

A comparative life cycle assessment for solar integration in CO₂ capture utilized in a downstream urea synthesis plant

R. Shirmohammadi^{a,*}, A. Aslani^a, E. Batuecas^b, R. Ghasempour^a, L.M. Romeo^c,
F. Petrakopoulou^c

^a Department of Renewable Energy and Environment, Faculty of New Sciences & Technologies, University of Tehran, Tehran, Iran

^b Department of Thermal and Fluid Engineering, University Carlos III of Madrid, Madrid, Spain

^c Escuela de Ingeniería y Arquitectura, Departamento de Ingeniería Mecánica, Universidad de Zaragoza, María de Luna 3, Zaragoza 50018, Spain

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ABSTRACT

This study assesses the environmental performance of an existing petrochemical plant that produces urea fertilizer and liquid ammonia. In urea production facilities, ammonia is always in excess. This excess can be converted back to urea if reacted with CO₂ in an ammonia reformer. Such a process can boost the production capacity of the plant without the need for further investment in major equipment, like reformers and reactors. In the plant studied here, a CO₂ capture and utilization unit (CCU) is used to capture CO₂ from the stack of the ammonia plant to further enhance urea production. The unit recovers about 5500 kg of CO₂ per hour. The environmental performance of the petrochemical plant is evaluated with and without CO₂ capture and under solar-assisted operation. Although the solar-assisted operation performs better than the plant with CCU in many environmental parameters, the differences between the two cases are relatively small. The outcomes of the life cycle assessment show that the carbon footprint of the solar-assisted operation with CCU is about 10% lower than that of the plant without CCU. In addition to some environmental benefits of the CCU plant, the plant with carbon capture increases the urea production by about 8%.

1. Introduction

Numerous economic activities and human needs today rely on the consumption of energy. However, the operation of the energy sector is linked to significant greenhouse gas (GHG) emissions that go against sustainable development goals set in the majority of the developing countries [1]. The per capita energy consumption in these countries (e. g., Iran) is much higher compared to the other countries, resulting in significant environmental impacts (EIs) [2]. Though human activities are not the only source of CO₂ emissions, and a large proportion of GHGs is related to natural sources, heavy industrial activities contribute towards the deterioration of the nature resilience and contribute to global warming [3]. Iran is considered as one of the main contributors to global total CO₂ emissions (TCE). The country released approximately 579 Mt of CO₂ in 2018, accounting for 1.74% of the global TCE [4]. Industry is considered the sector with the highest CO₂ emissions in Iran because of the high dependency on fossil fuels. A strict policy toward clean energies has been put in place globally to mitigate global warming [5]. After Kyoto Protocol in 1997, many other policies and protocols being

adopted worldwide such as Reo, Montreal, Paris, Glasgow and others [6]. However, the wider use of renewables and their availability and intermittency are still largely debated [7]. These challenges become even stronger in a fossil fuel rich country such as Iran. This has led to renewable energy (RE) sources taking a more supportive role to fossil fuels than a primary role in the industry, where fossil fuels being mainly used in power generation, refineries, petrochemical complexes and other energy intensive industries [8].

Carbon Capture and utilization (CCU) technologies are recognized as important bridging strategies on the way to REs transition. In order to decrease GHG emissions and to evaluate other carbon sources in the chemical industries, several methods of CCU have been evaluated in literature. However, most of the recent publications give emphasis on power-to-gas or fuels in various industries [9] than the utilization of CO₂ for the production of chemicals [10]. Among chemical productions, urea is considered as the most significant nitrogenous fertilizer and plants primary supplement. Granules urea under specific operating conditions are synthesized where CO₂ reacts with ammonia [11].

Some studies evaluate the EI for specific industries and offer them more environmentally friendly solutions [12–20]. These studies

* Corresponding author.

E-mail address: r.shirmohammadi1987@gmail.com (R. Shirmohammadi).

Nomenclature

CC	Climate Change
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
GHG	Greenhouse Gas
EI	Environmental Impact
ILCD	International Reference Life Cycle Data System
KPIC	Kermanshah Petrochemical Industries Co
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
MEA	Monoethanolamine
PCC	Post-combustion Carbon capture
RE	Renewable Energy
SPCC	Solar-assisted Post-combustion Carbon Capture
TCE	Total CO ₂ emissions

generally adopt a life-cycle perspective to evaluate such energy systems [21]. Life cycle assessment (LCA) allows the evaluation of the EIs of complete production systems, including upstream and downstream processes [22,23]. In LCA methods all the supply chain and EIs of different generation stages are systematically considered. From this point of view, such analyses can support studies related to the implications of water-energy-environment nexus. This is particularly relevant to large industries in Iran, a country with an energy system highly dependable on fossil fuels and freshwater consumption.

He et al. [24] He investigated CO₂ utilization benefits for the reverse water gas shift into syngas for the production of liquid fuel and power. The life cycle emission was calculated as 129.98 kg CO₂-eq/MW h, and the proportion of carbon emissions that correspond to the production of liquid fuel is 60%. This system achieved an energy savings of 18.19% and a life-cycle carbon emission reduction rate of 46.87% compared with the NGCC and GTL standalone generation system with the same amount of carbon capture.

Aldaco et al. [25] developed a dynamic LCA along with economic analysis to investigate a potential transition to low-carbon manufacture of formic acid. Evaluation of formic acid manufactured by electrochemical reduction of CO₂ (CCU), and comparing this production path to the traditional synthesis and to storing CO₂ in geological storage was conducted technically, environmentally and economically using the developed model. They concluded that the CO₂ capture and storage (CCS) technology obtained greater reductions in CO₂ emissions than the CCU scenarios and the traditional processes; whereas, CCU has lower fossil consumption and better economic justification, particularly when powered by green electricity.

Yoo et al. [26] developed a system via an incremental approach calculating identical carbon intensity, while avoiding the wide calculations in the expanded system boundary framework. The system allocates the obstacles of CO₂ capture to the CO₂ feedstock supplying the CCU. Zhang et al. [27] presented a united framework on the EI and energetic analyses of a CCS system. They studied three scenarios: a membrane process, a monoethanolamine-based (MEA) system, and a hybrid membrane-cryogenic process, for post-combustion CO₂ capture (PCC) in a power plant. The EI of the different scenarios, assessed with LCA, showed that MEA-based capture is linked to more challenges than membrane processes due to its higher energy consumption and the EI from solvent emissions and degradation. Cuéllar-Franca and Azapagic [28] investigated EIs of various CCS and CCU systems. They concluded that PCC with MEA is the most appropriate technology to integrate with different energy-intensive sectors. However, as MEA synthesis and ultimate degradation leads to CO₂ emissions and GWP, the development of more environmentally sustainable sorbents' pathway is desirable. Rosental et al. [29] studied the production of the large volume organic

