, while energy efficiency is the largest contributor to CO_2 emission reductions (45%), bioenergy plays a necessary role of 6% reduction in the transport sector and of 2% in power production.

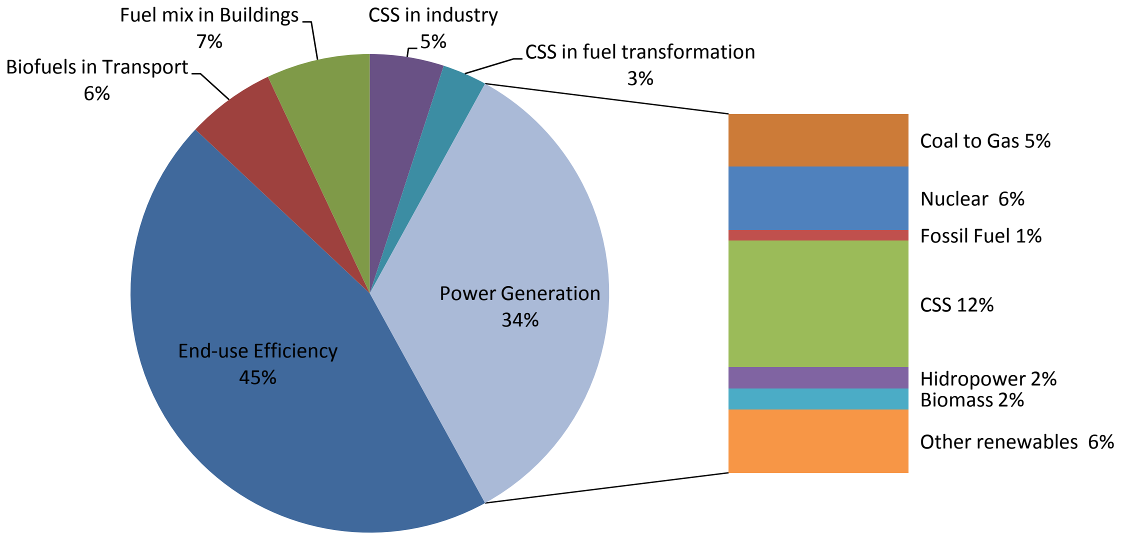

Figure 1.3: Relative contributing factors to bring CO_2 emissions to 2003 levels in 2050 by technology area, ACT-MAP Scenario. Source: IEA

The European Union also sees bioenergy as a great opportunity for renewable energy production. Bioenergy will play a crucial role in the achievement of the 2020 targets: it currently provides more than 2/3 of the renewable energy in the EU, and it is expected to account more than half of the EU's renewable energy in 2020, see fig. 1.4, and about 11% of the total EU energy consumption, according to the Member States' National Renewable Action Plans (NREAPs) [20, 113, 248].

Bioenergy has specific benefits that make of it a special renewable energy source, as is well explained by Volpi [248]. On the one hand, it provides versatility: it is the natural partner to wind and other variable sources of electricity production and, at the same time, can be used for controllable heat generation or to produce transport fuels. Secondly, it is cost effective as it can achieve lower costs than other renewable energy sources, building on existing infrastructure and protecting existing jobs. Thirdly, it is particularly effective as regards the security of energy supply especially when using domestic feedstocks, including wastes. Finally, it generates significant business and job opportunities across the supply chains, increasing the prosperity in rural areas, which in the EU are being slowly getting depopulated.

However, unlike other renewable energy sources, generating net greenhouse gas savings from bioenergy depends on the fuel production processes used. For this reason, in June 2012 the European Commission published a Communication on the renewable energy policy [87] where it stated that while bioenergy is key for decarbonisation, efficiency in biomass production and consumption is key to minimise unwanted side effects and it asks to reinforce and further develop the EU sustainability framework for bioenergy and will investigate the most appropriate use of bioenergy post–2020.

There are significant risks and uncertainties related to the conditions that need to be met if the full potential of GHG emissions reduction with bioenergy is to be realised, in particular: the availability of low-carbon biomass and biofuels, the GHG reduction they actually achieve, their cost and market uptake, and the biomass demand from other sectors, as gathered by Hill et al. [133].

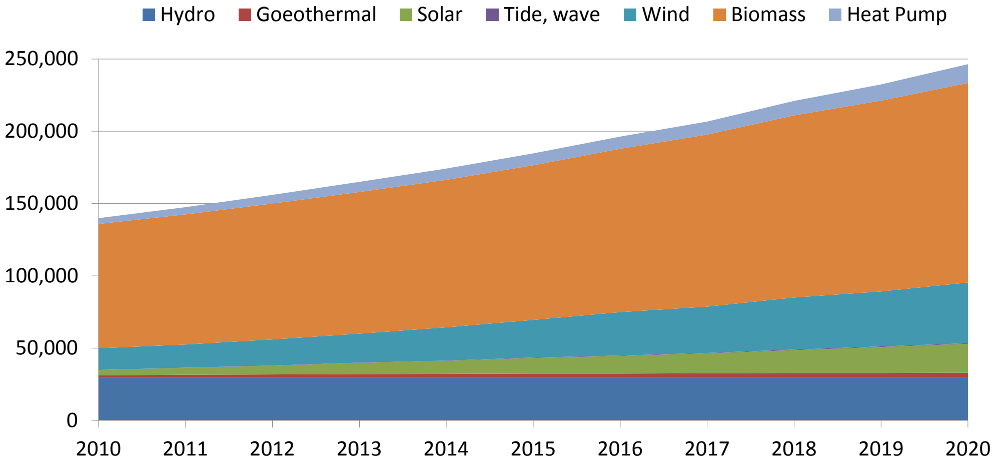

Figure 1.4: EU renewable energy outlook by 2020 (ktoe). Source: NREAPs

The EU has put in place policy instruments to ensure that bioenergy actually contributes to greenhouse gas reductions compared to their fossil counterparts. These instruments are the so-called sustainability criteria.

On 25 February 2010, the European Commission presented a report [79] on sustainability requirements for the use of solid biomass and biogas in electricity, heating and cooling. The report makes recommendations on sustainability criteria to be used by those Member States that wish to introduce a scheme at national level, in order to avoid obstacles for the functioning of the internal market for biomass. The calculations of greenhouse gas emission reductions follow a similar structure as the ones applied to liquid biofuels and bioliquids.

In the case of liquid biofuels and bioliquids (i.e. bioenergy in liquid form used in static devices for heating and/or electricity production, e.g. palm oil) the European Commission introduced mandatory minimum greenhouse gas reduction thresholds in the Directive 2009/28/EC on the promotion of the use of energy from renewable sources [99] and Directive 2009/30/EC amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions [100]. How this mechanism works is explained in a subsequent paragraph. The Directive 98/70/EC also introduced a mandatory target to achieve by 2020 a 6% reduction in the greenhouse gas intensity of fuels used in road transport and non-road mobile machinery.

In addition, on 17 October 2012, the European Commission published a new proposal for a Directive to limit global land conversion for biofuel production, and raise the climate benefits of biofuels used in the EU, limiting the use of food-based biofuels to meet the 10% renewable energy target of the Renewable Energy Directive to 5% [89]. As far as greenhouse gas emissions are concerned this new proposal aims at increasing to 60% the minimum greenhouse gas saving threshold for biofuels and bioliquids produced in new installations with effect from 1 July 2014 in order to improve their overall greenhouse gas balance as well as discouraging further investments in installations with low greenhouse gas savings performance. The estimated indirect land-use change (ILUC) emissions would be included in the reporting of greenhouse gas emissions from biofuels. The ILUC emissions correspond to the unintended consequence of releasing more carbon emissions due to land-use changes around the world induced by the expansion of croplands for ethanol or biodiesel production. The proposal also introduces higher regulatory incentives for advanced non-land using biofuels via quadruple accounting towards the mandatory national targets.

The Commission is of the view that in the period after 2020 biofuels which do not lead to substantial greenhouse gas savings (when emissions from indirect land-use change are included) and are produced from crops used for food and feed should not be subsidised.

Taking as a basis the above mentioned debate on net greenhouse gas savings, this work aims to propose a methodology to assess the sustainability of bioenergy using the principles and concepts of thermoeconomics and in line with the sustainability criteria proposed by the European Commission. This methodology will help to identify improvements to the production processes, for which it will be identified whether they contribute to reduction of greenhouse gas emissions.

1.4.1 European sustainability criteria

As commented above, in order to make sure that biofuels and bioliquids are indeed helping to fight climate change, whilst at the same time they do not harm the environment, the European Commission introduced in both Renewable Energy and Fuel Quality Directives [99, 100] a set of mandatory sustainability criteria.

In the European Union biofuels must be sustainable if they want to be accounted in the national mandatory targets established in the National Renewable Energy Action Plans developed by the EU Member States according to the Renewable Energy Directive, and if they want to have access to other promotion mechanisms such as tax exemptions.

The stakeholders that produce and trade biofuels for transport and bioliquids should be able to demonstrate that their products are sustainable under these criteria.

The sustainability criteria consist mainly in the following points:

- The greenhouse gas emission saving from the use of biofuels taken into account for the purposes of the Directive shall be at least 35%. This percentage is increased to 50% after 2017.
- Biofuels and bioliquids shall not be made from raw material obtained from land with recognized high biodiversity value.
- Biofuels and bioliquids shall not be made from raw material obtained from land with high carbon stock.

Concerning the first point, there are three ways for calculating the GHG emissions of a determined biofuel/bioliquid production pathway: using default values specified in the Directive; using a value calculated in accordance with the methodology laid down in the annexes and, finally, using a combined procedure taking into consideration the disaggregated default values in Annex V of the Renewable Energy Directive [99].

This methodology takes account of the emissions associated with direct land use change as well as emissions coming from the production cycle. Emissions from the manufacture of machinery and equipment are not taken into account.

Annex V sets the formula to calculate the specific GHG emissions. The equation is the following:

$$E_{GHG} = \mathrm{eec} + \mathrm{el} + \mathrm{ep} + \mathrm{etd} + \mathrm{eu} - \mathrm{eccs} - \mathrm{eccr} - \mathrm{eee} \quad [gCO_2/MJ]$$

where:

- E_{GHG}: are the total emissions from the use of the fuel
- eec: accounts for the emissions from the extraction or cultivation of raw materials
- el: are the annualised emissions from carbon stock changes caused by land use change
- ep: accounts for the emissions from processing
- etd: accounts for the emissions from transport and distribution
- eu: accounts for the emissions from the fuel in use
- $eccs$: accounts for the emission savings from carbon capture and sequestration
- $eccr$: accounts for the emission savings from carbon capture and replacement
- eee: accounts for the emission savings from excess electricity from cogeneration

If a biofuel/bioliquid producer decides to use the default values to prove the sustainability of its product, it has to take into account that the production step is penalized with 40% more emissions compared to the typical GHG emissions. This penalty is justified by the Commission for fostering energy efficiency at this specific stage. The default values do not include emissions for machinery manufacture, energy for irrigation or the emissions from direct land use change.

As far as the sustainability of solid and gaseous bioenergy used in static devices, the European Commission has taken a gradual approach. In [79] it proposed similar sustainability criteria than for biofuels and bioliquids with the following differences: greenhouse gas accounting includes end-use conversion, i.e. the step of electricity and/or heating & cooling; small bioenergy installations (below 1 MW) are exempted from compliance; the biomass origin and quality in small-scale uses such as households is to be monitored by the EU Member States. In a subsequent stage the Commission is assessing the approach effectiveness considering new markets and policy developments and will publish a new Communication with additional/different requirements.

In this context, improving the energy efficiency of bioenergy production plants and the entire life cycles becomes crucial. Performing thermoeconomic calculations to the production plants can be an effective way to discern where to act and what could be done to improve the energy efficiency. Furthermore, if thermoeconomics is applied throughout all its life cycle (from field-to-tank) in its variant called thermoecology or exergoecology, this methodology can help to analyse all the life cycle environmental aspects.

1.5 Special focus on biodiesel

1.5.1 The need to reduce the fossil fuel use in the transport sector

In the specific case of the European Union, which can be transposed to other industrialised regions and countries, the transport sector is a major contributor to climate change and fossil fuel dependence due to its high dependency on fossil fuels in all transport modes. Statistics indicate that the transport sector contributes to 23% of all the CO_2 emissions in the 27 EU Member States. If this trend continues, transport is expected to contribute 50% of all the CO_2 emissions in the EU by 2050, if not within the next two decades [230]. An overview of historic developments of CO_2 emissions and estimates for various sectors is shown in fig. 1.5, where a clear continuing growth of emissions from transport can be observed.

In order to fight this tendency the European Commission published in 2011 the Transport White Paper [85] which set the target of delivering 60% reduction in greenhouse gas emissions by 2050.

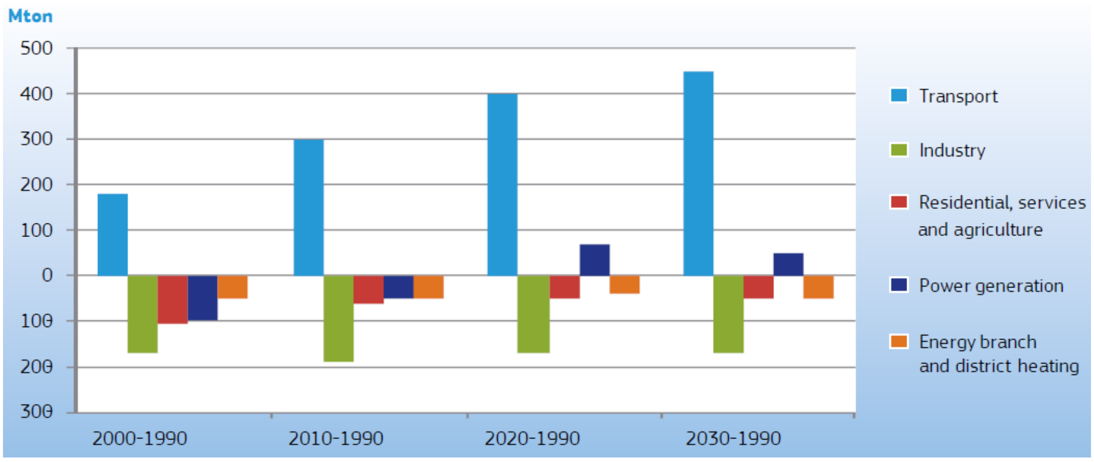

Figure 1.5: Change of CO_2 emissions since 1990 per sector. Source: EC, DG TREN, 2008

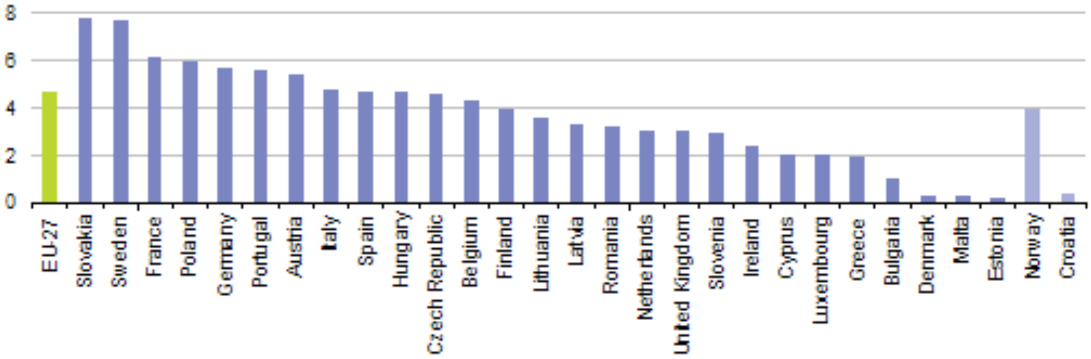

Figure 1.6: Renewable energy share in transport (2010 %). Source: Eurostat

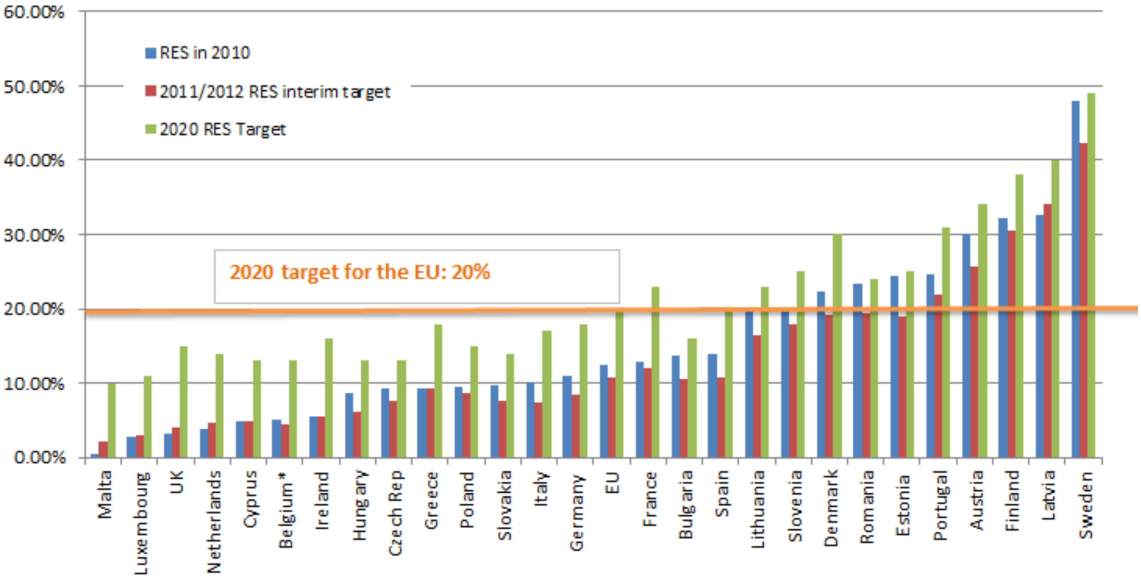

Figure 1.7: Renewable energy shares in final energy use (2011,%) and 2020 targets. Source: European Commission

This means that transport can no longer continue with the “business as usual” and needs to be decarbonised, or in other words defossilised, using a wide range of actions including the use of less and cleaner energy and making more efficient use of modern transport infrastructures and services. Nowadays, the renewable energy share in transport continues to be low, compared to the total renewable energy share in final energy use. See figs. 1.6 and 1.7.

As mentioned in section 1.4, in order to increase the renewable energy used in transport, the EU set a mandatory target in the Directive 2009/28/EC [99] of 10% in 2020. According to article 3.4 each Member State shall ensure that the share of energy from renewable sources in all forms of transport in 2020 is at least 10 % of the final consumption of energy in transport in that Member State. In order to calculate the percentage, the following provisions apply:

- for the calculation of the denominator, that is the total amount of energy consumed in transport, only petrol, diesel, biofuels consumed in road and rail transport, and electricity shall be taken into account
- for the calculation of the numerator, that is the amount of energy from renewable sources consumed in transport, all types of energy from renewable sources consumed in all forms of transport shall be taken into account.

1.5.2 The role of biofuels for transport

In the run to finding cleaner energies in the transport sector there are many policy options involving the use of alternative fuels and new propulsion systems to substitute the use of gasoline and diesel. These include electricity, hydrogen, biofuels, methane (natural gas and biomethane), LPG and others [34].

According to the World Economic Forum (WEF) [177], biofuels will provide about 18% of the worldwide energy used in transport by 2030, fig. 1.8. The IEA [29] states that by 2050 biofuels could provide about 27% of world transportation fuel.

Biofuels are currently the most important type of alternative fuels, accounting for 4.4% in EU transport [93, 94]. Biofuels are already in the market and can play a respectable paper in the aim of diversifying the energy mix, especially because, along with the electric vehicle (for short distances), they are the only present and short-term solution to the transport sector. The so-called conventional biofuels (i.e. mainly biodiesel and bioethanol) are expected to play a major role in the coming decade [163]. The great advantage of biofuels is that generally they require minimal changes in vehicle stocks and distribution infrastructure, and no new investments or infrastructure in the case of low blends with conventional fuels [82, 92]. This is an important competitive advantage in comparison to the other alternative fuels.

Biofuels are expected to contribute to the de-carbonisation of medium to long-distance road transport, rail transport, water transport and aviation [80, 81]. In the short-distance transport, for example inside cities, electric vehicles are seen as the main alternative.

Biofuels are of special importance for road transport [83], which is the responsible of most of the GHG emissions in transport as shown in the fig. 1.9, but can also play an important paper in water, air and rail transportation. Indeed, according to the World Economic Forum [177] biofuels are vital for the air, marine and heavy duty road transport where no other sustainable fuel alternatives are available, at least in the short to medium term.

This position is also shared by the NGO WWF in its Energy Report 100% Renewable Energies by 2050 [166, 251]. WWF considers that in order to achieve the 100% target bioenergy should be

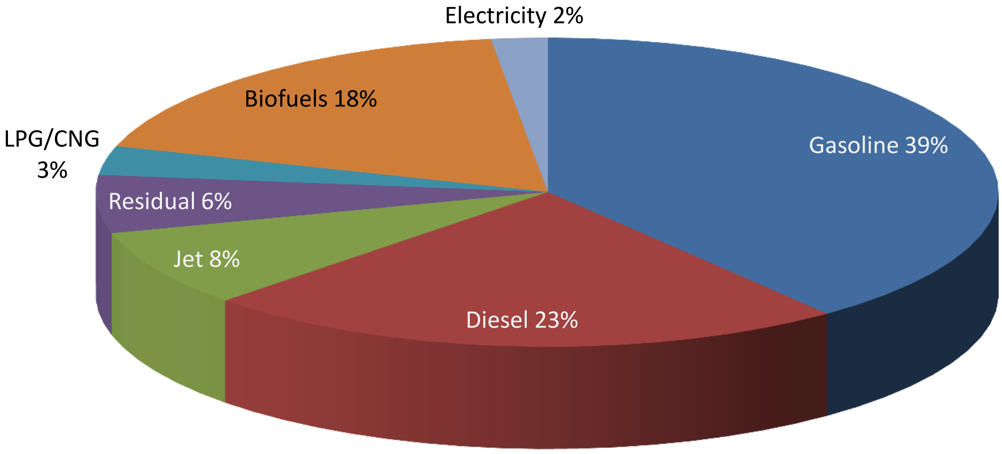

Figure 1.8: Transport energy consumption in 2030. Source: WEF

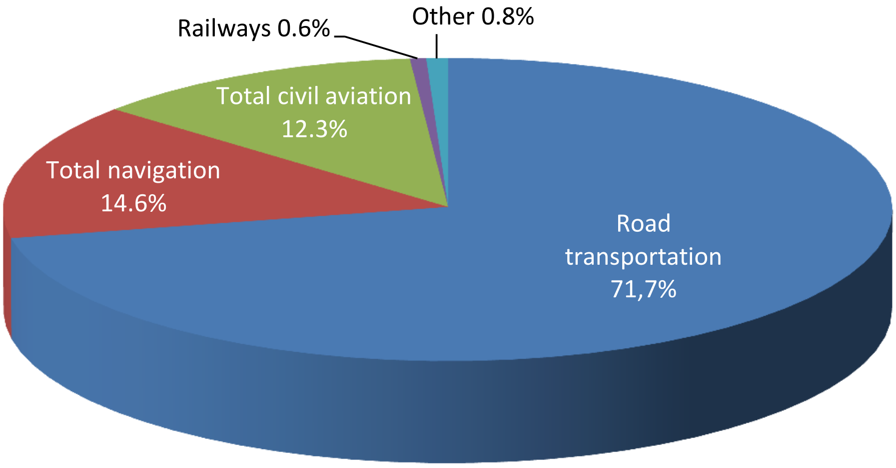

Figure 1.9: GHG emissions in the EU27 by transport mode. Source: EC, DG CLIMA, 2010 [96]

used where other renewable energy sources provide no alternative, or no complete alternative. Of course, bioenergy should be the last option; first other measures need to be put in place: reduction of energy consumption, energy efficiency measures, electrification of road transport and use of other renewable sources when possible. In the transport sector once these measures are applied, biofuels still remain important for the shipping, aviation and heavy duty road vehicle as shown in fig. 1.10. In the static applications, WWF recommends the use of bioenergy in high temperature industry processes. In all cases bioenergy should be sustainable.

In the case of aviation, promising sustainable alternatives to fossil kerosene are synthetic biomass-derived fuels and second generation biofuels [84, 93]. The "European Advanced Biofuels Flight path" aims to achieve an annual production of two million tonnes of sustainably produced biofuel for aviation by 2020 [229]. The American Society for Testing and Materials, ASTM, has approved the modification of the ASTM D7566 - 13 Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons, to allow the mixture of biofuels produced by Fischer-Tropsch process and the mixture of hydrotreated esters and fatty acids (HEFA) [9].

In water transport, where there is a challenging target to reduce by 40% the CO_2 emissions bellow 2005 levels in 2050, waterborne transport (maritime and inland waterways) could be supplied by biofuels (all vessels), hydrogen (inland waterways and small boats), LNG, (short sea shipping and inland waterways transport), and nuclear [80,83]. In this case, where there is also an important need to reduce the sulphur emissions, in the EU the Directive 2012/33/EU amending Council Directive 1999/32/EC as regards the sulphur content of marine fuels asks for the recognition of the use of biofuels as marine fuel by the European Union [101]. Without appropriate measures, sulphur emissions from maritime transport will exceed those from all land based sources in the EU by 2020 [183].

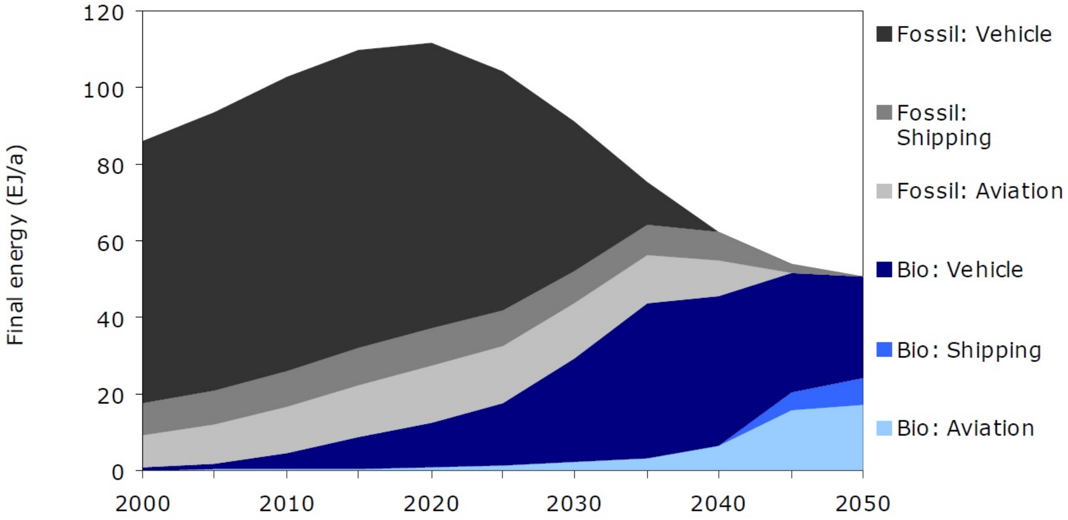

Figure 1.10: Biofuels in transport from 2000 to 2050 by WWF [166,251]

In the rail sector, the main policies to decarbonise are efficiency and electrification; however, where electrification is not possible the use of alternative biofuels in diesel engines is being researched. Taking into account that 50% of the railway network in Europe is not electrified which represents 20% of total transport volume and diesel traction is still relevant for freight services [59], biofuels represent an important alternative.

Whilst imported mineral oil still constitutes the vast bulk of fuel used in the transport sector, the share of biofuels obtained in 2010 in the EU is estimated to have generated 25.5 Mt $CO_{2\text{-eq}}$ savings, based on national reporting and 22.6 Mt $CO_{2\text{-eq}}$ based on the application of global default values [95]. These numbers represent 53% and 60% savings, compared to the situation where only fossil fuel would be used [91].

Figure 1.11 shows the % emission reduction compared to fossil fuels of the life-cycle production of different conventional and advanced biofuels according to the IEA [29].

As far as the problem of energy dependency is concerned, the production and use of biofuels displaces the crude oil needed to manufacture gasoline and distillate. According to a paper produced for the Global Renewable Fuels Association by John M. Urbanchuk [234] the global production of 110.8 billion litres of biofuels in 2010 is equivalent of 1.2 billion barrels of crude oil valued 135.4 billion US Dollars at 2011 prices. The displacement of crude oil with biofuels is projected to increase to nearly 2.3 billion barrels by 2020 valued at 253.6 billion US Dollars. This displacement has a positive effect on the balance of payments and international financial health of net oil importers. Urbanchuk states that the 14 major biofuel producers with net oil imports had an oil deficit equivalent to 639 billion US Dollars and produced an equivalent of 821 million barrels in the form of biofuels valued at 91.3 billion US Dollars. This means that biofuels contributed to reduce the oil deficit in more than 14%.

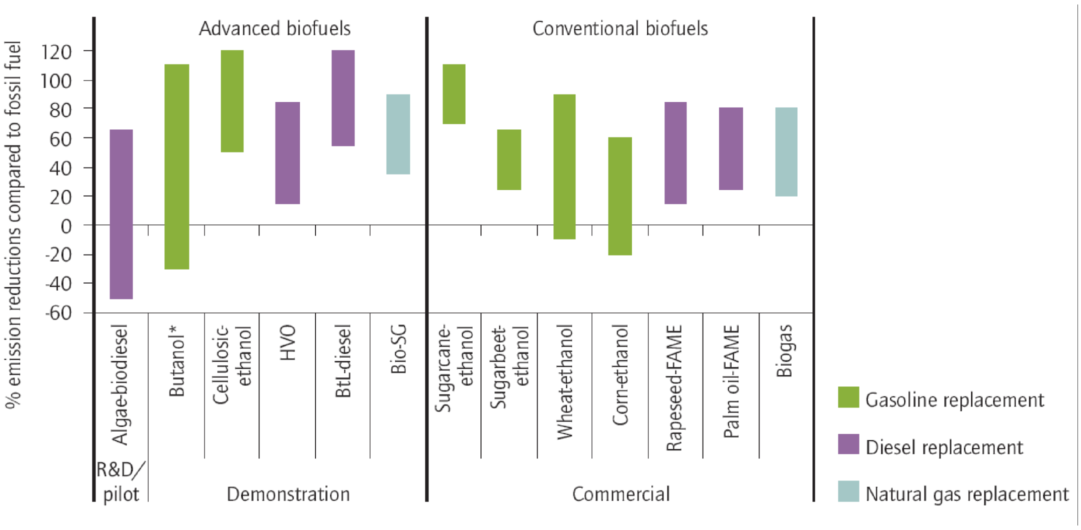

Figure 1.11: Life-cycle GHG balance of different conventional and advanced biofuels, and current state of technology. Source: IEA, 2012

Besides GHG reduction and energy security, another reason for which biofuels are being promoted is to foster socio-economic development of producing countries. Biofuels can contribute to create new sources of income especially in rural areas. In recent years the growth of biofuels production is making a significant contribution to the individual economies of the producing countries and to the global economy as a whole. Development of biofuels not only benefits farmers and the agricultural sector, but also stimulates the manufacturing sector. In total, biofuels contributed to 0.4% of the globe's GDP in 2010 (i.e. 277.3 billion US Dollars) and created 1,379,358 jobs, from which 291,129 were generated by the biodiesel industry, according to Urbanchuck [234]. Other sources estimate that biofuels have generated 220,000 jobs in the EU and 1.4 million jobs globally, in 2010 [95]. These jobs not only include the direct jobs of the biofuels production, but also the jobs in agriculture, other supplying industries and other sectors such as retail and wholesale trade that benefit from the economic activity generated by biofuels.

In 2020, it is expected that the biofuel industry will generate globally an output of 679,751 million US Dollars and will create 2,267,695 employments from which 673,380 will be in the biodiesel sector [234].

Other studies and reports [86, 197], state that only in the EU, the expected employment related to biofuels in 2020 could be around 400,000 jobs in total along the supply chain, including agriculture, logistics and at biofuels production facilities, but also in sectors that supply to or support biofuels supply chains.

In Spain, the Spanish Renewable Energy Association APPA commissioned a study on the macroeconomic impact of renewable energies in the country, where biofuels were analysed [6]. According to the authors, in 2008 the substitution of imported fossil fuels of 518,976 toe and 90,231 toe by biodiesel and bioethanol respectively (2.04% and 1.40% in terms of energy content) represented a contribution of the biofuels sector to the country's gross domestic product of 90.2 million Euros, where 43.3% corresponded to the direct biofuels production activity and 56.7% to the related industries such as service providers, components and equipment industry, and auxiliary industry. It is evident that to achieve the above mentioned aims, especially the climate change related one, biofuels production will need to contribute to net greenhouse gas emission reductions.

1.5.3 Especial focus on EU diesel consumption

Among the different possible biofuels, this work is focused on biodiesel. Biodiesel is the most important bioenergy derived fuel used in transport in Europe nowadays. It accounts approximately 78% of the biofuels consumption [72]. According to the National Renewable Action Plans (NREAPs) of the EU Member States, biodiesel will play an important role in reaching the 10% EU renewable energy target in transport in 2020. Biodiesel will count for as much as 65.9% of this objective [20]. Figure 1.12 shows the EU biofuels consumption forecast for up to 2020 where biodiesel consumption is almost three times higher than bioethanol [119].

The reason behind the commitment to biodiesel by most of the EU Member States is the widening EU mineral diesel deficit which represents a major strategic challenge, see fig. 1.13. The diesel deficit affects the EU from an economic perspective by reducing its competitiveness and from a security of supply perspective because it makes the EU dependent on foreign supply of diesel as the EU does not have sufficient production capacity. Around 90% of the diesel imports come from the Middle East and the rest from Russia. According to sources from Eurostat and OPEC, it is expected that EU net diesel imports will almost double from the approximately 15–17 million tonnes per year in 2000 to the around 27-29 million tonnes per year in 2030 [119]. Biodiesel can provide a practical and sustainable solution to this challenge. This is why petroleum refiners such as TOTAL consider that biodiesel is the only type of biofuel that contributes to Europe's energy security [123].

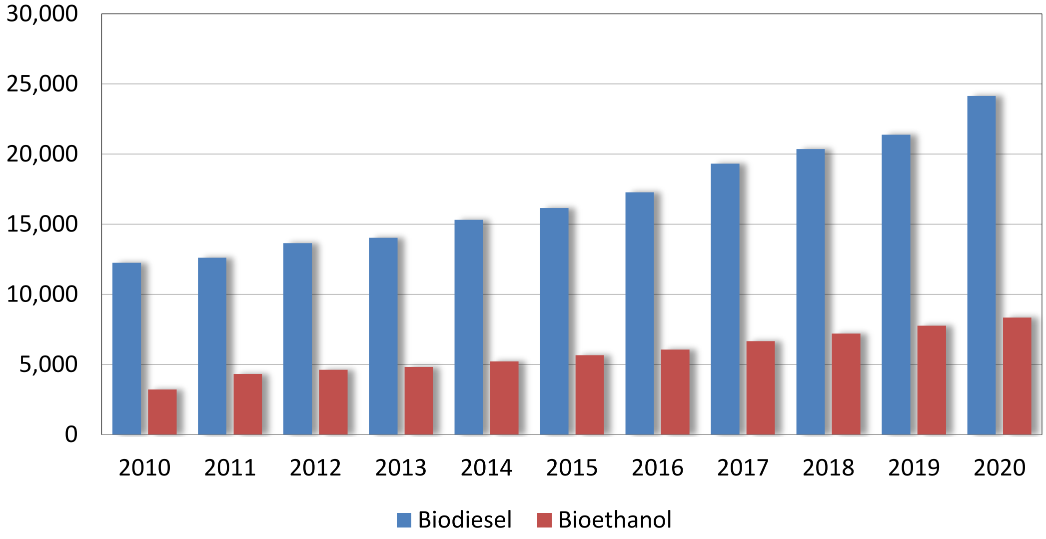

Figure 1.12: EU biofuels consumption forecast 2010-2020 in M tonnes. Source: NREAPs

As is described by [119], the main reasons for this increase in diesel consumption are, on the one hand, the policy framework which is favourable to diesel use, on the other hand, the commonness of diesel powered vehicles, not only for heavy duty but also for low duty passenger vehicles, and, finally, related to the previous ones, the relative cost advantage of diesel over gasoline due to considerably lower taxes.

The increase in diesel consumption is especially due to the heavy duty vehicle transport as shown in fig. 1.14 , where according to the White Paper from the European Commission biofuels are the most expected to contribute, while diesel use in light duty vehicles will decrease due to the possibility of using other fuels and electricity.

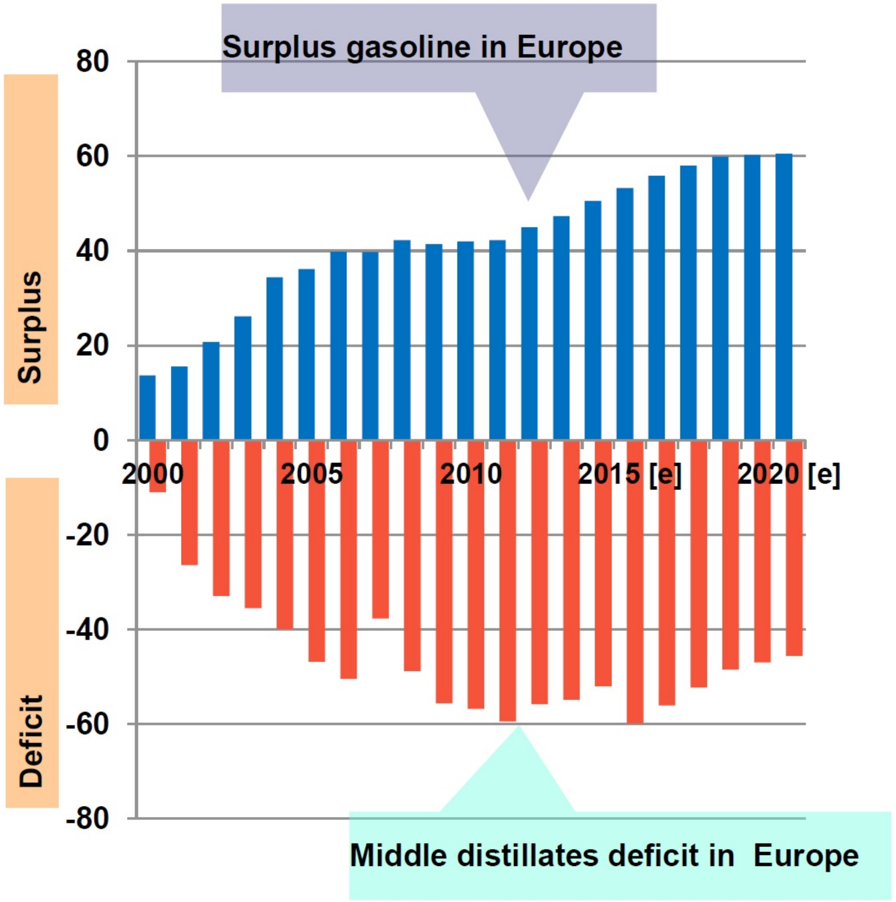

Figure 1.13: Gasoline-middle distillates balances in Europe (Million tonnes). Source: TOTAL [123]

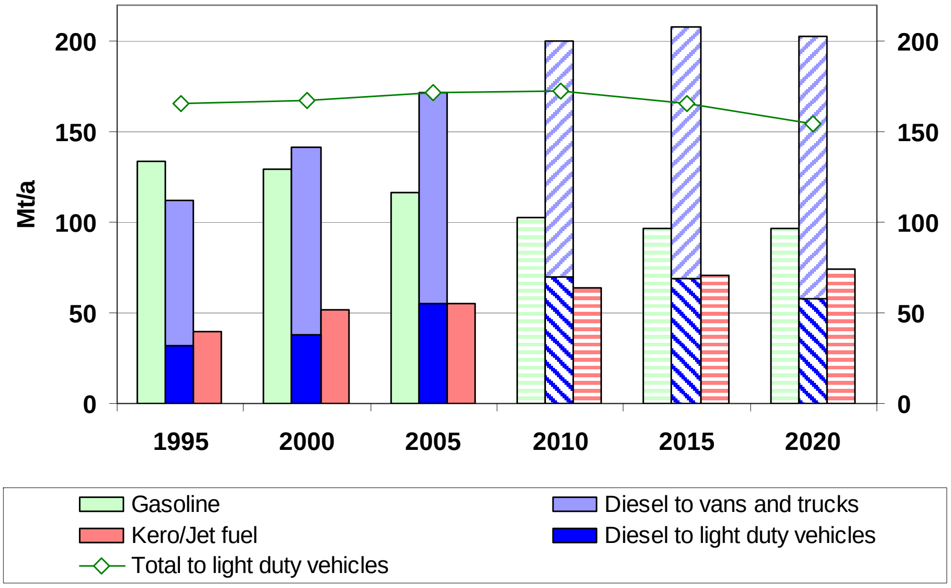

Figure 1.14: Progression of fuels for transport up to 2020. Source: Wood Mackenzie [119]

1.5.4 Biodiesel impact on greenhouse gas emissions

As seen above, biodiesel appears to be the most appropriate biofuel to reduce the consumption of fossil fuels in the transport sector, according to the constellation of the EU market. However, the impact of biodiesel on the greenhouse gas emissions is set to be higher than those of other biofuels, namely bioethanol, when indirect land use change emissions (ILUC) are taken into account as shown in table 1.1.

Table 1.1: Estimated indirect land use change emissions from biofuel and bioliquid feedstocks ($gCO_{2\text{-eq}}$ /MJ). Source: European Community [89]

Feedstock group	Estimated ILUC emissions
Cereals and other starch rich crops	12
Sugars	13
Oil crops	55

Aggregating the values of table 1.1 with the direct emissions savings for several energy crops used for biodiesel and bioethanol production the results of table 1.2 are obtained.

It is important to underline that the addition of the ILUC emissions to the direct emissions is not fully appropriate because they use different methodologies for their calculation. Also, the ILUC emission calculation methodology is put into question by many authors as commented in section 1.7.1.

However, these results show that if the EU aims to decrease the use in diesel fuel for transport by using biodiesel, actions need to be introduced in the production cycles in order to increase the efficiency and achieve higher direct CO_2 emissions reductions to compensate with the indirect ones.

Table 1.2: Typical annual direct savings compared to estimated indirect land use change emissions per crop ($gCO_{2\text{-eq}}$ /MJ). Source: European Community [86]

Feedstock group	Estimated ILUC emissions	Direct emissions savings	Total emissions
Maize for bioethanol	10	-57	-47
Sugar beet for bioethanol	7	-63	-56
Sugar cane for bioethanol	15	-70	-54
Palm oil for biodiesel	54	-39	15
Rapeseed for biodiesel	55	-50	5
Soybean	56	-43	13
Sunflower	54	-58	-4

The numbers of table 1.2, contained in the impact assessment of the European Commission's proposal [89] are calculated with assumptions regarding the expected improvements in greenhouse gas emissions performance of biofuels, as well as changes in the carbon intensity of fossil fuels, as gathered by Londo [162]. The baseline improvements to the GHG emissions of the different chains relate to:

- The introduction of fertiliser (N_2O, N) production in the EU emission trading scheme (ETS) as results of the ambitions of the Climate Directive to reduce greenhouse gas emissions in 20% by 2020.
- Improvements in the feedstock production due to reduction of transport of inputs, management of land, etc.
- Improvements in the efficiency of vehicle engines and long-distance transport.
- Improvements in biofuel processing, assuming a 10% emission reduction in 2020, based on the improvements realised by the food and beverage industry in the past.

In view that the above improvements have already been considered and the emissions are still too high, even higher than fossil diesel in some cases, other solutions need to be applied.

The need to improve the efficiency of biodiesel production and therefore reduce its CO_2 emissions is also very urgent if the proposition of the proposal for a Directive is approved, related to increasing the minimum greenhouse gas emissions savings threshold up to 60% for biofuels and bioliquids produced in installations starting operation after 1 July 2014. According to the Impact Assessment of the proposal [86] it is expected that a threshold of 60% will exclude biodiesel produced from palm oil without methane capture, rapeseed oil and soybean oil from being used, unless improvements are introduced in the production cycles.

Not introducing measures to ensure that these biodiesels exceed the threshold will have economic impacts in Europe if the proposal is approved. Raising the threshold to 60% will require industrial adjustment, and those countries with the largest biodiesel installed capacity (i.e. Germany, Spain, France, Italy and the Netherlands) will be most affected. Moreover, activity will be reduced in related industries such as those involved in the production of vegetable oils/crushing of oil crops for all food/feed/biofuels markets (mainly being present in Germany, France, Spain, the Netherlands and the UK) [86].

For this reason, assessing the biodiesel production plants and life cycles becomes crucial to improve their efficiency and reduce emissions. This PhD proposes the use of exergy for the reasons explained before.

1.6 Life cycle biodiesel exergy assessments

The concept of exergy has been used by many authors in different ways to assess the sustainability of production chains and life cycles, and some of them have specifically applied it to biofuels. Here a short list of papers is presented.

Cornelissen and Hirs [51] analysed the value of the so-called exergetic life cycle assessment (ELCA) and concluded that ELCA is a more appropriate instrument to quantify the environmental problem of the consumption and depletion of natural resources than the conventional life cycle assessments. In particular, they concluded that in the case of mineral resources there is no depletion at all but an increase of irreversibility caused by the need to obtain minerals from poorer and poorer ores which involves a higher loss of natural resources to obtain the same quantity of minerals. This measure of “loss” was done using the concept of exergy.

Dewulf et al. [54] analysed the production chain of soybean and rapeseed methyl esters and corn based ethanol using exergy values in order to evaluate their efficiency and renewability. They calculated the cumulative exergy consumption as the amount of resources both renewable and non-renewable that have to be extracted out of the ecosystem in order to deliver a product.

Unlike this paper, they considered the irreversibility provided by the renewable inputs. As results, they obtained that the biofuels under study had a non-renewable fraction between 24.3 and 34.2.

Hovelius and Hansson [135] studied the energy and exergy efficiency of rapeseed methyl ester production. The exergy analysis was performed for the energy flows according to the *process analysis method*. Unlike this paper, the chemical exergy of the materials was excluded. They concluded that the energy ratio of the production chain was 2.4 while the exergy ratio was 3.0 for the same process thus showing differences, specially caused in the processes where steam was used.

Laura Talens et al. [221] produced a so-called Exergy Flow Analysis (ExFA) to biodiesel production from used cooking oil, in order to analyse the loss of exergy along the production process. They also performed Extended Exergy Accounting [222] to biodiesel from used cooking oil and rapeseed oil by including in the analysis the externalities (capital, labour and environmental impact) measured in homogeneous units (GJ).

Velásquez et al. [246] used exergy accounting in palm oil biodiesel production process and proposed a renewability performance indicator defined as ratio of the net exergy associated to the products to the non-renewable energy used and the deactivation exergy of the wastes. As results they concluded that palm oil biodiesel production was a friendly environmental process with a renewability of 29.1.

Berthiaume et al. [19] also used exergy to calculate the renewability of a biofuel. In this case, the renewability indicator not only took into consideration the cumulative exergy consumption from non-renewable energy sources but also the exergy needed for the restoration of the altered environment to its initial state when these resources were used. Taking these factors into account they concluded that corn based bioethanol was not sustainable.

None of the articles calculated the exergy costs of the life cycle production using the exergy cost theory as applied in this PhD and explained in chapter 3. In addition, most of the analyses only consider the non-renewable energy consumption meanwhile this paper analyses the consumption of non-renewable resources, being these energy or material flows. In any case, independently of the specificities of the different analysis all the authors coincide to point out that the use of exergy provides a better instrument for life cycle and process analysis than the use of energy.

1.7 Environmental considerations not covered in this thesis

Besides the greenhouse gas emissions reductions, biodiesel production may have other positive and negative impacts. These impacts although considered very important, cannot be evaluated using thermoeconomics either because there is no clear methodology to calculate them or because they are of a social nature. Even if not the focus of analysis in this Ph.D., they deserve to be shortly mentioned in this introductory chapter as well as the possible solutions to tackle them. Here, only the negative impacts are mentioned, although it is clear that, according to the IEA [140], if well-managed and coordinated with investments in infrastructures and agriculture, biofuels can provide an opportunity for increasing land productivity and creating economic development, particularly in rural areas of developing countries, while reducing greenhouse gas emissions.

1.7.1 Indirect land use change (ILUC)

Indirect land use change (ILUC) has already been mentioned above as one of the possible factors of greenhouse gas emissions of biofuel production. This is one of the most important issues at stake in biofuels policy nowadays.

ILUC is defined as the land use change that would be produced when biofuel production displaces the production of other commodities (e.g. food or feed), which are then produced on forest land converted elsewhere (perhaps in another region or country). The deforestation of forest land would then contribute to increase the GHG emissions associated with biofuels production.

While it is generally acknowledged that biofuels provoke indirect land use change (as any other economic sector) there is no agreement on the magnitude of the impact.

No agreed methodology has been developed to measure the impact of biofuels in ILUC and there is a high uncertainty on the quantification of the impact. The European Commission stated in the report on indirect land use change related to biofuels and bioliquids [78] that there are several remaining deficiencies and uncertainties associated with the modelling of the indirect land use change and therefore, at the time when the Communication was published did not approve any specific measure. The new proposal for a Directive [89] has confirmed this point and even though it includes the proposal to monitor the ILUC emissions in the reporting of greenhouse gas emissions from biofuels these are not taken into consideration in the mandatory emission reduction thresholds.

The numbers of ILUC emissions shown in table 1.2 are obtained from the study known as IFPRI report [156]. The European Commission considers this work to represent the best available science with regards to the estimated indirect land use change impacts associated with biofuels consumed in the EU [86].

However, there are scientists that challenge the results and methodology used by IFPRI [129, 157]. A recent study [52] carried out by US and Canadian researchers and commissioned by the European Biodiesel Board using another methodology, based on the GTAP model, used by the Californian Low Carbon Fuel Standard [31]. Using a different method and different assumptions this new study shows discrepancies of up to 95%.

The ILUC methodology of the IFPRI study is based on the MIRAGE model, a general equilibrium model which is used to project the effects of increased biofuel production on a global land and commodity markets, following the next procedure, as described by Lahl [157]:

- first, the additional land brought into production to compensate for land removed from other uses to produce biofuels is calculated, determining the approximate location of this land.
- then, the resulting land use changes are mapped to specific land cover types based on historical patters of land use.
- for each category of land cover conversion, the quantity and time profile of GHG emissions from land use conversion are estimated.
- finally, the GHG emissions induced by the expanded biofuel production are attributed to a quantity of fuel, usually defined with reference to a time period of fuel production.

As compiled by Hamelinck [129], the criticisms to the methodology and calculations made by IFPRI are related, among other aspects, to the selection of the time period, which might me considered too short on the time scale of the climate problem; the data on soil carbon loss, which might be lower than considered; the accountability of the material or energy use of cleared biomass; the types of land converted and marginal activities considered; the yields on new land, which might be too low compared to practice; and the accountability of crop rotation, set-aside lands and unused land.

But the most important criticism is the scientific consistency of the principle of applying the ILUC concept in isolation only for biofuels. The indirect land use change is actually the direct land use change from another sector. Therefore the real causes of land use change are not solved. If direct land use change policies were applied to all sectors, there would not be indirect changes. However, applying such policies would be burdensome to some sectors risking their economic viability.

Establishing an ILUC policy for biofuels will set a precedent to evaluate other policies for indirect effects, for example, the EU policy on reduction in agricultural acreage which also causes ILUC.

On the other hand, if ILUC factors are applied to biofuels, for a fair competition, the same rules should apply to the fossil fuels for which they are compared. This would include for example the indirect military GHG emissions from Middle Eastern petroleum extraction. According to Liska and Perrin (2009) these emissions would rise the GHG intensity of gasoline by roughly twofold [157].

Finally, if biofuel replace the marginal fossil fuel productions, e.g. shale oil, deep sea oil, Arctic oil, tar sand oil and synthetic oil from coal, which are the most costly ones, the comparator should be the one having higher GHG emissions, which in the end may also have the highest ILUC emissions.

In view of the uncertainty raised by the ILUC concept and its calculation methodology, governments and organisations are opting for other solutions. Some government programmes (for example the California Low Carbon Fuel standard [31]) have opted for adding a penalty to the GHG balance so that biofuel producers should demonstrate higher emission reductions to be accounted for the target.

A different solution applied in Brazil has been introducing a zoning programme so that the biofuel producers are entitled to harvest the crops by increasing the cattle density, without the need to convert new land to pasture.

An amendment in the European Parliament to the proposal for a Directive introducing the ILUC term asks for the creation of an annual country list with regional direct land use changes so that biofuels from countries or regions in which emissions from direct land use changes (LUC) amount to more than 35% of the emissions of fossil fuels (30 g $CO_{2\text{-eq}}$ / MJ) calculated for the whole country or region in accordance with the established methodology shall not be taken into account in the renewable energy target for transport. This proposal is interesting taking into account that JRC studies assumes that around 75% of the entire ILUC provoked from EU biofuel goals will be caused in Indonesia/Malaysia and Brazil, as mentioned by Lahl [157]. The United Nations Collaborative Programme on Reducing Emissions from Deforestation and Forest Degradation in Developing Countries (REDD) could be part of the solution, as well as providing incentives for those countries introducing good governance practices to avoid the spread of deforestation.

Other organisations propose methodologies to limit the indirect impacts of biofuel policies, for example the Low Indirect Impact Biofuels (LIIB) methodology established by Ecofys or the Integrated Food Energy System (IFES) methodology defined by FAO.

Whatever the solution will be, it is clear that there is much uncertainty on how to measure the ILUC impact. Figure 1.15 shows the ranges of model-based quantifications of direct and indirect land-used chance which have been assessed by many authors [18, 29, 56].

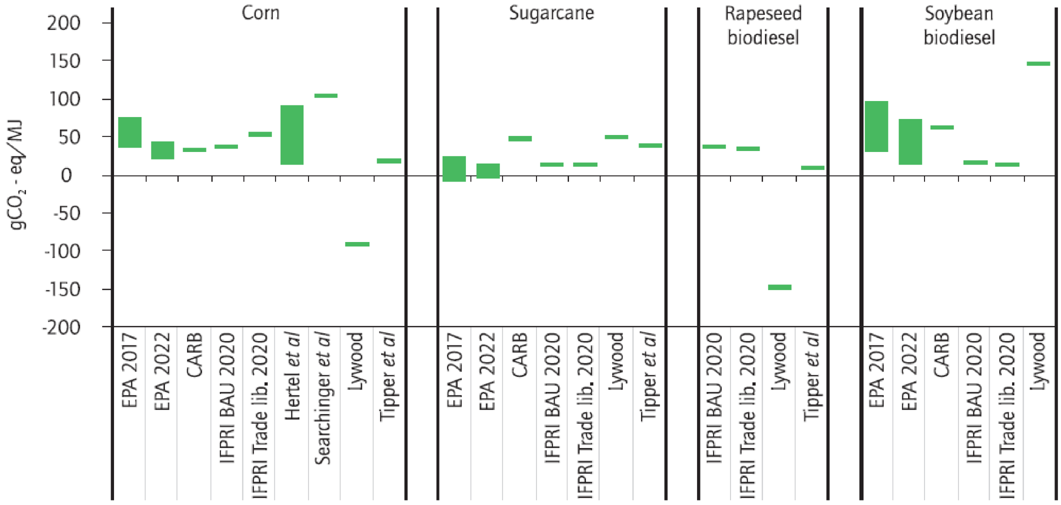

Figure 1.15: Ranges of model-based quantifications of land use change (direct and indirect) for selected biofuel/crop combinations. Source: IEA Bioenergy, 2012 [18]

At this stage, due to the uncertainty it is evident that there are not sufficient grounds to include greenhouse gas emissions from ILUC in the life cycle production assessments of this Ph.D.

On the other hand, it is important to note that emissions related to current biofuel production generate only around 1% of the total emissions caused by land-use change globally, according to [18], most of which are produced by changes in land use for food and fodder production, or other reasons. This is explained in the IEA biofuels technology roadmap [29].

In any case, as mentioned in a previous paragraph, it will be assessed whether the proposed improvements are enough to counterbalance the increase in the emissions due to this factor. In addition, it will be assessed in a qualitative point of view whether they may contribute to increase or reduce the land use change. In this respect, the IEA has identified routes where the risks of land use change and resulting emissions can be minimised and in some cases be negative. Some of these routes are considered in this PhD. and include:

- focusing on wastes and residues as feedstock;
- maximising land-use efficiency by sustainably increasing productivity and intensity and selecting high-yielding feedstocks;
- using perennial energy crops, particularly on unproductive or low-carbon soils;
- maximising the efficiency of feedstock use in the conversion processes;
- cascade utilisation of biomass, i.e. linking industrial and subsequent energetic use of biomass;
- co-production of energy and food crops.

1.7.2 Food security

Since the global food crises of 2007–2008 another debate that has increased considerably is the impact that biofuels (and bioenergy in general) may have over the food supply and prices (the so called "food vs. fuel" debate) when using arable land to produce energy crops. At that time, many international bodies, lobbies and NGOs blamed biofuels of the increase of food prices [30].

However, after the food crises ended and food prices were reduced to similar levels as before the crises, as shown in fig. 1.16 for wheat, maize and rice [158], reports concluded that the impact of biofuels had not been so great. The latest analyses suggest that a combination of high oil prices, poor harvests and use of commodities by financial investors probably had a considerably higher impact on food prices than biofuel production (World Bank, 2010) [29].

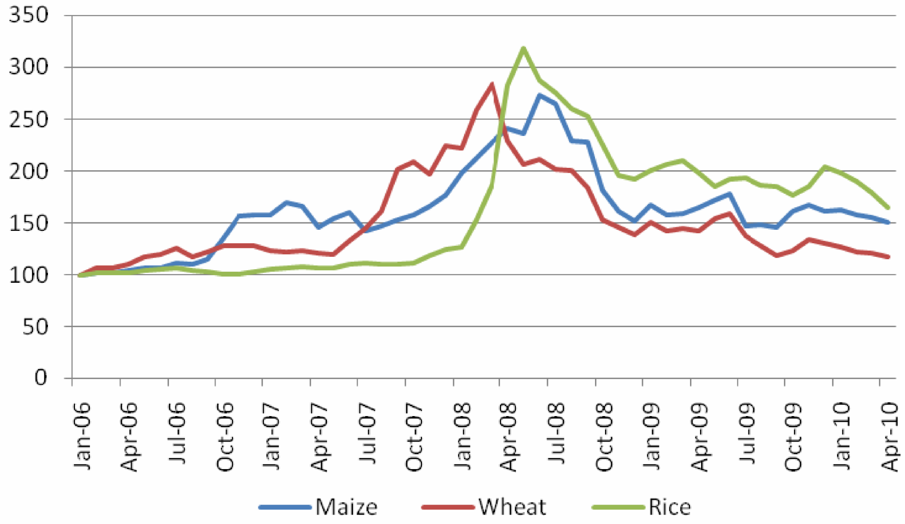

Figure 1.16: Cereal prices (US$) from January 2006 to April 2010. Source: IISD, 2012

The detailed overview of the main regional markets of importance to EU biofuel production, as provided by the report prepared for the Commission by Ecofys [62], does not suggest any direct link between the biofuel production and local food price increases [91]. The European Commission considers that biofuels could have influence only 4% in the price of vegetable oils from 2000 to 2010, which is a modest increase.

In addition to that, a report from FAO [126] suggests that roughly one-third of food produced for human consumption is lost or wasted globally, which amounts to about 1.3 billion tons per year. This inevitably also means that huge amounts of the resources used in food production are used in vain, and that the greenhouse gas emissions caused by production of food that gets lost or wasted are also emissions in vain. Figure 1.17 shows the part of the initial production lost or wasted at different stages in the food supply chain for oilseeds and pulses in different regions. This information downgrades the ILUC and food vs. fuel debates.

In spite of the above, the issue is still a hot topic. Recent studies published just before the vote at the European Parliament of the proposal for a Directive amending the Renewable Energy Sources Directive [89, 99] in September 2013, provide contradictory results: one prepared by the JRC, Institute for Prospective Technological Studies, suggesting that biofuel policies can have a great impact of food prices in 2020 [134] and another produced by Ecofys by order of ePURE concluding among other aspects that systemic factors, like reduced reserves, food waste, speculation, transportation issues, storage costs and problems, and hoarding play a much larger role in local food prices [128].

As this conflict still continues, food security remains a critical topic for the design of sound biofuel policies. International institutions work to understand better the role between the biofuels industry and the food market. The European Commission included in the Renewable Energy Directive [99] a provision to evaluate every second year the impact of biofuels on social sustainability in the Community and in third countries of increased demand for biofuel, on the impact of Community biofuel policy on the availability of food stuffs at affordable prices, in particular for people living in developing countries, and wider development issues.

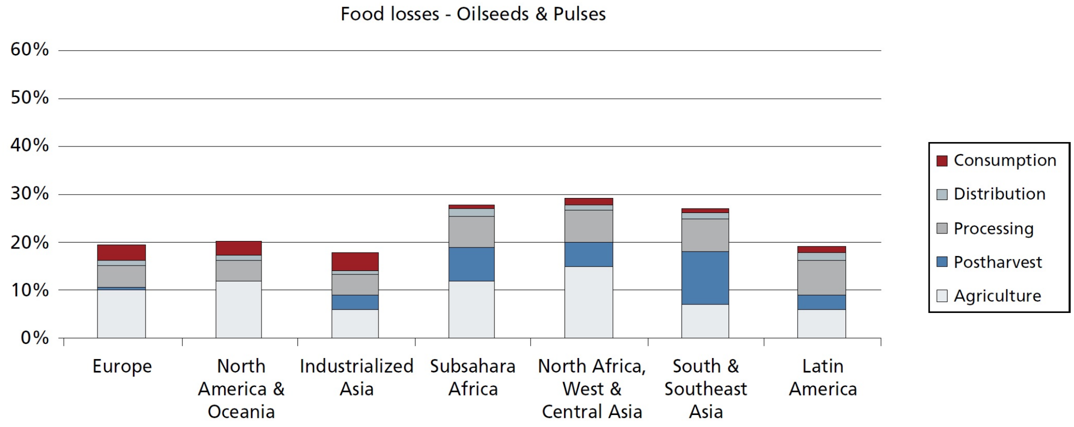

Figure 1.17: Part of the initial production lost or wasted at different stages in the food supply chain for oilseeds and pulses in different regions. Source: FAO, 2011

In addition, the United Nations Food and Agricultural Organisation (FAO) published a document providing guidance to governments on the way to assess and respond at national and project level to the potential impacts (either positive or negative) that the bioenergy production might have concerning food security [106]. This document is part of FAO efforts to better understand when bioenergy has positive or negative effects on food security. At the national level, the assessment focuses on the indicator of price and supply of a national food basket. At the project level the guidelines examine how an existing or planned agricultural operation comprises a number of indicators to address key environmental and socio-economic aspects of agriculture operations linked to food security. The guidelines identify a range of responses to address impacts at the national and project level. In examining the sustainability of bioenergy investments, the report notes the important role played by the time horizon of the activity, and the scale where impacts may be felt.

Also, the UK Department for Environment, Food and Rural Affairs (Defra) published in June 2012 a report proposing a system of flexible mandates [60]. With this system, mandates (i.e. mandatory targets for the introduction of biofuels into the transport sector) would be reduced temporarily during food price spikes. Indeed, biofuel mandates have led to increased agricultural production relative to a state of the world with no biofuel mandates - this extra supply could follow market forces onto food or animal feed markets during a price spike, if the mandates allowed it. Biofuels would therefore have the positive effect of creating a “virtual grain store”.

1.7.3 Land availability

One aspect to be considered when dealing with the ILUC and food versus fuel debate is the availability of arable land. This is of great importance if taking into account the world's population is estimated to reach 9.1 billion by 2050, leading to a 70% increase in global food demand (FAO, 2009). According to FAO projections, 90% of the additional crop demand could be met with higher yields and increased cropping intensity, but nonetheless a net expansion of arable land by about 70 million ha would be needed.

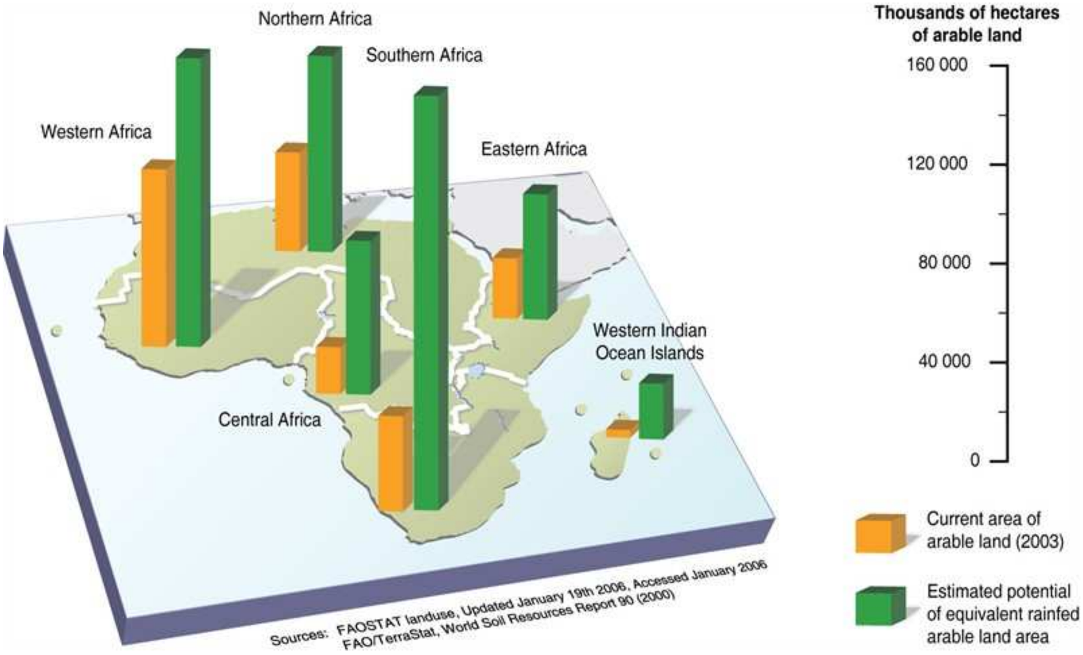

Figure 1.18: Areas of arable land in 2003 and estimated. Source: Ahlenius, UNEP

The exact extent to which land availability is limited globally and which percentage of land could be used for biofuels production is much debated. The globe has approximately 13,200 million ha of land, of which around 1,600 million ha is used for cropping (107 million ha in the EU). The land used for biofuels is 30 million ha (this number does not take into account the land savings due to the co-product production).

The IPCC special report on renewable energy estimates that 780 million ha of land are available for bioenergy production without irrigation worldwide (14% in Europe) amounting to more than 4,000 million toe [229].

Even though biofuel production is occupying arable land, compared to 1981 the harvested land has significantly declined in Europe, Commonwealth and North America, thus suggesting that there would be land available to increase food and biofuel production. Figure 1.18 [4] shows the potential arable land available in Africa. With regard to the EU, it is expected that the agricultural area will continue to reduce by around 0.5 million hectares each year [86].

On the other hand, there are estimates of the availability of marginal land for bioenergy production. Hoogwijk estimates that between 430 and 580 Mha of land is marginal and can potentially be used. However, other authors suggest that these estimates are at least 10-times too high [86].

It should be analysed whether the available land, be it marginal or not, could contribute to increase agricultural production without significant emission increases due to land use change. This analysis is not covered in this PhD.

1.7.4 Other impacts on sustainability and certification schemes

Besides the impacts mentioned above, there are other impacts on the environment, economy and society that need to be considered or studied. These are, for example:

- On the social pillar: Smallholder integration
- On the environmental field: Soil quality, water use and quality
- In the economic arena: Balance of payments, Financing, Fuel cost

The Renewable Energy Sources Directive 2009/28/EC [99] establishes that the Commission shall present a report, addressing, in particular, among other aspects, an assessment of the feasibility of reaching the target whilst ensuring the sustainability of biofuels production in the Community and in third countries, and considering economic, environmental and social impacts, including indirect effects and impacts on biodiversity, as well as the commercial availability of second-generation biofuels.

In March 2013, the European Commission published a first progress report [95] on the implementation of the Directive 2009/28/EC which assessed the sustainability of biofuels and bioliquids consumed in the EU and the impacts of this consumption in accordance with the Directive. The report concludes that additional separate biofuels-specific measures are not necessary. That said, the Commission will continue to monitor these impacts and might take future action if considered necessary.

Even though for the moment, no additional requirements are necessary, there are many initiatives worldwide that are trying to identify sustainability indicators for biofuels at global level regarding these additional issues to prevent future negative impacts.

One of them is the Global Bioenergy Partnership (GBEP). The GBEP is an initiative stemming from the G8 + 5 (Brazil, China, India, Mexico and South Africa) meeting in Gleneagles in 2005. The countries represented at that meeting agreed to "*... promote the continued development and commercialisation of renewable energy ... launching a Global Bioenergy Partnership to support wider, cost effective, biomass and biofuels deployment, particularly in developing countries where biomass use is prevalent*".

The GBEP comprises 23 countries and 13 international organizations and institutions: Argentina, Brazil, Canada, China, Colombia, Fiji Islands, France, Germany, Ghana, Italy, Japan, Mauritania, Mexico, Netherlands, Paraguay, Russian Federation, Spain, Sudan, Sweden, Switzerland, Tanzania, United Kingdom, United States of America, Economic Community of West African States (ECOWAS), European Commission, Food and Agriculture Organization of the United Nations (FAO), Inter-American Development Bank (IDB), International Energy Agency (IEA), International Renewable Energy Agency (IRENA), United Nations Conference on Trade and Development (UNCTAD), United Nations Department of Economic and Social Affairs (UN/DESA), United Nations Development Programme (UNDP), United Nations Environment Programme (UNEP), United Nations Industrial Development Organization (UNIDO), United Nations Foundation, World Council for Renewable Energy (WCRE) and European Biomass Industry Association (EUBIA).

In December 2011, The GBEP produced a first version of Sustainability Indicators for Bioenergy [124] which presents 24 voluntary sustainability indicators for bioenergy focusing in the three areas mentioned above.

In addition, the EU has recognised the following certification schemes to certify the sustainability of the biofuels consumed in the EU. These schemes need to comply with the mandatory sustainability criteria described in a previous paragraph, and may also include other criteria to cope with aspects of the three pillars mentioned above:

1. ISCC (International Sustainability and Carbon Certification)
2. Bonsucro EU
3. RTRS EU RED (Round Table on Responsible Soy EU RED)
4. RSB EU RED (Roundtable of Sustainable Biofuels EU RED)
5. 2BSvs (Biomass Biofuels voluntary scheme)
6. RBSA (Abengoa RED Bioenergy Sustainability Assurance)
7. Greenergy (Greenergy Brazilian Bioethanol verification programme)
8. Ensus voluntary scheme under RED for Ensus bioethanol production
9. Red Tractor Farm Assurance Combinable Crops & Sugar Beet (Red Tractor)
10. Scottish Quality Farm Assured Combinable Crops Limited (SQC)
11. REDcert
12. NTA 8080
13. Roundtable on Sustainable Palm Oil RED
14. Biograce GHG calculation tool

1.8 Scope, objectives and structure of the Thesis

The previous paragraphs have set the scope of this Ph.D. in a step-by-step conception which is summarised in the chart of fig. 1.19.

To sum up, the humankind is facing a two-sided climate and energy dilemma. Both issues are strongly related to the consumption of oil. In order to solve this problem Nations are putting forward policy instruments to reduce the consumption of fossil fuels, among them the promotion of the production and consumption of renewable energies. Bioenergy is the most used renewable energy source nowadays and its role in the future is set to increase. This is of special importance in the transport sector where the dependence from fossil fuels is more significant. The transport sector is dependent on oil in around 98% in the EU and is the only economic sector which emissions are set to increase in the future. Biodiesel, as a natural substitute to diesel fuel, is one of the most important transport fuels especially in Europe. However, the net greenhouse gas emission savings of bioenergy depend on the production process. It could be the case that bioenergy production can produce more greenhouse gas emissions than the diesel fuel comparator. This is especially the case of biofuels produced from energy crops and more specifically of biodiesel which has higher emission factors. For this reason the EU has proposed an amendment to the policy framework in order to ensure that biofuels produce actual net greenhouse gas savings to a specific threshold. If this framework is finally adopted, biodiesel from certain energy crops could be excluded from use in the EU if the production processes are not improved.

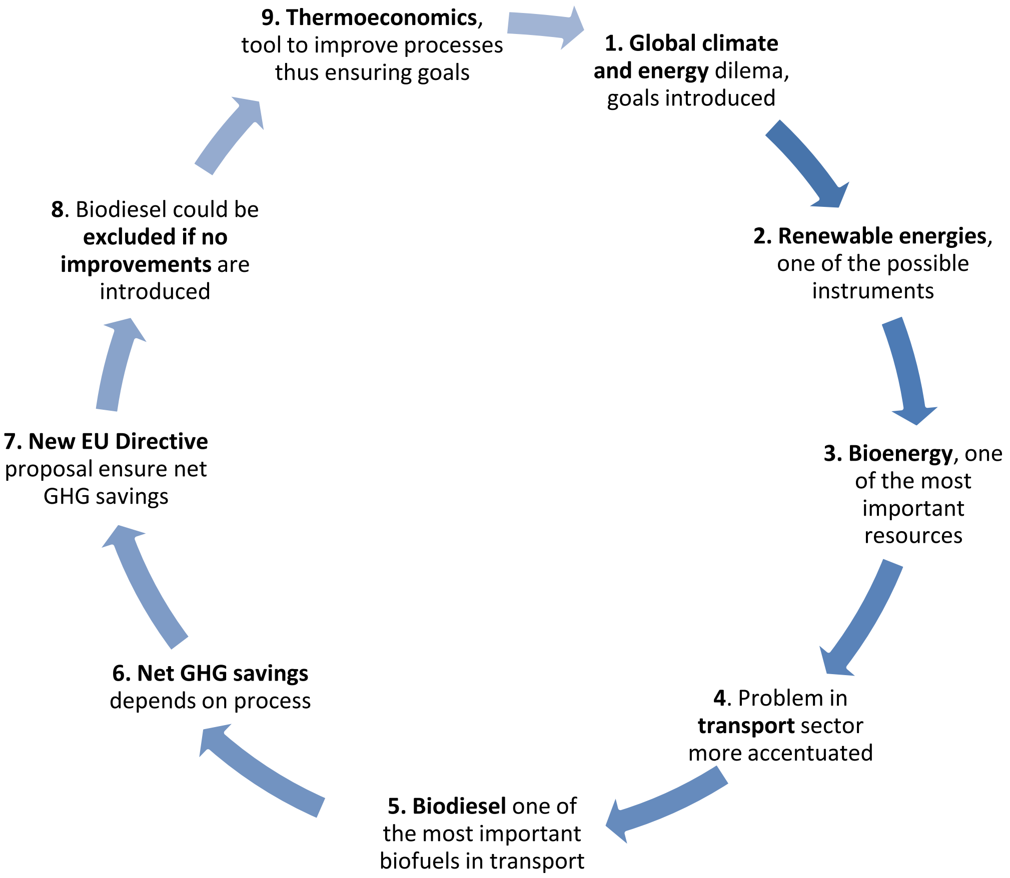

Figure 1.19: Step-by-step conception of this thesis

Thermoeconomics is proposed in this Ph.D. as method to analyse the additional improvements that can be introduced in order to maintain the biodiesel sector in Europe. It provides the tools to analyse the detailed processes to identify inefficiencies and propose solutions like:

- process integration
- substitution
- components' efficiency improvements
- flows recirculation

O'Connor [187] modelled the potential reductions in the GHG emissions that could be obtained by introducing improvements in the cycle. These include, no till management practices, the use of controlled release nitrogen fertilizer to reduce N_2O emissions, increased oil content of the seeds and lower energy consumption in the oilseed crushers and biodiesel processors. Part of the proposed improvements are re-assessed in this work from a thermoeconomic viewpoint, with other additional improvements such as the use of organic fertilisers, taking profit of the straw as valuable co-product in the cultivation, anaerobic digestion of cake in the oil extraction, use of bioethanol or biomethanol at the transesterification stage, recirculation of biodiesel in the process and anaerobic digestion of glycerol.

This work aims to provide an objective evaluation of the CO_2 emission reductions derived from the implementation of the proposed improvements stemming from the application of the thermoeconomic methodologies. It also assesses the socio-economic impacts of these measures.

In addition, this work also presents the application of thermoeconomics to a transesterification plant. The aims of this exercise are, on the one hand, demonstrating the usefulness of the exergy cost analysis applied to an industrial bioenergy production plant and, on the other hand, identifying which of the vegetable oil materials presents a higher consumption of exergy, where the irreversibilities are located and how these irreversibilities can be reduced.

The Ph.D. has been structured as shown in the fig. 1.20, in a sequential manner, to respond to the above mentioned aims.

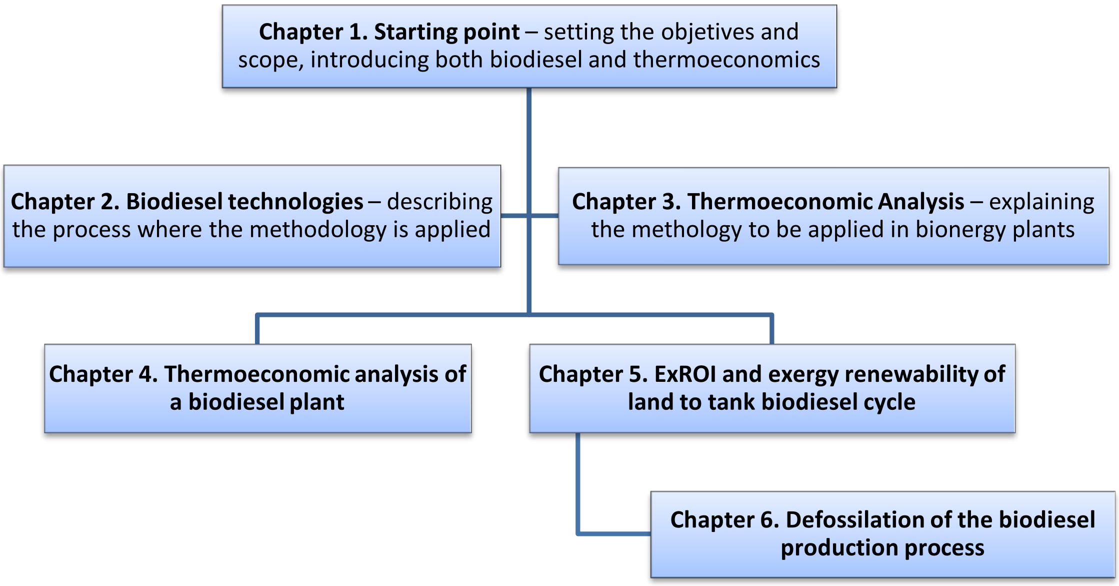

Figure 1.20: Logical structure of the Ph.D

1.8.1 Scientific publications derived from this Ph.D

Some of the developments and results obtained in this thesis have been presented in different scientific conferences and published in international journals:

The concepts and calculation methodologies of the ExROI and Renewability ratio and preliminary results applied to land-to-tank biodiesel productions were presented in the ECOS 2011 conference in Novi Sad, Serbia, and were published in the scientific journal Energy in 2012 [111].

Once the preliminary results of ExROI applying improvements in the life cycles were obtained, as explained in chapter 6, these were presented in the ECOS 2012 conference in Perugia, Italy and have been published in the International Journal of Thermodynamics in 2013 [112].

The results of the work have been used in a presentation to the International Energy Agency Advanced Motor Fuels IA ExCo 44 in 23 – 26 October 2012.

Other scientific publications published by the author related to the field of study are:

1. Font de Mora, E., Dubolino, D., Vivarelli, S., Bioenergy markets in the EU - How the Intelligent Energy – Europe is contributing, European Energy Innovation, 2012.

2. Font de Mora, E. The theory of exergy cost applied to various biodiesel production process and life cycles. Poster presentation at the 2009 UKERC Annual Assembly ans Summer School, July 9, 2009.
3. Lapuerta, M., Fernández-Rodríguez, J., Font de Mora, E. Correlation for the estimation of the cetane number of biodiesel fuels and implications on the iodine number. Energy Policy, 2009.
4. Balda, M., Font de Mora, E., Contreras, T., Manso, A. Desarrollo y aplicaciones de los biocarburantes, CONAMA9, Spanish National Environment Congress, 2008.
5. Font de Mora, E. Biocarburantes y ayuda al desarrollo. Ventajas sociales, oportunidades de financiación europea y proyectos de la ONU. Engineers without borders, 2006.

Chapter 2

Biodiesel technologies from land to tank

Biodiesel can be produced from many vegetable oils and animal fats, i.e. materials containing high contents of triglycerides. In a wider definition of biodiesel, it can be assumed that these raw materials can be processed in many ways to produce the final fuel called biodiesel. These processes are: vegetable oil direct use and blending, micro emulsification, hydrotreatment and transesterification.

Depending on the raw material and technology selected, the properties of biodiesel will vary significantly, and therefore also its ulterior use in vehicle engines. In addition, there are significant variations in the use of resources along the production chain.

Among the mentioned processes, transesterification has become the most accepted technology. This is the reason that many sources only consider as biodiesel the fatty acid alkyl esters obtained from transesterified oils and fats and this is why this Ph.D is mainly focused on this technology.

The main aim of transesterification is to lower the viscosity of the oil in order to make it useful in conventional internal combustion diesel engines. The main raw materials used nowadays are vegetable oils from agricultural origin, mainly rapeseed, soybean, sunflower and palm oils. Used cooking oils and animal fats are also common sources for biodiesel production. Other raw materials such as algae are being investigated.

This chapter gathers the main characteristics of the materials used for producing biodiesel and describes the technological steps for the production of biodiesel from land to tank. Finally, it shows the main properties of the biodiesel fuels obtained from these materials and processes.

2.1 Definition of biodiesel

Biodiesel can be defined as an alkyl ester produced by the transesterification reaction of triglycerides of a vegetable oil or an animal fat with a short-chain alcohol, normally methanol or ethanol. In Europe the alcohol commonly used is methanol due to its relative lower cost compared to ethanol. In this case, biodiesel is also called fatty acid methyl ester (FAME) [208].

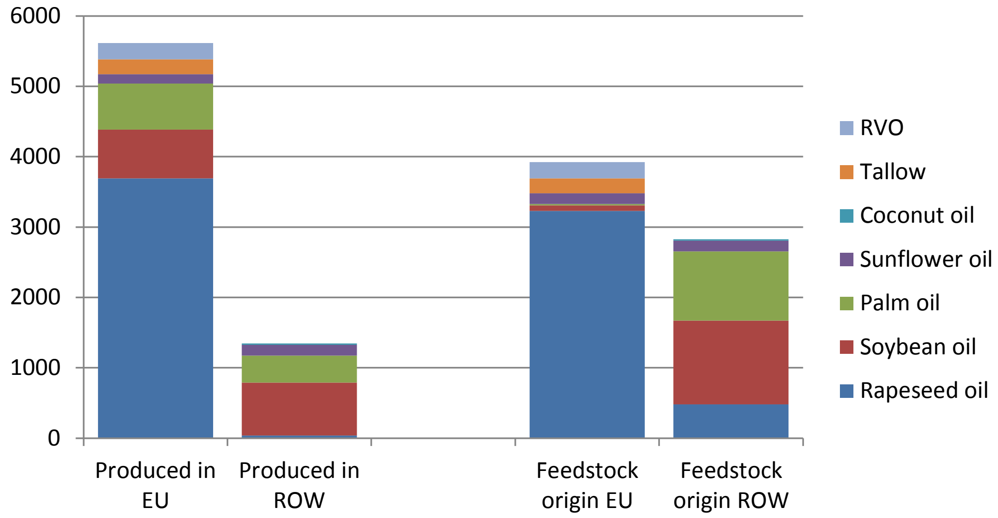

Figure 2.1: Feedstock used for biodiesel consumed in 2008 in the EU and the rest of the World (ktoe). Source: Peters et al. [62]

The fig. 2.1 shows [1] the main vegetable oils used for biodiesel production [193], where rapeseed oil is the most important one due to the higher production in the EU, followed by soybean and palm oils.

Due to its characteristics methyl esters can be used in compression-ignition engines, i.e. diesel vehicles, and in gas-oil static engines for the production of electricity and/or heat. As biodiesel has similar densities and viscosities to the conventional fossil diesel oil, a better lubricity and a higher cetane number, its combustion in a diesel engine is very suitable and even better than when fossil diesel is used [16].

Methyl esters may be used as a pure fuel (100% biodiesel, also called B100) or blended with conventional diesel [152]. In a pure state, vehicles may require small adaptations which should be homologated by the car manufacturer. As regards blends, there is some uncertainty regarding how much biodiesel can be blended with diesel, while maintaining associated warranties from car manufactures. In Europe, this is regulated by the Fuel Quality Directive 2009/30/CE [100] and the European quality standard EN 590 for diesel fuel used as an automotive fuel [37], which include a maximum blending level of 7% in volume. Work is currently under way in the European standardisation body (CEN) to develop standards for B10 (up to 10% v/v) for cars and B30 for heavy duty engines, probably only for captive fleets.

Even though generally, carmakers do not guarantee the use of blends higher than the percentage stipulated in EN 590, many studies have demonstrated that conventional engines can work without any modification with blends with less than 30% (in volume basis) of biodiesel.

In France, there is an association called *Partenariat Diester* [57] which objective is to promote the use of diesel/biodiesel blends at 30% (V/V) in captive fleets of light and heavy duty vehicles. According to data published by this association in 2006 more than 6,000 vehicles run with this type of blend. At the end of 2007, the number of vehicles exceeded the 8,000 vehicles.

Another experience described by Gateau in [121] evidences that high biodiesel blends can be used without problems: during twelve years (from 1993 to 2005) a fleet of 14 light duty vehicles

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[1] RVO stands for recycled vegetable oils/UCO

(10 direct injection engines and 4 common rail and particulate filter) and 20 trucks (Euro 0 and Euro 3) used a 50% (V/V) blend and pure diesel fuel (this last to be able to compare results). According to the results of the experience, none of the engines showed different behaviours when running with one or other fuel.

This thesis does not have as aim positioning on one side or another of this controversy. Either in low or high blends, biodiesel will continue to be consumed in compression-ignition engines.

Biodiesel, independently of its use (pure or blended) must comply in Europe with the quality standard EN 14214 [36,208] This standard sets the minimum and maximum contents of elements and compounds that fatty acid methyl esters may have. Table 2.1 shows the specifications.

Table 2.1: Biodiesel fuel quality requirements according to EN 14214

Property	Units	lower limit	upper limit	Test-Method
Ester content	% (m/m)	96.5	-	EN 14103
Density at 15 °C	kg/m^3	860	900	EN ISO 3675 EN ISO 12185 EN 12185
Viscosity at 40 °C	mm^2/s	3.5	5.0	EN ISO 3104 EN 14105
Flash point	°C	$>$ 101	-	EN ISO 2719 EN ISO 3679
Sulphur content	mg/kg	-	10	EN ISO 20846 EN ISO 20884
Carbon residue remnant (at 10% distillation remnant)	% (m/m)	-	0.3	EN ISO 10370
Cetane number	-	51.0	-	EN ISO 5165
Sulphated ash content	% (m/m)	-	0.02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper band corrosion (3 hours at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Oxidation stability,110 °C	hours	6	-	EN 15751 EN 14112
Acid value	mg KOH/g	-	0.5	EN 14104
Iodine value	-	-	120	EN 14111
Linolenic Acid Methyl ester	% (m/m)	-	12	EN 14103
Polyunsaturated (>= 4 Double bonds) Methyl ester	% (m/m)	-	1	EN 14103
Methanol content	% (m/m)	-	0.2	EN 14110
Mono-glyceride content	% (m/m)	-	0.8	EN 14105
Di-glyceride content	% (m/m)	-	0.2	EN 14105
Triglyceride content	% (m/m)	-	0.2	EN 14105

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Property	Units	lower limit	upper limit	Test-Method
Free Glycerine	% (m/m)	-	0.02	EN 14105 EN 14106
Total Glycerine	% (m/m)	-	0.25	EN 14105
Group I metals (Na+K)	mg/kg	-	5	EN 14108 EN 14109 EN 14538
Group II metals (Ca+Mg)	mg/kg	-	5	EN 14538
Phosphorus content	mg/kg	-	4	EN 14107

2.2 Overview on biodiesel developments

2.2.1 Worldwide, European and Spanish production and consumption

Biofuels have been produced commercially in both the United States and Brazil for several decades. However, the sector has grown the fastest in the past ten years, driven by policy support in over 50 countries. Figure 2.2 shows the blending mandates and targets in 20 countries worldwide [142].

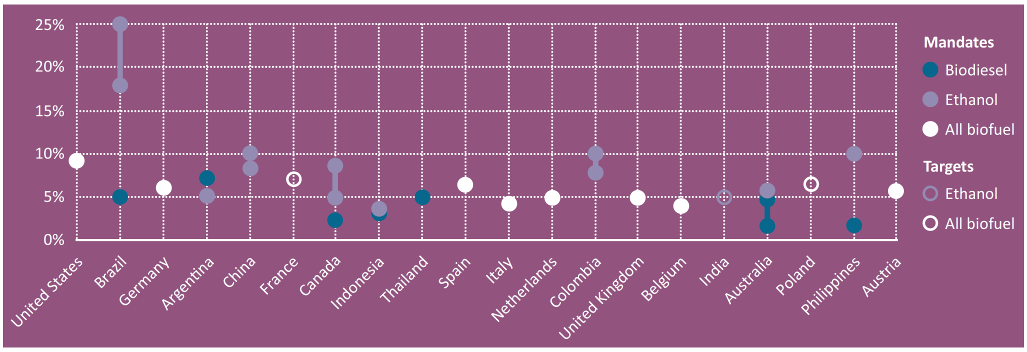

Figure 2.2: Blending mandates and targets in key countries. Source: IEA, 2013 [142]. Some mandates might have been modified at the time of defending this Ph.D, e.g. in Spain

Globally, in 2012 biofuels accounted for around 3.4% of road transport fuels [200] when in 2011 the share was 2.3%. The most considerable contribution is due to Brazil (21.1%) with an increasing share in the United States (about 4.4% in 2010) and the European Union (about 4.2% in 2010). Global biofuels production grew from 16 billion litres in 2000 to more than 110 billion litres in 2012 [142]. Worldwide, bioethanol is the most produced biofuel as it can be shown in fig. 2.2. Biodiesel is not as well established or developed as the bioethanol industry globally. According to [234], industry analysts indicated that in 2010 global biodiesel production accounted 17.6 billion litres and REN21 estimates a production of 22.5 billion litres in 2012 [200]. Although compared to bioethanol this is a small figure, it represents a nearly six-fold increase from 2005 production levels.

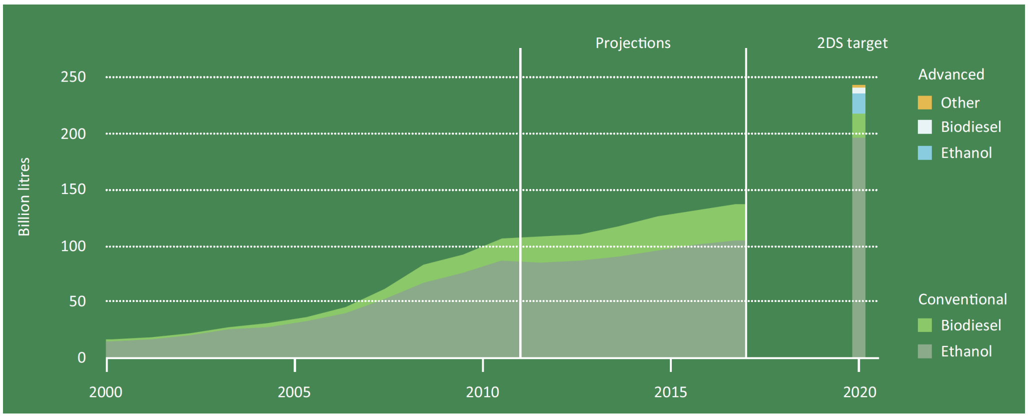

Figure 2.3: Worldwide biofuel production, 2000-2012 and projections to 2020. Source: IEA, 2013 [142]

The European Union is the world's largest biodiesel producer accounting for 41% of the global output [200]. Germany is the largest producer with 2.7 billion litres followed by France, Italy, the UK and Spain. Rapid expansion has also been detected in southeast Europe (Romania and Serbia) [27]. Outside Europe, Argentina, Brazil and the U.S. are the next largest producers. Production in these countries is mainly driven by the export markets to the EU. Figure 2.4 shows the trade of biodiesel worldwide. These export figures vary constantly and might be reduced in the future as results of the approval by the European Union of provisional anti-dumping duties against biodiesel imports from Argentina and Indonesia on 28 May 2013.

In the recent years also China, Singapore, Malaysia, Thailand and Indonesia as well as the Philippines and Vietnam are developing emerging biodiesel industries. This is shown in fig. 2.5.

The total installed capacity for biodiesel production in the EU amounted to 19.8 Mtoe, distributed as follows: in Germany (4.5 Mtoe), Spain (3.7 Mtoe), France (2.3 Mtoe), Italy (2.1 Mtoe) and the Netherlands (1.2 Mtoe), according to the European Biodiesel Board [86].

Production has increased significantly since the approval of the Directive 2003/30/EC on the promotion of biofuels [97] in 2003. This Directive established a non-binding consumption target of 5.75% (% in energy content) of biofuels in the transport sector in 2010. From this point on, the EU Member States started setting legal frameworks to promote biofuels which fostered a high increase in production and consumption. Although the installed biodiesel production capacity in Europe increased rapidly from 2006-7 onwards, it slowed down in 2010. In addition, due to a slow market uptake and the increase of imports, capacity utilization is at around 50%, standing at 8.2 Mtoe.

According to the 2013 European Commission's staff working document [91], 13.3 Mtoe of biofuels were consumed in the EU in 2010, representing 4.5% of all fuels consumed in road transport and the bulk of the total renewable energy share (4.7%) in transport. 9.9 Mtoe corresponded to biodiesel. This share however fell below the original indicative target of 5.75% for 2010 stipulated in the previously mentioned Directive.

In Spain, the target set by the Directive 2003/30/EC was transposed to the national legislation by the Royal-Decree 61/2006 which also set the blending limits for the incorporation of biofuels into fossil fuels. This Royal-Decree was repealed by the Law 12/2007 (which modified the Hydrocarbon Sector Law) in what refers to the consumption targets. The targets became mandatory and were set for a total biofuel consumption of 3.4% in 2009 and 5.83% in 2010.

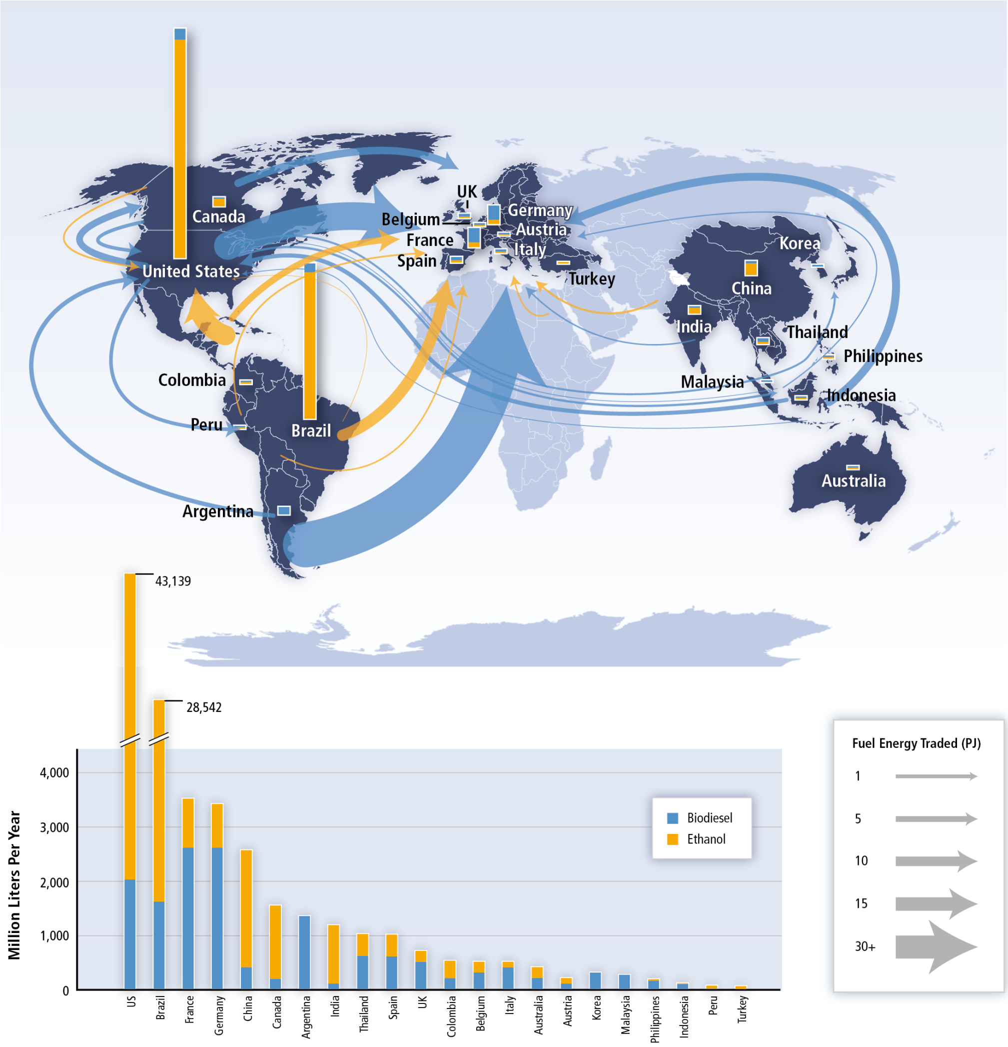

Figure 2.4: Worldwide biofuel trade. Source: IPCC, 2011 [42]

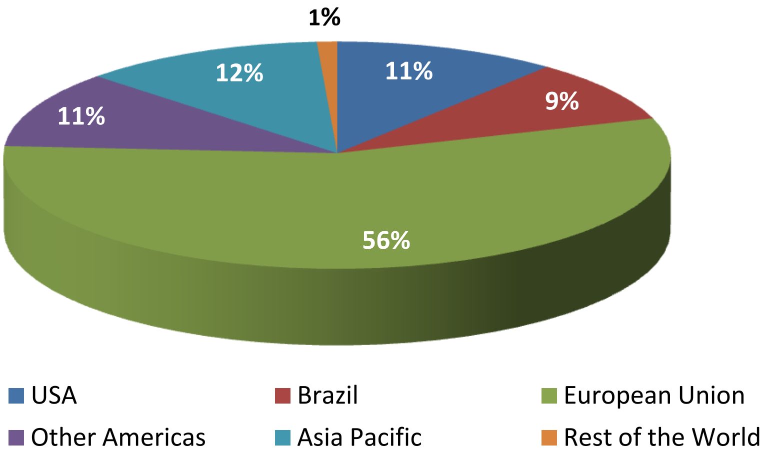

Figure 2.5: Contribution of different countries and regions to biodiesel production, 2009–2010. Source: CIFOR, 2012 [149]

The Ministerial Order ITC/2877/2008 established specific targets for the biofuels to be incorporated into diesel fuel and gasoline: 2.5% in 2009 and 3.9% in 2010. The targets for 2011 to 2013 were set by the Royal-Decree 459/2011. A recent Order has reduced the total biofuel target for 2013 from 6.5% to 4.1% and for biodiesel from 7% to 4.1%. The reason behind, according to the Spanish government, is to reduce the price of transport fuels at the pump. This reasoning has been challenged by the sector.

The legal framework established since 2006 has favoured biofuel consumption. The consumption of biodiesel in Spain has increased continuously in the last years, from 62,909 tonnes in 2006 to 1,632,782 tonnes in 2011, according to APPA, the Spanish Renewable Energy Association. The National Energy Commission (CNE) states that in 2011 biodiesel and *hidrobiodiesel* (HVO) accounted for 7.19% of the diesel volume consumed in the country [49]. However, most of the biodiesel comes from outside the national territory and the EU: in 2011, the internal production only accounted 647,199 tonnes which was 14% of the installed capacity. In addition, the biodiesel imports in the first nine months of 2012 equalled to 1,098,676 tonnes which brought the internal production to only 9% of the installed capacity. The changes to the legal framework established in 2012 and 2013 add uncertainty to the continuity of the sector in the coming years.

2.2.2 Future biodiesel consumption perspectives

In spite of the actual and potential re-shapes of the legal frameworks promoting biofuels, biodiesel produced with current technologies (transesterification) will continue to be produced worldwide. According to the IEA [29] in the transition from the conventional production technologies to advanced technologies currently under R&D, such as for example Fischer-Trops, DME and HVO, there will be a long period in which conventional biodiesel will still be produced. Figure 2.6 shows that biodiesel via transesterification (biodiesel – conventional) will be increasingly produced until 2030 and from then until around 2045 the production will start to be reduced.

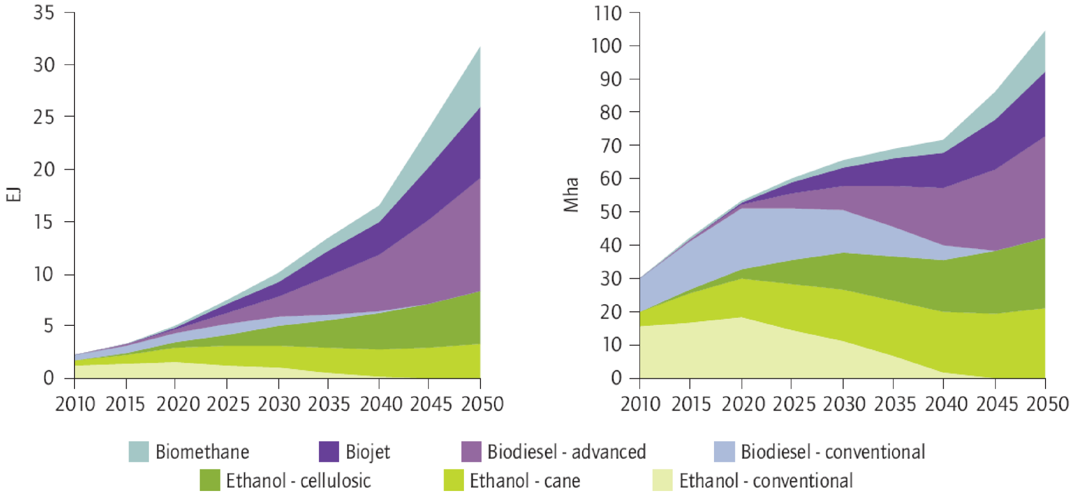

Figure 2.6: Demand for biofuels (in EJ) and resulting land demand (in Mha) in the IEA roadmap. Source: IEA, 2012

Biofuels are expected to cover 3.9% of global road transport by 2018, according to the IEA, in spite of the downside risk from the above mentioned growing policy uncertainty; and the slow progress of the market uptake of advanced biofuels [141].

The EU is expected to continue being the world's largest biodiesel producer and consumer, as shown in fig. 2.7. As it can be seen in the figure, biodiesel production is expected also to increase in the U.S., Argentina, Brazil and a significant increase is expected to take place in countries in Asia and Africa.

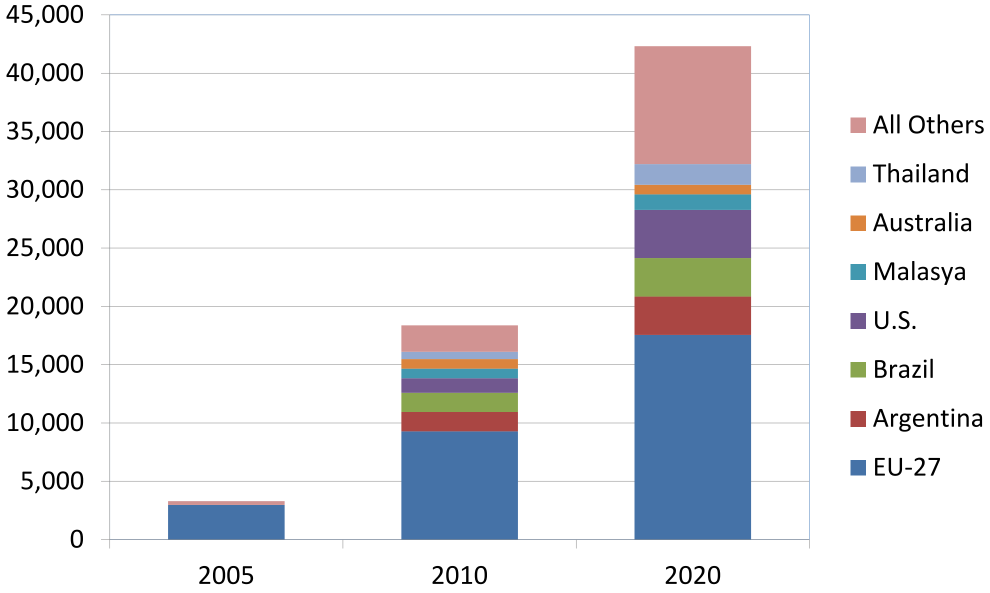

Figure 2.7: Global biodiesel production in 2005, 2010 and 2020. Source: Urbanchuk [234]

In the EU, the European Commission has pictured two different scenarios [90], the first one assumes that the EU policy will remain as it is now with the Renewable Energy Directive [99] and the second one assumes that the European Commission's proposal of limiting the consumption of first generation biofuels to 5% is approved. In the first one, biofuels will account for about 8.5% of the total EU transport energy consumed in 2020 with 22.9 million toe. The 10% target will be reached in 2022 with 24.5 million toe. Biodiesel will account 13.3 million toe in 2020, i.e. 58% of the total volume, and 13.8 million toe in 2022, i.e. 56% of the total volume, and a 7.2% of diesel fuel consumption. In the second scenario biodiesel will still count for as much of 6.4% of the diesel fuel consumption in 2022, only 0.8 percentage points below the baseline.

The progress report of the European Commission on the implementation of the Directive 2009/28/EC [95] and IEE project Keep on Track! [151] also foresee that, with the current trends and if nothing else is done at policy level, the 2020 target for renewable energies in transport will not be reached because EU Member States are not following the shares as planned in their National Renewable Energy Action plans. This is mainly due to the policy uncertainty and the lack of support from the national decision makers in some countries.

In Spain the Renewable Energy Plan PER 2011-2020 [136] sets a 2020 target of 2,313 ktoe of biodiesel in 2020. This represents around 72% of the renewable energy target for the transport sector and around 8.1% of the total transport fuels. In addition, the Spanish Biomass Technology Platform BioPlat set a vision of having 15% of biofuels in the market in 2030 [24]. The achievement of these targets is under question due to the above mentioned uncertainties.

2.3 Material and energy balances

As in every life cycle analysis the results depend greatly on the material and energy balances selected. For this work the material and energy balances selected are those that have been used by the European Commission to define the sustainability criteria of the Renewable Energy Directive. These balances have been produced by the European Commission's Joint Research Centre in collaboration with the European Automotive Industry Association (EUCAR) and the European Association of Oil Companies named CONCAWE (Conservation of Clear Air and Water in Europe).

Appendix 4 of the *Well-to-wheels Analysis of Future Automotive Fuels and Powertrains in the European Context* [148] sets the step-by-step input data for individual pathways, from which the pathways for biodiesel produced with rapeseed, sunflower, soybean and palm oils have been selected. Also the pathways for the production of the materials used in the respective steps have been considered.

In the case of biodiesel produced from used cooking oil (UCO), data have been obtained from the life cycle study produced by CIEMAT for the Spanish Institute for the Diversification and Savings of Energy (IDAE) [160].

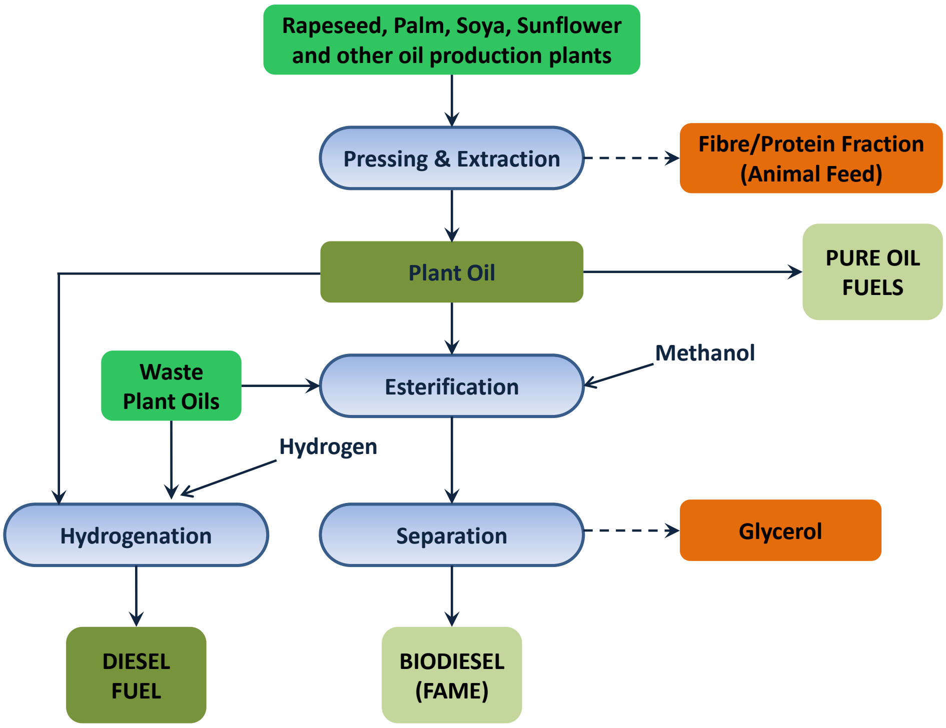

Figure 2.8: Biodiesel life cycle production process. Source: EBTP © 2007 CPL Press

2.4 Conventional life cycle processes and technologies

The pathways of biodiesel produced from crude vegetable oils are basically the same: first cultivation, then extraction of the oil and finally biodiesel production. Transport from one stage to the other needs also to be considered. All the processes are gathered in table B.1.

Following, a description of each process is presented. Other bibliographic sources may show varying combinations of processes and different descriptions of the detailed processes as shown in this chapter.

A mass and energy input/output qualitative diagram for a typical biodiesel production life cycle is shown in fig. 2.8. The hydrogenation pathway also shown in the figure is still not fully deployed and it is described in section 2.7.

2.4.1 Raw material production and refining

Cultivation of sunflower, rape and soy is different compared to the cultivation of palm. The main reason is that the first three crops are annual crops, i.e. they are collected every certain time, and palm is a permanent plant which can give fruits for more than 20 years.

Roughly, the typical cultivation process of rape, sunflower and soy is shown in the diagram of fig. 2.9. It shows all the labours that a farmer must carry out to produce the seeds. Most of the steps consume diesel fuel as they are performed using tractors.

Concerning palm, data just consider the cultivation stage where the palm is already mature to produce free fruit bunches (FFB). Given this, cultivation consists mainly in adding fertilisers and pesticides and harvesting the fruits.

The typical energy and mass inputs and outputs for these four crops are shown in table 2.2. As it can be observed taking into account the use of chemicals and fuel per hectare and year, the most sustainable crop is palm, as it consumes less fertilisers, pesticides and diesel fuel and, additionally, it has the highest yield.

Table 2.2: Consumption data at the cultivation stage. Source: JEC study [148]

Cultivation	I/O	Rapeseed	Sunflower	Palm	Soybean	Units
N fertiliser	Input	137.43	39.00	6.74	8.00	kg /(ha*yr)
CaO fertiliser	Input	19.00	0	0	0	kg /(ha*yr)
K_2O fertiliser	Input	49.46	22.00	10.53	62.00	kg /(ha*yr)
P_2O_5 fertiliser	Input	33.67	30.00	7.58	66.00	kg /(ha*yr)
Pesticides	Input	1.23	2.00	0.44	2.7	kg/(ha*yr)
Seeding material	Input	6.00	6.00	30.84	0	kg/(ha*yr)
Diesel	Input	2,963.00	2,963.00	108.72	2,100.00	MJ/(ha*yr)
Seeds, beans, FFB	Output	3,113.44	2,440.00	19,000,00	2,798.00	kg/(ha*yr)

The consumption of inputs in the cultivation process depends greatly on the edaphologic, geographic and climatic conditions of the crop land. Therefore, other studies present other consumption data. For example, the life cycle analysis produced by CIEMAT [160] for sunflower and rape grown in Spain, assuming the same quantity of seeds as the ones obtained in the JEC study [148], applying a proportional rule would give the consumptions of table 2.3. As it can be observed in this table there is a high variability of consumption data in the bibliography.

Once the rape and sunflower seeds, soy beans and palm FFB are obtained, the following processes depend on the raw material. Sunflower and rapeseed follow the same procedure while soybean and palm follow different ones.

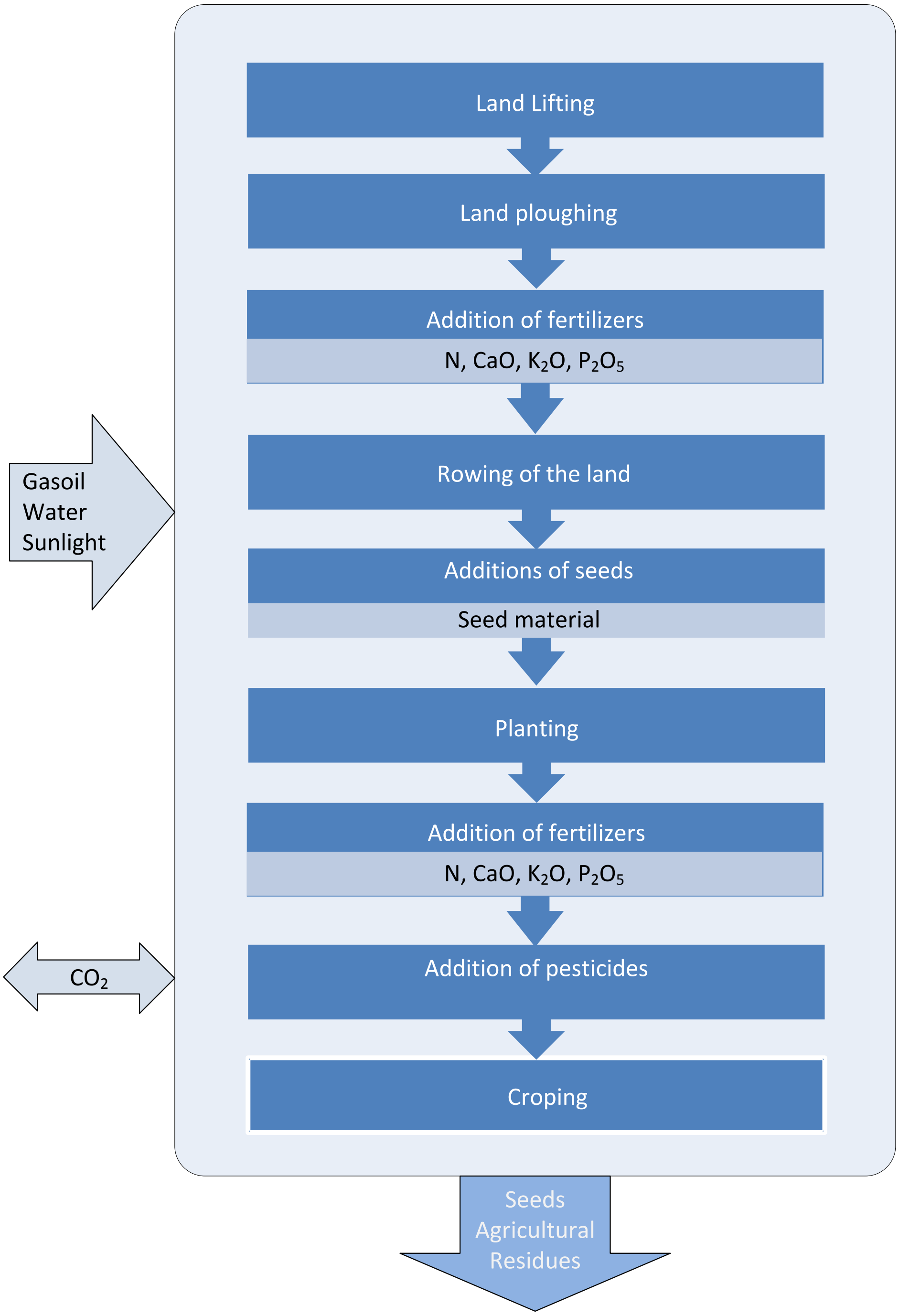

Figure 2.9: Rape, sunflower and soy cultivation process. Source: CIEMAT, 2005 [160]

Table 2.3: Consumption data at the cultivation stage comparing CIEMAT and JRC

	Rapeseed		Sunflower		
Material	JRC	CIEMAT	JRC	CIEMAT	**Units**
Fertiliser	239.56	1114	91	576	kg/ha*year
Pesticides	1.23	15.15	2	12.2	kg/ha*year
Seeding material	6	22	6	15.25	kg/ha*year
Diesel	2,963	3,606	2,963	4,310	MJ/ha*year

As far as rapeseed and sunflower are concerned [160], first of all, the seeds are dried. This can be done by ambient drying or using a circulating air stream. The consumption data of table 3.6 have been considered.

In this Ph.D. it has been assumed that the moisture of the seeds is 10% both for rapeseed and sunflower following the assumption of the JEC study [148]. Once dried, the seeds are processed to obtain the oil by extraction.

Soy beans are not dried. They are stored and transported by road and maritime transport to the EU normally from South America (namely, Argentina and Brazil). Once arrived in Europe, soy beans are directly sent to the oil extraction unit.

For the rape and sunflower seeds and soy beans the first step in the extraction unit consists in passing the seeds through filters in order to discard the smaller seeds and possible estrange particles. After this they are stored until needed.

Table 2.4: Consumption data at the drying process. Source: JEC study [148]

Drying	I/O	Rapeseed	Sunflower	Units
Diesel	Input	0.00018	0.00018	MJ/MJ seed
Electricity	Input	0.00308	0.00308	MJ/MJ seed

The second step is a cleaning process where the seeds are cleaned. Once cleaned, they are triturated and laminated. Triturating is performed in order to separate the meet of the seed from the shell. Here a residue is obtained. After these processes, the seeds are put at the temperature and moisture needed to proceed to the first extraction of the oil by pressing. The oil extracted at this point is filtered and stored. The rest of the meet which still contains a percentage of oil is transported to the second extraction process which uses solvents.

The solvent usually used for extracting oil is n-hexane. The stream coming from pressing is mixed with hexane so a mixture of oil and hexane is obtained (miscela). Another stream of plant-meal and hexane is also obtained. In both streams hexane must be separated.

For the stream composed of oil and hexane, both components are separated by distillation using water vapour. Two streams are obtained: one of hexane and one of oil. The hexane is condensed and reused in the process. The oil is decanted and added to the oil previously obtained by pressing. This final stream of oil is centrifuged in order to eliminate impurities and it is dried and stored until it is bought by a client.

For the stream of plant-meal and hexane, this last component is separated by a process called *desolventing-toasting*, which consists roughly in injecting vapour streams in order to obtain two products: hexane, which is reused and meal which is cooled, moulted and stored.

During all the process, seeds and meal seed are transported from one site to another usually by transporting conveyor belts.

In the case of palm oil the extraction process is considerably different from the process just described by Pleanjai [194]. A typical process is formed of seven basic steps: first, the palm fresh fruit bunches are received and transported using conveyor belts to a sterilization site. The sterilization consists in circulating steam at 120-130 °C through the FFB in a sterilization device for around one hour and a half. Vapour used during the sterilization is condensed and treated as a residue. The sterilized FFB are then threshed with the aim to separate the fruits from the bunch where they are connected. This bunch is considered a residue, which usually is left to rot in anaerobic conditions, generating CH_4 during fermentation [148]. The following step is pressing the fruits under vapour conditions.

The homogeneous mass obtained after pressing undergoes an oil-extraction process, which begins by pressing in a screw-shape pressing unit. The pressed material is filtered obtaining two products: on the one side oil with impurities and, on the other side, fruit fibber and kernel. The oil is circulated in a hydro-cyclone and a decantation device in order to eliminate impurities, water and particles. Water and meal without economic value are obtained and treated as a residue. The oil is centrifuged, vacuum dried and stored. The storage is performed at 60 °C by using water steam. This storage temperature is needed in order to avoid the solidification of fatty matter with low could points, relatively abundant in palm oil.

The kernel and fibre of the fruit are separated in a cyclone. Fibber is obtained in the upper side and will be used in the furnace of the extraction plant as a fuel. When circulating through the cyclone the kernel is pressed. The pressed kernel is then introduced in a separation unit where the meal and the shell of the kernel are segregated. The shell can be used as fuel in the furnace of the plant and the kernel meal is a valuable product that is sold to other companies that extract palm kernel oil. The consumption data in the oil extraction process are shown in table 2.5.

Table 2.5: Consumption data at the extraction process. Source: JEC study [148]

Extraction	I/O	Rapeseed	Sunflower	Palm	Soybean	Units
n-hexane	Input	1	1	0.7	-	kg/t seed
Seeds, beans or FFB	Input	2.469	2.298	5.319	4.444	kg/kg oil
Electricity	Input	34	34	60	-	kWh/ t seed
Steam	Input	580	580	1,000	-	MJ/t seed
Crude vegetable oil	Output	1	1	1	1	kg/kg oil
Meal	Output	1.468	1.299	4.318	0.111	kg/kg oil
CH_4 from waste	Output	-	-	-	0.94	g/MJ oil
Heat	Output	-	-	-	692	MJ/t FFB

As it can be observed, the different crops have different ratios oil: meal. While for soybean per each kg of oil it is possible to obtain 4.3 kg of meal, for palm oil per each kg of oil only 0.1 kg of meal is obtained. On the other hand, soybean oil extraction consumes more energy than any other process while in the case of palm oil the energy needed for the extraction is obtained by the consumption of own biomass having indeed a surplus of heat.

Once the oils are extracted they must be refined. Refining is performed at the same site of extraction for the rape and sunflower oils. The soybean and palm oils are refined after being transported by ship to Europe normally from South America and South-East Asia respectively. Refining is performed by passing the oil through a Fuller's earth filter. Table 2.6 shows the consumption of inputs in this process. As it can be observed, the database used for this work considers the same input consumption for all the oils under study. Once the oil is obtained it is transported to the transesterification unit.

Table 2.6: Consumption data at the refining process. Source: JEC study [148]

Extraction	I/O	Rapeseed	Sunflower	Palm	Soybean	Units
Fuller's earth	Input	6	6	6	6	kg/(t oil)
Electricity	Input	6	6	6	6	kWh/(t oil)
Steam	Input	296	296	269	296	MJ/(t oil)

2.4.2 Transformation into biodiesel

The first step of the process is the oil pre-treatment before the transesterification. This pre-treatment aims at removing impurities, such as phosphatides (also called phospo-lipides), water, free fatty acids, waxes, colourants and tocopherols. The pre-treatment consists of two major steps which are normally applied to all kinds of vegetable oils: degumming to eliminate phosphatides and neutralization to eliminate free fatty acids.

Degumming is needed to eliminate the content of phosphatides. These materials have negative impacts in the production plant. These compounds can act as emulsifiers and thus impede the phase separation during the transesterification process. They also make the oil become turbid during storage and promote the accumulation of water in the final product, as mentioned by Mittelbach et al. [176].

The neutralization consists in converting the free fatty acids (FFA) contained in the oil into soaps which are soluble in water. This is easily achieved by the simple addition of an alkali, normally NaOH at ambient temperature. It is also possible to use part of the alkaline glycerol phase of the subsequent transesterification step thus reducing the consumption of alkali. This step is performed at the same tank where degumming has been carried out. After this process, water must be eliminated.

FFA must be eliminated prior to transesterification because they have several negative effects. First of all because at the transesterification reaction they might react with the catalyst creating soaps and thus reducing the efficiency of the reaction, secondly, because a high degree of acidity in the methyl ester facilitates the ageing during storage. This has been linked with corrosion and the formation of deposits.

In addition, further steps can be applied if needed depending on the characteristics of the oil. One of these processes is the so called bleaching or whitening in order to reduce the content of pigments of the oil so that the final biodiesel fuel obtained has a colour closer to the one of diesel oil. This process is normally applied to palm oil, for example. Another additional process is the dewaxing or winterization, which is applied to reduce the content of waxes in the oil in oils having high content of waxes for example sunflower oil. This process is needed because waxes can reduce the yield of the transesterification reaction. In addition they can cause filter plugging if they solidify within an engine.

Finally, after all this stages, the oil is ready to be transesterified. The reaction of transesterification, also called alcoholisis, consists basically in transforming one molecule of triglyceride into three molecules of esters by adding methanol or another alcohol in the presence of a catalyst and producing glycerol as a co-product.

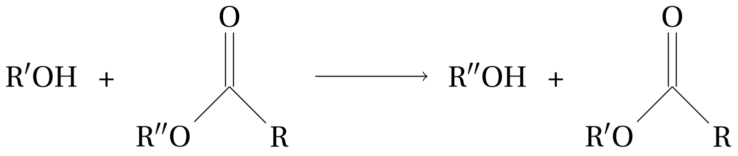

Figure 2.10: Glyceride transesterification reaction

As commented at the beginning of this chapter, the most commonly used alcohol for the transesterification is methanol. This is due mainly because it is cheaper compared to other alcohols such as ethanol and because when the alcohol is shorter, the better is its reactivity. Another reason is that methanol is more easily available in absolute form as compared to ethanol (which may contain small percentages of water) and so, there is no water content which can provoke the formation of FFA from soaps by hydrolysis.

As far as the catalysers are concerned, several catalysis types might be used: alkaline catalysis, acid catalysis, catalysis with metal compounds, enzymatic catalysis and catalysis by silicates. Alkayline catalysis using sodium hydroxide, potassium hydroxide or sodium methoxide is by far the most commonly used reaction type. The main advantage of this form over the acid catalysis is the high conversion under mild conditions in comparatively short times. Acid catalysis has the advantage of also esterifying free fatty acids contained in the fats and oils this is why acids such as sulphuric or phosphoric acids are normally used for the transesterification of used cooking oils and fats. The other types of catalysis contained in the literature – using metal compounds, enzymes and silicates - have not gained sufficient market.

In this Ph.D., sodium hydroxide has been considered as catalyser in chapter 5 for the life cycle ExROI calculation of pure vegetable oils – rapeseed, sunflower, soybean and palm – and sulphuric acid for the used cooking oils. For the in-depth calculation of chapter 4 based on real consumption data of a Spanish biodiesel production plant sodium methoxide has been considered.

After reaction, glycerol and biodiesel form different phases that are easily separable by decantation. Other authors suggest other separation methods, for example, centrifugation, although this increases the consumption of energy and costs. Others suggest adding water or hexane, which would stay in the middle, or solvents, but these options are not considered in this case.

The methyl ester flow obtained after transesterification contains a relatively high quantity of methanol, glycerol, catalyst and other compounds. In order to produce a high quality biodiesel this flow has to be washed and dried. Washing is performed by adding warm water and hydrochloric acid. Drying is performed using steam for heating the product. More and more, biodiesel producers in order to comply with the quality standards and specifications of the fuel blenders are opting for distilling the biodiesel even if this increases the production costs.

In order to be considered a co-product, the glycerol stream which contains water and other residues (FFA, methanol, soaps and methyl esters) is purified and then distilled. Purification consists in adding an acid to split the soaps into FFA and salts, which are then separated by decantation. The distillation unit is needed to eliminate the remaining methanol content. The recovered methanol can be sent to the beginning of the process in order to be reused.

The inputs and outputs considered in the JEC study [148] can be seen in table 2.7 It is considered that all the process works at 1 atm and, when not indicated, at ambient temperature. The energy sources consumed in the process are electricity from the grid and natural gas that is used to produce the steam used in the process.

Table 2.7: Consumption data at the transesterification process including pre-treatment and after-treatment units, for pure vegetable oils. Source: JEC study [148]

	I/O	Rape	Sunflower	Soy	Palm	Units
H_3PO_4	Input	1.7	1.7	1.7	1.7	kg/(t FAME)
HCl	Input	20	20	20	20	kg/(t FAME)
Na_2CO_3	Input	2.5	2.5	2.5	2.5	kg/(t FAME)
NaOH	Input	6.72	6.72	6.72	6.72	kg/(t FAME)
Methanol	Input	109	109	109	109	kg/(t FAME)
Plant oil	Input	1.04	1.04	1.04	1.04	kg oil/kg FAME
Electricity	Input	30	30	30	30	kWh/(t FAME)
Steam	Input	1,545	1,545	1,545	1,545	MJ/(t FAME)
FAME	Output	37.2	37.2	37.2	37.2	MJ/(kg FAME)
Glycerol	Output	0.1056	0.1056	0.1056	0.1056	kg/kg FAME

As it can be seen in the previous table the JEC study [148] does not differentiate the mass and energy inputs depending on the raw material used. However, they vary depending on the raw material due to their different composition. Also, it does not consider the production of valuable products other than biodiesel and glycerol. However, as it has been just described, other co-products may be obtained, e.g. soapstocks and waxes.

A specific in-depth analysis of the transesterification process including pre- and after-treatment with the possible variations is produced in chapter 4.

2.4.3 Pathway according to SIMAPRO and EcoInvent database

The processes involving biodiesel production might vary slightly from the ones described in previous sections, especially in what concerns the consumption of inputs. This has already been demonstrated by showing the numbers of different studies, i.e. JRC and CIEMAT. To have another source of information as a reference, the life cycle of biodiesel production from rapeseed oil has been simulated using SIMAPRO and the EcoInvent database.

SIMAPRO is a software tool developed by the Dutch company PRé Consultants, which enables producing Life Cycle Analysis (LCA), using as databases own inventories (user-created) and/or literature datasets (BUWAL, IDEMAT, ETH, IVAM). It allows complex life cycles to be modelled and analysed in a systematic and transparent way. SimaPro is the most widely used LCA software, used by major industries, consultants, research institutes and universities.

EcoInvent is the world's leading database with consistent and transparent, up-to-date Life Cycle Inventory (LCI) data. With more than 4,000 LCI datasets in the areas of agriculture, energy supply, transport, biofuels and biomaterials, bulk and speciality chemicals, as well as waste treatment, among others, EcoInvent offers one of the most comprehensive international LCI databases, based on industrial data and information compiled by internationally renowned research institutes and LCA consultants.

The main differences between the cycles with the different data sources are on the one hand, the specific consumption data of materials and energy in each process, and on the other hand the conversion factors. Table 2.8 shows the assumptions considered by EcoInvent.

Table 2.8: Conversion factors for the rapeseed biodiesel using EcoInvent

Ratio	**Value**	**Unit**
Rapeseed:FAME	0.524	Kg oil / kg rapeseed
Oil:FAME	0.89	Kg oil/kg FAME

Another difference is that some processes are aggregated into one, e.g. in EcoInvent the extraction process includes the oil refining, while in the JEC study [148] these processes are considered separately. In addition, in some processes, additional materials are considered, for example, the tap water. Finally, some inputs are specifically defined while the JEC study [148] they are put generically. This is the case of the fertilisers in the cultivation process. While the JEC study defines the fertilisers by the generic chemical element/molecule (i.e. N, CaO, K_2O and P_2O_5) without informing about the material, the EcoInvent clearly specifies the material, for example urine in the case of N fertiliser. The consumption data and relation of materials are shown in chapter 5.

2.5 Biodiesel production from used cooking oils

As its name indicates, used cooking oils (UCO) are vegetable oils that have been used in cooking, normally for frying purposes. Once the user considers the oil to have been sufficiently used, the oil is replaced and the used oil becomes a waste. UCO are part of the definition of bio-waste in the Waste Framework Directive. Indeed, the term bio-waste stands for biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises and comparable waste from food processing plants [98].

UCO produced in the EU are considered as non-hazardous waste according to the Consolidated European Waste Catalogue. They are classified as Municipal Wastes (household waste and similar commercial, industrial and institutional wastes) including separately collected fractions, under the code 20 01 25 (edible oils and fats). If the UCO is obtained from waste water treatment plants they are also considered non-hazardous materials with a different code: 19 08 09 (grease and oil mixture from oil/water separation containing edible oil and fats). These last types of UCO are mentioned in a subsequent paragraph.

It is important to highlight that the above definitions only apply to UCO produced in the EU. UCO obtained from means of international transport (i.e. which has come from outside the EU) is classified as category 1 under the animal by-products Regulations due to the risk to transmit exotic diseases and therefore should be treated as explained in the following section for category 1 materials. These UCO are considered hazardous waste regardless of any threshold concentrations.

The wrong disposal of UCO can have important negative effects on the environment: the increased amount of nutrients in the drains augments the number of rats and other plagues. If the waste is not eliminated in waste water treatment plants it can produce a negative effect on the capacity of auto regeneration of rivers, fauna and flora and can increase the population

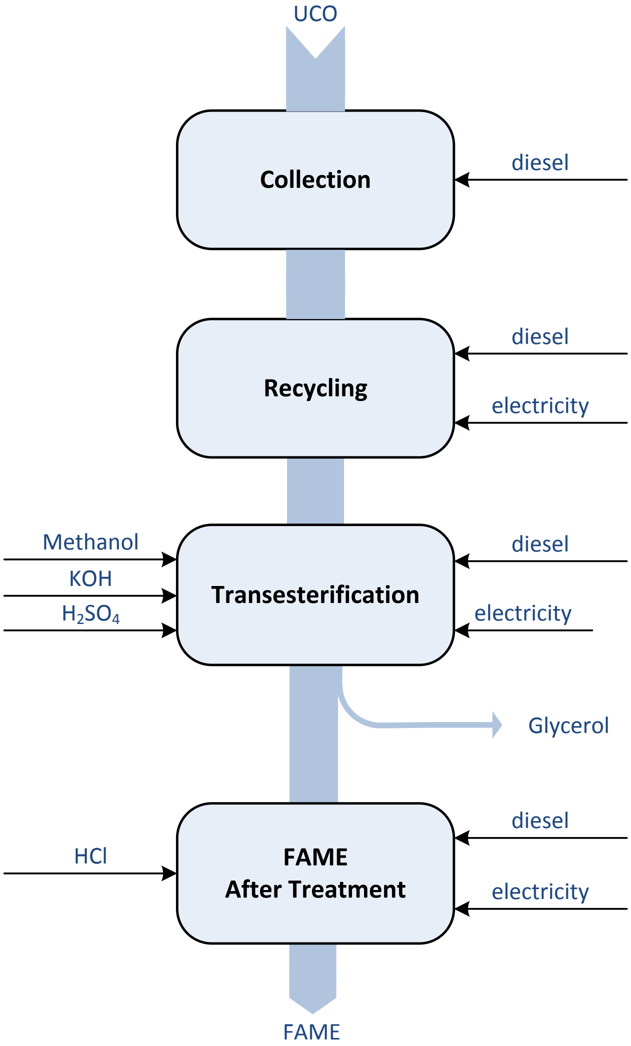

Figure 2.11: Flow diagram of a biodiesel plant producing with Used Cooking Oil. Source: CIEMAT, 2005

of jelly fish on coastlines [161]. Other negative effects are the increase in the cost of sewage treatment and clogging problems in drains with the consequent repair costs [161].

With the current legislation in place in the European Union the use of UCO for biodiesel production has gained importance. Indeed, according to article 21 of the Renewable Energy Directive [99] the contribution made by biofuels to the 2020 targets produced from wastes, residues, non-food cellulosic material, and ligno-cellulosic material are considered to be twice that made by other biofuels. Biofuels produced from these resources are called advanced or second generation biofuels. UCO enter in this definition. This means that for each tonne of biodiesel from UCO put into the market by the operators obliged to distribute biofuels, they will be accounted twice, therefore halving the effort to reach the target.

This regulation has had unexpected counter effects: international imports of UCO have started to take place, mainly from the U.S., the price of UCO has scaled up to even exceed the price of low quality (unused) edible vegetable oils, such as palm oil; and finally it has opened the door to fraud. As there is no real definition of used cooking oil and no possible way nowadays to determine when a vegetable oil is used or not, some actors are claiming to have UCO when in reality the vegetable oil has only been used once and they have used high quantities of oil to fry a small portion of food. In light of the revision of the Renewable Energy Directive [99] there are voices suggesting eliminating UCO from the list of advanced biofuels benefiting from double counting .

Be it considered or not an advanced biofuel, biodiesel produced from UCO will still play a role in achieving the renewable energy in transport 2020 target in the EU, in view of its beneficial lower GHG emissions. In the Annex V of the Renewable Energy Directive [99] while the typical GHG emission reduction for biodiesel produced from unused vegetable oils ranges from 40 to 62%, biodiesel from UCO shows reductions of 88%, which still makes it attractive for mandated operators.

There are three types of producers of used cooking oils: households, the HORECA sector (i.e. restaurants and caterers) and the food industry. According to Waste Framework Directive [98], EU Member States shall take measures to encourage the separate collection of bio-waste and the treatment in a way that fulfils a high level of environmental protection.

In line with these requests normally the HORECA sector and food industry have a high degree of implementation of selective collection systems by means of authorised collectors. This is because these sectors are easily controllable from the waste authority viewpoint.

In households the collection of UCO is not as manageable as in the other sectors and countries do not have established collection plans in place. The existing collection systems are generally encouraged by regional or local governments or stemming from private initiatives. In this sector the consideration of used oil is let to the discretion of the owner and normally the used oil is thrown away through the drain or disposed at the bean in a used container (empty plastic bottle or brick).

Estimating the potential of UCO collection that could be used in biodiesel production is a challenge. In the EU the consumption of vegetable oils in 2011 was about 19 million tonnes for rapeseed, soybean, sunflower and palm oils [108]. The worldwide vegetable oil production was about 145 million tonnes for the same oils plus olive oil [235]. However from this data, knowing the quantities of UCO that could be effectively recovered is not easy. This is especially the case in the households sector.

Some initiatives and institutions have made attempts to calculate how much biodiesel could be produced from UCO following two methodologies. One of these methodologies follows a top-down approach. Knowing the vegetable oil consumption of an area a certain percentage of losses is assumed (e.g. around 85%) in terms of the oil ingested by the consumer and potential shortfalls in oil collection and recycling, and from the final number they calculate the quantity of biodiesel produced.

The other methodology follows a bottom-up approach. By means of practical experiences they obtain the quantity of vegetable oil consumed per person/year. Knowing the population of a defined area with the same cultural conditions they can calculate the quantity of vegetable oil consumed in the entire region. Assuming a certain loss in UCO collection and recycling, they obtain a final number which then is converted to biodiesel.

The weakness in both methodologies is related to the assumptions made in terms of UCO losses in collection and recycling. The bottom-up approach also adds the uncertainty in data obtained per person/year and the extrapolation of these data to an entire region. As an example, the quantities obtained in the IEE project OILECO range from 4-18 kg/person/year [146] in EU countries (Italy, Spain, Hungary, Slovakia and Bulgaria). As mentioned, the potential UCO collection depends on the culinary culture of the country. Countries used to fry more than any other way of cooking will consume more oil than others.

Being this the situation, some projects have estimated the potential biodiesel production in the EU. The IEE project RecOil states that biodiesel produced from UCO could replace 1.5% of the EU-27 diesel consumption, whereas currently over 60% of the UCO produced is improperly disposed of [190]. The final report of the IEE project BioDieNet [21] states that the total amount of recoverable UCO available in the EU-27 in 2009 was about 3.5 million tonnes (3.95 million litres). As the EU-27 diesel consumption was 214 million litres in 2007, around 1.8% of the EU-27 diesel consumption could have potentially been replaced with biodiesel produced from UCO. Other calculations suggest a potential substitution between 0.2 to 0.8% of the European diesel consumption in 2020, which would be equivalent to 2.1 and 10.4% of the biofuels consumed.

The life cycle of biodiesel production from UCO starts by the collection and transport of the residue, and is followed by the recycling where the oil is filtered and decanted in order to separate solid particles and water. Once the oil is refined, it is sent to the transesterification plant.

The UCO collection potential from households can be higher than the HORECA one. Figure 2.12 shows the specific case of Spain. According to GEREGRAS, the Spanish association of vegetable oil and fat residues management companies, the potential for UCO collection in Spain in 2020 is about 280,000 tonnes from which more than 120,000 tonnes are from the HORECA sector and 160,000 tonnes from the domestic sector. However, in 2011 the quantity of UCO collected was about 90,000 tonnes which were mostly coming from the HORECA sector [136]. The main problems that the UCO collection from households is facing are non-technological. They are related to the lack of awareness of the possibility to collect UCO, lack of promotion about the benefits to the environment, and making the collection more attractive to the UCO holders for example by reducing the distances to the UCO collection points and having a strong hygiene maintenance of the containers.

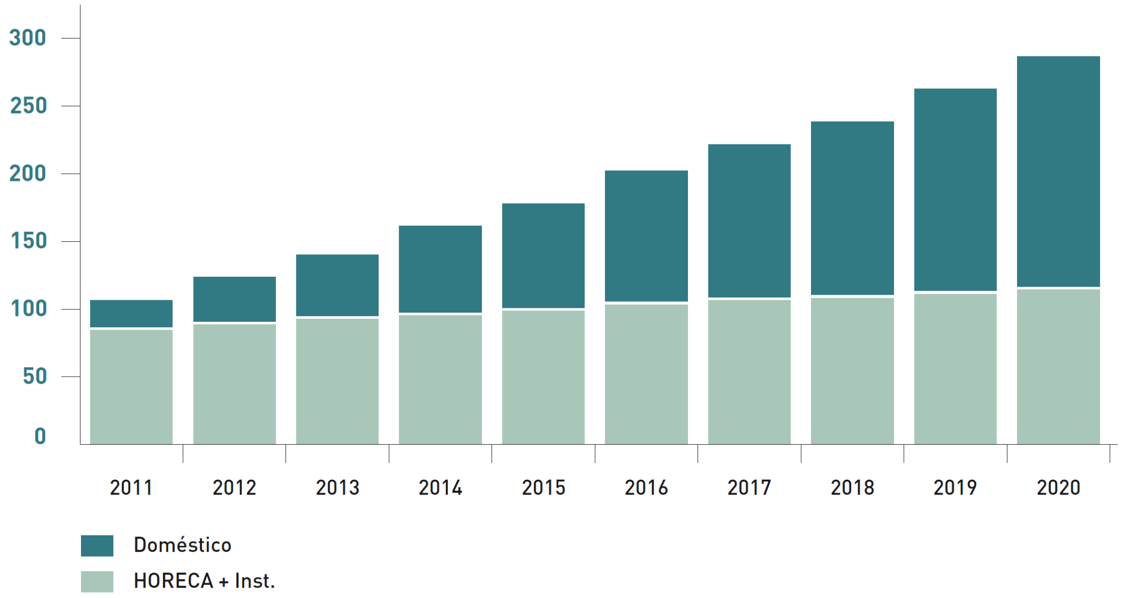

Figure 2.12: Collection of used cooking oil in Spain from 2011 to 2020 in domestic and HORECA sectors (million tonnes). Source: IDAE [136]

The collection and transport of the UCO is done by an authorised agent for waste management. In the collection and transport phase the only input is diesel fuel needed to run the vans and trucks that are used to transport the containers of UCO to the recycling, also called refining unit.

The collection can be organised in different ways. In the HORECA sector and food industry, normally the collection is done on-site by the authorised agent in medium-to-big containers that are transported via ban or truck to the recycling plant. In the case of households there are different possibilities: the collection can be done door-to-door or by setting distributed collection points though out an area with well identified containers. These containers can be adapted to receive UCO in recipients (such as used bricks or bottles, or reusable bottles designed for the purpose) or have a whole where the oil can be poured through. According to results of IEE projects OILECO and RecOiL the best practices are those having collection points with containers adapted to leave recipients. This system can also be the most sustainable if the transport of the oil to the collection point by the household consumer is not accounted in the life cycle.

In the recycling process the inputs are normally electricity and gasoil or natural gas. The gasoil or natural gas is consumed to produce steam which is used to clean the containers so that they can be reused again. The electricity is used as energy source in the filtration and decantation units.

As far as the transesterification is concerned, in this case the oil normally follows a different process compared to the case of crude vegetable oils, which affects the consumption of materials and energy sources. The main differences are:

- The pre-treatment is not so elaborated because the oil comes already "clean" from the recycling unit. Normally, only a cleaning is done via centrifugation and drying to eliminate possible small particles and excess water that might be contained in the oil.
- Afterwards, the oil is esterified with an acid catalyser to, as commented above, transform into esters the high quantity of free fatty acids that are normally present in UCO; this esterification is followed by a basic catalysed transesterification as explained in the previous paragraph. Some plants have the esterification and transesterification tanks in parallel. They treat in the esterification plant those oils having high FFA (more than 4%) and in the transesterification plant those oils with less FFA [160].
- The ester obtained after transesterification follows a cleaning and drying process. Other plants have opted to distillate it to ensure the fulfilment of the quality standards, EN 14214 [36] in the EU.
- The glycerol does not follow an after-treatment process. The crude glycerol is either treated as a residue or sold as a low added-value co-product. Some plants have after-treatment processes similar to the ones using vegetable oils to obtain a high quality glycerine product.

On the other hand, some biodiesel producers which do not have their plants adapted to work with UCO, if they aim to use UCO normally add a small part (e.g. 10%) to their main streams, e.g. rapeseed oil. With this, they do not need to adapt their plants to deal with this lower quality resource while producing a high quality biodiesel.

The inputs and outputs of the transesterification phase can be seen in table 2.9 together with flow diagram of fig. 2.11. These data have been obtained from a LCA carried out by CIEMAT [160] based on a supply chain established in the north of Spain and with data of two real biodiesel production plants using this resource. It is important to note that in this case for the production of steam, diesel fuel is considered instead of natural gas.

Table 2.9: Consumption data for processes considered in the life cycle analysis for UCO. Source: CIEMAT

Process	I/O	Value	Units
Collection			
Diesel	Input	0.48316	MJ/kg UCO
Recycling			
Diesel	Input	0.036	MJ/kg oil
Electricity	Input	0.35	MJ/kg oil
Transesterification			
Recycled oil	Input	1.03	kg/kg FAME
Methanol	Input	0.155	kg/kg FAME
KOH	Input	0.02770	kg/kg FAME
H_2SO_4	Input	0.017	kg/kg FAME
Diesel	Input	0.455	kWh/kg FAME
Electricity	Input	0.137	kWh/kg FAME
FAME	Output	1.00	kg/kg FAME
Glycerol crude	Output	0.20	kg/kg FAME

2.6 Biodiesel production from animal fats

In the European Union the production of biodiesel from animal fats mandatory involves the introduction of additional units as compared to biodiesel production from fresh vegetable oils. This is due to two main factors. First of all, in order to comply with the European legislation aimed at preventing the emergence and spread of contagious diseases from animals and animal-derived products (TSE), such as aftose fever, swine fever, contamination by dioxins and the bovine spongiform encephalopathy [2]. Secondly, due to the relatively poor "quality" of animal fats which makes that, without these additional equipments, it would be difficult to comply with the limits set at the European quality standard for biodiesel, EN 14214 [36].

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[2] Regulation (EC) 1774/2002 of the European Earliament and of the Council of 3 October 2002 laying down health rules on animal by-products not intended for human consumption

Regulation (EC) No 92/2005 of 19 January 2005 implementing Regulation (EC) No 1774/2002 of the European Parliament and of the Council as regards means of disposal or uses of animal by-products and amending its Annex VI as regards biogas transformation and processing of rendered fats

Regulation(EC) No 2067/2005 of 16 December 2005 amending Regulation (EC) No 92/2005 as regards alternative means of disposal and use of animal by-products

Regulation (EC) No 1678/2006 of 14 November 2006 amending Regulation (EC) No 92/2005 as regards alternative means of disposal of and use of animal by-products

Regulation (EU) No 142/2011 of 25 February 2011 implementing Regulation (EC) No 1069/2009 of the European Parliament and of the Council laying down health rules as regards animal by-products and derived products not intended for human consumption and implementing Council Directive 97/78/EC as regards certain samples and items exempt from veterinary checks at the border under that Directive

Concerning the first reason, legislation classifies animal fats under three different categories depending on their dangerousness in transmitting diseases:

Category 1: the most dangerous fats. Summing up, it comprises by-products (or any material containing such by-products) of animals killed by, or suspected of being infected by, a TSE or in which the presence of a TSE has been officially confirmed and by-products of animals other than farmed animals, including in particular pet animals, zoo animals and circus animals, experimental animals and wild animals, when suspected of being infected with diseases communicable to humans or animals. It also comprises products derived from animals to which prohibited substances have been administered as well as containing residues of environmental contaminants. All animal material collected when treating waste water from category 1 processing plants and other premises in which specified risk material is removed is also included. Finally, it also comprises catering waste (including cooking oils) from means of transport operating internationally.

Category 2: It comprises animal by-products (or any material containing such by-products) such as manure and digestive tract content, all animal materials collected when treating waste water from specific slaughterhouses, products of animal origin containing residues of veterinary drugs, products of animal origin, other than category 1 material, that are imported from non EU Member States and, in the course of the inspections provided for in Community legislation, fail to comply with the veterinary requirements for their importation into the Community.

Category 3: It comprises animal by-products (or any material containing such by-products) such as parts of slaughtered animals (including hides and skins, hooves, feathers, wool, horns, hair and fur, blood, raw milk, shells, hatchery by-products and cracked egg by-products), which are fit for human consumption in accordance with Community legislation, but are not intended for human consumption for commercial reasons because they are not affected by any signs of diseases communicable to humans or animals and derive from carcases that are fit for human consumption in accordance with Community legislation; animal by-products derived from the production of products intended for human consumption, including degreased bones and greaves; former foodstuffs of animal origin; fish or other sea animals, except sea mammals, caught in the open sea for the purposes of fishmeal production; fresh by-products from fish from plants manufacturing fish products for human consumption; and, finally catering waste (including cooking oils) other than that considered as category 1.

Depending on the classification, biodiesel producers must follow the next procedures:

- Except for category 3, animal fats must undergo a pre-esterification phase. In this stage, pH must be reduced to ≤ 1 by adding sulphur acid (H_2SO_4; 1.2-2 molar) or an equivalent acid and the blend must be heated at 72 °C during 2 hours being energetically mixed all the time.
- Once esterified, the flow must be subjected to two transesterification phases on a row. These phases must consist in increasing pH up to 14 with a 15% of KOH (1-3 molar) or an equivalent base at a temperature of 35-50 °C during 15-30 minutes.
- Finally, the methyl ester phase must be vacuum-distilled at least at 150 °C.

After Regulation (EC) 2067/2005, the competent authority may authorise the use of other process parameters for the aforementioned stages if these parameters provide for an equivalent reduction of risks for public and animal health.

All the animal fats that enter the production plant must be pre-treated previously by an authorised company. Regulation (EC) 1774/2002 provides for seven different pre-treatments but all consist in filtering up to a certain diameter (among 150 and 20 mm depending on the posterior heating process), heating between 70 and 130 °C during a determined time (among 13 and 125 minutes) and finally, eliminating all the proteins and insoluble impurities. After this pre-treatment, that is usually done before entering the producing plant, animal fats have a very small quantity of solid impurities. A scheme of a typical transesterification plant is shown in the fig. 2.13.

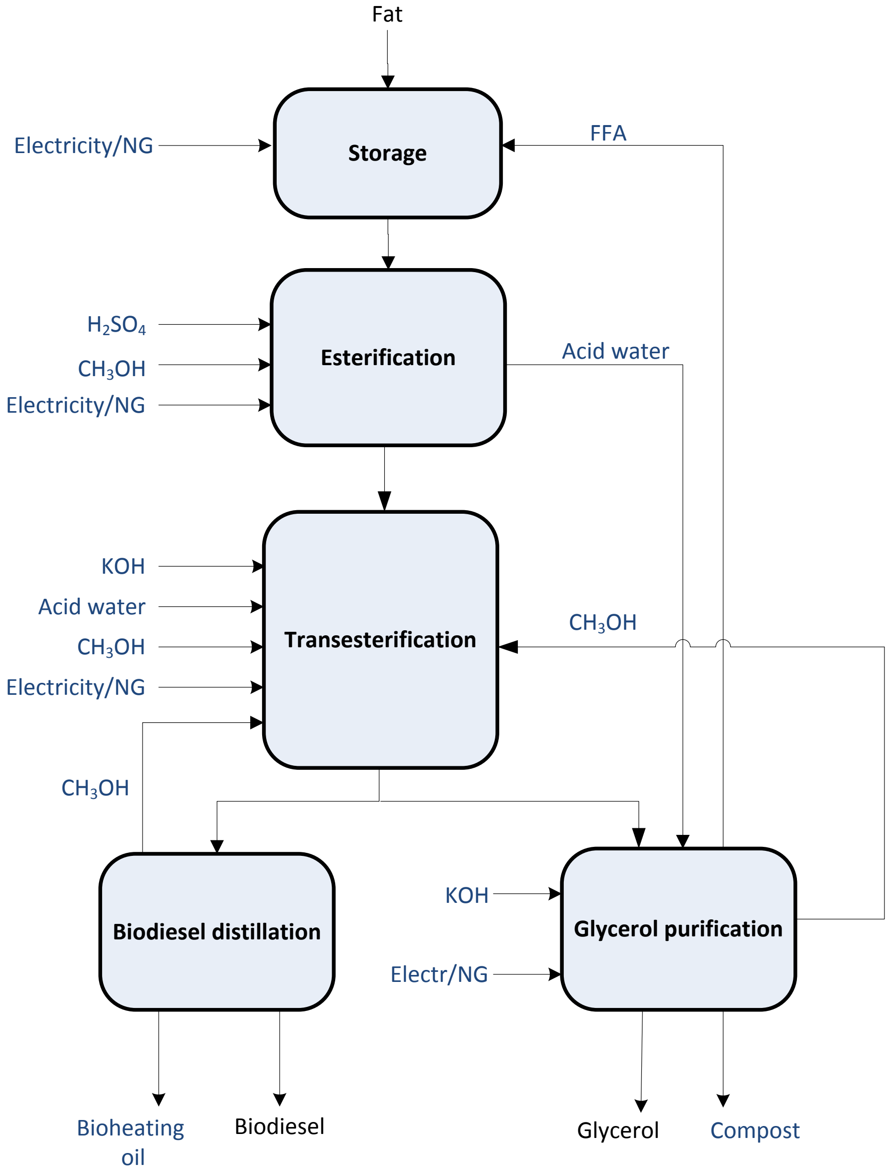


Figure 2.13: Scheme of the biodiesel plant producing with animal fats

These kinds of plants can operate in discontinuous or continuous regimes. Most plants also operate at a semi-continuous regime. This means that each unit works as an independent stage, so the output of each unit is not transferred to the following unit until certain conditions are reached. This makes easier the quality control of each unit and the plant in general.

Following a process of a real biodiesel plant producing from animal fats, located in the north of Spain is shortly described.

The first stage is storage. In order to make the animal fats stay in liquid phase, they have to be warmed to around 30 °C. Otherwise, they would solidify, especially during the night and in winter periods.

Then, it comes the pre-esterification, which is performed by adding methanol and sulphuric acid as catalyst in a mixing tank at 70 °C. In this phase the relative high percentage of free fatty acids that the raw material contains is transformed into methyl esters. By doing so, the production of soaps is reduced and the yield of the whole process is improved. It is important to note that, contrarily to vegetable oils, the FFA content of the raw material used in this plant can reach up to 15% and therefore, producing so much soaps reduces considerably the performance of the plant, what does not occur when using fresh oils. The problem of esterification is that the water content is increased as the reaction is as follows:

$$R - COOH \quad + \quad CH_3 - OH \quad \longrightarrow \quad H_2O + R - COO - CH_3$$

Water must be separated. This is done by decantation at the same tank as water settles down at the lowest part of it. After esterification, the content of the tank which is composed of triglycerides, methyl esters and remaining FFA, is transferred to the transesterification tanks.

The second step is the transesterification phase using methanol and KOH (previously mixed as potassium methoxide) as a catalyst. This is done in a mixing tank at 55 °C. The yield of the reaction is practically 100%. As the esterification time is shorter than the transesterification one, in order to optimise the semi continuous process there are three identical transesterification units, so this stage of the process does not become a bottleneck. The separation of the glycerol phase and the biodiesel phase is done at the same tank by decantation. In order to improve the separation, water and phosphoric acid are added. Water sets in the middle of the two phases so when extracting the lower phase (glycerol) it is possible to check when it has been all extracted by using a conductivity meter (water has less conductivity than glycerol). This avoids losing methyl esters in the glycerol phase.

The methyl ester phase, which contains unreacted glycerides, FFA, methanol and catalyst, is distilled at 200 °C, so an almost pure methyl ester phase is obtained (99.9%). The methanol extracted is reused. The rest of matter, which is a mixture of unreacted glycerides, FFA and catalyst, etc. is sold as bio-heating oil for heavy industries.

After transesterification, the glycerol phase is sent to an acidulation tank where possible soaps formed during transesterification are split into FFA and salts thanks to the addition of sulphuric acid. The acid waters obtained at the esterification phase can be added in order to reach the needed amount of sulphuric acid. FFA are sent back to the esterification tank. At a second stage, the glycerol phase is neutralised using potassium hydroxide. Then, the remaining methanol is recovered and the potassium salts plus the remaining substances are sold as an additive for compost production.

2.7 Other materials and processes under R&D

As explained in the introduction of this chapter, there are other processes to produce biodiesel that are under research and development. The reasons to try to find additional kinds of biodiesel respond to a number of drawbacks associated with their use. These include:

- The limitation on the extent to which these fuels can be used in current fleets (the so called blending wall). As seen in previous paragraphs, the current legislation in the EU does not allow blending more than 7% biodiesel into fossil diesel. This also affects the fuel infrastructure.
- The sensitivity of biodiesel (and biofuels) from crops to the feedstock prices, especially taking into account that in conventional biodiesel production the cost of vegetable oil can represent around 85% of the total production costs.
- The sustainability concerns mentioned in chapter 1 as for example the indirect land use change and influence in the food and feed prices.

These processes are often referred to as the ones producing advanced biodiesel. However, the definition of “advanced” in this context is not clear. The definition by most stakeholders, especially NGOs, is based on the feedstocks of origin, which are normally non-food feedstocks not requiring arable land for their production. This involves waste, residues and lignocellulosic materials in line with article 21 of the Renewable Energy Sources Directive [99] that sets the double counting of biofuels from these materials towards the achievement of the 2020 target.

Other actors base the definition on technological grounds. For these actors, especially fossil fuel companies, advanced biofuels are those produced with innovative technologies, not commercialised, which produce a fuel called "drop-in" fuel, which means that can be blended with conventional fossil fuels at all rates.

Finally, some other actors, like NGOs and decision makers define as advanced biofuels those ones having high greenhouse gas emission reduction levels and other environmental benefits.

Eventually, these three definitions overlap between each other as for example in the case of hydrotreated vegetable oil (HVO) from UCO. However, this would not be the case when the HVO is produced from unused vegetable oils, like palm oil.

An initiative funded by the European Commission under the 7th Framework Programme, the European Sustainable Biofuels Forum, ESBF, is working in finding an agreement on the definition of advanced biofuels.

Independently of the definition, this paragraph describes shortly some of the considered advanced biofuels for use in diesel engines,from information provided by EBTP, IEA and SETIS [73, 139, 208]. Figure 2.14 shows the commercialisation status of these technologies according to the IEA. The European project BIOMAP [23] shows the projects that have been funded in the European Union about these technologies:

- Hydrotreated vegetable oil (HVO). The production of HVO is normally carried out in existing refineries. The process consists in using hydrogen to remove the oxygen from the triglyceride. The oxygen-free product is the final fuel. The main advantages of the process is that additional chemicals, like methanol, are not needed and that it does not produce any glycerol [1]. Table 2.11 shows the consumption data for two existing HVO plants [148].

  According to the IEA , this biofuel is in an early commercial stage, and in some markets it is an already an established biofuel. This is the case of Spain where according to the

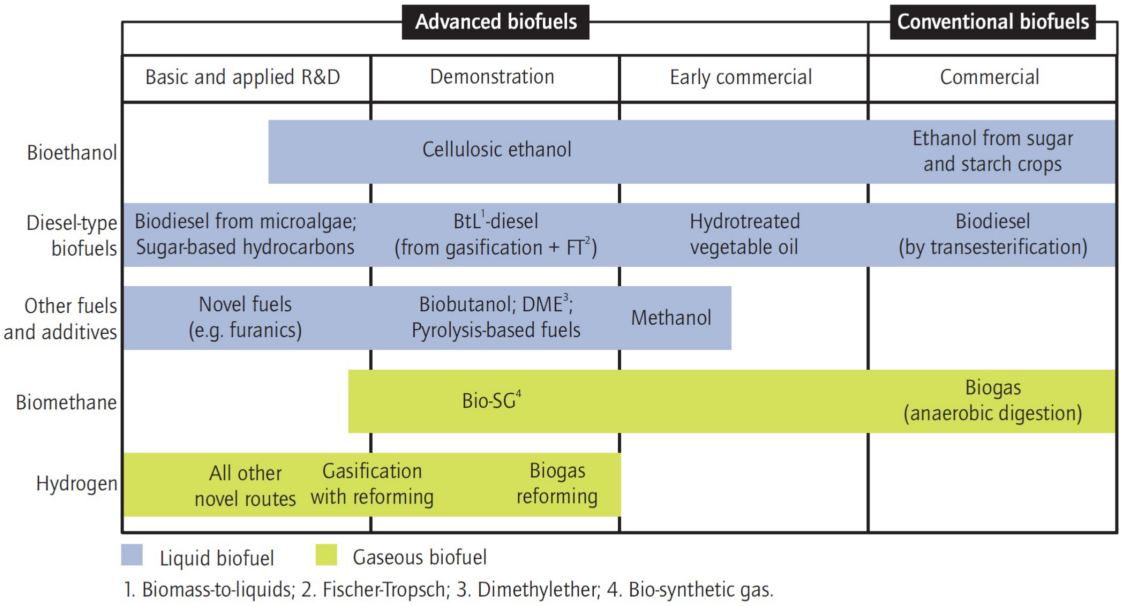


Figure 2.14: Commercialisation status of main biofuel technologies. Source: IEA, 2011 [29]

National Energy Commission (CNE) in its annual report published in 2013, in 2011 HVO already represented a 3.85% of the biofuel market (91,196 million litres) [49]. All the HVO produced was from palm oil origin, being one main technical barrier of this technology the use of waste oils and fats, which is not fully developed as stated Mittelbach [175]. Another barrier is the higher total costs compared to conventional biodiesel in part due to the high cost of the hydrogen used in the process.

This product is fully mixable with fossil diesel being the mixture still compliant with the diesel quality requirements (EN590); therefore this biofuel is highly accepted by the automotive and fuel industry as a substitute for fossil diesel.

This biofuel is an interesting option for the aviation sector. As mentioned in chapter 1, the American Society for Testing and Materials, ASTM, has approved the modification of the ASTM D7566 - 13 Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons, to allow the mixture of jet fuel with biofuels produced by Fischer-Tropsch process and hydrotreated esters and fatty acids (HEFA).

According to the Annex V of the Renewable Energy Directive [99], HVO can achieve typical greenhouse gas emissions savings from 40% to 68%, although this still needs further analysis.

- Biomass-to-liquid (BtL). This fuel is still under demonstration according to the IEA. The term BtL is applied to synthetic fuels made from biomass through a thermochemical route. It is also known as synfuel or sundiesel.

  Although the technology to produce this fuel is well known and has been applied during decades using fossil-feedstocks, such as methane (GtL) or coal, commercial advanced biofuels based on these technologies are not currently widely available in the market place [73].

  The thermochemical route consists of two steps, first gasification and then Fischer-Tropsh. According Rutz and Janssen [205], gasification consists basically in heating at high temperatures (in some demonstration plants to around 500 °C in others up to 1200 °C) and high pressure so that the material is broken down into synthetic gas. A gasification agent such as oxygen needs to be present as air or pure oxygen. The synthetic gas is composed mainly of hydrogen, carbon monoxide and carbon dioxide. This gas needs to be cleaned before entering the other step. The cleaning process is considered as the bottleneck of the process as it uses part of the output gas reducing the efficiency. The final step is the synthesis process known as Fischer-Tropsh which consists of putting in contact the reactive parts of the synthesis gas (CO and H_2) with a catalyst to form hydrocarbons.

One of the advantages of BtL is that it can be produced from many biomass resources besides energy crops such as agricultural residues, e.g. straw, and waste wood [205]. The other benefit is that the process allows producing fuel components that are similar to those of current fossil-derived petrol (gasoline) and diesel fuels and hence can be used in existing fuel distribution systems and with standard engines. As mentioned above, it can be used also as a jet fuel. For these reasons, this fuel is also highly accepted by the automotive and fuel industry.

The main specific technical barriers that this technology is facing are the high investment costs and the use of the waste obtained which is still not developed. More research is needed to scale-up the existing plants, according to Mittelbach [175].

Table 2.11 shows the greenhouse gases considered for this fuel in the Annex V of the Renewable Energy Directive [99].

- Biodiesel from micro-organisms, such as microalgae, bacteria and fungi, which are still under basic and applied R&D. According to EABA, the European Algae Biomass Association, algae and aquatic biomass have the potential to provide a new range of third generation biofuels, including jet fuels. The most important advantages of these resources are their high oil and biomass yields, widespread availability, absent (or very reduced) competition with agricultural land, high quality and versatility of the by-products, their efficient use as a mean to capture CO_2 and their suitability for waste water treatments and other industrial plants [61, 73, 211].

  Other authors state that a priori the strategy of aiming to generate lipids directly from microalgae for biodiesel production does not seem very profitable. A more suitable approach would be through thermochemical processes of the Fischer-Tropsch type, based on an algal biomass rich in polysaccharides. The problem is not so much the production of lipids, as knowing how to extract and process them adequately, according to a report produced by BIOPLAT [25]. However, these authors also mention existing examples of projects and research activities on biodiesel production from algae: Soladiesel, EXXON-Venter, PLANKTON POWER, SAPPHIRE ENERGY and PETROALGAE.

  The main challenges of using these resources are firstly finding species of an adequate composition for the production of fuels and secondly adjusting the technologies for the harvesting and extraction. Another drawback is that the biodiesel produced might need specific quality specifications as it may not comply with the standard EN 14214 [36]. Finally, as for the other advanced technologies, Mittelbach [175] identifies a need to reduce production costs.

  The life cycle greenhouse gas emissions need to be analysed although assuming the fact that they are a means to capture CO_2, the reductions should be high. According to Zhanga et al. [254], biodiesel production from phototrophic microalgae has negative GHG emissions, i.e. they are carbon dioxide capture processes.

- Hydrocarbons from catalysis of plant sugars and via synthetic biology. According to the European Biofuels Technology Platform [73], chemical catalysis of modified micro-organisms offer great potential for converting sugars into specific fuel molecules including biopetroleum, bio jet fuel and other drop-in fuels, which have very similar properties to their fossil fuel counterparts. This possibility is still under basic and applied research.

Table 2.10: Mass and energy for the production of 1MJ of HVO. Source: JEC study [148]

Products	**I/O**	**NExBTL** MJ/MJ HVO	**UOP** MJ/MJ HVO
Hydrogen	Input	0.0857	0.11
Vegetable oil	Input	1.0341	0.91
Electricity	Input	-	0.005
Electricity	Output	0.0015	-
Steam	Input	-	0.013
Steam	Output	0.008	-
Heavy fuel oil	input	-	0.013

Another possibility of producing advanced biodiesel not mentioned by the IEA in its biofuels technology report [29] is using the waste oils and fats obtained from sewage sludge in waste water treatment plants. Several researchers have studied the potentialities of this resource [5, 178, 189, 195, 209, 210, 257].

According to Navia and Mittelbach, taking into account that the lipid content is, on a dry basis, in the range of 20 to 26% in the primary sludge and 6% in the secondary sludge, with about 65% of free fatty acids, the estimated potential for biodiesel in Europe and the U.S. could reach 700,000 tonnes/year [184].

The main challenges of this resource are the drying of sewage sludge and the extraction process for recovery of the lipids fraction, according to [184]. Also, the composition of free fatty acids could result in non-compliance of the biodiesel fuel with the quality standard EN 14214 [36], especially the cold weather related properties. This could be solved by mixing it with high quality biodiesel in small percentages. The high amount of free fatty acids (up to 65%) of this resource requires a first esterification phase as when using UCO and described before. It might also require distillation as after-treatment process [184].

According to Zhanga et al. [254], biodiesel production from sludge has negative GHG emissions, which suggests that they are carbon dioxide capture processes.

Other advanced biofuels for transport that can be used in conventional petrol vehicles or vehicles provided of a gas engine are: biobutanol, cellulosic ethanol, bioDME/methanol, biosynthetic natural gas (BioSNG) and biohydrogen.

These technologies may offer advantages over the conventional biodiesel produced from energy crops: first, the use of non-food raw materials or feedstocks that have lower land requirements; secondly, production of drop-in that can be blended in any proportion with fossil-based fuels; and finally, better overall greenhouse gas balances.

As far as greenhouse gas emissions are concerned, the Renewable Energy Sources Directive [99] assigns very high reduction values compared to conventional biodiesel. Table 2.11 shows the estimated typical and default values for future biofuels that were not on the market or were on the market only in negligible quantities in January 2008, if produced with no net carbon emissions from land-use change.