chemicals i.e. methanol, ethylene, propylene, benzene, toluene, and mixed xylenes. Investigated process chains comprise CO₂ capture from an industrial point-source or from the atmosphere through direct air capture; alkaline water electrolysis for hydrogen production; methanol synthesis; methanol-to-olefins and methanol-to-aromatics synthesis including aromatics separation. The boundary of the developed system included all related processes with a cradle-to-gate approach. They defined scenarios by replacing processes to produce important infrastructure materials, such as aluminum, copper, steel, and concrete, with other less resource (carbon) intensive processes and higher rates of recycling. The LCA results showed that the synthesis of the studied chemicals from CCU processes can diminish the GHG emissions by 88–97%, when utilizing electricity from offshore wind turbines instead of fossil fuel-based production routes. The replacement of all production processes with CCU processes in Germany was found to increase the total primary energy demand between 2% and 7%. However, they estimated an overall decrease of emissions via enhanced base material production processes and the recycling of copper, steel, aluminum, and concrete. Such measures could reduce the undesirable impacts of the basic chemical production with CCU technologies in case of economic justification. Young et al. [30] explored the cradle-to-gate LCA of amine-based CO₂ capture systems in petroleum refineries, ammonia production, natural gas combined cycle plants, and supercritical and coal-fired power plants in the USA. They found that the eutrophication potential, the particulate matter formation potential, and the water consumption increased in all sectors because of the operation and installation of CCS technologies per kg CO₂ avoided. On the other hand, the influence on particulate matter formation and acidification potentials was not straightforward. Trade-off variation among the different systems was primarily determined by the combustion emissions of the fuel recovered by the capture unit, the upstream supply chain to prepare that fuel, and the relative impact of the CO₂ capture from the flue gas. Khojasteh-Salkuyeh et al. [31] conducted process design and LCA of several methanol production processes. The LCA results showed that the direct CO₂ hydrogenation is an environmentally friendly option, only when the electricity GHG intensity is lower than 0.17 kg CO₂ equivalent per kWh of electricity. They concluded that in the context of Canada, it can be suggested for the states where low-carbon electricity is accessible.

Khoo et al. [32] investigated the potential of carbon reduction for a CO₂ mineralization technology for CO₂ utilization in Singapore. The carbon reduction potential, net carbon emissions and life cycle were analyzed with LCA. Their results showed that the studied technology abated 115.78 kg CO₂-eq per tonne of CO₂ input. Gaikwad et al. [33] conducted LCA analysis for various scenarios of the Carbon2Chem® project, where process gases of steel mills used carbon to produce methanol and urea. They compared the integrated production with the conventional one and concluded that including Carbon2Chem® technologies in a steelmaking plant results in strong reductions of global warming impact in all examined scenarios. Shi et al. [34] investigated the energy consumption performance and GHG emissions in the life cycle of urea production. The average energy consumption reported was about 30.1 GJ/t urea. They concluded that in any process or method employed in urea production, reducing coal consumption is vital. Attention has been paid to the integration of RE with conventional industrial fossil fuel-based systems to obtain CO₂ reduction [35]. Several choices can be considered: using RE in CO₂ capture processes, converting RE to fuel for industrial processed, and/or utilizing captured CO₂ as a raw material in another process. Generally, there would be no consistent concept for all industries, each industrial sector and production process can reduce CO₂ emissions differently [36]. Attention has been paid to the integration of RE technologies with conventional energy intensive fossil fuel based systems [37]. Solar energy has been regarded as the most promising solution to tackle CC challenges due to its sustainability and availability characteristics [38]. Recently, the implementations of solar energy to provide the required energy in industrial applications have increased [39]. The solar-assisted

Table 1

Life Cycle Inventory for 50 ton/h of ammonia production in the (i) base scenario, (ii) CCU scenario and (iii) SPCC scenario.

Products		Base scenario	CCU scenario	SPCC scenario	Units
NH ₃		50	50	50	ton/h
CO ₂		63	63	63	ton/h
Steam to urea plant		97	86	93.7	ton/h
Steam for other processes			11	3.3	ton/h
<i>Inputs</i>	<i>Dataset (or proxy)</i>				
Process air	Air (resources)	292	292	292	m ³ /h
Natural gas (feed)	Natural gas, high pressure market group for APOS, U	30084	30084	30084	m ³ /h
Natural gas (fuel)	Natural gas, high pressure market group for APOS, U	15535	15535	15101.2	m ³ /h
AMDEA solution	Amine oxide amine oxide production APOS, U	7	7	7	kg/h
Chemicals for demi water treatment	Phosphate rock, as P ₂ O ₅ , beneficiated, dry market for APOS, U	7.5	7.5	7.5	kg/h
	Diethanolamine market for APOS, U	0.25	0.25	0.25	kg/h
Steam	Steam, in chemical industry market for steam, in chemical industry APOS, U	167.98	167.98	167.98	ton/h
Electricity	Electricity, medium voltage IR= market for APOS, U	2347	2347	2347	kWh
<i>Emissions to air</i>		273.9	210.6	210.6	ton/h
Nitrogen		198.33	152.50	152.50	ton/h
Carbon dioxide		18.57	14.28	14.28	ton/h
Oxygen		8.93	6.87	6.87	ton/h
Water		48.10	36.99	36.99	ton/h
<i>Waste</i>					
Wastewater		5	5	5	m ³ /h

post-combustion carbon capture (SPCC) alternative provides a possibility to offset the high energy consumption of the PCC process [40]. However, the implementation of SPCC depends on its GHG reduction potential and its cost, compared to other low-carbon technologies. Wibberley [41] first proposed the SPCC where the required thermal energy for solvent regeneration was provided by solar energy. Overall, several studies on MEA-based SPCC have been carried out. Parvareh et al. [42] divided the system into full and partial systems by means of solar fraction. Saghafifar and Gabra [43] categorized the system into indirect and direct solar-assisted PCC depending on the assembly between solar thermal collectors and CO₂ capture facilities. Wang et al. [44] analyzed a 300MWe coal-fired power generation in China considering three scenarios: i) base-case equipped with PCC; ii) base-case equipped with PCC and SPCC; iii) base-case integrated with PCC and solar-assisted repowering process. Their results showed significant benefits for the solar-assisted cases in both GHG mitigation potential and costs.

To the best of the author's knowledge, there is no published work on the comprehensive LCA feasibility of a CCU system along with a solar-assisted system for the utilization of CO₂ in the production of chemicals and, specifically, urea and ammonia plants. This work presents an input-output LCA study of the annual EI of a petrochemical complex located in west of Iran. The study includes a comprehensive analysis of the EIs of different impact categories (ICs), to reveal the environmental performance of all technologies used. The environmental performance of the CCU plant is compared to the base scenario without CO₂ capture, as well as the solar-assisted CCU system. The analysis involves a conventional cradle-to-gate LCA analysis realized using the software SimaPro. This study is meant to fill the knowledge gap of the implications on how solar-assisted and CCU scenarios could improve the life cycle and potentially increase the rate of urea production of the integrated systems.