Table 2.11: Estimated typical and default values for future biofuels for diesel engines. Source: Directive 2009/28/EC

Biofuel production pathway	Typical greenhouse emission saving	Default greenhouse emission saving
Waste wood Fischer-Tropsch diesel	95 %	95 %
Farmed wood Fischer-Tropsch diesel	93 %	93 %
Waste wood dimethylether (DME)	95 %	95 %
Farmed wood DME	92 %	92 %
Farmed wood methanol	91 %	91 %

There are two main reasons why these advanced biodiesels are not analysed in this Ph.D. On the first hand, the high greenhouse savings already achieved by these fuels makes that no technological improvements need to be applied in terms to make them comply with the new proposal of a Directive [89]. On the other hand, most of them are still under demonstration, or research and development, what means that they will not become available in the market in the short term.

2.8 Conclusions

In this chapter a definition is presented on what exactly is meant by biodiesel in the context of this thesis. This is the fatty acid alkyl esters produced from triglyceride containing materials. The current production and consumption rates in the World, Europe and Spain and which are the future consumption perspectives have been gathered from relevant sources. This information has shown that biodiesel is nowadays an important biofuel and will continue being a significant contributor to transport fuel diversification. In spite the potential re-shaping of the European legal framework, biodiesel will continue being produced worldwide in the next two decades.

The life cycle processes and technologies for biodiesel production from vegetable oils, used cooking oils and animal fats is described. The consumption data at each step of the process provide the information to be used in the forthcoming chapters. There are different consumption data depending on the source of information. The differences may be due to several factors, among them climatic, geographical, etc. The reason for selecting the data of the well-to-wheels analysis of future automotive fuels and powertrains in the European context, developed by the European Commission's Joint Research Centre has been justified, as this information has formed the basis for defining the sustainability criteria of the Renewable Energy Sources Directive [99].

Chapter 3

Thermoeconomic analysis

As shortly mentioned in chapter 1, biodiesel is considered a renewable energy source. However, although renewable, as for every industrial system, biofuel manufacturing consumes natural resources. The production cycle is not reversible which means that resources are consumed and lost forever. The great advantage of biofuels production is that a great part of the resources consumed is renewable: solar radiation used to grow the plant from which the biofuel is obtained

Still, part of the resources consumed –the non-renewable resources– are not regenerated and this contributes to accelerate the natural increase of the earth's entropy, fostered by the economic progress [122]. The consumption of natural resources can be assessed following the concepts and tools defined by thermoeconomics. Acording to Valero [237], thermoeconomics is a resources saving science connecting physics and economics, thus setting the perfect frame to the aim of this Thesis.

This chapter presents the thermoeconomic methodologies used to assess biodiesel production in the subsequent chapters. It defines the concept of exergy cost, exergoecologic cost including Life Cycle Assessment and the *Exergy Return on Exergy Investment* (ExROI) on the basis of the exergy cost theory [165]. In other words, it provides the description of the methodology to calculate the ratio of non-renewable exergy consumed in the system (exergy cost) to the exergy that the biodiesel has.

3.1 Exergy Analysis

It is well-known that to have something with a high potential to carry out an action has a great value. In terms of physics this intensive potential is measured using pressure, temperature, chemical potential…The real value of the things is not to have but to have more than our environment.

If we liberate the bounds that maintain the high potential of our system, it will evolve toward the environment conditions, without producing any useful work. The energy and the mass of our system will not change, but we will note that something has changed.

To quantify these changes the entropy concept is used. The entropy of a system is a function of its intensive potentials, and it is defined in such a way that the entropy increases as much as less useful effects take place when the system evolves toward its environment. Therefore, we have introduced the Second Law and we have related the concepts of entropy and usefulness. What is the usefulness from the point of view of Physics?

On one hand, the thermodynamic usefulness or availability always has a reference. The usefulness is measured with regard to a reference level, the farther away the intensive potentials from a reference level are, more usefulness the process has. On the other hand, the magnitude we use in physics to account the availability to do something is the energy (kilowatts per hour). Although, in accordance with the First Law the energy that we pay in our electricity bill is the same one that the heat vanished by a stove that consumes those kilowatts per hour.

3.1.1 Exergy definition

Not all the energy types have the same quality, for that reason the thermodynamic usefulness will have to be measured in some type of magnitude that indicates quality and quantity at the same time. The ability to perform mechanical work has been accepted as a measure of the quality of a kind of energy, characterizing their ability to be transformed into other kinds of energy. This ability depends not only on the composition and state parameters of the considered matter (determining its energy) but also on the composition and state parameters commonly appearing in the environment in which the transformation process takes place. This quality index for energy was termed by Z. Rant *exergy* [219], and can be defined as follows:

> *Exergy expresses the maximum quantity of work that we could obtain from a flow that evolves toward the reference environment, by means a sequence of reversible processes.*

There are other ways to define the exergy concept:

- Exergy is the minimum work required to produce a material in its specific state from components common in the natural environment, in a reversible way [219].
- Exergy is the noble part of energy as it is the part of energy capable of producing work [164].
- Exergy is a synonym of the capacity to create changes [154]. For a flow, it is the maximum quantity of work obtainable when the flow is transferred from its initial state to a final state through processes in which the flow interacts exclusively with the environment [154].
- The exergy content of a natural resource input can be interpreted as a measure of its quality or potential usefulness, or its ability to perform *useful work* [13].
- Exergy is the standard used to measure which is the part of a flow of disordered energy capable of producing work. Disordered energy is the type of energy which capacity of producing work, i.e. its quality, depends on the parameters of the environment and of the system [154]. As examples, thermal and chemical energies are disordered energies and potential energy is an ordered energy.

An example of what exergy means is that of steam: it does not produce the same amount of useful energy a stream of steam at atmospheric pressure than when it is under big pressure. Pressured steam can be used to produce electricity in a turbine while atmospheric steam is useless.

As exergy is a measure of the deviation of the state of a system from that of the environment, exergy is an attribute of the system and environment altogether. Once the environment is specified, however, a value can be assigned to exergy in terms of property values for the system only, so exergy can be regarded as an extensive property of the system.

Exergy can be destroyed and generally is not conserved. A limit case would be when exergy is completely destroyed, as occurs when a system comes into equilibrium with the environment spontaneously with no provision to obtain work. The capability to develop work in the initial states would be completely wasted in the spontaneous process. Moreover, because no work needs to be done to produce such a spontaneous change, it may be concluded that the value of exergy is at least zero and therefore cannot be negative.

3.1.2 Reference environment

Any system, be it a component in a larger system such as a steam turbine in a power plant or the power plant itself, operates within surroundings of some kind. Distinguishing between the environment and the system's surroundings is important. The term *surroundings* refers to everything not included in the system. The term *environment* applies to a portion of the surroundings, in which the intensive properties are uniform and do not change significantly as a result of any process under consideration. The environment is regarded as free of irreversibilities. All significant irreversibilities are located within the system and its immediate surroundings.

Because the physical world is complicated, models with various levels of specificity have been proposed for describing the environment. In the present discussion the environment is modelled as a simple compressible system, large in extent, and uniform in temperature, T_0, and pressure, p_0. In keeping with the idea that the environment has to do with the actual physical world, the values for p_0 and T_0 used throughout a particular analysis are normally taken as typical environmental conditions, such as 1 atm. and 25 °C.

The environment is regarded as composed of common substances existing in abundance within the atmosphere, the oceans, and the crust of the Earth. The substances are in their stable forms as they exist naturally, and developing work from interactions –physical or chemical– between parts of the environment is not possible. Although its intensive properties do not change, the environment can experience changes in its extensive properties as a result of interactions with other systems. Kinetic and potential energies are evaluated relative to coordinates in the environment, all parts of which are considered to be at rest with respect to one another. Accordingly, a change in the energy of the environment can be a change in its internal energy only.

When the pressure, temperature, chemical composition, velocity, or elevation of a system is different from the environment, an opportunity to develop work exists. As the system changes state toward that of the environment, the opportunity diminishes, ceasing to exist when the system and the environment, at rest relative to one another, are in equilibrium. This state of the system is called the *dead state*. At the dead state, the conditions of mechanical, thermal and chemical equilibrium between the system and the environment are satisfied: the pressure, temperature, and chemical potentials of the system are equal to those of the environment, respectively. In addition, the system has zero velocity and zero elevation relative to coordinates in the environment. Under these conditions, no possibility exists of spontaneous change within the system or the environment, nor can they interact.

3.1.3 Exergy components

In the absence of nuclear, magnetic, electrical, and surface tension effects, the exergy of a stream of matter E, crossing the system boundaries can be divided into four components: physical exergy, E^{PH}, kinetic exergy, E^{K}, potential exergy, E^{P}, and chemical exergy, E^{CH}, that is:

$$E = E^{PH} + E^{K} + E^{P} + E^{CH} \tag{3.1}$$

The sum of the kinetic, potential, and physical exergies is also referred to as thermomechanical exergy. Although exergy is an extensive property, it is often convenient to work with it on a unit mass basis. The specific exergy, e is given by

$$e = e^{PH} + \frac{c^2}{2} + g\,z + E^{CH} \tag{3.2}$$

In equation (3.2), c and z denote velocity and elevation relative to coordinates in the environment. When evaluated relative to the environment, the kinetic and potential energies of the system are, in principle, fully convertible to work as the system is brought to rest relative to the environment, and so they correspond to the kinetic and potential exergies, respectively.

Considering a system at rest relative to the environment ($E^{K} = E^{P} = 0$) the physical exergy is the maximum theoretical useful work obtainable as the system passes from the initial state, where the temperature is T and the pressure is p, to the reference environment, where the temperature is T_0 and pressure is p_0.

The specific physical exergy of a flow at a specified state is given by the expression:

$$e^{PH} = (h - h_0) - T_0(s - s_0) \tag{3.3}$$

where h and s denote, respectively, the enthalpy and entropy of the system at the specific state. h_0, and s_0 denote the enthalpy and entropy on the reference environment.

When working with liquids, it can be considered that the variations of pressure do not affect the exergies, then eq. (3.3) could be written as:

$$e^{PH} = c_p(T)\left(T - T_0 - T_0 \ln\frac{T}{T_0}\right) \tag{3.4}$$

where $c_p(T)$ represents the specific heat when pressure is constant. In this work c_p values are taken from bibliography when available or calculated using the Joback aggregation method [198]. The calculation method for biodiesels is explained in appendix A.

3.1.4 Chemical Exergy

The chemical exergy expresses the exergy of a substance at environment temperature and pressure. It is defined as the maximum work which can be obtained when the considered substance is brought from its initial state in a reversible way to the state of reference substances present in the environment, using the environment as a source of heat and of reference substances necessary for the realization of the described process. Standard chemical exergy results from a conventional assumption of a standard ambient temperature and pressure and standard concentration of reference substances in the natural environment.

The chemical composition of a substance is the key factor for fixing the final use of a certain substance. Furthermore, it has a direct influence on the energy required for processing the considered resource. For instance, the energy required to extract pure copper from its sulphide is significantly smaller than from its oxide, therefore copper sulphides such as chalcopyrite ($CuFeS_2$) are preferred as copper ores.

The chemical exergy of any chemical compound e^{CH}, can be calculated in terms of chemical potential by means of the expression:

$$e^{CH} = \sum_i \mu_{0,i} \left(N_i - N_{0,i}\right) \tag{3.5}$$

where $\mu_{0,i}$ is the chemical potential of the substances in the environment, $N_{0,i}$ is number of moles of substance i in the environment.

The chemical exergy can be also calculated by means of the exergy balance of a reversible formation reaction:

$$e^{CH} = \Delta G_f + \sum_i n_i e_i^{CH} \tag{3.6}$$

This expression is usually more convenient to use, as the Gibbs free energy of formation and the chemical exergy of the elements that compose the compound can be found in the bibliography [217] or be calculated [43]. The standard Gibbs free energy of formation of a compound is the change of Gibbs free energy that accompanies the formation of 1 mole of that substance from its component elements, at their standard states. Table 3.1 shows values of chemical exergy for pure elements from different bibliographic sources .

Table 3.1: Chemical exergies of the pure elements

		Szargut 2005 [217]		Szargut 1983 [154]		Rivero 2006 [202]	
Element	Reference Substance	e^{ch} kJ/mol	e^{ch} kJ/kg	e^{ch} kJ/mol	e^{ch} kJ/kg	e^{ch} kJ/mol	e^{ch} kJ/kg
C	C	410.25	34,157.0	410.82	34,204.5	410.27	34,158.7
H	H_2	236.10	117,116.6	238.49	118,302.1	236.12	117,126.5
O	O_2	3.97	124.1	3.97	124.07	122.5	3.88
N	N_2	0.72	25.7	0.72	25.7	0.67	23.9
P	P	861.42	27,811.3	859.60	27,752.5	861.30	27,807.4
Na	Na	336.71	14,646.1	343.83	14,955.8	336.70	14,645.6
K	K	366.66	9,377.0	371.52	9,501.3	366.70	9,378.0

For organic compounds the chemical exergy can be calculated by means of group contribution techniques. The two techniques considered in this Ph.D. are the ones developed by Van-Krevelen Chermin and Jankowski. Although originally created to be used for gaseous compounds the Van-Krevelen Chermin method has been also applied to liquids [185, 221]. These methods are described in appendix B

The chemical exergy of gaseous and liquid organic fuels can be determined by means of equation (3.6). This is, however, not possible in the case of the majority of solid and liquid organic fuels consisting of complex solutions and mixtures of many compounds. An approximate formula could be obtained expressing the ratio β of their chemical exergy to the lower heating value LHV as a function of the atomic ratio of the elements C, H, O, N, S.

$$e^{CH} = \beta \cdot LHV \tag{3.7}$$

- For solid C, H, O, N compounds

$$\beta = 1.0347 + 0.0140\frac{H}{C} + 0.0968\frac{O}{C} + 0.0493\frac{N}{C} \tag{3.8}$$

- For liquid C, H, O, S compounds

$$\beta = 1.047 + 0.0154\frac{H}{C} + 0.0562\frac{O}{C} + 0.5904\frac{S}{C}\left(1 - 0.175\frac{H}{C}\right) \tag{3.9}$$

The exergy of some biodiesel computed by eq. (3.7) are show in table 3.2. More detailed methods for calculation of exergy can be found in [58, 217, 245]. All the calculations of the exergies for the compounds considered in this Ph.D. are further explained in the following chapters and in the appendix B.

Table 3.2: Chemical exergy calculation by LHV for methil esters (data provided by UCLM)

	Atoms				LHV	Exergy
Sustance	C	H	O	β	kJ/kg	kJ/kg
Sunflower	18.91	34.76	2	1.0726	37,274.63	39,981.33
Rape	18.97	35.33	2	1.0730	37,336.83	40,062.28
Palm	18.31	35.05	2	1.0740	37,215.54	39,970.70
UCO	18.40	34.46	2	1.0733	37,311.32	40,047.84

3.1.5 Exergy balance

It is usually considered that performing mass and energy balances to a process is an effective way to optimize such process. These balances are based on the First Law of thermodynamics i.e. energy and mass are neither created nor destroyed. For this reason, these balances just consider as losses of a process the mass and energy flows that exit the boundaries of the system.

These balances do not take into consideration the losses of energy quality that might be caused because of the degradation of the mass and energy along the process, i.e. they do not consider the Second Law. The loss of quality of the mass and energy along the process might have important consequences in the efficiency of the process and need to be taken into account for a correct process optimisation. For example, a reduction in the quality of mass and energy flows might lead to increases in the use of resources or to increases in the production of wastes. The Second Law states that energy can only be transformed by the consumption of quality. The level of deterioration of quality is measured through the entropy property. In a system with identified borders, the only processes than can occur are those for which the entropy of the isolated system increases.

Therefore, in order to produce an adequate optimisation of a process, both First and Second Laws should be combined to take into account both the losses due to the mass and energy flows that exit the boundaries of the system and the losses due to a deterioration of the quality of the flows. This is captured by the exergy content of the flows. In all physical transformations of matter or energy, it is always exergy that is lost.

For this fundamental reason, performing an exergy balance to a producing process is a more powerful tool for designing and auditing industrial installations. The exergy balance for a closed system is obtained with the combination of energy and entropy balances. Exergy can be applied for resource accounting because all material and energy flows have a definable and calculable exergy content, with respect to a defined external environment. Therefore, the exergy concept has the capability of aggregating heterogeneous energy and material assets.

Most applications of engineering thermodynamics are conducted on control volume basis, see fig. 3.1.

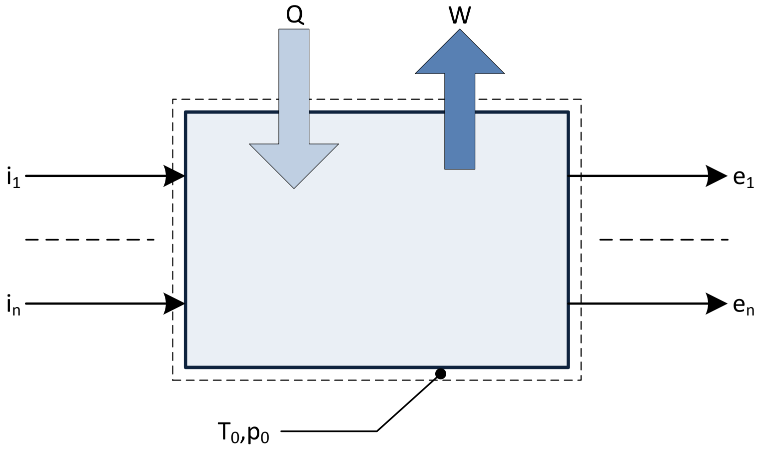


Figure 3.1: Control volume diagram

For applications in which inward and outward flows occur, each through one or more flows, the mass balance in steady state is expressed as:

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e \quad [\mathrm{kg/s}] \tag{3.10}$$

where dm/dt represents the time rate of change of mass contained within the control volume, $\dot{m}_i$ denotes the mass flow rate at an inlet stream, and $\dot{m}_e$ denotes the mass flow rate at an exit stream.

The energy rate balance in a steady state for such a system is:

$$\dot{W} - \dot{Q} = \sum_i \dot{m}_i \left(h_i + \frac{c_i^2}{2} + g z_i \right) - \sum_e \dot{m}_e \left(h_e + \frac{c_e^2}{2} + g z_e \right) \quad [\mathrm{W}] \tag{3.11}$$

The terms $\dot{Q}$ and $\dot{W}$ account, respectively, for the net of energy rates by heat and work. The right side of the equation accounts the energy rate balance of mass streams.

The entropy balance in steady state is written as:

$$0 = \frac{\dot{Q}}{T} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \dot{S}_g \quad [\mathrm{W/°K}] \tag{3.12}$$

$\dot{Q}$ represents the rate of heat transfer at the location on the boundary where temperature is T. The terms $\dot{m}_i s_i$, $\dot{m}_e s_e$ account, respectively, for rates of entropy transfer into and out the control volume accompanying mass flow. $\dot{S}_g$ denotes the time rate of entropy generation due to irreversibilities within the control volume.

Combining energy and entropy balances at steady state, we get:

$$\left(1 - \frac{T_0}{T}\right) \dot{Q} - \dot{W} + \sum_i \dot{m}_i \, e_i - \sum_e \dot{m}_e \, e_e = T_0 \dot{S}_g. \tag{3.13}$$

The term $(1 - T_0/T)\dot{Q}$ represents the exergy associated with heat transfer Q, by definition of exergy transfer associated with work is equal to its energy W. The term $\dot{m}_i\ e_i$ accounts for the time rate of exergy transfer accompanying mass flow at inlet i. Similarly, $\dot{m}_e\ e_e$ accounts for the time rate of exergy transfer accompanying mass flow at exit e, the value of specific exergy e correspond with the physical exergy given by eq. (3.3) The last term $T_0\dot{S}_g$ accounts for the time rate of exergy destruction due to irreversibilities within the system, that is defined as:

$$\dot{I} = T_0\dot{S}_g \geq 0 \quad [\mathrm{W}] \tag{3.14}$$

A First Law energy analysis generally fails to identify energy waste or effective use of fuels and resources. For instance, the First Law does not recognize any loss in an adiabatic throttling process, one of the worst processes from the thermodynamic point of view.

The Second Law shows that, in some energy carriers (e.g., enthalpy of a flow stream) a part of the energy is useless. Exergy is the part of energy that can be converted into any other form of energy. An exergy analysis based on both the First and Second Laws, calculates the useful energy associated with thermodynamic system or with each flow stream in the process. It also identifies and evaluates the inefficiencies of an energy system. This analysis shows that useful energy is destroyed during any step of an energy conversion process, while the total energy remains constant. An energy analysis is the way to unmask the high irreversibilities in processes such as combustion, heat transfer throttling or mixing. The causes of irreversibilities or exergy destruction could be located and quantified and the effects of inefficiencies of other components could be detected.

3.2 Exergy Efficiency

The thermal efficiency and coefficient of performance based only on the First Law make no reference to the best possible performance. However, the exergetic efficiency or Second Law efficiency overcomes this deficiency and gives a measure of approximation to reversible operation. Exergetic efficiencies are useful for distinguishing means for utilizing energy resources that are thermodynamically effective from those that are less so. They can be used to evaluate the effectiveness of engineering measures taken to improve the performance of a thermal system. The exergetic efficiency is defined in a generic form as the ratio between the exergy recovered (P) and the exergy supplied (F):

$$\epsilon_i = \frac{P_i}{F_i} \leq 1 \tag{3.15}$$

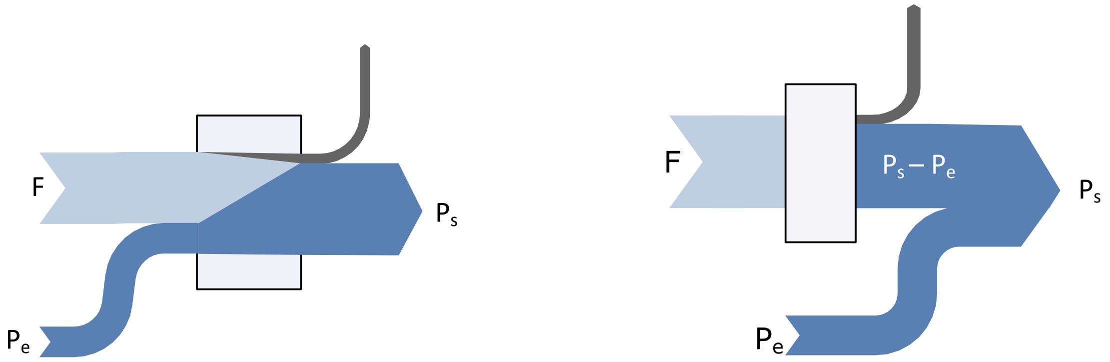
Equivalently, the inverse value is the unit consumption, i.e. the amount of resources required per product obtained:

$$k_i = \frac{F_i}{P_i} \geq 1 \tag{3.16}$$

The definition of exergetic efficiency includes a classification of the flows crossing the boundaries of the system: the flows that are the production objective and the resources supplied to carry out the production. This information is not implicit in the Second Law or in the exergy balance. According to the exergetic efficiency definition, the exergy balance could be written as:

$$F_i - P_i = I_i \geq 0 \quad [J] \tag{3.17}$$

Exergy streams associated with energy streams (e.g., heat or work) appear either at the component inlet, and then are part of the fuel, or at the outlet, and then are part of the product of the component being considered. When working with mass streams, it is meaningful and appropriate to operate with exergy differences associated with each material stream between inlet and outlet.



(a) Physical Diagram (b) Productive Diagram

Figure 3.2: Product Streams modelling

The product consists of:

- all the exergy values to be considered at the outlet (including the exergy of energy streams generated in the component)
- all the exergy increases between inlet and outlet.

Product streams, see fig. 3.2, appear when the process purpose is to increase the exergy of a mass input flow: $P_s > P_e$. The product of the process is the exergy difference between output and input flows. The input fuel comes from the output of another process and it is added to the product of the process, which will be used as input in other process or as final product.

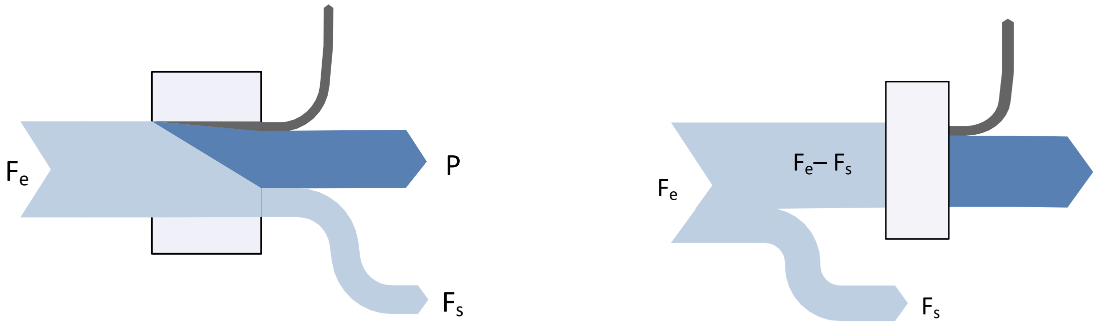
On the other side, the fuel consists of:

- all the exergy values to be considered at the inlet (including the exergy of energy streams supplied to the component) and
- all the exergy decreases between inlet and outlet.

A Fuel stream, see fig. 3.3 provides exergy to the process decreasing the quality of the mass: $F_e > F_s$. The process fuel is the exergy difference between input and output. The output flow will be used as input of other process.

It is usually considered that performing mass and energy balances to a process is an effective way to optimize such process as it applies the First Law of thermodynamics. However these balances just consider as losses the mass and energy flows that exit the process, without taking into consideration the losses of energy quality that might be caused because of the degradation of the mass and energy along the process, i.e. without considering the Second Law.

For this fundamental reason, performing an exergy analysis to a producing process is a more powerful tool for designing and auditing industrial installations, as it analyses the equipments/units using as a basis the Second Law, i.e. the degradation of the energy (or the quality of energy) along the process, or in other words, the loss of quality of the energy, which is an effective way to have information on the efficiency of the processes.



(a) Physical Diagram (b) Productive Diagram

Figure 3.3: Fuel Streams modelling

In addition, exergy can be applied for resource accounting because all material and energy flows have a definable and calculable exergy content, with respect to a defined external environment. Therefore, the exergy concept has the capability of aggregating heterogeneous energy and material assets.

The exergy is always higher at the beginning of the process (summing the exergy of all the inputs), and it is reduced along it, so the sum of the exergies of the outputs is always lower than the sum of the exergies of the inputs. The difference of the input exergy and the output exergy gives a picture of the efficiency of the system: the bigger the difference, the higher will be the degradation of the energy, i.e. the irreversibility (I) of the process, so the less efficient it will be, see (3.18). It is evident that the irreversibility cannot be negative, as if it were so it would contradict the Second Law.

3.3 Exergy Cost

In ideal conditions, the exergy needed to produce a certain substance or energy flow is the same as the exergy contained by the substance or flow. However, the actual processes produced by man are far from the ideal conditions and the energy and mass requirements to obtain a resource are always greater. For this reason, a system should not be evaluated in terms of the exergy obtained since this would ignore the technological limits of the processes. Therefore the cumulative exergy that has been consumed or in other words the exergy cost, need to be consider. The exergy costs take into account the technological limits of processes [237]. Another perspective to treat the same matter arises by making the following question: What is the exergy content of a beautifully designed bohemian glass? Or that of a stone sculpture? Or that of gold? The answer is zero in practical terms. Many things we value, thermodynamics does not. The source of value may be or may not be related to its exergy content, even for the case of fuels. The only thing that physics can do is to assess the physical cost of objects, i.e. the amount of energy units required to produce a given product, namely *embodied energy*.

The concept of embodied energy comes from the 1970s, when there was a great concern with the first global energy crisis. The problem with energy is the lack of techniques to allocate values of embodied energy when two products are produced simultaneously. A more precise concept then came: the *exergy cost* proposed by Valero or the *cumulative exergy consumption* proposed by Szargut [218], which are in fact the same concepts as embodied energy but using exergy.

Cost could be defined as the amount of resources needed to obtain a functional product. On one hand, resources take a general meaning. On the other hand, cost is associated to the purpose of production. It is associated neither with price nor with the resources that could be saved if the production process were less efficient.

Cost is an emergent property. It cannot be measured as a physical magnitude of a flow stream as temperature or pressure; it depends on the system structure and appears as an outcome of the system analysis. Therefore, it needs precise rules for calculating it from physical data. Cost is a property that cannot be found in the product itself.

The *exergy cost* of a mass or energy stream is the amount of exergy required to produce it. The *unit exergy cost* of a mass or energy stream represents the amount of exergy required to obtain a unit of exergy of the product stream. If E_i represents the exergy of the i-th product stream and E_i^* its exergy cost, the unit average exergy cost is written as:

$$k_i^* = \frac{E_i^*}{E_i} > 1 \tag{3.18}$$

Then, what is, for example, the exergy cost of electricity? A first answer would be 3 units of exergy, because we suppose that it is produced in a conventional thermal power plant burning fuel-oil or coal, with an efficiency of 33%. If we consider electricity at the consumer's point, we must add the losses in transmission and distribution. This adds a 10% to the unit cost giving now a cost of 3.3 units. However coal or fuel-oil must be mined, treated and transported to the plant. Additionally, each time we produce electricity we produce wastes that need to be disposed. Disposal of wastes requires more exergy: flue gas desulfuration, special NO_x burners and CO_2 capture and storage. Different studies indicate that electricity of thermal origin at the consumer's point can range between 4.5 and 5.5, which means that we need 4.5–5.5 units of exergy of coal in mine to produce one unit of electrical exergy. On the other hand, electricity, figuratively speaking, is a "raw fuel" used in most industrial processes. We can question ourselves what is the physical cost measured in exergy units of all manufactured products as well as the exergy needed for their use, maintenance, repair and disposal. This comprehensive analysis is named Exergy Life Cycle Assessment [51] and provides average exergy costs because it is focused in obtaining round numbers which could be used as ecological indexes of sustainability.

However, the problem comes up when two or more products, by-products and residues are produced simultaneously. How to allocate costs? We need rules mathematically supported rather than considering concepts of usefulness. We need to look inside the system in order to understand the process of cost formation, by identifying the internal relationships of all the structure components.

Indeed, the main problem of allocating costs has been to find a function that adequately characterizes all of the internal flows in a system and distributes cost proportionally. This function needs to be universal, sensitive and additive. That is, it needs to have an objective value for every possible material manifestations, it needs to be able to vary when these manifestations do so and each internal flow property needs to be represented additively. There is a wide international consensus that the best function, at least for energy systems, is exergy, which can contain in its own analytical structure the flow history.

The problem with allocating costs to flow bifurcations can be solved in a classical way. If the bifurcation does not affect the quality of the bifurcated flow, the costs are proportional to the quantity of each exiting flow. If the bifurcation affects quality, we must perform a detailed analysis of the change of exergy components and their proportion to allocate a cost to the bifurcated flow. Each exergy component is a reflection of a qualitative flow property which, in turn, has passed on to the flow throughout the history of the productive process with a specific resource consumption cost.

Therefore three conditions are needed to allocate costs. First, the definition of the boundaries of the system; second, a structure of the system in which all the components or processes are described in terms of black boxes interacting to each other through energy flows, or more generalized: energy, economic or information flows; and third, the definition of the productive purpose for each and every component.

In the cost formation process, it is essential to analytically search for the locations and physical mechanisms that make up a specific productive flow. The resources are used up to provide physico–chemical qualities to the intermediate products until a finished product is obtained. The main problem to be solved using exergy is how to measure and homogenize the accounting of these qualities.

Exergy, not only, is an objective measure of the thermodynamic value of an energy carrier but also is related closely to the cost of the exergy carrier, because users should pay only for the useful part of energy. Consider two energy carriers that consist of the same material (e.g. water) and have the same pressure and the same total energy; one operates at high temperature (superheated steam) an the other at a low temperature (saturated liquid water). The second carrier must have a larger mass. A thermal engineer would probably be willing to pay more for the first carrier than the second one because the cost of the heat exchanger, where the thermal energy would be used, will be lower if the high temperature energy carrier were used instead of the lower temperature carrier. This example indicates that exergy rather than mass or energy should serve as a basis for assigning cost to energy carriers. Thus, the Second Law sheds light on the cost formation process while the First Law could lead to erroneous conclusions.

Exergy costs are able to give this information and therefore they constitute the tool to understand the origin of losses, i.e. the origin of operative problems. The exergy cost of a flow is defined as the quantity of exergy needed to produce the flow in a determined process, understanding that the object of the process is to transfer the exergy of the fuel to the exergy of the main product. The more the exergy is transferred, the lower the exergy losses will be and, therefore, the more efficient.

By calculating the exergy costs of all the flows of the system, which enter and exit its units, one will have a picture of which exiting flow will have the higher exergy cost and also when, along the process, the cost is more or less increased. Knowing this, one can be able to discern where the actions will be more effective to reduce the exergy consumption of the system.

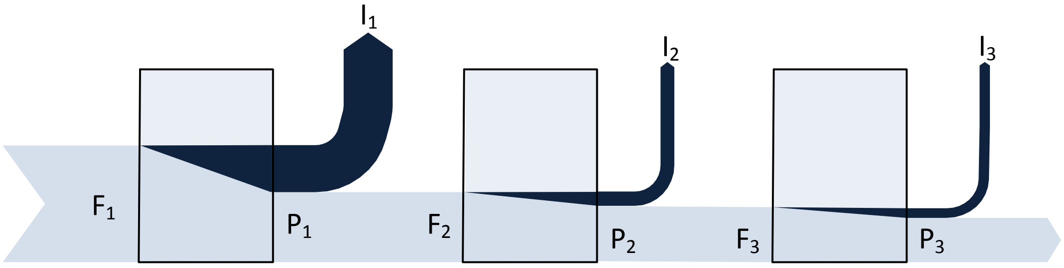


Figure 3.4: Exergy Diagram of a sequential system

Consider, for example, a system composed by several sequential processes, see fig. 3.4. it verifies: $P_i^* = F_1$, and the exergy cost of a product is the sum of the exergy of the product plus all the irreversibilities cumulated along the producing process. Due to $I_j \geq 0$, the exergy cost of a product is always bigger than its exergy and its unit cost bigger than one.

$$P_i^* = P_i + \sum_{j=1}^{i} I_j \tag{3.19}$$

On the other hand, eq. (3.20) shows, that the unit exergy cost of a product is equal to the product of the unit exergy consumption of the processes taking part in the production. These expressions could be generalized for any system, it does not matter how complex is it, see eqs. (3.38) and (3.45).

$$k_{P,i}^* = \prod_{j=1}^{i} \kappa_j \geq 1 \tag{3.20}$$

The concept of exergy cost could be extended to *exergoecologic* or *total exergy* cost, increasing the boundaries of the system, and considering that the exergy cost of the flows entering the system are accounted using exergy life cycle assessment. When these assessments are being incorporated, the exergy costs will include a greater part of the external irreversibilities. These irreversibilities have their origin in the manufacture, installation, maintenance of the physical units which constitute the logical process, in the elimination of residues and in the production of the external resources used in the system.

3.4 Thermoeconomic Input-Output Analysis

Thermoeconomic Input-Output analysis, formerly Symbolic exergoeconomics [224,225], provides general relationships between the production demand and the resources cost with the efficiency and irreversibilities of each individual process in an energy system. As explained in previous sections, the distinguishing element in thermoeconomics from conventional energy and exergy analysis is purpose. Matter and energy flows entering and exiting a given system are classified into fuel and product. Fuel (F) refers to the resources that the component uses to achieve its purpose, and product (P) corresponds to the flows related to that purpose.

The methodology presented here is closely related to the Input–Output analysis [174]. The mathematical principles are very similar, but the input–output table is transformed into a Fuel–Product model, in which the Second Law is used in the analysis of the processes.

Other studies such as those of Hau and Bakshi [132] have applied exergy to Input–Output analysis to a sample of industrial and ecological systems. In the same way, emergy has been also used as a unit of measure for I–O analysis. Emergy values resources, services and commodities in common units of the solar energy it took to make them [188].

The physical structure of a system (where all physical flows appear), needs to be converted into a productive structure represented by the fuel–product table,see table 3.3, which describes how the production processes are related.

Let us consider a system formed by, say n processes. Let P_i denote the exergy of the process i production, which is used in part to meet the intermediate requirement as input resources of other processes and in part to meet the final demand of the system. If E_{ij} denotes the exergy of process i uses as resource for process j, and E_{i0} denotes the final demand produced in process i, the following expression is formed:

$$P_i = E_{i0} + \sum_{j=1}^{n} E_{ij}, \quad i = 1, \ldots, n \tag{3.21}$$

Table 3.3: Fuel-Product Table

		Final Product	Process Resources					Total
			1	$\cdots$	j	$\cdots$	n	
External Resources			E_{01}	$\cdots$	E_{0j}	$\cdots$	E_{0n}	P_0
	1	E_{10}	E_{11}	$\cdots$	E_{1j}	$\cdots$	E_{1n}	P_1
Process Products	$\vdots$	$\vdots$	$\vdots$		$\vdots$		$\vdots$	$\vdots$
	i	E_{i0}	E_{i1}	$\cdots$	E_{ij}	$\cdots$	E_{in}	P_i
	$\vdots$	$\vdots$	$\vdots$		$\vdots$		$\vdots$	$\vdots$
	n	E_{n0}	E_{n1}	$\cdots$	E_{nj}	$\cdots$	E_{nn}	P_n
Total		F_0	F_1	$\cdots$	F_j	$\cdots$	F_n	

P_0 represents in this model the production of the environment, i.e. from the point of view of the system is the total exergy of the external resources, which denote as F_T

$$F_T \equiv P_0 = \sum_{j=1}^{n} E_{0j} \tag{3.22}$$

On the other hand, the input resources of each process i, say F_i, is in part coming from external resources, say E_{0i} and in part from the production of other processes, then we have the condition:

$$F_i = E_{0i} + \sum_{j=1}^{n} E_{ji}, \quad i = 1, \ldots, n \tag{3.23}$$

In this case, F_0 represents the fuel of the environment, that from of view of the system is its total production P_T:

$$P_T \equiv F_0 = \sum_{j=1}^{n} E_{j0} \tag{3.24}$$

The Second Law states that the difference between fuel and product is a positive value and equal to the irreversibility, accounting for the losses appearing in the process: $F_i - P_i = I_i \geq 0$.

The fuel and product equations (3.21) and (3.23) could be written in terms of exergy costs as:

$$\begin{aligned} P_i^* &= E_{i0}^* + \sum_{j}^{n} E_{ij}^*, \quad i = 1, \ldots, n \\ F_i^* &= E_{0i}^* + \sum_{j}^{n} E_{ji}^*, \quad i = 1, \ldots, n \end{aligned} \tag{3.25}$$

where E_{ij}^* denotes the exergy costs of the flow E_{ij}, and P_i^* and F_i^* are the cost of product and fuel of process i respectively.

The exergy cost theory defines three propositions in order to determine the production exergy costs [227]:

P1. In the absence of external assessment, the exergy costs of the flows entering the system equals their exergy. This indicates that, for the given boundaries of the system, the entering flows have no irreversibilities. For this reason, selecting an appropriate limit of the system is a crucial point of the analysis.

$$E^*_{0i} = E_{0i} \tag{3.26}$$

P2. The exergy cost is a conservative property, i.e. for each process in the system, the exergy cost of fuel is equal to the exergy cost of product.

$$F^*_i = P^*_i \tag{3.27}$$

P3. Exergy efficiency is used as allocation property: the exergy costs of the flows produced in a process are proportional to their exergies.

$$E^*_{ij} = k^*_{P,i} E_{ij} \tag{3.28}$$

The previous equations could be combined in the way of the following equation:

$$P^*_i = E_{0i} + \sum_{j=1}^{n} k^*_{P,i} E_{ji}$$

Then, the direct exergy cost of the products of each process of the system P^*_i can be determined by solving the set of linear equations, given by:

$$P^*_i - \sum_{j=1}^{n} \frac{E_{ji}}{P_j} P^*_j = E_{0i} \quad i = 1, l \ldots, n \tag{3.29}$$

or in an equivalent way, for the unit exergy cost, $k^*_{P,i}$:

$$k^*_{P,i} - \sum_{j=1}^{n} \frac{E_{ji}}{P_i} k^*_{P,j} = \frac{E_{0i}}{P_i} \quad i = 1, l \ldots, n \tag{3.30}$$

This methodology provides two possible representations of the system under study: a Resources driven model, from fuel to product (FP) or a Demand driven model, from product to fuel (PF), introduced in the next sections.

3.4.1 The FP representation

The FP representation allows one to obtain all flows of the productive structure of the system starting from the external resources (those consumed by the system from the environment). It is based on the distribution coefficients y_{ij}, see fig. 3.4, which indicate the proportion of the production of the i-th process used as resource in the j-th process. In other words, the coefficients indicate how the product of a component is distributed among the other components and the environment, see fig. 3.5.

The distribution coeficients are defined as:

$$y_{ij} = \frac{E_{ij}}{P_i} \tag{3.31}$$

and satisfy

$$\sum_{i=0}^{n} y_{ij} = 1 \tag{3.32}$$

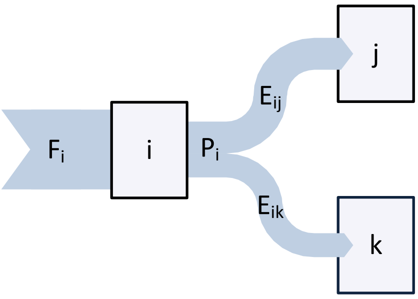


Figure 3.5: Distribution parameters

If eq. (3.31) is substituted into eq. (3.21), it yields:

$$F_i = E_{0i} + \sum_{j=1}^{n} y_{ji} P_j \tag{3.33}$$

In matrix notation, the previous equation becomes:

$$\mathbf{F} = \mathbf{F}_e + {}^{\mathrm{t}}\langle \mathbf{FP} \rangle \mathbf{P} \quad [J] \tag{3.34}$$

where $\langle \mathbf{FP} \rangle$ is a $(n \times n)$ matrix made up of elements y_{ij}, $\mathbf{F}$ and $\mathbf{P}$ are vectors containing Fuel and Products of all components and $\mathbf{F}_e$ is the vector of the external resources; i.e. resources consumed from the different processes and coming from the environment.

If eq. (3.16) is combined with eq. (3.34) it is possible to obtain:

$$\mathbf{P} = {}^{\mathrm{t}}\langle \mathbf{P} | \mathbf{F}_e \quad \text{where } \langle \mathbf{P} | \equiv (\mathbf{K}_{\mathrm{D}} - \langle \mathbf{FP} \rangle)^{-1} \tag{3.35}$$

$\mathbf{K}_{\mathrm{D}}$ is a $(n \times n)$ diagonal matrix containing the unit exergy consumption κ_i of all components, defined in eqs. (3.16) and (3.35). allows one to calculate the products $\mathbf{P}$ of all components from:

- The exergy external resources: $\mathbf{F}_e \equiv (E_{01}, \ldots, E_{0n})$
- The efficiency of each process or equivalently the unit consumption of each process: $\mathbf{K}_{\mathrm{D}}$
- The distribution ratios defined in $\langle \mathbf{FP} \rangle$

In other words, it uses external fuel to obtain all products, what explains the name of FP representation.

If we use the distribution ratios definition y_{ij} into cost equation (3.36) we get in matrix notation:

$$\mathbf{P}^* = \mathbf{F}_e + {}^{\mathrm{t}}\langle \mathbf{FP} \rangle \mathbf{P}^* \quad [J] \tag{3.36}$$

which let to determine the production exergy cost of all the processes of the system, as a function of the external resources and the distribution ratios, by means of the equation:

$$\mathbf{P}^* = {}^{\mathrm{t}}\left\langle \mathbf{P}^* \right| \mathbf{F}_e \quad \text{where } \left\langle \mathbf{P}^* \right| \equiv (\mathbf{U}_{\mathrm{D}} - \langle \mathbf{FP} \rangle)^{-1} \tag{3.37}$$

Comparing eqs. (3.35) and (3.37) it can be said that exergy cost is the maximum exergy we can obtain from a given resource if the system is composed by reversible processes $\mathbf{K}_{\mathrm{D}} = \mathbf{U}_{\mathrm{D}}$.

Subtracting the characteristic equation of FP representation for exergy eq. (3.34) from the corresponding equation for exergy cost eq. (3.36), we obtain:

$$\mathbf{P}^* - \mathbf{F} = {}^{\mathrm{t}}\langle\mathbf{FP}\rangle\left(\mathbf{P}^* - \mathbf{P}\right)$$

and applying exergy balance equation (3.17):

$$\mathbf{P}^* - \mathbf{P} = \mathbf{I} + {}^{\mathrm{t}}\langle\mathbf{FP}\rangle\left(\mathbf{P}^* - \mathbf{P}\right)$$

we get the following equation that relates cost and irreversilities:

$$\mathbf{P}^* = \mathbf{P} + {}^{\mathrm{t}}\left\langle\mathbf{P}^*\right|\mathbf{I} \quad [J] \tag{3.38}$$

which means that *the production cost of a product is equal to its exergy plus the sum of all irreversibilities generated to produce it.* In this way, we link the physical production cost of any process with the irreversibilities ocurred in its production. The coefficients π^*_{ij} of the matrix $\langle\mathbf{P}^*|$ represents the portion of exergy destroyed in the i-th process to obtain the product of process j-th.

It should be stated that the resulting costs of products depend on the way in which the external resources of the considered system are assessed. If these are evaluated in exergy terms, as it is proposed here, products will be valued in exergy cost terms as expressed in eq. (3.38). However, if external resources are valued in cumulative exergy terms, i.e. accounting for the exergy required to obtain those external resources, then the associated costs (exergoecological costs) of products will be defined as the amount of resources (of a renewable and non–renewable nature) required to obtain the given product. In the same way, if external resources are assessed in monetary terms, using the price of natural gas, oil, coal, electricity, etc., the methodology still allocates costs in proportion to the exergy of flows, as expressed in eq. (3.37), but the obtained costs of products are given in monetary terms, relative to the initial price given to the external resources.

3.4.2 The PF representation

The idea of PF representation is to complement the FP representation, allowing one to obtain all flows of the productive structure of the system starting from the final (those produced by the system to the environment). It is based on the technical coefficients κ_{ij}, see fig. 3.6, which indicate the quantity (exergy) of the production of process i required to obtain a unit of product in process j:

$$\kappa_{ij} = \frac{E_{ij}}{P_j} \tag{3.39}$$

The technical coefficients are related with the efficiency of the process, in particular with the unit exergy consumption. Applying these ratios definition to eq. (3.21) we have:

$$k_i = \kappa_{0i} + \kappa_{1i} + \cdots + \kappa_{ni} \tag{3.40}$$

Meanwhile, applying eq. (3.39) to eq. (3.23) we obtain:

$$P_i = E_{i0} + \sum_{j=1}^{n} \kappa_{ij} P_j \tag{3.41}$$

In matrix notation, eq. (3.41) may be compactly expressed as:

$$\mathbf{P} = \mathbf{P}_s + \langle\mathbf{KP}\rangle\mathbf{P} \quad [J] \tag{3.42}$$

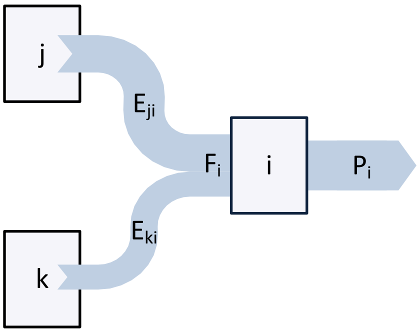


Figure 3.6: Technical coefficients

in which $\langle \mathbf{KP} \rangle \equiv [k_{ij}]$ is the $(n \times n)$ matrix of technical coefficients, and $(P)_s \equiv [E_{i0}]$ is the vector of the final demand of the system. The matrix $\langle \mathbf{KP} \rangle$ is, in the input–output methodology, the matrix of *direct requirement* because it shows the quantity of product i required directly in the production of one unit of process j, and the technical coefficients could also considered as unit exergetic consumptions.

Therefore, the production of each process could be expressed as a function of:

- the exergy of the final demand: $\mathbf{P}_s$
- the efficiency of the processes: $\langle \mathbf{KP} \rangle$

by means of the equation:

$$\mathbf{P} = |\mathbf{P}\rangle \, \mathbf{P}_s \quad \text{where } |\mathbf{P}\rangle = (\mathbf{U}_{\mathrm{D}} - \langle \mathbf{KP} \rangle) \tag{3.43}$$

The matrix $|\mathbf{P}\rangle$ is call, in the input–output methodology, the *Leontief inverse* matrix, and its elements, say p_{ij} represents the total production requirement of process i in the production of a unit of process j, both direct and indirect.

The cost equation (3.30) could be expressed in terms of the technical coefficients as:

$$\mathbf{k}_P^* = \langle \mathbf{KP} \rangle \mathbf{k}_P^* + \kappa_e \quad [\,\mathrm{J/J}\,] \tag{3.44}$$

which let to obtain the unit exergetic cost of each process as a function of the local unit exergetic consumptions of all the processes of the system:

$$\mathbf{k}_P^* = {}^{\mathrm{t}}|\mathbf{P}\rangle \, \kappa_e \tag{3.45}$$

We have seen two different ways for the evaluation of the cost of the products: as a function of the distribution or the technical coefficients. The information flow in the FP representation has the direction of the productive process. If the external resources are known, it is possible to evaluate the rest of the thermoeconomic properties of the flows, including the exergy and the cost of the final products. The PF representation uses an equivalent logic structure, but the information has the opposite direction. If we know the plant product it is possible to determine the resources required for obtaining any internal product, and its cost. Both representations are complementary and figure out the complete picture of the production process and cost formation.

The variables of both representations are related by the relationship:

$$P_i y_{ij} = \kappa_{ij} P_j \tag{3.46}$$

Or in matrix form:

$$\langle \mathbf{FP} \rangle = \mathbf{P}_{\mathrm{D}}^{-1} \langle \mathbf{KP} \rangle \mathbf{P}_{\mathrm{D}} \tag{3.47}$$

which allows obtaining the operators of the FP representation from the PF operator and vice versa:

$$\langle \mathbf{KP} \rangle = \mathbf{P}_{\mathrm{D}} \langle \mathbf{FP} \rangle \mathbf{P}_{\mathrm{D}}^{-1} \tag{3.48}$$

And the same relationship for the cost matrices:

$$\left\langle \mathbf{P}^* \right| = \mathbf{P}_{\mathrm{D}}^{-1} \left| \mathbf{P} \right\rangle \mathbf{P}_{\mathrm{D}} \tag{3.49}$$

$$\left| \mathbf{P} \right\rangle = \mathbf{P}_{\mathrm{D}} \left\langle \mathbf{P}^* \right| \mathbf{P}_{\mathrm{D}}^{-1} \tag{3.50}$$

As an example of the use of the correspondence between both representations, the equivalent formula of the cost/irreversibility relationship could be obtained in the PF representation.

Substituting eq. (3.47) in eq. (3.38), we get:

$$\mathbf{P}^* = \mathbf{P} + \mathbf{P}_{\mathrm{D}}{}^{\mathrm{t}} \left| \mathbf{P} \right\rangle \mathbf{P}_{\mathrm{D}}^{-1} \mathbf{I}$$

and multiplying both sides of equation by $\mathbf{P}_{\mathrm{D}}^{-1}$:

$$\mathbf{k}_P^* = \mathbf{u} + {}^{\mathrm{t}} \left| \mathbf{P} \right\rangle \mathbf{P}_{\mathrm{D}}^{-1} \mathbf{I}$$

On other hand, $\mathbf{I} = (\mathbf{K}_{\mathrm{D}} - \mathbf{U}_{\mathrm{D}})\, \mathbf{P}$ and substituting in previous equation, we get:

$$\mathbf{k}_P^* = \mathbf{u} + {}^{\mathrm{t}} \left| \mathbf{I} \right\rangle \mathbf{u} \quad [\mathrm{J/J}] \tag{3.51}$$

where ${}^{\mathrm{t}} \left| \mathbf{I} \right\rangle \equiv (\mathbf{K}_{\mathrm{D}} - \mathbf{U}_{\mathrm{D}})\, {}^{\mathrm{t}} \left| \mathbf{P} \right\rangle$ is the irreversibility operator. Equation (3.51) could be written in scalar format as:

$$k_{P,i}^* = 1 + \sum_{j=1}^{n} \phi_{ji}$$

This relationship represents an alternative method for evaluating the unit exergy cost of the product, as sum of contribution of the component irreversibilities. The term ϕ_{ij} represents the irreversibility generated in the $j-$th component to obtain a unit of the $i-$th product.

3.4.3 Exergoecologic Cost

Life cycle assessment (LCA) allows taking into account all renewable and non-renewable resources to obtain a product, including the production of the required inputs. Meanwhile exergy cost analysis permits the correct cost assessment, taking into account the energy quality of the production flows. The combination of both ideas permit to extend easily the model introduced in previous sections, taking into account the LCA of external resources.

According these ideas, eq. (3.37) could be rewritten as:

$$\mathbf{C}_P = {}^{\mathrm{t}} \left\langle \mathbf{P}^* \right| \mathbf{C}_e \quad [\mathrm{J}] \tag{3.52}$$

where $\mathbf{C}_e$ is the LCA value in terms of exergy of the external resources and $\mathbf{C}_P$ is the *exergoecological cost* or *total exergy cost*, defined as the total amount of resources, renewable and non-renewable required to obtain a product, as an extension of the “direct” exergy cost, in which only the exergy of the direct inputs of the system are considered.

The *unit exergoecological cost* is also defined as the total amount of resources, renewable and non-renewable required to obtain one unit of product.

$$c_{P,i} = \frac{C_{P,i}}{P_i} \tag{3.53}$$

and could be also computed by rewriting eq. (3.45) as:

$$\mathbf{c}_P = {}^{\mathrm{t}}|\mathbf{P}\rangle\, \mathbf{c}_e \quad [\,\mathrm{J/J}\,] \tag{3.54}$$

where $\mathbf{c}_e \equiv \mathbf{P}_{\mathrm{D}}^{-1}\mathbf{C}_e$ are the modified technical coefficients for external resources.

The production cost can be decomposed, see reference [227], considering the different types of resources required. The resources cost vector can be separated into two terms:

$$\mathbf{C}_e = \mathbf{C}_e^{\mathrm{rs}} + \mathbf{C}_e^{\mathrm{nrs}} \quad [\,\mathrm{J}\,] \tag{3.55}$$

The first term represents the cumulative exergy of the renewable resources and the latter the non-renewable of fossil resources. Therefore, the exergoecologic cost can be broken down into the renewable and fossil parts: $\mathbf{C}_P = \mathbf{C}_P^{\mathrm{rs}} + \mathbf{C}_P^{\mathrm{nrs}}$, where:

$$\begin{aligned} \mathbf{C}_P^{\mathrm{rs}} &\equiv {}^{\mathrm{t}}\langle \mathbf{P}^* \big| \mathbf{C}_e^{\mathrm{rs}} \\ \mathbf{C}_P^{\mathrm{nrs}} &\equiv {}^{\mathrm{t}}\langle \mathbf{P}^* \big| \mathbf{C}_e^{\mathrm{nrs}} \end{aligned} \tag{3.56}$$

Similar expresions can be used to compute unit exergoecologic costs.

The *renewability ratio* defined as follows establishes the weight of the renewable exergy cost with respect to the total exergoecologic cost:

$$\rho_i = \frac{C_{P,i}^{\mathrm{rs}}}{C_{P,i}} \quad [J/J] \tag{3.57}$$

Consider now the exergoecologic cost table, as an extension of the exergy FP table, depicted in table 3.4,

Table 3.4: Generic FP Exergoecologic cost table

	$C_{F,0}$	$C_{F,1}$	$\dots$	$C_{F,n}$
$C_{P,0}$		C_{01}	$\dots$	C_{0n}
$C_{P,1}$	C_{10}	C_{11}	$\dots$	C_{1n}
$\dots$	$\dots$	$\dots$	C_{ij}	$\dots$
$C_{P,n}$	C_{n0}	C_{n1}	$\dots$	C_{nn}

where $C_{ij} = c_{P,i}E_{ij} = C_{P,i}\,y_{ij}$ are the exergoecologic cost of the internal flows of the system, and C_{0i} are the cost of external resources, then the exergoecological cost balance is written as:

$$C_{P,i} = C_{0,i} + \sum_{j=1}^{n} C_{ij} \tag{3.58}$$

Now we introduce the *exergoecology ratio* which provides the relationship between exergy cost and exergoecologic cost:

$$c^*_{P,i} = \frac{C_{P,i}}{P^*_i} \quad [\mathrm{J/J}] \tag{3.59}$$

Substituting the exergoecologic ratio into eq. (3.58) we obtain:

$$c^*_{P,i} P^*_i = C_{0,i} + \sum_{j=1}^{n} c^*_{P,i} E^*_{ji}$$

and dividing by P^*_i

$$C_{P,i} = c^*_{P,i} = q^*_{0,j} + \sum_{j=1}^{n} c^*_{P,i} q^*_{ji} \tag{3.60}$$

where $q^*_{ij} = E^*_{ij} / P^*_j$ are called *exergy cost junction ratios*, see fig. 3.7, which explain the direct cost formation of a process, i.e. the portion of the resources cost of process j-th that come from process i-th, and verifies:

$$q^*_{ij} = \frac{k^*_{P,i}}{k^*_{P,j}} \kappa_{ij} = \frac{P^*_i}{P^*_j} y_{ij} \tag{3.61}$$

$$\sum_{i=0}^{n} q^*_{ij} = 1 \tag{3.62}$$

In matrix notation, the exergoecologic ratio could be written as:

$$\mathbf{c}^*_P = {}^{\mathrm{t}}\left|\mathbf{P}^*\right\rangle \mathbf{c}^*_e \quad \text{where} \quad {}^{\mathrm{t}}\left|\mathbf{P}^*\right\rangle \equiv \left(\mathbf{U}_{\mathrm{D}} - \langle\mathbf{PF}^*\rangle\right) \tag{3.63}$$

and $\langle\mathbf{PF}^*\rangle$ is the matrix of exergy cost junction ratios. $\mathbf{c}^*_e$ is the vector which contains the ratio exergy cost of external resources per cost of total fuel of the process (q^*_{0i}). The exergy consumption operator matrix $|\mathbf{P}^*\rangle$ will play a relevant role in sensitivity analysis.

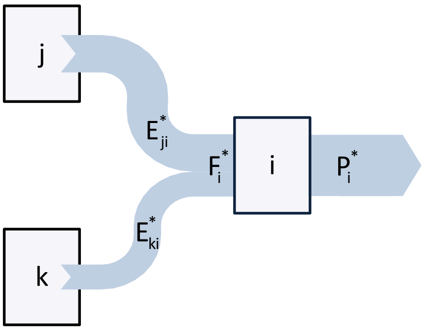


Figure 3.7: Exergy cost juntion ratios.

Note the equivalence between eqs. (3.54) and (3.63), the last one is the normalized value respect exergy cost instead of exergy. Matrix $|\mathbf{P}^*\rangle$ is a PF representation operator, which could be easily obtained from $\langle\mathbf{P}^*|$ and $|\mathbf{P}\rangle$ matrices.

$$p^*_{ij} = \frac{P^*_i}{P^*_j} \pi^*_{ij} = \frac{k^*_{P,i}}{k^*_{P,j}} p_{ij} \tag{3.64}$$

Equation (3.63) lets to obtain exergoecologic ratios as a function of exergy and the valuation of external resources, and to decompose the exergoecologic cost into two factors: the exergy cost, independent of the valuation of the external resources, and the exergoecologic ratio which takes into account the relative cost of external resources.

Figure 3.8 gives the relationship between exergy, exergy cost and exergoecologic cost. Exergy, which is the minimum cost in terms of exergy resources, and exergy cost, which gives the impact of resources on the product can be obtained from the thermodynamic analysis of the primary processes. Meanwhile, the exergoecologic cost requires the thermodynamics and LCA interaction. Exergy and exergoecologic cost are related by the exergoecologic factor which evaluates the weight of external resources.

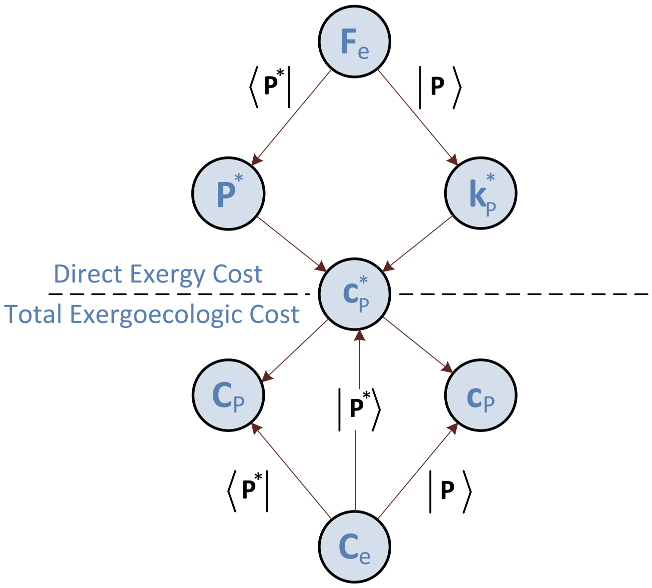


Figure 3.8: Exergy and exergoecologic cost relationships

3.5 The EROI and ExROI concepts

In order to make sure that biofuels achieve the aims for which they are being promoted, it is necessary that they have a positive resource balance, which means that they do not imply the consumption of more non-renewable resources than the resource they are by themselves. One instrument to measure this property is the Energy Return on Energy Investment (EROI). The EROI concept, was defined by Cleveland et al. [46] in 1984 as the ratio of the amount of usable energy acquired from a particular energy resource to the amount of energy expended to obtain that energy resource.

The calculation of EROI does not usually include the consumption of natural sources, only the human-applied ones. The EROI concept brings an indication of the sustainability of a product only from an energy perspective (energy sustainability) and cannot be used to indicate the sustainability of a product as a whole because it does not take into account other factors such as the potential deforestation, land use changes, pollutant emissions, etc.

When applying this concept, the selection of the system boundaries is of upmost importance and always needs to be considered when obtaining conclusions of the analysis of results. For one specific product, different EROI values can be obtained if the control volume considered varies. Therefore without sufficient information two EROI results may not be comparable.

This concept has already been applied to several biofuel production processes, giving differing results depending on the control volume, raw material, production chains and energy allocation method. Thus, Russi [204] obtained that, according to different bibliographic sources, the EROI for biodiesel [247] could vary between 0.2 for soybean based biodiesel without allocation of energy consumption to the by-products and 4.5 for sunflower based biodiesel if meal is used as fuel [150]

However, the concept of EROI does not take into account the quality of energy, which, according to Cleveland could bring misleading conclusions in an energy balance. For this reason, he started using exergy in EROI calculations. Cleveland and Herendeen [44] applied it in solar parabolic collectors. They demonstrated that not taking into account the quality of energy (i.e. exergy or capacity to produce work) could derive in considering as qualitative the same heat at 50 and at 350 °C despite the different capacity to produce work. In a latter study focused on oil and gas extraction in the US [45], Cleveland concluded that quality corrections have important effects on the results of energy analysis, thus proposing to calculate the so-called "quality-corrected EROI". The reason is that, as explained in a previous paragraph, exergy does not only takes into account the quantity of flows entering and exiting the system but also the losses of useful energy caused by the degradation of the flows along the process (irreversibility) and the capacity to produce work of the outputs. This degradation of the biodiesel cycle is "captured" by the exergy concept but not by a typical energy balance.

Based on Cleveland's work, we define the *Exergy Return on Exergy Investment* (ExROI) as the ratio of non-renewable consumed by the system (exergoecologic cost) to the exergy that the product (biodiesel) has.

$$\mathrm{ExROI} = \frac{P}{C_P^{\mathrm{nrs}}} = \frac{1}{c_P^{\mathrm{nrs}}} \tag{3.65}$$

The only relevant costs for sustainability purposes are those associates to the non-renewable use. The lower exergy cost due the fossil resources is, the higher ExROI will be.

The allocation of the exergy cos to the different products obtained along the production chain can be summarised as follows: in a specific stage of the process the exergoecologic cost is distributed to all the products (main product and by–products) of the stage proportionally by their exergy value; there is no exergy cost allocated to the residues generated, and the exergy cost of the resources entering into the system depends on the boundaries selected.

3.6 Sensitivity Analysis

As mentioned in previous sections, an adequate selection of the boundaries is required to perform an life cycle analysis, thus depending on the process included, the values obtained could vary significantly. On the other hand, exergoecologic cost are obtained from data provided by LCA software as EcoInvent database [63] or in case of biodiesel also by organizations like JRC. These numbers are fixed and based on specific assumptions. However, consumption in biodiesel production can vary significantly depending on many circumstances, for example, temperature and soil conditions at cultivation, carrying distance, quality of the oil at the transesterification plant, etc. This variation influences the exergy costs of the external resources entering the system and therefore the exergoecologic costs value of the product. In order to understand the effect that variations in the consumption of external resources may have in the costs values, a sensitivity analysis must be performed.

According to eq. (3.52) the external costs do not depend of the production matrix, thus the effect in the exergoecologic cost due to a variation in the external cost can be calculated as:

$$\Delta \mathbf{C}_P = {}^{\mathrm{t}}\langle \mathbf{P}^* | \Delta \mathbf{C}_e \tag{3.66}$$

then the elements of the production matrix π^*_{ij} also represent the exergoecologic cost variation of process j-th when the external resources of component i-th vary. Introducing the elasticity coefficient $\%\Delta x = \Delta x / x$, eq. (3.66) could be written as:

$$\%\Delta C_{P,i} = \frac{\Delta C_{P,i}}{C_{P,i}} = \sum_{j=1}^{n} \frac{\pi^*_{ji} C_{e,j}}{C_{P,i}} \Delta C_{e,j} \tag{3.67}$$

or in matrix form $\%\Delta \mathbf{C}_P = \left[\mathbf{A}^e_P\right] \%\Delta \mathbf{C}_e$ where the coefficients of the elasticity matrix $\left[\mathbf{A}^e_P\right]$ are defined as:

$$\alpha_{ij} = \frac{C_{e,j}\, \pi^*_{ji}}{C_{P,i}} = c^*_{e,j} p^*_{ji}$$

On the other hand, taking into account how the process aggregation is in complex systems such as the biodiesel production, the evaluation of the efficiency of the primary processes considered could vary depending on the chosen model; then we could also analyse the variation of exergoecologic cost due to changes in the efficiency of processes.

According to exergy cost theory [165], the fuel impact is the effect on total resources consumption, which can be achieved if the efficiency of a process, or equivalently its unit consumption, is improved. Torres and Valero [227] state that the variation of unit exergy cost, caused by the variation of local efficiency of the internal processes on the system could be approximated by:

$$\%\Delta \mathbf{C}_P \approx {}^{\mathrm{t}}|\mathbf{P}^*\rangle \%\Delta \mathbf{k} \tag{3.68}$$

The accuracy of this expression depends on the degree of linearity (or recirculation) of the system. In this case the elasticity matrix is the transpose of exergy consumptions matrix, and:

$$p^*_{ij} = \frac{\%\Delta C_{P,j}}{\%\Delta k_i}$$

3.7 Conclusions

In this chapter the tools used in this Ph.D to analyse the efficiency and sustainability of biodiesel production and the improvements that can be introduced have been defined. As explained in the introductory chapter thermoeconomics uses exergy as quality and quantity measure of the mass and energy flows for cost assessment purposes. Thermoeconomics input-output analysis integrates Second Law and economic input-output analysis together with material flows and life cycle analysis to provide a rigorous evaluation procedure for energy saving, sustainability and renewability of bioenergy processes, see fig. 3.9.

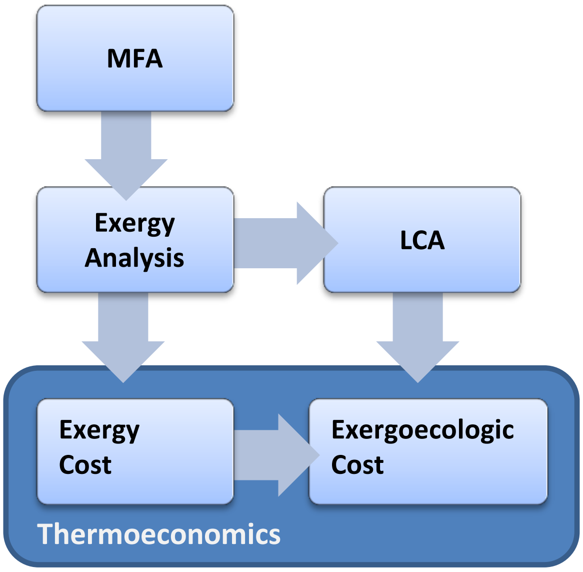


Figure 3.9: Thermoeconomic Input-Output analysis methodology

First the methods to evaluate the exergy of biodiesel production flows are described, and then the concepts of exergy cost and exergocologic cost are used to evaluate the amount of renewable and non-renewable resources required to obtain bioenergy products in a complete process from land to tank.

Three new ratios have been defined: The *renewability ratio* that measures the portion of renewable exergy used respect the total exergy consumption. The *exergy rate of investment* (ExROI) that evaluates the amount of biodiesel exergy obtained for each unit of non-renewable resources and the *exergoecologic factor* that evaluates the ratio between the exegy and exergoecologic cost, and gives an indication of the capability of improvement of the direct processes of the land to tank cycles. These ratios will be used in the next chapters to evaluate different bioenergy production processes and potential improvements.

Chapter 4

Thermoeconomic analysis of a biodiesel plant

This chapter presents a study of the exergy costs obtained when analysing in detail the processes included in a typical transesterification plant. As the composition of the oils in terms of impurities (materials different than triglycerides) varies from one type to another, the process needs to be adjusted in order to produce a final product complying with the specifications of the quality standards. The aims of this exercise are, on the one hand, demonstrating the usefulness of the exergy cost analysis applied to bioenergy production and, on the other hand, identifying which of the vegetable oil materials presents a higher consumption of exergy, where the irreversibilities are located and how these irreversibilities can be reduced.

The data used to produce the exercise of this chapter are real data provided by an existing biodiesel plant operating in Spain. As not all data needed to produce an exergy cost analysis are normally recorded by the plant operators, some assumptions have been made. Given this, the reader has to understand that, although based on real data, this is a theoretical analysis.

4.1 Data, assumptions and procedure

The specific plant analysed is located in the north of Spain. The transesterification unit has an annual vegetable oil treatment capacity of around 35,000 tonnes/year and it is operative during 8,016 hours/year. It consumes only refined vegetable oils from rapeseed, sunflower and palm. These oils could be mixed or used individually, their consumption being based on the market price. This exercise is assuming that the oils are treated separately in order to analyse the effect of the oil characteristics in the process.

A normal quality assurance procedure applied in biodiesel production plants consists in ensuring a good quality of the refined crude oil entering the plant and before the transesterification unit, in terms of water content and impurities; and ensuring a good quality of the final product according to the European norm EN 14214 [36]. Not all the parameters of the standard are controlled. Those that are expensive to monitor or require expensive technologies and are normally compliant with the standard limits are not analysed. This is the case, for example, of the cetane number, which is measured each certain time (e.g. twice a year) by an external laboratory.

Biodiesel production plants do not normally control the exact composition of each of the flows entering and exiting the intermediate units of the process. For the intermediate processes what is normally controlled is the temperature and time. Whenever the resource entering the system has adequate values for the measured parameters (water and impurities), and the temperature and time are ensured within a certain range in each unit, the final product will presumably be of good quality.

Regarding the energy consumption, plant operators do not control the energy consumption in each single unit. They either control the total consumption or the consumption in aggregated processes. For example, normally they consider the transesterification and after-treatment processes as a unique process.

On the other hand, in order to produce an exergy cost analysis of a given system, the mass composition of every flow and the energy consumption of every unit have to be known to the extent of the chosen disaggregation level.

Given these two circumstances, in order to calculate the exergies of all the flows, what will allow performing the exergy cost calculations, several assumptions need to be considered. The following sub-paragraphs show the information displayed by the plant operators, the assumptions that have been made and the procedure followed to calculate the remaining missing information.

4.1.1 Material balances

The diagrams from figs. 4.1(a) to 4.1(c) show the material balances in kg/h of the pre-treatment units for the three different vegetable oils as provided by the plant operator. The processes have been explained in detail in chapter 2.

The quantities of alcohol and catalyser consumed in the transesterification tank according to the data provided by the plant operator are shown in the table 4.1 in kg per tonne of pre-treated oil entering the transesterification tank.

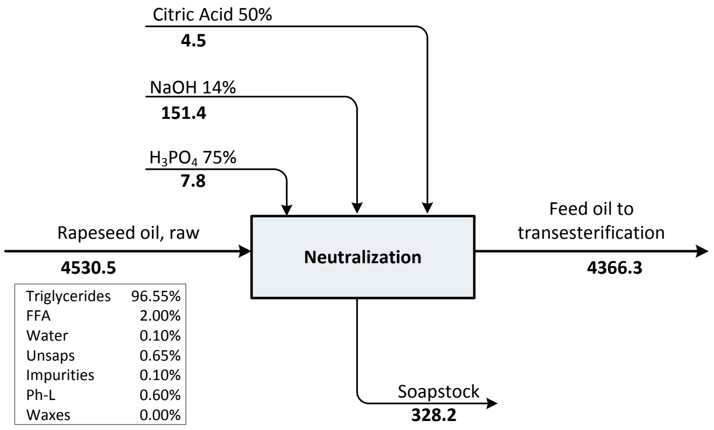
Table 4.1: Quantities of inputs for the transesterification reaction (kg/tonne oil)

Material	Rapeseed oil	Sunflower oil	Palm oil
Methanol	108.8	108.3	111.8
Sodium methoxide	5.1	5.1	5.1

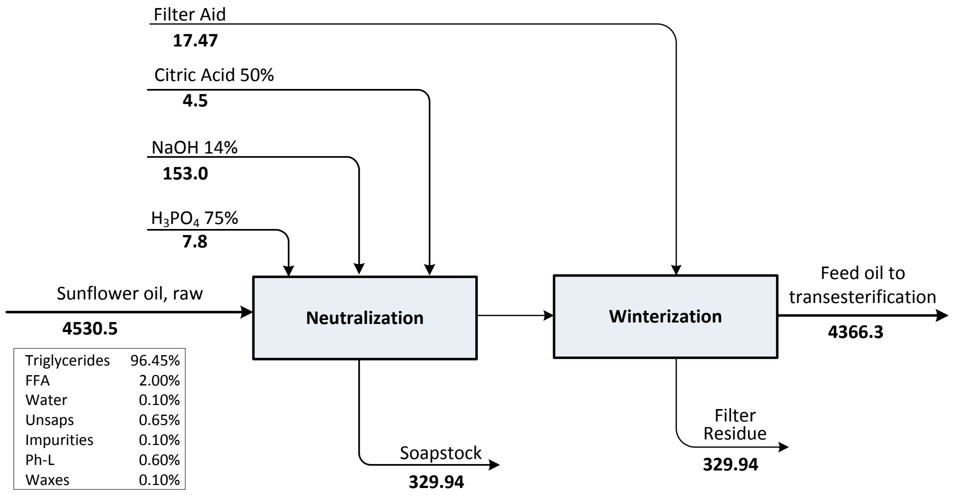
The material balances of the tank where the transesterification reaction and decantation are taking place are shown in table 4.2.

Table 4.2: Material balances for the transesterification and decantation processes (kg/h)

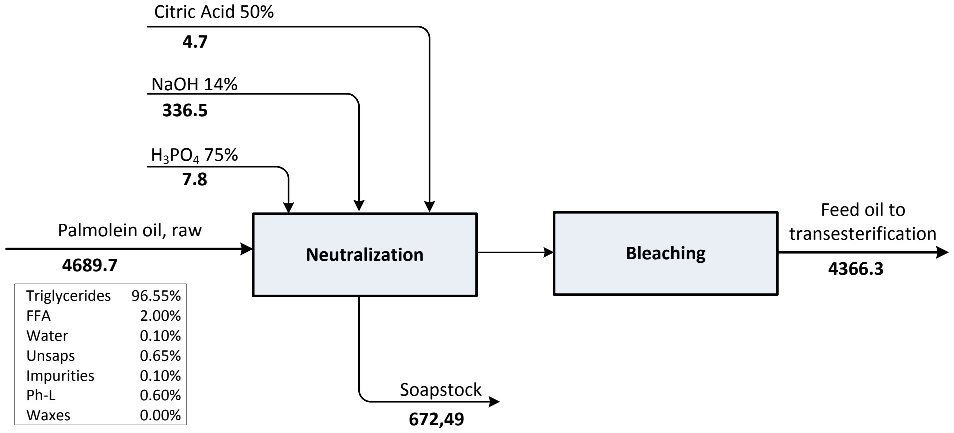
Material	Rapeseed	Sunflower	Palm
Pre-treated oil	4,366.27	4,366.27	4,366.27
Methanol	472.87	475.05	488.14
Sodium methoxide	22.27	22.27	22.27
Crude biodiesel	4,324.38	4,324.04	4,326.49
Crude glycerol	537.03	539.54	550.2



(a) rapeseed oil



(b) sunflower oil



(c) palm oil

Figure 4.1: Material balance for pre-treatment process

The after-treatment of the biodiesel and glycerol phases is produced using hydrochloric acid. In the first case, the HCl is used as a solution with water at 30% in a quantity of 51.3 kg/h, as provided by the plant operator; in the latter case the stoichiometric quantity needed to eliminate the soaps following the unsaponification reaction has been considered. With this, the material balances are the ones shown in table 4.3.

Table 4.3: Material balances for biodiesel and glycerol after–treatment (kg/h)

Material	**Rapeseed**	**Sunflower**	**Palm**
Biodiesel			
Crude biodiesel	4,324.38	4,324.04	4,326.49
HCl solution	51.3	51.3	51.3
Washed biodiesel	4,283.82	4,283.19	4,284.81
Waste waters	91.86	92.15	92.97
Evaporate	12.23	12.47	12.95
Final biodiesel	4,271.59	4,270.72	4,271.87
Glycerol			
Crude glycerol	537.03	539.54	550.2
HCl	5.09	5.11	5.24
Purified glycerol	500.64	503.17	513.96
FFA	41.48	41.48	41.48
Final glycerol	430.45	431.79	442.78
Methanol	8.61	8.92	9.55
Residues	61.58	62.46	61.63

4.1.2 Composition of the oil, soapstock, biodiesel and glycerol streams

For the composition of the vegetable oil, biodiesel and glycerine flows going through the different units, besides the content of triglycerides, fatty acid methyl esters (FAME) and glycerol, respectively, there is the need to consider the content of undesired materials such as free fatty acids, water, soaps, phosphatides, waxes, etc.

The only information provided by the biodiesel plant operators is the composition of the oil before transesterification after going through the pre-treatment phase. This is a crucial piece of information as an adequate composition of the oil before transesterification will ensure an adequate FAME yield. The composition of the other flows, i.e. the oil before pre-treatment and the flows after transesterification, need to be conjectured taking into account several assumptions.

The tables in figs. 4.1(a) to 4.1(c) show the information provided by the plant operator regarding the composition of the oil before transesterification. As it can be seen, the plant operator assumes that the oils entering the transesterification tank have the same percentage of undesired materials regardless of the origin, except for the wax content where a certain content has been considered (0.10% m/m) in the case of sunflower oil.

The composition of the vegetable oils that enter the plant has not been provided by the plant operator. Therefore, some assumptions have been made backwards in the process. The composition of the vegetable oil before entering the pre-treatment units by means of producing mass balances, have been obtained. To allocate real values to each of the components of the crude oils, the typical references contained in the Norma CODEX for oils (CODEX STAN-210, 2005) [48] and the specifications provided by FEDIOL, the European Oil and Protein meal Federation [107], have been taken as reference.

Table 4.4 shows the compositions in percentage of the vegetable oils that have been considered, as well as the reference compositions provided by the Norma CODEX and FEDIOL.

Table 4.4: Composition of the refined vegetable oils before pre-treatment (% m/m)

Material	Rapeseed	Sunflower	Palm	Reference for rapeseed and sunflower	Reference for palm oil
FFA	3	3	7.5	2	5
Water	0.5	0.5	0.2	0.5	0.2
Unsaponified	2	2	1.2	2	1.2
Impurities	0.5	0.5	0.5	0.5	n/a
Phospholipides	0.9	0.9	0.66	0.075	0.005
Waxes	-	0.3	-	n/a	n/a

As it can be observed, the compositions of the sunflower and rapeseed oil are practically the same except for the wax content. The most important differences are in the palm oil which has a higher content of free fatty acids and phospholipids and a lower content of water and unsaponified matter.

The content of water, unsaponified matter, impurities and waxes is the same as the one provided by the Norma CODEX and FEDIOL. There are two slight differences regarding the composition of the oils compared to the reference oils: namely the percentage of free fatty acids (FFA) and phosphatides. As far as the phosphatides are concerned, a higher percentage is considered because the percentage given by the company for the oil after pre-treatment was already higher than the reference. The content of the free fatty acids had also to be increased in the mass balance due to the same reason and in order to balance the mass before and after the pre-treatment process.

This is in concordance with the oil composition provided by other authors: Riegel' s handbook of industrial chemistry [201]; Mittelbach's comprehensive handbook on biodiesel [176] and Erickson's proceedings on edible fats and oils processing: basic principles and modern practices (World conference proceedings) [71]. Riegel states that the phosphatide content of rapeseed oil is between 1 and 3% and for sunflower between 0.5 and 0.9%. In this work, the same percentage -0.9%- has been assumed for both oils. Erickson confirms that the phosphatide content of palm oil is lower than for sunflower and rapeseed oils. Although Erickson considers that this content is between 0.05 and 0.1%, in this case, a 0.66% content has been considered because the plant operators consider already a 0.6% after the pre-treatment phase. Finally, Mittelbach provides information about the FFA composition of rapeseed and sunflower oil which is only higher than 5% in extreme cases. In this work a 3% has been considered. As far as for palm oil, the FFA content is normally higher than for rapeseed and sunflower; this is why higher amounts of alkali is needed for the neutralisation. In this case, it is assumed that the crude palm oil is a high-FFA crude palm oil with a FFA content of 7.5%.

The composition of the crude biodiesel and crude glycerol streams after the transesterification reaction and the decantation process are calculated based on the following assumptions:

First, in the transesterification tanks, three reactions take place in parallel: the oils (mainly formed of triglycerides, with small amounts of mono and di-glycerides) react with the alcohol to form the methyl esters and glycerol molecules; the free fatty acids react with the alcohol to form a mono-glyceride and water; and the free fatty acids react with the catalyser to form soaps and methanol. The stoichiometric reactions are the following:

$$\underset{\text{FFA}}{\mathrm{R-COOH}} + \underset{\text{Catalyser}}{\mathrm{CH_3ONa}} \longrightarrow \underset{\text{Soap}}{\mathrm{R-COO-Na}} + \underset{\text{Methanol}}{\mathrm{CH_3OH}}$$

$$\underset{\text{FFA}}{\mathrm{R-COOH}} + \underset{\text{Methanol}}{\mathrm{CH_3OH}} \longrightarrow \underset{\text{Mono-glyceride}}{\mathrm{R-COO-CH_3}} + \underset{\text{Water}}{\mathrm{H_2O}}$$

$$\underset{\text{Trigyceride}}{\mathrm{3R-3COO-2CH_2-CH}} + \underset{\text{Methanol}}{\mathrm{3CH_3OH}} \longrightarrow \underset{\text{FAME}}{\mathrm{3[R-COO-CH_3]}} + \underset{\text{Glycerol}}{\mathrm{C_3H_8O_3}}$$

It is assumed that the yield of the transesterification reaction is 98.8% [116], i.e. oils are transformed in a 98.8% into methyl esters. For the other secondary reactions the yield is assumed to be 100%. It is also assumed that ½ of the free fatty acids are transformed into soaps, while ¼ is transformed in mono-glycerides and ¼ remains unreacted.

On the second hand, it is assumed that the complete separation of the substances is unfeasible; therefore there will be a certain quantity of all components in both streams. The only exception considered are methyl esters and the unreacted oil, which are considered to be 100% in the biodiesel phase. In order to produce a realistic allocation of materials in both the biodiesel and glycerol streams, the following considerations have been taken into account, in line with an experienced plant operator:

- Glycerol has three hydroxyl groups and therefore it is a very polar and hydrophilic substance. On the other hand, methyl esters are less polar and therefore less hydrophilic. Taking into consideration the polarities of the substances, and knowing the tolerance of polar substances to dissolve in polar media and the incapacity of non-polar substances to dissolve in polar media, it is possible to discern which substances will tend to go to one phase or the other:
    1. Soaps, water and phospholipids (this latter due to the phosphate group which is very polar) will tend to stay at the glycerol part. It is assumed that 90% of the soaps, 90% of the phospholipids and 85% of the water remain in the glycerol phase;
    2. FFA (for long chain FFA the non-polar hydrocarbon chain dominates over the polar acid functional group), unsaponifiables and waxes will tend to stay in the methyl ester phase. It is assumed that 90% of the FFA, 70% of the unsaponifiable matter and 80% of the waxes remain in the biodiesel phase.
- Methanol will be shared almost equally by both phases. A 40/60 % relation has been considered for the glycerol/methyl ester phases after Wieyang Zhou et al, 2006 [256], which state an experimental separation of 42/58 %.
- Concerning the catalyser, Wieyang Zhou et al. [256] and Chuang-Wei et al. [41] report that the catalyser goes practically completely to the glycerol phase. In this exercise it has been assumed that 90% of the catalyser stays in the glycerol phase.

- It is assumed that 90% of the impurities stay in the glycerol phase. Impurities tend to stay at the bottom of the tank where the glycerol phase stays due to its higher density.

With the above mentioned premises, the composition of the crude biodiesel and crude glycerol phases is shown in table 4.5.

Table 4.5: Composition of the crude biodiesel and crude glycerol (% m/m)

Material	Rapeseed	Sunflower	Palm
Crude biodiesel			
Methyl ester	97.29	97.19	97.25
Oil	1.17	1.17	1.17
Glycerol	0.1	0.1	0.1
Methanol	0.3	0.31	0.33
Sodium methoxyde	0.03	0.03	0.03
Soaps	0.11	0.11	0.11
FFA	0.45	0.45	0.45
Water	0.02	0.02	0.02
Unsaponified matter	0.46	0.46	0.46
Impurities	0.01	0.01	0.01
Phosphatides	0.06	0.06	0.06
Waxes	0	0.08	0
Crude glycerol			
Glycerol	80.15	80.03	80.48
Oil	0	0	0
Methanol	1.6	1.65	1.74
Sodium methoxide	2.33	2.31	2.23
Soaps	7.89	7.86	7.72
FFA	0.41	0.4	0.4
Water	0.91	0.91	0.9
Unsaponified matter	1.59	1.58	1.55
Impurities	0.73	0.73	0.71
Phosphatides	4.39	4.37	4.29
Waxes	0	0.16	0

In the biodiesel after-treatment processes it has been considered that the final methyl ester phase, i.e. the biodiesel product, fulfils all the requirements of the European norm EN 14214 [36], what influences the biodiesel streams after washing and drying.

In the biodiesel washing the reaction taking place to convert the soaps into free fatty acids is the following. It is assumed that all the soaps are converted into free fatty acids. This is the only change considered for the washing reaction in relation to the crude biodiesel after transesterification.

$$\mathrm{R-COO-Na} + \mathrm{HCl} \longrightarrow \mathrm{R-COOH} + \mathrm{NaCl}$$

The specifications of the European norm EN 14214 [36] used to calculate the composition of the final biodiesel product are shown in the table 4.6.

Table 4.6: Parameters of the EN 14214 considered

Parameter	Unit	Lower limit	Upper limit
Ester content	% (m/m)	96.5	-
Monoglyceride content	% (m/m)	-	0.8
Diglyceride content	% (m/m)	-	0.2
Triglyceride content	% (m/m)	-	0.2
Free glycerine	% (m/m)	-	0.02
Methanol content	% (m/m)	-	0.2
Acid value	mg KOH/g	-	0.5
Water content	mg/kg	-	500
Total contamination	mg/kg	-	24
Group I metals	mg/kg	-	5
Group II metals	mg/kg	-	5
Phosphorous content	mg/kg	-	4

The acid value represents a measure of the content of FFA. The acid value or neutralization number is a measure of mineral acids and free fatty acids contained in a fuel sample. It is expressed in mg KOH required to neutralize 1g of fatty acid methyl esters and is set to a maximum value of 0.5 mg KOH/g in the European norm.

For this exercise it is assumed that this parameter is only influenced by the free fatty acids. The chemical reaction taking place is the following one:

$$\mathrm{R{-}COOH} + \mathrm{KOH} \longrightarrow \mathrm{R{-}COO{-}K} + \mathrm{H_2O}$$

Following this stoichiometric reaction and taking into account the molecular weights of the FFA for the different kind of oils, each mg of KOH would be able to neutralise around 5 mg of FFA. In each g of methyl ester there should not me more than 2.5 mg of FFA.

The acidity of the biodiesel needs to be controlled because it mirrors the degree of fuel ageing during storage as it gradually increases due to hydrolytic scission of the ester bonds. Fuels with high acid values are linked with corrosion and the formation of deposits in the engine [176].

The total contamination is used in this exercise as the parameter limiting the content of unsaponified matter. The maximum limit is fixed at 24 mg/kg of biodiesel. Total contamination can also be due to contents in other materials such as leftover of catalysers. This parameter is defined as the quota of insoluble material retained after the filtration of a heated fuel sample over a standardised filter. High total contamination values are related to blockages of fuel filters and injection pumps in the engine.

The content of group I (Sodium and Potassium) and II metals (Calcium and Magnesium) has been used to limit the content of impurities. In both cases the limits are set at 5 mg/kg of biodiesel. The alkali metals are introduced in the final biodiesel from catalyst residues whereas alkaline-earth metals may come from hard water used in the washing process. Na and K are linked with the formation of ash in the engine and Ca and Mg might cause problems in the engine fuel injectors [2].

The phosphorus content has been assumed to be the limiting parameter for the phosphatides (also called phospholipids). The phosphorus content can also be increased when using phosphoric acid as catalyser, which is not the case in this plant. The phosphorous content in biodiesel is limited to 4 mg/kg in the standard because the automotive industry argues that higher quantities can damage the emission after-treatment devices of their vehicles causing higher particulate matter emissions [2].

Table 4.7: Composition of the washed and final biodiesels (% m/m)

	Rapeseed		**Sunflower**		**Palm**	
Material	Washed biodiesel	Final biodiesel	Washed biodiesel	Final biodiesel	Washed biodiesel	Final biodiesel
Methyl ester	97.8	98.49	97.71	98.41	97.79	98.5
Oil	1.18	1.18	1.17	1.18	1.18	1.18
Glycerol	0.02	0.02	0.02	0.02	0.02	0.02
Methanol	0.15	0	0.16	0	0.17	0
Sodium methoxyde	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
Soaps	0	0	0	0	0	0
FFA	0.249	0.2507	0.2479	0.2497	0.2417	0.2435
Water	0.6	0.05	0.6	0.1	0.6	0.1
Unsaponified matter	0.0021	0.0021	0.0021	0.0021	0.0023	0.0023
Impurities	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009
Phosphatides	0.0003	0.0004	0.0003	0.0004	0.0003	0.0004
Waxes	-	-	0.08	0.1	-	-

The contents of mono-, di- and triglycerides are used as a measure of the content of unreacted oil in the biodiesel after transesterification. The European norm EN 14214 limits the amounts of mono-, di- and triglycerides to 0.8%, 0.2% and 0.2% respectively. Fuels exceeding the content of glycerides are prone to cocking and may thus cause the formation of deposits in the injector nozzles, pistons and valves of the engine [176].

The free glycerine content is used to measure the content of glycerol in the biodiesel fuel. High quantities of glycerol in biodiesel are the result of a bad crude biodiesel washing. Glycerol may also be formed by hydrolysis of remaining mono-, di- and triglycerides in stored biodiesel fuel [176]. The content of glycerol in the final fuel needs to be limited up to 0.02% (m/m) because it might cause damage to the injection system of the engine. This is because it sets at the bottom and attract polar substances like water and soaps that when burnt have negative effects. It can also cause glycerol depositions in the fuel filter and increase aldehyde emissions [176]. The EN 14214 [36] contains another parameter to control the content of glycerol in the fuel; this is the total glycerol content. The total glycerol takes into account the content of free glycerol plus the glycerol bound in the form of mono-, di- and triglycerides. To simplify the exercise, only the free glycerol content is considered as a parameter to limit the content of glycerol in the final biodiesel product. The content of methanol in the final biodiesel is limited to 2% (m/m). The reason for limiting it is that high methanol contents pose safety risks in the biodiesel transport and storage due to the correspondingly low flashing points [176].

The water content is limited to 500 mg per kg of biodiesel. Free water in the biodiesel fuel is not desired in vehicle engines for many reasons: it can drive to corrosion of parts of the engine as for example the injection system; it can also react, partly converting fatty acid methyl esters into free fatty acids which are related to filter blockages. Some authors relate it to biological growth in the biodiesel fuel which can create sludge and slime leading to blockage of fuel filters. When blended with fossil diesel it may cause phase separation. The maximum water concentration level of biodiesel is higher than the one for fossil diesel because biodiesel has the drawback of being hydrophilic thus attracting water during ulterior transport and storage.

Having all these premises into account, the compositions of table 4.7 have been considered for the washed and final biodiesel streams. In the case of the glycerol streams, it is assumed that in the purification tank using HCl all the soaps are converted into free fatty acids and all the free fatty acids are completely separated from the glycerol stream. With this, the composition of the glycerol stream after purification is the one shown in table 4.8.

Table 4.8: Composition of the purified glycerol (% m/m)

Material	**Rapeseed**	**Sunflower**	**Palm**
Glycerol	85.98	85.81	86.15
Oil	0	0	0
Methanol	1.72	1.77	1.86
Sodium methoxide	2.5	2.48	2.39
Soaps	0	0	0
FFA	1.63	1.63	1.64
Water	0.98	0.97	0.96
Unsaponified matter	1.7	1.69	1.66
Impurities	0.78	0.78	0.76
Phosphatides	4.71	4.69	4.59
Waxes	-	0.17	-

Finally for the distilled glycerol stream i.e. the final glycerol product, it is assumed that it is formed 100% by glycerol molecules. Pharmaceutical grade glycerol should have percentages of glycerol no less than 99.7%.

4.1.3 Energy balances

As far as the energy balances are concerned, as commented above, plant operators do not control the energy consumption in all the processes. Normally they consider the transesterification and after-treatment processes as an aggregation for which the overall consumption is monitored. Therefore, in order to distribute the energy consumption per process, assumptions have been made in agreement with the plant operators. The data provided by the plant operator are the ones of table 4.9.

The data concerning transesterification, besides the consumption in the transesterification tank, also includes the consumption of energy of the biodiesel washing and biodiesel drying. Also, the data related to glycerol after-treatment does not differentiate between the consumption in the glycerol washing and in the distillation. In order to produce an adequate allocation of exergy consumption there is a need to disaggregate between these processes. The assumptions of table 4.10 were provided by the plant operator. The steam is entirely produced with natural gas. The relation between the natural gas consumed and the steam produced is given by the plant operator and corresponds to 0.85 kWh NG/kg steam. With the above data and assumptions it is possible to know the consumption of electricity and natural gas in each of the processes, as shown in table 4.11.

Table 4.9: Energy consumption data provided by plant operator

Process	**Electricity** kWh/tonne biodiesel	**Steam** kg [12-16 bar]/ tonne biodiesel
Degumming + neutralisation	12	25
Winterization	12	55
Bleaching	6	15
Transesterification	13	340
Glycerol after-treatment	9	335

Table 4.10: Energy consumption distribution for the transesterification and after–treatment processes

Process	**Electricity** (%)	**Steam** (%)
Transesterification	54.6	80
Biodiesel washing	27.3	0
Biodiesel drying	18	20
Glycerol washing	70	41
Glycerol distillation	30	59

Table 4.11: Energy consumption data per process

Process	**Rapeseed**	**Sunflower**	**Palm**
Electricity (kWh/tonne biodiesel)			
Degumming + neutralisation	11.74	11.74	11.74
Winterisation	-	11.74	-
Bleaching	-	-	5.87
Transesterification	6.95	6.95	6.95
Biodiesel washing	3.48	3.48	3.48
Biodiesel drying	2.29	2.29	2.29
Glycerol washing	6.16	6.16	6.16
Glycerol distillation	2.64	2.64	2.64
Natural gas (kJ/kg biodiesel)			
Degumming + neutralisation	74.84	74.83	74.85
Winterisation	-	164.62	-
Bleaching	-	-	-
Transesterification	814.27	814.11	814.32
Biodiesel washing	-	-	-
Biodiesel drying	203.57	203.53	203.58
Glycerol washing	411.18	411.09	411.20
Glycerol distillation	591.69	591.57	591.73

4.2 Exergy calculation

This paragraph presents the assumptions and data that have been considered to calculate the chemical and physical exergies of the materials and energy sources consumed and produced in the transesterification plant.

The exergy values have been calculated using the calculation methods described in chapter 3. Some chemical exergies have been obtained from the Exergy Calculator of the Exergoecology portal developed by CIRCE [43].

The chemical exergies of the oil, soapstock, biodiesel and glycerol streams have been obtained by calculating the chemical exergies of their constituent materials, i.e. the vegetable oils, free fatty acids, phosphatides, soaps, waxes and methyl esters, taking into account their share in % m/m in each stream.

The chemical exergies of these constituent materials have been calculated taking into account the fatty acid compositions of each type of oil. It has been assumed that the materials of one kind of oil have all the same average acid chain which is calculated taking into account the fatty acid composition of the oil. The fatty acid compositions of sunflower, rapeseed and palm oils are shown in table A.1. The chemical exergies have been calculated using eq. (3.6), and their values are shown in table A.20.

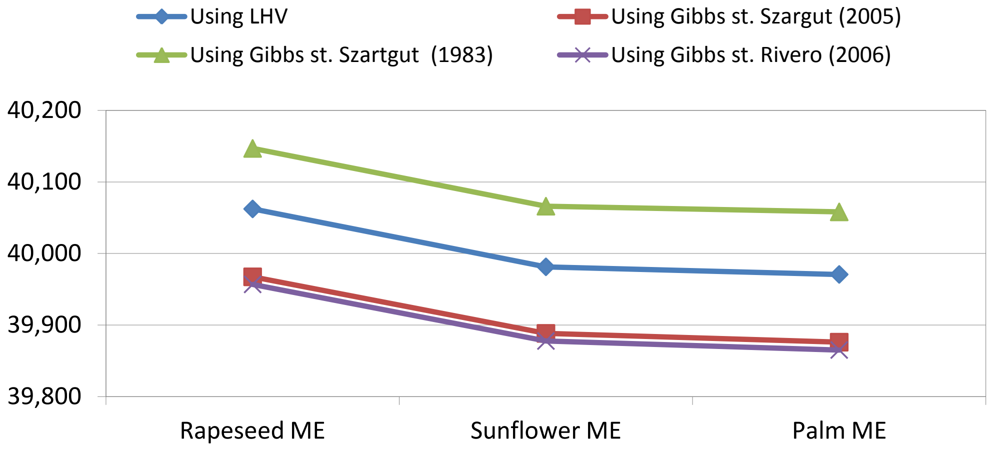


Figure 4.2: Comparison of the chemical exergies (kJ/kg) of the crude oil methyl esters, calculated by different methods

In order to check if the chemical exergies are correctly calculated, the exergies of the methyl esters have also been calculated by eq. (3.7), as the Low Heating Values are known. As it can be observed in fig. 4.2, there is a difference of ± 90 kJ/kg for all the types of methyl esters, if the results of the method that uses the heating value are compared to the other three results. This short difference is negligible.

In the case of unsaponifiables, the chemical exergy has been calculated assuming that this material is uniquely composed of tocopherols and sterol glucosides, both at a 50% share. The chemical exergies of the glycerol, sodium methoxide, citric acid, tocopherol and glucosides have been calculated using the standard Gibbs free energy of formation which has been calculated by the aggregation method of Jankousky.

The chemical exergies of tocopherols and glucosides have been calculated assuming that they are formed by a unique kind of molecule. Figure 4.3 shows the molecule of tocopherol. The molecule of glucoside is assumed to be formed by the molecular formula $C_{36}H_{65}O_6$.

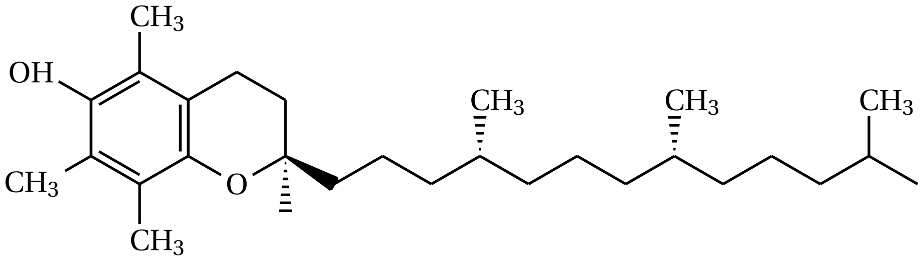


Figure 4.3: Molecule of tocopherol

The chemical exergy of the impurities has been calculated assuming that they are composed of metallic salts of Ca, Mg (group II metals), Na and K (group I metals) in equal percentages. These metallic salts are typical in vegetable oils.

The chemical exergies of methanol and natural gas have been calculated knowing the LHV and composition of C, H and O by eq. (3.7), see table 4.12. For the electricity streams entering the system the consumption value is the exergy value.

Table 4.12: Chemical exergies of methanol, n-hexane, toluene and natural gas using LHV method (3.7)

				Atoms		
Material	e^{CH} (kJ/kg)	**LHV** (kJ/kg)	β	C	H	O
Methanol	23,154.00	20,000	1.1577	1	4	1
Hexane	49,476.43	46,046	1.0745	6	14	0
Toluene	42,842.48	40,587	1.0556	7	8	0
Methane	55,050.00	50,000	1.1010	1	4	0

The chemical exergies of the remaining materials have been obtained from the bibliography or by means of the Exergy Calculator of the Exergoecology portal [43].

The physical exergies are calculated using eqs. (3.3) and (3.4). The $c_p(T)$ values have been obtained from the bibliography or applying the Joback method explained in chapter 3. All the results are shown in appendix A. The temperatures of each process are explained in the following paragraph. The exergy values of the rest of material flows are shown in table A.21.

4.3 Thermoeconomic model of biodiesel production

Once the chemical and physical exergies of all the materials and energy sources used and produced in the processes are calculated it is possible to calculate the exergy of each of the flows, which are composed of one or more of the mentioned materials or energy sources.

The processes considered in this model are the ones shown in fig. 4.4. The system has been described in detail in chapter 2, where justifications to apply these units where provided. The following paragraphs go deeper in the description of the specific units in terms of consumption of materials and energy.

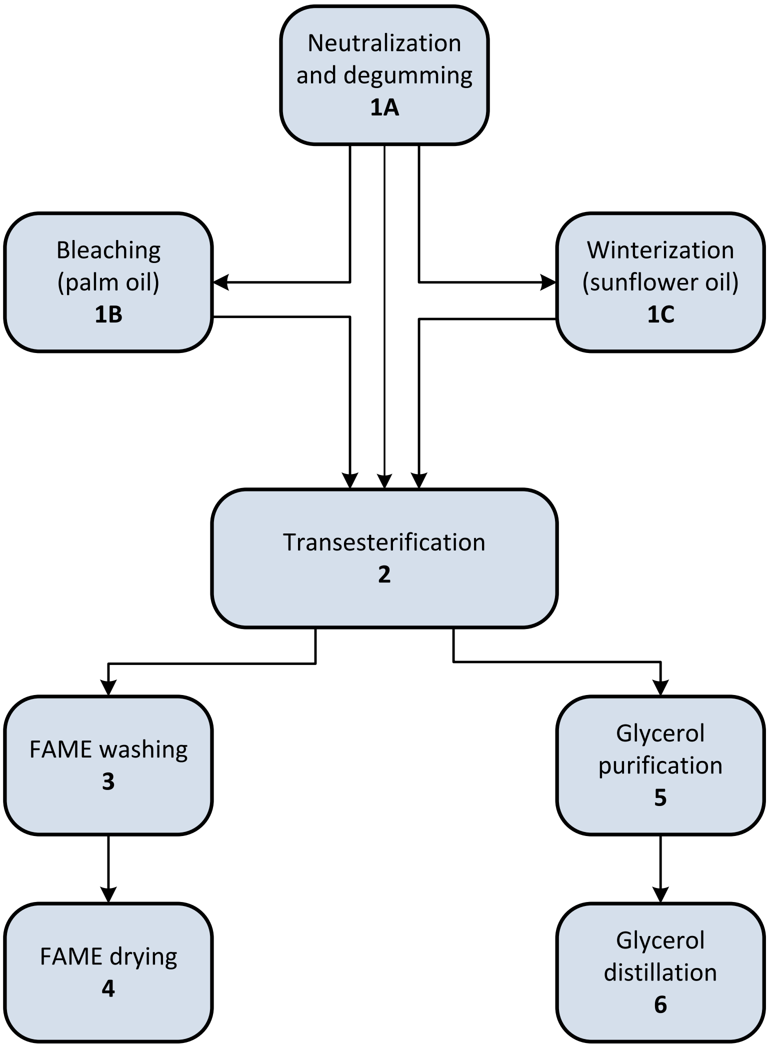


Figure 4.4: Scheme of the biodiesel plant producing with refined vegetable oils

4.3.1 Degumming and neutralisation

The degumming and neutralization of the refined vegetable oil is produced sequentially in the same tank provided with a mixer. Depending on the moisturability of the phosphatides they can be eliminated in two different ways: water degumming and acid degumming. The first one, which consists of adding water at 60-90 °C and centrifuging the mixture, only eliminates the hydrable phosphatides. The oil that enters the biodiesel plant might have been previously degummed by this process at the oil mills and therefore, it is not necessary to carry it out again. However, in order to eliminate the non-hydrable phosphatides there is the need to apply an acid degumming.

In practice in order to eliminate all possible phosphatides present in the oil, what it is usually done according to an experienced plant operator is, at the same tank, heating the oil up to 75 °C and firstly add an acid at ambient temperature (in this process both phosphoric and/or citric acid are commonly used) in order to make hydrable the non-hydrable phosphatides and, secondly, add warm water (around 75 °C) in order to hydrate all the phosphatides, which, once hydrated can be easily eliminated. When the non-hydrable phosphatides are scarce, it is advisable to add water and acid at the same time in order to save time, having a good efficiency in separating the phosphatides.

After degumming the oil is neutralized by converting the free fatty acids into soaps by the simple addition of an alkali, in this case NaOH [1] at ambient temperature. This step is performed at the same tank where degumming has been carried out. After this process, water must be eliminated. This is done by heating the oil up to 90 °C.

After degumming and neutralization a side-product of the system is obtained: soapstocks which contains mainly soaps, water and unsaponifiable matter. This product is normally treated as a residue. It can be sold to soap unfolders which produce FFA that are then sold to edible industries.

In order to calculate the soap content in the soapstock flow, the following saponification reaction has been considered. The mass balance is shown in table 4.13.

$$\mathrm{R{-}COOH} + \mathrm{NaOH} \longrightarrow \mathrm{R{-}COO\cdot Na} + \mathrm{H_2O}$$

Table 4.13: Mass balance for saponification reaction (kg/h)

	FFA	NaOH	Soaps	H_2O
Rapeseed oil	48.59	6.91	52.39	3.11
Sunflower oil	48.90	6.98	52.74	3.14
Palm oil	292.54	42.83	316.08	19.29

The quantity of FFA reacted is the difference between the free fatty acids contained in the vegetable oil entering the plant and the ones contained in the oil after the pre-treatment, which were given by the plant operator. The term R- in the chemical reaction refers to the average fatty acid chain of each type of oil.

Knowing the material balance, the energy consumption, the temperature and the exergy values of each material, it is possible to calculate the exergy cost for this specific process. Table 4.14 shows the exergy values of the inputs and outputs of the process. Performing the exergy balance gives the results per each type of oil as shown in table 4.15.

Table 4.14: Exergies of the degumming and neutralisation process (kJ/kg biodiesel)

Material	**I/O**	**Rapeseed**	**Sunflower**	**Palm**
Raw oil	Input	41,708.47	41,728.44	43,170.59
H_3PO_4	Input	1.59	1.59	1.59
Citric acid	Input	9.47	9.47	9.89
NaOH	Input	10.57	10.68	23.48
Electricity	Input	42.26	42.25	42.27
Natural gas	Input	74.84	74.83	74.85
Soapstock	Residue/Output	1,204.86	1,202.86	2,770.96
Neutralised oil	Output	40,531.78	40,553.76	40,427.28

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[1] It is also possible to use alkaline glycerol phase of the subsequent transesterification step

Table 4.15: Unit exergy consumption in degumming and neutralisation process (kJ/kg FAME)

	Fuel	**Product**	**k**
Rapeseed	41,847.20	40,531.78	1.0325
Sunflower	41,867.26	40,553.76	1.0324
Palm	43,322.67	40,427.28	1.0716

As it can be seen in fig. 4.5, the exergetic efficiency of neutralised oil from palm is slightly lower than for rapeseed and sunflower. This is mainly due to the higher exergy value of the palm oil that enters the plant. The entering palm oil has a higher exergy value due to the higher quantity of free fatty acids which have a relevant exergy value. Also, the higher use of NaOH needed to neutralise the free fatty acids influences slightly on the exergy efficiency.

An action that can be done to improve the exergy costs in this process is to sell the soapstock stream as a valuable product. As already said, soapstocks can be sold to soap unfolders which produce FFA that are then sold to edible industries. Attributing a value to the soapstocks reduces the exergy costs in around 3% for rapeseed and sunflower and around 6.5% for palm oil. This can be seen in fig. 4.5. The higher reduction in the palm oil neutralised oil is caused by the higher exergy value of the soapstock in this case due to the higher amount of free fatty acids.

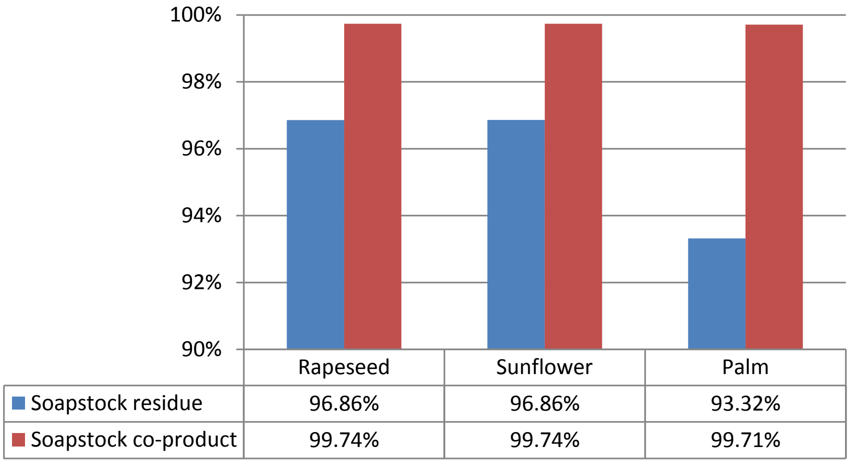


Figure 4.5: Comparison of exergy efficiency of neutralised oil

The efficiency values are high which means that not much exergy is lost in the process. The main factor influencing the reduction of efficiency is the consumption of energy in the process.

In any case, these results are a good example to show how knowing the composition of the oils and the exergy of the components allows understanding which is the cause of the inefficiency of the process, which reduces the useful energy that can be transferred from the input material to the desired outgoing product: as said before, the reason for the lower efficiency of the palm oil process is the higher content in free fatty acids in the entering palm oil.

4.3.2 Bleaching or whitening

Whitening, also called bleaching, is a simple step which consists in making the oil go through an adsorbent layer (calcic bentonite) which eliminates the pigments of the oil. This step is carried out normally only for palm oil because it has a typical red colour which is better to eliminate due to aesthetical purposes. This step is carried out at around 90 °C. The exergy values for this specific process are shown in table 4.16.

Performing the exergy balance, the exergetic efficiency of the process is 99.50%. This is a very good efficiency only being the low consumption of electricity the influencing factor, as no loss of exergy is due to the loss of matter.

Table 4.16: Exergies of the bleaching process (kJ/kg biodiesel)

Material	I/O	Palm
Neutralised oil	Input	40,427.28
Electricity	Input	21.13
Bleached oil	Output	40,427.22

4.3.3 Dewaxing or winterization

The content of waxes has to be eliminated because waxes might solidify during low temperature weather conditions leading to the formation of deposits. Dewaxing, also called winterization, consists in controlling the temperature of a filtering tank where the oil is circulated. The relative low temperatures of the tank make the waxes solidify and get retained on the filters. Temperature has to be lower than the cloud point temperature of the oil. This temperature is defined as that at which certain dissolved constituents in the fuel (such as waxes) start to crystallize and separate from the oil [7]. For sunflower oil, typical cloud points can range from 7 to 8 °C. The temperature applied in this case is 5 °C.

As result a vegetable oil practically free of waxes (only 0.1%) and a residue consisting of the filter layer impregnated of waxes are obtained. Performing the exergy balance, it is shown that the efficiency of this process is 98.99% due to the consumption of energy and the loss of matter in the form of filter residue.

Table 4.17: Exergies of the winterisation process (kJ/kg biodiesel)

Material	I/O	Sunflower
Neutralised oil	Input	40,553.76
Electricity	Input	42.25
Natural gas	Input	164.62
Filter residue	Residue	98.66
Winterised oil	Output	40,445.30

4.3.4 Transesterification

Transesterification can be performed at different temperatures and pressures. The speed of the reaction is very dependent on these two parameters. For base catalysed reactions, as in this case, the temperature can range from room temperature up to 80 °C at atmospheric pressure. The lower the temperature, the lower the reaction speed will be. In this case, the temperature is around 55 °C according to the plant operators.

The stoichiometric relationship entails 3 mole of methanol per 1 mole of triglyceride (3:1), but usually the reaction requires excess amounts of alcohol in order to force the reaction equilibrium towards the products. Other parallel reactions that can also take place are the esterification of free fatty acids into methyl esters and the formation of soaps by the reaction of FFA with the catalyst, as explained before. After reaction, glycerol and biodiesel form different phases that are separated by decantation.

Table 4.18: Exergies of the transesterification process (kJ/kg biodiesel)

Material	I/O	Rapeseed	Sunflower	Palm
Pre–treated oil	Input	40,531.78	40,445.30	40,427.22
Sodium methoxide	Input	106.41	106.43	106.4
Methanol	Input	2,563.16	2,575.52	2,645.82
Electricity	Input	25.03	25.02	25.03
Natural gas	Input	814.27	814.11	814.32
Crude glycerol	Output	3,163.33	3,174.73	3,231.87
Crude methyl ester	Output	40,462.65	40,385.74	40,381.49

As it can be seen in table 4.18 the exergies of the outputs are very similar; however, it is clear that the exergy of the crude rapeseed methyl ester stream is slightly higher compared to the other oils. In this case the main influencing factor is that the exergy value of the rapeseed methyl ester component in the stream which is the major component, is higher than for the other types of oils.

The main factor influencing the higher exergy value of the glycerol stream in the case of palm is that, following the stoichiometric reaction between the oil and the alcohol, there is a higher production of glycerol; this is due to the lower molecular weight of palm oil which is composed of shorter fatty acid chains.

In the case of sunflower, the production of glycerol is practically the same as for rapeseed, however, the exergy value of the crude glycerol stream is slightly higher due to the content of waxes, which stay in this stream. Also, the exergy value of the crude methyl ester stream is a little bit lower. This is because although there is practically the same production of crude methyl esters in terms of kg/h, when dividing by the kg/h of final biodiesel to obtain the kg/tonne of biodiesel, a lower value is obtained, because in the case of sunflower, the production of final biodiesel is slightly lower.

Performing the exergy balance, the exergy efficiency for each type of oil is shown in table 4.19, which distinguishes if crude glycerol is used as co-product or a residue of the process.

Table 4.19: Efficiencies of the transesterification process (%)

	Glycerol as co-product	Glycerol as residue
Rapeseed	99.06	91.88
Sunflower	99.08	91.86
Palm	99.08	91.77

The efficiencies in this process are also very high if the glycerol is considered co-product. In case of glycerol being a residue, the efficiency is much lower than in the case of the neutralisation process because the exergy lost in the co-product is higher. The exergy efficiency of palm when glycerol is a residue is slightly lower due to the higher formation of glycerol.

4.3.5 Biodiesel washing

Washing is performed by adding warm water (80 °C) and hydrochloric acid. Acidifying the water helps to better eliminate glycerol, methanol and catalyst. An important drawback of this process is that it may cause ester losses due to hydrolysis. In this Ph.D, no losses have been considered. The exergy values are shown in table 4.20. Performing the exergy balance, the results of table table 4.21 per each type of oil, are obtained.

Table 4.20: Exergies of the biodiesel washing process (kJ/kg biodiesel)

Material	I/O	Rapeseed	Sunflower	Palm
Crude methyl ester	Input	40,462.65	40,385.74	40,381.49
Acid waters	Input	6.5	6.5	6.5
Electricity	Input	12.51	12.51	12.52
Waste water	Residue	398.47	399.4	405.02
Washed methyl ester	Output	40,070.65	39,992.81	39,982.94

Table 4.21: Exergy efficiency of the biodiesel washing process (kJ/kg FAME)

	Fuel	Product	k
Rapeseed	40,481.66	40,070.65	1.0103
Sunflower	40,404.75	39,992.81	1.0103
Palm	40,400.51	39,982.94	1.0104

As it can be seen the exergy cost values are very similar here being the only influence to the numbers obtained, the difference between the exergies of the crude methyl esters. The efficiencies are very high because the residue stream is very low.

4.3.6 Biodiesel drying

Drying is performed using steam for heating the product. The boiling point of methanol and water are 65 °C and 100 °C at 1 atm [255], much lower than that of methyl esters (approximately 320 °C at 1 atm) so heating to a temperature close to 110 °C ensures a good degree of methanol and water elimination. The exergy values are shown in table 4.22. The exergy values are very similar; the short variation is due to the different exergy values of the entering washed methyl esters.

Even if the efficiency is very high, the exergy cost can be improved slightly by taking measures to recover the methanol from the waste water evaporate stream. The unit exergy consumption of the final biodiesel when recovering methanol as a valuable co-product is compared in table 4.23 with the exergy costs when methanol is as waste.

Table 4.22: Exergy of the biodiesel drying process (kJ/kg biodiesel)

Material	**I/O**	**Rapeseed**	**Sunflower**	**Palm**
Washed methyl ester	Input	40,070.65	39,992.81	39,982.94
Electricity	Input	8.24	8.24	8.24
Natural gas	Input	203.57	203.53	203.58
Residual waters (evaporate)	Residue	35.52	31.8	31.36
Final biodiesel	Output	40,049.51	39,970.27	39,958.01

Table 4.23: Exergy balance in biodiesel washing including recovering methanol

		Metanol recovered		**Metanol as waste**	
	F (kJ/kg)	P (kJ/kg)	k	P (kJ/kg)	k
Rapeseed	40,282.46	40,083.82	1.0050	40,049.51	1.0058
Sunflower	40,204.58	40,005.86	1.0050	39,970.27	1.0059
Palm	40,194.76	39,996.16	1.0050	39,958.01	1.0059

4.3.7 Glycerol purification

Purification consists in adding an acid, in this case HCl, to split the soaps into FFA and salts, which are then separated by decantation. Glycerine for industrial use at 65 °C is obtained although it still contains residues, water and methanol that must be eliminated in the distillation unit. The exergy values are shown in table 4.24.

Table 4.24: Exergies of the glycerol purification process (kJ/kg FAME)

Material	**I/O**	**Rapeseed**	**Sunflower**	**Palm**
Crude glycerol	Input	3,163.33	3,174.73	3,231.87
HCl	Input	1.6	1.61	1.65
Electricity	Input	22.19	22.18	22.19
Natural gas	Input	411.18	411.09	411.2
FFA	Residue/Co-product	385.09	384.3	384.02
Purified glycerol	Output	2,780.59	2,792.81	2,850.29

The process efficiency of the purified glycerol is show in table 4.25. As for the residue of the neutralisation and degumming process, here the residue composed of free fatty acids could be sold to edible industries.

Compared to the biodiesel after-treatment processes, the unit exergy costs are higher and the efficiency is lower. The main reason for this is the high consumption of energy per kg/h of product obtained.

4.3.8 Glycerol distillation

The distillation consists in heating the glycerol up to 130 °C so that methanol evaporates and is separated from the glycerol stream. The recovered methanol can be sent to the beginning of the

Table 4.25: Efficiency of the glycerol purification process

		FFA recovered		FFA as waste	
	F (kJ/kg)	P (kJ/kg)	k	P (kJ/kg)	k
Rapeseed	3,598.30	3,165.68	1.1367	2,780.59	1.2941
Sunflower	3,609.61	3,177.11	1.1361	2,792.81	1.2925
Palm	3,666.91	3,234.31	1.1338	2,792.81	1.3130

process in order to be reused. The exergy values of the flows entering this process are shown in table 4.26.

The exergy balance of the purified glycerol flow is the one shown in table 4.27. As it can be seen distillation of glycerol is an energy-intensive process. This is why there are authors proposing other techniques including chromatography, ion-exchange, membranes, crystallization and evaporation. However, these techniques have not been implemented so widely and plant owners see distillation as the desired option to obtain pharma grade glycerol.

Table 4.26: Exergies of the glycerol distillation process (kJ/kg FAME)

Material	I/O	Rapeseed	Sunflower	Palm
Purified glycerol	Input	2,780.59	2,792.81	2,850.29
Electricity	Input	9.51	9.51	9.51
Natural gas	Input	591.69	591.57	591.73
Methanol	Output	46.7	48.39	51.79
Glycerol	Output	2,388.35	2,394.96	2,455.26

Table 4.27: Exergy balance in the glycerol distillation process (kJ/kg FAME)

	Fuel	Product	k
Rapeseed	3,381.79	2,435.05	1.3888
Sunflower	3,393.89	2,443.35	1.3890
Palm	3,451.53	2,507.05	1.3767

4.4 Exergy Cost Analysis

In the previous paragraphs the exergy balances of the different processes were calculated individually to understand which losses of exergy are produced in each of them and why. However, the processes altogether constitute a global production process and the irreversibilities caused in one process can influence the exergy cost of the following. Therefore, it is always necessary to carry out an exergy cost analysis for the whole plant.

Tables 4.28(a) to 4.28(c) represent the Fuel-Product tables of the transesterification plant studied in this chapter for each of the oil types studied. Figure 4.6 shows the F-P diagram for the case of rapeseed oil.

Table 4.28: F–P Tables for each of the oil types studied for the BAU scenario (kJ/kg FAME)

(a) Rapeseed

	F_0	F_{1A}	F_2	F_3	F_4	F_5	F_6	Total
P_0		41,847	3,509	19	212	435	601	46,623
P_{1A}	0	0	40,532	0	0	0	0	40,532
P_2	0	0	0	40,463	0	3,163	0	43,626
P_3	0	0	0	0	40,071	0	0	40,071
P_4	40,050	0	0	0	0	0	0	40,050
P_5	0	0	0	0	0	0	2,781	2,781
P_6	2,388	0	0	0	0	0	0	2,388
Total	42,438	41,847	44,041	40,482	40,282	3598	3,382	

(b) Sunflower

	F_0	F_{1A}	F_{1B}	F_2	F_3	F_4	F_5	F_6	Total
P_0		41,867	207	3,521	19	212	435	601	46,862
P_{1A}	0	0	40,554	0	0	0	0	0	40,554
P_{1B}	0	0	0	40,445	0	0	0	0	40,445
P_2	0	0	0	0	40,386	0	3,175	0	43,560
P_3	0	0	0	0	0	39,993	0	0	39,993
P_4	39,970	0	0	0	0	0	0	0	39,970
P_5	0	0	0	0	0	0	0	2,793	2,793
P_6	2,395	0	0	0	0	0	0	0	2,395
Total	42,365	41,867	40,761	43,966	40,405	40,205	3,610	3,394	

(c) Palm

	F_0	F_{1A}	F_{1C}	F_2	F_3	F_4	F_5	F_6	Total
P_0		43,323	21	3,592	19	212	435	601	48,202
P_{1A}	0	0	40,427	0	0	0	0	0	40,427
P_{1C}	0	0	0	40,427	0	0	0	0	40,427
P_2	0	0	0	0	40,381	0	3,232	0	43,613
P_3	0	0	0	0	0	39,983	0	0	39,983
P_4	39,958	0	0	0	0	0	0	0	39,958
P_5	0	0	0	0	0	0	0	2,850	2,850
P_6	2,455	0	0	0	0	0	0	0	2,455
Total	42,413	43,323	40,448	44,019	40,401	40,195	3,667	3,452	

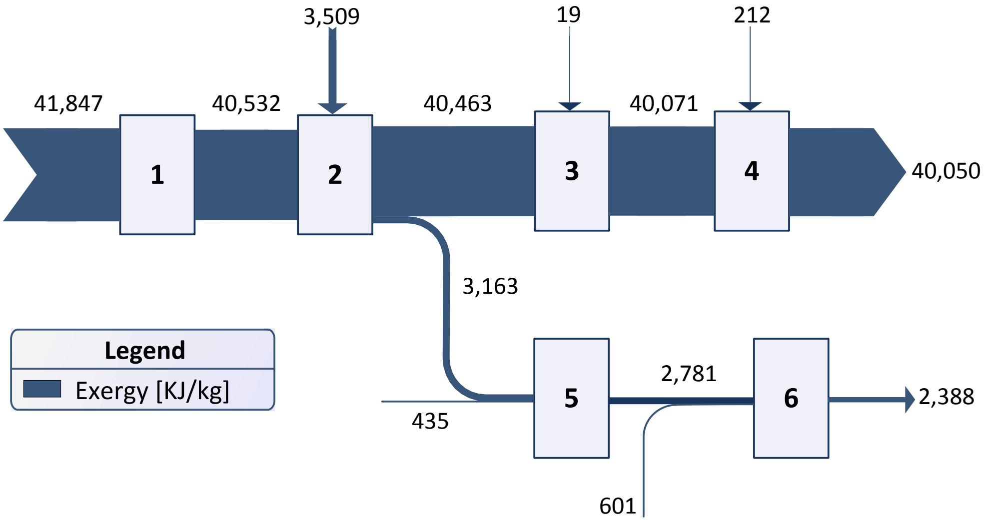


Figure 4.6: Fuel-Product diagram of rapeseed biodiesel production (kJ/kg FAME)

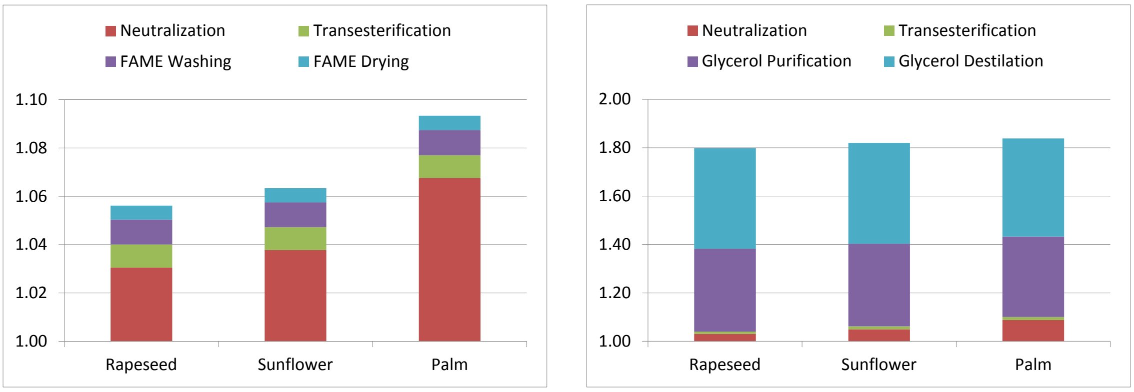
Table 4.29: Exergy costs (kJ/kg FAME) of the processes for the business as usual scenario

		Rapeseed		Sunflower		Palm	
Process		**P***	**k**$_P^*$	**P***	**k**$_P^*$	**P***	**k**$_P^*$
Pre-treatment	1A	41,847	1.0325	41,867	1.0324	43,323	1.0716
	1B	-	-	42,074	1.0403	-	-
	1C	-	-	-	-	43,344	1.0721
Transesterification	2	45,356	1.0397	45,595	1.0467	46,935	1.0762
Biodiesel washing	3	42,086	1.0503	42,291	1.0575	43,476	1.0874
Biodiesel drying	4	42,298	1.0561	42,503	1.0634	43,688	1.0934
Glycerol purification	5	3,724	1.3392	3,758	1.3456	3,913	1.3729
Glycerol distillation	6	4,325	1.8108	4,359	1.8201	4,514	1.8386

The exergy cost obtained from are shown in table 4.29. As it can be seen, the values of the different biodiesels (obtained after the biodiesel drying) are quite similar, although there are differences that need to be analysed: palm oil biodiesel has the highest exergy cost, followed by sunflower. While for palm the main reason for having a higher value is the exergy inputs in the beginning of cycle due to the higher exergy value of the oil (as seen in a previous paragraphs), in the case of sunflower oil where the oil has a similar exergy value than rapeseed, the main factor is the exergy consumed in the winterization unit.

The transesterification process is the one having higher exergy costs compared to the other processes. This is due to the higher consumption of exergy in the form of methanol. After this process the exergy costs are reduced for the biodiesel process because a significant part of the exergy costs are attributed to the co-product glycerol.

Figure 4.7 shows the cost formation process of biodiesel and glycerol along their production chain for the different types of oil studied, using eq. (3.38) .In the case of biodiesel, the biggest increase is due to the pre-treatment phase, in particular for the palm oil case, meanwhile the increase of irreversibilities after this phase is practically constant. In case of glycerol production the cost formation is due, mainly, to the purification and distillation phases.



(a) Biodiesel (b) Glycerol

Figure 4.7: Exergy cost formation of biodiesel and glycerol

4.4.1 Possible actions to reduce the exergy cost of biodiesel

As commented in previous paragraphs, there are several residues that can be recovered and re-used in the process or sold as co-product. This is the case for the soapstocks obtained in the neutralisation and degumming process and the free fatty acids obtained in the glycerol purification, which can be sold to soap unfolders or edible industries; and also the case of the methanol obtained after the biodiesel drying and glycerol distillation, which can be reintroduced in the process at the transesterification unit. Introducing these improvements in the Fuel-Product tables, these are modified as shown in tables 4.30(a) to 4.30(c). The numbers highlighted in bold are the ones modified compared to the previous Fuel-Product tables.

The exergy cost obtained due to these improvements can be seen in table 4.31 and fig. 4.8. As it can be observed by comparing tables 4.29 and 4.31, the exergy costs are improved for the three types of biodiesel. With these actions, the exergy cost of palm oil biodiesel is lower than for rapeseed and sunflower. This is due mainly to the higher exergy cost of the co-product obtained in the degumming and neutralisation process. In average, while the exergy cost of rapeseed and sunflower biodiesel is improved around 2.6% in the case of palm oil biodiesel the improvement is close to 5.8%.

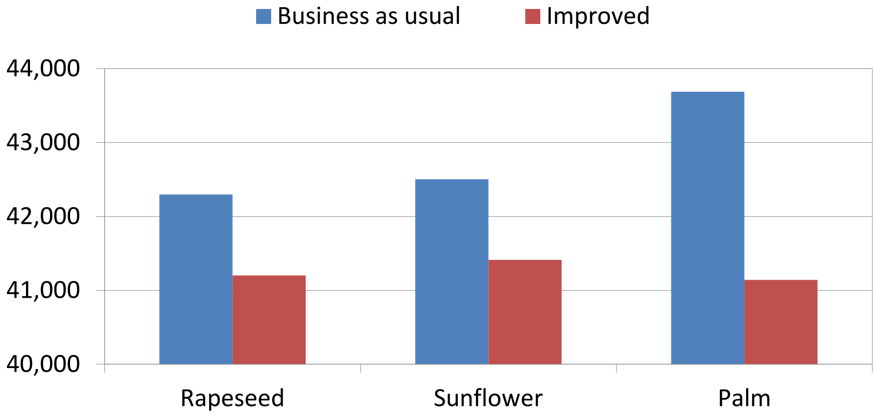


Figure 4.8: Comparison of exergy costs of final biodiesel products in BAU and improved scenarios (kJ/kg FAME)

Table 4.30: F–P Tables for each of the oil types studied for the improved scenario (kJ/kg FAME)

(a) Rapeseed

	F_0	F_{1A}	F_2	F_3	F_4	F_5	F_6	Total
P_0		41,847	**3,428**	19	212	435	601	46,542
P_{1A}	**1,205**	0	40,532	0	0	0	0	41,737
P_2	0	0	0	40,463	0	3,163	0	43,626
P_3	0	0	0	0	40,071	0	0	40,071
P_4	40,050	0	**34**	0	0	0	0	40,084
P_5	**385**	0	0	0	0	0	2,781	3,166
P_6	2,435	0	**47**	0	0	0	0	2,482
Total	44,075	41,847	44,041	40,482	40,282	3,598	3,382	

(b) Sunflower

	F_0	F_{1A}	F_{1B}	F_2	F_3	F_4	F_5	F_6	Total
P_0		41,867	207	**3,437**	19	212	435	601	46,778
P_{1A}	**1,203**	0	40,554	0	0	0	0	0	41,757
P_{1B}	0	0	0	40,445	0	0	0	0	40,445
P_2	0	0	0	0	40,386	0	3,175	0	43,560
P_3	0	0	0	0	0	39,993	0	0	39,993
P_4	39,970	0	0	**36**	0	0	0	0	40,006
P_5	**384**	0	0	0	0	0	0	2,793	3,177
P_6	2,395	0	0	**48**	0	0	0	0	2,443
Total	43,952	41,867	40,761	43,966	40,405	40,205	3,610	3,394	

(c) Palm

	F_0	F_{1A}	F_{1C}	F_2	F_3	F_4	F_5	F_6	Total
P_0		43,323	21	**3,502**	19	212	435	601	48,113
P_{1A}	**2,772**	0	40,427	0	0	0	0	0	43,199
P_{1C}	0	0	0	40,427	0	0	0	0	40,427
P_2	0	0	0	0	40,381	0	3,232	0	43,613
P_3	0	0	0	0	0	39,983	0	0	39,983
P_4	39,958	0	0	**38**	0	0	0	0	39,996
P_5	**384**	0	0	0		0	0	2,850	3,234
P_6	2,455	0	0	**52**	0	0		0	2,507
Total	45,569	43,323	40,448	44,019	40,401	40,195	3,667	3,452	

Table 4.31: Exergy costs (kJ/kg FAME) of the processes for the improved scenario

		Rapeseed		Sunflower		Palm	
Process		**P***	**k**$^*_P$	**P***	**k**$^*_P$	**P***	**k**$^*_P$
Pre-treatment	1A	41,847	1.0026	41,867	1.0026	43,323	1.0029
	1B	-	-	40,868	1.0105	-	-
	1C	-	-	-	-	40,564	1.0034
Transesterification	2	44,174	1.0126	44,418	1.0197	44,185	1.0131
Biodiesel washing	3	40,990	1.0229	41,200	1.0302	40,930	1.0237
Biodiesel drying	4	41,201	1.0279	41,411	1.0351	41,142	1.0286
Glycerol purification	5	3,638	1.1492	3,672	1.1558	3,709	1.1468
Glycerol distillation	6	3,797	1.5298	3,829	1.5671	3,870	1.5437

4.4.2 Effects on the exergy costs due to malfunctions in the process

In previous paragraphs the exergy costs of biodiesel for a business as usual scenario have been calculated. It has been shown how the exergy cost analysis can be used to assess possible improvements to be introduced in the processes. Another added value of the thermoeconomic analysis is that it can help to detect malfunctions in the processes and to assess the impact of the malfunction in the exergy costs. In this section the effect of two hypothetical examples applied to the process when using rapeseed oil are analysed.

The first example is a break down in the degumming and neutralisation tank so that no free fatty acids are converted into soaps and the phosphatides remain in the oil flow, even if the inputs and conditions of temperature are kept as usual. The rest of assumptions taken into consideration for the calculation of the exergy costs in the business as usual scenario are considered to be maintained: the efficiencies of the chemical reactions and the distribution of the components between the different phases and with the residues, as explained previously.

Another malfunction that can occur in the process is that the yield of the transesterification reaction is drastically reduced so that lower quantities of biodiesel and glycerol are obtained and higher quantities of oil remain in the tank. In this case, the yield of the reaction is assumed to be only 60%.

The Fuel-Product tables 4.32 show the exergy values in these two cases.These values are modified because:

- The final biodiesel production is modified; as the exergy values are calculated in relation to the kg of biodiesel produced, all the values are generally modified.
- In the case of the malfunction in the neutralisation process the exergy of the neutralised oil is increased because it retains the free fatty acids and phosphatides. This also occurs for the crude methyl ester and crude glycerol, where the exergy also increases because there is a higher production of mono-glycerides and soaps due to the reaction of FFA with methanol and sodium methoxide respectively. The final biodiesel and glycerol have similar exergies because it is assumed that the after-treatment processes are capable of cleaning the products of the higher amounts of undesired materials, namely FFA and soaps. In the biodiesel washing there is sufficient quantity of acid water to cope with the additional quantities of soaps to be converted into FFA. This would normally require

Table 4.32: Fuel–Product tables for malfunction analysis in rapeseed oil (kJ/kg FAME)

(a) Malfunction in neutralization

	F_0	F_{1A}	F_2	F_3	F_4	F_5	F_6	Total
P_0	0	41,723	3,503	19	212	436	603	46,497
P_1	0	0	40,861	0	0	0	0	40,861
P_2	0	0	0	40,587	0	3,350	0	43,937
P_3	0	0	0	0	40,073	0	0	40,073
P_4	40,050	0	0	0	0	0	0	40,050
P_5	0	0	0	0	0	0	2,756	2,756
P_6	2,381	0	0	0	0	0	0	2,381
Total	42,431	41,723	44,364	40,606	40,286	3,786	3,359	

(b) Malfunction in transesterification

	F_0	F_{1A}	F_2	F_3	F_4	F_5	F_6	Total
P_0	0	41,920	3,512	19	211	434	600	46,697
P_1	0	0	40,603	0	0	0	0	40,603
P_2	0	0	0	40,337	0	2,230	0	42,568
P_3	0	0	0	0	39,945	0	0	39,945
P_4	39,924	0	0	0	0	0	0	39,924
P_5	0	0	0	0	0	0	1,847	1,847
P_6	1,453	0	0	0	0	0	0	1,453
Total	41,377	41,920	44,115	40,356	40,156	2,664	2,447	

more energy, however, in this theoretical exercise the increases in energy consumption are difficult to quantify. The most conservative assumption is that the consumption of energy remains the same.

- In the case of a malfunction in the transesterification tank, the exergy values of crude biodiesel and crude glycerol are modified because there is no formation of methyl esters and glycerol. This is more significant for the glycerol stream because the unreacted oils tend to go practically all to the methyl ester phase. As in the previous case the exergy values of the final products do not vary significantly because of the same assumption, i.e. the after-treatment processes are capable of cleaning the products of the higher amounts of undesired materials. However, the limits of the parameters of mono-, di- and triglycerides which are accounted as the amount of oil in the final biodiesel are exceeded. This would also make that the minimum quantity of methyl esters would not be reached. This would increase the viscosity of the final fuel probably exceeding the limit of the standard and having potential negative consequences in the engine.

To compute the exergy cost variation, the formula (3.68) is used, which relates the variation of production cost with the efficiency variation of the individual processes by means of matrix $|\mathbf{P}^*\rangle$.

In our example this matrix for BAU scenario is:

$$\left|\mathbf{P}^{*}\right\rangle = \begin{bmatrix} 1.0000 & 0.9226 & 0.9222 & 0.9176 & 0.8149 & 0.7016 \\ 0.0000 & 1.0000 & 0.9995 & 0.9945 & 0.8832 & 0.7604 \\ 0.0000 & 0.0000 & 1.0000 & 0.9950 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.8610 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 \end{bmatrix}$$

In the case of the neutralisation an increase in the exergy costs of the after-treatment processes is observed. This is more evident in the glycerol streams as the volume of product that enters the glycerol after-treatment is higher. In the distillation unit there is a much higher formation of residues. The exergy costs would be included if part of the methyl esters that go with the glycerol phase were recirculated into the process.

As it can be observed in table 4.32(b), a problem in the transesterification unit affects mainly the biodiesel drying and washing units where a higher volume of residues is formed, while the transesterification unit appears to be almost not affected. The exergy costs of glycerol after-treatment processes are increased considerably due to the lower glycerol production.

These two examples are good to show that the exergy cost analysis is a good tool to detect where the inefficiencies of the processes are in case of malfunctions. For example, when a plant suffers a problem in the glycerol distillation an operator might think immediately that there is a specific problem in the distillation tower however, this example shows that indeed the problem might be at the very first process of the plant, i.e. the neutralisation tank.

Table 4.33: Relative variation of exergy cost due to malfunctions in the rapeseed oil production

		Malfunction in Neutralization		**Malfunction in Transestrification**	
Process		$\%\Delta k$	$\%\Delta k_P^*$	$\%\Delta k$	$\%\Delta k_P^*$
Neutralization	1A	-1.10	-1.10	0.00	0.00
Transesterification	2	0.02	-0.99	2.66	2.66
Biodiesel washing	3	0.30	-0.69	0.01	2.66
Biodiesel drying	4	0.01	-0.68	0.00	2.65
Glycerol purification	5	6.17	5.29	11.49	13.84
Glycerol distillation	6	-0.38	4.17	18.93	30.85

4.5 PINCH analysis

A general action that can be introduced in the process to reduce the exergy inputs is to use the residual heat and the temperature of colder flows to heat and cool other streams. This would allow the reduction of natural gas used to produce steam.

In order to see whether this action can be applied in the transesterification plant the PINCH methodology is applied to the plant for the rapeseed case.

The PINCH analysis was developed in 1977 by Ph.D. student Bodo Linnhoff under the supervision of Dr John Flower at the University of Leeds. It is a simple methodology for analysing chemical processes and the surrounding utility systems based on the Laws of thermodynamics, in order to check whether better possible heat integration is possible, thus allowing energy savings.

In order to produce the PINCH analysis, the temperatures of the flows (T_s) and the target temperature (T_t), which is the temperature required for a given flow, need to be identified. Also, the heat load, which is the amount of enthalpy change H of the process stream and therefore the maximum amount of heat that could be transferred to or from the stream, need to be known. The heat load is calculated with the thermal capacity, which is the specific heat capacity C_p of the stream multiplied by its mass flow (m) rate:

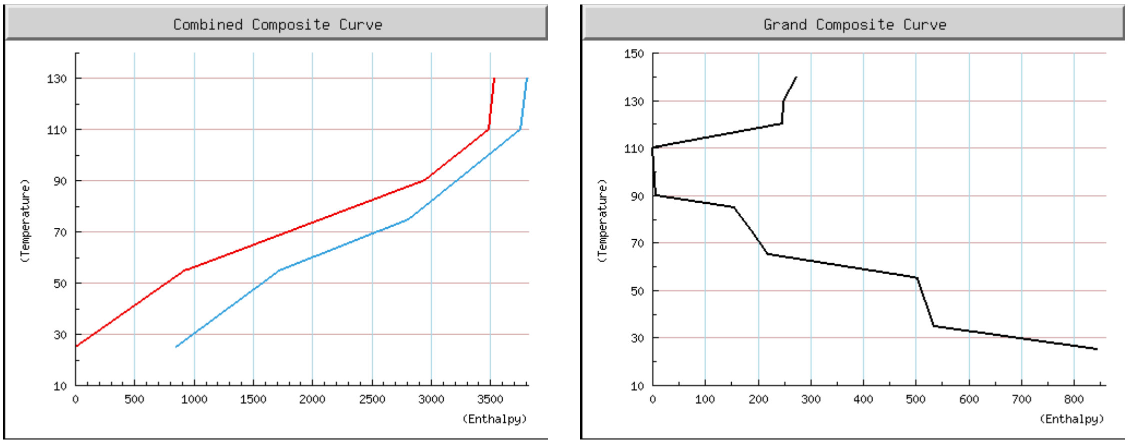
$$H = m\, c_p\, (T_s - T_t)$$

Knowing the temperatures in °C and the enthalpies in kW, it is possible to design the composite curve, which is a set of individual temperature vs. enthalpy curves for each flow that are combined to create a single curve. The composite curve gives a visual profile of the availability of heating or cooling available from the process streams. Table 4.34 shows the cold streams to be heated and the hot streams that can be cooled. With the information in table 4.34 the combined composite curve is the one shown in fig. 4.9(a). This curve has been calculated using the *Online Pinch Analysis Tool* © 2010, developed by Jeffrey S. Umbach. The grand composite curve for DT_{min}=10 in fig. 4.9(b) helps to identify the results obtained in table 4.35.

Table 4.34: Hot and cool streams on Pinch analysis of biodiesel production

ID	Stream	Min Temp. °C	Max Temp. °C	Heat Load kW	Thermal Capacity kW °C
Cool Streams					
1	Raw oil	25	75	1,222.06	24,441,127
3	Crude methyl ester	55	55.3	7.29	24,313,528
4	Washed methyl ester	55.3	110	1,338.67	24,468,451
6	Crude glycerol	55	65	26.08	2,608,335
7	Purified glycerol	65	130	159.46	2,453,225
9	NaOH solution	25	75	100.94	2,018,722
10	Methanol input	25	55	66.5	2,216,823
11	Acid waters	25	80	41.72	758,470
Hot Streams					
2	Neutralised Oil	55	90	945.78	27,022,161
5	Final methyl ester	25	110	2,094.49	24,641,116
8	Glycerol	25	130	232.11	2,210,574
12	Soapstock	25	90	212.49	3,269,043
13	Waste waters	25	55.3	16.79	554,375
14	Evaporate	25	110	17.29	314,336
15	FFA	25	65	9.47	236,630
16	Methanol from glycerol distillation	25	130	5.24	49,885

The Pinch temperature is the temperature at which the ability to transfer heat between the process streams is most constraint. By finding this point and starting the design there, the



(a) Combined Composite curve

(b) Grand Composite curve

Figure 4.9: Pinch composite curves for DT$_{min}$ = 10

energy targets can be achieved using heat exchangers to recover heat between hot and cold streams in two separate systems, one for temperatures above Pinch temperatures and one for temperatures below Pinch temperatures.

The ideal minimum heating and cooling requirements are the ideal amounts of heating and cooling utility required to make up for that cannot be performed via the process streams.

DT$_{\text{min}}$ is the minimum approach distance between the hot and cold composite curves on the temperature axis. It is determined by the overall heat transfer coefficients and the geometry of the heat exchanger. The amount of heat recovered depends on this factor, which is chosen by the designer of the system. Normally for chemical process this temperature varies from 10 to 20 °C. Higher values lead to higher utility requirements and lower area required for the exchangers.

Table 4.35: Results of PINCH analysis

	DT Min (°C)	
Parameter	10	20
Pinch temperature (°C)	110	90
Ideal minimum cooling (kW)	844.06	1,247.41
Ideal minimum heating (kW)	273.11	676.47

As explained by Umbach, the combination of hot and cold streams for the design on the exchanger has to be done following the following rules, depending on whether the streams are above or below the Pinch temperature:

- Above the Pinch: All hot streams that contact the Pinch must be cooled before hot streams that do not contact the Pinch may be cooled. When matching streams at the Pinch, the thermal capacity of the hot stream must be less than or equal to thermal capacity of the cold stream.
- Below the Pinch: All cold streams that contact the Pinch must be warmed before cold streams that do not contact the Pinch may be warmed. When matching streams at the

Pinch, the thermal capacity of the hot stream must be greater than or equal to thermal capacity of the cold stream.

- In either case, at any point inside the heat exchanger the difference of the temperatures of the hot and cold streams must be greater than or equal to the value of $\mathrm{DT_{MIN}}$.

As an example, with the results of the Pinch analysisit is posible to exchange heat between the final methyl ester and the washed methyl ester and between the purified glycerol and final glycerol. In the first heat exchanger the washed methyl ester is fully heated to 110 °C and therefore the natural gas that would be needed to heat it in the drying unit could be reduced. In the second exchanger, the purified glycerol is heated up to 118 °C which would reduce the natural gas needed to heat the stream up to the 130 °C needed for the distillation. Therefore, the exergy cost reduction would take place in the biodiesel drying unit and in the glycerol distillation unit.

According to table 4.35, the plant would need from 273.11 to 676.47 kW of natural gas (utility considered in this chapter) for heating purposes. This plant does not require cooling of streams for any specific purpose. The hot streams are let to cool naturally after being produced.

Taking into account that the plant works to produce 35,000 tonnes of biodiesel during 8,016 hours/year, the natural gas consumption for heating purposes would be between 216 and 540 kJ/kg FAME. This represents from 10 to 26% of the natural gas consumption of the plant (out of a total consumption of 2,095.55 kJ/kg FAME).

If the percentage reductions explained above are applied to the natural gas consumption in the plant and these are introduced in the F-P table of the business as usual scenario for the rapeseed shown in table 4.28(a), the unit exergy cost of final biodiesel is reduce up to 1.0536 – 1.0495, and in case of purified glycerol up to 1.766 – 1.695.

This improvement has also positive environmental impacts due to the substitution of natural gas by a free heat source with no GHG emissions. This action reduces the emissions in 3.03-3.68 $\mathrm{gCO_{2\text{-}eq}}$ /MJ for the biodiesel stream, which implies a reduction of GHG emissions of biodiesel of about 42 – 46% compared to diesel fuel with an emission level of 83.8 – 90.3 $\mathrm{gCO_{2\text{-}eq}}$ /MJ, being the reduction for the business as usual scenario of biodiesel production from rapeseed of 38% (using the default value). This option also implies a reduction of costs. Assuming a price of 10.97 €/GJ, the savings could be up to 17.0 – 20.7 €/tonne of biodiesel produced.

4.6 Energy cost analysis

In order to justify the use of exergy values and the calculation of the exergy costs, we have also calculated the energy consumption (or energy costs) and the unit energy cost. These terms are equivalent to the exergy cost P^* and unit exergy cost k_p^* calculated in previous paragraphs.

For this, only the energy flows entering and exiting the plant are considered. The energy consumption has been allocated taking into account the energy content of the products. The energy consumption of each process is the one shown in section 4.1.3

The energy contents of the glycerol and biodiesel are shown in table 4.36. The table also shows the energy content of the vegetable oil and methanol. Although these products in this process are not to be considered energy inputs but as chemical materials, they have been considered in the analysis because they can be used indeed as energy sources. These values need to be multiplied by the kg/kg of biodiesel consumed in the process.

Table 4.36: Energy content of the products

Product	**Energy** (kJ/kg)
Glycerol	19,000
Biodiesel	37,000
Pure vegetable oil	37,000
Methanol	19,700

With this information, the energy costs obtained are shown in fig. 4.10, and they are compared to the exergy costs for the business as usual scenario. As it can be observed the energy cost values follow a similar pattern as the exergy cost, i.e. the energy cost of palm is the highest value compared to the other types. This can be better observed in fig. 4.10. However, the values are much lower because many material flows entering the system are not taken into consideration.

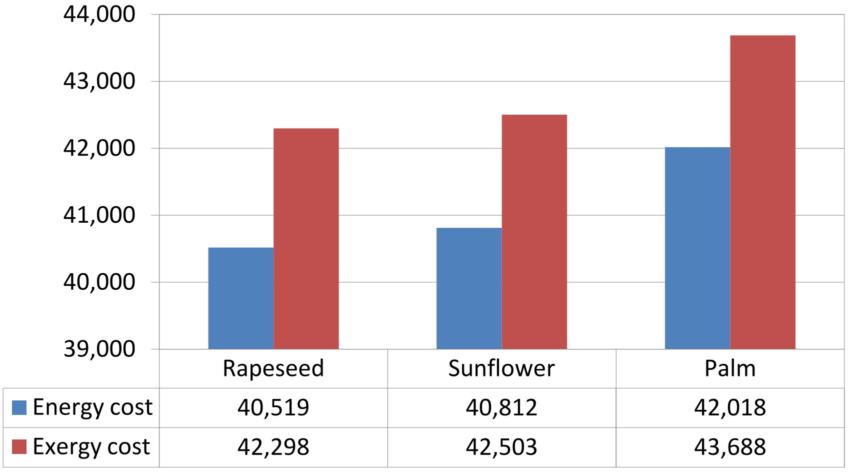


Figure 4.10: Energy and exergy cost of biodiesel (kJ/kg FAME)

An aspect that has to be highlighted between the energy and exergy analysis is that in an energy analysis where only energy inputs and outputs are considered, it is not possible to introduce improvement measures such as those related to the re-circulation of materials or consideration of materials as valuable products. It cannot be used to identify malfunctions in the process due to for example the poor yield in the chemical reactions as seen in a previous paragraph.

4.7 Summary and conclusions

This chapter demonstrates the applicability of thermoeconomics to bioenergy production processes and in particular to biodiesel production via transesterification. It shows that the exergy cost analysis is an appropriate tool to identify the inefficiencies of the process, how these inefficiencies can be minimised and how the exergy costs are affected by malfunctions in the process. Also, it shows the differences in terms of results between an energy and an exergy cost analysis.

The results obtained show that the compositions of the flows affect the individual efficiencies of the processes. It is also demonstrated that the inefficiencies of some processes can affect the exergy costs of ulterior processes. For example, it is observed that the higher exergy costs of the biodiesel fuels made from palm oil and sunflower oil, compared to the rapeseed oil biodiesel, are mainly due to the initial processes of the system. Also, the process with the highest irreversibility has been identified: the transesterification tank and this irreversibility has been quantified and compared with the other processes.

This chapter also shows how the improvements in the process in terms of recirculations and taking profit of wastes can improve the exergy costs of the products, having as a result that the biodiesel made with palm oil becomes the one with the lowest exergy cost.

Moreover, it shows how the malfunctions in the processes affect the subsequent processes in the cycle. It is demonstrated that while a malfunction happening in one process might affect the exergy costs of that process negligibly, it can have important effects in the subsequent processes. On the other hand, it also shows that, in view of the quality management procedures normally applied in this type of plants, where not all the properties are measured and not all the intermediate flows are controlled, applying thermoeconomics is a complex exercise.

Finally, the differences between an energy assessment and an exergy assessment have been demonstrated.

Chapter 5

ExROI and exergy renewability of land-to-tank biodiesel cycle

Chapter 2 described the different biodiesel technologies from land-to-tank and chapter 3 introduced the definition of Exergy Return on Investment (ExROI). This chapter aims at putting together these preceding chapters so once the main biodiesel technology pathways have been identified and the ExROI concept has been defined, the objective is to apply the ExROI concept to the biodiesel life cycles.

The ExROI concept as used here conjugates two important factors, life cycle assessment and exergy cost analysis. Life cycle assessment from land to tank allows taking into account all non-renewable resources required from crop cultivation to the transesterification plant (primary processes), including the production of the required inputs (secondary processes), meanwhile exergy cost analysis permits the correct cost assessment taking into account the energy quality of the production flows.

5.1 Borders of the system

As in every life cycle assessment, when performing an ExROI analysis it is very important to select adequate boundaries of the system, as this decision will have a great impact on the results to be obtained. In this work, two scenarios have been considered: on the one hand, one scenario puts the boundaries of the system in the direct processes related to biodiesel production, identified as primary processes. For biodiesel from energy crops this layer involves the cultivation, oil extraction, refining, transesterification and the intermediate transport stages. On the other hand, the other scenario considers also a second layer constituted by the production processes of the raw materials used in the first layer. This involves for example the production of fertilisers, diesel fuel, pesticides, n-hexane, methanol, etc.

The difference between the two scenarios considered from the point of view of the exergy cost theory is basically that if only the first layer is considered, the exergy cost of the raw materials is assumed to be their exergy values. This reduces the overall exergy costs of the system and therefore as results the ExROI value is increased. The results of the two scenarios considered are presented in the following paragraphs. With this it is possible to discern which is the impact of the production of the inputs in the system. This is calculated with the exergoecology factor as explained in chapter 3.

This PhD does not take into account a possible third layer which would be constituted by the production processes needed to build the machinery and technologies used to produce the biodiesel. This is a layer that is not normally considered in life cycle assessments and therefore has been neglected.

It is worth mentioning that the Renewable Energy Sources Directive [99] in its Annex V that sets the sustainability criteria for biofuels and bioliquids, requests to take into account the first and second layers in order to calculate the GHG emission savings, being the third layer not requested.

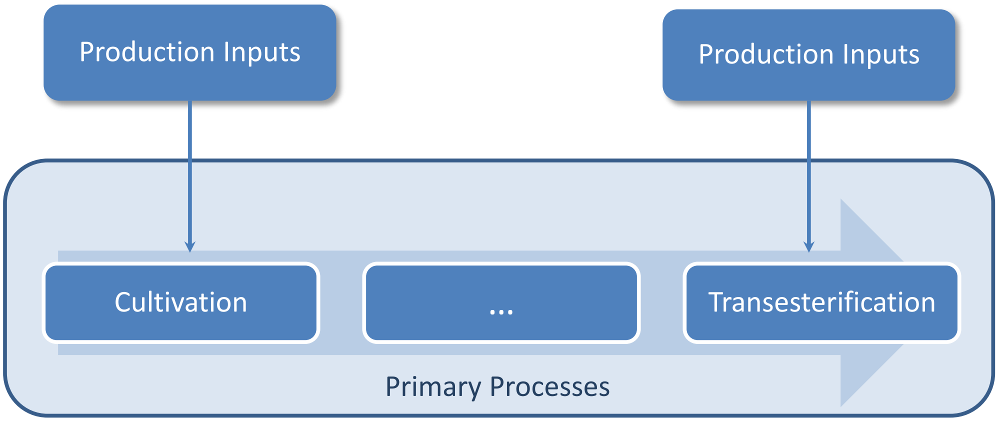


Figure 5.1: Boundaries of the system

The processes considered in the first layer, this is the primary processes, are shown in table B.1. As it can be seen in the table, some processes have been grouped (e.g. the transport phases) so that the processes numbers 5 to 8 coincide with those of the biodiesels considered. This will facilitate the comparison of results.

5.2 Exergy calculations

This paragraph presents the assumptions and data that have been considered to calculate the exergies of the materials and energy sources consumed and produced in the production processes.

The exergy values have been calculated using the calculation methods described in chapter 2. Other have been obtained from the *Exergy Calculator* of the Exergoecology portal developed by CIRCE [43].

The fatty acid composition taken into account to calculate the exergies of the oils and biodiesel for the different raw materials of vegetable origin and used cooking oil (UCO), are shown in table A.1. The fatty acid composition of soybean raw materials has been considered to be the same as the sunflower oil due to their high similarity [176].

The chemical exergies of the vegetable oils and the respective biodiesels have been calculated using eq. (3.6), except for the UCO methyl ester where the result of applying eq. (3.7) has been considered. The Gibbs free energy of formation has been determined using the Van Krevelen Chermin method. The chemical exergies for methanol, n-hexane, toluene and natural gas have been calculated using eq. (3.7), assuming the heating values and C, H and O composition of table 4.12.

The chemical exergies for glycerol and pesticide have been calculated using the standard Gibbs free energy which has been calculated by the aggregation method of Jankousky.

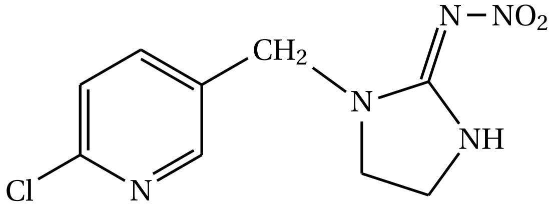


Figure 5.2: Molecule of pesticide used for the exergy calculation

The composition of the pesticide is unknown and therefore, in order to calculate the chemical exergy, the molecule of imidacloprid, a common pesticide widely used [32], has been considered. See fig. 5.2.

The chemical exergy of the remaining chemicals has been obtained from the bibliography or by means of the Exergy Calculator of the Exergoecology portal [43]. The results are shown in table A.21.

5.3 Life cycle exergy cost calculation

Once the exergy has been calculated for all the chemicals, materials and energy sources used in the processes, to obtain the exergoecologic cost of the system flows it is required to calculate the cumulative cost of external resources, i.e. the life cycle exergy of the flows crossing the boundaries of the system. For those flows, renewable and non-renewable sources will be distinguished.

5.3.1 Fertilizers

Nitrogenated fertiliser production and transport. For the calculation of the exergy cost in the production of N fertiliser the following data sources and assumptions have been considered.

The energy inputs for the production and transport of the nitrogenated fertiliser are the ones provided in the JEC study [148]. As for the consumption of materials, it has been assumed that the nitrogenated fertiliser is urea $CO(NH_2)_2$.

Urea is the most popular and economical of all nitrogenous fertilisers being used worldwide [206]. More than 90% of world production of urea is destined for use as a nitrogen-release fertiliser. Urea has the highest nitrogen content of all solid nitrogenous fertilisers in common use. Therefore, it has the lowest transportation costs per unit of nitrogen nutrient [109]. The standard crop-nutrient rating of urea is 46-0-0. Urea is commonly produced by the reaction of liquid ammonium and carbon dioxide following the chemical reaction shown below [39]. Taking into account the molar relation, the molecular weights and the nitrogen content of the urea, it is possible to calculate the quantity of chemical reagents needed to obtain 1 kg of N. Also, knowing the chemical exergies of the chemical reagents, obtained from [43] it is possible to obtain the exergy of the chemicals in kJ/kg N.

$$2\,NH_3 + CO_2 \longrightarrow CO(NH_2)_2 + H_2O$$

The exergies in kJ/kg N of all the inputs needed for the production of nitrogenate fertiliser are shown in table table 5.1. The cumulative cost of the product is the addition of all the exergies.

Table 5.1: Cumulative exergy for the production of N fertiliser

Inputs	**e** (kJ/kg N)
NH_3	23,740.52
CO_2	709.49
Hard coal	3,950.00
Diesel oil	860
Electricity	626.4
Fuel oil	4,380.00
Natural gas	33,000.00
N fertiliser	**67,266.41**

CaO fertiliser production and transport. The calcium oxide, commonly known as quicklime or lime, is obtained normally by the decomposition of carbonate calcium to obtain calcium oxide and carbon dioxide as a by-product, following the next chemical reaction. Knowing the molar relation, the molecular weights and the chemical exergies of the chemical reagents it is possible to obtain the exergy of the chemicals in kJ/kg CaO.

$$CaCO_3 \longrightarrow CaO + CO_2$$

The energy inputs for the production of the fertiliser are the ones provided in the JEC study [148]. The transport needs are also included in the values. The exergies in kJ/kg CaO of all the inputs needed for the production of CaO fertiliser are shown in table 5.2.

Table 5.2: Exergies and cumulative exergy for the production of CaO

Inputs	**e** (kJ/kg CaO)
$CaCO_3$	1,166.25
Diesel oil	185
Electricity	399.6
Hard coal	94
Lignite	230
Natural gas	300
CaO	**2,374.85**

Potassium oxide fertiliser production and transport. The K_2O fertiliser is assumed to be obtained from potassium chloride (KCl) [172]. KCl is the most common source to obtain K_2O fertiliser used worldwide [143]. KCl is present in nature in the form of several minerals: silvinite, silvite, kainite and carnalite, having each of them a different percentage of KCl in their composition. For this work, in order to obtain the cumulative exergy provided by the material, it is assumed that the KCl is obtained from silvite, which is the mineral that has the highest KCl content, around 60% [145]. Knowing the molecular weights and the chemical exergies of the chemical materials it is possible to obtain the exergy.

The energy inputs for the production of the fertiliser are the ones provided in the JEC study [148]. The transport needs are also included in the values. The exergies in kJ/kg K_2O of all the inputs needed for the production of K_2O fertiliser are shown in table 5.3.

Table 5.3: Exergies and cumulative exergy for the production of K_2O

Inputs	**e** (kJ/kg K_2O)
KCl	430.13
Diesel oil	540
Electricity	219.6
Natural gas	7,500.00
K_2O	**8,689.73**

Phosphate fertilizers production and transport. The P_2O_5 is obtained commonly from the reaction of mineral rocks phosphorite $Ca_3(PO_4)_2$ or apatite $3\,Ca_3(PO_4)_2Ca(ClF)_2$ with phosphoric acid or sulphuric acid. As a result calcium dihydrogen phosphate is obtained. This chemical compound contains around 46% of P_2O_5. For this work it has been assumed that the fertiliser is produced from phosphorite and phosphoric acid.

$$Ca_3(PO_4)_2(s) + 4\,H_3PO_4(aq) \longrightarrow 3\,Ca(H_2PO_4)_2$$

As in the previous products, the energy inputs for the production and transport of the fertiliser are the ones provided in the JEC study [148]. Knowing the molecular weights and the chemical exergies of the mineral it is possible to obtain the exergy the chemicals in kJ/kg as shown in table 5.4.

Table 5.4: Exergies and cumulative exergy for the production of P_2O_5 fertiliser

Inputs	**e** (kJ/kg P_2O_5)
$Ca_3(PO_4)_2$	113.32
H_3PO_4	210.09
Hard coal	570
Diesel oil	1,120.00
Electricity	1,602.00
Fuel oil	5,000.00
Natural gas	3,150.00
P_2O_5	**11,442.00**

5.3.2 Pesticide production and transport

As mentioned in the previous paragraph, to compute its exergy value, it is assumed that the pesticide is imidacloprid. Imidacloprid is currently the most widely used insecticide in the world.

It is very versatile as it can be applied by soil injection, tree injection, application to the skin of the plant, broadcast foliar, ground application as a granular or liquid formulation, or as a pesticide-coated seed treatment. Recently it has been linked to the disease and reduction in the number of bees. Although it is now off patent, the primary manufacturer of this chemical is Bayer CropScience.

It has not been possible to obtain information about the production process. Therefore, only the inputs provided by the JEC study [148] for its production and consumption are considered as the input values. The resulting exergy cost is shown in table 5.5.

Table 5.5: Exergies and cumulative exergy for the production of pesticide

Inputs	**e** (kJ/kg pesticide)
Hard coal	7,620.00
Diesel oil	58,100.00
Electricity	28,476.00
Fuel oil	32,500.00
Natural gas	71,400.00
Pesticide	**198,096.00**

5.3.3 Winter rape and sunflower seeding material production

The winter rape seeding material and the sunflower seeding material are produced from vegetable plants. Historically, the production of seeding material consisted in taking aside part of the seeds of a normal crop cultivation as a by product to be used for the next season or to sell them to other farmers. Although some seeds may still be produced in this manner, for example in developing countries, currently the commercial seeds production has evolved to become a specialised intensive industry with its own processes [223].

Table 5.6: Exergies and cumulative exergy for the production of seeding material

Inputs	**Rapeseed** **e** (kJ/kg seed)	**Sunflower** **e** (kJ/kg seed)
Hard coal	400	400
Diesel oil	1,600.00	1,600.00
Electricity	360	360
Fuel oil	800	800
Natural gas	3,300.00	3,300.00
Seeding material	**6,460.00**	**6,460.00**

The procedure for producing and handling a commercial seed lot, according to [223], go from the genetic selection to develop superior varieties, the seed production in specialised growing areas for which it is necessary to select adequate planting density, pest control and availability of insect pollinators; the collection at optimum stage of maturity; the seed conditioning to remove the seeds from the non-seed material and weed seeds; the seed treatment to enhance the germination or facilitate sowing; and, finally, the packaging and storage to retain the seed quality until sale to or use by crop producer.

For its production and transport in this work only the energy inputs provided by the JEC study are considered [148]. The input seeds and the water needs are considered as renewable products and therefore they are not taken into account for the non-renewable exergoecologic cost calculation. See table 5.6.

5.3.4 n-Hexane supply

n-Hexane is a minor constituent of crude oil and natural gas, obtained by the refining operations that separate the hydrocarbons within specific ranges of boiling points. It may also be a metabolic by-product from certain types of fungi, although this is not the current production method. For its purification electricity is needed [10]. n-Hexane is required to enhance the extraction of vegetable oil from seeds. The values of table 5.7 are obtained from the JEC study [148].

Table 5.7: Exergies and cumulative exergy for the supply n-hexane

Inputs	**e** (kJ/kg n-hexane)
Hard coal	326.65
Crude oil	51,611.37
Hydropower	30.62
Lignite	275.61
Natural gas	622.68
Nuclear	265.41
n-Hexane (rs)	**30,63**
n-Hexane (nrs)	**53,101.73**

5.3.5 Fuller's earth supply

Fuller's earth is the name received by any non-plastic clay or clay-like earthy material used to decolorize, filter, and purify animal, mineral, and vegetable oils and greases [68]. Its name originated with the textile industry, in which textile workers (or fullers) cleaned raw wool by kneading it in amixture of water and fine earth that adsorbed oil, dirt, and other contaminants from the fibres.

Fuller's earth consists chiefly of hydrated aluminum silicates that contain metal ions such as magnesium, sodium, and calcium within their structure. In this case, it has been considered as that the filtering material is bentonite of the type montmorillonite, which is the principal clay mineral in fuller's earth. For its extraction, milling and purification, energy inputs are needed.