2. Case study

Three different scenarios are considered and evaluated using a comprehensive LCA analysis: the base scenario, the CCU, and the SPCC scenario. The main difference between the base scenario and the other two is the reduction of emissions in the ammonia plant. The CCU and SPCC scenarios use part of the flue gas of the ammonia plant to produce CO₂ that is then used in the urea production unit. Furthermore, the SPCC scenario produces the required thermal energy of the carbon capture unit from steam generated in a concentrating solar plant. In the SPCC scenario the amount of energy consumption is reduced by 3.8 million m³ natural gas annually relative to the base case [45]. This leads to a reduction in the amount of natural gas feed by 433.8 m³/h (3.8 million (m³/year)/(365 * 24)) (shown in Table 1).

2.1. Base scenario

Kermanshah Petrochemical Industries Co. (KPIC) is an Iranian fertilizer producer, founded in 1996 with headquarters in Tehran. Its establishment was driven by the growing fertilizer demand and facilitated by the abundance of gas and related raw materials. The industrial complex, located in Kermanshah, western Iran, approximately produces 1200 tons of liquid ammonia and 2000 tons of granulated urea daily basis [46]. Flow diagrams of the ammonia and urea plants are shown in Fig. 1 (A) and (B).

The production of urea is carried out with the following units: i) Feed pressure increase unit: Liquid ammonia from the Haber-Bosch process and CO₂ as the main feedstocks are pumped and compressed respectively and sent to the urea synthesis unit. ii) Urea synthesis unit: ammonia and CO₂ are converted to urea under appropriate temperature and pressure conditions. iii) Evaporation and purification unit: the purity of the produced urea is increased and sent to the granulation unit. iv) Granulation unit: the urea produced is granulated into solid granules and stored in a special warehouse.

2.2. CCU scenario

In this scenario, a CO₂ recovery unit is used to capture the CO₂ from the first reformer of an ammonia plant. The project began in 2013 with a duration of 20 months. The project at KPIC was licensed, designed and constructed by Shahrekord Carbon Dioxide Co. (SCD) to capture 132 metric tons per day of CO₂ with capture efficiency of about 81% from the ammonia stack. The stripper thermal energy demand of the system is approximately 26784 MJ [47]. The CCU plant includes three columns, i. e., washing, absorption, and stripper columns. The washing column consists of a two-packed section. The absorber has 5 sections. Cooling and washing segments are placed at the top with two intercoolers in the middle section of the absorber. The lean solvent is sent to the third section, where the absorption with MEA is done. The rich solution then

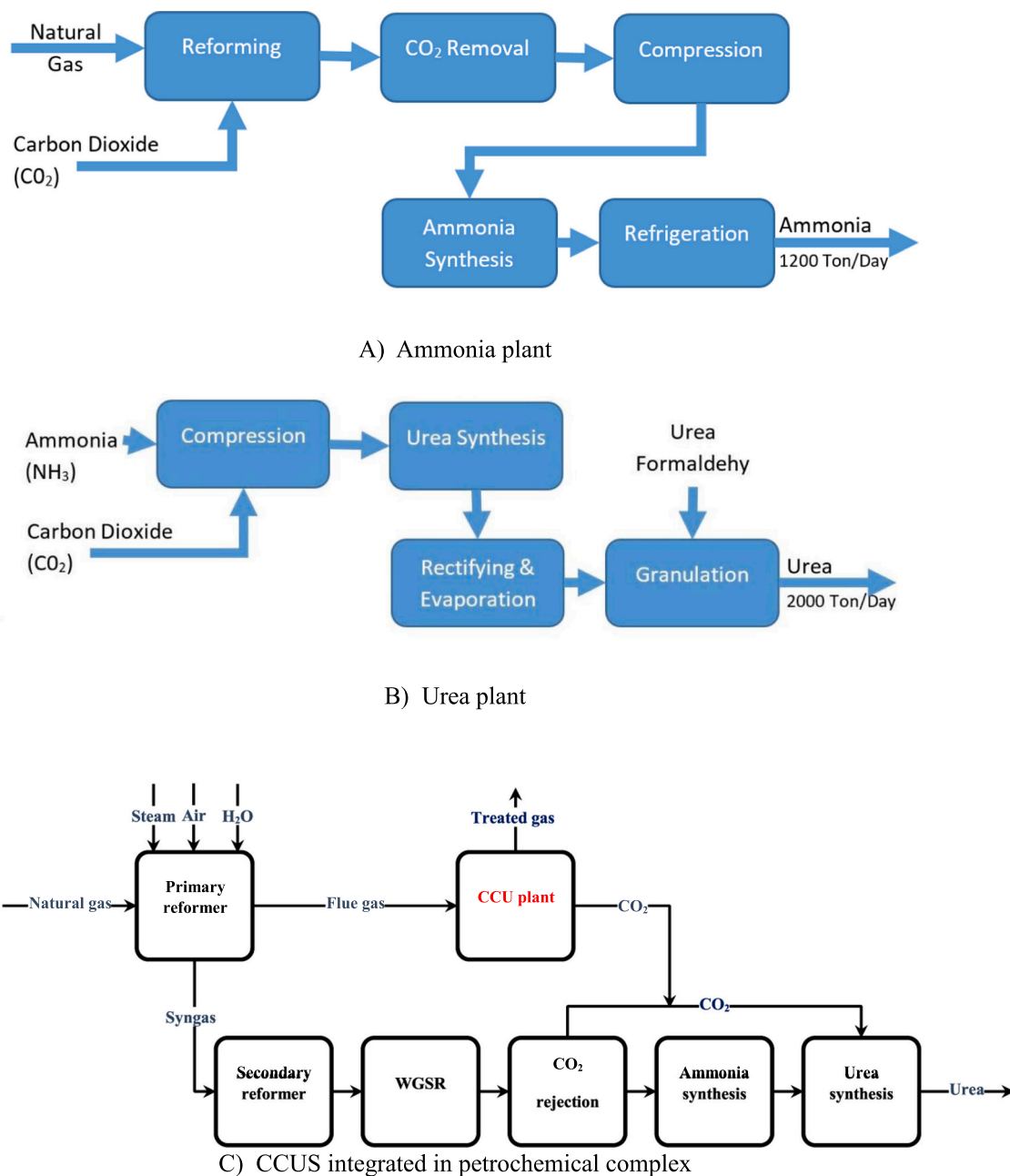


Fig. 1. Block flow diagram of the case study. A) Ammonia plant B) Urea plant C) CCUS integrated in petrochemical complex.

exchanges heat in the two-stage rich-lean heat exchangers. The rich solvent is sent to the top section of the stripper, where the solvent regeneration takes place. The required energy for the regeneration of the solvent is provided by a part of steam generated in the reformer of the ammonia plant. The CO₂ gas, exiting from the top of the stripper is directed to the compressor's knockout drums of the urea plant [48]. A flow diagram of the CCU plant integrated in the petrochemical complex is shown in Fig. 1 (C).