The energy inputs of the JEC study [148] are considered. It's chemical formulation is $Ca_{0.17}Al_{2.33}Si_{3.67}O_{10}(OH)_2$, its molecular weight 366.7625 kg/kmol and its chemical exergy 17.8 kJ/kmol. Table 5.8 shows the exergoecology cost of Fuller's earth formation.

5.3.6 Transterification inputs

The transesterification process requires a set chemical compounds to obtain biofuel and glycerol from vegetable oil. The following compounds are considered.

Table 5.8: Exergies and cumulative exergy for the supply of Fuller's earth

Inputs	**e** (kJ/kg F.E.)
Montmorillonite	48.53
Hard coal	10
Crude oil	2,480.00
Lignite	20
Natural gas	20
Electricity	10
Fuller's earth	**2,588.53**

Sodium hydroxide production. NaOH is produced by the electrolysis of an aqueous solution of sodium chloride. The sodium hydroxide builds up at the cathode, where water is reduced to hydrogen gas and hydroxide ion [69]. All the input data assumed for this work have been obtained from the JEC study [148] which for this product includes the mass and energy balances. For this study, it has been assumed that the hydrogen production is a by-product of the process so that exergy costs can be attributed to it. See table 5.9.

Table 5.9: Exergies and cumulative exergy for the supply of NaOH

Inputs	**e** (kJ/kg NaOH)
Na_2CO_3	10.03
NaCl	287.93
H_2O	7,893.81
Electricity	4,320.00
Heat	240.12
H_2 (g)	7,724.59
NaOH	**5,027.30**

Chlorhydric acid production. HCl can be generated in many ways, and thus several precursors to hydrochloric acid exist. In this work it is assumed that the chemical is produced by a chlor-alkali process using salted water and sodium carbonate [196]. As a first step chlorine and hydrogen are obtained and then these chemicals are reacted to obtain the final product. The input data considered are those provided by the JEC study [148] which for this product includes the mass and energy balances. Hydrogen is obtained as a valuable co-product. See table 5.10.

Sodium carbonate production. Sodium carbonate is synthetically produced in large quantities from salt (sodium chloride) and limestone in a process known as the Solvay method [186] following the next chemical reaction:

$$2\,\mathrm{NaCl} + \mathrm{CaCO_3} \longrightarrow \mathrm{Na_2CO_3} + \mathrm{CaCl_2}$$

Knowing the molecular weights and the chemical exergies of the reactants it is possible to obtain the exergy the chemicals in kJ/kg. Adding the consumption of energy in the process in kJ/kg to the exergy of the chemicals, the exergy costs and non-renewable exergy costs are obtained.

Table 5.10: Exergies and cumulative exergy for the supply of HCl

Inputs	**e** (kJ/kg HCl)
Na_2CO_3	10.72
NaCl	315.8
H_2O	8,753.33
Cl_2	120.59
Electricity	4,735.45
Heat	262.54
H_2 (g)	8,950.06
HCl	**5,248.38**

It is assumed that the input data provided by the JEC study [148] are all allocated to the main product due to the lack of information; this is the most conservative option as all the exergy costs are then allocated to the main product. See table table 5.11.

Table 5.11: Exergies and cumulative exergy for the supply of Na_2CO_3

Inputs	**e** (kJ/kg Na_2CO_3)
NaCl	100.58
$CaCO_3$	165.96
Hard coal	11,701.08
Crude oil	217.08
Energy (rs)	735.48
Energy (nrs)	13,061.52
Na_2CO_3 (rs)	**735.48**
Na_2CO_3 (nrs)	**13,328.06**

Phosphoric acid production. H_3PO_4 is produced following the sulphuric acid route which is the most commonly used in Europe according to EFMA, the European Fertiliser Manufacturers' Association [65]. This route consists of the following chemical reaction from which the exergies of the reactants in kJ/kg are obtained, knowing the molar relation, the molecular weight and the individual exergy values.

$$Ca_3(PO_4)_2(s) + 3\,H_2SO_4(aq) \longrightarrow 2\,H_3PO_4 + 3\,CaSO_4$$

The exergy cost and non-renewable exergy cost are obtained taking into account the energy inputs provided by the JEC study [148]. As in the previous case, it is assumed that the input data are all allocated to the main product due to the lack of information. See table 5.12.

Sulphuric acid production. Sulphuric acid is produced by the reaction of sulphur and water. In this study the mass and energy inputs of the JEC study [148] are considered. The exergies of the inputs and exergy costs and non-renewable exergy cost are shown in table 5.13.

Table 5.12: Exergies and cumulative exergy for the supply of H_3PO_4

Inputs	**e** (kJ/kg H_3PO_4)
$Ca_3(PO_4)_2$	1,184.80
H_2SO_4	1,636.15
Energy (rs)	102.6
Energy (nrs)	33,362.29
H_3PO_4 (rs)	**102.60**
H_3PO_4 (nrs)	**36,183.24**

Table 5.13: Exergies and cumulative exergy for the supply of H_2SO_4

Inputs	**e** (kJ/kg H_2SO_4)
Sulphur	198.47
H_2O	31.81
Electricity	761.19
Natural gas	1,637.96
H_2SO_4 (rs)	**31.81**
H_2SO_4 (nrs)	**2,597.63**

Potasium hydroxide production. KOH is produced by the reaction of potassium chloride and water. In this study the mass and energy inputs from the EcoInvent inventory [63] are considered as no information is provided in the JEC study [148]. The exergies of the inputs and exergy costs and non-renewable exergy cost are shown in table 5.14.

Table 5.14: Exergies and cumulative exergy for the supply of KOH

Inputs	**e** (kJ/kg KOH)
KCl	127.23
H_2O	93.82
Electricity	6,500.00
Heat	6,200.00
Transport	464.17
KOH (rs)	**93.82**
KOH (nrs)	**13,291.40**

5.3.7 Electricity production

The electricity production considered in this work is assumed to be produced in Europe. Given this, an EU electricity mix is considered. The data of table 5.20 are the ones considered in the JEC study [148]. These numbers also include the transport and distribution losses. It is assumed that there is a loss of 1.2% in the distribution from high voltage to low voltage. The distribution of electricity sources renewable and non-renewable is shown in the same table.

Table 5.15: Energy consumption for electricity supply in the EU [148]

Source	%	**e** (kJ/kJ elec)
Biomass	0.25%	0.00708
Hard coal	19.79%	0.56773
Geothermal	0.07%	0.00202
Hydropower	4.44%	0.12751
Lignite	7.02%	0.20139
Crude oil	8.61%	0.24693
Natural gas	12.35%	0.3542
Nuclear	40.74%	1.16886
Waste	6.60%	0.18924
Wind power	0.14%	0.00405
Electricity (rs)	11.50%	**0.33**
Electricity (nrs)	88.50%	**2.54**
Total	100.00%	**2.87**

5.3.8 Diesel production

For the diesel production the inputs from the JEC study [148] have been considered. This study assumes that the crude oil is extracted outside Europe and then transported consuming heavy fuel oil. The refinement is produced in a refinery located in the European Union. Then it is considered that 20% of the diesel product is transported via inland navigation for 500 km, 60% is transported via pipeline and another 20% via train over a distance of 250 km, to the depot where then it is distributed to the specific point of consumption. In this work transport of diesel to the fuel station is not considered as this is not the final use of the product. Taking into account all these steps the exergy cost can be calculated as the aggregation of the exergies obtained in kJ/MJ of diesel. During the oil refinement many products are obtained for which exergy costs could be allocated. However, the JEC study [148] only includes the consumption related to the marginal production of diesel so the quantities are allocated entirely to this product.

Table 5.16: Exergy and cumulative exergy for diesel supply

Process	**e** (kJ/MJ diesel)
Crude oil production	1,163.80
Crude oil transport	11.11
Transport via inland navigation	1.17
Transport via pipeline	0.12
Transport via train	0.24
Diesel depot	0.84
Diesel	**1,177.28**

5.3.9 Steam generation

Steam can be generated using many resources being them fossil (diesel oil and natural gas mainly) or renewable. Steam can also be obtained as a co-product from a close industry is an industrial symbiosis scheme. For the purpose of this work, in this chapter, which is setting the baseline ExROI value, it has been assumed that the steam is produced from natural gas. This is in fact the energy vector normally being used nowadays by the industry for their heating needs.

There are many pathways that can be considered for the production and distribution of natural gas. The JEC study [148] considers many possibilities for example the production from Russia with transport via pipeline. Other possibilities are the extraction from the north of Africa or the North Sea and transport via pipeline or as compressed natural gas via vessel. Although most of the natural gas supplied to Europe comes from Russia [88], an EU mix needs to be considered. For this reason the inputs of the EU mix included in the JEC study [148] have been considered.

The selected pathway starts by the extraction of the natural gas and process at the place of extraction; then it is followed by pipeline transport over 1,000 km and by high pressure transport over 510 km. Losses due to pipeline transport and mechanical processes for the compression are taken into consideration. For the steam production it has been assumed that it is produced in a conventional boiler consuming the inputs shown in the table below.

In this case, besides the consumption of energy, a certain increase in the exergy cost has to be considered due to the exergetic efficiency of the steam production process.

Table 5.17: Exergies and cumulative exergy for the steam production

Process	**e** (kJ/kg steam)
Steam production	2,300
Natural gas transport via pipeline	14.90
Natural gas extraction	310.89
Steam	**2,625.79**

5.3.10 Methanol production

Methanol can be produced from many sources: coal, natural gas and biomass. For this chapter, which is setting the baseline, it has been considered that the production is from natural gas. The pathway considered involves the natural gas extraction and processing taking into consideration an EU mix of all possible origins of the natural gas arriving into the EU; natural gas transport by pipeline over 1,000 km; the high pressure distribution over 500 km and the methanol production and transport over a distance of 150 km for which diesel is consumed. Losses due to pipeline distribution and mechanical work for compression are taken into account. For the diesel consumption it has been considered a consumption of 0.94 MJ per tkm and a relation of 0.0081 tkm per MJ of methanol. See table 5.18.

Table 5.18: Exergies and cumulative exergy for the methanol production

Process	**e** (kJ/kg methanol)
Natural gas extraction	29,896.92
Natural gas transport via pipeline	170.76
Natural gas distribution	87.46
Methanol production and transport	152.28
Methanol	**30,307.42**

5.4 Exergy analysis of land to tank biodiesel cycles

The different steps for the production of the biodiesels from the different energy crops and used cooking oil have been explained in detail in chapter 2. Consumption data were also shown in different tables. In order to calculate the exergies of the flows these data need to be transformed into kg/kg of biodiesel or MJ/kg of biodiesel. Then, by multiplying the consumption data in these units per the exergy cost (or exergy) of the product (kJ/kg of product) it will be possible to obtain the exergy of the specific flow in kJ/kg of biodiesel. In order to obtain the consumption data in kg/kg of biodiesel the following conversion factors shown in table 5.19 have been considered.

Table 5.19: Conversion factors and other assumptions

Parameter	**Rape**	**Sunflower**	**Palm**	**Soybean**
Energy content of seeds, FFB and beans (MJ/kg)	23.8	23.8	15.84	20
Loss of seeds, beans or FFB due to transport (%)	1	1	2.04	1
Oil content (kg crude oil/kg of seed)	0.405	0.435	0.225	0.188
Loss of oil at refining (%)	4	4	1	4
Ratio refined oil:biodesel	1.04	1.04	1.04	1.02

After applying the conversion factors shown in table 5.19, as summary of the section the tables B.2, B.6, B.10 and B.14 show the values of the exergoecologic costs for all flows entering the primary processes. In the material or energy sources, all costs taken into account are considered as non-renewable energy sources.

Until now in this chapter, the transesterification plant has been considered as a single process where two main products are obtained: biodiesel and glycerol. In order to make an adequate distribution of the exergy costs between both products, the plant needs to be disaggregated into smaller units. By doing this, there will be a better allocation of the exergy costs.

The transesterification plant for the vegetable oil based biodiesels has been divided in three logic processes: the pre-treatment and transesterification on one hand, the biodiesel after-treatment on another side and finally the glycerol after-treatment. The reason for applying this disaggregation level is that the input for the pre-treatment and transesterification processes is the vegetable oil whilst after transesterification there are two differentiated streams: one stream of biodiesel and another of glycerol that follow different processes until the final desired products are produced.

The three logic processes considered have common inputs such as electricity, heat and HCl that are consumed in all or several of the processes. However, the consumption data available in the JEC study [148] are total consumption data for the entire plant. Therefore it is necessary to find a way to distribute the consumption between the three logic processes selected. In order to do this, the consumption data of a real biodiesel plant have been taken into account (the same one of chapter 4), for which the consumption per each of the logic processes selected is known.

This plant operates with rapeseed oil, sunflower oil and palm oil. For each type of oil different consumption of these inputs is observed as for example the pre-treatment of the vegetable oil varies in terms of the processes undergone. For the assessment of soybean biodiesel cycle, the same distribution as for the sunflower has been considered due to the similarities of the oils.

Knowing the specific consumption inputs in each of the logic processes considered and the total consumption, it is possible to obtain percentages of consumption. It has been assumed that these percentages can be applied to the consumption data provided by the JEC study [148] therefore obtaining a disaggregation of inputs, as shown in table 5.20.

In a similar way the exergy of products of direct processes of the studied biodiesel cycles are shown in tables B.3, B.7, B.11 and B.15.

Table 5.20: Distribution of consumption data in transesterification plant (%)

	Rapeseed	**Sunflower**	**Palm**
Electricity			
Transesterification	58.3	69.0	64.6
Glycerol purification	26.5	19.7	22.7
FAME after-treatment	15.2	11.3	12.7
Steam			
Transesterification	42.4	46.4	41.8
Glycerol purification	47.9	44.6	48.6
FAME after-treatment	9.7	9.0	9.6
HCl			
Transesterification	0.0	0.0	0.0
Glycerol purification	78.6	80.4	80.0
FAME after-treatment	21.4	19.6	20.0

Concerning the exergy values, it can be observed in fig. 5.3 that the life cycle biodiesel production is a process where exergy is lost stage after stage, except for the transport periods where exergy is conserved. As it can be observed, soy beans have a very high exergy value compared to the rapeseed and sunflower seeds and the palm FFB. This is due to the higher quantities of beans needed to produce a kg of biodiesel. While 5.7 kg of soy beans are needed, only 2.7 kg of rape seeds or 2.5 kg of sunflower seeds are required to obtain a kg of biodiesel. In the case of palm, there is also a need of high quantities of FFB, around 4.8 kg. However, as the exergy of the FFB is lower, the result is similar to the rape and sunflower seeds, see fig. 5.3.

There is a big loss of exergy at the oil extraction plant where crude oil is obtained. This reduction is attributable to the loss of matter as the oil content represents the lowest fraction in relation to the protein meal. The case of soy beans is the most dramatic one where oil only represents around 19% followed by the palm FFB where the oil content is account 22%. In the case of rape seeds the oil content is 40.5% and 43.5% for the sunflower seeds. This loss of matter outweighs the higher exergy value of the oil compared to the exergy of the seeds, beans and FFB.

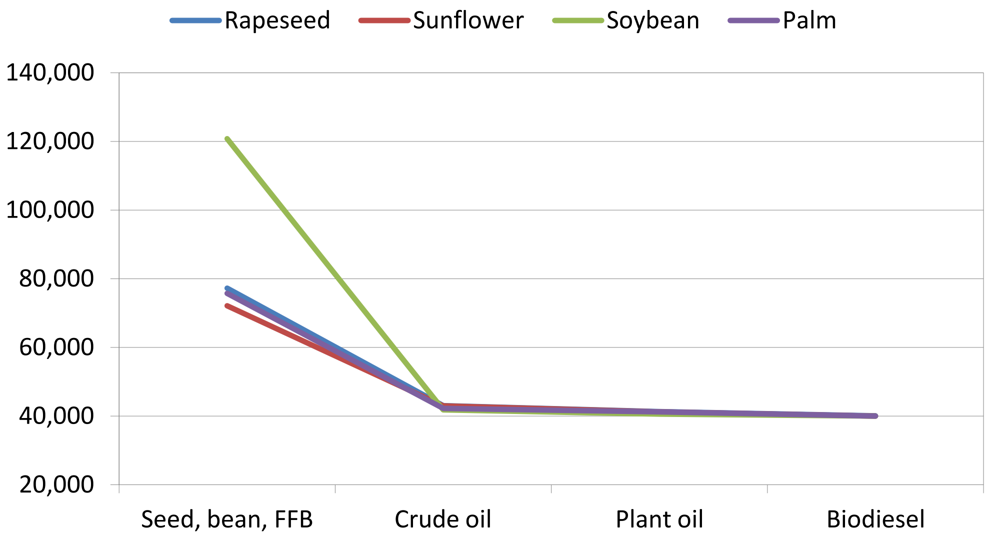


Figure 5.3: Exergy of the main products of the biodiesel life cycles (kJ/kg FAME)

Figure 5.4 shows the *exergy efficiency* of the main processes in the life cycles (i.e. excluding transport) as the coefficient between the exergy of the desired product of the process and the exergy that is consumed in it. As it can be observed in the figure, the oil extraction phase is the most inefficient one, especially for the soybean oil. This is mainly due to the high loss of mass, and not to the consumption of external resources.

It is worth noticing that for the palm oil, even when there is a reduction in the consumption of external inputs, namely energy sources, due to the self consumption of biomass resources, the efficiency of the process is not improved in comparison to the rapeseed and sunflower oils. This can be explained by the lower oil content per kg of FFB.

The efficiency of the cultivation phase varies from source to source. The less efficient one is the rapeseed cultivation, mainly due to the higher consumption of external inputs. The one that consumes fewer inputs is the palm cultivation; however, this crop is negatively affected due to the low exergy of the FFB obtained and the low yield. This can be better seen in Fig. 5.5 where the difference between the exergy inputs and outputs, the ratio seed-beans-FFB per FAME (in %) and yields of seed-beans-FFB in tonne per ha and year are shown. This figure shows the complexity of the analysis.

Taking into account the exergy of the co-products into the analysis in the extraction phase, so that the *exergy performance* is calculated as the ratio between the exergy of all the products of the process and the exergy that is consumed in it, the results are shown in fig. 5.5. As it can be observed, the performance of soy beans is increased due to the high yield in meal production and to the high exergy of the meal. The performance of palm is reduced due to the low meal yield.

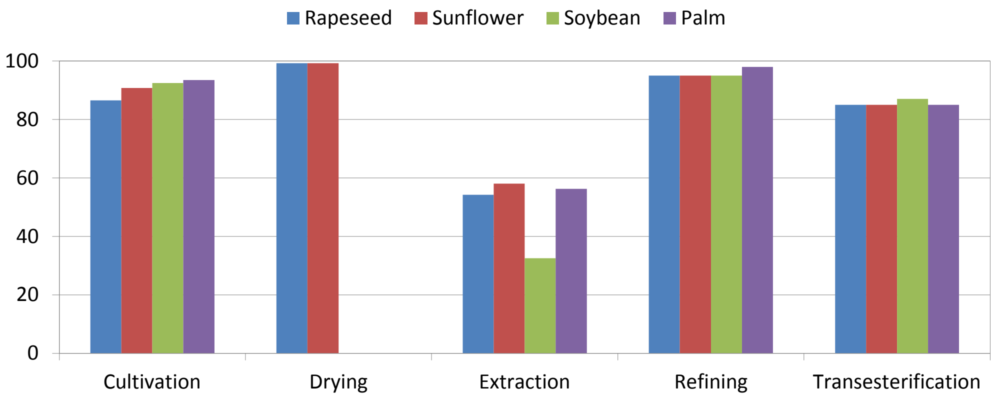


Figure 5.4: Exergy efficiencies (%) of the main processes of the biodiesel life cycles

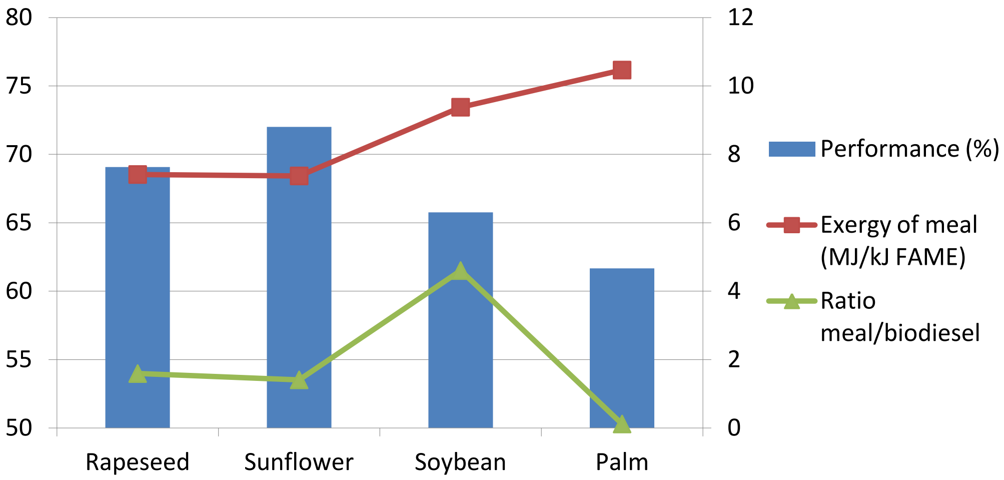


Figure 5.5: Exergy performance (%) of the extraction process of the biodiesel life cycle

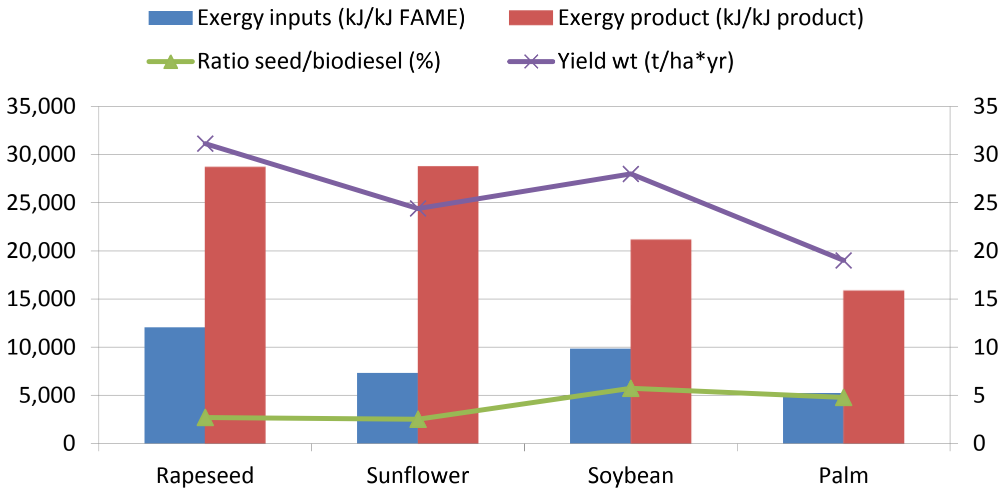


Figure 5.6: Exergy inputs, exergy of the product (left), yield for the cultivation processes (t/ha*yr) and ratio seeds-beans-FFB/biodiesel (%) (right)

5.5 Exergoecologic cost and ExROI calculations

Once the exergy costs of the material and energy flows entering the direct processes of the pathways are known, it is possible to obtain the exergies of all the flows entering and exiting the processes. This will lead to obtaining of the Fuel-Product tables as explained in chapter 3. Using the TAESS calculation tool, Thermoeconomic Analysis of Energy Systems (TAESS) [43], it is possible to obtain the unit exergy costs of the biodiesel flows.

For carrying out the calculations, the renewable natural resources consumed in the process, for example the solar energy consumed, the water needs in cultivation (it is considered that crops are rain fed) and CO_2 absorbed by the plant, need to be considered otherwise one could get the impression that the cultivation process is creating matter and energy, something completely impossible from the point of view of the First Law: the exergy of the outputs would be higher than the exergy of the inputs, which would imply a negative irreversibility, due to the creation of matter/energy from nothing.

However, the JEC study [148] does not include such information. For this reason, a compromise solution must be found in order to make the irreversibility of this stage coherent. It has been assumed that the sum of the exergy provided by the renewable natural resources equals the exergy of the product (seeds for rape and sunflower, FFB for palm and beans for soybean cultivation). By doing this, the only irreversibilities taken into account for calculating the exergy costs are the ones provided by the non-renewable resources, i.e. the fertilisers, pesticides and diesel fuel consumptions. According with the values introduced in previous sections the fuel–product for BAU scenario are presented in appendix B

Applying the mathematical model introduced in chapter 3, the production cost and ExROI values for all biodiesel considered in the study are shown in table 5.21, and the exergy and exergoecologic cost for all direct process of biodiesel cycles are shown in tables 5.22 and 5.23.

Table 5.21: Exergocologic cost, ExROI and renewable factor for biodiesel

Source	c_P	c_P^{nrs}	c_P^{nrs}	ExROI	ρ
Rapeseed	1.80	0.40	1.40	2.49	0.78
Sunflower	1.66	0.32	1.35	3.15	0.81
Palm	1.91	0.28	1.63	3.54	0.85
Soybean	1.98	0.59	1.38	1.68	0.70
UCO	1.43	0.24	1.19	4.10	0.83

As it can be observed in table 5.21, all the biodiesel sources have ExROI values higher than one, which means that for one unit of non-renewable resources used in their production, more than one unit of biodiesel is obtained. From the point of view of the consumption of non-renewable resources, the most sustainable one is the biodiesel produced from used cooking oil, studied in next section, followed by palm, sunflower and rapeseed. The less sustainable is the soybean oil one which almost has a 1:1 relation.

The term ρ *renewability ratio* establishes the weight of the renewable exergy cost with respect the total exergy cost. This can be seen also in fig. 5.7. As it can be seen palm oil biodiesel has the highest renewability followed by UCO. The soybean is the least “renewable” fuel although still has a 70% of renewable costs.

Table 5.22: Exergy and Exergoecologic costs from different biodiesel sources

	Rapeseed			Sunflower			Palm			Soybean		
Process	k^*	c_p	c_p^*	k^*	c_p	c_p^*	k^*	c_p	c_p^*	k^*	c_p	c_p^*
1	1.070	1.158	1.082	1.059	1.104	1.042	1.036	1.069	1.032	1.046	1.082	1.034
2	1.073	1.166	1.086	1.062	1.111	1.047	1.064	1.099	1.033	1.186	1.245	1.050
3	1.085	1.179	1.086	1.074	1.124	1.047	1.753	1.811	1.033	1.744	1.864	1.069
4	1.533	1.698	1.108	1.454	1.555	1.070	1.787	1.852	1.037	1.775	1.901	1.071
5	1.600	1.779	1.112	1.517	1.631	1.075	1.814	1.888	1.041	1.857	1.991	1.072
6	1.574	1.779	1.130	1.497	1.641	1.096	1.776	1.882	1.059	1.789	1.950	1.090
7	1.592	1.803	1.132	1.514	1.663	1.098	1.797	1.907	1.062	1.810	1.976	1.092
8	2.210	2.766	1.251	2.100	2.554	1.216	2.463	2.887	1.172	2.481	2.957	1.192

Table 5.23: Non renewable exercoecologic costs from different biodiesel sources (MJ/kg FAME)

	Rapeseed			Sunflower			Palm			Soybean		
Process	C_e^{nrs}	C_P^{nrs}	c_p^{nrs}	C_e^{nrs}	C_P^{nrs}	c_p^{nrs}	C_e^{nrs}	C_P^{nrs}	c_p^{nrs}	C_e^{nrs}	C_P^{nrs}	c_p^{nrs}
1	12.06	12.06	0.156	7.314	7.314	0.101	5.250	5.250	0.069	9.856	9.856	0.082
2	0.58	12.65	0.164	0.542	7.856	0.109	0.573	5.823	0.078	18.257	28.114	0.235
3	0.15	12.79	0.167	0.139	7.995	0.112	0.000	5.823	0.129	10.300	38.414	0.450
4	2.88	15.68	0.286	2.682	10.678	0.200	1.726	7.129	0.171	1.567	20.570	0.487
5	0.44	12.74	0.308	0.438	9.040	0.219	0.438	7.567	0.184	0.438	21.008	0.518
6	4.37	17.11	0.391	4.473	13.512	0.309	4.376	11.943	0.273	4.473	25.481	0.583
7	0.24	16.06	0.401	0.217	12.705	0.318	0.233	11.276	0.282	0.217	23.771	0.595
8	1.02	2.32	0.927	0.946	1.971	0.788	1.026	1.926	0.770	0.946	2.873	1.149

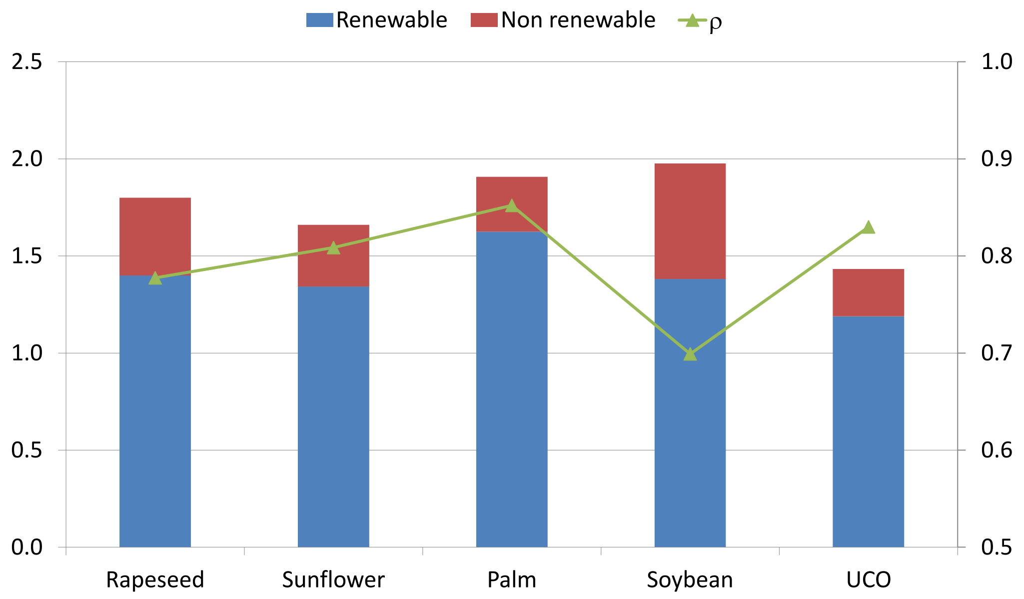


Figure 5.7: Renewable factor (kJ/kJ) in the production of biodiesel oils

The term c_P^* is the *exergoecologic ratio or factor* that relates the exergy and exergoecologic cost and measure the weight of the external resources cost. This relationship is also shown in fig. 5.8. As it can be observed, the rapeseed biodiesel has the highest exergoecologic ration while palm and UCO have the lowest.

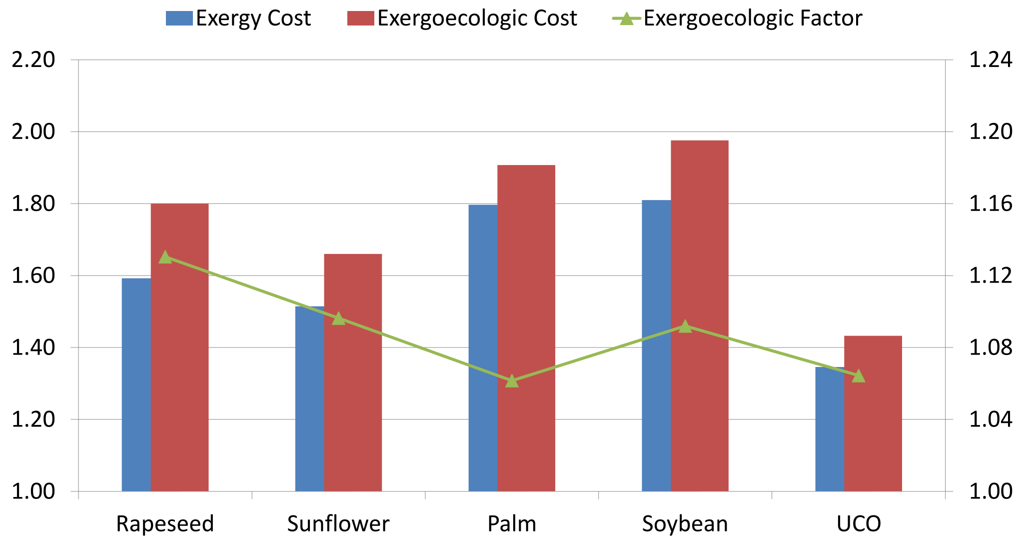


Figure 5.8: Exergoeconomic factors (kJ/kJ) in the production of biodiesel oils

Figure 5.9 shows how the unit non-renewable costs evolve in the life cycle of biodiesel production. Soybean and palm are the cycles that begin with the lowest unit exergy costs; however, the soybean biodiesel ends with the highest one. The main irreversibilities are found in the oil extraction plants. The maritime transport of the soybeans to the EU also adds irreversibility to this specific cycle. After the extraction and refining of the oil, all of the cycles remain practically constant in the unit exergy costs, not adding much irreversibilities to the whole process.

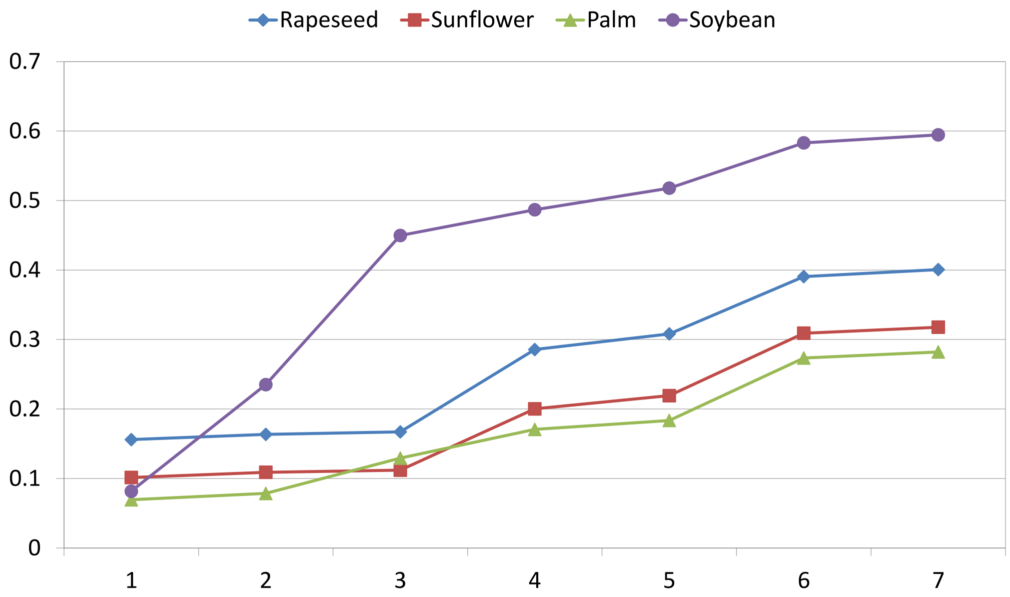


Figure 5.9: Evolution of unit non-renewable Exergoecologic Cost (kJ/kJ) in the production of biodiesel oils

It is worth noticing that the exergy cost of the refined glycerol is higher than the one of the final biodiesel. The reason behind this high value is that the exergy of glycerol is low while the exergy consumption is considerably high in the glycerol purification phase where a lot of energy per kg of glycerol is consumed in the distillation unit.

In fig. 5.10 is shown of the cost of glycerol is increase in the purification process form crude, which cost is the same cost than crude biodiesel.

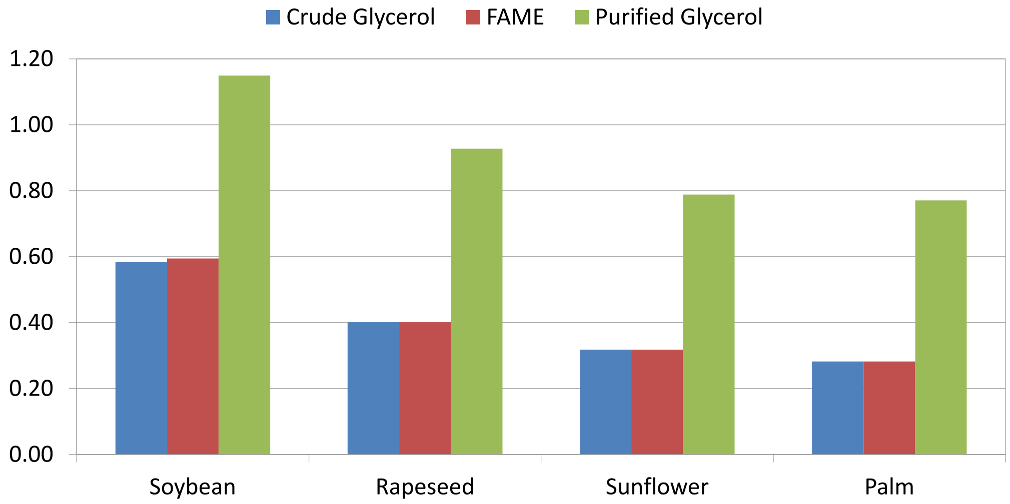


Figure 5.10: Comparison of unit non-renewable exergoecologic cost (kJ/kJ) of crude and purified glycerol for different biodiesel oils

It is worth noticing that the exergy cost of the refined glycerol is higher than the one of the final biodiesel. The reason behind this high value is that the exergy of glycerol is low while the exergy consumption is considerably high in the glycerol purification phase where a lot of energy per kg

of glycerol is consumed in the distillation unit. Figure 5.10 shows the cost of glycerol is increased in the distillation process. The crude glycerol and crude FAME have similar values.

5.6 Thermoeconomic analysis of used cooking oils

The results of the thermoeconomic analysis of biodiesel produced from used cooking oil have been presented in the previous paragraph to compare them with the biodiesel production from vegetable oils. In this section the data used for the calculation are detailed as well as the main assumptions taken into account. The main steps for the production have been explained in detail in section 2.5, where energy and mass consumption data are shown.

Here assumptions to discern between the inputs of the esterification process and the inputs of the after-treatment have been considered because the data obtained from the CIEMAT study [160] where aggregated to the entire plant. The assumptions are the following:

1. The after-treatment process of FAME is the same as that of the other oils: washing and drying.
2. The consumption values for these processes in u/kg FAME are the result of calculating the average consumption of the three vegetable oils in chapter 4.
3. The consumption in the esterification tank results from the difference of the total consumption and the consumption in the after-treatment process.
4. The results show that the consumption in the esterification tank is much higher in relation to the after-treatment than for the vegetable oils. This can be justified because there are two phases: esterification and transesterification which need to be heated and mixed.
5. In order to calculate the steam production from diesel fuel, the same assumptions as the ones for steam production from natural gas in chapter 4 have been considered, which correspond to 0.85 kWh/kg steam.
6. The enthalpy of steam considered at 1MPa is 2.777 MJ/kg.
7. A certain consumption of HCl in the after-treatment is assumed. This consumption was not quantified in the LCA of CIEMAT [160], which is the life cycle basis of these calculations.
8. In this plant there is no after-treatment of the glycerol phase. The crude glycerol is sold as a low value added by-product.

Table 5.24 shows the specific consumption in each unit as well as the exergy and exergoecologic costs and the mass balance and exergy values of the intermediate and final products. Table 5.25 shows the Fuel-Product table obtained with the given data and assumptions.

Table 5.26 presents the results of the exergy costs calculations, which are also shown in fig. 5.11. As it can be seen the costs are increased mostly in the esterification phase. This increase is due to the consumption of non-renewable energy sources.

Table 5.24: Exergy and cost of flows of the UCO biodiesel pathway

					Exergy		**Cost**	
Material	**Process**	I/O	**Unit** (u)	u/kg FAME	MJ/u	MJ/kg FAME	MJ/u	MJ/kg FAME
Diesel	1	Input	MJ	0.6459	1.0000	0.6459	1.1773	0.7604
UCO	1	Output	kg	1.3368	39.5994	52.9364	-	-
Diesel	2	Input	MJ	0.0371	1.0000	0.0371	1.1773	0.0437
Electricity	2	Input	MJ	0.4679	1.0000	0.4679	2.8690	1.3423
UCO recycled	2	Output	kg	1.0300	39.5994	40.7873	-	-
Methanol	3	Input	kg	0.1550	23.1540	3.5889	30.3074	4.6977
KOH	3	Input	kg	0.0277	0.8229	0.0228	13.3852	0.3708
H2SO4	3	Input	kg	0.0170	1.6417	0.0279	2.6295	0.0447
Diesel	3	Input	MJ	1.5651	1.0000	1.5651	1.1773	1.8426
Electricity	3	Input	MJ	0.4713	1.0000	0.4713	2.8690	1.3522
Crude FAME	3	Output	kg	1.0100	39.8548	40.2533	-	-
Crude Glycerol	3	Output	kg	0.2000	23.6779	4.7356	-	-
HCl	4	Input	kg	0.0406	1.3409	0.0544	5.2484	0.2131
Diesel	4	Input	MJ	0.0749	1	0.0749	1.1773	0.08820186
Electricity	4	Input	MJ	0.0187	1.0000	0.0187	2.869	0.0535
FAME	4	Output	kg	1	39.8376	39.8376	-	-

Table 5.25: F–P Tables UCO biodiesel (MJ/kg FAME)

	F_0	F_1	F_2	F_3	F_4	Total
C_0^{nrs}		52.94	0.00	0.00	0.00	52.94
C_0^{nrs}		0.76	1.39	8.31	0.35	10.81
P_1	0.00	0.00	52.94	0.00	0.00	52.94
P_2	0.00	0.00	0.00	40.79	0.00	40.79
P_3	4.74	0.00	0.00	0.00	40.25	44.99
P_4	39.84	0.00	0.00	0.00	0.00	39.84
Total	44.58	53.70	54.32	49.10	40.61	

Table 5.26: Cost analysis for UCO biodiesel (MJ/kg FAME)

Process	P^* MJ/kg	C_p MJ/Kg	c_P^* MJ/MJ	C_P^{nrs} MJ/kg	c_P^{nrs} MJ/MJ
1	53.582	53.697	1.0021	0.760	0.0144
2	54.087	55.083	1.0184	2.146	0.0526
3	59.763	63.391	1.0607	10.454	0.2324
4	53.621	57.073	1.0644	9.709	0.2437

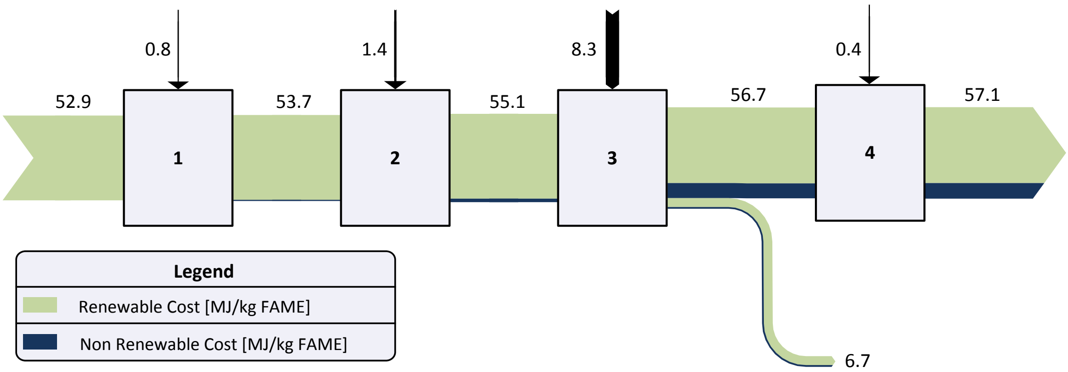


Figure 5.11: Cost diagram of UCO biodiesel production

5.7 Sensitivity analysis

As it has been explained above, the results obtained are based mostly on the consumption data of the life cycle assessments produced by the JRC, EUCAR and CONCAWE, which are fixed numbers based on specific assumptions. Additionally, consumption in the biodiesel production cycle can vary significantly depending on many circumstances, for example, temperature and soil conditions at cultivation, distance for transport, quality of the oil at the transesterification plant, etc. This variation influences the exergy costs of the external resources entering the system and therefore the ExROI value of the product. In order to understand the effect that variations in the consumption of external resources may have in the ExROI result, a sensitivity analysis needs to be produced.

By using eq. (3.67) it is possible to compute the impact of the variation in the cost of non-renewable resources in the FAME production cost:

$$\%\Delta C_{FAME}^{\text{nrs}} = \alpha_{in}\,\%\Delta C_{in}^{\text{nrs}}$$

where C_{in}^{nrs} is the cost of the input materials. Table 5.27 shows the impact values α_{in} for in the production cost of FAME, for each external resource considered.Note that the sum by columns of that table is equal to 1. In term of ExROI, it could be written as:

$$\%\Delta\text{ExROI} = -\frac{\%\Delta C_{FAME}^{\text{nrs}}}{1+\%\Delta C_{FAME}^{\text{nrs}}}$$

The values shown in table 5.27, could be used to estimate the effect of a change on cost of external resources on the production cost of FAME, these changes could be due to a reduction in the consumption of the materials or by the replacement of non-renewable resources by renewable ones. It can helped to identify improvement policies. For example, in case of FAME produced from rapeseed the most important factor is the use of fertilizers, a reduction or replacement by organic fertilizers of 10% causes an improvement of 3.75% in the cost of FAME. Or in case of FAME obtained from palm oil a reduction of 10% in the consumption of methanol for transesterification represents a improvement of 2.5% in the cost of biodiesel.

Other example of application, is to consider electricity as a renewable resource. In the JEC study 15% of electricity is from renewable origin, in case of rapeseed, this would suppose a reduction of FAME cost of 1.27% which is not relevant.

Table 5.27: Relative impact on the production cost of FAME due to a relative variation of external resources

Material	Rapeseed	Sunflower	Palm	Soybean
Fertilizer	0.3752	0.1790	0.2121	0.0696
Methanol	0.1793	0.2245	0.2496	0.1237
Diesel	0.1365	0.2061	0.0882	0.1745
Steam	0.1941	0.2388	0.1630	0.2030
Electricity	0.0848	0.1026	0.0355	0.0793
Heavy fuel oil	0.0000	0.0000	0.1187	0.3163
Others	0.0301	0.0490	0.1329	0.0336

5.8 Maximum allowance transport distance

Besides the general sensitivity analysis carried out in the previous paragraph, another aspect that can be analysed is the maximum allowance transport distance. This concept is defined as the maximum distance in km that can be allowed in the transport process while obtaining an ExROI value $\geqslant 1$. Beyond this distance, the product would have an ExROI value lower than 1 which means that it would consume more non-renewable exergy than the exergy contained in the product.

In the case of rapeseed the only transport process considered is the transport of the rape seed by truck from the drying plant which is close to the cultivation field to the mill where the oil is extracted, which is assumed to be besides the transesterification plant. In this case 47.5 MJ of diesel per kg of rape seed are consumed. This consumption is translated in an exergy value of 149.46 kJ/kg FAME.

Calculating the exergy value for this stream that would be necessary for obtaining an ExROI value of 1 while maintaining the other exergy values constant, the exergy value obtained would be 33,215 kJ/kg FAME.

Taking into account the conversion factor from FAME to rapeseed and the consumption of diesel per tkm (940 kJ/tkm) a distance of 13,209 km to transport one tonne of seeds is obtained. This is equivalent to a trip go and return by road between Lisbon and Teheran through the Bosporus Strait, following the path shown in fig. 5.12.

Figure 5.12: Distance between Lisbon and Teheran by road transport

In the case of palm based biodiesel there are several transport processes: road transport of the fresh fruit bunches from the palm field to the mill where the oil is extracted; road transport of the crude oil to the depot in the port where the oil is shipped; and maritime transport of the crude oil to Europe where it is refined and transesterified.

This exercise is only applied to the maritime transport because the road transport distances are less significant. In the business as usual scenario there is a heavy fuel consumption of 1,263 kJ per kg of crude oil which translated into an exergy value of 1,567.45 kJ/kg FAME.

In this case, for obtaining an ExROI value of 1, the exergy value would need to be 32,547.07 kJ/kg FAME. Taking into account the conversion factor from FAME to crude palm oil and the consumption of heavy fuel oil per tkm (124 kJ/tkm) a distance of 249,004 km to transport one tonne of crude oil is obtained. If the distance between the port of Valencia and Sydney is around 37,000 km, the value obtained would be equivalent to 7 trips go and return from both ports through the Strait of Suez, following the path in the fig. 5.13.

Figure 5.13: Distance between Valencia and Sydney by maritime transport

With this results obtained it is possible to conclude that the transport processes will not make the ExROI value be bellow 1 because such maximum allowance transport distances will be difficultly reached.

5.9 Results using EcoInvent database

In the results shown in the previous paragraphs have been obtained for a life cycle based mainly in the JEC study database [148]. This paragraph shows the results that are obtained by using the EcoInvent database [63] using the SimaPro program [212]. EcoInvent is currently the world leading life cycle inventory data source. Taking into account this database the processes and consumption data considered in the cycle are slightly different than the ones considered in the JEC study. This can be seen in table 5.28. Moreover, the bounding of direct processes is also slightly different, transportation process is included in cultivation and extraction, and this last one also includes the refining process.

If EcoInvent database is used instead of the data used in the JEC study, the ExROI value obtained is equal to 2.99, which is 19%higher than when the JEC study database is used. This example shows the disparity of results that can be obtained by using different data sources.

Table 5.28: Exergy of flows for rapeseed oil biodiesel pathway using EcoInvent

Stream	**Process**	I/O	**Unit** (u)	u/kg$_{FAME}$	**e** (kJ/kg$_{FAME}$)
Rape seed IP, at regional storehouse/CH U	1	Input	kg	0.00175	87.26
Urea, as N, at regional storehouse/ RER U	1	Input	kg	0.01165	401.06
Triple superphosphate, as P2O5, at regional storehouse/RER U	1	Input	kg	0.02582	175.02

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Stream	**Process**	I/O	**Unit** (u)	u/kg_{FAME}	e (kJ/kg_{FAME})
Potassium chloride, as K2O, at regional storehouse/RER U	1	Input	kg	0.06462	342.26
Lime, from carbonation, at regional storehouse/CH U	1	Input	kg	0.49881	54.02
Pesticide unspecified, at regional storehouse/RER U	1	Input	kg	0.00036	1250.12
Transport, lorry 20-28t, fleet average/CH U	1	Input	tkm	0.15526	182.79
Transport, freight, rail/RER U	1	Input	tkm	0.02055	24.19
Transport, barge/RER U	1	Input	tkm	0.19469	229.21
Transport, tractor and trailer/CH U	1	Input	tkm	0.04752	55.95
Rape seed conventional, at farm/DE U	1	Output	kg	1.70243	48689.49
Grain drying, low temperature/CH U	2	Input	kg	1.70243	48689.49
Light fuel oil, burned in industrial furnace 1MW, non-modulating/CH U	2	Input	MJ	0.8125	956.54
Electricity, medium voltage, production RER, at grid/kWh/RER	2	Input	MJ	0.41786	1198.84
Grain drying, low temperature/CH U	2	Output	kg	1.70243	48689.49
Rape seed conventional, at farm/DE U	4	Input	kg	1.70243	48689.49
Bentonite, at processing/DE U	4	Input	kg	0.00399	6.38
Hexane, at plant/RER U	4	Input	kg	0.00187	49.66
Phosphoric acid, industrial grade, 85% in H2O, at plant/RER U	3	Input	kg	0.0006	1.88
Heat, natural gas, at industrial furnace >100kW/RER U	4	Input	MJ	1.20483	1399.60
Electricity, medium voltage, production RER, at grid/kWh/RER	3	Input	MJ	0.26176	751.01
Transport, freight, rail/RER U	4	Input	tkm	0.00093	1.09
Transport, lorry >16t, fleet average/RER U	3	Input	tkm	0.00077	0.91
Transport, lorry 3.5-16t, fleet average/RER U	3	Input	tkm	0.38228	450.05
Rape oil, at oil mill/RER U	4	Output	kg	0.89314	35487.93
Rape oil, at oil mill/RER U	6	Input	kg	0.89314	35487.93
Methanol, at plant/GLO U	6	Input	kg	0.09869	4006.08
Phosphoric acid, industrial grade, 85% in H2O, at plant/RER U	4	Input	kg	0.004	54.11
Potassium hydroxide, at regional storage/RER U	4	Input	kg	0.00987	395.24
Heat, natural gas, at industrial furnace >100kW/RER U	4	Input	MJ	0.80254	932.28
Electricity, medium voltage, production RER, at grid/kWh/RER	4	Input	MJ	0.13228	379.52
Transport, freight, rail/RER U	6	Input	tkm	0.01614	19.00

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Stream	**Process**	I/O	**Unit** (u)	u/kg_{FAME}	e (kJ/kg_{FAME})
Transport, lorry >16t, fleet average/RER U	6	Input	tkm	0.01349	15.89
Tap water, at user/RER U	6	Input	m3	0.023738	1.17
Rape methyl ester, at esterification plant/RER U	6	Output	kg	1	40062.28

5.10 Summary and conclusions

In this chapter thermoeconomics is applied to the land-to-tank cycles of biodiesel fuels from different origins following the methodology of chapter 3. The exergy values, exergy costs for all the products in each process and the ExROI values of the final desired product are computed.

From the exergy point of view, it is shown how the exergies of the main valuable products are reduced after each process and the reasons behind these values have been explained, in relation with the efficiencies of the processes and the production of co-products. This has also been shown for the unit exergy costs. Finally, it has been shown which processes add more exergy costs to the final product, the main one being the oil extraction.

As far as the ExROI value is concerned, all the biodiesel sources have ExROI values higher than one, which means that for one unit of non-renewable resources used in their production, more than one unit of biodiesel is obtained. From the point of view of the consumption of non-renewable resources, the most sustainable one is the biodiesel produced from used cooking oil, followed by palm, sunflower and rapeseed. The less sustainable is the soybean oil one which almost has a 1:1 relation.

In terms of the *renewability* ratio which establishes the weight of the renewable exergy cost with respect the total exergy cost, the product with the highest renewability if the palm oil biodiesel followed by the biodiesel produced from used cooking oil.

The *sensitivity analysis* shows that in face of possible variations, errors or deviations in the introduction of non-renewable resources consumption data into the system, the exergy cost does not vary significantly and, as a result, it indicates that the ExROI value is a consistent indicator.

Other calculations that have been carried out are the maximum allowance transport distances for rapeseed and palm oil biodiesels, which show that these distances are too big to ensure ExROI values higher than 1 in their normal geographic scopes, and the ExROI value using data from the EcoInvent database which shows the disparity of results that can be obtained when using different data sources.

Yet another calculation done is the exergoecologic factor, which shows the relative weight of the external inputs in the results, therefore underlining the need to take into account the secondary processes. Taking as a basis the results obtained in this chapter, the following one shows ways to improve the ExROI values.

Chapter 6

Defossilisation of the production process

In the previous chapter the ExROI values of the land-to-tank cycles of the biodiesel fuels considered in this Ph.D., has been calculated and it has been shown that the values are higher than 1, which means that they do not require more non-renewable useful energy than the useful energy they are by themselves.

However, it could also be considered that even though the values are higher than 1, they are still low. According to Charles A.S. Hall et al. [127], the minimum EROI value that society must attain from its energy exploitation to support continued economic activity and social function is about 3:1 and therefore, biodiesel fuels which life cycle provides an ExROI value lower than 3 should introduce measures to improve their values or be discouraged.

In addition, the ExROI values of biodiesel fuels should be compared to the direct competitor, i.e. fossil diesel fuel. According to Cleveland [45], the EROI value of gasoline (and therefore of diesel as they are products of the same process) is in the range of 6 to 10. Other authors provide lower EROI values for fossil oil from unconventional sources. This is the case of Brandt [26] who observed a decline in the life-cycle EROI of the oil extracted in California from 6.5 to 3.5 increasing need for steam-based thermal enhanced oil recovery. Murphy et al. [182] estimate the EROI value of Canadian tar sands to be presently about 3 and Cleveland and O'Connor [47] that shale oil is around 1.5. In these last cases the EROI is calculated for the crude oil and therefore the EROI of the gasoline and diesel final products would be presumably lower. The life cycle biodiesel production processes should be defossilised in order to obtain higher ExROI values than the fossil diesel fuel.

On the other hand, when introducing improvements in the cycles to increase the ExROI value one should be careful to not produce negative impacts, for example, increasing the greenhouse gas emissions, adding pressure to the competition for land use, etc.

This chapter shows which defossilisation measures could be introduced in the different stages of the biodiesel land-to-tank cycle in order to improve the ExROI values. It also analyses the consequences that these measures could have from the environmental and socio-economic point of view. This exercise is only produced for rapeseed based biodiesel but it could also be done for the other biodiesel fuels.

6.1 Fossil fuel comparator

The greenhouse gas emission reductions due to the application of the defossilisation measures are compared with a fossil fuel comparator. The emissions of the fossil fuel comparator are taken from the Renewable Energy Directive and Fuel Quality Directive [99, 100] which are the ones that should be used by the actors in the biofuel supply chains to comply with the sustainability criteria established by the Directives. These emissions are 83.8 $gCO_{2\text{-eq}}$ /MJ.

In addition, the latest updates from the Joint Research Centre are also used. In [86], the Joint Research Centre has calculated the expected fossil fuel comparator to be 90.3 $gCO_{2\text{-eq}}$ /MJ in 2020.

According to the assumptions of the JRC, the extraction emissions for existing oilfields will gradually rise with time because the energy needed to extract the crude increases. The resulting average production emissions from fields supplying the EU in 2020 are expected to reach 6.8 gCO_2/MJ crude, or 7.2 gCO_2/MJ final fuel, ignoring any potential effect of the Fuel Quality Directive, which requires a reduction of 6% greenhouse gases by 2020.

Updated figures from CONCAWE suggest that the production (upstream emissions) greenhouse gas intensity (not including transport) is 5.6 gCO_2/MJ final fuel. The 2020 gasoline value would become $87.6 - 5.6 + 7.2 = 89.2$ and the 2020 diesel value becomes $89.1 - 5.6 + 7.2 = 90.7$. If the diesel/gasoline split is 75:25 the weighted average is 90.3 g/MJ final fuel.

6.2 Defossilisation in the cultivation process

As shown in the sensitivity analysis of chapter 5 the processes more sensible to changes, in the case of rapeseed based biodiesel, are the cultivation and transesterification. This section evaluates the improvements applicable in the cultivation process.

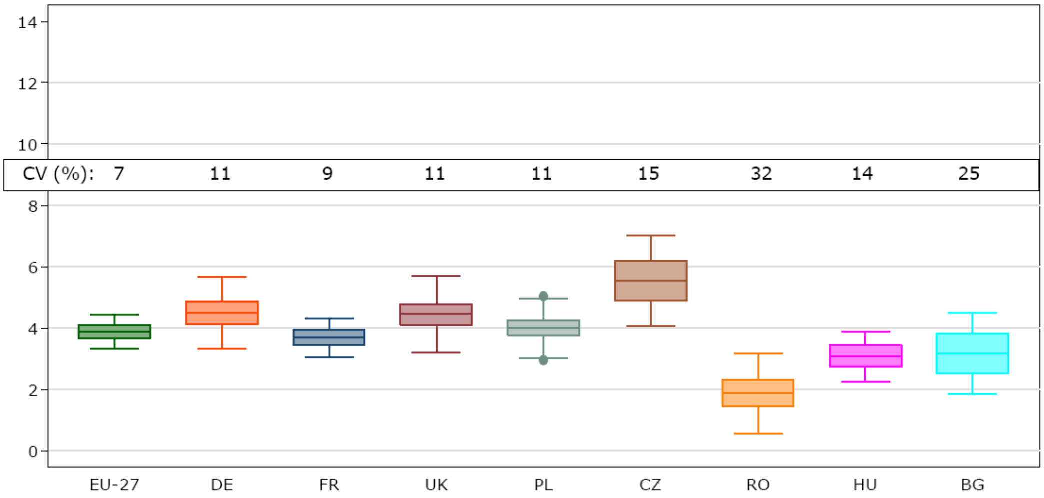

Figure 6.1: Distribution of rapeseed yield for the EU and in some selected Member States (t/ha). Source: DG AGRI, EC [90]

6.2.1 Increasing the yield of rapeseed production per hectare

Starting from the cultivation process, the first possible action is increasing the yield of rape seed production per hectare.

The JEC study [148] considers that the yield is 3.1 tonnes of seed per hectare/year. However, with a coefficient of variation of 7.2% at the aggregate EU level, rapeseed presents a high yield uncertainty, according to the European Commission, DG Agriculture [90]. As it can be seen in fig. 6.1 the yield can vary substantially. The EU average is close to 4 tonnes per hectare and in countries like the Czech Republic the yield can be higher than 6 tonnes per hectare.

A high rape seed yield of 6 t/ha has been selected, which is possible according to fig. 6.1. If the same energy and materials consumption per hectare are assumed there is a reduction in the consumption of inputs per kg of rape seeds. The input values and exergies obtained are shown in table 6.1. For the following steps, i.e. drying, seed's transport, oil extraction and transesterification the values remain the same as in the business as usual scenario because these values are calculated taking as a basis the kg of rape seeds.

With the inputs costs of table 6.1 the input costs of the cultivation process are reduced by 48.12%, if compared with the business as usual situation. Using the sensitivity analysis eq. (3.67) a reduction of 26.22% in the non-renewable cost of FAME is obtained, and the ExROI value is improved to 3.38.

Table 6.1: Exergy and cost of input resources for high yield rapeseed cultivation

			Exergy		Cost	
Inputs	**Unit** (u)	u/kg$_{\text{FAME}}$	MJ/u	MJ/kg$_{\text{FAME}}$	MJ/u	MJ/kg$_{\text{FAME}}$
N fertiliser	kg	0.0620	20.0376	1.2423	67.2664	4.1705
CaO fertiliser	kg	0.0086	2.1330	0.0183	1.5223	0.0204
K_2O fertiliser	kg	0.0223	4.5173	0.1008	8.6897	0.1939
P_2O_5 fertiliser	kg	0.0152	2.2512	0.0342	11.4420	0.1738
Pesticides	kg	0.0006	19.3270	0.0106	198.0960	0.1090
Seeding material	kg	0.0027	28.6600	0.0777	6.4600	0.0175
Diesel	MJ	1.3367	1.0000	1.3367	1.1773	1.5737
Total				**2.8206**		**6.2587**

Environmental impact: This improvement leads to reductions of land use. For each hectare of land, with a production of 6 tonne of seeds per ha, a production of biodiesel of 2.2 tonne FAME/ha is obtained, while for a production of 3.1 tonnes of seeds per ha the yields is 1.2 tonnes of biodiesel.

If a consumption of 13.3 Mtoe of biodiesel in 2020 as foreseen by [90] with the current targets of the RES Directive [99] is taken into account, the land yield is increased from 3.1 tonnes of seeds/ha to 6 tonnes of seeds/ha, which would result in a reduction in the use of land of around 6.3 millions ha.

This improvement also leads to higher greenhouse gas emission reductions. Knowing the reduction in the consumption of inputs per kg of seed obtained and the $CO_{2\text{-eq}}$ emission factors of each of the inputs it is possible to calculate the $CO_{2\text{-eq}}$ emissions in the cultivation. The values are shown in table 6.2 and reflect a reduction in 50% of CO_2 emissions. They have been calculated using the standard emission values according the BioGrace project, co-funded by the Intelligent Energy – Europe programme [22] of the European Commission.

Table 6.2: Comparison of the GHG emissions in rapeseed cultivation ($gCO_{2\text{-eq}}$ /MJ FAME)

Inputs	**BAU**	**High yield**
N fertilizer	18.99	9.85
CaO fertilizer	0.06	0.03
K_2O fertilizer	0.67	0.35
P_2O_5 fertilizer	0.8	0.41
Pesticides	0.32	0.16
Seeding material	0.1	0.053
Diesel	6.1	3.17
TOTAL	**27.04**	**14.03**

Not all these emission reductions should be allocated to the biodiesel product. According to point 17 of the Annex V of the Renewable Energy Directive establishing the methodology to calculate the GHG emissions of biofuels [99], where a fuel production process produces, in combination, the fuel for which emissions are being calculated and one or more other products (co-products), greenhouse gas emissions shall be divided between the fuel or its intermediate product and the co-products in proportion to their energy content (determined by the lower heating value –LHV- in the case of co-products other than electricity).

The LHV assumed for rapeseed meal, glycerol and biodiesel are the ones considered in the IEE project BioGrace [22], which are shown in table 6.3. This table also shows the GHG emission reduction allocation.

Table 6.3: LHV of life cycle co-products and emission allocation

Co-product	MJ/kg	kg/kg FAME	MJ/kg FAME	$gCO_{2\text{-eq}}$ /MJ
Rapeseed meal	18.7	1.59	29.76	5.64
Glycerol	16	0.11	1.69	0.32
Biodiesel	37.2	1	37.2	7.05

The total GHG emissions of rapeseed oil based biodiesel in its life cycle in a business as usual scenario are 52 $gCO_{2\text{-eq}}$ /MJ according to the Annex V of the Renewable Energy Sources Directive [99] (default value). This is a reduction of 38% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and a reduction of 42% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

For high yield lands the total GHG emissions in its life cycle would be reduced to 44.9 $gCO_{2\text{-eq}}$ /MJ. This is a reduction of 46% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and a reduction of 50% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

It is important to note that these calculations do not include the possible emissions that could be due to land use change, both direct and indirect. In this work it is considered that the rapeseed is cultivated in land that was previously used for the same purpose.

It is also necessary to mention that the comparisons are made for the default values of the Directive and not to the typical greenhouse gas emission values, also established in the Directive. The default values are higher than the typical because there is penalisation of 40% in the disaggregated values of the processing.

Socio-economic impact: This improvement increases the farmer's income per hectare of land. If a price of rape seeds of 400–500 €/tonne is considered as shown in fig. 6.2, the farmer gets an increase of income of around 1,160–1,450 Euros.

Overall, the cost of producing biodiesel with this option is also reduced. If the following prices are considered: fertilisers 375-440 €/tonne; pesticides 50-80 €/tonne; seeds 400-500 €/tonne, and diesel fuel 1.9 €/litre average EU [88], there could be around 90 to 107 €/tonne of biodiesel in savings, compared to the business as usual.

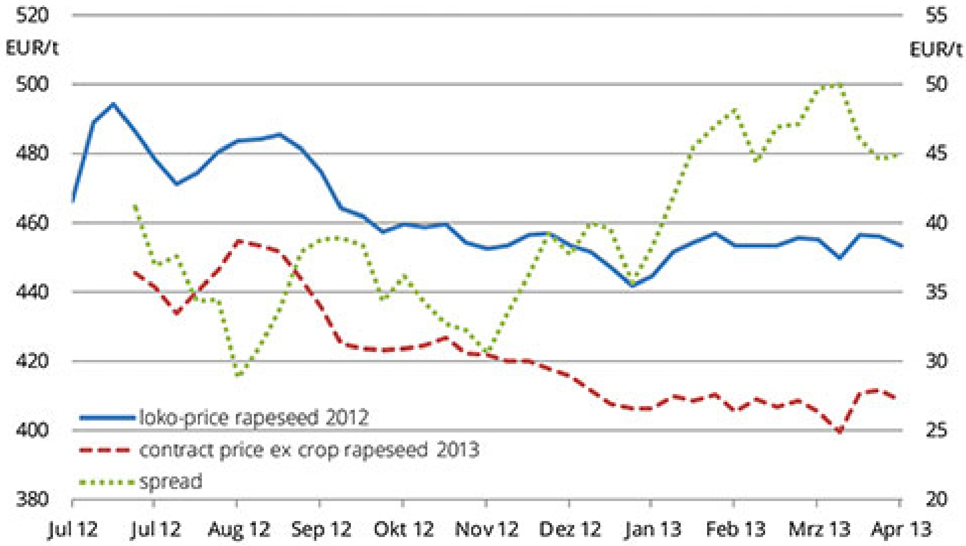

Figure 6.2: Variation of rape seed prices in Germany. Source: UFOP [232]

6.2.2 Use of compost as fertiliser

Another possible improvement is the use of organic fertilisers, instead of inorganic fertilisers which consume high quantities of non-renewable resources in their production.

The organic fertiliser considered is compost. Compost is essentially stable aerobically decomposed organic matter. Compost is the result of a managed decomposition process in which successions of aerobic micro-organisms break down and transform organic material into a range of increasingly complex organic substances [192].

Compost provides NPK nutrients to the soil therefore constituting an adequate material to substitute the use of fossil fuel based fertilisers.

In this work, the mass and energy consumption data for the production of compost have been obtained from the EcoInvent database [63]. Taking into account that the materials used to produce the compost are wastes, their exergy values are not taken into account to calculate the non-renewable energy cost. Therefore, only the energy consumption is considered. The consumptions of diesel and electricity are 115.24 kJ/kg of compost and 42.48 kJ/kg of compost, respectively. The NPK content of the compost could be obtained from [203].

Knowing the consumption of energy in kJ/kg compost and the NPK content of the compost in kg/kg compost we can calculate the energy needed to produce a kg of each NPK component. Taking into account the need of NPK for cultivating rape following the data obtained from the JEC study [148], it is possible to obtain the exergy cost in the cultivation process when compost is used as fertiliser. Data are shown in table 6.4. It is assumed that the use of compost, in such quantities that the NPK levels are maintained constant, leads to the same yield as when inorganic fertilisers are used.

Table 6.4: Cumulative exergy of non-renewable resources for rapeseed cultivation using organic fertilisers

			Cost	
Inputs	**Unit** (u)	u/kg FAME	MJ/u	MJ/kg FAME
N fertiliser	kg	0.1195	3.7330	0.4460
CaO fertiliser	kg	0.0165	2.3748	0.0391
K_2O fertiliser	kg	0.0430	3.3963	0.1460
P_2O_5 fertiliser	kg	0.0293	3.7330	0.1093
Pesticides	kg	0.0011	198.0960	0.2120
Seeding material	kg	0.0052	6.4600	0.0337
Diesel	MJ	2.5760	1.1773	3.0327
Total				**4.0189**

With the values of table 6.4 the cost of the external non-renewable resources are reduced by 8 MJ/kg FAME (66.8%) when organic fertilizers are used, compared with the use of conventional inorganic fertilizers. Introducing this value in eq. (3.67), the non-renewable cost of FAME is reduced by 36.39% and the ExROI value is improved to 3.92.

It is important to note [1] that, when substituting inorganic fertilisers by compost providing the same amount of NPK, in theory, if all the NPK needs are covered by the material either organic or inorganic, there should not be a reduction in yield. However, the key element, Nitrogen, when provided in organic form by the compost needs more time to be absorbed by the plant, which in fact may reduce the production for a specific period of time. In principle, a yield reduction of around 10–15% could be considered in the first years of compost usage. On the other hand, there could be other elements, which are needed in less quantity than NPK but still are necessary, which might not be provided by compost. This is the case of sulphur, for example. The lack of these elements might affect the productivity of the plants.

High quality compost should be used to ensure high yields, for example compost from manure. Also, high yields are ensured when the use of compost has been done for several years in the field, included in the rotation of crops.

Environmental impact: The use of compost as fertiliser besides reducing the consumption of non-renewable resources has other benefits. According to [192], these can be summarised as follows:

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[1] Information obtained in consultation with experts of the University of Torino and the Spanish Agricultural Cooperatives' Association.

1. Improved crop performance and lower production costs through:
    - improved yields, product quality and storage life.
    - more efficient and reduced use of fertilisers and pesticides, including soil fumigants.
    - better utilisation of irrigation.
    - increased crop resistance to pests and diseases.
2. Improved soil quality through:
    - better organic matter levels and organic cycles.
    - increased available water to plants.
    - increased nutrient availability and nutrient-holding capacity.
    - improved structure.
    - reduced soil-borne plant pathogens and pests.

On the other hand, there could be also disadvantages: applying rates that are too low can lead to nutrient deficiency and low yields. On the other hand, too high rates can lead to nitrate leaching, phosphorus run-off, accelerated eutrophication of lakes, and excessive vegetative growth of some crops [203].

Thus, understanding how to manage compost is crucial to maintain the same yield while avoiding the negative impacts.

There are studies that suggest that the use of compost increases indeed the yield. According to a report produced by FAO [64] in degraded lands the use of compost gives higher yields than the use of chemical fertilisers.

From the climate change perspective, compost production can reduce significantly the $CO_{2\text{-eq}}$ emissions.

Knowing the standard emission values of N, P, K fertilisers of inorganic origin in $gCO_{2\text{-eq}}$ /kg obtained from the BioGrace project [22] and taking into account the consumption of N, P, K in the cultivation of rapeseed, it is possible to calculate the $gCO_{2\text{-eq}}$ emissions per MJ of FAME as shown in table 6.5.

Table 6.5: GHG emissions on the use of inorganic fertilizers

	$gCO_{2\text{-eq}}$ /kg	kg/kg FAME	$gCO_{2\text{-eq}}$ /kg FAME	$gCO_{2\text{-eq}}$ /MJ FAME
N fertiliser	5,880.60	0.1195	702.61	18.99
P_2O_5 fertiliser	1,010.70	0.0293	29.59	0.8
K_2O fertiliser	576.1	0.043	24.77	0.67
TOTAL			**756.97**	**20.46**

In the case of compost, the emissions to take into account are the ones derived by the consumption of diesel and electricity in its production, for which the emission standard values of the BioGrace project [22] can be used. Taking into account the consumption of electricity (EU mix) and diesel in the production of compost and the consumption of compost in the cultivation field, it is possible to calculate the emissions per MJ of FAME, as shown in table 6.6.

As it can be observed, GHG emissions are reduced in 20.38 $gCO_{2\text{-eq}}$ per MJ of biodiesel. Taking into account the distribution of emissions in relation to the LHV of the biodiesels and

Table 6.6: GHG Emisions of the use of compost as fertilizer

	$gCO_{2\text{-eq}}$ /MJ	MJ/kg compost	$gCO_{2\text{-eq}}$ /kg compost	kg/kg FAME	$gCO_{2\text{-eq}}$ /kg FAME	$gCO_{2\text{-eq}}$ /MJ FAME
Electricity	129.19	0.0425	5.49	0.19	1.05	0.03
Diesel	87.64	0.1152	10.1	0.19	1.94	0.05
Total					**2.99**	**0.08**

co-products obtained in the cycle, the emission reductions allocated to biodiesel are 11.04 $gCO_{2\text{-eq}}$ per MJ.

When using organic compost as fertiliser instead of conventional inorganic fertilisers, the emissions of the entire life cycle allocated to biodiesel would be 41.0 $gCO_{2\text{-eq}}$ /MJ, which is a reduction of 51% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and a reduction of 55% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

Socio-economic impacts: The average price of NPK fertilisers is around 375–400 €/tonne, according to data from the Spanish Agricultural Cooperatives' Association and around 420–440 €/tonne according to information provided by the University of Torino. On the other hand, the price of compost is around 50 €/tonne (data obtained in consultation with the University of Torino). In some places compost might even be given for free under certain circumstances.

However, the price per fertiliser unit, i.e. the price that the fertiliser has in terms of its content of NPK [105] needs to be taken into consideration. The price of the fertilisers is shown in table 6.7. As it can be observed, the organic fertiliser, although cheaper in tonnes is more expensive per unit of fertiliser because the content of fertiliser is lower.

Therefore, the use of organic fertilisers increases the costs of rape seeds production and therefore the final price of biodiesel. If the fertiliser prices of table 6.7 are considered, the use of compost as organic fertiliser increases the biodiesel production in between 152.85 and 472.81 €/tonne.

Table 6.7: Price of fertilizers per fertilizer unit

	Organic fertiliser Compost	N fertiliser Urea	K_2O fertiliser KCl	P_2O_5 fertiliser Phosphorite	Complex fertiliser
% N	0.499	46	0	0	15
% P	0.499	0	0	46	15
% K	0.454	0	60	0	15
€/kg	500	3,000	3,350	2,450	4,000
€/unit	3.4	0.7	0.6	0.5	0.9

6.2.3 Use of high oil content varieties

Another possibility in the cultivation process to increase the ExROI value is the selection of crop varieties with high oil content. The JEC study [148] considers that rape seeds have an oil content of 40.5%. According to [187], the yields from different refined rape seeds in Europe vary from 39 to 42%. However, there are life cycle analysis that consider that rapeseed planted under certain circumstances may have yields up to 44.5% [3].

This higher oil yield (44.5%) has been considered assuming that the inputs of energy and materials in the cultivation, drying, seed's transport and oil extraction remain the same for the high oil content variety compared to the initial one. The input values and exergies obtained for this variety are shown in table 5.6.

Table 6.8: Exergy of flows for high oil content rapeseed cultivation

Material	**Process**	I/O	**Unit** (u)	u/kg FAME	MJ/kg FAME
N fertiliser	1	Input	kg	0.1087	7.311
CaO fertiliser	1	Input	kg	0.0150	0.036
K_2O fertiliser	1	Input	kg	0.0391	0.340
P_2O_5 fertiliser	1	Input	kg	0.0266	0.305
Pesticides	1	Input	kg	0.0010	0.193
Seeding material	1	Input	kg	0.0048	0.031
Diesel	1	Input	MJ	2.5353	2.985
Rape seed	1	Output	kg	2.4578	70.294
Rape straw	1	Output	kg	3.5638	65.931
Rape seed	2	Input	kg	2.4578	70.294
Diesel	2	Input	MJ	0.0105	0.012
Electricity	2	Input	MJ	0.1820	0.517
Rapeseed dry	2	Output	kg	2.4578	70.294
Rapeseed	3	Input	kg	2.4578	70.294
Diesel	3	Input	MJ	0.0020	0.136
Rapeseed	3	Output	kg	2.4578	69.598
n-hexane	4	Input	kg	0.0026	0.139
Steam	4	Input	MJ	0.5521	1.802
Electricity	4	Input	MJ	0.3274	0.929
Rapeseed	4	Input	kg	2.4578	69.598
Rapeseed meal	4	Output	kg	1.3501	10.005
Crude oil	4	Output	kg	1.0834	43.047

With the information of table 6.8 it is possible to build the F-P table 6.9 for this scenario. The changed values compared to the BAU situation of the previous chapter (see table B.4) are marked in bold. Calculating the non-renewable cost of biodiesel, by means of eq. (3.56) a value of 15.75 MJ/kg FAME, and an ExROI value of 2.54 are obtained, which means a relative improvement of 1.93%.

Environmental impacts: In this case, as the production of oil per hectare and year is increased, while considering that the consumption of inputs remains constant, there is an evident reduction of GHG emissions. However, this reduction is not considerable; around 2.08 $gCO_{2\text{-eq}}$ per MJ of biodiesel of which 1.13 would be allocated to the biodiesel product. The GHG emissions of the cultivation, drying and transport to the extraction plant both for the business as usual seeds and the high-oil content seeds are shown in table 6.10.

This GHG emission reduction constitutes a reduction of 39% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and a reduction of 44% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

Table 6.9: F–P Table of rapeseed biodiesel for high oil content seeds (MJ/kg FAME)

	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0	rs	**70.43**	0.00	0.00	0.00	0.00	0.00	0.00	0.00	70.43
	nrs	**11.20**	**0.53**	**0.14**	2.88	0.44	4.37	0.24	1.02	20.82
P_1	0.00	0.00	**70.29**	0.00	0.00	0.00	0.00	0.00	0.00	70.29
P_2	0.00	0.00	0.00	**70.29**	0.00	0.00	0.00	0.00	0.00	70.29
P_3	0.00	0.00	0.00	0.00	**69.60**	0.00	0.00	0.00	0.00	69.60
P_4	**10.01**	0.00	0.00	0.00	0.00	43.05	0.00	0.00	0.00	53.05
P_5	0.00	0.00	0.00	0.00	0.00	0.00	41.33	0.00	0.00	41.33
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.48	3.31	43.79
P_7	40.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.06
P_8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Total	52.57	81.63	70.82	70.43	72.48	43.49	45.69	40.72	4.34	

Table 6.10: Comparison of GHG emissions of high oil content and BAU seeds

			Bussines as Usual		**High-oil content**	
Streams	**Unit** (u)	$gCO_{2\text{-eq}}$ /u	u/kg_{FAME}	$gCO_{2\text{-eq}}$/MJ	u/kg_{FAME}	$gCO_{2\text{-q}}$/MJ
N fertiliser	kg	5,880.6	0.1195	18.99	0.1087	17.27
CaO fertiliser	kg	129.5	0.0165	0.06	0.015	0.05
K_2O fertiliser	kg	576.1	0.043	0.67	0.0391	0.61
P_2O_5 fertiliser	kg	1,010.7	0.0293	0.8	0.0266	0.73
Pesticides	kg	10,971.3	0.0011	0.32	0.001	0.29
Seeds- rapeseed	kg	729.9	0.0052	0.1	0.0047	0.09
Diesel cultivation	MJ	87.64	2.576	6.1	2.5353	6.01
Diesel drying	MJ	87.64	0.0116	0.03	0.0105	0.02
Electricity drying	MJ	129.19	0.1981	0.69	0.1802	0.63
Diesel transport	MJ	87.64	0.127	0.3	0.1155	0.27
Total				**28.06**		**25.97**

Another advantage of this solution is the reduction of agricultural land use. In the business as usual situation for each tonne of biodiesel produced, there is an actual use of land of 0.87 ha. For this calculation, it is taken into account that for each kg of biodiesel, 2.70 kg of seeds are needed. Also, it has been assumed a production of rape seeds of 3,113.44 kg/(ha*yr) according to the JEC study [148].

In the case of high oil seeds, for each kg of biodiesel there is a need of 2.46 kg of seeds. If the same production of seeds per ha and year is considered, the need of land is equal to 0.79 ha. Hence there is a reduction of 0.08 ha/tonne of biodiesel. This is not a big amount. Considering a consumption of 13.3 Mtoe of biodiesel in 2020 as foreseen by [90] with the current targets of the RES Directive [99] the reduction in the use of land would equal to around 1.2 million ha.

Socio-economic impact: There is a direct reduction of consumption per kg of oil obtained, which results in a reduction of costs. If the following prices are considered: fertilisers 375–440

€/tonne; pesticides 50–80 €/tonne; seeds 400–500 €/tonne, diesel fuel 1.19 €/litre average EU, and electricity 10.29 €/100 kWh average EU [88], there would be around 10 Euros per tonne of biodiesel in savings.

6.3 Defossilisation in the oil extraction process

In the oil extraction, the most interesting action is the production of biogas from the rapeseed meal, which is a co-product of the process. The anaerobic digestion of rapeseed meal can yield the production of 274 m^3 CH_4/tonne of fresh feedstock [205]. The generation of biogas from rapeseed meal has been studied since de beginning of biodiesel production at industrial scale as a measure to improve the sustainability of the cycle [120]. However, to our knowledge it has not been analysed from an exergy cost viewpoint. Other possible uses of rapeseed meal that have been analysed are the direct combustion or co-firing with coal in coal fire power stations [120, 214].

This action does not reduce the biodiesel yield and provides a renewable energy source that can be reintroduced in the biodiesel cycle in order to reduce the consumption of fossil fuels for electricity and steam generation. As an additional benefit, it produces a digestate with a high N content that can be reintroduced in the system reducing the need of inorganic N fertiliser.

Table 6.11: Exergy of flows for scenario when rapeseed meal is converted in biogas

Stream	I/O	**Unit** (u)	u/kg FAME	MJ/kg FAME
n-hexane	Input	kg	0.0026	0.139
Rapeseed	Input	kg	2.6750	76.506
Crude oil	Output	kg	1.0834	43.047
N fertiliser	Output	kg	0.0047	0.029
Steam	Output	MJ	3.6038	3.604
Electricity	Output	MJ	4.6112	4.611

Table 6.11 shows the input/output balance and exergy values in the extraction phase when the meal is used to produce biogas. The data are based on the JEC study [148], and the F-P table is given in table 6.12.

The assumptions done to obtain this numbers, marked in bold, are the following:

- The N-fertiliser obtained in the meal anaerobic digestion is used in the cultivation;
- The electricity and steam from biogas are used in the subsequent processes without losses;
- There is still exceeding electricity and steam that are used in other external processes.

Calculating the non-renewable cost of biodiesel, by means of eq. (3.56) a value of 13.59 MJ/kg FAME, and an ExROI value of 2.95 are obtained, which means a relative improvement of 15.4%.

Enviromental impact: As main environmental drawback, this action eliminates the production of a valuable product used for feeding purposes. It can be thought that as a result of the reduction of meal production, other feeding materials must increase their production (for example, soybean meal) in order to maintain a constant production of feeding material; from this it can be deduced that more land is therefore needed which may lead to land use changes. In this case, these changes would be indirect land use changes which are difficult to quantify.

Table 6.12: F–P Table of rapeseed biodiesel using meal as biogas (MJ/kg FAME)

	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0	rs	77.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	77.42
	nrs	**12.03**	0.58	0.15	**0.14**	0.02	**3.42**	**0.02**	**0.08**	16.44
P_1	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	0.00	77.27
P_2	0.00	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	77.27
P_3	0.00	0.00	0.00	0.00	76.51	0.00	0.00	0.00	0.00	76.51
P_4	**5.73**	**0.03**	0.00	0.00	0.00	**43.46**	**0.92**	**0.22**	**0.93**	51.29
P_5	0.00	0.00	0.00	0.00	0.00	0.00	41.33	0.00	0.00	41.33
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.48	3.31	43.79
P_7	40.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.06
P_8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Total	48.29	89.48	77.85	77.42	76.65	43.48	45.67	40.72	4.32	

From the climate change point of view, this action may save 28.12 g of $CO_{2\text{-eq}}$ per MJ of biodiesel. To obtain this number the $CO_{2\text{-eq}}$ emissions that would be emitted in the business as usual scenario have been compared with this scenario.

Table 6.13 shows the emissions due to the use and production of n-hexane, electricity and steam in the process and also the emissions for the production of steam from natural gas. In total the emissions are 4.68 $gCO_{2\text{-eq}}$ /MJ FAME.

Taking into account that the anaerobic digestion of rape meal provides sufficient energy to cover the electricity and steam needs of the extraction process, there is a direct emission saving of 4.42 $gCO_{2\text{-eq}}$ /MJ FAME.

In addition, there is a surplus production of electricity and steam that has been assumed that is used in other processes of the life cycle. As this energy, which is considered GHG neutral, replaces electricity from the grid and steam produced from natural gas, there are additional savings of GHG emissions amounting 23.70 $gCO_{2\text{-eq}}$ /MJ FAME.

Table 6.13: GHG emisions of rapeseed in BAU scenario and reduction due tu surplus energy production ($gCO_{2\text{-eq}}$ /MJ FAME)

Stream	**BAU**	**Energy surplus**
n-hexane	0.26	-
Electricity	1.25	16.35
Steam	0.02	0.04
Natural gas (EU mix)	3.15	7.31
Total	**4.68**	**23.7**

Adding the 23.70 $gCO_{2\text{-eq}}$ and the 4.42 $gCO_{2\text{-eq}}$ a total emission reduction of 28.12 g of $CO_{2\text{-eq}}$ per MJ of biodiesel is obtained. Allocating these emissions to the products and co-products, this GHG emission reduction constitutes a decrease in biodiesel production of 66% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and a reduction of 68% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

Socio-economic impacts: Economically, this action is not favourable. Indeed, if a price of N-fertiliser of 375–440 €/kg is considered there could be 1.77 – 2.08 €/tonne of biodiesel in savings due to the consumption reduction. Additionally, assuming a price of electricity of 10.29 c€/kWh and of natural gas of 10.97 €/GJ [88] (this last one for the production of steam [2] have been assumed) savings of 177 €/tonne of biodiesel are obtained due to the reduction of consumption. The overall savings would be 179 €/tonne of biodiesel.

Table 6.14: Benefit comparison of selling rapeseed meal or produce biogas from it

(a) Extraction of vegetable oil in BAU

Stream	I/O	**Unit** (u)	u/kg FAME	**MIN** €/kg FAME	**MAX** €/kg FAME
Rapeseed meal	Output	kg	1.5913	0.398	0.477
Electricity	Input	MJ	0.3274	0.009	0.009
Steam	Input	MJ	1.5515	0.019	0.019
Balance				**0.370**	**0.449**

(b) Extraction of vegetable oil when meal is converted to biogas

Stream	I/O	**Unit** (u)	u/kg FAME	**MIN** €/kg FAME	**MAX** €/kg FAME
N fertiliser	Output	kg	0.0047	0.002	0.002
Electricity	Output	MJ	4.6112	0.132	0.132
Steam	Output	MJ	3.6038	0.045	0.045
Balance				**0.179**	**0.179**

However, assuming a price of rape seed meal of 250 – 300 €/tonne, obtained from the statistics of UFOP, the German Union of Oil and Protein producers [232] taking as a basis fig. 6.3, the benefit of selling the meal is 369 – 449 €/tonne. With this benefit the cost of paying for the energy needed in the extraction process is exceeded. All these numbers are gathered in table 6.14(b). However, rape seed meal price is declining in the latest months as shown in fig. 6.3.

An important consideration that has to be made in the extraction process is the impact that the exergy content of the meal has in the ExROI calculations for the biodiesel fuel. In this work, the exergy content of the meal has been considered to be 7.4 MJ/kg, which is the metabolisable energy according to [144]. This is the useful energy animals can profit of when eating the meal. If instead this value, it is considered a value of 21.1 MJ/kg, which is the value assumed by Lechon et al. [160], for the allocation of CO_2 emissions and energy consumption in the life cycle analysis, at the same conditions, the ExROI value is increased in 25%, i.e. up to 3.14.

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[2] To convert natural gas into steam a relation of 0.85 kWh N.G/kg of steam and an enthalpy of steam of 2,676 kJ/kg steam at 100 °C.

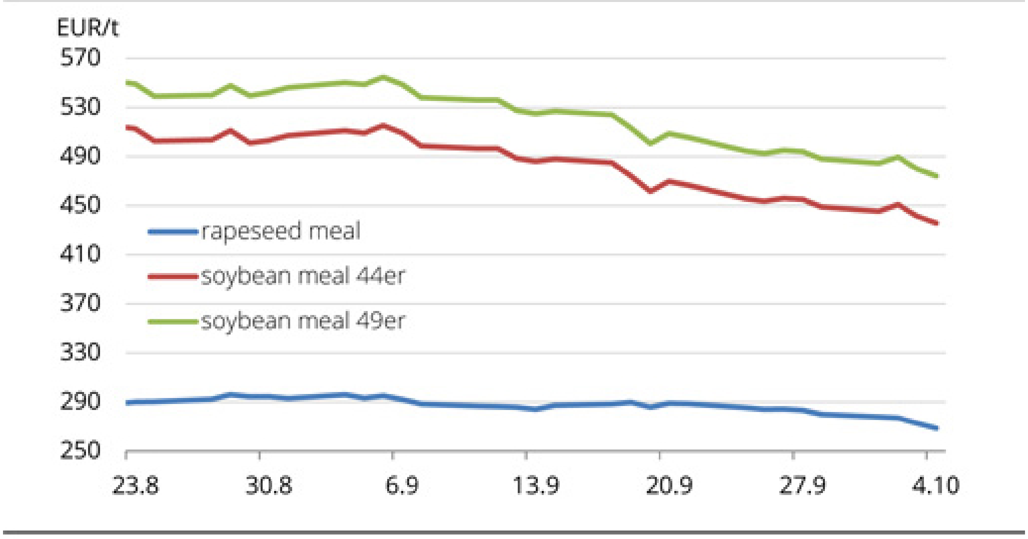

Figure 6.3: Price of rapeseed meal and soybean meal in August–October 2012. Source: UFOP [90]

6.4 Defossilation in the transesterification process

Chapter 4 showed the application of the PINCH methodology to reduce the exergy costs in the transesterification plant. There was a direct reduction of natural gas consumption used for heating purposes, which provided benefits in terms of greenhouse gas emissions and economic costs. This paragraph explains other measures that can be applied to reduce the consumption of non-renewable resources.

6.4.1 Use of bioethanol from wheat instead methanol

In the business as usual scenario analysed in chapter 5, it has been considered that the alcohol used as reactive in the transesterification reaction is methanol, assuming that this methanol is produced from fossil crude oil. Indeed, this is the actual situation of the biodiesel production plants in Europe.

A possibility to reduce the consumption of non-renewable resources is the substitution of fossil derived methanol by a bio-product. Bioethanol or simply, ethanol, is an alcohol produced by the fermentation of sugar with yeast. Ethanol can also be produced from petrol through the hydration of ethylene but this is not the process considered in this work.

When bioethanol is used as the alcohol in the transesterification reaction, instead of fatty acid methyl esters (FAME) we obtain fatty acid ethyl esters (FAEE). FAEE has slightly different properties than FAME like significantly higher but still acceptable viscosity and lower cold flow properties [130], and can also be used in vehicle engines.

The production of bioethanol considered in this study is based on wheat. Wheat has been selected as raw material because it is the most important raw material for bioethanol production in Europe. Also, high quantities of sugar cane and maize bioethanol are exported to the EU annually as shown in fig. 2.4 so these two materials could have also been considered.

The production of wheat based bioethanol starts from the cultivation of the wheat. In the cultivation NPK fertilisers, pesticides, seeding material and diesel fuel are consumed. As a result, wheat grains and straw are obtained. In this work, only the production of wheat grains has been considered. The following steps are the storage and transport of the grains to the conversion plant which follows the process shown in fig. 6.4. In the conversion plant the grains are mashed and liquefied to separate the non-sugar components. As co-products, starch and bran are obtained. The sugars are fermented using microbial yeast. The alcohol resulting from the fermentation needs to be distilled to eliminate the excess water content. After distillation the product contains maximum 96.5% (V/V) ethanol and 3.5% (V/V) water. This mixture is called hydrous ethanol. Hydrous ethanol is not miscible in all ratios with gasoline, so the water fraction is typically removed in a further treatment called dehydration in order to allow burning bioethanol in combination with gasoline in gasoline engines. As a result of distillation an appreciated co-product is obtained: Distiller's Dried Grains with Solubles (DDGS), a valuable protein-rich cattle feed co-product. DDGS have a high protein content, which can be used as animal feed. For every tonne of cereals used for ethanol production, on average one third of these cereals will enter the animal feed stream as DDGS [70].

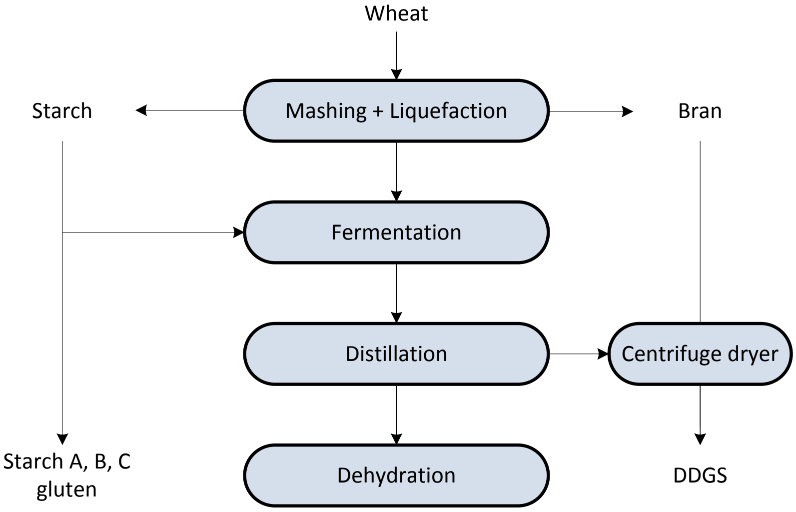

Figure 6.4: Bioethanol production process with cereal as feedstock. Source: ePure [70]

In order to obtain the final value of ethanol (kJ/kg) the following conversion factors have been used:

- Energy content of grain: 16.7 MJ/kg wheat grain, 13.5% H_2O;
- Ratio grain:bioethanol: 3.01 kg what grain/kg ethanol;
- Energy content of bioethanol: 27 MJ/kg ethanol.

Table 6.15 shows the calculation of the cumalitive exergy costs for the non-renewable resources of bioethanol. The costs to ethanol and DDGS have been distributed proportionally to their exergy, considering the exergy of bioethanol 27,000 kJ/kg ethanol and DDGS 18,370 kJ/kg ethanol.

Taking into account the cost of external resources, the balance table 6.16 for the transesterification process is obtained. The main difference of the transesterification process with methanol and bioethanol is that the second requires higher quantities of alcohol but with less non-renewable cost. The result is an average decrease of 33% in the use of non-renewable resources in the transesterification. Using eq. (3.67) there is a relative improvement of the ExROI value of 8.24%, which is increased to 2.72.

Table 6.15: Non renewable cumulative exergy cost for bioethanol production

Material	**e** (kJ/kg ethanol)
Wheat Cultivation	
N fertiliser	450.41
K_2O fertiliser	49.11
P_2O_5 fertiliser	32.37
Pesticides	29.99
Seeding material	1,332.18
Diesel	2,470.00
Handling and storage of wheat grain	
Electricity	20.02
Transport of wheat grain via 4t truck over a distance of 50 km	
Diesel	167.2
Ethanol conversion from wheat grain (DDGS used as animal fooder)	
Electricity	1,460.28
Steam	9,819.10
Output	
DDGS	5,870.33
Ethanol	8,628.29

Environmental impacts: As environmental drawbacks of this action, there is an increase of agricultural land use due to the need to produce wheat from which the bioethanol is obtained. Per each kg of bioethanol, there is a need to consume 3.04 kg of wheat grains. Considering that each hectare produces 5,200 kg of wheat, for each tonne of bioethanol produced 0.59 ha are used. Taking into consideration that to produce 1 kg of biodiesel, 0.21 kg of bioethanol are needed, the increase of land use is 0.12 ha/tonne biodiesel. All in all, the agricultural land needed to produce one tonne of biodiesel from rape seed using bioethanol as alcohol in the transesterification reaction is 0.99 ha.

If a consumption of 13.3 Mtoe of biodiesel in 2020 as foreseen by [90] with the current targets of the Renewable Energy Sources Directive [99] is considered, there would be a total use of land of 14.9 million ha, which represents 1.8 million ha more.

From a climate change point of view the substitution of conventional methanol with bioethanol from wheat leads to lower greenhouse gas emission reductions than the business as usual situation. Although greenhouse gas emissions from the production of bioethanol are lower than for the production of methanol (99.6 and 70.0 g of $CO_{2\text{-eq}}$ /MJ of product, respectively), the production of biodiesel with bioethanol consumes higher amounts of alcohol than the production of biodiesel with methanol (0.11 MJ/MJ FAEE and 0.06 MJ/MJ FAME, respectively, according to the JEC study [148]). This increase of alcohol consumption offsets the lower GHG emissions of bioethanol so the emissions of biodiesel are increased in 1.69 $CO_{2\text{-eq}}$ per MJ. It is important to note that in the case that the bioethanol is obtained from sugar cane (which has an emission factor of 24 of $CO_{2\text{-eq}}$ per MJ) there would be an increase of greenhouse gas reductions of 3.09 $CO_{2\text{-eq}}$ per MJ allocated to biodiesel.

Table 6.16: Exergy cost balance in transesterification using bioethanol form wheat

				Cost	
Stream	**I/O**	**Unit** (u)	u/kg FAEE	MJ/u	MJ/kg FAEE
H_3PO_4	Input	kg	0.0018	36.2858	0.065
HCl	Input	kg	0.0209	5.2484	0.110
Na_2CO_3	Input	kg	0.0026	14.0635	0.037
NaOH	Input	kg	0.0047	5.0273	0.024
Electricity	Input	MJ	0.1129	2.8690	0.324
Steam	Input	MJ	0.5749	3.2644	1.877
Bioethanol	Input	MJ	0.2102	8.6283	1.813
Plant oil	Input	MJ	1.0400	39.7339	41.325
FAEE	Output	kg	1.0000	40.0623	40.062
Glycerol	Output	kg	0.1056	23.6779	2.500

All in all when using wheat, the GHG emission reduction is decreased to 36% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and a reduction of 41% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

If bioethanol produced from sugar cane is used, there would be an increase in the GHG emission reductions of 42% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and a reduction of 46% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

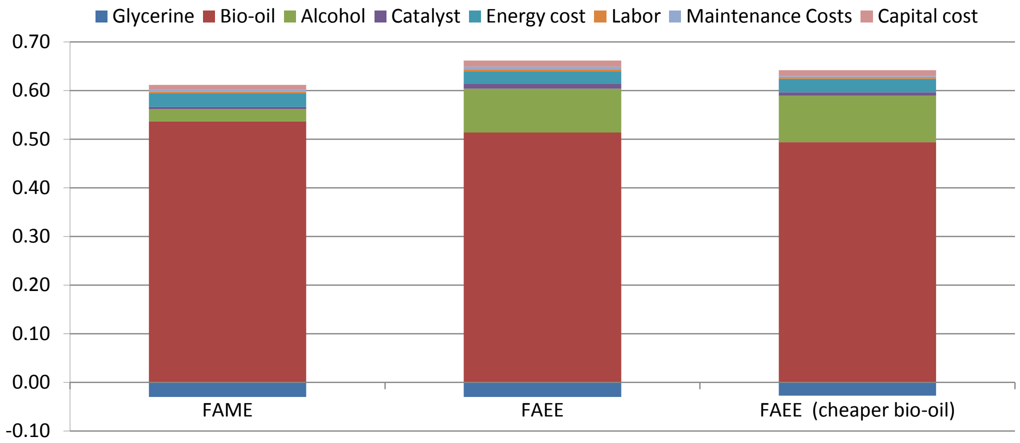

Figure 6.5: Costs of FAME and FAEE €/l FAME. Sources: BIOScopes [130]

Socio-economic impacts: The use of bioethanol instead of methanol is not advantageous from an economic point of view. Figure 6.5 shows the price difference between a biodiesel produced with methanol (FAME) and two biodiesels produced with bio-ethanol (FAEE) and the influence of each cost category in the total price, according to the European project BIOScopes [130]. As it can be seen, the difference between the price of ethanol compared to the price of methanol is the most important factor driving the difference in costs between FAME and FAEE. The price of ethanol almost triples the price of methanol in the economic analysis carried out in BIOScopes [130]. However, the prices of ethanol and methanol depend strongly on the geographical location and fluctuate strongly over time, therefore these results should be considered carefully.

In view that the environmental and socio-economic impacts of this action are negative, the use of bioethanol from wheat for biodiesel production should be disregarded even if the ExROI value is higher. This option has been seen as positive by some authors [169].

6.4.2 Use of methanol from wood

A better solution than the previous one is provided by the use of methanol from wood instead of methanol from crude oil. In this case, nothing changes in the process and the only parameter that changes is the exergoecologic cost of methanol, See table 6.17.

The production of methanol from wood starts by the cultivation of the trees. In this case, data have been obtained from the JEC study [148] where the trees are assumed to be poplar cultivated in a short rotation forestry system (SRF) which includes the addition of fertilisers. Diesel is needed to cut the trees and process the trunks. It is assumed that the N-fertiliser is urea which is the same assumption considered in chapter 5. The next process is the chipping of the wood which consists in mechanically breaking the wood to pieces of small size (<5 cm long). In this case, the source of energy is biomass obtained from the same chipping process (wood dust, wood cortex and discarded wood parts). After chipping, the wood is suitable for transport to the gasification plant where the methanol is produced.

Table 6.17: Exergy consumption in the production of methanol from wood

Source	**e** (kJ/kg methanol)
N fertilizer	33.67
Diesel in cultivation	200.94
Diesel in transport	580.18
Diesel in syntesis and gasification	152.28
Methanol	**967.07**

Gasification is a process that converts carbonaceous materials into carbon monoxide, hydrogen and carbon dioxide. The process is described by Dermibas [53]. It consists in reacting the material at high temperatures >700 °C, without combustion, with a controlled amount of oxygen and/or steam. The resulting gas mixture is called syngas (from synthesis gas or synthetic gas) or producer gas and is itself a fuel. In order to convert the syngas in the desired methanol the gas follows a conventional steam-reforming/WGS reaction followed by high-pressure catalytic methanol synthesis:

$$\begin{gathered} CH_4 + H_2O \longrightarrow CO + 3\,H_2 \\ CO + H_2O \longrightarrow CO_2 + H_2 \\ CO + 2\,H_2 \longrightarrow CH_3OH \\ CO_2 + 3\,H_2 \longrightarrow CH_3OH + H_2O \end{gathered}$$

The first two chemical reactions are called gasification/shift reactions. The latest ones are the methanol synthesis reaction. The whole process is shown in fig. 6.6. In this work, the energy needed in the gasification plant it is assumed to come from diesel.

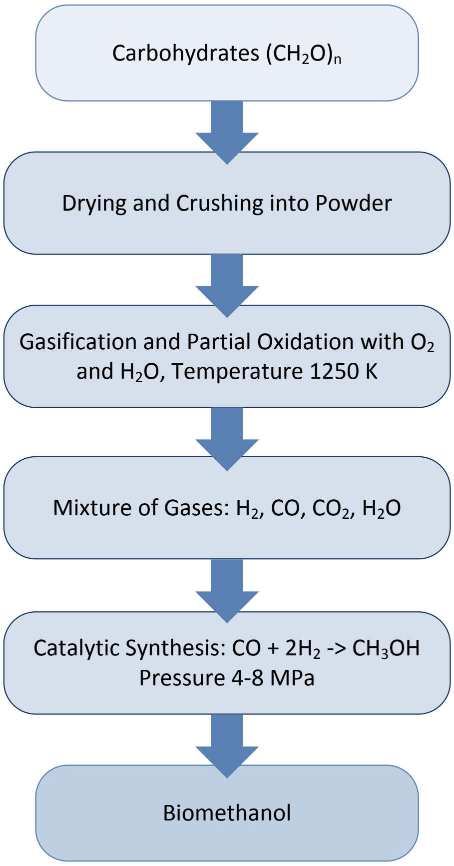

Figure 6.6: Process for methanol production from carbohydrates by gasification an partial oxidation. Source: Demirbas [53]

The exergy cost balance in the transesterification process using this alcohol is shown in table 6.18. The reduction in the cost of external resources in the transesterification process equals 73%, and applying eq. (3.67) the relative reduction of the non-renewable cost of biodiesel is 18.36% (73.04 × 0.2514). The ExROI value is increased to 3.06.

Environmental impacts: From the climate change point of view, the substitution of conventional methanol for biomethanol from wood helps to reduce the $CO_{2\text{-eq}}$ emissions of the cycle. The amount of emission reductions allocated to biodiesel follows the same scheme as explained in the previous case. The emission reduction is 5.18 $gCO_{2\text{-eq}}$ /MJ of biodiesel. The GHG emission reduction is increased to 44% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and to 48% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

In this case, if the wood comes from residues of sustainable managed forest land there would not be any direct agricultural land use. In any case, the land needed to obtain the biomethanol is 0.25 ha/tonne. In view that in the transesterification process, there is a need of 0.11 kg methanol per kg of biodiesel, the additional land required is 0.03 ha/tonne. All in all the land use is 0.90 ha per tonne of biodiesel produced.

If a consumption of 13.3 Mtoe of biodiesel in 2020 as foreseen by [90] with the current targets of the Renewable Energy Sources Directive [99] there would be a total use of land of 13.5 Mha, which is 0.4 Mha more.

Table 6.18: Exergy cost balance in transesterification using methanol form wood

Stream	**I/O**	**Unit** (u)	u/kg FAEE	**Cost** MJ/u	MJ/kg FAEE
H_3PO_4	Input	kg	0.0017	36.286	0.062
HCl	Input	kg	0.0200	5.248	0.105
Na_2CO_3	Input	kg	0.0025	14.064	0.035
NaOH	Input	kg	0.0067	5.027	0.034
Electricity	Input	MJ	0.1080	2.869	0.310
Steam	Input	MJ	0.5499	3.264	1.795
Methanol	Input	MJ	0.1087	0.967	0.105
Plant oil	Input	MJ	1.0400	39.734	41.325
FAME	Output	kg	1.0000	40.062	40.062
Glycerol	Output	kg	0.1056	23.678	2.500

Socio-economic impacts: From the economic point of view, this action is relatively competitive. The production of methanol from biomass is more cost intensive due to complications with biomass gasification [28]. However, the calculations from Faaij [104] show that the breakeven gate price for methanol from biomass in Europe of 10 – 15 €/GJ in the short term, evolving to 6-8 €/GJ in the long term, due to improved technology, as more production facilities employing biomass gasification are built and operated. With these data the price of biomethanol from wood would be of 200-300 €/tonne in the short term.

The price of methanol from natural gas depends on the price of natural gas. The MIT Natural Gas report [179] estimates that for a price of natural gas of 4 – 8 US Dollars/MMBtu the price of methanol is 1.3 – 2 US Dollars/GGE. Translated in to €/tonne this would give a price of methanol from natural gas of 166 – 256 €/tonne (conversion Euro to Dollar of 5 March 2013).

The numbers above should be taken with caution because the price of natural gas varies significantly as it can be observed in fig. 6.7. Natural gas prices are set to decrease in the U.S. due to the high increases in shale gas production, however, in the EU prices are foreseen to remain high.

6.4.3 Recirculation of biodiesel to the primary processes

The recirculation of part of the biodiesel produced in the cycle, to substitute the use of fossil diesel in the primary processes is another action that can be applied to reduce the use of non-renewable resources and increase the ExROI value.

In this case, only the direct substitution of diesel fuel is considered. This means that for this example no biodiesel is used to produce electricity or steam that then would be consumed in the cycle. With this consideration, the only primary processes that consume diesel fuel are the cultivation process, the drying of the seeds and the transport of the seeds to the extraction unit.

As the cultivation and drying processes occur in areas far away of the transesterification unit, an extra loss of 0.15 MJ/kg FAME for the transport to the cultivation and drying areas is considered.

The Fuel-Product table is the one shown in table 6.19, showing in bold the values changed compared to the business as usual scenario, and applying the theory of exergy cost it is possible to obtain the exergy cost and unit non-renewable exergy cost of the biodiesel fuel. The inverse

Figure 6.7: Natural gas prices in the U.S. Source: Infomine

of the last one gives as a result the ExROI value. In this case, the ExROI is increased up to 2.75 which is a relative increase of 9.2%.

Environmental impacts: Considering that diesel fuel production emits 87.64 $gCO_{2\text{-eq}}$ /MJ of fuel, and that the rapeseed biodiesel re-circulated into the cycle emits 46 $gCO_{2\text{-eq}}$ /MJ, this action can save the emission of 3.59 $gCO_{2\text{-eq}}$ /MJ FAME, of which 1.95 $gCO_{2\text{-eq}}$ are allocated to the biodiesel product. The GHG emission reduction is increased to 42% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and to 46% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

In this case, there is a very small increase of agricultural land use. As a part of the biodiesel obtained in the process is reused internally, to produce the same amount of biodiesel as output of the process more hectares are needed. The extra biodiesel needed in terms of exergy is in total 3.35 MJ/kg FAME. Taking into account the exergy of biodiesel (40.06 MJ/kg) and the land use needed to produce a tonne of biodiesel (0.87 ha), the extra land needed is this case is 7.24·10-5 ha/tonne of biodiesel. This is a negligible increase.

Socio-economic impacts: This action results in a reduction of the use of diesel fuel of 3.19 MJ/kg FAME. For a price of diesel fuel 1.19 €/litre average EU [102] the savings in diesel purchase are 105 €/tonne of FAME. For a cycle involving a production capacity of 50,000 tonnes of biodiesel/year, the savings would amount 5.25 million €/year.

6.4.4 Use of biodiesel for the production of inputs

Another possibility is the partial use of biodiesel in the secondary processes, i.e. in the production of the inputs that enter the refining and transesterification plants, which are assumed to be close to each other.

Table 6.19: F–P Table of rapeseed biodiesel with direct recirculation (MJ/kg FAME)

		F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0	rs	77.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	77.42	
	nrs	**9.03**	**0.57**	**0.00**	2.88	0.44	4.37	0.24	1.02	18.56	
P_1	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	0.00	77.27	
P_2	0.00	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	77.27	
P_3	0.00	0.00	0.00	0.00	76.51	0.00	0.00	0.00	0.00	76.51	
P_4	11.79	0.00	0.00	0.00	0.00	43.05	0.00	0.00	0.00	54.84	
P_5	0.00	0.00	0.00	0.00	0.00	0.00	41.33	0.00	0.00	41.33	
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.48	3.31	43.79	
P_7	**36.87**	**3.03**	**0.01**	**0.15**	0.00	0.00	0.00	0.00	0.00	40.06	
P_8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50	
Total	51.17	89.48	77.85	77.42	79.39	43.49	45.69	40.72	4.34		

In this case, it has been assumed that biodiesel is a direct substitute of the hard coal, crude oil, lignite and natural gas used in the production of n-hexane, Fuller's earth, NaOH, HCl, Na_2CO_3 and H_3PO_4. The MJ of these energy carriers are substituted by MJ of biodiesel from the transesterification plant. In the cases of HCl and Na_2CO_3 where electricity and steam are also used a 25% electrical conversion efficiency, and 85% thermal conversion efficiency have been assumed. These are the efficiencies considered in the Communication of the European Commission COM(2010)11 for the sustainability of solid biomass [79].

As this exercise is calculating the non-renewable exergy costs, it is necessary to assume that part of the MJ of biodiesel are renewable and only account the non-renewable part for the analysis. Taking into account the results obtained in chapter 5, shown in table 5.21, a renewability factor of 78% has been considered.

The total biodiesel consumed to substitute these energy carriers is 4.13 MJ/kg FAME. The Fuel-Product table is modified as shown in table 6.20 compared to the business as usual scenario, with the modified values highlighted in bold.

Table 6.20: F–P Table of rapeseed biodiesel with indirect recirculation (MJ/kg FAME)

		F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0	rs	77.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	77.42	
	nrs	12.06	0.58	0.15	**0.90**	**0.11**	**3.54**	**0.06**	**0.22**	17.62	
P1	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	0.00	77.27	
P2	0.00	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	77.27	
P3	0.00	0.00	0.00	0.00	76.51	0.00	0.00	0.00	0.00	76.51	
P4	11.79	0.00	0.00	0.00	0.00	43.05	0.00	0.00	0.00	54.84	
P5	0.00	0.00	0.00	0.00	0.00	0.00	41.33	0.00	0.00	41.33	
P6	0.00	0.00	0.00	0.00	**1.98**	**0.33**	**0.83**	**36.35**	**4.12**	43.60	
P7	34.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	34.54	
P8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50	
Total	48.83	89.48	77.85	77.42	79.39	43.49	45.69	36.41	4.34		

From the F–P table applying the theory of exergy cost it is possible to obtain the exergy cost and unit non-renewable exergy cost of the biodiesel fuel. The inverse of the last one gives as a result the ExROI value. In this case, the ExROI is increased up to 2.69 which is a 4.3% more.

Environmental impacts: In this case, the reduction of $gCO_{2\text{-eq}}$ emissions is 1.17 $gCO_{2\text{-eq}}$ /MJ FAME, of which 1.06 gr $gCO_{2\text{-eq}}$ are allocated to the biodiesel fuel. The GHG emission reduction is increased to 39% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and to 44% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

In this case the increase in the use of agricultural land is also negligible amounting $2{\cdot}10^{-5}$ ha/tonne of biodiesel.

Socio-economic impacts: This action also results in a reduction of the use of fossil fuels. In this case the reduction is 1,037.44 kJ/kg FAME. In this case the fossil fuels substituted are hard coal, crude oil, lignite and natural gas, which have different prices. In order to compare with the previous case, a similar average price to that of diesel fuel for all these energy carriers has been assumed, obtaining that the savings are 34 €/tonne FAME. For a cycle involving a production capacity of 50,000 tonnes of biodiesel/year, the savings would amount 1.7 million €/year.

6.4.5 Production of Pure Vegetable Oil as fuel

If instead of producing biodiesel, the refined vegetable oil is considered as a biofuel to be used directly in adapted engines, the ExROI value of this product, for which no transesterification is needed, would be 3.24, which is a 23% higher than for biodiesel. This provides an indication of the weight that transesterification has in the biodiesel life cycle production.

It is worth noticing that the use of PVO has as inconvenient that it can only be used in adapted engines with adequate after-treatment systems. In various projects [168] it has been shown that with the use of PVO in direct injection engines, even after a relatively short duration, problems may occur. A build-up of deposits in the combustion chamber and damage to the injectors have been found. Existing diesel engines have to be converted to be able to operate with PVO. Changes may be needed in the fuel lines, combustion chamber and fuel injectiors. In agriculture, there have been engines for several years that have been manufactured to be able to operate with PVO, for example John Deeree, Fendt and Deutz.

The fact of not transforming the oil into biodiesel avoids the consumption of the inputs needed in the transesterification plant and therefore reduces the greenhouse gas emissions. The emissions are reduced in 1.40 $gCO_{2\text{-eq}}$ /MJ FAME. With this, the GHG emission reduction is increased to 40% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and to 44% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

In addition, it does not make a big difference compared to the market price of biodiesel as shown in fig. 6.8. As can be observed, the price of rapeseed PVO is still higher than that of fossil diesel and similar to biodiesel.

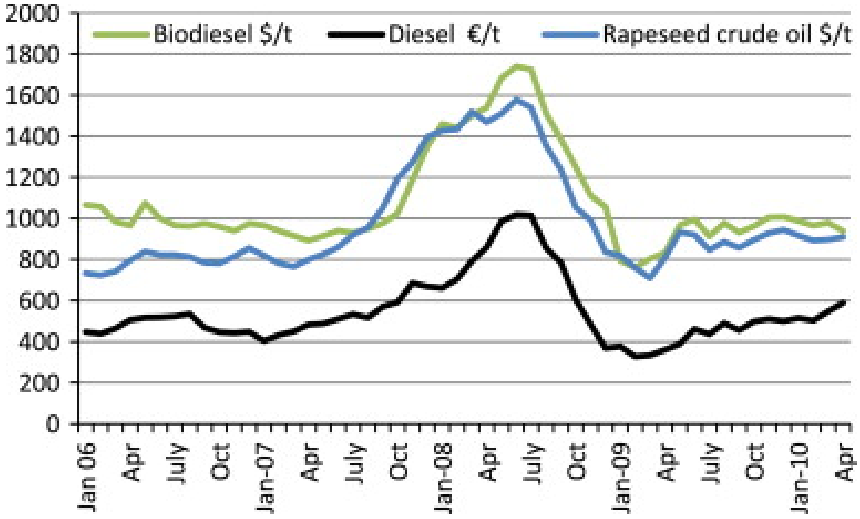

Figure 6.8: Market prices of diesel, biodiesel and rapeseed crude oil in the EU from 2006 to 2010. Source: Di Lucia [55]

6.5 Alternatives of the use of glycerol

The co-product glycerol of the transesterification process plays an important role in the ExROI value of the final biodiesel. Depending on the use given to this product, which ranges from a high added value substance to a residue in saturated markets, the effect that glycerol production has in the ExROI value is positive or negative. When glycerol is considered a waste there is no possibility to divert exergy costs to it and therefore the (non-renewable) exergy cost of biodiesel increases and the ExROI value decreases. This paragraph discusses the possible uses of glycerol besides the business as usual considered in chapter 5 and analyses the consequences in the ExROI value and the environmental and socio-economic impacts.

Chapter 4 showed that the unit exergy cost of the glycerol after-treatment processes (purification and distillation) are relatively high compared to the after-treatment of the biodiesel stream. This section presents also an analysis, when pertinent, about the effect on the unit exergy cost of the final glycerol product obtained.

6.5.1 Partial distillation of glycerol

In the case that all the glycerol produced in the transesterification process could not be sold as a product but instead treated as a residue due to the saturation of the glycerol market, the ExROI value of biodiesel would be decreased to 2.31 i.e. an 8% lower than the case when glycerol is sold as a valuable product.

Crude glycerol while having a lower economic value can also be used in many processes. In markets where the high quality distilled glycerol is saturated and therefore its price is dramatically reduced, while still involving high costs in the after-treatment, there is a need to find high added value uses for the crude glycerol. This allows reducing the production costs (no purification and distillation) while still having a valuable product which divert exergy costs from the biodiesel stream. Yang et al. [252] provide a review of the the current and potential value-added applications of crude glycerol from biodiesel production.

The chemical composition of crude glycerol mainly varies with the type of catalyst used to produce biodiesel, the transesterification efficiency, recovery efficiency of the biodiesel, other impurities in the feedstock, and whether the methanol and catalysts were recovered [252]. All of these considerations contribute to the composition of the crude glycerol fraction.

The uses considered by [252] are animal feedstuff, feedstock for chemicals produced via biological conversions (1, 3-propanediol, citric acid, hydrogen and other lower molecule fuels, poly-hydroxyalkanoates, docosahexaenoic acid, lipids), chemicals produced through conventional catalytic conversions (oxygenated chemicals, hydrogen or syngas, and other chemicals from conventional catalytic conversions) and other uses.

The ExROI value of biodiesel depends only on the crude glyclerol produced in the transesterification, i.e. it is independent on whether the glycerol is purified or sold as crude glycerol. If there is a part of the crude glycerol that cannot be used in further processes, the ExROI value decreases from the BAU value of 2.49 to 2.31 when all the glycerol is considered as a residual stream.

Environmental impacts: When not all the crude glycerol is upgraded, there is a decrease in the $CO_{2\text{-eq}}$ emissions due to the reduction of the consumption of inputs in the glycerol purification and distillation. These emission reductions should be entirely allocated to the glycerol stream as this is the only product of these processes. If only 25% of the crude glycerol is treated and therefore there is a reduction of 75% of inputs consumption in the processes, there would be a reduction of emissions of 75% per each kg of glycerol produced. On the other hand, the environmental impacts of disposing the waste glycerol stream need to be taken into account.

Socio-economic impacts: From the economic point of view, while there is a reduction in the consumption of inputs in the purification and distillation which reduces the overall costs of the process, there is a shift of the production of a high added value product to a lower added value product. Whereas the cost of distilled glycerol can reach from less than 500 up to 2,500 US Dollars per metric tonne in the period from 2005 to 2009 as seen in fig. 6.9, the price of crude glycerol is much lower, from around 22 US Dollars during 2008-2009 to 353 US Dollars in 2010 (source: ICIS, 2010).

6.5.2 Anaerobic digestion of glycerol

When glycerol finds no value in the market, the anaerobic digestion of glycerol could be alternatively considered to produce biogas, which could be consequently used in the transesterification cycle to substitute fossil sources and produce the required steam.

Using data of the JEC study [148], table 6.21 shows the consumption inputs and the production of outputs when glycerol is digested and converted to steam and this steam is used in the process. As it can be observed, there is reduction of 1.4 MJ/kg FAME of steam, but extra steam is still needed as there is not sufficient production from glycerol to supply all the steam needed.

This operation means a reduction of resources consumption in transesterification process of 9.3% with respect the previous case and 2.35% in the non-renewable cost of biodiesel, but the ExROI value 2.37 is still smaller than in the BAU scenario. Therefore on the contrary to what could be considered, anaerobic digestion of glycerol does not improve the ExROI value of biodiesel, and the digestion of glycerol to produce biogas which is used in the cycle does not have practically any effect in the greenhouse gas emission reductions.

Table 6.21: Exergy cost balance in transesterification when glycerol is digested

				Cost	
Stream	**I/O**	**Unit** (u)	u/kg FAME	MJ/u	MJ/kg FAME
H_3PO_4	Input	kg	0.0017	36.286	0.062
HCl	Input	kg	0.0200	5.248	0.105
Na_2CO_3	Input	kg	0.0025	14.064	0.035
NaOH	Input	kg	0.0067	5.027	0.034
Electricity	Input	MJ	0.1080	2.869	0.310
Steam	Input	MJ	0.1101	3.264	0.359
Methanol	Input	MJ	0.1087	30.307	3.295
Plant oil	Input	MJ	1.0400	39.734	41.325
FAME	Output	kg	1.0000	40.062	40.062

Socio-economic impacts: From an economical point of view, this action is not attractive. Glycerol is a valuable product. The price of refined glycerol is very variable, as shown in fig. 6.9. Only in very saturated markets glycerol may be practically considered a residue instead of a co-product. Depending on its price, selling refined glycerol provides incomes to biodiesel production or losses. If a price of 200 to 2,000 €/tonne based on the variability shown in fig. 6.9 is considered, for the lower range there is a reduction of benefit of about 100 €/tonne of biodiesel while for the higher range the production of glycerol brings an additional benefit of around 190 €/tonne of biodiesel. In the case that glycerol is digested to produce electricity and steam consumed in the process, it is observed that the energy savings do not outweigh the loss of the co-product so there are losses of about 700 €/tonne of biodiesel. These results are shown in tables 6.22(a) and 6.22(b) and explain why it is not a normal practice for biodiesel producers to digest glycerol.

Table 6.22: Benefit comparison of selling glycerol or used to produce biogas

(a) Esterification BAU

				MIN	**MAX**
Stream	**I/O**	**Unit** (u)	u/kg FAME	€/kg FAME	€/kg FAME
Glycerol	Output	kg	1.5913	0.398	0.477
Electricity	Input	MJ	0.3274	0.009	0.009
Steam	Input	MJ	1.5515	0.019	0.019
Balance				**0.370**	**0.449**

(b) Esterification (glycerol to steam)

				MIN	**MAX**
Stream	**I/O**	**Unit** (u)	u/kg FAME	€/kg FAME	€/kg FAME
Electricity	Output	MJ	0.1008	0.003	0.003
Steam	Output	MJ	0.1101	0.004	0.004
Balance				**-0.007**	**-0.007**

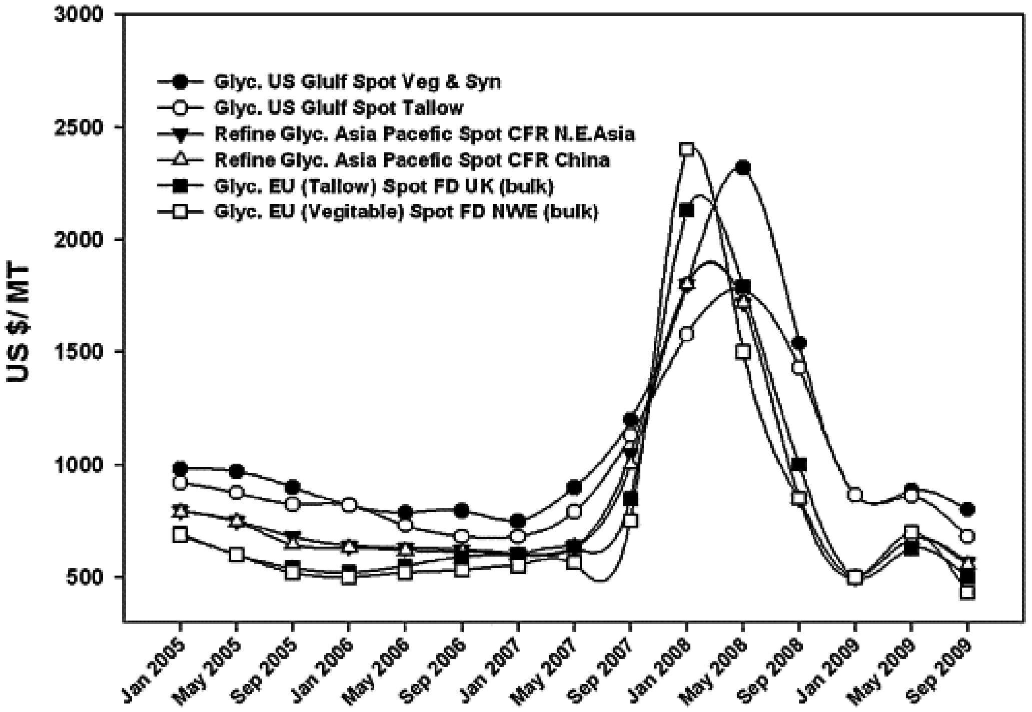

Figure 6.9: Price trend of diferent types of glycerol during 2005-2009. Source: Ayoub, 2012 [11]

6.5.3 Glycerol as biofuel

McNeil et al. [170] consider glycerol as the perfect diesel fuel in their paper "Glycerine from biodiesel: the perfect diesel fuel". They studied the combustion of glycerol in standard modified compression ignition engines, from the point of view of engine performance and emissions.

In spite of previous studies, which state that glycerol does not ignite in a diesel engine or that when combusting glycerol the engine would become clogged with polymerization products and toxic acrolein would be emitted [170], McNeil et al. demonstrate that with modified engines it is possible to produce heat and electricity from the combustion of glycerol with electrical efficiencies of 37.5-37.8% and a total engine efficiency of 42%, and with extremely low emissions.

The glycerol used in the experiments was distilled glycerol from a biodiesel plant with a purity of 98.5%. Assuming the results obtained by McNeil, the exergy costs of biodiesel and glycerol could be added together, because both would be biofuels to be used in diesel engines.

By doing this, the Fuel-Product table is modified as shown in table 6.23. In this case the values of the table are not referenced to kg of FAME but to kg of biofuel which includes both biodiesel and glycerol. There is a reduction of exergy consumption as the production of *biofuel* is higher than the production of FAME.

From the Fuel-Product table applying the theory of exergy cost the ExROI value in this case is reduced to 2.23. There is an increase of the exergy costs allocated to the main product, in this case the biofuel (considering both biodiesel and the glycerol) because the after-treatment of glycerol consumes high quantities of exergy that cannot be, in this case, allocated to any co-product.

Table 6.23: F–P Table of rapeseed biodiesel with glycerol as biofuel (MJ/$kg_{Biofuel}$)

		F_1	F_2	F_3	F_4	F_5	F_6	F_7	Total
	F_0								
C_0	rs	69.89	0.00	0.00	0.00	0.00	0.00	0.00	69.89
	nrs	10.90	0.47	0.14	2.51	0.39	3.93	1.97	20.31
P_1	0.00	0.00	69.89	0.00	0.00	0.00	0.00	0.00	69.89
P_2	0.00	0.00	0.00	69.89	0.00	0.00	0.00	0.00	69.89
P_3	0.00	0.00	0.00	0.00	69.20	0.00	0.00	0.00	69.20
P_4	10.67	0.00	0.00	0.00	0.00	38.94	0.00	0.00	49.61
P_5	0.00	0.00	0.00	0.00	0.00	0.00	37.38	0.00	37.38
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	39.95	39.95
P_7	38.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	38.50
Total	49.17	80.79	70.36	70.03	71.71	39.33	41.31	41.92	

Environmental impacts: In spite of reducing the ExROI value this option increases the emission reductions compared to diesel fuel as it is considered that more quantity of biofuel is being produced with the same quantity of raw materials. The emissions are reduced to 48.72 $gCO_{2\text{-eq}}$ /MJ. This implies a reduction of 42% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and a reduction of 46% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ.

This option reduces the land needed to obtain a MJ of biofuel. Taking into account the same seed yield as in the business as usual (3.113,44 kg/(ha*yr)), in view that in this case less quantities of seeds are needed to obtain the same quantity of biofuel (2.44 kg of seeds), the need of land is equal to 0.78 ha/tonne of biofuel. This is a reduction of 0.09 ha per tonne. For a consumption of 13.3 Mtoe of biodiesel in 2020 as foreseen by [90] the reduction in the use of land would equal to around 1.3 million ha.

Socio-economic impacts: From a socio-economic point of view, the combustion of glycerol only makes sense in saturated markets where the price of glycerol is lower than the price of diesel fuel. As shown in fig. 6.9 the price of glycerol can vary widely from less than 500 US Dollars to almost 2,500 US Dollars per metric tonne. In view of this, it might be more economically viable to sell the crude glycerol. With this at least it is possible to obtain a reduction of costs as the glycerol after-treatment process consumes high quantities of energy. This is studied in the next subsection.

6.6 Industrial symbiosis

One possible action to improve the ExROI of the cycle stems from the definition of Industrial Ecology. The aim of Industrial Ecology is to achieve a more rational and balanced industrial organization, trying to imitate the structure and operation of natural ecosystems [15]. A key issue in Industrial Ecology is the Industrial Symbiosis, which aims at the transformation of the conventional linear productive chains into a material cycle by using waste flows from industries as raw materials for others [236].

Any combination of industries allowing the use of residual products or heat or the reduction of transport costs for the inputs or the outputs is subject to Industrial Symbiosis. Herewith two possible examples of industrial symbiosis involving the biodiesel life cycle are analysed. Examples of industries with high energy losses that could be recovered for industrial symbiosis are shown in fig. 6.10.

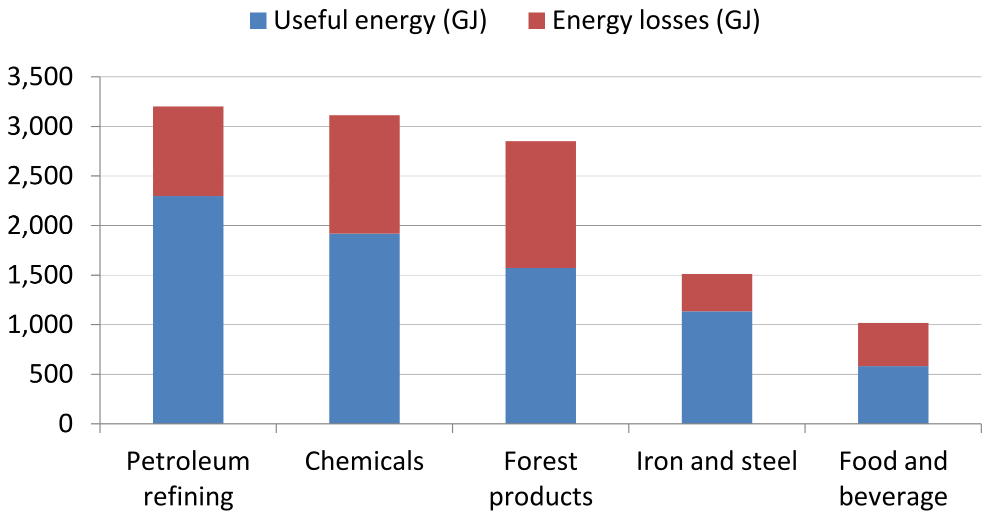

Figure 6.10: Energy use and energy losses in energy systems for the main sectors in the US. Source: IEA–IETS [138]

6.6.1 Biodiesel plant – Oil refinery industrial symbiosis

A case would be the installation of the biodiesel plant besides a petroleum oil refinery. The possible "interactions" between the two sites could result in the use of excess heat produced in the refinery by the vegetable oil refining and transesterification plants, and then, the biodiesel produced could be blended with the diesel fuel in a percentage allowing the transport of the blend via pipeline. With this, there are savings in heat production by using a waste heat, and in transport costs, as the final fuel blend is transported via pipeline. As the heat in this example is considered a waste, it does not count for the calculation of the ExROI value.

The Fuel-Product table for all the cycle is shown in table 6.24. In bold the values changed compared to the business as usual scenario are shown. In this case, there is a reduction of 36% of the external resources used in transesterification processes and the ExROI is increased up to 2.71 which is a relative change of 7.8% more. Is also interesting to note that the cost of glycerol is reduced 41%.

Environmental impacts: In this case, there is a reduction of greenhouse gas emissions due to the substitution of natural gas as energy source to produce steam, by residual steam for which no greenhouse gas emissions are allocated. The reduction amounts 4.20 $gCO_{2\text{-eq}}$ /MJ. This is a reduction of 43% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and a reduction of 47% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ, which is the same as in the business as usual scenario.

Socio-economic impacts: This action also implies a reduction of production costs if it is assumed that the excess heat is given for free. Assuming a price of natural gas of 10.97 €/GJ [88] savings up to 23 Euro per tonne of biodiesel produced could be obtained.

Table 6.24: F–P Table of rapeseed biodiesel for oil-refinery industrial symbiosis (MJ/kg FAME)

	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	Total	
C_0	rs	77.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	77.42
	nrs	12.06	0.58	0.15	2.88	**0.07**	**3.58**	**0.06**	**0.16**	19.55
P1	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	0.00	77.27
P2	0.00	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	77.27
P3	0.00	0.00	0.00	0.00	76.51	0.00	0.00	0.00	0.00	76.51
P4	11.79	0.00	0.00	0.00	0.00	43.05	0.00	0.00	0.00	54.84
P5	0.00	0.00	0.00	0.00	0.00	0.00	41.33	0.00	0.00	41.33
P6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.48	3.31	43.79
P7	40.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.06
P8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Total	54.35	89.48	77.85	77.42	79.39	43.12	44.91	40.54	3.47	

6.6.2 Cultivation - CHP plant - Oil extraction industrial symbiosis

Another industrial symbiosis could be the case of having a combined heat and power production plant using biomass as combustible material where part of the biomass is the straw produced in the cultivation of rapeseed and where part of the heat and power produced is used in the oil drying and oil extraction processes. This material cycle promotes the use of an agricultural residue while substitutes part of the fossil fuel consumption in the biodiesel life cycle.

It has been assumed that only 50% of the straw is collected. By taking half of the straw which otherwise would stay on the ground, no additional use of fertilisers to recover potential soil losses are needed. According to the MixBioPells project [155] taking this percentage of straw out of the field does not affect the fertility of the soil. The quantity of straw produced is 1:2.9 as ratio seed:straw [155].

Rape straw has a net calorific value of about 18.5 MJ/kg of dry matter and a water content of 45 – 60 wt % after the harvest. Thus, rape straw should be dried at the field before it is used as fuel [253]. Kristofel et al. [253] report the following combustion-relevant properties: ash content 3.4 %db, N content 1.48 %db, S content 0.20 %db.

The rape straw can be combusted directly or can be transformed into pellets. Experiences of both combustion and pelletizing exist showing combustion characteristics similar to other bio-materials that are normally used for these purposes according to [155]. To Chico-Santamarta et al. [40] rape (canola) straw pellets are a superior combustion fuel to straw bales due to lower moisture content and less microbial deterioration during storage.

There are authors that report that the combustion of rape straw has negative effects on emissions and can lead to problems in the boiler [131]; others that pelletizing rape straw is comparatively difficult compared to wood pellets and that they have relatively high concentrations of ash, sulphur, nitrogen and chloride which would be expected to lead to higher emissions in addition to boiler corrosion [110]. On the other hand, there are positive experiences of co-combustion and production of mixed pellets involving rape straw and other bio-materials such as wheat straw [173].

Carroll and Finnan [33] conclude that even though rape straw pellet combustion has negative emission and technical problems, with advances in boiler design and emission control measures which would counteract the harmful emissions of cereal straw combustion, it is likely, that in the future, cereal straw and energy crop pellets will be able to make a significant contribution to renewable energy supply.

The Fuel-Product table obtained in this case is shown in table 6.25. The variations to the business as usual scenario are highlighted in bold. As it can be observed, there is an increase in the production of the cultivation process (P_1), due to the consideration of the rape straw as a final product. The non-renewable cost of biodiesel obtained by applying eq. (3.56) is 9.4 MJ/kg FAME, which represents an improvement of 41.4% and an ExROI value of 4.26.

Table 6.25: F–P Table for rapeseed oil with straw production (MJ/kg FAME)

	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0	rs	**149.90**	0.00	0.00	0.00	0.0	0.0	0.0	0.00	149.75
	nrs	12.06	**0.00**	0.15	**0.14**	0.44	4.37	0.24	1.02	18.41
P_1	**72.48**	0.00	77.27	0.00	0.00	0.00	0.00	0.00	0.00	149.75
P_2	0.00	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	77.27
P_3	0.00	0.00	0.00	0.00	76.51	0.00	0.00	0.00	0.00	76.51
P_4	11.79	0.00	0.00	0.00	0.00	43.05	0.00	0.00	0.00	54.84
P_5	0.00	0.00	0.00	0.00	0.00	0.00	41.33	0.00	0.00	41.33
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.48	3.31	43.79
P_7	40.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.06
P_8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Total	126.84	161.80	77.27	77.42	76.65	43.49	45.69	40.72	4.34	

Environmental impacts: In this case, there is a reduction of greenhouse gas emissions due to the substitution of fossil energy sources in the drying and oil extraction processes. The reduction amounts 3 $gCO_{2\text{-eq}}$ /MJ. This implies a reduction of 42% compared to diesel fuel with an emission level of 83.8 $gCO_{2\text{-eq}}$ /MJ and a reduction of 46% compared to diesel with an emission level of 90.3 $gCO_{2\text{-eq}}$ /MJ, which is the same as in the business as usual scenario.

For this case, it is important to note that the Renewable Energy Sources Directive [99] does not allow diverting emissions of the cultivation process to the straw. The Annex V of the Directive establishing the rules for calculating the greenhouse gas impact of biofuels, bioliquids and their fossil fuel comparators, indicates that all co-products shall be taken into account for the purposes of the greenhouse gas emission reductions calculation, except the agricultural crop residues, including straw, bagasse, husks, cobs and nut shells.

Socio-economic impacts: The use of rape straw can constitute a new source of income for the farmers. According to a study by Bloomberg New Energy Finance [35], if only 17.5% of the one billion tonnes of agriculture residues available in Europe were used to produce biofuels an average farmer could increase its revenues by up to 40%.

On the other hand, the electricity produced in the CHP plant is introduced in the electricity grid therefore the price of the electricity used in the cycle remains the same as in the BAU and no reduction of costs are expected. As for the heat used which substitutes the consumption of diesel fuel and natural gas in the drying and oil extraction processes, there could be some savings depending on the price fixed by the CHP plant to the heat production.

6.7 Defossilisation using combinations of measures

All the actions explained above applied separately do not provide an ExROI value higher than the EROI of fossil diesel fuel, according to Cleveland [45] and some of them are below the Charles A.S. Hall limit mentioned in the introduction of this chapter. In this section the ExROI value is calculated for two combinations of some of the actions to see if by combining them it is possible to achieve higher values than the EROI of diesel fuel.

Two options have been considered. In both cases, only actions leading to greenhouse gas reductions have been considered. The first one only takes into account the improvements that avoid having negative impacts in land use change while also provide positive socio-economic impacts. The second one considers in addition other actions regardless of the negative socio-economic impacts or in land use.

Table 6.26 shows a summary of the impacts of each of the actions analysed in the previous paragraphs. Grey colour highlight indicates the actions considered in both options, meanwhile in light grey the ones considered only in the second option. The results of the greenhouse gas emission reductions are shown in fig. 6.11.

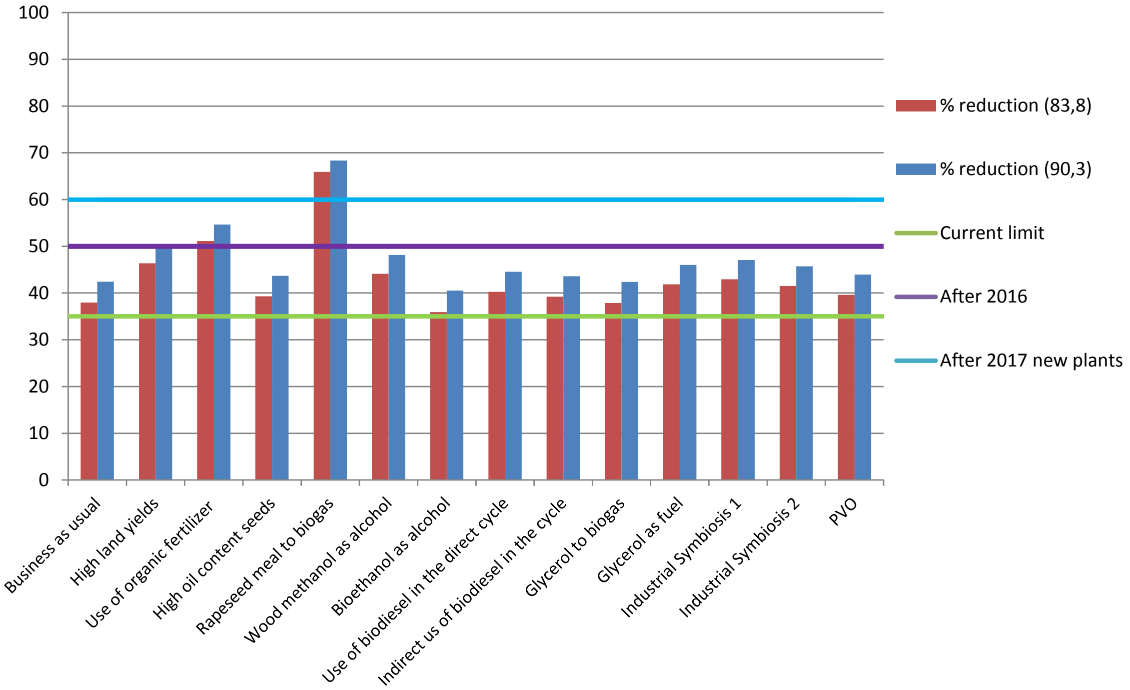

Figure 6.11: Greenhouse gas emission reductions of the different actions

Tables 6.27(a) and 6.27(b) shows the F–P tables for options A and B. The first option includes the following actions together: increasing the yield of rapeseed, using high oil content seeds, use of methanol from waste wood as alcohol in transesterification, recirculation of biodiesel in the cycle and for the production of inputs, and measures of industrial symbiosis, such as using waste heat from neighbouring industries and using the straw of rapeseed as valuable co-product to CHP.

Option B considers all the actions of option A plus the use of organic fertilisers and the anaerobic digestion of rapeseed meal regardless if they lead to increases in land use or negative socio-economic impacts.

Table 6.26: Sumary of impacts under study

Nr	Action	GHG emission reductions to 83.8 $gCO_{2\text{-eq}}$	Land use Mha needed for 13.3 Mtoe FAME	Socio economic impact
0	Business as usual	38%	(=)	(=)
1	Increasing seed yields	46% (+)	-6.3 (+)	(+)
2	Use of compost as fertiliser	51% (++)	N.A.	(-)
3	High oil content varieties	39% (+)	-1.2 (+)	(+)
4	AD of cake	66% (+++)	(-) ILUC	(-)
5	Bioethanol as alcohol in transesterification	36% (-)	+1.8 (-)	(-)
6	Methanol from waste wood as alcohol in transesterification	44% (+)	(=)	(=)
7	Methanol from wood as alcohol in transesterification (non waste)	44% (+)	+0.4 (-)	(=)
8	Recirculation of biodiesel in cycle	42% (+)	(=)	(+)
9	Reuse of biodiesel for the production of inputs	39% (+)	(=)	(+)
10	Industrial symbiosis 1 - waste heat recovery	43% (+)	(=)	(+)
11	Industrial symbiosis 2 - rape straw to CHP	42% (+)	(=)	(+)
12	AD of glycerol	38% (=)	(=)	(-)
13	Glycerol as biofuel	42% (+)	-1.3 (+)	(-)
14	Partial distillation of glycerol	-	-	-
15	No transesterification process	40% (+)	(=)	(-)

(+): actions leading to improvements <50%

(++): actions leading to improvements >50%

(+++) actions leading to improvements >66%

(=): actions leading to no improvements

(-): actions leading to increases in GHG emissions

N.A.: in the case of using straw as a co-product of cultivation

The ExROI value obtained for option A is 14.41, which means a relative increase of 82% compared to the business as usual scenario, for option B the ExROI value increases up to 23.85 which represents near an increase of 90%. The renewability factor ρ increases from 78% in the BAU scenario up to 97.5% in option B.

Table 6.28 shows the non-renewable exergoecologic cost comparing the BAU scenario values per process and values obtained from option A and B.

Table 6.27: F-P tables for combination measures improvements (MJ/kg FAME)

(a) Option A

	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0	rs	142.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	142.77
	nrs	2.71	0.46	0.00	0.90	0.04	0.25	0.04	0.10	4.50
P_1	72.48	0.00	70.29	0.00	0.00	0.00	0.00	0.00	0.00	142.77
P_2	0.00	0.00	0.00	70.29	0.00	0.00	0.00	0.00	0.00	70.29
P_3	0.00	0.00	0.00	0.00	69.60	0.00	0.00	0.00	0.00	69.60
P_4	10.01	0.00	0.00	0.00	0.00	43.05	0.00	0.00	0.00	53.06
P_5	0.00	0.00	0.00	0.00	0.00	0.00	41.33	0.00	0.00	41.33
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.60	3.12	43.72
P_7	32.70	1.55	0.01	0.14	0.00	0.00	0.00	0.00	0.00	34.40
P_8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Total	117.69	147.03	70.76	70.43	70.50	43.09	41.58	40.64	3.22	

(b) Option B

	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0	rs	142.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	142.77
	nrs	0.41	0.46	0.00	0.90	0.00	0.16	0.02	0.06	2.01
P_1	72.48	0.00	70.29	0.00	0.00	0.00	0.00	0.00	0.00	142.77
P_2	0.00	0.00	0.00	70.29	0.00	0.00	0.00	0.00	0.00	70.29
P_3	0.00	0.00	0.00	0.00	69.60	0.00	0.00	0.00	0.00	69.60
P_4	7.14	0.03	0.00	0.00	0.00	43.08	0.09	0.02	0.04	50.40
P_5	0.00	0.00	0.00	0.00	0.00	0.00	41.33	0.00	0.00	41.33
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.60	3.12	43.72
P_7	32.70	1.55	0.01	0.14	0.00	0.00	0.00	0.00	0.00	34.40
P_8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Total	114.82	144.76	70.76	70.43	70.50	43.08	41.58	40.64	3.22	

6.7.1 Environmental and socio-economic impacts

From the climate change point of view both options offer the greenhouse gas emission reductions shown in fig. 6.12. As it can be observed, with option A the greenhouse gas emission reductions are higher than 60%. With option B the production of biodiesel exceeds 100%. For each MJ of biodiesel produce, the $CO_{2\text{-eq}}$ in the atmosphere is reduced by -4.97 $gCO_{2\text{-eq}}$.

Other research studies have found that applying improvements to the production cycles can increase the greenhouse savings in more than 100% compared to diesel fuel. This is the case of Stephenson et al. [214] which state that if the application rate of nitrogenous fertiliser was changed from the UK average of 211 kg/ha to 100 kg/ha, glycerol and rape meal were sent to CHP plants and cold pressing was used to extract the oil from the rapeseed, the total energy requirement would be reduced to $-31,000$ MJ/tonne of biodiesel and the global warming

Table 6.28: Non-renewable production cost of rapeseed based biodiesel applying improvement measures (C_P^{nrs} in MJ/kg FAME)

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Process		BAU		Option A		Option B	
		C_P^{nrs}	c_P^{nrs}	C_P^{nrs}	c_P^{nrs}	C_P^{nrs}	c_P^{nrs}
1	Seeds	12.06	0.156	2.82	0.020	0.48	0.003
2	Dried seeds	12.65	0.164	1.85	0.026	0.69	0.010
3	Dried seeds	12.79	0.167	1.86	0.027	0.70	0.010
4	Crude Vegetable Oil Rapeseed Meal	15.68	0.286	2.76	0.052	1.60	0.032
5	Refined Oil	12.74	0.308	2.28	0.055	1.37	0.033
6	Crude Biodiesel Crude Glycerol	17.11	0.391	2.53	0.058	1.53	0.035
7	FAME	16.06	0.401	2.39	0.069	1.44	0.042
8	Glycerol	2.32	0.927	0.28	0.112	0.17	0.068

requirement would reduce to −750 kg $CO_{2\text{-eq}}$, corresponding to net energy and global warming savings from using biodiesel rather than ultra low sulphur diesel of 170% and 120%, respectively.

On the other hand, both options reduce the use of land. Option A requires 7.5 Mha less land that the BAU scenario to achieve the 13.3 Mtoe of biodiesel in 2020 as projected by the European Commission [90]. Option B requires 5.3 Mha less land that the BAU scenario. In this case there is a reduction due to the increases of land needed when using biodiesel in the cycle or to produce some inputs; however, this increase is outweighed by the huge reductions of land use due to improved seed yields and higher oil content of the seeds. Nevertheless, in option B there could be indirect land use changes due to the withdrawal of rapeseed cake in the feed market which could provoke that this gap is filled by increasing the cultivation of soybeans, for example. This ILUC effects have not been measured in this work as there is no scientific methodology established to do so. Table 6.29 shows the impact in land use of the actions driving to variations in land use.

Table 6.29: Land use impacts of different actions driving to land use variation

	kg/(ha · year)	Mha for 13.3 Mtoe biodiesel in 2020	ha/t biodiesel
Business as usual	1,152.37	13.1	0.87
High seed yeilds	2,220.76	6.8	0.45
High oil seeds	1,266.75	11.9	0.79
Bioethanol as alcohol	1,008.99	14.9	0.99
Wood methanol as alcohol	1,117.17	13.5	0.9
Wood waste as methanol	1,152.37	13.1	0.87
Direct use of biodiesel	1,152.27	13.1	0.87
Indirect use of biodiesel	1,152.34	13.1	0.87

From the socio-economic point of view, both options offer greater incomes at farm level due to the higher seed production and the profit that can be obtain from the consideration of straw as a valuable co-product. In terms of Euro per tonne of biodiesel, option A would produce up to 262–279 Euros in savings. In option B can produce either savings or increases in costs depending on the price of the fertilisers compared. For the price of fertilisers used in this work, the production of biodiesel using compost as fertiliser in option B could produce either savings of 109.15 €/tonne or increases of costs of 193.81 €/tonne.

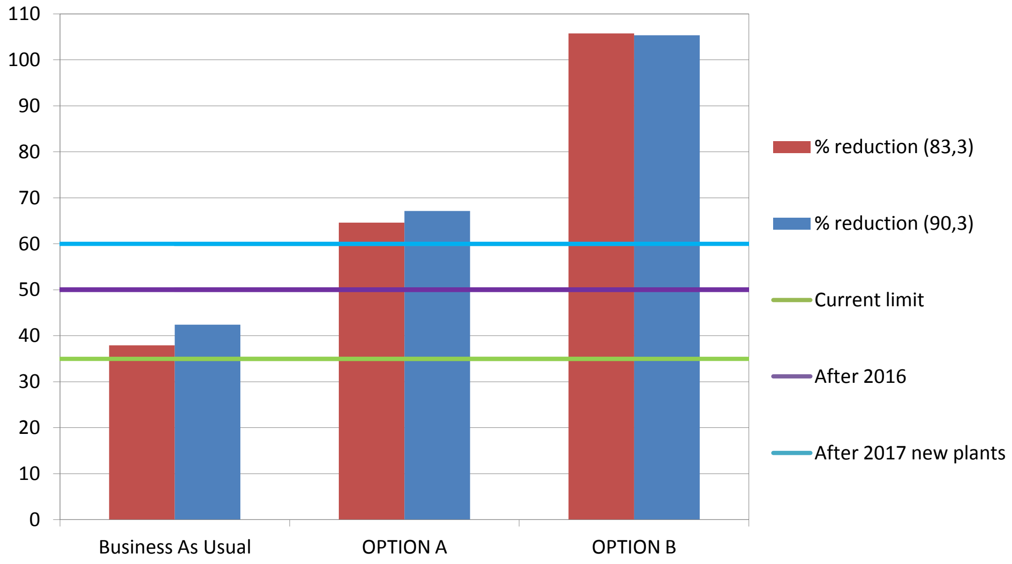

Figure 6.12: GHG emissions reductions of options A and B

6.8 Summary and conclusions

This chapter demonstrates that the ExROI methodology is an adequate tool to analyse the detailed processes to identify inefficiencies and propose solutions. The ExROI methodology can complement the greenhouse gas emissions calculations and the socio-economic impacts as a sustainability indicator.

Figure 6.13 shows the summary of the results obtained in this chapter. It reflects ExROI values of the previous individual cases, the results of the combinations analysed and the EROI values of fossil fuel sources according to the bibliography. As it can be seen, whilst the ExROI value can be improved by introducing improvements to the production cycles, the EROI (and ExROI) of fossil fuels is declining due to the depletion of the conventional sources and the need to obtain fuels from energy intensive unconventional fields such as shale oil, tar sands or deep off-shore. In the best case, per each MJ of non-renewable energy it is possible to produce 24 MJ of biodiesel. This is 2 to 4 times more than the EROI value of gasoline according to Cleveland. It is also 8 times more than the level mentioned by Charles A.S. Hall et al. [127] as the minimum EROI that society must attain from its energy exploitation to support continued economic activity and social function.

It is important to note that not all the options analysed in this chapter can be applied to all biodiesel plants. This depends on the specific characteristics of the plant and its geographical location and the location of other processes involved in the life cycle. Its application also depends on the technological developments driving, for example, to improve the yield and oil content of the crops, or the deployment of wood methanol at large scale.

Also, it is important to underline that not all the possible improvements are applicable right now due to the high costs involved or the insufficient maturity of the technologies or processes. However, the results obtained give clear signal of the results that can be obtained in the future.

This chapter demonstrates that introducing improvements in the production cycles as those identified using thermoeconomics, such as process integration, substitution, components' efficiency improvements and flow recirculation, can drive to higher greenhouse gas emission reductions and even to cycles that reduce the $CO_{2\text{-eq}}$ in more than 100% compared to diesel fuel. All of this with socio-economic benefits.

As mentioned in the chapter 1, the European Commission has issued a proposal aiming at increasing the minimum greenhouse gas emissions savings threshold up to 60% for biofuels and bioliquids produced in installations starting operation after 1^{st} July 2014.

The Impact Assessment of the proposal [86] expects that a threshold of 60% will exclude biodiesel produced from palm oil without methane capture, rapeseed oil and soybean oil from being used, unless improvements are introduced in the production cycles. This chapter demonstrates that these improvements are possible and therefore first generation biofuels should not be disregarded.

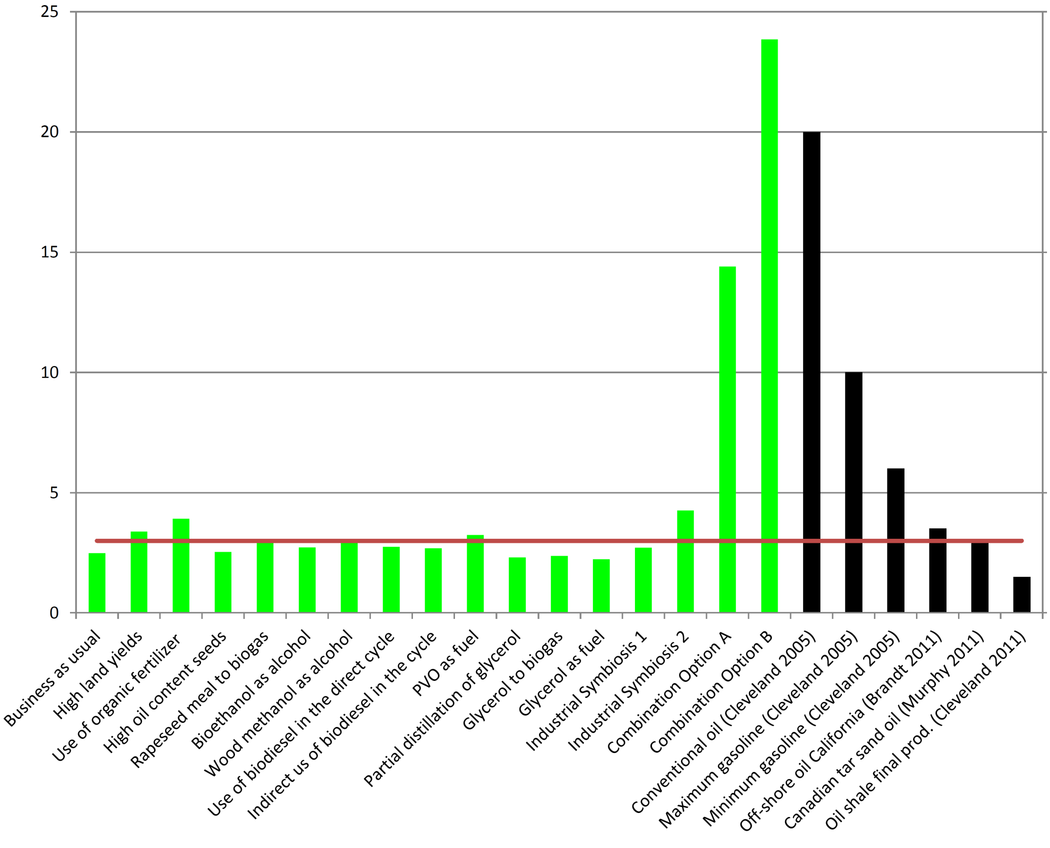

Figure 6.13: ExROI values of the different improvement options for rapeseed biodiesel

Chapter 7

Conclusions

This last chapter presents the synthesis of this thesis aiming to respond to the fundamental questions what? why? how?: what have we done, why have we done it and how have we proceeded. It also highlights the main contributions of the work done and results obtained to the scientific arena as well as to the society in general. And, finally, it mentions which perspectives for further research can be derived from the thesis, i.e. how could the work done be continued.

7.1 Synthesis

The aim of this PhD was applying thermoeconomics to improve the efficiency of bioenergy production plants and land-to-tank cycles. Therefore, three fields of knowledge or research lines can be distinguished: thermoeconomics, bioenergy and life cycle assessment.

Chapter 1 explains the reasons for putting these three fields together, which is summarised herewith. Bioenergy is playing an ever increasing role in the energy mix and will substantially contribute to the achievement of renewable energy targets in those countries that have set policies to fight climate change and energy dependence. In the EU, bioenergy currently provides more than 2/3 of the renewable energy, and it is expected to account more than half of the EU's renewable energy in 2020 and about 11% of the total EU energy consumption.

However, unlike other renewable energy sources, generating net greenhouse gas savings from bioenergy depends on the production processes. Inefficient bioenergy processes may produce more greenhouse gases than the fossil fuel counterpart that bioenergy pretends to substitute. The efficiency of bioenergy processes both at the plant scale and the life cycle needs to be optimized in order to ensure that the greenhouse gas emissions are minimized.

This thesis focuses specifically on biodiesel because as a renewable transport fuel it can contribute to reduce the fossil energy dependency of this sector, which is of about 98%, and the greenhouse gas emissions. In the EU, statistics indicate that the transport sector contributes to 23% of all the CO_2 emissions and if the trend continues, transport is expected to contribute 50% of all the CO_2 emissions in the EU by 2050. Biodiesel is the most important bioenergy resource used in transport in Europe nowadays due to the widening EU mineral diesel deficit which represents a major strategic challenge. It accounts approximately 78% of the biofuels consumption and will play an important role in reaching the 10% EU renewable energy target in transport in 2020.

However, the impact of biodiesel on the greenhouse gas emissions is set to be higher than those of other biofuels, namely bioethanol. If the mandatory emission thresholds are increased in view of modifications in the legal framework, or if the indirect land use change emissions are taken into account, biodiesel produced from palm oil, rapeseed oil and soybean oil could risk of not being promoted, unless improvements are introduced in the production cycles. If the EU aims to decrease the use in diesel fuel for transport by using biodiesel, actions need to be introduced in the production cycles in order to increase the efficiency and achieve higher direct CO_2 emissions reductions.

Besides the direct greenhouse gas emissions, biodiesel production may have other positive and negative impacts. These are related to indirect land use changes (ILUC), food security, land availability, and other social and environmental aspects. The ILUC and food vs. fuel debates are especially very controversial and studies have been produced both blaming and exonerating biodiesel of these impacts. In spite of the impossibility to assess these impacts using thermoeconomics, this chapter makes an objective description of the matter and provides information of initiatives undertaken to better understand the impacts.

Once the framework is set, **chapter 2** gathers the main characteristics of the materials used for producing biodiesel and describes the technological steps for the production of biodiesel from land to tank. It explains the production of biodiesel from vegetable oils (rapeseed, sunflower, palm and soybean oils), used cooking oils and animal fats. It shows the main properties of the biodiesel fuels obtained from these materials and processes. In addition, it also describes the main advanced processes under research and development.

Chapter 3 presents the thermoeconomic methodologies used to assess biodiesel production and land-to-tank cycles. Thermoeconomics provides an effective tool to identify inefficiencies, to discern where to act, what can be done to improve the efficiency of a process and propose solutions like process integration, substitution, components' efficiency improvements and flow recirculation.

It defines the concepts of exergy, exergy cost, exergetic efficiency and exergoecologic cost. It also explains how to perform a thermoeconomic input-output analysis based on the exergy cost theory. While these concepts are already well established concepts used by a wide number of scientists and researchers, this thesis also introduces newly defined concepts: the ExROI concept, based on the EROI concept, is used to calculate the ratio of non-renewable exergy consumed in the system to the exergy that the biodiesel contains. The less non-renewable exergy consumed, the higher the ExROI value will be. The ExROI concept as used conjugates two important factors, life cycle assessment and exergy cost analysis. Life cycle assessment allows taking into account all non-renewable resources required from crop cultivation to the transesterification plant (primary processes), including the production of the required inputs (secondary processes), meanwhile exergy cost analysis permits the correct cost assessment taking into account the energy quality of the production flows. The need to take into account the quality of energy in EROI calculations had been identified in previous studies by authors like Cleveland, the innovation of this thesis relies in the calculation methodology, from the non-renewable exergoecologic costs.

By discerning between the renewable and non-renewable cost, the renewability ratio is defined, which establishes the weight of the renewable costs with respect to the total exergoecologic cost. While similar renewability indicators have been defined by previous authors that can be assimilated to this one, the renewability ratio defined in this thesis is based on the exergy cost theory using the exergoecologic costs.

Also, as this thesis identifies two different boundaries of a system: primary processes which are the ones of the system, and secondary processes, which are the ones of the life cycle assessment (to produce the inputs to the system), the exergoecologic ratio is introduced. This ratio provides information on the relationship between the exergy cost and the exergoecologic cost and therefore helps to understand the weight of the external costs with respect the costs of the system.

Finally, taking into account that in LCA the results depend greatly on the source of information and assumptions made, this thesis introduces a sensitivity analysis of exergy and exergoecologic cost system assessments. With this methodology it is possible to measure the degree of variation in the results due to changes in the system conditions. The following chapters consist in applying the methodologies of chapter 3 to the processes described in chapter 2.

Chapter 4 presents an in-depth study of the exergy costs obtained when analysing in detail the processes included in a typical transesterification plant. This chapter demonstrates the applicability of thermoeconomics to bioenergy production processes and in particular to biodiesel production via transesterification. It shows that the exergy cost analysis is an appropriate tool to identify the inefficiencies of the process, how these inefficiencies can be minimised and how the exergy costs are affected by malfunctions in the process. Also, it shows the differences in terms of results between an energy and an exergy cost analysis.

Chapter 5 presents the application of thermoeconomics to the land-to-tank cycles of biodiesel fuels from different origins following the methodology of chapter 3. The exergy values, exergy costs and exergoecologic have been calculated for all the products in each process and the ExROI values and renewability ratio of the final desired product have been obtained.

As far as the ExROI value is concerned, all the biodiesel sources have ExROI values higher than one (varying from 1.68 to 4.10), which means that for one unit of non-renewable resources used in their production, more than one unit of biodiesel is obtained. From the point of view of the consumption of non-renewable resources, the most sustainable one is the biodiesel produced from used cooking oil, followed by palm, sunflower and rapeseed. The less sustainable is the soybean oil one which almost has a 1:1 relation. In terms of the renewability ratio the product with the highest renewability is the palm oil biodiesel followed by the biodiesel produced from used cooking oil.

According to Charles A.S. Hall et al. the minimum EROI that society must attain from its energy exploitation to support continued economic activity and social function is about 3:1 and therefore, biodiesel fuels which life cycle provides an ExROI value lower than 3 should introduce measures to improve their values or be discouraged. In addition, the ExROI values of biodiesel fuels should be compared to its direct competitor, i.e. fossil diesel fuel. According to Cleveland, the EROI value of gasoline (and therefore of diesel as they are products of the same process) is in the range of 6 to 10, while other authors provide lower values for unconventional oil sources.

Chapter 6 presents measures to defossilise the biodiesel land-to-tank cycle from rapeseed, in order to obtain higher ExROI values than fossil diesel fuel. It also analyses the consequences that these measures could have from the environmental and socio-economic point of view.

The measures analysed in this chapter are applied to the cultivation: use of organic fertilisers, increasing the yield per hectare, selecting high-oil content seeds; to the oil extraction process: anaerobic digestion of the meal; and in the transesterification plant: use of alcohols of biological origin, recirculation of part of the final product to substitute fossil fuels, and alternative uses for the glycerol by-product, like partial distillation, anaerobic digestion and use as fuel.

It also analyses to example of industrial symbiosis, one related to the use of waste heat in the oil refining and transesterification plants, and the other to the use of agricultural residues (straw) to partially cover the energy needs in the subsequent stages.

Finally, taking into account the environmental and socio-economic impacts of the different measures, it analyses the ExROI value of a combination of measures. It demonstrates that introducing improvements in the production cycles as those identified using thermoeconomics, such as process integration, substitution, components' efficiency improvements and flow recirculation, can drive to ExROI values higher than the limit of 10, to higher greenhouse gas emission reductions and even to cycles that reduce the GHG emissions in more than 100% compared to fossil diesel fuel. This can be achieved also with socio-economic benefits.

7.2 Contributions

The main contributions of this Ph.D. are outlined herewith. They can also be classified in the three research lines outlined before: thermoeconomics, bioenergy and life cycle assessment.

1. The main overarching contribution of this thesis is the combination of the three mentioned areas in the way it has been done. It is not the first time that bioenergy, life cycle assessment and exergy are put together; however innovation of this thesis relies in the methodologies provided, which are based on thermoeconomics and the exergy cost theory.

   Thermoeconomics input-output analysis integrates Second Law and economic input-output analysis together with material flows and life cycle analysis to provide a rigorous evaluation procedure for energy saving, sustainability and renewability of bioenergy processes. It puts together the pieces of a puzzle combining them to produce a methodology which is then applied to a specific system. The methodology does not just provide basic cost information but also how these costs are cumulated by the addition of irreversibility.