2.3. SPCC scenario

The solar plant includes parabolic trough collectors gathering thermal energy from the sun. The thermal energy is transferred from the solar field to the regenerator with the use of a working fluid (Hitec XL). The system has a solar multiple of 3.1 and 18-hours of storage, resulting in a solar share of 0.7 and a LCOH of 3.85 (¢/kWh). The thermal energy required for the regeneration of the solvent in the reboiler of the stripper

can be provided via solar energy and a part of steam generated in the reformer. Here, it is assumed that most of the energy needed is provided with solar energy, whereas the remaining is supplied by a part of steam generated in the reformer of the ammonia plant. When there is sufficient solar radiation, the working medium is heated up. Part of it is stored in tanks and a part produces steam used to regenerate the solvent. When solar energy is not sufficient, the thermal energy storage with additional extracted steam from a part of steam generated in the reformer of ammonia plant are used for the regeneration of the solvent. The benefits of this system are the use of solar energy and the CO₂ captured for urea production. The system can operate independently and solely based on solar thermal energy during the summer [45]. Fig. 2 presents a flow diagram of the SPCC system. In the figure, LPS and MPS stand for low and medium pressure steam respectively, and SA-DCC stands for soda ash wash-direct contact column.

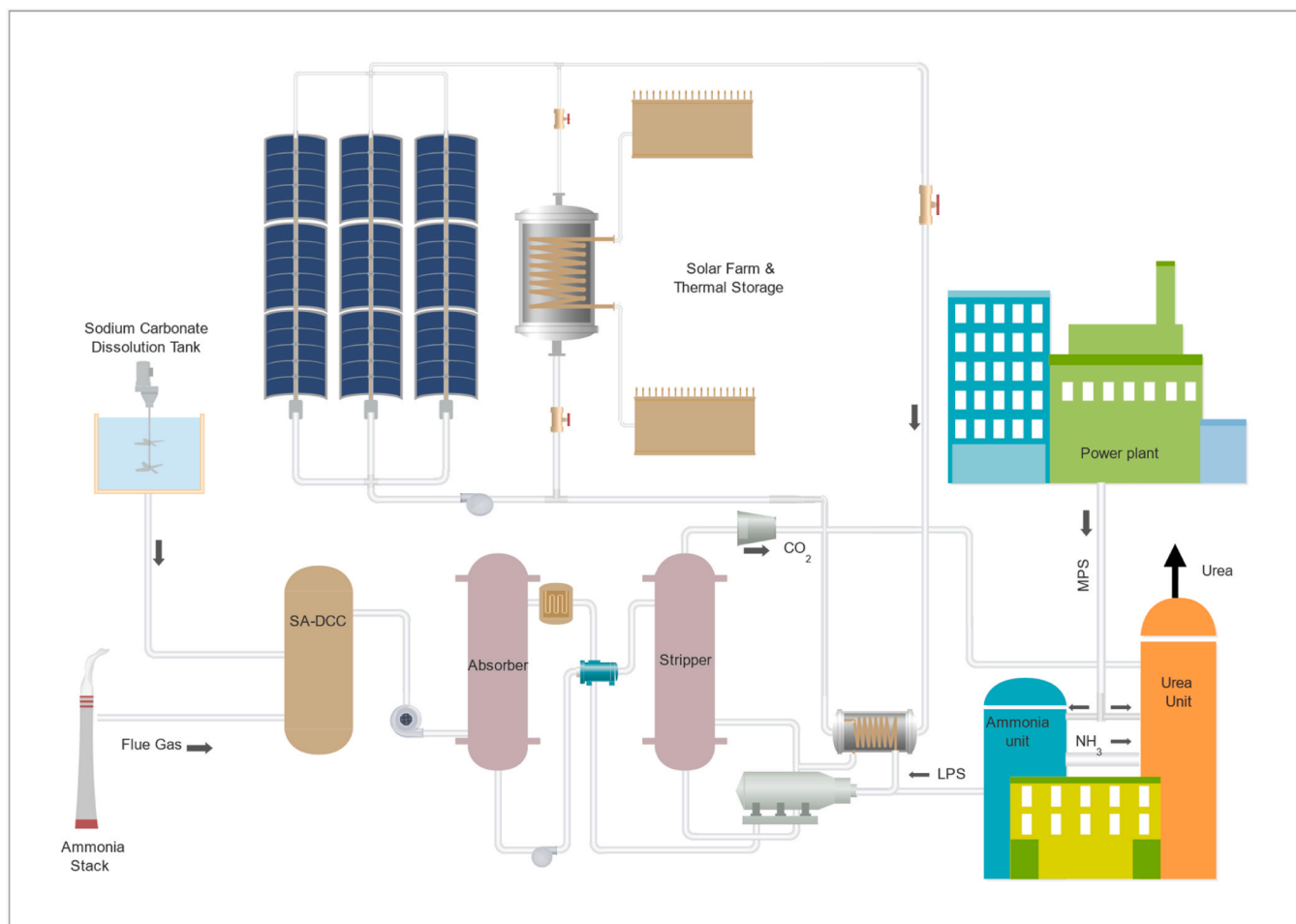


Fig. 2. Schematic of the SPCC system.

3. LCA methodology

The LCA is based on ISO 14040 and ISO 14044 standards. These LCA standards define four basic steps: i) the definition of the goal and the scope, ii) the definition of a Life Cycle Inventory (LCI), iii) an impact assessment and iv) the interpretation of the results [49].

To obtain 16 midpoint impact categories in the LCA, the international reference life cycle data system (ILCD) method is used. The impact categories included in this study are the following: 1) Climate change (CC), also called Global Warming Potential, has been established by the Intergovernmental Panel Climate Change (IPCC), is obtained by calculating the radiative forcing over a time horizon of 100 years. 2) Ozone Depletion (OD) represents the destructive effects on the stratospheric ozone layer over a time horizon of 100 years. 3) Human toxicity, cancer effects (HTC) and 4) non-cancer effects (HTNC) are calculated in Comparative Toxic Units for humans (CTUh). This indicator expresses the increase in morbidity in the human population. 5) Particulate matter formation (PMF) estimates the impact of PM_{2.5} particulates. 6) Ionizing radiation on human health (IRHH) quantifies the impact of ionizing radiation on the population, in comparison to Uranium 235. 7) Ionizing radiation on ecosystems (IRE) expresses the potentially affected ecosystems in terms of toxicity. 8) Photochemical ozone formation (POF) refers to the potential contribution to photochemical ozone formation. 9) Acidification (AC) characterizes the potential of acidifying substances deposits in terrestrial and main freshwater ecosystems. 10) Terrestrial eutrophication (TE) refers to eutrophying substances (i.e., nutrients) deposited to the soil. 11) Freshwater eutrophication (FWEU) represents the potential of nutrients reaching the freshwater or 12) the marine end

compartment (Marine eutrophication, ME). 13) Freshwater ecotoxicity (FEW) expresses the potential of species affected by toxicity in freshwater. 14) Land use (LU) represents changes in the soil organic matter. 15) Water resource depletion (WRD) is the scarcity-adjusted amount of water used. Finally, 16) resource depletion (RD) is the scarcity of a mineral resource.