2. Regarding life cycle assessment, it provides an innovative methodology to assess the impacts of production processes with an objective allocation system, avoiding the subjectivity of substitution methods and also the negative aspects of energy allocation using low heating values. The exergoecologic cost allocation life cycle assessment permits the correct cost assessment, taking into account the energy quality of the production flows, be them energy or material flows. It represents a useful tool to asses non-linear production cycles for which substitution methods may not be valid. It provides a methodology to assess the sustainability of bioenergy sources from the point of view of the consumption of finite i.e. non-renewable resources. This methodology takes into account not only the consumption of fossil energy sources but also other finite materials, all of them quantified with the same units.

3. In the field of thermoeconomics one of the main contributions is providing the innovative conception of the decomposition of costs between renewable and non-renewable sources. This distinction between costs allows the definition of innovative calculation methodologies and concepts using the exergy cost theory: the ExROI value and the renewability ratio. These concepts and methodologies can be applied to any production process where both renewable and non-renewable energy sources are consumed. They are useful to assess the sustainability of processes and life cycles from the perspective of non-renewable resource consumption.

4. Another innovation is the decomposition of the costs between those costs related to the direct processes of a cycle (named exergy costs) and the secondary costs, related to the production of the inputs that enter into the direct processes (named exergoecologic costs). This differentiation allows the definition of an innovative concept: the exergoecologic factor, which permits understanding the weight of the external and internal inputs in the cost of the final products of the system.

5. In addition, this thesis presents a methodology to produce sensitivity assessments to the thermoeconomic calculations. Based on elasticity matrices, it allows to understand the effect of potential improvements in the process, such as efficiency improvements or non-renewable sources substitutions, on the final cost. This methodology allows to diagnose potential modifications of the process with a simpler process than thermoeconomic diagnosis. It is a methodology linking somehow thermoeconomics and ecological modelling.

6. From the point of view of bioenergy, the results of this thesis confirm (even though the author is of the opinion that this should not have needed any confirmation) that biodiesel is a renewable source of energy. The contribution of this Ph.D consists in providing an innovative methodology to calculate the grade of renewability of the fuel by calculating the renewability ratio. While other authors have defined also renewability indicators to biofuel production this thesis provides an innovative methodology to calculate it based on the theory of exergy cost using exergoecologic costs.

7. The results demonstrate that biodiesel production, with the data provided by the European Commission's Joint Research Centre and other institutional sources, contains more exergy than the non-renewable exergy consumed in its production. However, it also demonstrates that the production processes need to be improved to in order to have fuels with ExROI values higher than the EROI of fossil diesel and to have higher GHG emission reductions.

   With the proposed improvements,in the best case, per each MJ of non-renewable energy consumed up to 24 MJ of biodiesel can be obtained. This is 2 to 4 times more than the EROI value of gasoline (and therefore of diesel as they are products of the same process) which is in the range of 6 to 10. It is also 8 times more than the level mentioned by Charles A.S. Hall et al. as the minimum EROI that society must attain from its energy exploitation to support continued economic activity and social function. The results obtained can give policy makers a clue to shape policy frameworks to favour those life cycles with higher sustainability and propose a range of measures to foster the achievement of climate and energy targets.

8. These results give also another message: while according to the bibliography the EROI (and ExROI) values of fossil fuels are declining over time due to the depletion of conventional oil wells and the need to obtain oil from energy intensive unconventional oil fields like deep off-shore fields or tar sands, the ExROI of bioenergy can be improved by introducing improvement measures.

9. The thesis also demonstrates that introducing improvements in the production cycles as those identified using thermoeconomics, such as process integration, substitution, components' efficiency improvements and flow recirculation, can drive to higher greenhouse gas emission reductions and even to cycles that reduce $CO_{2\text{-eq}}$ emissions in more than 100% compared to diesel fuel applying the methodology established in the renew-

able energy Directive of the European Union, all of it with socio-economic benefits and reductions in the need for land.

The Impact Assessment of the European Commission's proposal to review the greenhouse gas threshold expects that a threshold of 60% will exclude biodiesel produced from palm oil without methane capture, rapeseed oil and soybean oil from being used, unless improvements are introduced in the production cycles. This thesis demonstrates that these improvements are possible and therefore first generation biofuels should not be disregarded.

7.3 Perspectives

The perspectives of this Ph.D. dissertation could be distinguished both from the methodologies provided and the results obtained.

This Ph.D. provides methodologies for a detailed thermoeconomic analysis of the Exergy Return on Investment (ExROI), renewability and exergoecologic ratios, as well as sensitivity analysis of systems. The developments presented here can be subject to improvements or modifications in future works in several aspects.

For example, the methodology could be modified to take into account the analysis of residues costs originated in the process. In the current methodology, the residues (that are not recirculated) are not taken into account so that no exergy costs are allocated to them. However, residues can also provide costs due to the consumption of exergy needed to their treatment.

The methodologies can be applied to other bioenergy life cycles, for example, second generation biofuels or to bioethanol or biomethane fuels. In the case of bioethanol production it could be interesting to see how the use of exergy in LCA allows diverting costs to an important by-product of the process (a high concentrated CO_2 flow that can be used for example in greenhouses aimed at flower production) that cannot be taken into consideration when applying low heating value as the proportionality measure.

It would also be interesting to widen the analysis of UCO derived biodiesel; and apply the methodology to biodiesel produced from animal by-products or oils from sewage sludge. These biodiesels are more sustainable and may have lower production costs, while at the same time make use of a waste. Therefore, they should be promoted. As seen in chapter 5the exergoecologic factor for the UCO biodiesel is basically increased in the transesterification. In the previous steps the consumption of external resources is lower.

Also, the analysis of industrial symbiosis with other industrial sectors could be widened for example to gather together different bioenergy production plants, e.g. biogas-biodiesel-wood pellets; and also to link with slaughterhouses, agri-food and beverage industry.

The European Commission is expected to issue an update of the values of Annex V since 31 December 2012 (as required in article 19 of the Renewable Energy Directive), in which the calculations of chapter 5 and chapter 6 are based, however, this Communication is being delayed. The update will include data for pathways not included in Annex V and may include corrections to the values when considered necessary. Although it is not expected that the changes introduced will lead to dramatic changes in the life cycles, a future work will consist in adapting the calculations to the new data and check the potential variation of results using the sensitivity analysis defined in this thesis.

The life cycles could be amplified to take into account the production of the machinery used in the cycle. This would be the third layer, as mentioned in chapter 5, and also the treatment of residues (e.g. residual waters, etc) and the final use of the fuel in the vehicle.

The measures identified in chapter 6 to improve the life cycles can be applied to the other biodiesel cycles. As the exergoecologic factor is different, the impact of these measures could vary. This is especially the case of palm and soybean oil biodiesels.

Another interesting aspect to analyse is the scalability of the model. The methodology has been applied to MJ/kg of biodiesel as reference unit. It could be interesting to know what would happen if the scale used is higher, for example, in terms of the costs, efficiencies and impacts. Would they be maintained?

Finally, the methodologies here defined, can also be applied to other processes and cycles where both renewable and non-renewable resources are being used, beyond bioenergy.

As far as the results are concerned, they can serve the stakeholders in the bioenergy arena to better understand the production cycles and how these can be improved to maximise the environmental and socio-economic impacts.

In view of the results obtained, decision makers have a better perspective of which measures should be fostered to improve the processes and therefore maximise the greenhouse gas emission reductions, which should contribute to achieve the climate change and renewable energy goals. Also, planners have a tool to help designing new plants and production cycles to take advantage of measures such as recirculation of flows, the use of new, more sustainable materials and valorisation of waste streams, reductions of resource consumption, and potential industrial symbiosis.

Appendix A

Calculation of exergy values of biodiesel

This appendix describes the calculation and shows the information required to compute the exergy flows of the direct processes of the land-to-tank biodiesel plants.

The main flows of the direct processes of biodiesel production are composed by free fatty acids. Table A.1 shows the FFA composition of the different vegetable and recycled oils studied in this Ph.D. The characteristic of the molecules for different kind of FFA are shown in tables A.2 and A.3.These tables will be used for further calculations.

Table A.1: Fatty acid composition of the vegetable oils and UCO % m/m

Fatty acid		**Sunflower oil**	**Rapeseed oil**	**Palm olein**	**UCO**
Caproic	C6:0	0	0	0	0.2
Lauric	C12:0	0	0	0.5	0.1
Miristic	C14:0	0	0	1	0.4
Palmitic	C16:0	6.7	4.7	31.5	14.1
Palmitoleic	C16:1	0.1	0.2	0	0.7
Estearic	C18:0	3.5	1.5	3	5.8
Oleic	C18:1	24.9	63.3	49.3	39.4
Linoleic	C18:2	63.9	18.6	14	38.1
Linolenic	C18:3	0.1	9.2	0.3	0.7
Araquic	C20:0	0.2	0.5	0.4	0.3
Eicosenoic	C20:1	0.1	1.3	0	0.3
Behenic	C22:0	0.6	0.3	0	0.0
Eruric	C22:1	0	0.4	0	0.0

A.1 Physical exergies

To compute the exergy of biodiesel, the Jobback aggregation method to compute the specific heat of liquids when pressure is constant is used, that follows eq. (A.1):

$$c_p(T) = A + B\,T + C\,T^2 + D\,T^3 \tag{A.1}$$

where

$$A = \sum_j g_j \Delta_a - 37.93 \qquad B = \sum_j g_j \Delta_b - 0.21$$

$$C = \sum_j g_j \Delta_c - 3.91 \cdot 10^{-4} \qquad D = \sum_j g_j \Delta_d - 2.06 \cdot 10^{-7}$$

where g_j is the number of groups of type j, Δ is the contribution for the j group and T the temperature in Kelvin degrees. The contribution values for the groups considered to calculate the exergy of FFA are shown in table A.4.

Table A.4: Contribution values for the groups in Joback method

Group	Δ_a (J/mol K)	Δ_b (J/mol K)	Δ_c (J/mol K)	Δ_d (J/mol K)
CH_3-	1.95E+01	-8.08E-03	1.53E-04	-9.67E-08
CH_2-	-9.09E-01	9.50E-02	-5.44E-05	1.19E-08
$CH-$	-2.30E+01	2.04E-01	-2.65E-04	1.20E-07
$CH=$	-8.00E+00	1.05E-01	-9.63E-05	3.56E-08
COOH	2.41E+01	4.27E-02	8.04E-05	-6.87E-08
$COO-$	2.45E+01	4.02E-02	4.02E-05	-4.52E-08
$O-$	2.55E+01	-6.32E-02	1.11E-04	-5.48E-08
$O=$	6.82E+00	1.96E-02	1.27E-05	-1.78E-08
$N-$	-3.11E+01	2.27E-01	-3.20E-04	1.46E-07
$C-$	-6.62E+01	4.27E-01	-6.41E-04	3.01E-07

Table A.2: Characteristic of molecules for different kind of FFA. Part 1

	Chemical structure		
Name	FFA	ME	Crude Oil
Caproic	CH_3-4CH_2-COOH	$CH_3-4CH_2-COO-CH_3$	$3CH_3-12CH_2-3COO-2CH_2-CH$
Lauric	CH_3-10CH_2-COOH	$CH_3-10CH_2-COO-CH_3$	$3CH_3-30CH_2-3COO-2CH_2-CH$
Miristic	CH_3-12CH_2-COOH	$CH_3-12CH_2-COO-CH_3$	$3CH_3-36CH_2-3COO-2CH_2-CH$
Palmitic	CH_3-14CH_2-COOH	$CH_3-14CH_2-COO-CH_3$	$3CH_3-42CH_2-3COO-2CH_2-CH$
Palmitoleic	$CH_3-12CH_2-CH=CH-COOH$	$CH_3-12CH_2-CH=CH-COO-CH_3$	$3CH_3-36CH_2-3(CH=CH)-3COO-2CH_2-CH$
Estearic	CH_3-16CH_2-COOH	$CH_3-16CH_2-COO-CH_3$	$3CH_3-48CH_2-3COO-2CH_2-CH$
Oleic	$CH_3-14(CH_2)-CH=CH-COOH$	$CH_3-14CH_2-CH=CH-COO-CH_3$	$3CH_3-42CH_2-3(CH=CH)-3COO-2CH_2-CH$
Linoleic	$CH_3-12CH_2-2(CH=CH)-COOH$	$CH_3-12CH_2-2(CH=CH)-COO-CH_3$	$3CH_3-36CH_2-6(CH=CH)-3COO-2CH_2-CH$
Linolenic	$CH_3-10CH_2-3(CH=CH)-COOH$	$CH_3-10CH_2-3(CH=CH)-COO-CH_3$	$3CH_3-30CH_2-9(CH=CH)-3COO-2CH_2-CH$
Margaric	CH_3-15CH_2-COOH	$CH_3-15CH_2-COO-CH_3$	$3CH_3-45CH_2-3COO-2CH_2-CH$
Margaroleic	$CH_3-13CH_2-CH=CH-COOH$	$CH_3-13CH_2-CH=CH-COO-CH_3$	$3CH_3-39CH_2-3(CH=CH)-3COO-2CH_2-CH$
Araquic	CH_3-18CH_2-COOH	$CH_3-18CH_2-COO-CH_3$	$3CH_3-54CH_2-3COO-2CH_2-CH$
Eicosenoic	$CH_3-16CH_2-CH=CH-COOH$	$CH_3-16CH_2-CH=CH-COO-CH_3$	$3CH_3-48CH_2-3(CH=CH)-3COO-2CH_2-CH$
Behenic	CH_3-20CH_2-COOH	$CH_3-20CH_2-COO-CH_3$	$3CH_3-60CH_2-3COO-2CH_2-CH$
Eruric	$CH_3-18CH_2-CH=CH-COOH$	$CH_3-18CH_2-CH=CH-COO-CH_3$	$3CH_3-54CH_2-3(CH=CH)-3COO-2CH_2-CH$

Table A.3: Characteristic of molecules for different kind of oils. Part 2

	Chemical structure		
Name	Phosphatides	NA/K Soap	Sunflower wax *
Caproic	$2CH_3-8CH_2-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-4CH_2-COO-K$	$CH_3-4CH_2-COO-C-R$
Lauric	$2CH_3-20CH_2-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-10CH_2-COO-K$	$CH_3-10CH_2-COO-C-R$
Miristic	$2CH_3-24CH_2-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-12CH_2-COO-K$	$CH_3-12CH_2-COO-C-R$
Palmitic	$2CH_3-28CH_2-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-14CH_2-COO-K$	$CH_3-14CH_2-COO-C-R$
Palmitoleic	$2CH_3-24CH_2-2(CH=CH)-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-12CH_2-CH=CH-COO-K$	$CH_3-12CH_2-CH=CH-COO-C-R$
Estearic	$2CH_3-32CH_2-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-16CH_2-COO-K$	$CH_3-16CH_2-COO-C-R$
Oleic	$2CH_3-28CH_2-2(CH=CH)-2COO-2CH_2-CH-(O-PO_2-O)-2CH_2-N-3CH_2$	$CH_3-14CH_2-CH=CH-COO-K$	$CH_3-14CH_2-CH=CH-COO-C-R$
Linoleic	$2CH_3-24CH_2-4(CH=CH)-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-12CH_2-2(CH=CH)-COO-K$	$CH_3-12CH_2-2(CH=CH)-COO-C-R$
Linolenic	$2CH_3-20CH_2-6(CH=CH)-2COO-2CH_2-CH-(O-PO_2-O)-2CH_2-N-3CH_2$	$CH_3-10CH_2-3(CH=CH)-COO-K$	$CH_3-10CH_2-3(CH=CH)-COO-C-R$
Margaric	$2CH_3-30CH_2-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-15CH_2-COO-K$	$CH_3-15CH_2-COO-C-R$
Margaroleic	$2CH_3-26CH_2-2(CH=CH)-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-13CH_2-CH=CH-COO-K$	$CH_3-13CH_2-CH=CH-COO-C-R$
Araquic	$2CH_3-36CH_2-2COO-2CH_2-CH-(O-PO_2-O)-2CH_2-N-3CH_2$	$CH_3-18CH_2-COO-K$	$CH_3-18CH_2-COO-C-R$
Eicosenoic	$2CH_3-32CH_2-2(CH=CH)-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-16CH_2-CH=CH-COO-K$	$CH_3-16CH_2-CH=CH-COO-C-R$
Behenic	$2CH_3-40CH_2-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-20CH_2-COO-K$	$CH_3-20CH_2-COO-C-R$
Eruric	$2CH_3-36CH_2-2(CH=CH)-2COO-2CH_2-CH-(O-PO2-O)-2CH_2-N-3CH_2$	$CH_3-18CH_2-CH=CH-COO-K$	$CH_3-18CH_2-CH=CH-COO-C-R$

* the $-R$ group in the wax is assumed to be equal to the inverse chain before the $COO-$ group

Table A.5: Joback's constants for FFA composition

	Groups					**Constants values** (J/mol °K)			
	CH3−	CH2−	CH−	CH =	COOH	A	B	C	D
Caproic	1	4	0	0	1	2.03	0.62	-3.75E-04	-3.24E-07
Lauric	1	10	0	0	1	-3.42	1.19	-7.02E-04	-2.52E-07
Miristic	1	12	0	0	1	-5.24	1.38	-8.10E-04	-2.29E-07
Palmitic	1	14	0	0	1	-7.06	1.57	-9.19E-04	-2.05E-07
Palmitoleic	1	12	1	1	1	-36.24	1.69	-1.17E-03	-7.30E-08
Estearic	1	16	0	0	1	-8.87	1.76	-1.03E-03	-1.81E-07
Oleic	1	14	1	1	1	-38.06	1.88	-1.28E-03	-4.92E-08
Linoleic	1	12	2	2	1	-67.24	2.00	-1.53E-03	8.26E-08
Linolenic	1	10	3	3	1	-96.42	2.12	-1.79E-03	2.14E-07
Margaric	1	15	0	0	1	-7.97	1.67	-9.74E-04	-1.93E-07
Margaroleic	1	13	1	1	1	-37.15	1.79	-1.23E-03	-6.11E-08
Araquic	1	18	0	0	1	-10.69	1.95	-1.14E-03	-1.57E-07
Eicosenoic	1	16	1	1	1	-39.87	2.07	-1.39E-03	-2.54E-08
Behenic	1	20	0	0	1	-12.51	2.14	-1.25E-03	-1.33E-07
Eruric	1	18	1	1	1	-41.69	2.26	-1.50E-03	-1.60E-09

Table A.6: Joback's constants for methyl ester composition

	Groups					**Constants values** (J/mol °K)			
	CH3−	CH2−	CH−	CH =	COO−	A	B	C	D
Caproic	2	4	0	0	1	21.93	0.61	-2.62E-04	-3.97E-07
Lauric	2	10	0	0	1	16.48	1.18	-5.89E-04	-3.26E-07
Miristic	2	12	0	0	1	14.66	1.37	-6.98E-04	-3.02E-07
Palmitic	2	14	0	0	1	12.84	1.56	-8.06E-04	-2.78E-07
Palmitoleic	2	12	1	1	1	-16.34	1.68	-1.06E-03	-1.46E-07
Estearic	2	16	0	0	1	11.03	1.75	-9.15E-04	-2.54E-07
Oleic	2	14	1	1	1	-18.16	1.87	-1.17E-03	-1.22E-07
Linoleic	2	12	2	2	1	-47.34	1.99	-1.42E-03	9.40E-09
Linolenic	2	10	3	3	1	-76.52	2.11	-1.67E-03	1.41E-07
Margaric	2	15	0	0	1	11.94	1.66	-8.61E-04	-2.66E-07
Margaroleic	2	13	1	1	1	-17.25	1.78	-1.11E-03	-1.34E-07
Araquic	2	18	0	0	1	9.21	1.94	-1.02E-03	-2.30E-07
Eicosenoic	2	16	1	1	1	-19.97	2.06	-1.28E-03	-9.86E-08
Behenic	2	20	0	0	1	7.39	2.13	-1.13E-03	-2.07E-07
Eruric	2	18	1	1	1	-21.79	2.25	-1.39E-03	-7.48E-08

Table A.7: Joback's constants for crude oil composition

	Groups					**Constants values** (J/mol °K)			
	CH3−	CH2−	CH−	CH =	COO−	A	B	C	D
Caproic	3	14	1	0	3	58.34	1.84	-8.38E-04	-3.45E-07
Lauric	3	32	1	0	3	41.98	3.55	-1.82E-03	-1.31E-07
Miristic	3	38	1	0	3	36.53	4.12	-2.14E-03	-5.95E-08
Palmitic	3	44	1	0	3	31.07	4.69	-2.47E-03	1.19E-08
Palmitoleic	3	38	4	3	3	-56.47	5.05	-3.23E-03	4.07E-07
Estearic	3	50	1	0	3	25.62	5.26	-2.80E-03	8.33E-08
Oleic	3	44	4	3	3	-61.93	5.62	-3.55E-03	4.79E-07
Linoleic	3	38	7	6	3	-149.47	5.97	-4.31E-03	8.74E-07
Linolenic	3	32	10	9	3	-237.02	6.33	-5.07E-03	1.27E-06
Margaric	3	47	1	0	3	28.35	4.98	-2.63E-03	4.76E-08
Margaroleic	3	41	4	3	3	-59.20	5.33	-3.39E-03	4.43E-07
Araquic	3	56	1	0	3	20.17	5.83	-3.12E-03	1.55E-07
Eicosenoic	3	50	4	3	3	-67.38	6.19	-3.88E-03	5.50E-07
Behenic	3	62	1	0	3	14.71	6.40	-3.45E-03	2.26E-07
Eruric	3	56	4	3	3	-74.03	6.76	-4.21E-03	6.22E-07

Table A.8: Joback's constants for sunflower wax composition

	Groups					**Constants values** (J/mol °K)			
	CH3−	CH2−	CH−	CH =	COO−	A	B	C	D
Caproic	2	9	0	0	1	17.39	1.09	-5.34E-04	-3.38E-07
Lauric	2	21	0	0	1	6.48	2.23	-1.19E-03	-1.95E-07
Miristic	2	25	0	0	1	2.85	2.61	-1.40E-03	-1.47E-07
Palmitic	2	29	0	0	1	-0.79	2.99	-1.62E-03	-9.95E-08
Palmitoleic	2	25	2	2	1	-59.16	3.23	-2.13E-03	1.64E-07
Estearic	2	33	0	0	1	-4.43	3.37	-1.84E-03	-5.19E-08
Oleic	2	29	2	2	1	-62.79	3.61	-2.35E-03	2.12E-07
Linoleic	2	25	4	4	1	-121.16	3.85	-2.85E-03	4.75E-07
Linolenic	2	21	6	6	1	-179.52	4.08	-3.36E-03	7.39E-07
Margaric	2	31	0	0	1	-2.61	3.18	-1.73E-03	-7.57E-08
Margaroleic	2	27	2	2	1	-60.97	3.42	-2.24E-03	1.88E-07
Araquic	2	37	0	0	1	-8.06	3.75	-2.06E-03	-4.30E-09
Eicosenoic	2	33	2	2	1	-66.43	3.99	-2.56E-03	2.59E-07
Behenic	2	41	0	0	1	-11.70	4.13	-2.28E-03	4.33E-08
Eruric	2	37	2	2	1	-70.06	4.37	-2.78E-03	3.07E-07

Table A.9: Joback's constants for phosphatides composition

	Groups								**Constants values** (J/mol °K)			
	CH3−	CH2−	CH−	CH =	O−	O =	N	COO−	A	B	C	D
Caproic	2	15	1	0	3	1	1	2	65.66	1.96024	-1.06E-03	1.85E-07
Lauric	2	27	1	0	3	1	1	2	54.75	3.10024	-1.71E-03	3.27E-07
Miristic	2	31	1	0	3	1	1	2	51.11	3.48024	-1.93E-03	3.75E-07
Palmitic	2	35	1	0	3	1	1	2	47.48	3.86024	-2.15E-03	4.23E-07
Palmitoleic	2	31	3	2	3	1	1	2	-10.89	4.09824	-2.65E-03	6.86E-07
Estearic	2	39	1	0	3	1	1	2	43.84	4.24024	-2.37E-03	4.70E-07
Oleic	2	51	3	2	3	1	1	2	-29.07	5.99824	-3.74E-03	9.24E-07
Linoleic	2	31	5	4	3	1	1	2	-72.89	4.71624	-3.38E-03	9.97E-07
Linolenic	2	27	7	6	3	1	1	2	-131.25	4.95424	-3.88E-03	1.26E-06
Margaric	2	37	1	0	3	1	1	2	45.66	4.05024	-2.26E-03	4.46E-07
Margaroleic	2	33	3	2	3	1	1	2	-12.71	4.28824	-2.76E-03	7.10E-07
Araquic	2	43	1	0	3	1	1	2	40.20	4.62024	-2.58E-03	5.18E-07
Eicosenoic	2	39	3	2	3	1	1	2	-18.16	4.85824	-3.09E-03	7.81E-07
Behenic	2	47	1	0	3	1	1	2	36.57	5.00024	-2.80E-03	5.65E-07
Eruric	2	43	3	2	3	1	1	2	-21.80	5.23824	-3.31E-03	8.29E-07

Table A.10: Joback's constants for Na/K soap composition

	Groups						Constants values (J/mol °K)			
	CH3−	CH2−	CH−	CH =	COO−	Na/K	A	B	C	D
Caproic	1	4	0	0	1	1	2.43	0.62	-4.15E-04	-3.00E-07
Lauric	1	10	0	0	1	1	-3.02	1.19	-7.42E-04	-2.29E-07
Miristic	1	12	0	0	1	1	-4.84	1.38	-8.51E-04	-2.05E-07
Palmitic	1	14	0	0	1	1	-6.66	1.57	-9.59E-04	-1.81E-07
Palmitoleic	1	12	1	1	1	1	-35.84	1.69	-1.21E-03	-4.95E-08
Estearic	1	16	0	0	1	1	-8.47	1.76	-1.07E-03	-1.58E-07
Oleic	1	14	1	1	1	1	-37.66	1.88	-1.32E-03	-2.57E-08
Linoleic	1	12	2	2	1	1	-66.84	2.00	-1.57E-03	1.06E-07
Linolenic	1	10	3	3	1	1	-96.02	2.12	-1.83E-03	2.38E-07
Margaric	1	15	0	0	1	1	-7.57	1.67	-1.01E-03	-1.69E-07
Margaroleic	1	13	1	1	1	1	-36.75	1.79	-1.27E-03	-3.76E-08
Araquic	1	18	0	0	1	1	-10.29	1.95	-1.18E-03	-1.34E-07
Eicosenoic	1	16	1	1	1	1	-39.47	2.07	-1.43E-03	-1.90E-09
Behenic	1	20	0	0	1	1	-12.11	2.14	-1.29E-03	-1.10E-07
Eruric	1	18	1	1	1	1	-41.29	2.26	-1.54E-03	2.19E-08

Table A.11: Joback's constant values and molecular weights of biodiesel obtained from different sources

	Molecular weight	Constant Values (J/mol °K)			
Substance		A	B	C	D
Sunflower					
FFA	280.19	-53.493	1.939	-1.41E-03	1.95E-08
ME	294.19	-33.573	1.928	-1.30E-03	-5.38E-08
Oil	878.55	-108.186	5.782	-3.94E-03	6.85E-07
Ph-L	802.61	-48.960	4.967	-3.35E-03	9.19E-07
Na soap	302.19	-53.093	1.936	-1.45E-03	4.30E-08
K soap	318.32	-53.093	1.936	-1.45E-03	4.30E-08
Wax	528.34	-93.652	3.717	-2.60E-03	3.49E-07
Rapeseed					
FFA	281.38	-46.780	1.916	-1.35E-03	-1.01E-08
ME	295.41	-26.880	1.906	-1.24E-03	-8.33E-08
Oil	882.19	-88.102	5.715	-3.78E-03	5.96E-07
Ph-L	890.99	-41.179	5.505	-3.57E-03	9.32E-07
Na soap	303.36	-46.380	1.914	-1.39E-03	1.34E-08
K soap	319.47	-46.380	1.914	-1.39E-03	1.34E-08
Palm					
FFA	273.19	-31.065	1.792	-1.19E-03	-8.62E-08
ME	287.22	-11.165	1.781	-1.08E-03	-1.59E-07
Oil	857.63	-40.954	5.342	-3.28E-03	3.68E-07
Ph-L	843.20	-7.714	5.044	-3.11E-03	7.54E-07
Na soap	295.18	-30.665	1.789	-1.23E-03	-6.27E-08
K soap	311.29	-30.665	1.789	-1.23E-03	-6.27E-08
UCO					
FFA	273.40	-42.517	1.847	-1.29E-03	-2.83E-08
ME	287.70	-22.912	1.836	-1.18E-03	-1.00E-07
UCO	859.12	-76.084	5.508	-3.59E-03	5.32E-07
Ph-L	817.16	-29.994	4.983	-3.22E-03	8.37E-07
Na soap	295.06	-42.123	1.844	-1.33E-03	-5.13E-09
K soap	310.93	-42.123	1.844	-1.33E-03	-5.13E-09

A.2 Chemical exergies

To compute the chemical exergies of biodiesel, eq. (3.6) is applied, which built the standard free Gibbs energy of formation $\Delta_f G^0$.

Two methods, based on group contribution methods, are use to compute it. According to Van-Krevelen Chermin, the standard Gibbs free energy of formation can be written as [250]:

$$\Delta_f G^0 = \sum_j A_j + B_j T \tag{A.2}$$

where the values of the constant A_j and B_j at 298°K for the relevant groups of the substances analyzed in this thesis are shown in table A.12.

Table A.12: Constants used in Van Krevelen-Chermin method

			ΔG_f	
Group	A	$B \times 10^2$	T=298.15 °K	T=313.15 °K
CH_3-	-10.943	2.215	-18.137	-16.748
CH_2-	-5.193	2.430	8.578	10.101
CH	-0.705	2.910	33.319	35.144
$CH=CH$	17.663	1.965	98.320	99.553
COOH	-98.390	2.860	-375.627	-373.834
OH	-41.560	1.280	-157.769	-156.966
$COO-$	-92.620	2.610	-354.624	-352.988
C	1.958	3.735	54.733	57.074

The method developed by Jankowski [147] uses the following equation:

$$\Delta_f G^0 = \sum_{i=1} N_i \Delta_f G_i^0 \tag{A.3}$$

where $\Delta_f G_i^0$ is the standard free Gibbs contribution of group i, and N_i is the number of instances of group i in the molecular structure. The values of the relevant groups for the calculation of FFA are shown in table A.13.

Table A.13: Values of standard free Gibbs contributions of chemical groups for Jankowsky method [147]

Group	$\Delta_f G^0$ (kJ/mol)
CH_3-	-15.257
CH_2-	6.7716
$CH-$	21.234
$CH=$	53.504
$COO-$	-347.36
$O-PO_2-O$	-978.12
$N-$	101.99
Na [202]	-262.05
K [202]	-282.44

Table A.14: Standard Gibbs free energy of formation and molecular weight for FFA composition using Van Krevelen-Chermin method

	Groups				Molecular weight	$\Delta_f G^0$ kJ/mol	$\Delta_f G^0$ kJ/kg
	CH_3-	CH_2-	$CH=CH$	COOH			
Caproic	1	4	0	1	116.16	-359.45	-3094.52
Lauric	1	10	0	1	200.32	-307.99	-1537.50
Miristic	1	12	0	1	228.37	-290.83	-1273.51
Palmitic	1	14	0	1	256.42	-273.68	-1067.29
Palmitoleic	1	12	1	1	254.41	-192.51	-756.71
Estearic	1	16	0	1	284.48	-256.52	-901.74
Oleic	1	14	1	1	282.46	-175.36	-620.82
Linoleic	1	12	2	1	280.45	-94.19	-335.87
Linolenic	1	10	3	1	278.43	-13.03	-46.79
Margaric	1	15	0	1	270.45	-265.10	-980.22
Margaroleic	1	13	1	1	268.43	-183.94	-685.21
Araquic	1	18	0	1	312.53	-239.37	-765.90
Eicosenoic	1	16	1	1	310.51	-158.20	-509.49
Behenic	1	20	0	1	340.58	-222.21	-652.45
Eruric	1	18	1	1	338.57	-141.05	-416.60

Table A.15: Standard Gibbs free energy of formation and molecular weight for methylester composition using Van Krevelen-Chermin method

	Groups				Molecular weight	$\Delta_f G^0$ kJ/mol	$\Delta_f G^0$ kJ/kg
	CH_3-	CH_2-	$CH=CH$	$COO-$			
Caproic	2	4	0	1	130.18	-356.59	-2739.09
Lauric	2	10	0	1	214.34	-305.12	-1423.52
Miristic	2	12	0	1	242.40	-287.97	-1188.00
Palmitic	2	14	0	1	270.45	-270.81	-1001.34
Palmitoleic	2	12	1	1	268.43	-189.65	-706.49
Estearic	2	16	0	1	298.50	-253.66	-849.76
Oleic	2	14	1	1	296.49	-172.49	-581.78
Linoleic	2	12	2	1	294.47	-91.33	-310.14
Linolenic	2	10	3	1	292.46	-10.16	-34.74
Margaric	2	15	0	1	284.48	-262.23	-921.81
Margaroleic	2	13	1	1	282.46	-181.07	-641.04
Araquic	2	18	0	1	326.56	-236.50	-724.23
Eicosenoic	2	16	1	1	324.54	-155.34	-478.63
Behenic	2	20	0	1	354.61	-219.35	-618.56
Eruric	2	18	1	1	352.59	-138.18	-391.90

Table A.16: Standard Gibbs free energy of formation and molecular weight for crude oil composition using Van Krevelen-Chermin method

	Groups					Molecular weight	$\Delta_f G^0$ kJ/mol	$\Delta_f G^0$ kJ/kg
	CH_3-	CH_2-	$CH-$	$CH=CH$	$COO-$			
Caproic	3	14	1	0	3	386.52	-964.88	-2496.30
Lauric	3	32	1	0	3	639.00	-810.48	-1268.36
Miristic	3	38	1	0	3	723.16	-759.02	-1049.58
Palmitic	3	44	1	0	3	807.32	-707.55	-876.42
Palmitoleic	3	38	1	3	3	801.27	-464.06	-579.15
Estearic	3	50	1	0	3	891.48	-656.09	-735.95
Oleic	3	44	1	3	3	885.43	-412.59	-465.98
Linoleic	3	38	1	6	3	879.38	-169.09	-192.29
Linolenic	3	32	1	9	3	873.34	74.40	85.19
Margaric	3	47	1	0	3	849.40	-681.82	-802.71
Margaroleic	3	41	1	3	3	843.35	-438.32	-519.74
Araquic	3	56	1	0	3	975.64	-604.62	-619.72
Eicosenoic	3	50	1	3	3	969.59	-361.12	-372.45
Behenic	3	62	1	0	3	1059.80	-553.16	-521.94
Eruric	3	56	1	3	3	1053.75	-309.66	-293.86

Table A.17: Standard Gibbs free energy of formation and molecular weight for sunflower wax composition using Van Krevelen-Chermin method

	Groups					Molecular weight	$\Delta_f G^0$ kJ/mol	$\Delta_f G^0$ kJ/kg
	CH_3-	CH_2-	$C-$	$CH=CH$	$COO-$			
Caproic	2	8	1	0	1	198.30	-267.54	-1349.18
Lauric	2	20	1	0	1	366.62	-164.61	-449.00
Miristic	2	24	1	0	1	422.73	-130.30	-308.25
Palmitic	2	28	1	0	1	478.83	-95.99	-200.47
Palmitoleic	2	24	1	2	1	474.80	66.34	139.71
Estearic	2	32	1	0	1	534.94	-61.68	-115.31
Oleic	2	28	1	2	1	530.91	100.65	189.58
Linoleic	2	24	1	4	1	526.88	262.98	499.13
Linolenic	2	20	1	6	1	522.84	425.31	813.45
Margaric	2	30	1	0	1	506.89	-78.84	-155.54
Margaroleic	2	26	1	2	1	502.85	83.49	166.04
Araquic	2	36	1	0	1	591.05	-27.37	-46.31
Eicosenoic	2	32	1	2	1	587.01	134.96	229.90
Behenic	2	40	1	0	1	647.15	6.94	10.72
Eruric	2	36	1	2	1	643.12	169.27	263.20

Table A.18: Standard Gibbs free energy of formation and molecular weight for phosphatide composition using Jankowsky method

	Groups							Molecular weight	$\Delta_f G^0$ kJ/mol	$\Delta_f G^0$ kJ/kg
	CH_3-	CH_2-	$CH-$	$CH=$	$O-PO_2-O$	N	$COO-$			
Caproic	2	15	1	0	1	1	2	450.48	-1478.55	-3282.14
Lauric	2	27	1	0	1	1	2	618.80	-1397.29	-2258.06
Miristic	2	31	1	0	1	1	2	674.91	-1370.20	-2030.21
Palmitic	2	35	1	0	1	1	2	731.02	-1343.12	-1837.33
Palmitoleic	2	31	3	2	1	1	2	726.98	-1220.73	-1679.17
Estearic	2	39	1	0	1	1	2	787.12	-1316.03	-1671.95
Oleic	2	51	3	2	1	1	2	1007.51	-1085.30	-1077.20
Linoleic	2	31	5	4	1	1	2	779.06	-1071.25	-1375.06
Linolenic	2	27	7	6	1	1	2	775.03	-948.86	-1224.29
Margaric	2	37	1	0	1	1	2	759.07	-1329.57	-1751.59
Margaroleic	2	33	3	2	1	1	2	755.04	-1207.18	-1598.84
Araquic	2	43	1	0	1	1	2	843.23	-1288.94	-1528.58
Eicosenoic	2	39	3	2	1	1	2	839.20	-1166.55	-1390.09
Behenic	2	47	1	0	1	1	2	899.33	-1261.86	-1403.10
Eruric	2	43	3	2	1	1	2	895.30	-1139.47	-1272.72

Table A.19: Standard Gibbs free energy of formation and molecular weight for Na/K soap composition using Van Krevelen-Chermin method

	Groups					Na Soap			K Soap		
	CH_3-	CH_2-	$CH = CH$	$COO-$	Na/K	Molecular weight	$\Delta_f G^0$ kJ/mol	$\Delta_f G^0$ kJ/kg	Molecular weight	$\Delta_f G^0$ kJ/mol	$\Delta_f G^0$ kJ/kg
Caproic	1	4	0	1	1	138.14	-600.50	-4347.03	154.25	-620.89	-4025.16
Lauric	1	10	0	1	1	222.30	-549.03	-2469.79	238.41	-569.43	-2388.41
Miristic	1	12	0	1	1	250.35	-531.88	-2124.52	266.46	-552.27	-2072.58
Palmitic	1	14	0	1	1	278.41	-514.72	-1848.82	294.52	-535.12	-1816.92
Palmitoleic	1	12	1	1	1	276.39	-433.56	-1568.65	292.50	-453.95	-1551.95
Estearic	1	16	0	1	1	306.46	-497.57	-1623.60	322.57	-517.96	-1605.72
Oleic	1	14	1	1	1	304.44	-416.40	-1367.75	320.56	-436.79	-1362.62
Linoleic	1	12	2	1	1	302.43	-335.24	-1108.49	318.54	-355.63	-1116.44
Linolenic	1	10	3	1	1	300.41	-254.07	-845.75	316.52	-274.46	-867.12
Margaric	1	15	0	1	1	292.43	-506.15	-1730.81	308.54	-526.54	-1706.52
Margaroleic	1	13	1	1	1	290.42	-424.98	-1463.35	306.53	-445.37	-1452.95
Araquic	1	18	0	1	1	334.51	-480.41	-1436.16	350.62	-500.81	-1428.32
Eicosenoic	1	16	1	1	1	332.50	-399.25	-1200.76	348.61	-419.64	-1203.76
Behenic	1	20	0	1	1	362.57	-463.26	-1277.72	378.68	-483.65	-1277.21
Eruric	1	18	1	1	1	360.55	-382.09	-1059.75	376.66	-402.48	-1068.56

Table A.20: Chemical exergies of the vegetable oils, free fatty acids, phosphatides, soaps, waxes, unsaponifiable matter and methyl esters (kJ/kg)

		Molar fraction (N_i)							Exergy (kJ/kg)		
Sustance	$\Delta_f G^0$ (kJ/kg)	C	H	O	P	N	Na	K	Szargut [217]	Szargut [154]	Rivero [202]
Sunflower											
FFA	-479.72	0.768	0.118	0.114	0.000	0.000	0.000	0.000	39,563.49	39,739.65	39,552.21
ME	-446.89	0.772	0.119	0.109	0.000	0.000	0.000	0.000	39,888.26	40,066.09	39,877.65
Oil	-329.08	0.776	0.115	0.109	0.000	0.000	0.000	0.000	39,653.88	39,827.09	39,643.18
Ph-L	-1,401.45	0.716	0.109	0.120	0.039	0.017	0.000	0.000	36,263.08	36,424.80	36,250.84
Na soap	-1,314.49	0.712	0.106	0.106	0.000	0.000	0.076	0.000	36,536.20	36,719.13	36,525.68
K soap	-1,311.96	0.676	0.101	0.101	0.000	0.000	0.000	0.123	34,715.03	34,881.60	34,705.20
Wax	-218.03	0.816	0.123	0.061	0.000	0.000	0.000	0.000	42,102.89	42,287.82	42,098.18
Rapeseed											
FFA	-539.81	0.767	0.119	0.114	0.000	0.000	0.000	0.000	39,652.31	39,830.26	39,641.10
ME	-504.36	0.771	0.121	0.108	0.000	0.000	0.000	0.000	39,967.33	40,146.84	39,956.79
Oil	-387.52	0.775	0.117	0.109	0.000	0.000	0.000	0.000	39,733.89	39,908.81	39,723.26
Ph-L	-1,246.56	0.729	0.113	0.108	0.035	0.016	0.000	0.000	37,334.81	37,502.48	37,324.08
Na soap	-1,365.44	0.711	0.107	0.105	0.000	0.000	0.076	0.000	36,635.12	36,819.71	36,624.66
K soap	-1,365.44	0.675	0.102	0.100	0.000	0.000	0.000	0.122	34,812.37	34,980.57	34,802.59
Palm											
FFA	-741.03	0.761	0.122	0.117	0.000	0.000	0.000	0.000	39,546.21	39,726.89	39,534.61
ME	-694.15	0.766	0.123	0.111	0.000	0.000	0.000	0.000	39,875.98	40,058.14	39,865.08
Oil	-574.68	0.769	0.119	0.112	0.000	0.000	0.000	0.000	39,635.59	39,813.04	39,624.60
Ph-L	-1,452.26	0.719	0.113	0.114	0.037	0.017	0.000	0.000	36,880.07	37,047.70	36,868.58
Na soap	-1,575.19	0.704	0.109	0.108	0.000	0.000	0.078	0.000	36,452.63	36,639.93	36,441.83
K soap	-1,558.54	0.668	0.104	0.103	0.000	0.000	0.000	0.126	34,597.19	34,767.53	34,587.10
UCO											
FFA	-588.51	0.765	0.120	0.117	0.000	0.000	0.000	0.000	39,581.13	39,759.43	39,569.52
ME	-549.85	0.768	0.121	0.111	0.000	0.000	0.000	0.000	39,837.55	40,017.13	39,826.66
Oil	-433.30	0.772	0.117	0.112	0.000	0.000	0.000	0.000	39,599.35	39,774.28	39,588.36
Ph-L	-1,384.51	0.719	0.111	0.117	0.038	0.017	0.000	0.000	36,687.44	36,852.43	36,675.49
Na soap	-1,408.80	0.709	0.108	0.108	0.000	0.000	0.078	0.000	36,559.52	36,744.87	36,548.70
K soap	-1,399.95	0.673	0.102	0.103	0.000	0.000	0.000	0.126	34,726.33	34,894.96	34,716.23

Table A.21: Chemical exergies obtained from the bibliography

	e^{CH} (kJ/kg)	e^{CH} (kJ/kmol)	$\Delta_f G^0$ (kJ/kmol)	Source
$CaCO_3$	175.75	17,590.00	-1,130.02	[43]
CaO	2,133.02	119.62	n.a.	[154]
$Ca_3(PO_4)_2$	748.64	23,221.00	-3,700.71	[43]
CH_3ONa	20,411.59		-89.48	
Citric acid	17,795.39		-203.88	
Cl_2	1,749.07	124,020.00	n.a.	[43]
Fresh fruit bunches	15,840.00		n.a.	[148]]
Glucosides	37,806.66		-153.32	
Glycerol	23,677.92		-116.18	[147]
H_2	117,119.25	236,100.00	n.a.	[43]
HCl	1,340.88	48,890.00	-131.17	[43]
H_2O liquid	173.19	3,120.00	n.a.	[154]
H_2O steam	650.00	11,710.00	n.a.	[154]
H_3PO_4	1,098.32	98,850.00	n.a.	[154]
H_2SO_4	1,641.67	161,010.00	n.a.	[154]
Impurities	756.66		n.a.	
K_2O	4,517.27	425,540.00	n.a.	[154]
KOH	822.86	46,170.00	-440.53	[43]
Methanol	23,154.00		n.a.	
Mo	7,611.74	730,270.00	n.a.	[43]
Montmorillonite	48.53	17,800.00	-5,355.92	[43]
NaCl	379.86	22,200.00	n.a.	[154]
Na_2CO_3	501.28	53,130.00	n.a.	[154]
$NaHCO_3$	649.24	54,540.00	-816.43	[43]
Natural gas	55,050.00		n.a.	
NaOH	968.32	38,730.00	-418.02	[43]
NH_3	20,037.58	341,250.00	n.a.	[154]
Ni	3,964.84	23,271.00	n.a.	[43]
N2O	2,413.39	106,220.00	104.25	[154]
Palm kernel meal	10,465.00		n.a.	[103]
Pesticide	19,326.96		156.44	[147]
P_2O_5	2,251.16	319,540.00	n.a.	[154]
Rape seed	28,660.00		n.a.	[135]
Rapeseed meal	7,410.64		n.a.	[144]
Silvite (KCl)	258.08	19,240.00	-409.43	[43]
Soybean meal	9,378.43		n.a.	[144]
Soybean seed	21,100.00		n.a.	[54]
Sunflower meal	7,368.77		n.a.	[144]
Sunflower seed	28,660.00		n.a.	*
Tocopherol	42,557.85		77.99	
Unsaponifiables	40,182.26		n.a.	

* Same as rape seed

Appendix B

Thermoeconomic models for Land-to-tank bioenergy plants

This appendix shows the information about the thermoeconomic models of the four examples of land-to-tank biodiesel cycles analysed in this Ph.D. The description of direct process considered in the LCA are show in table B.1.

For each example, the flow diagram fig. B.1 and the tables with the exergy values of the external resources B.2 and internal flows B.3 are shown. With this information the F–P table B.4 is built and the distribution matrix, production operator and elasticity matrices are computed, see table B.5. Finally the cost and renewability diagram is also shown for each example, see fig. B.2.

Table B.1: Direct processes considered in the life cycle analysis

Process	Rapeseed and sunflower	Soybean	Palm
1	Cultivation	Cultivation	Cultivation
2	Drying	Road and maritime transport	Road transport and storage
3	Transport	Extraction	Extraction
4	Extraction	Maritime transport	Road transport, Depot and Maritime transport
5	Refining	Refining	Refining
6	Pretreatment and transesterification	Pretreatment and transesterification	Pretreatment and transesterification
7	FAME washing	FAME washing	FAME washing
8	Glycerol refining	Glycerol refining	Glycerol refining

B.1 Biodiesel plant model using rapeseed or sunflower oil

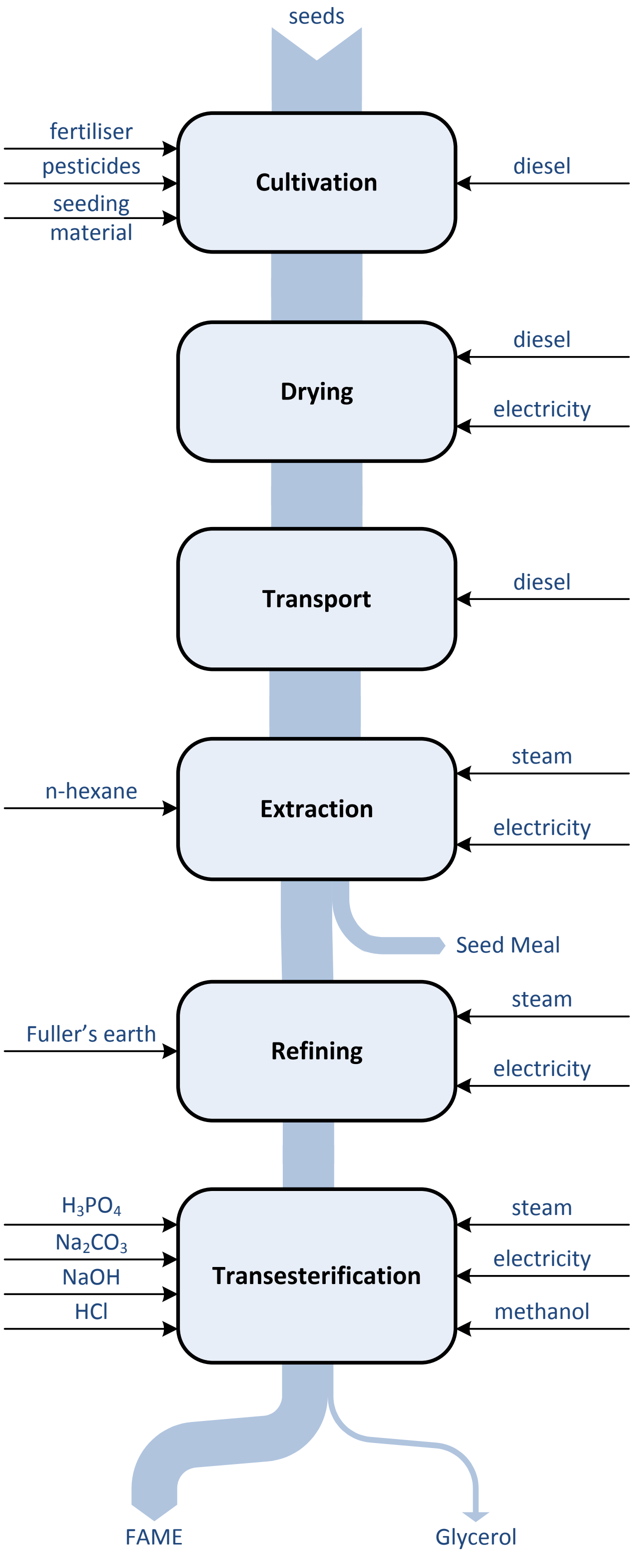

Figure B.1: Flow Diagram for biodiesel production from rapeseed and sunflower oil

Table B.2: Exergy and exergoecologic cost of input flows for the rapeseed biodiesel pathway

				Exergy		Cost	
Inputs	Process	Unit (u)	u/kgFAME	MJ/u	MJ/kg FAME	MJ/u	MJ/kg FAME
N fertiliser	1	kg	0.1195	20.0376	2.3941	67.2664	8.0370
CaO fertiliser	1	kg	0.0165	2.1330	0.0352	1.5223	0.0251
K_2O fertiliser	1	kg	0.0430	4.5173	0.1942	8.6897	0.3737
P_2O_5 fertiliser	1	kg	0.0293	2.2512	0.0659	11.4420	0.3349
Pesticides	1	kg	0.0011	19.3270	0.0207	198.0960	0.2120
Seeding material	1	kg	0.0052	28.6600	0.1496	6.4600	0.0337
Diesel	1	MJ	2.5760	1.0000	2.5760	1.1773	3.0327
Diesel	2	MJ	0.0116	1.0000	0.0116	1.1773	0.0136
Electricity	2	MJ	0.1981	1.0000	0.1981	2.8690	0.5683
Diesel	3	MJ	0.1270	1.0000	0.1270	1.1773	0.1495
n-hexane	4	kg	0.0026	49.4764	0.1296	53.1324	0.1392
Steam	4	MJ	1.8253	1.0000	1.8253	2.6258	4.7929
Electricity	4	MJ	0.3274	1.0000	0.3274	2.8690	0.9394
Fuller’s earth	5	kg	0.0062	0.0178	0.0001	2.5885	0.0162
Steam	5	MJ	0.3079	1.0000	0.3079	1.1617	0.3576
Electricity	5	MJ	0.0225	1.0000	0.0225	2.8690	0.0645
H_3PO_4	6	kg	0.0017	1.0983	0.0019	36.2858	0.0617
HCl	6	kg	0.0200	1.3409	0.0268	5.2484	0.1050
Na_2CO_3	6	kg	0.0025	0.5013	0.0013	14.0635	0.0352
NaOH	6	kg	0.0067	0.9683	0.0065	5.0273	0.0338
Methanol	6	kg	0.1087	23.1540	2.5175	30.3074	3.2953
Steam	6	MJ	1.5452	1.0000	1.5452	1.1617	1.7950
Electricity	6	MJ	0.1080	1.0000	0.1080	2.8690	0.3099

Table B.3: Exergy of products and intermediate flows in rapeseed biodiesel cycle

Flow	Process	Mass ratio kg/kg $_{\text{FAME}}$	Exergy MJ/kg	Exergy MJ/kg $_{\text{FAME}}$
Rape seed	1	2.7018	28.600	77.271
Dry rape seed	2	2.7018	28.600	77.271
Rape seed after transport	3	2.675	28.600	76.506
Crude oil	4	1.0834	39.734	43.047
Rapeseed meal	4	1.5913	7.411	11.792
Plant oil	5	1.0401	39.734	41.325
Crude FAME	6	-	-	40.476
Crude glycerol	6	-	-	3.312
FAME	7	1.0000	40.062	40.062
Glycerol	8	0.1056	23.678	2.500

Table B.4: F–P Table for rapeseed oil (MJ/kg FAME)

	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0^{rs}		77.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	77.42
C_0^{rs}		12.06	0.58	0.15	2.88	0.44	4.37	0.24	1.02	21.75
P_0		82.71	0.21	0.13	1.01	0.13	2.82	0.08	0.31	87.40
P_1	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	0.00	77.27
P_2	0.00	0.00	0.00	77.27	0.00	0.00	0.00	0.00	0.00	77.27
P_3	0.00	0.00	0.00	0.00	76.51	0.00	0.00	0.00	0.00	76.51
P_4	11.79	0.00	0.00	0.00	0.00	43.05	0.00	0.00	0.00	54.84
P_5	0.00	0.00	0.00	0.00	0.00	0.00	41.33	0.00	0.00	41.33
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.48	3.31	43.79
P_7	40.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.06
P_8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Total	54.36	89.48	77.85	77.42	79.39	43.49	45.69	40.72	4.34	

Table B.5: Distribution ratios, production operator and elasticity matrices for rapeseed BAU (MJ/MJ)

$$\langle \mathbf{FP} \rangle = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.7850 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.9244 & 0.0756 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\langle \mathbf{P}^{*} | = \begin{bmatrix} 1.0000 & 1.0000 & 1.0000 & 1.0000 & 0.7850 & 0.7850 & 0.7256 & 0.0594 \\ 0.0000 & 1.0000 & 1.0000 & 1.0000 & 0.7850 & 0.7850 & 0.7256 & 0.0594 \\ 0.0000 & 0.0000 & 1.0000 & 1.0000 & 0.7850 & 0.7850 & 0.7256 & 0.0594 \\ 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.7850 & 0.7850 & 0.7256 & 0.0594 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 1.0000 & 0.9244 & 0.0756 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.9244 & 0.0756 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 \end{bmatrix}$$

$$[\mathbf{A}_{P}^{\mathrm{nrs}}] = \begin{bmatrix} 1.0000 & 0.9540 & 0.9428 & 0.7696 & 0.7431 & 0.5534 & 0.5450 & 0.3089 \\ 0.0000 & 0.0460 & 0.0455 & 0.0371 & 0.0358 & 0.0267 & 0.0263 & 0.0149 \\ 0.0000 & 0.0000 & 0.0117 & 0.0095 & 0.0092 & 0.0069 & 0.0068 & 0.0038 \\ 0.0000 & 0.0000 & 0.0000 & 0.1838 & 0.1775 & 0.1322 & 0.1302 & 0.0738 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0344 & 0.0256 & 0.0252 & 0.0143 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.2553 & 0.2514 & 0.1425 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0152 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.4418 \end{bmatrix}$$

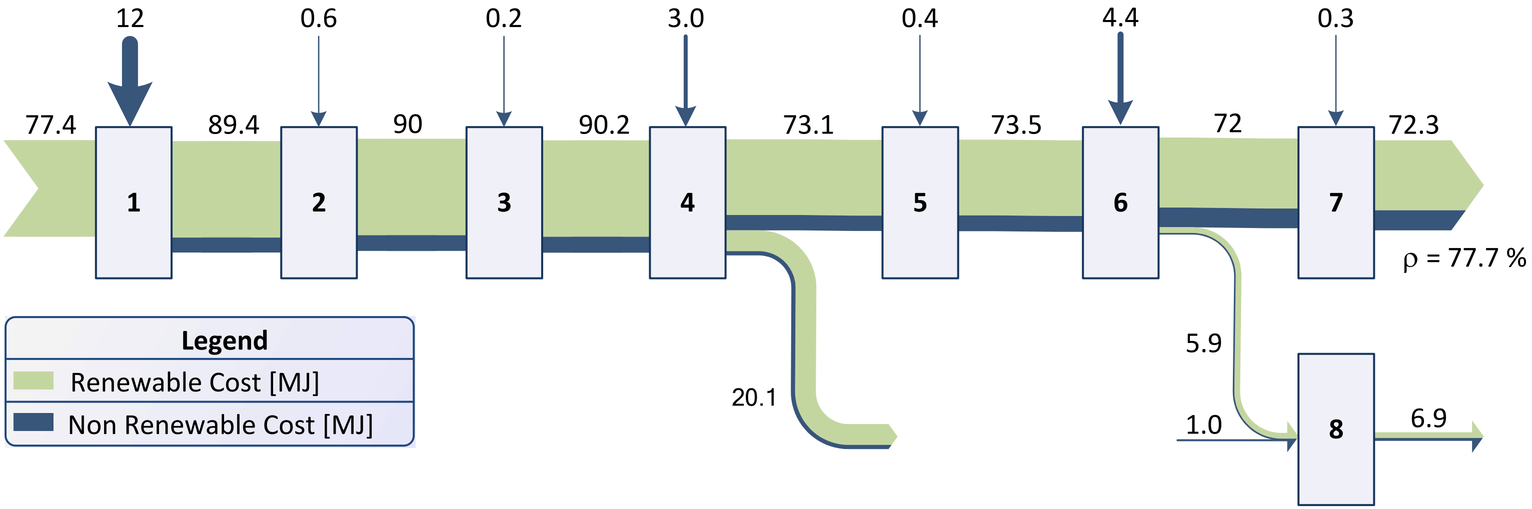

Figure B.2: Cost and renewability diagram for biodiesel production from rapeseed (MJ/kg FAME)

Table B.6: Exergy and exergoecologic cost of input flows for the sunflower biodiesel pathway

				Exergy		Cost	
Inputs	Process	Unit (u)	u/kgFAME	MJ/u	MJ/kg FAME	MJ/u	MJ/kg FAME
N fertiliser	1	kg	0.0403	20.0376	0.8071	67.2664	2.7095
K_2O fertiliser	1	kg	0.0227	4.5173	0.1026	8.6897	0.1974
P_2O_5 fertiliser	1	kg	0.0310	2.2512	0.0697	11.4420	0.3545
Pesticides	1	kg	0.0021	19.3270	0.0400	198.0960	0.4101
Seeding material	1	kg	0.0062	28.6000	0.1773	6.4600	0.0401
Diesel	1	MJ	3.0603	1.0000	3.0603	1.1773	3.6028
Diesel	2	MJ	0.0108	1.0000	0.0108	1.1773	0.0127
Electricity	2	MJ	0.1844	1.0000	0.1844	2.8690	0.5291
Diesel	3	MJ	0.1182	1.0000	0.1182	1.1773	0.1392
n-hexane	4	kg	0.0024	49.4764	0.1207	53.1324	0.1296
Steam	4	kg	1.6994	0.8500	1.4445	2.6258	4.4623
Electricity	4	MJ	0.3048	1.0000	0.3048	2.8690	0.8746
Fuller’s earth	5	kg	0.0062	0.0178	0.0001	2.5885	0.0162
Steam	5	MJ	0.3079	1.0000	0.3079	1.1617	0.3576
Electricity	5	MJ	0.0225	1.0000	0.0225	2.8690	0.0645
H_3PO_4	6	kg	0.0017	1.0983	0.0019	36.2858	0.0617
HCl	6	kg	0.0200	1.3409	0.0268	5.2484	0.1050
Na_2CO_3	6	kg	0.0025	0.5013	0.0013	14.0635	0.0352
NaOH	6	kg	0.0067	0.9683	0.0065	5.0273	0.0338
Methanol	6	kg	0.1087	23.1540	2.5175	30.3074	3.2953
Steam	6	MJ	1.5452	1.0000	1.5452	1.1617	1.7950
Electricity	6	MJ	0.1080	1.0000	0.1080	2.8690	0.3099

Table B.7: Exergy of products and intermediate flows in sunflower biodiesel cycle

Flow	**Process**	**Mass ratio** kg/kg$_{\text{FAME}}$	**Exergy** MJ/kg	MJ/kg$_{\text{FAME}}$
Soybean seed	1	5.7249	21.100	120.795
Soybean seed transport	2	5.66822	21.100	119.599
Crude oil	3	1.06563	39.654	42.256
Soybean seed meal	3	4.60259	9.378	43.165
Crude oil after transport	4	1.06563	39.654	42.256
Plant oil	5	1.023	39.654	40.566
Crude FAME	6	-	-	40.399
Crude glycerol	6	-	-	3.306
FAME	7	1.0000	39.981	39.981
Glycerol	8	0.1056	23.678	2.500

Table B.8: F–P Table for sunflower oil (MJ/kg FAME)

	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0^{rs}		72.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	72.27
C_0^{nrs}		7.31	0.54	0.14	2.68	0.44	4.47	0.22	0.95	16.75
P_0		76.35	0.20	0.12	0.86	0.13	2.86	0.07	0.29	80.87
P_1	0.00	0.00	72.09	0.00	0.00	0.00	0.00	0.00	0.00	72.09
P_2	0.00	0.00	0.00	72.09	0.00	0.00	0.00	0.00	0.00	72.09
P_3	0.00	0.00	0.00	0.00	71.38	0.00	0.00	0.00	0.00	71.38
P_4	10.37	0.00	0.00	0.00	0.00	42.96	0.00	0.00	0.00	53.33
P_5	0.00	0.00	0.00	0.00	0.00	0.00	41.24	0.00	0.00	41.24
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.40	3.31	43.71
P_7	39.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	39.98
P_8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Total	52.85	79.58	72.63	72.23	74.06	43.40	45.71	40.61	4.26	

Table B.9: Distribution ratios, production operator and elasticity matrices for sunflower BAU (MJ/MJ)

$$\langle \mathbf{FP} \rangle = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.8056 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.9242 & 0.0758 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\langle \mathbf{P}^* | = \begin{bmatrix} 1.0000 & 1.0000 & 1.0000 & 1.0000 & 0.8056 & 0.8056 & 0.7445 & 0.0611 \\ 0.0000 & 1.0000 & 1.0000 & 1.0000 & 0.8056 & 0.8056 & 0.7445 & 0.0611 \\ 0.0000 & 0.0000 & 1.0000 & 1.0000 & 0.8056 & 0.8056 & 0.7445 & 0.0611 \\ 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.8056 & 0.8056 & 0.7445 & 0.0611 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 1.0000 & 0.9242 & 0.0758 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.9242 & 0.0758 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 \end{bmatrix}$$

$$[\mathbf{A}_P^{\mathrm{nrs}}] = \begin{bmatrix} 1.0000 & 0.9310 & 0.9148 & 0.6850 & 0.6518 & 0.4361 & 0.4286 & 0.2267 \\ 0.0000 & 0.0690 & 0.0678 & 0.0507 & 0.0483 & 0.0323 & 0.0317 & 0.0168 \\ 0.0000 & 0.0000 & 0.0174 & 0.0130 & 0.0124 & 0.0083 & 0.0082 & 0.0043 \\ 0.0000 & 0.0000 & 0.0000 & 0.2512 & 0.2390 & 0.1599 & 0.1572 & 0.0831 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0485 & 0.0324 & 0.0319 & 0.0169 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.3310 & 0.3253 & 0.1721 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0171 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.4801 \end{bmatrix}$$

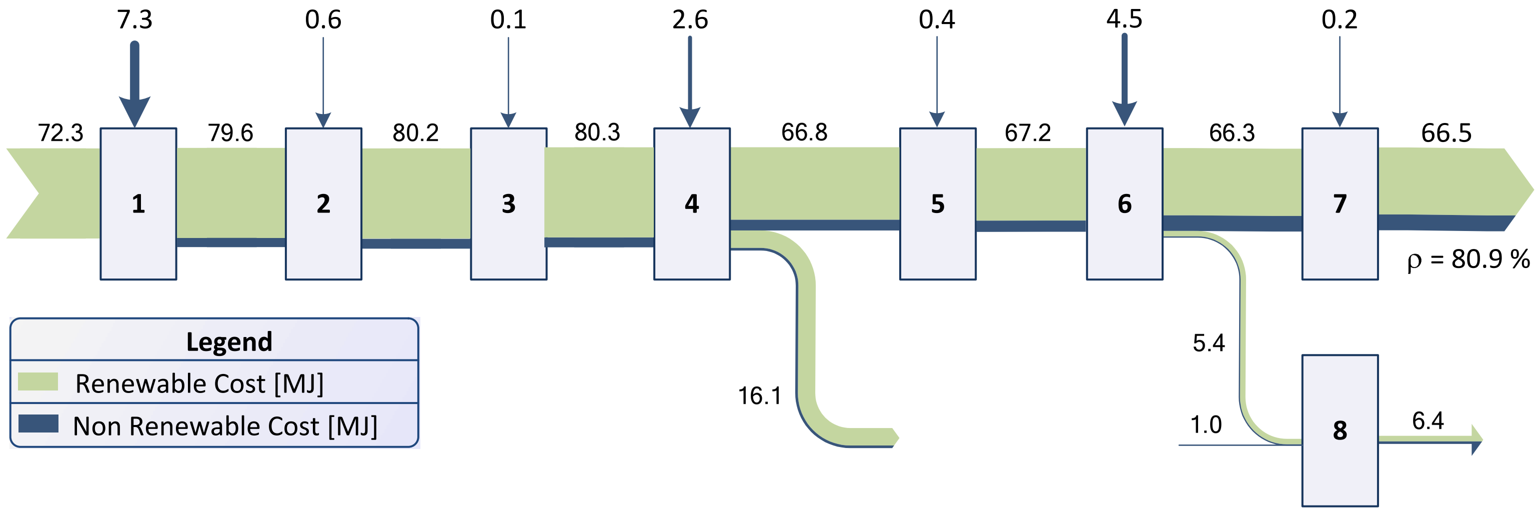

Figure B.3: Cost and renewability diagram for biodiesel production from sunflower (MJ/kg FAME)

B.2 Biodiesel plant model using palm oil

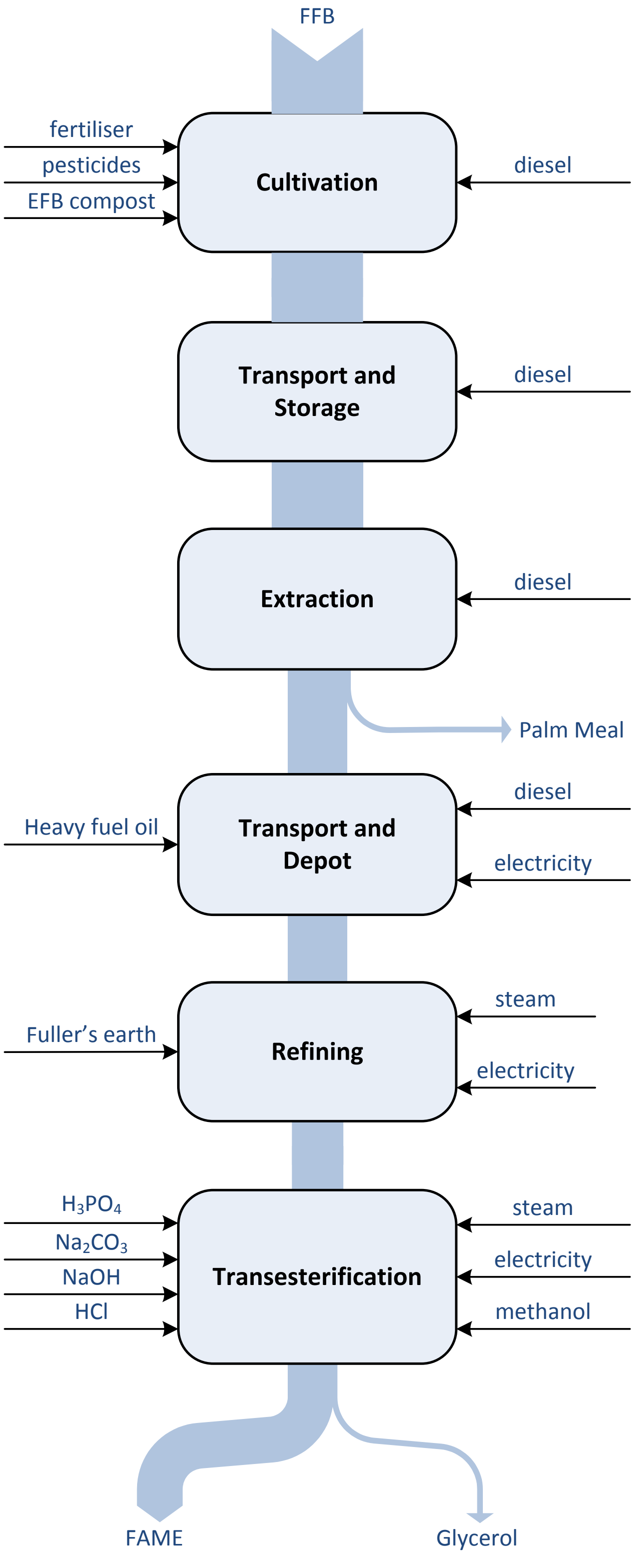

Figure B.4: Flow Diagram for biodiesel production from palm tree

Table B.10: Exergy and exergoecologic cost of input flows for the palm oil biodiesel pathway

				Exergy		Cost	
Inputs	Process	Unit (u)	u/kgFAME	MJ/u	MJ/kg FAME	MJ/u	MJ/kg FAME
N fertiliser	1	kg	0.0322	20.0376	0.6454	67.2664	2.1667
K_2O fertiliser	1	kg	0.0503	4.5173	0.2273	8.6897	0.4373
P_2O_5 fertiliser	1	kg	0.0362	2.2512	0.0816	11.4420	0.4145
Pesticides	1	kg	0.0021	19.3270	0.0406	198.0960	0.4160
EFB compost	1	kg	0.1474	8.1627	1.2033	8.1627	1.2033
Diesel	1	MJ	0.5197	1.0000	0.5197	1.1773	0.6119
Diesel	2	MJ	0.4871	1.0000	0.4871	1.1773	0.5734
Diesel	4	MJ	0.0550	1.0000	0.0550	1.1773	0.0647
Electricity	4	MJ	0.0328	1.0000	0.0328	2.8690	0.0940
Heavy fuel oil	4	MJ	1.3314	1.0000	1.3314	1.1773	1.5674
Fuller's earth	5	kg	0.0062	0.0178	0.0001	2.5885	0.0162
Steam	5	kg	0.3622	0.8500	0.3079	2.6258	0.9510
Electricity	5	MJ	0.0225	1.0000	0.0225	2.8690	0.0645
H_3PO_4	6	kg	0.0017	1.0983	0.0019	36.2858	0.0617
HCl	6	kg	0.0200	1.3409	0.0268	5.2484	0.1050
Na_2CO_3	6	kg	0.0025	0.5013	0.0013	14.0635	0.0352
NaOH	6	kg	0.0067	0.9683	0.0065	5.0273	0.0338
Methanol	6	kg	0.1087	23.1540	2.5175	30.3074	3.2953
Steam	6	kg	1.8179	0.8500	1.5452	2.6258	4.7734
Electricity	6	MJ	0.1080	1.0000	0.1080	2.8690	0.3099

Table B.11: Exergy of products and intermediate flows in palm oil biodiesel cycle

Flow	Process	Mass ratio kg/kg $_{\text{FAME}}$	Exergy MJ/kg	MJ/kg $_{\text{FAME}}$
FFB	1	4.7805	15.8400	75.723
FFB after transport and storage	2	4.6849	15.8400	74.209
Crude oil	3	1.0541	39.6356	41.780
Palm kernel meal	3	0.1171	10.4650	1.226
CH_4 from waste	3	0.0368	55.0500	2.027
Crude oil after transport and depot	4	1.0541	39.6356	41.780
Plant oil	5	1.0401	39.6356	41.223
Crude FAME	6	-	-	40.394
Crude glycerol	6	-	-	3.291
FAME	7	1.0000	39.9707	39.971
Glycerol	8	0.1056	23.6779	2.500

Table B.12: F–P Table for palm oil production process (MJ/kg FAME)

	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0^{rs}		75.72	0.00	0.00	0.00	0.00	0.00	0.00	0.00	75.72
C_0^{nrs}		5.25	0.57	0.00	1.73	0.44	4.38	0.23	1.03	13.62
P_0		78.44	0.49	0.00	1.42	0.12	2.83	0.07	0.31	83.68
P_1	0.00	0.00	75.72	0.00	0.00	0.00	0.00	0.00	0.00	75.72
P_2	0.00	0.00	0.00	74.21	0.00	0.00	0.00	0.00	0.00	74.21
P_3	3.25	0.00	0.00	0.00	41.78	0.00	0.00	0.00	0.00	45.03
P_4	0.00	0.00	0.00	0.00	0.00	41.78	0.00	0.00	0.00	41.78
P_5	0.00	0.00	0.00	0.00	0.00	0.00	41.22	0.00	0.00	41.22
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.39	3.29	43.69
P_7	39.97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	39.97
P_8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Total	45.72	80.97	76.30	74.21	43.51	42.22	45.60	40.63	4.32	

Table B.13: Distribution ratios, production operator and elasticity matrices for palm oil BAU (MJ/MJ)

$$\langle \mathbf{FP} \rangle = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.9278 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.9247 & 0.0753 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\left\langle \mathbf{P}^{*} \right| = \begin{bmatrix} 1.0000 & 1.0000 & 1.0000 & 0.9278 & 0.9278 & 0.9278 & 0.8579 & 0.0699 \\ 0.0000 & 1.0000 & 1.0000 & 0.9278 & 0.9278 & 0.9278 & 0.8579 & 0.0699 \\ 0.0000 & 0.0000 & 1.0000 & 0.9278 & 0.9278 & 0.9278 & 0.8579 & 0.0699 \\ 0.0000 & 0.0000 & 0.0000 & 1.0000 & 1.0000 & 1.0000 & 0.9247 & 0.0753 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 1.0000 & 0.9247 & 0.0753 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.9247 & 0.0753 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 \end{bmatrix}$$

$$[\mathbf{A}_{P}^{\mathrm{nrs}}] = \begin{bmatrix} 1.0000 & 0.9015 & 0.9015 & 0.6832 & 0.6437 & 0.4078 & 0.3994 & 0.1905 \\ 0.0000 & 0.0985 & 0.0985 & 0.0746 & 0.0703 & 0.0445 & 0.0436 & 0.0208 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.2421 & 0.2281 & 0.1445 & 0.1415 & 0.0675 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0579 & 0.0367 & 0.0359 & 0.0171 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.3664 & 0.3589 & 0.1712 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0207 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.5329 \end{bmatrix}$$

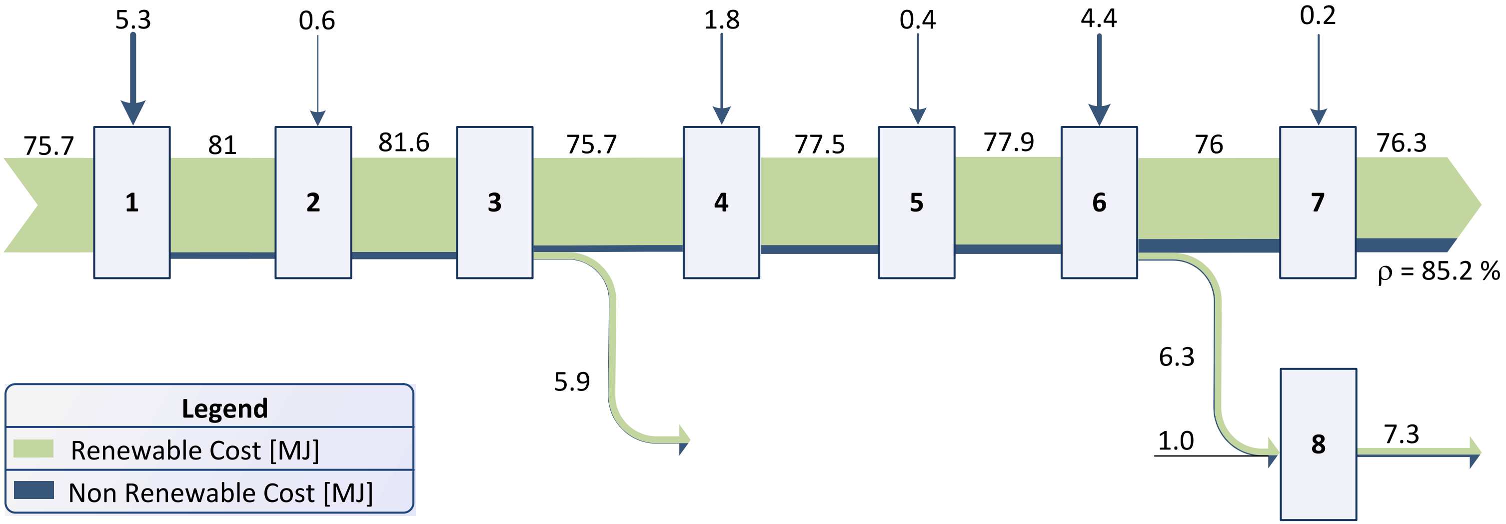

Figure B.5: Cost and renewability diagram for biodiesel production from palm oil

B.3 Biodiesel plant model using soybean oil

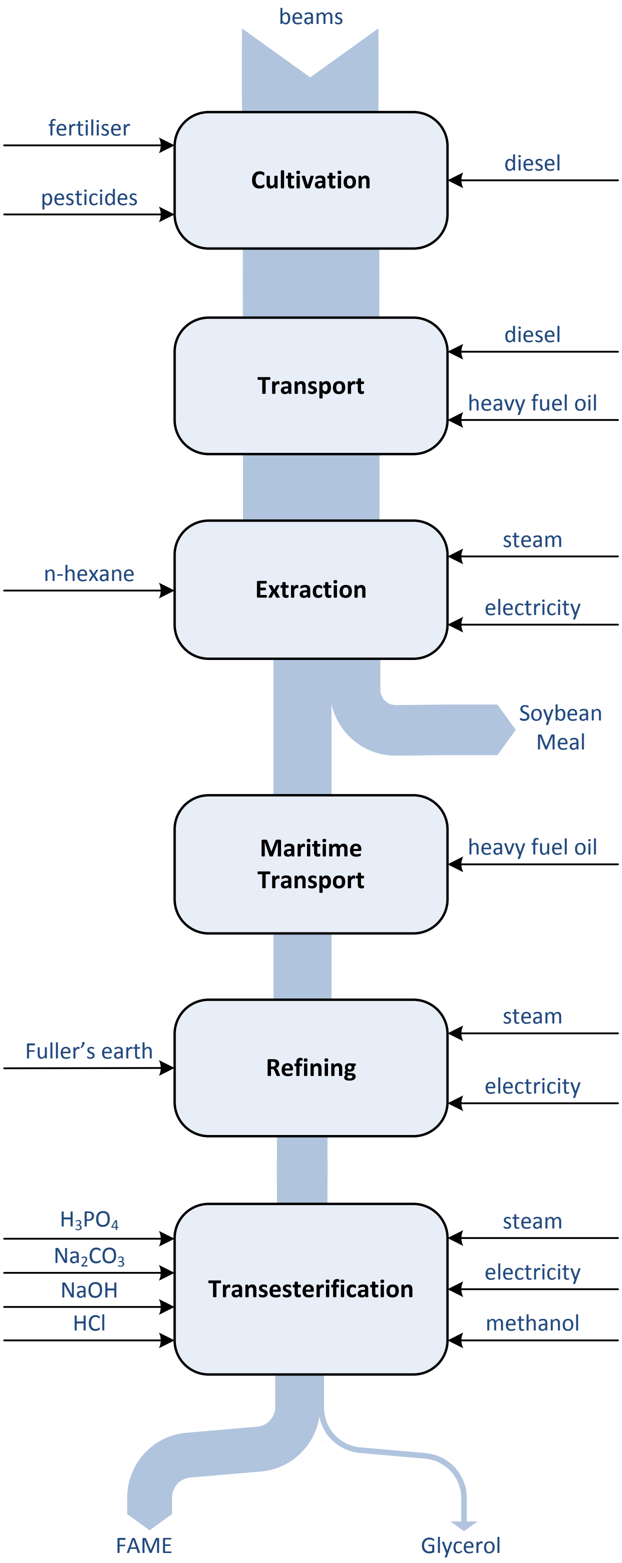

Figure B.6: Flow Diagram for biodiesel production from soybean

Table B.14: Exergy and exergoecologic cost of input flows for the soybean biodiesel pathway

				Exergy		Cost	
Inputs	Process	Unit (u)	u/kgFAME	MJ/u	MJ/kg FAME	MJ/u	MJ/kg FAME
N fertiliser	1	kg	0.0164	20.0376	0.3280	67.2664	1.1012
K_2O fertiliser	1	kg	0.1269	4.5173	0.5731	8.6897	1.1024
P_2O_5 fertiliser	1	kg	0.1350	2.2512	0.3040	11.4420	1.5451
Pesticides	1	kg	0.0056	19.3270	0.1073	198.0960	1.0994
Soybean seed	1	kg	5.7249	21.1000	120.7954	21.1000	120.7954
Diesel	1	MJ	4.2542	1.0000	4.2542	1.1773	5.0084
Diesel	2	MJ	3.7297	1.0000	3.7297	1.1773	4.3909
Heavy fuel oil	2	MJ	11.7782	1.0000	11.7782	1.1773	13.8663
n-hexane	3	kg	0.0038	49.4764	0.1890	53.1324	0.2030
Steam	3	MJ	6.6685	0.8500	5.6682	1.1617	7.7465
Electricity	3	MJ	1.2243	1.0000	1.2243	2.8690	3.5126
Heavy fuel oil	4	MJ	1.3314	1.0000	1.3314	1.1773	1.5674
Fuller's earth	5	kg	0.0062	0.0178	0.0001	2.5885	0.0162
Steam	5	MJ	0.3622	0.8500	0.3079	1.1617	0.4207
Electricity	5	MJ	0.0225	1.0000	0.0225	2.8690	0.0645
H_3PO_4	6	kg	0.0017	1.0983	0.0019	36.2858	0.0617
HCl	6	kg	0.0200	1.3409	0.0268	5.2484	0.1050
Na_2CO_3	6	kg	0.0025	0.5013	0.0013	14.0635	0.0352
NaOH	6	kg	0.0067	0.9683	0.0065	5.0273	0.0338
Methanol	6	kg	0.1087	23.1540	2.5175	30.3074	3.2953
Steam	6	MJ	1.8179	0.8500	1.5452	1.1617	2.1118
Electricity	6	MJ	0.1080	1.0000	0.1080	2.8690	0.3099

Table B.15: Exergy of products and intermediate flows in soybean oil biodiesel cycle

Flow	Process	Mass ratio	Exergy	
		kg/kg $_{\text{FAME}}$	MJ/kg	MJ/kg $_{\text{FAME}}$
Soybean seed	1	5.725	21.100	120.795
Soybean seed transport	2	5.668	21.100	119.599
Crude oil	3	1.066	39.654	42.256
Soybean seed meal	3	4.603	9.378	43.165
Crude oil after transport	4	1.066	39.654	42.256
Plant oil	5	1.023	39.654	40.566
Crude FAME	6	-	-	40.399
Crude glycerol	6	-	-	3.306
FAME	7	1.000	39.981	39.981
Glycerol	8	0.106	23.678	2.500

Table B.16: F–P Table for soybean oil (MJ/kg FAME)

	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	Total
C_0^{rs}		120.80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	120.80
C_0^{nrs}		9.86	18.26	10.30	1.57	0.44	4.47	0.22	0.95	46.06
P_0		126.36	15.51	7.08	1.33	0.33	2.86	0.07	0.29	153.83
P_1	0.00	0.00	120.80	0.00	0.00	0.00	0.00	0.00	0.00	120.80
P_2	0.00	0.00	0.00	119.60	0.00	0.00	0.00	0.00	0.00	119.60
P_3	43.17	0.00	0.00	0.00	42.26	0.00	0.00	0.00	0.00	85.42
P_4	0.00	0.00	0.00	0.00	0.00	42.26	0.00	0.00	0.00	42.26
P_5	0.00	0.00	0.00	0.00	0.00	0.00	40.57	0.00	0.00	40.57
P_6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	40.40	3.31	43.70
P_7	39.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	39.98
P_8	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50
Total	85.65	130.65	139.05	129.30	43.82	42.69	45.04	40.62	4.25	

Table B.17: Distribution ratios, production operator and elasticity matrices for soybean oil BAU (MJ/MJ)

$$\langle \mathbf{FP} \rangle = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.4947 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.9244 & 0.0756 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$\left\langle \mathbf{P}^* \right| = \begin{bmatrix} 1.0000 & 1.0000 & 1.0000 & 0.4947 & 0.4947 & 0.4947 & 0.4573 & 0.0374 \\ 0.0000 & 1.0000 & 1.0000 & 0.4947 & 0.4947 & 0.4947 & 0.4573 & 0.0374 \\ 0.0000 & 0.0000 & 1.0000 & 0.4947 & 0.4947 & 0.4947 & 0.4573 & 0.0374 \\ 0.0000 & 0.0000 & 0.0000 & 1.0000 & 1.0000 & 1.0000 & 0.9244 & 0.0756 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 1.0000 & 0.9244 & 0.0756 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.9244 & 0.0756 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 1.0000 \end{bmatrix}$$

$$[\mathbf{A}_P^{\mathrm{nrs}}] = \begin{bmatrix} 1.0000 & 0.3506 & 0.2566 & 0.2370 & 0.2321 & 0.1914 & 0.1896 & 0.1284 \\ 0.0000 & 0.6494 & 0.4753 & 0.4391 & 0.4299 & 0.3544 & 0.3512 & 0.2377 \\ 0.0000 & 0.0000 & 0.2681 & 0.2477 & 0.2425 & 0.2000 & 0.1981 & 0.1341 \\ 0.0000 & 0.0000 & 0.0000 & 0.0762 & 0.0746 & 0.0615 & 0.0610 & 0.0413 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0209 & 0.0172 & 0.0170 & 0.0115 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.1755 & 0.1739 & 0.1177 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0091 & 0.0000 \\ 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.0000 & 0.3292 \end{bmatrix}$$

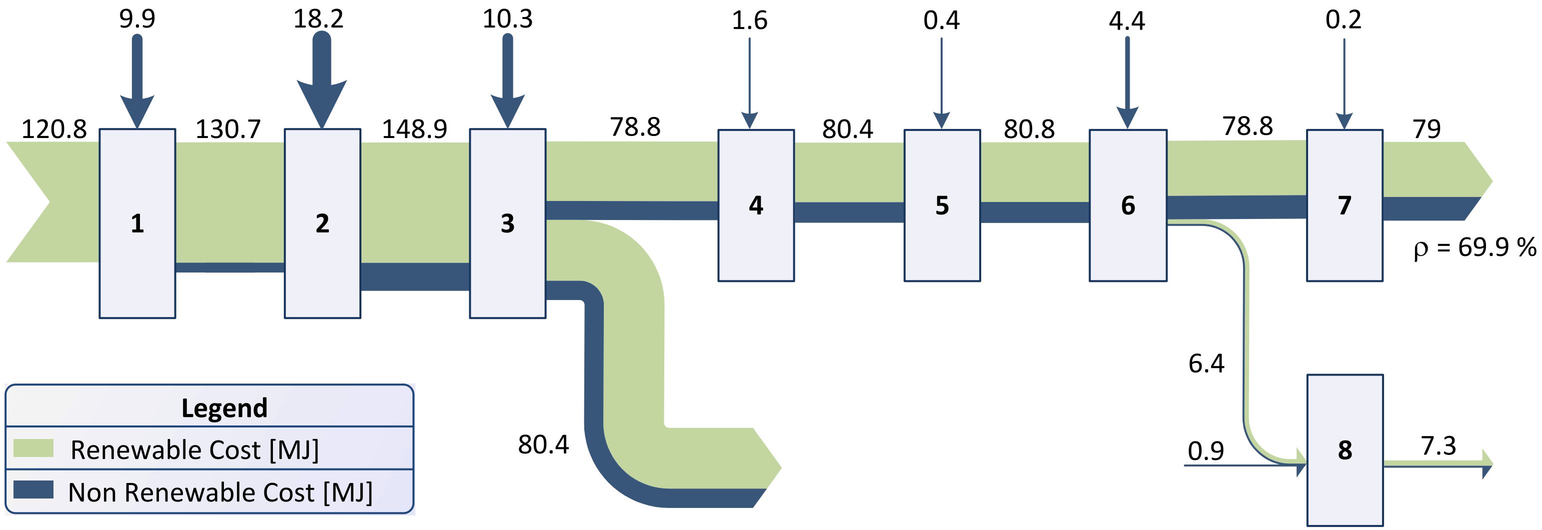

Figure B.7: Cost and renewability diagram for biodiesel production from soybean oil

Appendix C

Review of Lineal Algebra

This appendix reviews some aspects of linear algebra and Matrices that been used in the book. Special attention is paid in notation aspects.