The goal of this analysis is to determine the EI of the CCU in the production of urea. To this purpose, 1 kg of urea is chosen as the Functional Unit of the analysis. The production of the function unit (1 kg of urea) in the base scenario is compared with the CCU and SPCC scenarios. The third scenario that integrates a solar-assisted post-combustion carbon capture (SPCC scenario) is assessed to evaluate a more sustainable operation. The LCA-scenarios follow a cradle-to-grave approach, considering all inputs/outputs necessary to generate the main product. The LCA model has been conducted by taking the hourly average urea production. There are probably periods with more production and others with lower production; however, as an average the amount of urea production is considered hourly. It would be the best way to calculate the EIs as this is a static LCA model.

Fig. 3 displays the boundaries of the three scenarios. As seen, part of the flue gas released in the ammonia plant i.e. %23 (63.3 ton/h) is used in the CCU unit. For clarification and reproducibility, the LCI of the process with all input/output material and energy flows and the Ecoinvent 3 item used in the LCA model, are presented in Tables 1, 2 and 3. The LCI of the production of NH₃ in the ammonia plant, the production of CO₂ in the CCU unit, and the production of urea in the urea plant are presented in units per hour. The EIs are based on the product generated and they are thus reported per kg of urea produced. The LCA

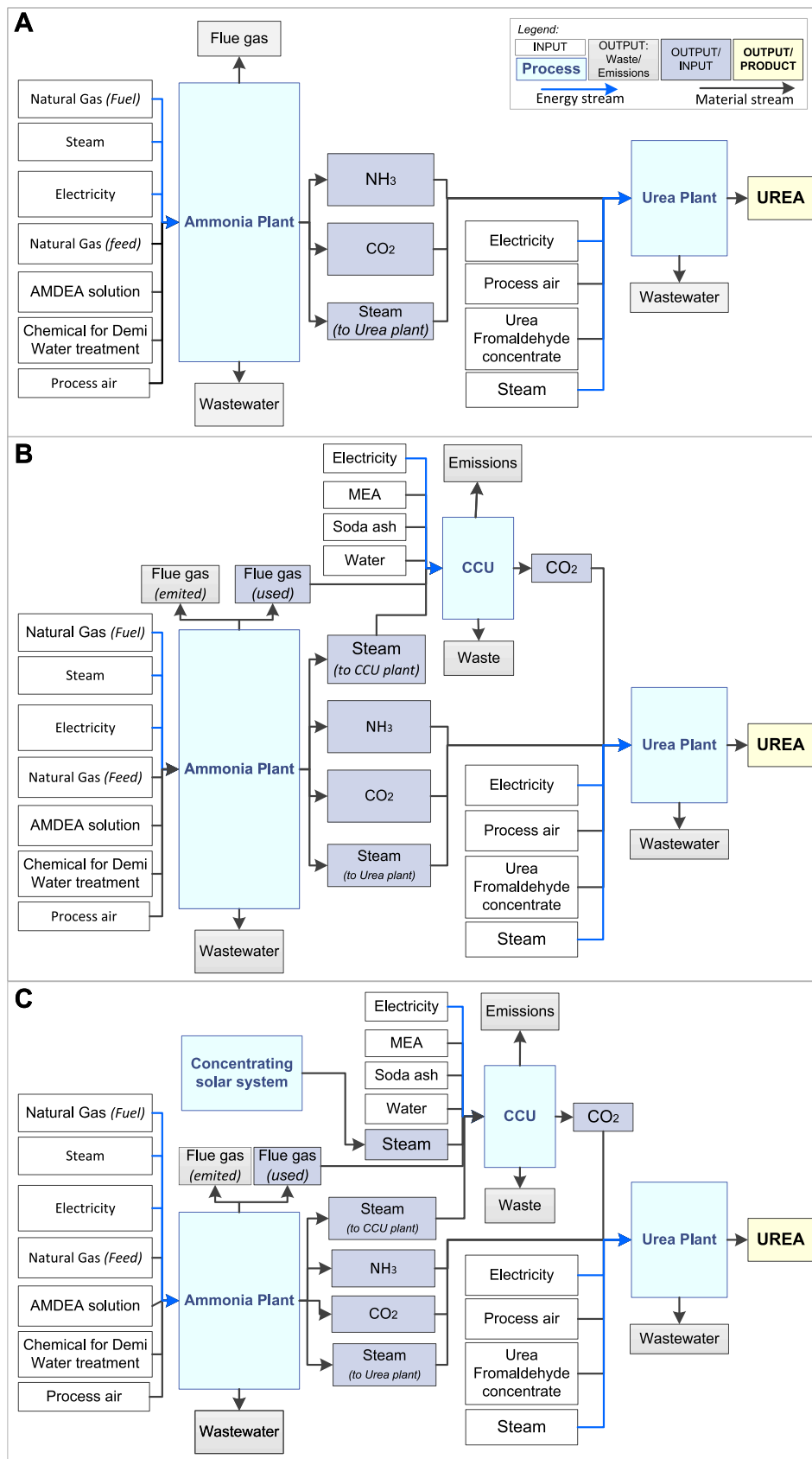


Fig. 3. Flowchart of the LCA boundaries for the three studied scenarios. A) Base scenario. B) CCU scenario. C) SPCC scenario.

Table 2

Life Cycle Inventory of the CCU. (*) As shown in Fig. 3, depending on the scenario, the steam comes from the ammonia plant (CCU scenario) or from both the ammonia and the solar plants (SPCC scenario).

Products		CCU scenario	SPCC scenario	Units
CO ₂ from CCU		5500	5500	kg/h
Inputs	<i>Dataset (or proxy)</i>			
Steam from Ammonia plant	*	11	3.3	ton/h
Steam from solar system	*		7.7	ton/h
Flue gas		63.3	63.3	ton/h
MEA	Monoethanolamine {RoW} ethanolamine production APOS, U	4.52	4.52	kg/h
Na ₂ CO ₃	Soda ash, dense {GLO} market for APOS, U	1.48	1.48	kg/h
Cooling water	Tap water {RoW} market for APOS, U	1387.45	1387.45	kg/h
Electricity	Electricity, medium voltage {IR} market for APOS, U	278.42	278.42	kWh
Emissions to air				
Nitrogen		42,120	42,120	kg/h
Carbon dioxide		961.20	961.20	kg/h
Oxygen		1760.40	1760.40	kg/h
Waste				
Wastewater		7920	7920	m ³

is conducted using the SimaPro software that allows the estimation of the EIs of the plant per unit of product.