C.1 Vectors

A vector is an ordered set of real numbers. For instance, $\mathbf{a} = (a_1, a_2, \ldots, a_n)$ is a vector of n elements or components. Let two vectors $\mathbf{a} = \{a_1, a_2, \ldots, a_n\}$ and $\mathbf{b} = \{b_1, b_2, \ldots, b_n\}$, then the sum is defined as:

$$\mathbf{a} + \mathbf{b} = (a_1 + b_1, \ldots, a_n + b_n)$$

The scalar product for any real number α is:

$$\alpha\ \mathbf{a} = (\alpha\ a_1, \ldots, \alpha\ a_n)$$

The vector $\mathbf{0} = (0, 0, \ldots, 0)$ is called null vector. The vector $\mathbf{u} = (1, 1, \ldots, 1)$ is called unity vector.

The inner product of two vector, written $\mathbf{a} \cdot \mathbf{b}$, is a real number given by:

$$\mathbf{a} \cdot \mathbf{b} = \sum_{i=1}^{n} a_i\ b_i$$

C.2 Matrices

A *matrix* **A** of size $n \times m$ is a rectangular array (table) of numbers with m rows an n columns, as for example:

$$\underset{(2\times 3)}{\mathbf{A}} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \end{bmatrix}$$

In this example **A** is matrix of two rows and three columns. In general an $n \times m$ matrix is written as

$$\underset{(n\times m)}{\mathbf{A}} = \left[a_{ij}\right]_{i=1,\ldots,n}^{j=1,\ldots m}$$

each element a_{ij} of the matrix, is the element in the i-th row and j-th column of **A**

The elements a_{ij} for $i = j$ are called the *diagonal* elements; while the a_{ij} for $i \neq j$ are called *off-diagonal* elements.

A square matrix whose off-diagonal elements are all zero is called diagonal matrix. The identity matrix, denoted by or $\mathbf{U}_{\mathrm{D}}$, is a diagonal matrix whose diagonal elements are all 1. A matrix whose elements are all zero is called a *null* matrix.

The elements of each column of a matrix define a vector called *column vector*. Similarly, each row of a matrix defines a *row vector*. In the previous example, the vectors

$$a_1 = \begin{pmatrix} 1 \\ 4 \end{pmatrix} \qquad a_2 = \begin{pmatrix} 2 \\ 5 \end{pmatrix} \qquad a_3 = \begin{pmatrix} 3 \\ 6 \end{pmatrix}$$

are the column vector of the matrix (A), while the vectors

$$b_1 = (1,2,3) \qquad b_2 = (4,5,6)$$

are the row vectors of A. Thus a vector may be treated as a special matrix with just one row or one column. A matrix with an equal number of rows and columns is called a *square matrix*.

The transpose of a matrix $\mathbf{A} = [a_{ij}]$, denoted by ${}^{\mathrm{t}}\mathbf{A}$ or $\mathbf{A}^T$ is a matrix obtained by interchanging the rows and columns of $\mathbf{A}$. In other words, ${}^{\mathrm{t}}\mathbf{A} = [a'_{ij}]$ where $a'_{ij} = a_{ji}$. For example, the transpose matrix defined in the example is given by:

$$\underset{(3\times 2)}{\mathbf{A}} = \begin{bmatrix} 1 & 4 \\ 2 & 5 \\ 3 & 6 \end{bmatrix}$$

The matrix $\mathbf{A}$ is said to be symmetric if ${}^{\mathrm{t}}\mathbf{A} = \mathbf{A}$.

C.3 Matrix Operations

The *sum* or *difference* of two matrices $\mathbf{A}$ and $\mathbf{B}$ is a matrix $\mathbf{C} = \mathbf{A} \pm \mathbf{B}$ where the elements of $\mathbf{C}$ are given by:

$$c_{ij} = a_{ij} \pm b_{ij}$$

For two matrices $\mathbf{A}$ and $\mathbf{B}$ the product $\mathbf{AB}$ is defined if and only if the number of columns of the matrix $\mathbf{A}$ is equal to the number of rows of $\mathbf{B}$. If $\mathbf{A}$ is a $m \times n$ matrix and $\mathbf{B}$ is a $n \times r$ matrix, the product $\mathbf{AB} = \mathbf{C}$ is defined as a matrix whose size is $m \times r$, and the (i, j)-th element of $\mathbf{C}$ is given by:

$$c_{ij} = \sum_{k=1}^{n} a_{ik} b_{kj} \quad i = 1, \ldots, m \quad j = 1, \ldots, r$$

For example, let:

$$\underset{(2\times 3)}{\mathbf{A}} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \end{bmatrix} \qquad \underset{(3\times 2)}{\mathbf{B}} = \begin{bmatrix} 1 & 2 \\ 3 & 4 \\ 5 & 6 \end{bmatrix}$$

$$\mathbf{AB} = \underset{(2\times 2)}{\mathbf{C}} = \begin{bmatrix} 22 & 28 \\ 49 & 64 \end{bmatrix}$$

For any scalar α, the product is defined as $\alpha\mathbf{A} = \left[\alpha a_{ij}\right]$

Matrix operations satisfy the following properties:

- $(\mathbf{A}+\mathbf{B})+\mathbf{C}=\mathbf{A}+(\mathbf{B}+\mathbf{C})$
- $\mathbf{A}+\mathbf{B}=\mathbf{B}+\mathbf{A}$
- $(\mathbf{A}+\mathbf{B})\,\mathbf{C}=\mathbf{AC}+\mathbf{BC}$
- $(\mathbf{A}\,\mathbf{B})\,\mathbf{C}=\mathbf{A}\,(\mathbf{B}\,\mathbf{C})$
- $\mathbf{U}_{\mathrm{D}}\mathbf{A}=\mathbf{A}\mathbf{U}_{\mathrm{D}}=\mathbf{A}$
- $(\mathbf{A}+\mathbf{B})^{T}=\mathbf{A}^{T}+\mathbf{B}^{T}$
- $(\mathbf{A}\,\mathbf{B})^{T}=\mathbf{B}^{T}\mathbf{A}^{T}$
- In general, $\mathbf{AB}\neq\mathbf{BA}$

There are some special cases of matrices product.

- A row matrix ${}^{\mathrm{t}}\mathbf{x}$ $(1\times n)$ multiplied by a matrix $\mathbf{A}$ $(n\times m)$ is a row matrix ${}^{\mathrm{t}}\mathbf{y}$ $(1\times m)$ whose elements are given by:

  $$y_i=\sum_{j=1}^{n}x_j a_{ji}\qquad i=1,\ldots,m$$

  If the row matrix is the unitary vector ${}^{\mathrm{t}}\mathbf{u}$ then this products becomes the sum of the columns of the matrix $\mathbf{A}$.

  $${}^{\mathrm{t}}\mathbf{u}\,\mathbf{A}=\left(\sum_{j=1}^{n}a_{ji}\right)_{i=1,\ldots,m}$$

- A matrix $\mathbf{A}$ $(n\times m)$ multiplied by a column matrix ${}^{\mathrm{t}}\mathbf{x}$ $(m\times 1)$ is a column matrix ${}^{\mathrm{t}}\mathbf{y}$ $(n\times 1)$ whose elements are:

  $$y_i=\sum_{j=1}^{m}a_{ij}x_j\qquad i=1,\ldots,n$$

  If the column matrix is the unitary vector ${}^{\mathrm{t}}\mathbf{u}$ then this products becomes the sum of the rows of the matrix $\mathbf{A}$.

  $$\mathbf{A}\,\mathbf{u}=\left(\sum_{j=1}^{m}a_{ij}\right)_{i=1,\ldots,n}$$

- A column matrix $\mathbf{x}$ $(n\times 1)$ multiplied by a row matrix ${}^{\mathrm{t}}\mathbf{y}$ $(1\times m)$ is matrix $\mathbf{A}$ $(n\times m)$ whose elements are given by:

  $$a_{ij}=x_i\,y_j$$

  This operation is also called outer product and it is represented as:

  $$\mathbf{A}=\mathbf{x}\otimes\mathbf{y}=\mathbf{x}\,{}^{\mathrm{t}}\mathbf{y}$$

In ordinary algebra, 1 is known as the *identity element* for multiplication, which means that a number remains unchanged when multiplied by it. There is an analogous concept in matrix algebra. An *identity matrix* is one that leaves a matrix unchanged when the matrix is multiplied by it.

The identity matrix, which denote by $\mathbf{U}_n$ is a square matrix to satisfy the conformability requirement for the particular operation in which appears. It has 1's along its *main diagonal*, from upper left to lower right, and 0's everywhere else.

$$\mathbf{U}_n = \begin{bmatrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 1 \end{bmatrix}$$

Given a rectangular matrix $\mathbf{A}$ $(n \times m)$ the identity matrix verify:

$$\mathbf{A} \cdot \mathbf{U}_m = \mathbf{U}_n \, \mathbf{A} = \mathbf{A}$$

C.4 Inverse Matrices

A square matrix $\mathbf{A}$ $(n \times n)$ is called *invertible*, *regular* or *non-singular* if there exists an square matrix $\mathbf{B}$ $(n \times n)$ such that:

$$\mathbf{A}\,\mathbf{B} = \mathbf{B}\,\mathbf{A} = \mathbf{U}_n$$

In this case the matrix $\mathbf{B}$ is uniquely determined by $\mathbf{A}$ and is called the inverse of $\mathbf{A}$, denoted by $\mathbf{A}^{-1}$.

The inverse of an invertible matrix $\mathbf{A}$ is itself invertible, with:

$$\left(\mathbf{A}^{-1}\right)^{-1} = \mathbf{A}$$

The inverse of an invertible matrix $\mathbf{A}$ multiplied by a non-zero scalar k yields the product of the inverse of both the matrix and the scalar:

$$(k\,\mathbf{A})^{-1} = \frac{1}{k}\,\mathbf{A}^{-1}$$

The product of two invertible matrix $\mathbf{A}$ and $\mathbf{B}$ of the same size is invertible with the inverse given by:

$$(\mathbf{A}\,\mathbf{B})^{-1} = \mathbf{B}^{-1}\,\mathbf{A}^{-1}$$

For an invertible matrix, its transpose matrix is invertible with the inverse given by:

$$\left(\mathbf{A}^{T}\right)^{-1} = \left(\mathbf{A}^{-1})\right)^{T}$$

An square matrix $\mathbf{A}$ is called diagonal dominant if its coefficients verify:

$$|a_{ii}| \geq \sum_{i \neq j} \left|a_{ij}\right| \qquad 1 \leq i \leq n$$

and it is called strong diagonal dominant if it at least exists a row i_0 such as:

$$\sum_{j} \left|a_{i_0 j}\right| > 0$$

If a matrix $\mathbf{A}$ $(n \times n)$ is strong diagonal dominant then it is invertible, and its inverse is definite positive (all its element are positives), and verifies that if $\mathbf{x} \geq 0$ then $\mathbf{A}^{-1}\mathbf{x} \geq 0$.

An special kind of this matrices, like ⟨**FP**⟩ studied in this PhD. has the form $\mathbf{U}_{\mathrm{D}} - \mathbf{A}$, where the element of $\mathbf{A}$ verifies:

(i) $a_{ij} > 0 \quad \forall i, j$

(ii) $\sum_j a_{ij} \leq 1 \quad \forall i$

(iii) $\exists i_0$ such us $\sum_j a_{i_0 j} < 1$

Then this type of matrices are always invertibles and its inverse verifies:

$$(\mathbf{U}_n - \mathbf{A})^{-1} = \mathbf{U}_n + \sum_{r=1}^{\infty} \mathbf{A}^r$$

A sketch of proof is shown below:

The matrix $\mathbf{U}_n - \mathbf{A}$ is invertible if the homogeneous system $(\mathbf{U}_n - \mathbf{A})\mathbf{x} = 0$ has only the trivial solution $\mathbf{x} = 0$. Suppose $\mathbf{x} = \mathbf{A}\mathbf{x}$ for some $\mathbf{x} \neq 0$, then let index l so that

$$|x_l| = \max(|x_1|, \ldots, |x_n|) > 0$$

then we have the inequality:

$$|x_l| = \left|\sum_j a_{lj} x_j\right| \leq \sum_j a_{lj} |x_j|$$

and dividing both side of expression by $|x_l|$ we have:

$$1 \leq \sum_j a_{l_j} \frac{|x_j|}{|x_l|} \leq \sum_j a_{l_j}$$

wherever, by definition of $\mathbf{A}$, it must be $\sum_j a_{lj} = 1$ and $|x_j| = |x_l|$ for each j, therefore $\sum_j a_{ij} = 1$ for each i which contradicts hypothesis (iii) and then $\mathbf{U}_n - \mathbf{A}$ is invertible.

Two square matrix $\mathbf{A}$ and $\mathbf{B}$ $(n \times n)$ are called similar if $\mathbf{B} = \mathbf{P}^{-1}\mathbf{A}\mathbf{P}$, for some invertible matrix $\mathbf{P}$ $(n \times n)$. Similar matrix represents the same linear transformation under two different bases, with $\mathbf{P}$ being the change of base matrix. Similar matrix share many properties like: rank, determinant, trace or eigenvalues.

The matrix studied in this PhD: $\langle \mathbf{P}|$, $\langle \mathbf{P}^*|$, $|\mathbf{P}\rangle$ and $|\mathbf{P}^*\rangle$ are similar matrices and all of them has the same diagonal.

C.5 Diagonal Matrices

Diagonal matrices are square matrices with elements on the diagonal from upper left to lower right and zeros elsewhere. In general a $\mathbf{A}(n \times n)$ diagonal matrix is defined as:

$$a_{ij} = \begin{cases} a_{ii} & \text{if} \quad i = j \\ 0 & \text{elsewhere} \end{cases}$$

A useful notation is creating a diagonal matrix from a vector. Suppose ${}^t\mathbf{x} = [x_1, x_2, x_3]$, then the diagonal matrix the elements of $\mathbf{x}$ strung out along its main diagonal is denoted as:

$$\mathbf{x}_\mathrm{D} = \begin{bmatrix} x_1 & 0 & 0 \\ 0 & x_2 & 0 \\ 0 & 0 & x_3 \end{bmatrix}$$

One useful fact about diagonal matrices is, if all the elements of a vector vmx are non-equal zero, the inverse of the corresponding diagonal matrix is another diagonal matrix, each of whose elements is just the reciprocal of the original element. For $\mathbf{x}_{\mathrm{D}}$ this means:

$$\mathbf{x}_{\mathrm{D}}^{-1} = \begin{bmatrix} 1/x_1 & 0 & 0 \\ 0 & 1/x_2 & 0 \\ 0 & 0 & 1/x_3 \end{bmatrix}$$

and it verifies $\mathbf{x}_{\mathrm{D}}^{-1}\mathbf{x}_{\mathrm{D}} = \mathbf{x}_{\mathrm{D}}\mathbf{x}_{\mathrm{D}}^{-1} = \mathbf{U}_3$, notice also that transposition of a diagonal matrix leaves the matrix unchanged $\mathbf{x}_{\mathrm{D}}^{T} = \mathbf{x}_{\mathrm{D}}$.

When a diagonal matrix, $\mathbf{D}$, post-multiply another matrix, $\mathbf{A}$, the j-th element in $\mathbf{D}$, d_j, multiplies all of the elements in the j-th column of $\mathbf{A}$, and when a diagonal matrix pre-multiplies $\mathbf{A}$, d_j multiplies all the elements in the j-th row of $\mathbf{A}$.

Putting facts about inverses of diagonal matrix together with this observation about post and pre-multiplication by a diagonal matrix, post-multiplying $\mathbf{A}$ by $\mathbf{D}^{-1}$ will divide each element in column j of $\mathbf{A}$ by d_j and pre-multiplying $\mathbf{A}$ by $\mathbf{D}^{-1}$ will divide each element in row j of $\mathbf{A}$ by d_j.

For example, let:

$$\mathbf{x} = \begin{bmatrix} 1 \\ 2 \end{bmatrix} \qquad \mathbf{A} = \begin{bmatrix} 3 & 4 \\ 5 & 6 \end{bmatrix}$$

then

$$\mathbf{x}_{\mathrm{D}} \cdot \mathbf{A} \cdot \mathbf{x}_{\mathrm{D}}^{-1} = \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix} \cdot \begin{bmatrix} 3 & 4 \\ 5 & 6 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 \\ 0 & 1/2 \end{bmatrix} = \begin{bmatrix} 3 & 2 \\ 10 & 6 \end{bmatrix}$$

Note that both matrices are *similar* and they have the same diagonal and trace.

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Nomenclature

Scalar

C	Exergoecologic cost [kJ]
c	Unit exergoecologic cost [kJ/kJ]
c_p	Specific heat when pressure is constant
c^*	Exergoecologic factor [kJ/kJ]
E	Exergy [kJ]
e	Specific exergy [kJ/kg]
F	Exergy of fuel [kJ]
g_j	Number of groups j
ΔG_f	Standard Gibbs free energy of formation [kJ]
h	Enthalpy [kJ/kg]
I	Irreversibility [kJ]
k	Unit exergy consumption [kJ/kJ]
k^*	Unit exergy cost [kJ/kJ]
$\dot{m}$	Mass flow rate [kg/s]
N_i	Number of moles
n	Number of processes
P	Exergy of product
p	Pressure [bar]
$\dot{Q}$	Heat transfer rate [kW]
R	Generic chain component in an organic compound
s	Entropy [kJ/°C]
$\dot{S}_g$	Entropy generation rate [kW/°C]
T	Temperature [°C]
$\dot{W}$	Work transfer rate [kW]
y	Exergy distribution ratios [kJ/kJ]
z	Elevation [m]

Matrices and vectors

$\langle \mathbf{FP} \rangle$	Fuel–Product matrix ($n \times n$)
$\langle \mathbf{KP} \rangle$	Technical coefficients matrix ($n \times n$)
$\langle \mathbf{P}\|$	Production resources driven matrix ($n \times n$)
$\langle \mathbf{P}^*\|$	Production cost resources driven matrix ($n \times n$)
$\|\mathbf{P} \rangle$	Production demand driven matrix ($n \times n$)
$\|\mathbf{P}^* \rangle$	Production cost demand driven matrix ($n \times n$)
$\mathbf{U}_{\mathrm{D}}$	Identity matrix ($n \times n$)

u	Unit vector (1 × n)

Greek letters

α	elements of elasticity matrix
β	Ratio of chemical exergy
Δ	Group of contribution
ε	Exergy efficiency
κ	technical coefficients
μ	Chemical potential
π	elements of the production resources driven matrix
ρ	Renewability ratio

Subscripts and Superscripts

0	Environment
D	Diagonal matrix
e	Exit stream
eq	Equivalent
gr	Group
i	Inlet stream
CH	Chemical
K	Kinetic
P	Potential
PH	Physical
nrs	Non renewable source
rs	Renewable source
t	Transpose matrix
-1	Inverse matrix
*	Exergy cost

Abbreviations

APPA	Spanish Renewable Energy Association
AEBIOM	European Biomass Association
BAU	Business as usual
BtL	Biomass to liquid
CEN	European standardization body
CHP	Combined heat and power
db	Dry basis
DEFRA	Department of environment, food and rural affairs, UK
DG AGRI	Directorate-General of Agriculture and Rural Development, European Commission
DG CLIMA	Directorate-General of Climate Action, European Commission
DG ENER	Directorate-General of Energy, European Commission
DG TREN	Directorate-General of Transport and Energy, European Commission
DME	Dimethylether
EABA	European Algae Biomass Association
EBB	European Biodiesel Board

EBTP	European Biofuels Technology Platform
EC	European Commission
ECEC	Ecological cumulative exergy consumption
ELCA	Exergy life cycle assessment
EROI	Energy return on energy investment
ESBF	European Sustainable Biofuels Forum
ExFA	Exergy flow analysis
ExROI	Exergy return on exergy investment
EU	European Union
EU-27	European Union comprising 27 member states (excluding Croatia)
FAME	Fatty acid methyl ester (biodiesel)
FAO	Food and Agriculture Organisation of the United Nations
FEDIOL	EU Vegetable Oil and Protein meal Industry Association
FFA	Free fatty acid
FFB	Fresh fruit bunches
GBEP	Global Bioenergy Partnership
GEREGRAS	Spanish association of vegetable oil and fat residues management companies
GHG	Greenhouse gas
GtL	Gas to liquid
HORECA	Sector of the food service industry
HVO	Hydrotreated vegetable oil
IEA	International Energy Agency
IFES	Integrated Food Energy System
ILUC	Indirect land use change
IPCC	Inter-governmental Panel on Climate Change
JB	Joback contribution method
JK	Jankowski method
LCA	Life cycle assessment
LCI	Life cycle inventory
LIIB	Low Indirect Impact Biofuels
LHV	Lower heating value
ME	Methyl ester
NG	Natural gas
NGO	Non-governmental organisation
OPEC	Organization of the Petroleum Exporting Countries
Ph-L	Phospholipids
Ppm	parts per million
PVO	Pure vegetable oil
RES	Renewable Energy Sources
SNG	Synthetic natural gas
Toe	Tonne of oil equivalent
TSE	Transmissible spongiform encephalopathies
UCO	Used cooking oil
UN	United Nations
VK	Van Krevelen-Chermin method
WEF	World Economic Forum

References

[1] Aatola, H., Larmi, M., Sarjovaara, T. and Mikkonen, S. *Hydrotreated vegetable oil (HVO) as a renewable diesel fuel: trade-off between NOx, particulate emission, and fuel consumption of a heavy duty engine.* SAE International, volume 2008–01–2500, p. 12, 2008. URL `http://biofuelstp.eu/downloads/SAE_Study_Hydrotreated_Vegetable_Oil_HVO_as_a_Renewable_Diesel_Fuel.pdf`.

[2] ACEA. *Worldwide Fuel Charter (WWFC) biodiesel guidelines*, 2008. URL `http://www.acea.be/images/uploads/files/20080717_Proposed_WWFC_B100_Guideline_final_draft_June_2008.pdf`.

[3] ADEME. *Life cycle assessment applied to first generation biofuels consumed in France.* Technical report, Department of Bioresources. Directorate of Renewable Energies, Energy Networks and Markets, ADEME, 2009.

[4] Ahlenius, H. *Current and potential arable land use in Africa.* Technical report, UNEP/GRID-Arenda, 2006. URL `http://www.grida.no/graphicslib/detail/current-and-potential-arable-land-use-in-africa_a9fd#`.

[5] Angerbauer, C., Siebenhofer, M., Mittelbach, M. and Guebitz, G. *Conversion of sewage sludge into lipids by lipomyces starkeyi for biodiesel production.* Bioresource Technology, volume 99(8), pp. 3051 – 3056, 2008. URL `http://www.sciencedirect.com/science/article/pii/S0960852407005111`.

[6] APPA. *Estudio del impacto macroeconómico de las energías renovables en España.* Technical report, APPA, Spanish Renewable Energy Association, 2010. URL `http://www.appa.es/02appa/02b-documentosappa.php`.

[7] Arcari, P. *Biodiesel in Australia, benefits, issues and opportunities for local government uptake.* Technical report, ICLEI, 2007. URL `http://www.iclei.org/fileadmin/user_upload/documents/ANZ/CCP/CCP-AU/Projects/Biodiesel/BiodieselReportMain_V14_071018.pdf`.

[8] Arvanitoyannis, I. *ISO 14040: Life cycle assessment (LCA) – Principles and guidelines. Ch. 3.* In I. Arvanitoyannis (editor), *Waste management for the food industries*, pp. 97–132. Academic Press, Amsterdam, 2008.

[9] *ASTM D7566 – 13. Standard specification for aviation turbine fuel containing synthesized hydrocarbons.* URL `http://www.astm.org/Standards/D7566.htm#an00001`.

[10] ATSDR. *Toxicological profile for n-hexane.*

[11] Ayoub, M. and Abdullah, A.Z. *Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry.* Renewable and Sustainable Energy Reviews, volume 16(5), pp. 2671 – 2686, 2012. URL `http://www.sciencedirect.com/science/article/pii/S1364032112000664`.

[12] Ayres, R. *Eco-thermodynamics: economics and the second law.* Ecological Economics, volume 26(2), pp. 189 – 209, 1998. URL `http://www.sciencedirect.com/science/article/pii/S0921800997001018`.

[13] Ayres, R. and Ayres, L. *Accounting for resources, 2: the life cycle of materials.* Edward Elgar Publishing Ltd., 1999.

[14] Ayres, R., Ayres, L. and Martinas, K. *Eco-Thermodynamics: exergy and life cycle analysis.* Technical report, INSEAD's Centre for the Management of Environmental Resources, 1996.

[15] Ayres, R.U. and Ayres, L. *Industrial Ecology. Towards closing the materials cycle.* Elgar Publishing Ltd., UK, 1996.

[16] Balda, M., Font de Mora, E., Contreras, T. and Manso, A. *Desarrollo y aplicaciones de los biocarburantes.* Technical report, Congreso Nacional del Medio Ambiente, Madrid, 2009. URL `http://www.conama9.org/conama9/download/files/GTs/GT_BIOC//BIOC_final.pdf`.

[17] Bejan, A., Tsatsaronis, G. and Moran, M.J. *Thermal Design and Optimization.* Wiley, 1996.

[18] Berndes, G., Bird, N. and Cowie, A. *Bioenergy, land-use change and climate change mitigation.* Bioenergy:ExCo:2010:03, volume 3, 2010. URL `www.ieabioenergy.com`.

[19] Berthiaume, R., Bouchard, C. and Rosen, M.A. *Exergetic evaluation of the renewability of a biofuel.* Exergy, An International Journal, volume 1(4), pp. 256 – 268, 2001. URL `http://www.sciencedirect.com/science/article/pii/S1164023501000292`.

[20] Beurskens, L., Hekkenberg, M. and Vethman, P. *Renewable energy projections as published in the national renewable energy action plans of the European Member States. Covering all 27 EU Member States with updates for 20 Member States.* Technical report, ECN, financed by the European Environmental Agency, 2011. URL `http://www.ecn.nl/docs/library/report/2010/e10069.pdf`.

[21] BioDieNet Project. *The future of small scale, localised biodiesel production from used cooking oil and its use in higher blends.* Technical report, Project supported by the Intelligent Energy – Europe (IEE) Programme of the European Commission, 2009.

[22] BioGrace Project. *Harmonised calculations of bioenergy greenhouse gas emissions in Europe.* Technical report, Supported by the Intelligent Energy – Europe Programme (IEE) of the European Commission, 2013. URL `http://www.biograce.net/`.

[23] *BIOMAP - Time-enabled mapping and dissemination tool for biofuel projects.* 7th Framework Programme Coordination and Support Action.

[24] BIOPLAT. *Documento de visión a 2030.* Technical report, BioPlat, Spanish Biomass Technology Platform, 2012. URL `http://www.bioplat.org/setup/upload/modules_docs/content_cont_URI_625.pdf`.

[25] BIOPLAT. *Energy from algae. Present and future.* Technical report, BioPlat, Spanish Biomass Technology Platform, 2012. URL `http://www.bioplat.org/setup/upload/modules_docs/content_cont_URI_2104.pdf`.

[26] Brandt, A.R. *Oil depletion and the energy efficiency of oil production: the case of California.* Sustainability, volume 3(10), pp. 1833–1854, 2011. URL `http://www.mdpi.com/2071-1050/3/10/1833`.

[27] Bringezu, S., Schütz, H., O´Brien, M. et al. *Towards sustainable production and use of resources: assessing biofuels.* Technical report, UNEP, 2009.

[28] Bromberg, L. and Cheng, W. *Methanol as an alternative transportation fuel in the US: Options for sustainable and/or energy-secure transportation.* Technical report, Sloan Automotive Laboratory, Massachusetts Institute of Technology and Cambridge, 2010. URL `http://www.afdc.energy.gov/pdfs/mit_methanol_white_paper.pdf`.

[29] Brown, A. and Fulton, L. *Technology roadmap, biofuels for transport.* Technical report, OECD/IEA, 2011. URL `http://www.iea.org/publications/freepublications/publication/biofuels_roadmap.pdf`.

[30] Bustos, M. and Font de Mora, E. *Biocarburantes y desarrollo sostenible. Mitos y realidades.* Technical report, APPA, Spanish Renewable Energy Association, 2007.

[31] California Environmental Protection Agency. *Low Carbon Fuel Standard Program pursuant to the California Assembly Bill AB 32 and the Governor's Executive Order S-01-07*, 2013. URL `http://www.arb.ca.gov/fuels/lcfs/lcfs.htm`.

[32] Canadian Council of Ministries of the Environment. *Canadian water quality guidelines: imidacloprid. Scientific supporting document*, 2007.

[33] Carroll, J. and Finnan, J. *Emissions and efficiencies from the combustion of agricultural feedstock pellets using a small scale tilting grate boiler.* Biosystems Engineering, volume 115(1), pp. 50 – 55, 2013. URL `http://www.sciencedirect.com/science/article/pii/S1537511013000172`.

[34] *CARS 21 High level group on the competitiveness and sustainable growth of the automotive industry in the European Union. Final report 2012*, 2012. URL `http://ec.europa.eu/enterprise/sectors/automotive/files/cars-21-final-report-2012_en.pdf`.

[35] CEI-Bloomberg. *Next generation biofuels and other bioproducts: opportunities for the countries of the central European initiative*, 2012.

[36] CEN, European Committee for Standardization. *EN14214 - Liquid petroleum products - Fatty acid methyl esters (FAME) for use in diesel engines and heating applications - Requirements and test methods*, 2008.

[37] CEN, European Committee for Standardization. *EN590 - Automotive fuels - Diesel - Requirements and test methods*, 2009.

[38] Chen, C., Habert, G., Bouzidi, Y., Jullien, A. and Ventura, A. *LCA allocation procedure used as an incitative method for waste recycling: an application to mineral additions in concrete.* Resources, Conservation and Recycling, volume 54(12), pp. 1231 – 1240, 2010. URL `http://www.sciencedirect.com/science/article/pii/S0921344910000935`.

[39] Cheremisinoff, N.P. *Handbook of solid waste management and waste minimization technologies.* Elsevier Science, 2003.

[40] Chico-Santamarta, L., Humphries, A.C., Chaney, K. et al. *Microbial changes during the on-farm storage of canola (oilseed rape) straw bales and pellets.* Biomass and Bioenergy, volume 35(7), pp. 2939 – 2949, 2011. URL `http://www.sciencedirect.com/science/article/pii/S0961953411001693`.

[41] Chiu, C.W., Goff, M.J. and Suppes, G.J. *Distribution of methanol and catalysts between biodiesel and glycerin phases.* AIChE Journal, volume 51(4), pp. 1274–1278, 2005. URL `http://dx.doi.org/10.1002/aic.10385`.

[42] Chum, H., Faaij, A., Moreira, J. et al. *Bioenergy. In IPCC special report on renewable energy sources and climate change mitigation.* Technical report, IPCC, 2011. URL `http://srren.ipcc-wg3.de/report/IPCC_SRREN_Ch02.pdf`.

[43] CIRCE. *The Exergoecology Portal*, 2013. URL `http://www.exergoecology.com/`.

[44] Cleveland, C. and Herendeen, R. *Solar parabolic collectors: succeeding generations are better net energy and exergy producers.* Energy Systems and Policy, volume 13, pp. 63–77, 1989.

[45] Cleveland, C.J. *Net energy from the extraction of oil and gas in the United States.* Energy, volume 30(5), pp. 769 – 782, 2005. URL `http://www.sciencedirect.com/science/article/pii/S0360544204002890`.

[46] Cleveland, C.J., Costanza, R., Hall, C.A.S. and Kaufmann, R. *Energy and the U.S. economy: a biophysical perspective.* Science, volume 225(4665), pp. 890–897, 1984. URL `http://www.sciencemag.org/content/225/4665/890.abstract`.

[47] Cleveland, C.J. and O'Connor, P.A. *Energy Return on Investment (EROI) of oil shale.* Sustainability, volume 3(11), pp. 2307–2322, 2011. URL `http://www.mdpi.com/2071-1050/3/11/2307`.

[48] CODEX. *Standard for names vegetable oils.* URL `http://www.codexalimentarius.org/`.

[49] Comisión Nacional de la Energía, CNE. *Informe anual sobre el uso de biocarburantes en España en 2011.* Technical report, CNE, 2013. URL `http://www.cne.es/cne/doc/prensa/NP_1_3_13.pdf`.

[50] Cornelissen, R. *Thermodynamics and sustainable development; the use of exergy analysis and the reduction of irreversibility.* Ph.D. thesis, University of Twente, 1997.

[51] Cornelissen, R. and Hirs, G. *The value of the exergetic life cycle assessment besides the LCA.* Energy Conversion and Management, volume 43(12), pp. 1417 – 1424, 2002. URL `http://www.sciencedirect.com/science/article/pii/S0196890402000250`.

[52] Darlington, T., Kahlbaum, D., O'Connor, D. and Mueller, S. *Land use change greenhouse gas emissions of European biofuel policies utilizing the Global Trade Analysis Project (GTAP) Model.* Technical report, Air Improvement Resource, Inc., S&T Consultants, University of Illinois, 2013.

[53] Demirbas, A. *Progress and recent trends in biofuels.* Progress in Energy and Combustion Science, volume 33(1), pp. 1 – 18, 2007. URL `http://www.sciencedirect.com/science/article/pii/S0360128506000256`.

[54] Dewulf, J., Van Lagenhove, H. and de Velde B, V. *Exergy-based efficiency and renewability assessment of biofuel production.* Environmental Science and Technology 2005;39:3878e82, volume 39, pp. 3878–3882, 2005. URL `http://pubs.acs.org/doi/abs/10.1021/es048721b`.

[55] Di Lucia, L. *External governance and the EU policy for sustainable biofuels, the case of Mozambique.* Energy Policy, volume 38(11), pp. 7395 – 7403, 2010. URL `http://www.sciencedirect.com/science/article/pii/S0301421510006294`.

[56] Di Lucia, L., Ahlgren, S. and Ericsson, K. *The dilemma of indirect land-use changes in EU biofuel policy: an empirical study of policy-making in the context of scientific uncertainty.* Environmental Science & Policy, volume 16, pp. 9 – 19, 2012. URL `http://www.sciencedirect.com/science/article/pii/S1462901111001754`.

[57] *Diester Partenaires.* URL `http://www.partenaires-diester.com/`.

[58] Dincer, I. and Rosen, M.A. *Exergy: energy, environment and sustainable development.* Newnes, 2012.

[59] Doppelbauer, J. *ERRAC. For a sustainable and efficient rail transport sector.* In *Sustainable energy for transport with alternative fuels. EU Sustainable Energy Week.* 2013. URL `http://eusew.eu/upload/events/553_1207_presentation%20josef%20doppelbauer%20errac%20.pdf`.

[60] Durham, C., Davies, G. and Bhattacharyya, T. *Can biofuels policy work for food security?* Technical report, DEFRA, 2012.

[61] EABA. *European Algae Biofuels Association.* URL `http://www.eaba-association.eu/`.

[62] ECOFYS. *Renewable energy progress and biofuel sustainability.* Technical report, Report for the European Commission, 2012. URL `http://ec.europa.eu/energy/renewables/reports/doc/2013_renewable_energy_progress.pdf`.

[63] *EcoInvent.* URL `www.ecoinvent.org`.

[64] Edwards, S., Asmelash, A., Araya, H. and Berhan Gebre Egziabher, T. *Impact of compost use on crop yields in Tigray, Ethiopia.* Technical report, FAO, 2007. URL `http://betuco.be/compost/Impact%20of%20Compost%20Use%20on%20Crop%20Yields%20in%20Tigray,%20Ethiopia.pdf`.

[65] EFMA. *Best available techniques for pollution prevention and control in the European fertilizer industry, booklet No. 4 of 8: production of phosphoric acid.* 2000.

[66] El-Sayed, Y. *The Thermoeconomic of Energy Conversion.* Elsevier Ltd. Oxford U.K., 2003.

[67] El-Sayed, Y.M. and Evans, R.B. *Thermoeconomics and the Design of Heat Systems.* Journal for Engineering for Power, volume 92(1), pp. 27–35, 1970. URL `http://dx.doi.org/10.1115/1.3445296`.

[68] Encyclopædia Britannica. *Fuller's earth*, 2013. URL `http://www.britannica.com/EBchecked/topic/221929/fullers-earth`.

[69] Epina eBook Team. *Sodium hydroxide*. URL `http://www.vias.org/genchem/inorgcomp_sodiumhydroxide.html`.

[70] ePURE. *The production of renewable ethanol*. URL `http://www.epure.org/product/production-renewable-ethanol`.

[71] Erickson, D. (editor). *Edible fats and oils processing. Basic principles and modern practices. (World Conference Proceedings)*. American Oil Chemists' Society, 1990.

[72] EurObserv'ER Project. *Biofuels barometer*. Technical report, Supported by the Intelligent Energy – Europe (IEE) Programme of the European Commission, 2012. URL `http://www.eurobserv-er.org/downloads.asp`.

[73] European Biofuels Technology Platform. *Biofuels production. Advanced biofuels*. URL `http://www.biofuelstp.eu/fuelproduction.html#second`.

[74] European Commission. *Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions. Limiting global climate change to 2 degrees Celsius, the way ahead for 2020 and beyond*. COM(2007) 2 final. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2007:0002:FIN:EN:HTML`.

[75] European Commission. *European Platform on Life Cycle Assessment (LCA)*. URL `http://ec.europa.eu/environment/ipp/lca.htm`.

[76] European Commission. *Communication from the Commission to the Council and the European Parliament, Integrated product policy, building on environmental life-cycle thinking*. COM(2003) 302 final, 2003. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2003:0302:FIN:en:PDF`.

[77] European Commission. *Communication from the Commission on the practical implementation of the EU biofuels and bioliquids sustainability scheme and on counting rules for biofuels*. COM/160/16, 2010. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:C:2010:160:0008:01:EN:HTML`.

[78] European Commission. *Report from the Commission on indirect land-use change related to biofuels and bioliquids*. COM(2010) 811 final, 2010.

[79] European Commission. *Report from the Commission to the Council and the European Parliament on sustainability requirements for the use of solid and gaseous biomass sources in electricity, heating and cooling*. COM(2010) 11, 2010. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2010:0011:FIN:EN:HTML`.

[80] European Commission. *Commission staff working document accompanying the White Paper - Roadmap to a single European Transport Area. Towards a competitive and resource efficient transport system*, 2011. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=SEC:2011:0391:FIN:EN:PDF`.

[81] European Commission. *Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions. Energy Roadmap 2050*, 2011. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2011:0885:FIN:EN:PDF`.

[82] European Commission. *EG FTF - 1st report of the expert group: future transport fuels.* Technical report, European Commission Expert Group on Future Transport Fuels, 2011. URL `http://ec.europa.eu/transport/themes/urban/cts/future-transport-fuels_en.htm`.

[83] European Commission. *EG FTF - 2nd report of the expert group: infrastructure for alternative fuels.* Technical report, European Commission Expert Group on Future Transport Fuels, 2011. URL `http://ec.europa.eu/transport/themes/urban/cts/future-transport-fuels_en.htm`.

[84] European Commission. *Flightpath 2050. Europe's vision for aviation. Maintaining global leadership serving society needs.* Technical report, European Commission High Level Group on Aviation Research, 2011. URL `http://ec.europa.eu/transport/modes/air/doc/flightpath2050.pdf`.

[85] European Commission. *White Paper roadmap to a single European Transport Area. Towards a competitive and resource efficient transport system*, 2011. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2011:0144:FIN:EN:HTML`.

[86] European Commission. *Commission staff working document accompanying the proposal for a Directive of the European Parliament and of the Council amending Directive 98/70/EC relating to the quality of petrol and diesel fuels and amending Directive 2009/28/EC on the promotion of the use of energy from renewable sources*, 2012. URL `http://ec.europa.eu/energy/renewables/biofuels/doc/biofuels/swd_2012_0343_ia_en.pdf`.

[87] European Commission. *Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions. Renewable energy: a major player in the European energy market.* COM(2012) 271 final, 2012. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2012:0271:FIN:EN:PDF`.

[88] European Commission. *EU energy statistics in figures, statistical pocketbook 2012.* 2012.

[89] European Commission. *Proposal for a Directive of the European Parliament and of the Council amending Directive 98/70/EC relating to the quality of petrol and diesel fuels and amending Directive 2009/28/EC on the promotion of the use of energy from renewable sources*, 2012. URL `http://ec.europa.eu/energy/renewables/biofuels/doc/biofuels/com_2012_0595_en.pdf`.

[90] European Commission. *Prospects for agricultural markets and income in the EU 2012-2020.* Technical report, European Commission, Directorate-General for Agriculture and Rural Development, 2012. URL `http://ec.europa.eu/agriculture/publi/caprep/prospects2012/fullrep_en.pdf`.

[91] European Commission. *Commission Staff working Document Accompanying the Report from the Commission to the European Parliament and the Council on the renewable energy progress report*, 2013. URL `http://ec.europa.eu/energy/renewables/reports/doc/swd_2013_0102_res_en.pdf`.

[92] European Commission. *Commission Staff working Document Impact Assessment Accompanying the document Proposal for a Directive on the deployment of alternative fuels infrastructure*, 2013. URL `http://ec.europa.eu/transport/themes/urban/cpt/doc/swd(2013)5-2-impact-assessment-part1.pdf`.

[93] European Commission. *Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions. Clean Power for Transport: A European alternative fuels strategy*, 2013. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2013:0017:FIN:EN:PDF`.

[94] European Commission. *Proposal for a Directive of the European Parliament and of the Council on the deployment of alternative fuels infrastructure*, 2013. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2013:0018:FIN:EN:PDF`.

[95] European Commission. *Report from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the renewable energy progress report*, 2013. URL `http://ec.europa.eu/energy/renewables/reports/doc/com_2013_0175_res_en.pdf`.

[96] European Commission, DG AGRI. *Reducing emissions from transport*. Technical report, European Commission, 2011. URL `http://ec.europa.eu/clima/policies/transport/index_en.htm`.

[97] European Union. *Directive 2003/30/EC of the European Parliament and of the Council of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport*, 2003. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2003:123:0042:0042:EN:PDF`.

[98] European Union. *Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives*, 2008. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:312:0003:0030:en:PDF`.

[99] European Union. *Directive 2009/28/EC of the European Parliament and the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC*, 2009. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=Oj:L:2009:140:0016:0062:en:PDF`.

[100] European Union. *Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009 amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amending Council Directive 1999/32/EC as regards the specification of fuel used by inland waterway vessels and repealing Directive 93/12/EEC*, 2009. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0088:0113:EN:PDF`.

[101] European Union. *Directive 2012/33/EU of the European Parliament and of the Council of 21 November 2012 amending Council Directive 1999/32/EC as regards the sulphur content of marine fuels*, 2012. URL `http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2012:327:0001:0013:EN:PDF`.

[102] Eurostat. *Energy consumption, EU27 energy dependence rate at 542011.* News release, 2013. URL `http://epp.eurostat.ec.europa.eu/cache/ITY_PUBLIC/8-13022013-BP/EN/8-13022013-BP-EN.PDF`.

[103] Ezieshi, E. and J.M, O. *Biochemical evaluation of millet offal as feeds for broiler chickens.* Pakistan Journal of Nutrition, volume 7, pp. 421–425, 2008. URL `http://www.pjbs.org/pjnonline/ab702.htm`.

[104] Faaij, A. *Modern biomass conversion technologies.* Mitigation and adaptation strategies for global change, volume 11, pp. 343–375, 2006. URL `http://igitur-archive.library.uu.nl/chem/2007-0621-201531/NWS-E-2006-109.pdf`.

[105] *FAO – Advances in citriculture 4. Sustainability of citrus plant nutrition and fertilization.* FAO – LEBANON GCP/LEB/021/ITA.

[106] FAO. *Impacts of bioenergy on food security. Guidance for assessment and response at national and project levels.* Environment and Natural Resources Working paper 52, FAO, 2012.

[107] FEDIOL. *The EU Vegetable Oil and Proteinmeal Industry.* URL `http://www.fediol.eu/`.

[108] FEDIOL. *Vegetable oils production, import, exports and consumption 2011 annual statistics, rev. Feb 2013*, 2013. URL `http://www.fediol.eu/data/1362407733Stat%20oils%202011rev%20feb2013.pdf`.

[109] FERTGAS. *Urea.* URL `http://www.fertgas.at/en/urea`.

[110] Finnan, J. *Feasibility of production and combustion of pellets from straw and energy crops.* Technical report, Irish Agriculture and Food Development Authority, 2010. URL `http://www.teagasc.ie/publications/2009/1320/Pelleting_5613.pdf`.

[111] Font de Mora, E., Torres, C. and Valero, A. *Assessment of biodiesel energy sustainability using the exergy return on investment concept.* Energy, volume 45(1), pp. 474 – 480, 2012. URL `http://www.sciencedirect.com/science/article/pii/S0360544212001867`.

[112] Font de Mora, E., Torres, C., Valero, A. and Zambrana, D. *Defossilisation assessment of biodiesel life cycle production using the ExROI indicator.* In *Proceedings of ECOS 2012. The 25th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems (June 26-29, 2012, Perugia, Italy)*, pp. 240–249. 2012. URL `http://www.scopus.com/scopus/inward/record.url?eid=2-s2.0-0031388275&partnerID=40&rel=R6.5.0`.

[113] Font de Mora, E., Vivarelli, S. and Dubolino, D. *Bioenergy Markets in the EU - How Intelligent Energy-Europe is Contributing.* European Energy Innovation, volume Summer 2012, pp. 12–13, 2012. URL `http://www.europeanenergyinnovation.eu/Articles/Autumn2012/BioenergyMarketsintheEU.aspx`.

[114] Frangopoulos, C. *Thermo-economic functional analysis and optimization.* Energy, volume 12(7), pp. 563–571, 1987.

[115] Frangopoulos, C.A. and Caralis, Y.C. *A method for taking into account environmental impacts in the economic evaluation of energy systems.* Efficiency, Cost, Optimization, Simulation and Environmental Aspects of Energy Systems, volume 38(15–17), pp. 1751–1763, 1997.

[116] Freedman, B., Pryde, E. and Mounts, T. *Variables affecting the yields of fatty esters from transesterified vegetable oils.* Journal of the American Oil Chemists Society, volume 61, pp. 1638–1643, 1984. URL `http://dx.doi.org/10.1007/BF02541649`.

[117] Gaggioli, R. and Wepfer, W. *Exergy economics - I. Cost accounting applications.* Energy, volume 5(8), pp. 823–837, 1980. URL `http://www.sciencedirect.com/science?_ob=GatewayURL&_origin=ScienceSearch&_method=citationSearch&_piikey=0360544280900997&_version=1&_returnURL=&md5=70ab8a252c23162f6326a9913fe282cb`.

[118] Gaggioli, R.A. and El-Sayed, Y.M. *A Critical Review of Second Law Costing Methods.* In *Proceedings of the IV Internatonal Symposium on Second Law Analysis of thermal Systems*, pp. 59–73. ASME, 1987.

[119] Garofalo, R. *Incentives to promote the use of biofuels, EBB perspectives.* In *Incentives for Biofuels in Aviation, Biofuels FlightPath Workshop, June 20th 2012*. 2012.

[120] Gartner, S.O. and Reinhard, G.A. *Life cycle assessment of biodiesel: update and new aspects.* Technical report, IFEU, Institute for Energy and Environmental Research Heidelberg, 2003. URL `http://www.co2star.eu/publications/ifeu_berichte/Biodiesel-engl-IFEU.pdf`.

[121] Gateau, P. *Twelve years of using 50% RME fuel mixture in heavy trucks and light vehicles.* In *AEA 2006 Poitiers, Futuroscope, European Conference Alternative Energies for Automotive Industry*. 2006.

[122] Georgescu-Roegen, N. *The Entropy Law and the economic process in retrospect.* Eastern Economic Journal, volume 12, pp. 3–25, 1986. URL `http://www.jstor.org/stable/40357380`.

[123] Gillmann, M. *Advanced biofuels in the energy mix and their industralisation in Europe.* In *AEBIOM European Bioenergy Conference 2013*. 2013.

[124] Global BioEnergy Partnership. *The Global Bioenergy Partnership sustainability indicators for bioenergy.* Technical report, GBEP, 2011. URL `http://www.globalbioenergy.org/programmeofwork/task-force-on-sustainability/gbep-report-on-sustainability-indicators-for-bioenergy/en/`.

[125] Goedkoop, M., De Schryver, A. and Oele, M. *Introduction to LCA with SimaPro 7.* Technical report, PRé Consultants, 2008.

[126] Gustavsson, J., Cederberg, C., van Otterdijk, R. and Meybeck, A. *Global food losses and food waste. Extent, causes and prevention.* Technical report, FAO, 2011. URL `http://www.fao.org/docrep/014/mb060e/mb060e00.pdf`.

[127] Hall, C.A.S., Balogh, S. and Murphy, D.J. *What is the minimum EROI that a sustainable society must have?* Energies, volume 2(1), pp. 25–47, 2009. URL `http://www.mdpi.com/1996-1073/2/1/25`.

[128] Hamelinck, C. *Biofuels and food security. Risks and opportunities.* Technical report, Ecofys by order of ePURE, 2013. URL `http://www.ecofys.com/files/files/ecofys-2013-biofuels-and-food-security.pdf`.

[129] Hamelinck, C. *Calculating greenhouse gas savings from biofuels.* In *European Sustainable Biofuels Forum (ESBF), Stakeholders Committee Meeting.* 2013.

[130] Hamelinck, C., Schober, S., Mittelbach, M., Verolet, J. and Dehue, B. *BIOScopes. Fatty acid ethyl esters.* Technical report, BIOScopes: Biodiesel Improvement On Standards, Coordination of Producers and Ethanol Studies, 2007. Project supported by the European Commission.

[131] Hardy, T., Musialik-Piotrowska, A., Coilek, J., Moscicki, K. and Kordylewski, W. *Negative effects of biomass combustion and co-combustion in boilers.* Environment Protection Engineering, volume 38, pp. 25 – 33, 2012. URL `http://epe.pwr.wroc.pl/2012/1_2012/03hardy.pdf`.

[132] Hau, J. and Bakshi, B. *Expanding exergy analysis to account for ecosystem products and services.* Environmental Science and Technology, volume 38, pp. 3768–3777, 2004.

[133] Hill, N., Brannigan, C., Smokers, R. et al. *Developing a better understanding of the secondary impacts and key sensitivities for the decarbonisation of the EU's transport sector by 2050. Final project.* Technical report, European Commission Directorate-General Climate Action and AEA Technology plc, 2012. URL `www.eutransportghg2050.eu`.

[134] Hélaine, S., M'barek, R. and Gay, H. *Impacts of the EU biofuel policy on agricultural markets and land use. Modelling assessment with AGLINK-COSIMO (2012 version).* Technical report, JRC, Institute for Prospective Technological Studies, 2012.

[135] Hovelius, K. and Hansson, P.A. *Energy and exergy analysis of rape seed oil methyl ester (RME) production under Swedish conditions.* Biomass and Bioenergy, volume 17(4), pp. 279 – 290, 1999. URL `http://www.sciencedirect.com/science/article/pii/S0961953499000471`.

[136] IDAE. *Plan de Energías Renovables (PER) 2011-2020*, 2011. URL `http://www.idae.es/index.php/mod.documentos/mem.descarga?file=/documentos_11227_PER_2011-2020_def_93c624ab.pdf`.

[137] IEA. *Energy Technology Perspectives: scenarios and strategies to 2050.* Technical report, OCDE/IEA, 2006.

[138] IEA. *Industrial excess heat recovery technologies and applications, draft annex.* Technical report, International Energy Agency, Industrial Energy-related Technologies and Systems (IETS), 2010. URL `http://www.iea-iets.org/oslo/iea-iets.nsf/Attachments/47DF4BDBEA3A3AB5C12577DC0034B388/$FILE/Draft+Annex_ExcessHeatRecovery_oct+26.pdf`.

[139] IEA. *Renewable energy: markets and prospects by technology.* Technical report, OECD/IEA, 2011. URL `http://www.iea.org/publications/freepublications/publication/name,20554,en.html`.

[140] IEA. *CO2 emissions from fuel combustion. Highlights.* Technical report, OECD/IEA, 2012. URL `http://www.iea.org/publications/freepublications/publication/CO2emissionfromfuelcombustionHIGHLIGHTS.pdf`.

[141] IEA. *Medium-term renewable energy market report 2013.* Technical report, OECD/IEA, 2013.

[142] IEA. *Tracking Clean energy Progress 2013. IEA input to the Clean Energy Ministerial.* Technical report, OECD/IEA, 2013. URL `http://iea.org/etp/tracking/`.

[143] International Potash Institute. *Optimizing crop nutrition, potassium in soil, plant and agro ecosystem.* URL `http://www.ipipotash.org/en/`.

[144] Iowa Soybean Association. *Comparative composition of various oilseed meals.* URL `http://www.soymeal.org/table1.html`.

[145] ISQUISA. *Cloruro de potasio. Ficha técnica.* URL `http://www.isquisa.com/site/files/productos/Cloruro_de_Potasio.pdf`.

[146] István, Z. *Analyses of the state of the art, main barriers and market potential of UCOs.* Technical report, Project OILECO, supported by the Intelligent Energy – Europe (IEE) Programme of the European Commision, 2011.

[147] Jankowski, M.D., Henry, C.S., Broadbelt, L.J. and Hatzimanikatis, V. *Group contribution method for thermodynamic analysis of complex metabolic networks.* Biophysical Journal, volume 95(3), pp. 1487 – 1499, 2008. URL `http://www.sciencedirect.com/science/article/pii/S0006349508702157`.

[148] JEC - Joint Research Centre-EUCAR-CONCAWE. *Well-to-Wheels analysis of future automotive fuels and powertrains in the European context.* Technical report, DG JRC, European Commission, 2011.

[149] Johnson, F.X., Pacini, H. and Smeets, E. *Transformations in EU biofuels markets under the Renewable Energy Directive and the implications for land use, trade and forests. Occasional Paper 78.* Technical report, Center for International Forestry Research, 2012. URL `http://www.cifor.org/online-library/browse/view-publication/publication/3775.html`.

[150] Kallivroussis, L., Natsis, A. and Papadakis, G. *Rural development: the energy balance of sunflower production for biodiesel in Greece.* Biosystems Engineering, volume 81(3), pp. 347 – 354, 2002. URL `http://www.sciencedirect.com/science/article/pii/S1537511001900212`.

[151] Keep on Track! Project. *EU Tracking Roadmap 2013.* Technical report, Project supported by the Intelligent Energy – Europe (IEE) of the European Commission, 2013.

[152] Knothe, G., Krahl, J. and Van Gerpen, J. *The biodiesel handbook.* Amer Oil Chemists Society, 2005.

[153] Koltun, P. *Materials and sustainable development.* Progress in Natural Science: Materials International, volume 20, pp. 16 – 29, 2010. URL `http://www.sciencedirect.com/science/article/pii/S1002007112600021`.

[154] Kotas, T.J. *The exergy method of thermal plant analysis.* Krieger Publishing Company, Malabar, Florida, 1995.

[155] Kristöfel, C. and Wopienka, E. *Biomass report.* Technical report, MixBioPells project, supported by the Intelligent Energy – Europe (IEE) Programme of the European Commission, 2011. URL `http://www.mixbiopells.eu/fileadmin/user_upload/WP2/D2_3_biomass_report_enhanced_final_2.pdf`.

[156] Laborde, D. *Assessing the land use change consequences of European biofuel policies. Final report.* Technical report, IFPRI, 2011. URL `http://trade.ec.europa.eu/doclib/docs/2011/october/tradoc_148289.pdf`.

[157] Lahl, U. *Life cycle analysis and scientific challenges: is science mature enough to quantify ILUC?* In *European Sustainable Biofuels Forum (ESBF), Stakeholders Committee Meeting.* 2013.

[158] Lang, K. *Policy brief. Should we be concerned about competition between food and fuel?* Technical report, International Institute for Sustainable Development, 2012. URL `www.iisd.org/gsi`.

[159] Lazzaretto, A. and Tsatsaronis, G. *SPECO: A systematic and general methodology for calculating efficiencies and costs in thermal systems.* Energy, volume 31(8), pp. 1257–1289, 2006. URL `http://www.sciencedirect.com/science?_ob=GatewayURL&_origin=ScienceSearch&_method=citationSearch&_piikey=S0360544205000630&_version=1&_returnURL=&md5=4ef3e7ac682652d84e122a35f9f24cbe`.

[160] Lechon, Y., Cabal, H., De la Rua, C. et al. *Análisis de ciclo de vida de combustibles alternativos para el transporte. Fase I. Análisis de ciclo de vida comparativo del biodiesel de cereales y de la gasolina.* Technical report, Ministerio de Educación y Ciencia y Ministerio de Medio Ambiente, 2005.

[161] LIFE Programme. *Ecobus - Collecting used cooking oils to their recycling as biofuel for diesel engines.* Technical report, European Commission, 2012. URL `http://ec.europa.eu/environment/life/project/Projects/index.cfm`.

[162] Londo, M. *Technical assistance for an evaluation of international schemes to promote biomass sustainability.* Technical report, COWI Consortium: ECN, Copernicus Institute, University of Copenhagen, COWI A/S, ControlUnion Certifications, 2009.

[163] Lonza, L., Reid, A., Rose, K., Hass, H. and Maas, H. *EU renewable energy targets in 2020: Analysis of scenarios for transport.* Technical report, JEC Biofuels Programme (JRC, EUCAR, CONCAWE), 2011.

[164] Lozano, M. and Valero, A. *Determinación de la exergía para sustancias de interés industrial.* In *Ingeniería Química.* Universidad de Zaragoza, 1986.

[165] Lozano, M. and Valero, A. *Theory of the exergetic cost.* Energy, volume 18(9), pp. 939 – 960, 1993. URL `http://www.sciencedirect.com/science/article/pii/036054429390006Y`.

[166] Luebbeke, I. *WWF's view on advanced biofuels in their 100 % renewable energy vision.* In *AEBIOM European Bioenergy Conference 2013.* AEBIOM, 2013.

[167] Marelli, L. and Edwards, R. *Life cycle GHG emissions in the EU biofuels legislation.* In *Workshop on GHG life cycle analysis.* European Commission - DG Joint research Centre (JRC), Institute for Energy and Transport, 2011. URL `http://www.globalbioenergy.org/fileadmin/user_upload/gbep/docs/2011_events/Workshop_on_GHG_LCA_Tokyo_15Nov2011/9._Edwards_Marelli.pdf`.

[168] Martens, R. and Antonini, E. *Pure plant oil as fuel. Technical aspects and legislative context.* 2011. Project Agriforenergy II, supported by the Intelligent Energy – Europe Programme (IEE) of the European Commission.

[169] Martin, M. and Eklund, M. *Improving the environmental performance of biofuels with industrial symbiosis.* Biomass and Bioenergy, volume 35(5), pp. 1747 – 1755, 2011. URL `http://www.sciencedirect.com/science/article/pii/S0961953411000171`.

[170] McNeil, J., Day, P. and Sirovski, F. *Glycerine from biodiesel: the perfect diesel fuel.* Process Safety and Environmental Protection, volume 90(3), pp. 180 – 188, 2012. URL `http://www.sciencedirect.com/science/article/pii/S0957582011001017`.

[171] Meyer, L., Tsatsaronis, G., Buchgeister, J. and Schebek, L. *Exergoenvironmental analysis for evaluation of the environmental impact of energy conversion systems.* Energy, volume 34(1), pp. 75–89, 2009. URL `http://www.sciencedirect.com/science/article/pii/S0360544208001837`.

[172] Mido, Y. and Satake, M. *Chemistry for agriculture and ecology.* Discovery Publishing House, 1995.

[173] Mika, M., Volakova, P., Verner, V., Jankovsky, O. and Klapste, B. *New straw combustion technology for cleaner energy.* World Academy of Science, Engineering and Technology, volume 64, pp. 929 – 932, 2012. URL `http://www.waset.org/journals/waset/v64/v64-177.pdf`.

[174] Miller, R.E. and Blair, P.D. *Input-Output analysis: foundations and extensions.* Cambridge University Press, 2009.

[175] Mittelbach, M. *Advanced biofuels. Definition, technical and non-technical barriers.* In *European Sustainable Biofuels Forum (ESBF), Stakeholders Committee Meeting.* 2013.

[176] Mittelbach, M. and Remschmidt, C. *Biodiesel: the comprehensive handbook.* Boersedruck Ges.m.b.H, 2004.

[177] Moavenzadeh, J., Chiesa, T., Ammirati, S. et al. *Sustainable transportation ecosystem. Addressing sustainability from an integrated systems perspective.* Technical report, World Economic Forum, 2012. URL `http://www.weforum.org/reports`.

[178] Mondala, A., Liang, K., Toghiani, H., Hernandez, R. and French, T. *Biodiesel production by in situ transesterification of municipal primary and secondary sludges.* Bioresource Technology, volume 100(3), pp. 1203 – 1210, 2009. URL `http://www.sciencedirect.com/science/article/pii/S0960852408007207`.

[179] Moniz, E.J., Jacoby, H.D. and Meggs, A.J.M. *The Future of natural gas. An interdisciplinary MIT study.* Technical report, MIT Massachusetts Institute of Technology, 2010.

[180] Moran, M. and Shapiro, H.N. *Fundamentals of Engineering Thermodynamic.* 2nd Edition. Wiley and Sons. New York., 2003.

[181] Morris, D.R. and Szargut, J. *Standard chemical exergy of some elements and compounds on the Earth planet.* Energy, volume 11, pp. 733–755, 1986.

[182] Murphy, D.J., Hall, C.A., Dale, M. and Cleveland, C. *Order from chaos: a preliminary protocol for determining the EROI of fuels.* Sustainability, volume 3(10), pp. 1888–1907, 2011. URL `http://www.mdpi.com/2071-1050/3/10/1888`.

[183] Mylly, M. *Sustainable energy for transport with alternative fuels. A maritime transport perspective.* In *Sustainable energy for transport with alternative fuels. EU Sustainable Energy Week.* 2013. URL `http://eusew.eu/upload/events/553_1207_presentation%20markku%20mylly%20emsa.pdf`.

[184] Navia, R. and Mittelbach, M. *Could sewage sludge be considered a source of waste lipids for biodiesel production?* Waste Management and Research, volume 30(9), pp. 873–874, 2012. URL `http://wmr.sagepub.com/content/30/9/873.full.pdf+html?rss=1`.

[185] Nisworo, A.P. *Biodiesel by supercritical transesterification: process design and economic feasibility.* Master's thesis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology (Technische Universiteit Eindhoven), 2005. URL `http://alexandria.tue.nl/repository/books/629823.pdf`.

[186] NSW HSC, online. *Industrial chemistry: Solvay process.* URL `http://hsc.csu.edu.au/chemistry/options/industrial/2765/Ch956.htm`.

[187] O'Connor, D. *Biodiesel GHG emissions, past, present and future.* Technical report, IEA Bioenergy Task 39, 2011. URL `http://www.task39.org/LinkClick.aspx?fileticket=E5r1rznoEzU%3D&tabid=4348`.

[188] Odum, H.T. *Environmental accounting: emergy and environmental decision making.* Wiley, 1996.

[189] Olkiewicz, M., Fortuny, A., Staber, F. et al. *Evaluation of different sludges from WWTP as a potential source for biodiesel production.* Procedia Engineering, volume 42, pp. 634 – 643, 2012. URL `http://www.sciencedirect.com/science/article/pii/S1877705812028561`.

[190] Paraiba, O., Tsoutsos, T., Tournaki, S. et al. *Strategies for the optimization of the domestic used cooking oil to biodiesel chain. The European project RecOil.* In *Proceedings of the 20th European Biomass Conference and Exhibition.* 2012. Project RecOil, supported by the Intelligent Energy – Europe Programme (IEE) of the European Commission.

[191] Parry, M., Canziani, O., Palutikof, J., van der Linden, P. and Hanson, C. *IPCC Fourth Assessment Report, Climate Change 2007: Impacts, adaptation and vulnerability, contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* Technical report, IPCC, 2007. URL `http://www.ipcc.ch/publications_and_data/publications_ipcc_fourth_assessment_report_wg2_report_impacts_adaptation_and_vulnerability.htm`.

[192] Paulin, B. and O'Malley, P. *Compost production and use in horticulture.* Technical report, Western Australian Agriculture Authority, 2008. URL `http://www.agric.wa.gov.au/objtwr/imported_assets/content/hort/compost_bulletin08.pdf`.

[193] Peters, D., van den Bos, A. and van de Staaij, J. *Assessing grandfathering options under an EU ILUC policy.* Technical report, ECOFYS, 2012.

[194] Pleanjai, S., Gheewala, S. and Garivait, S. *Environmental evaluation of biodiesel production from palm oil in a life cycle perspective.* Asian Journal of Energy and Environment, volume 8, pp. 15–32, 2007. URL `http://www.jseejournal.com/AJEE%202007/3.Environmental%20evaluation%20p.15-32.pdf`.

[195] Pokoo-Aikins, G., Heath, A., Mentzer, R.A. et al. *A multi-criteria approach to screening alternatives for converting sewage sludge to biodiesel.* Journal of Loss Prevention in the Process Industries, volume 23(3), pp. 412 – 420, 2010. URL `http://www.sciencedirect.com/science/article/pii/S0950423010000173`.

[196] Products, O.C.A. *Hydrochloric acid (HCl).* URL `http://www.olinchloralkali.com/Products/HydrochloricAcid.aspx`.

[197] Ragwitz, M., Schade, W., Breitschopf, B. et al. *EmployRES. The impact of renewable energy policy on economic growth and employment in the European Union. Final report.* Technical report, EmployRES partnership: Fraunhofer ISI, Ecofys, EEG, Rütter + Partner, LEI and SEURECO, 2009. Project supported by the Intelligent Energy – Europe (IEE) of the European Commission.

[198] Reid, R.C., Prausnitz, J. and Sherwood, T.K. *The properties of gases and liquids.* McGraw-Hill, 1987.

[199] Reistad, G.M. *Availability: Concepts and Applications.* Ph.D. thesis, University of Wisconsin, USA, 1970.

[200] *REN21. 2013. Renewables 2013 global status report*, 2013. URL `http://www.ren21.net/`.

[201] Riegel, E. and Kent, J. *Riegel's Handbook of Industrial Chemistry.* Kluwer Academics / Plenum Publishers, 2003.

[202] Rivero, R. and Garfias, M. *Standard chemical exergy of elements updated.* Energy, volume 31(15), pp. 3310 – 3326, 2006. URL `http://www.sciencedirect.com/science/article/pii/S0360544206000569`.

[203] Rosen, C.J. and Bierman, P.M. *Using manure and compost as nutrient sources for fruit and vegetable crops*, 2005. URL `http://www.extension.umn.edu/distribution/horticulture/M1192.html`. Department of Soil, Water, and Climate, University of Minnesota.

[204] Russi, D. *An integrated assessment of a large-scale biodiesel production in Italy: killing several birds with one stone?* Energy Policy, volume 36(3), pp. 1169 – 1180, 2008. URL `http://www.sciencedirect.com/science/article/pii/S0301421507005083`.

[205] Rutz, D. and Janssen, R. *Biofuel technology handbook.* Technical report, Project Biofuel Marketplace, supported by the Intelligent Energy – Europe Programme (IEE) of the European Commission, 2008.

[206] SABIC. *Prilled urea and granular urea.* URL `http://www.sabic.com/corporate/en/productsandservices/fertilizers/prilled-rea-granular-rea`.

[207] Sciubba, E. *Extended exergy accounting applied to energy recovery from waste: The concept of total recycling.* Strategies of Waste Energy Usage: Belin-Brandenburg Academy of Sciences Conference Dec 1999, volume 28(13), pp. 1315–1334, 2003.

[208] SETIS. *2011 Technology map of the European strategic energy technology plan (SET-Plan). Technology descriptions.* Technical report, JRC-IET, European Commission, 2011. URL `http://setis.ec.europa.eu/about-setis/technology-map/2011_Technology_Map1.pdf/view`.

[209] Siddiquee, M.N. and Rohani, S. *Experimental analysis of lipid extraction and biodiesel production from wastewater sludge.* Fuel Processing Technology, volume 92(12), pp. 2241 – 2251, 2011. URL `http://www.sciencedirect.com/science/article/pii/S0378382011002785`.

[210] Siddiquee, M.N. and Rohani, S. *Lipid extraction and biodiesel production from municipal sewage sludges: A review.* Renewable and Sustainable Energy Reviews, volume 15(2), pp. 1067 – 1072, 2011. URL `http://www.sciencedirect.com/science/article/pii/S1364032110003989`.

[211] Sikes, K., McGill, R. and Van Walwijk, M. *Algae as a feedstock for biofuels, an assessment of the current status and potential for algal biofuels production.* Technical report, IEA Advanced Motor Fuels Implementing Agreement and IEA Bioenergy Task 39, 2011. URL `http://www.iea-amf.vtt.fi/pdf/annex34b_joint_t39_algal_biofuels_summary_report_sept2011.pdf`.

[212] *SimaPro software.* URL `htLtp://www.pre-sustainability.com/`.

[213] Solomon, S., Qin, D., Manning, M. et al. *IPCC Fourth Assessment Report, Climate Change 2007: The physical science basis, contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* Technical report, IPCC, 2007.

[214] Stephenson, A., Dennis, J. and Scott, S. *Improving the sustainability of the production of biodiesel from oilseed rape in the UK.* Process Safety and Environmental Protection, volume 86(6), pp. 427 – 440, 2008. URL `http://www.sciencedirect.com/science/article/pii/S0957582008000815`.

[215] Stern, N. *Stern review on the economics of climate change.* Technical report, Cabinet Office - HM Treasury, UK Government, 2007. URL `http://www.cambridge.org/gb/knowledge/isbn/item1164284/?site_locale=en_GB`.

[216] Szargut, J. *Minimization of the consumption of natural resources.* Technical report, Polish Academy of Sciences, 1978.

[217] Szargut, J. *Exergy method. Technical and ecological applications.* WIT Press, New York, 2005.

[218] Szargut, J. and Morris, D. *Cumulative exergy consumption and cumulative degree of perfection of chemical processes.* Energy Research, volume 11(11), pp. 245–261, 1987.

[219] Szargut, J., Morris, D.R. and Steward, F. *Exergy analysis of thermal, chemical, and metallurgical processes.* Hemisphere, New York, 1988.

[220] Szargut, J., Ziabik, A. and Stanek, W. *Depletion of the non-renewable natural exergy resources as a measure of the ecological cost.* Energy Conversion and Management, volume 43(9–12), pp. 1149–1163, 2002. URL `http://www.sciencedirect.com/science/article/pii/S0196890402000055`.

[221] Talens, L., Villalba, G. and Gabarrell, X. *Exergy analysis applied to biodiesel production.* Resources, Conservation and Recycling, volume 51(2), pp. 397 – 407, 2007. URL `http://www.sciencedirect.com/science/article/pii/S0921344906002473`.

[222] Talens, L., Villalba, G., Sciubba, E. and Gabarrell, X. *Extended exergy accounting applied to biodiesel production.* Energy, volume 35(7), pp. 2861 – 2869, 2010. URL `http://www.sciencedirect.com/science/article/pii/S0360544210001337`.

[223] Texas A&M University. *Techniques of seed production and handling. Chapter 6*, 2010.

[224] Torres, C. *Symbolic exergoeconomics: methodology for thermoeconomic analysis of energy systems.* Ph.D. thesis, Universidad de zaragoza, 1991.

[225] Torres, C. *Symbolic thermoeconomic analysis of energy systems.* In C. Frangopoulos (editor), *Exergy, energy system analysis and optimization, from Encyclopedia of Life Support Systems (EOLSS)*. EOLSS Publishers, 2006.

[226] Torres, C., Valero, A., Serra, L. and Royo, F.J. *Structural theory and thermoeconomic diagnosis Part I. On malfunction and disfunction analysis.* Energy Conversion and Management, volume 43, pp. 1503–1518, 2002.

[227] Torres, C., Valero, A. and Valero, A. *Exergoecology as a tool for ecological modelling. The case of the US food production chain.* Ecological Modelling, volume 255, pp. 21–28, 2012.

[228] Tribus, M. and Evans, E. *A Contribution to the Theory of Thermoeconomics.* Technical Report 62, University of California, Los Angeles, 1962.

[229] Tricas, A. *Clean Power for Transport package. An EU sustainable alternative fuels strategy including the appropriate infrastructure. The role of biofuels.* In *AEBIOM European Bioenergy Conference 2013*. 2013.

[230] TRIP Innovation Portal consortium on behalf of the European Commission's Directorate-General for Mobility and Transport DG MOVE. *Towards a low carbon transport in Europe, Communicating transport research and innovation*, 2012. URL `http://www.transport-research.info/Upload/Documents/201204/20120423_214705_81522_PB02_web.pdf`.

[231] Tsatsaronis, G. and Winhold, M. *Exergoeconomic analysis and evaluation of energy-conversion plants-I. A new general methodology.* Energy, volume 10(1), pp. 69–80, 1985.

[232] UFOP. *Chart of the week (41). Oilseed meal prices in decline.* URL `http://www.ufop.de/english/news/chart-of-the-week/archive-chart-of-the-week/`.

[233] UNIDO. *Cleaner Production Toolkit, Volume 3 - Material flow analysis.* URL `http://www.unido.org/resources/publications/energy-and-environment/industrial-energy-efficiency/cp-toolkit-english.html`.

[234] Urbanchuk, J.M. *Contribution of biofuels to the global economy.* Technical report, Global Renewable Fuels Association, 2012. URL `http://www.mvo.nl/Portals/0/duurzaamheid/biobrandstoffen/nieuws/2012/05/Global_Economic_Impact_of_Biofuels_FINAL.pdf`.

[235] USDA - United States Department of Agriculture Foreign Agricultural Service. *PDS - Production, Supply and Distribution Online.* URL `http://www.fas.usda.gov/psdonline/`.

[236] Usón, S., Valero, A. and Agudelo, A. *Thermoeconomics and Industrial Symbiosis. Effect of by-product integration in cost assessment.* Energy, volume 45(1), pp. 43 – 51, 2012. URL `http://www.sciencedirect.com/science/article/pii/S0360544212002964`.

[237] Valero, A. *Thermodynamic process of cost formation.* In C. Frangopoulos (editor), *Exergy, energy system analysis and optimization, Vol. II from Encyclopedia of Life Support Systems (EOLSS).* EOLSS Publishers, 2006. URL `http://teide.cps.unizar.es:8080/pub/publicir.nsf/codigospub/0251/$FILE/CP0251.pdf`.

[238] Valero, A., Correas, L., Zaleta, A. et al. *On the Thermoeconomic Approach to the Diagnosis of Energy System Malfunctions. Part 1: the TADEUS problem.* Energy, volume 29, pp. 1875–1887, 2004.

[239] Valero, A., Lozano, M. and Muñoz, M. *A general theory of exergy saving. I. On the exergetic cost.* In R.A. Gaggioli (editor), *Computer-aided engineering and energy systems,* Vol. 3: Second Law Analysis and Modelling, pp. 1–8. ASME, New York, 1986.

[240] Valero, A., Lozano, M.A., Serra, L. et al. *{CGAM} problem: Definition and conventional solution.* Energy, volume 19(3), pp. 279 – 286, 1994. URL `http://www.sciencedirect.com/science/article/pii/0360544294901120`. <ce:title>Invited Papers on Exergoeconomics</ce:title>.

[241] Valero, A., Muñoz, M. and Lozano, M. *A general theory of exergy saving. II. On the thermoeconomic cost.* In R.A. Gaggioli (editor), *Computer-aided engineering and energy systems,* Vol. 3: Second Law Analysis and Modelling, pp. 9–16. ASME, New York, 1986.

[242] Valero, A., Muñoz, M. and Lozano, M. *A general theory of exergy saving. III. Energy saving and thermoeconomics.* In R.A. Gaggioli (editor), *Computer-aided engineering and energy systems,* Vol. 3: Second law analysis and modeling, pp. 17–21. ASME, New York, 1986.

[243] Valero, A. and Torres, C. *Thermoeconomic analysis.* In *Exergy, energy system analysis and optimization.* UNESCO - EOLSS, 2004.

[244] Valero, A., Usón, S., Torres, C. and Valero, A. *Application of thermoeconomics to industrial ecology.* Entropy, volume 12(3), pp. 591–612, 2010. URL `http://www.mdpi.com/1099-4300/12/3/591`.

[245] Valero, A. and Valero, A. *Exergy analysis of resources and processes.* Prensas Universitarias de Zaragoza, 2010.

[246] Velásquez, H., Benjumea, P. and De Oliveira, S. *Exergy and environmental analysis of the palm oil biodiesel production process.* In *Proceedings of the 20th international conference on efficiency, cost optimization and environmental impact of energy systems. ECOS 2007,* pp. 777–784. Padova, Italy, 2007.

[247] Venturi, P. and Venturi, G. *Analysis of energy comparison for crops in European agricultural systems.* Biomass and Bioenergy, volume 25(3), pp. 235 – 255, 2003. URL `http://www.sciencedirect.com/science/article/pii/S0961953403000151`.

[248] Volpi, G. *State of play of EU bioenergy policy.* Technical report, Inteligent Energy Europe. European Commission, 2013.

[249] von Spakovsky, M.R. and Evans, R.B. *Engineering Functional Analysis.* Journal of Energy Resources Technology, volume 115(2), pp. 86–99, 1993.

[250] Wilde, J. *Enthalpy and entropy of organic compounds from group contributions.* Delft University of Technology, Prins Maurits Laboratory, Delft, Rijswijk, The Netherlands, 1990. URL `http://repository.tudelft.nl/view/ir/uuid%3Aebd538b4-ee5f-4c92-96b0-2fde6c69dd1d/`.

[251] WWF, Ecofys and OMA. *The energy report 100% renewable energy by 2050.* Technical report, WWF, 2011. URL `http://wwf.panda.org/what_we_do/footprint/climate_carbon_energy/energy_solutions/renewable_energy/sustainable_energy_report/`.

[252] Yang, F., Hanna, M.A. and Sun, R. *Value-added uses for crude glycerol, a byproduct of biodiesel production.* Biotechnology for Biofuels, volume 5, p. 13, 2012. URL `http://www.biotechnologyforbiofuels.com/content/5/1/13`.

[253] Zeng, T., Kallio, M. and Ovarainen, H. *Critical review on the pelletizing technology, combustion technology and industrial-scale systems.* Technical report, MixBioPells project, supported by the Intelligent Energy – Europe (IEE) Programme of the European Commission, 2012. URL `http://www.mixbiopells.eu/fileadmin/user_upload/WP3/D31_Critical_Review_about_pelletising_and_combustion_technology_FINAL.pdf`.

[254] Zhang, X., Yan, S., Tyagi, R.D. and Surampalli, R.Y. *Energy balance and greenhouse gas emissions of biodiesel production from oil derived from wastewater and wastewater sludge.* Renewable Energy, volume 55, pp. 392 – 403, 2013. URL `http://www.sciencedirect.com/science/article/pii/S0960148113000086`.

[255] Zhang, Y., Dubé, M., McLean, D. and Kates, M. *Biodiesel production from waste cooking oil: 1. Process design and technological assessment.* Bioresource Technology, volume 89, pp. 1–16, 2003. URL `http://www.ncbi.nlm.nih.gov/pubmed/12676496`.

[256] Zhou, W. and Boocock, D. *Phase distributions of alcohol, glycerol, and catalyst in the transesterification of soybean oil.* Journal of the American Oil Chemists' Society, volume 83, pp. 1047–1052, 2006. URL `http://dx.doi.org/10.1007/s11746-006-5161-4`.

[257] Zhu, F., Zhao, L., Zhang, Z. and Jiang, H. *Preliminary study at lipids extraction technology from municipal sludge by organic solvent.* Procedia Environmental Sciences, volume 16(0), pp. 352 – 356, 2012. URL `http://www.sciencedirect.com/science/article/pii/S1878029612005889`.