There is no allocation among the various products of the base scenario. The generated streams of the ammonia plant (NH₃, CO₂ and steam to urea plant) are treated as a single output and delivered to the urea plant. In the CCU and SPCC scenarios, the production of steam is divided into two branches. As in all scenarios, 86 ton/h steam is sent to the urea plant (see Table 1). A smaller quantity is directed to the reboiler of the stripper in the CCU (11 ton/h in the CCU and SPCC scenarios). The concentrating solar system in the SPCC case provides 70% of the steam needed in the CCU plant (i.e., 7.7 ton/h of steam). The steam considered in the expanded system in this case, thus, is 3.3 ton/h. In other words, 97 ton/h of steam used in the urea plant are divided into 93.7 ton/h sent to the urea plant and 3.3 ton/h sent to the CCU unit.

Table 1 shows the reduction in natural gas (fuel) in the different cases. The use of concentrating solar in the SPCC scenario leads to a

Table 3

Life Cycle Inventory of urea production in every scenario.

Product		Base scenario	CCU scenario	SPCC scenario	Units
UREA		76.67	83.33	83.33	ton/h
Inputs	<i>Dataset (or proxy)</i>				
NH ₃	<i>Previously modelled</i>	50	57	57	ton/h
CO ₂	<i>Previously modelled</i>	63	63	63	ton/h
Steam to urea plant	<i>Previously modelled</i>	97	86	93.7	ton/h
CO ₂ from CCU	<i>Previously modelled</i>		5.5	5.5	ton/h
Process air	Air (resources)	61,500	61,500	61,500	kg/h
Urea formaldehyde concentrate	Urea formaldehyde resin {RoW} production APOS, U	0.7	0.7	0.7	kg/h
Electricity	Electricity, medium voltage {IR} market for APOS, U	1227.5	1227.5	1227.5	kWh
Steam	Steam, in chemical industry {RoW} market for steam, in chemical industry APOS, U	79.5	90.5	82.8	ton/h
Waste					
Wastewater		15	15	15	m ³ /h

reduction of 433.8 m³/h of natural gas, with respect to the base and CCU scenarios. From the previous study [45], it was found that almost 5.5 million m³ natural gas would be required to deliver the demand of the stripper annually. If the system were fully supported by natural gas, it would release over 10 million kg CO₂ annually. The natural gas consumption is reduced by about 3.8 million m³ considering 70% of the thermal required covered by the solar system. As expected, the scenario with the highest emissions to the air is the base scenario, resulting in a total of 273.9 ton/h. In the other two scenarios part of these emissions i.e. 23 (63.3 ton/h) is captured in the CCU unit.

Table 2 presents the LCI of the CCU unit included in both the CCU and SPCC scenarios. The simulation assumes that 63.3 ton/h of the flue gas is used for CO₂ recovery. After the CO₂ production, N₂, CO₂ and O₂ emissions are released to the air, while there is also a wastewater stream. As mentioned, in the case of the CCU and SPCC scenarios, 11 ton/h of steam is necessary to be delivered in to the reboiler of stripper to produce 5500 kg/h of CO₂.

As seen in Table 3, the different scenarios result in different amounts of generated urea. The base scenario produces 76.67 ton/h urea, while the production in the CCU and SPCC scenarios increases to 83.33 ton/h since the captured CO₂ is fed to urea plant to increase the production rate. Accordingly, the required amount of NH₃ is increased in the CCU and SPCC scenarios. This is basically due to the additional CO₂ captured in the retrofitted PCC unit in the CCU scenario. Interestingly, there are also differences in the steam required in the different processes. In the base scenario, all the steam production in the ammonia plant goes directly to the urea plant. It is needless to say that the differences between the CCU and SPCC scenarios in the process of producing urea is based on a Stamicarbon license. It is a CO₂ stripping method in which steam is used in urea Stripper. The other place where steam is consumed is the synthesis compressor, which is a heavy-duty equipment. In the CCU and SPCC scenarios, on the other hand, the situation is different. In the CCU and SPCC scenarios, 11 ton/h of the steam is supplied by the ammonia plant, while 70% of the necessary steam in the SPCC scenario comes from the concentrating solar system. The extra steam requirement in the different cases are 79.5 ton/h in the base case, 90.5 ton/h in the CCU scenario, and 82.8 ton/h in the SPCC scenario (7.7 ton/h covered by the solar unit).

4. Results and discussion

The results of the LCA analysis for 1 kg of urea production are shown in Table 4. It is seen that the CCU scenario results in lower EIs than the base scenario in all of the assessed environmental categories. In

Table 4

LCA results. EIs for the production of 1 kg of urea in the base, CCU and SPCC scenarios.

Impact Category Abb.	Units	Base scenario	CCU scenario	SPCC scenario
CC	kg CO ₂ eq	1.543	1.382	1.380
OD	kg CFC-11 eq	2.29·10 ⁻⁷	2.11·10 ⁻⁷	2.10·10 ⁻⁷
HTC	CTUh	9.01·10 ⁻⁸	8.30·10 ⁻⁸	8.28·10 ⁻⁸
HTNC	CTUh	5.74·10 ⁻⁹	5.29·10 ⁻⁹	5.26·10 ⁻⁹
PMF	kg PM2.5 eq	6.62·10 ⁻⁴	6.09·10 ⁻⁴	6.09·10 ⁻⁴
IRHH	kq U ²³⁵ eq	2.62·10 ⁻²	2.41·10 ⁻²	2.41·10 ⁻²
IRE	CTUe	1.92·10 ⁻⁷	1.77·10 ⁻⁷	1.77·10 ⁻⁷
POF	kg NMVOC eq	2.96·10 ⁻³	2.73·10 ⁻³	2.72·10 ⁻³
AC	molc H ⁺ eq	5.53·10 ⁻³	5.09·10 ⁻³	5.08·10 ⁻³
TE	molc N eq	7.98·10 ⁻³	7.36·10 ⁻³	7.34·10 ⁻³
FWEU	kg P eq	1.76·10 ⁻⁵	1.62·10 ⁻⁵	1.62·10 ⁻⁵
ME	kg N eq	7.34·10 ⁻⁴	6.77·10 ⁻⁴	6.76·10 ⁻⁴
FWE	CTUe	7.61·10 ⁻¹	7.01·10 ⁻¹	6.98·10 ⁻¹
LU	kg C deficit	2.081	1.917	1.909
WRD	m ³ water eq	2.85·10 ⁻⁴	2.52·10 ⁻⁴	2.53·10 ⁻⁴
RD	kg Sb eq	5.05·10 ⁻⁶	4.66·10 ⁻⁶	4.64·10 ⁻⁶

addition, the SPCC has environmental benefits in all the environmental categories, when compared to the base scenario. Moreover, when compared to the CCU case, the SPCC scenario improves the environmental behavior of all environmental categories to some extent. The results for WRD are 2.85·10⁻⁴, 2.52·10⁻⁴, 2.53·10⁻⁴ m³ water equivalent per kg of produced urea for base, CCU and SPCC scenarios respectively. An exception is the WRD, where 3.31·10⁻⁵ m³/kg urea are saved in the CCU scenario, compared to the base case and 3.18·10⁻⁵ m³/kg urea are saved in the production of urea in the SPCC scenario. As shown in Table 4, 0.161 kg CO₂ eq per kg of urea production are saved when the urea is produced in the CCU scenario instead of the base case. In addition, in the SPCC scenario 0.163 kg CO₂ eq per kg urea are saved when compared to the base case. Fig. 4 shows the relative EIs of the three scenarios. When the CCU is integrated in the urea production system (in both the CCU and SPCC scenarios), a reduction of more than 7% is achieved in all the environmental categories, resulting in a reduction of more than 10% in impact categories like CC and WRD. The most important observation is that the CCU and SPCC scenarios reduce all environmental categories with respect to the base scenario. The differences between the CCU and SPCC scenarios are almost conspicuous. According to Fig. 4, the SPCC scenario shows noticeable improvements in all EI categories compared to other two scenarios.

Fig. 5 presents the analysis of the stand-alone CCU process for

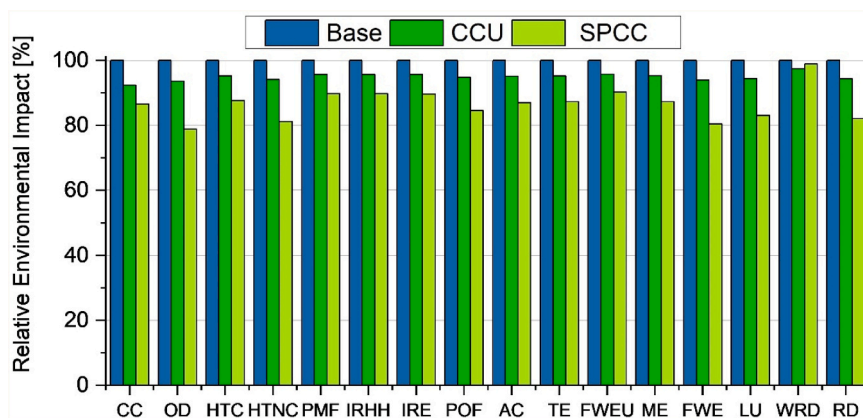


Fig. 4. LCA characterization results. Relative EIs of the three scenarios per 1 kg of urea production.

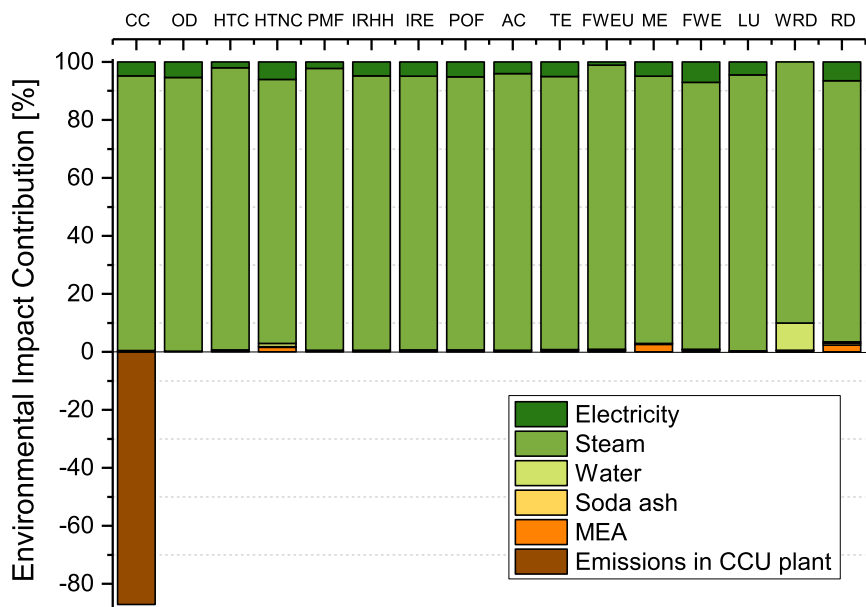


Fig. 5. CCU unit stand-alone LCA analysis. Relative contributions to CO₂ production in the CCU unit.

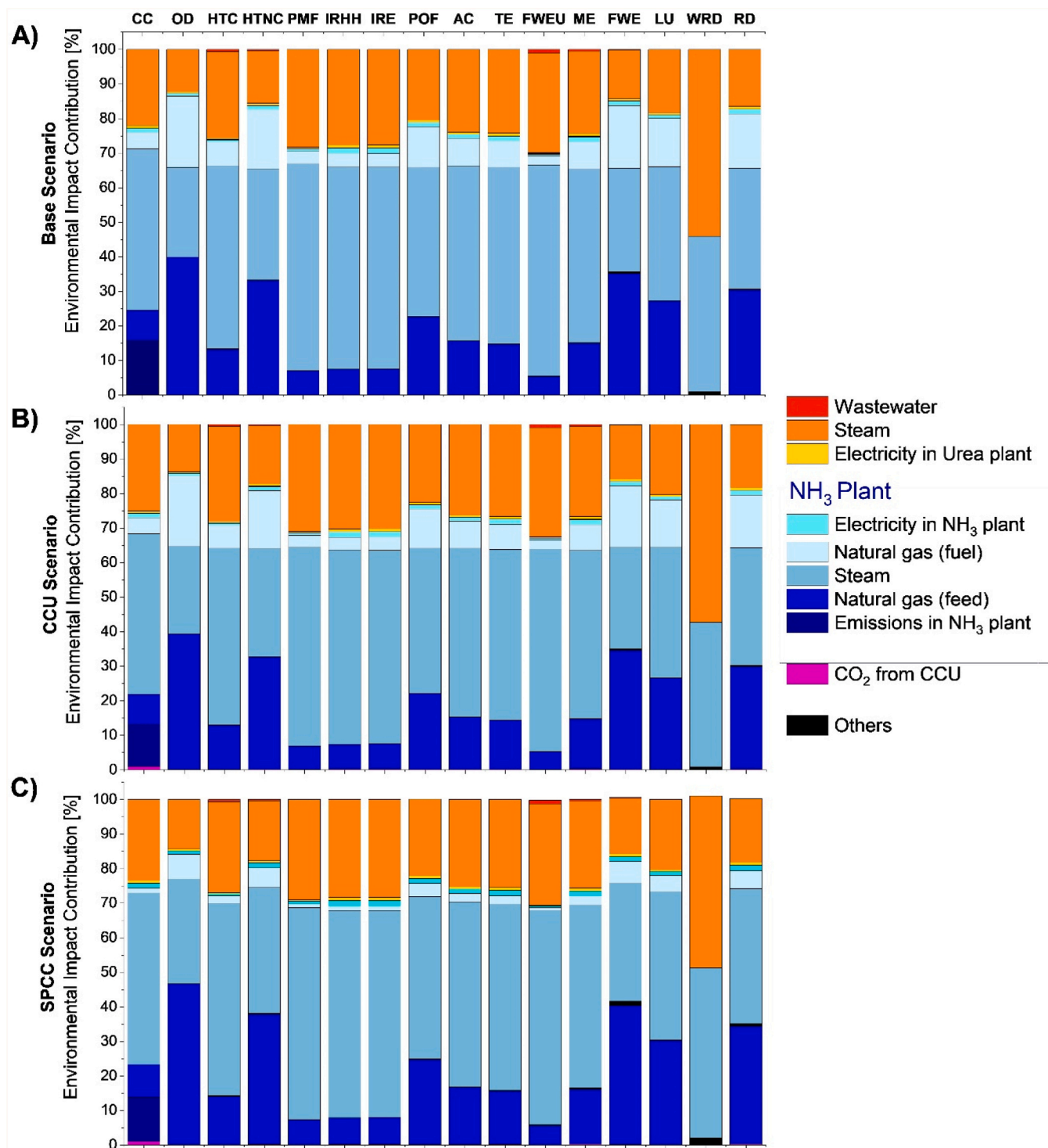


Fig. 6. EI contribution [%] of the selected input/outputs in each case study of urea production. A) Base scenario. B) Scenario with CCU and C) Scenario SPCC.

capturing CO₂ in the urea plant. The 11ton/h steam necessary to produce 5500 kg/h of CO₂ has the highest relative EI in the CCU unit. In fact, this CO₂ comes from the natural gas combustion to produce this steam. The study of the stand-alone CCU shows that electricity, soda ash and MEA have minor contributions to the different EI categories of this process. Regarding the emissions, a negative contribution in the CC category is noted (i.e., environmental benefit). This is primarily because the CO₂ production recovers 63.3 ton/h of flue gas.

Fig. 6 presents the contributions of the inputs/outputs of the urea production of every scenario to the environmental categories. Other

items referred to as “others” and their contribution to the environmental profile of the urea production is very small. The steam category highlights how this contribution affects the different environmental categories. It is obvious that a reduction in the required steam, would reduce the EI of the CCU unit overall. With this in mind, other processes like the ammonia production in the CCU scenario or even the solar energy in the SPCC scenario are considered to provide the necessary steam. Using steam from other processes and accounting for the environmental benefit in the CC, makes the final CCU contribution to this CO₂ almost negligible (see Fig. 6B for the CCU scenario and Fig. 6C for the SPCC

scenario).

Except for WRD, the NH₃ process (blue color group of items in Fig. 6) has a prominent role in all impact categories when it takes part of the production of urea. When looking at the NH₃ production (i.e., blue items), the impact of the steam is significantly higher than that of electricity or natural gas. A significant reduction in the CC is achieved when the CCU is included. The results also show the reduction in emissions in the CCU and SPCC scenarios (210.6 ton/h), when compared to the base scenario (273.9 ton/h). The emissions in the NH₃ plant represent 16% of the total CC in the base scenario and 12% in the CCU (Fig. 4B) and SPCC scenarios (Fig. 4C). Analyzing the urea production, it is noted that after the NH₃, the steam is the item with the highest contribution to all the environmental categories. The impacts of the wastewater and the electricity in the urea plant are relatively negligible.

In the SPCC scenario the amount of energy consumption is reduced. This reduces in turn the natural gas feed by the relatively small amount of 433.8 m³/h (Table 1). The reduction from 15,535 m³/h (base and CCU scenarios) to 15,101.2 m³/h (SPCC scenario) changes the EI slightly. Further efforts should be focused on the steam reduction in the NH₃ plant. Fig. 4 also reveals the big influence of the steam in both ammonia and urea production. A closer inspection of the environmental categories, such as the WRD, also supports that there is a need to reduce the EI of the steam.

5. Conclusion

A life cycle assessment is realized to evaluate the environmental impact of an existing industrial process, a petrochemical plant in Iran. The plant generating urea fertilizer and liquid ammonia is studied under three scenarios: (i) as is (base case), (ii) with carbon capture and utilization and (iii) with carbon capture and utilization supported by solar energy. The analysis includes a conventional cradle-to-gate LCA analysis, using the SimaPro software. The carbon footprint of the base plant, the plant with CO₂ capture, and the plant with solar-assisted CO₂ capture are found to be 1.543 kg CO₂ eq, 1.383 kg CO₂ eq and 1.380 kg CO₂ eq per kg of urea production, respectively. In addition to the environmental benefits of the CO₂ capture plant, the system boosts the capacity of the urea production by about 8%. However, although the solar unit reduces the natural gas consumption by 3.8 million m³ annually, the reduction of the environmental impact is rather small relative to the plant with CO₂ capture without solar input. The analysis carried out in this work shows that the plant with CO₂ capture results in the overall best performance under the defined considerations. The integration of similar systems in chemical industries in Iran is thus seen as a promising solution.

CRedit authorship contribution statement

Reza Shirmohammadi: Conceptualization, Methodology, Software, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. **Alireza Aslani:** Project administration, Supervision, Writing – review & editing. **Esperanza Batuecas:** Supervision, Methodology, Writing – review & editing. **Roghayeh Ghasempour:** Project administration, Supervision, Writing – review & editing. **Luis M. Romeo:** Supervision, Writing – review & editing. **Fontina Petrakopoulou:** Supervision, Methodology, Writing – review & editing.

Declaration of Competing Interest

The Authors declare that there is no conflict of interest.

Data availability

Data will be made available on request.

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References

- [1] R. Shirmohammadi, A. Aslani, R. Ghasempour, Challenges of carbon capture technologies deployment in developing countries, *Sustain. Energy Technol. Assess.* 42 (2020), 100837.
- [2] A.H. Saedi, A. Ahmadi, Life cycle assessment of Iran energy portfolio: Renewable energy replacement approach, *Energy Science & Engineering* n/a(n/a).
- [3] M. Chehrizi, B.K. Moghadas, A review on CO₂ capture with chilled ammonia and CO₂ utilization in urea plant, *J. CO₂ Util.* 61 (2022), 102030.
- [4] IEA, CO₂ emissions by sector, Islamic Republic of Iran, International Energy Agency, 2020.
- [5] T. Dixon, G. Leamon, P. Zakkour, L. Warren, CCS projects as Kyoto Protocol CDM activities, *Energy Procedia* 37 (2013) 7596–7604.
- [6] H. Bulkeley, P. Newell, *Governing Climate Change*, Taylor & Francis, 2023.
- [7] B. Johansson, Security aspects of future renewable energy systems-A short overview, *Energy* 61 (2013) 598–605.
- [8] R. Shirmohammadi, M. Soltanieh, L.M. Romeo, Thermo-economic analysis and optimization of post-combustion CO₂ recovery unit utilizing absorption refrigeration system for a natural-gas-fired power plant, *Environ. Prog. Sustain. Energy* 37 (3) (2018) 1075–1084.
- [9] M. Bailera, P. Lisbona, B. Peña, L.M. Romeo, A review on CO₂ mitigation in the Iron and Steel industry through Power to X processes, *J. CO₂ Util.* 46 (2021), 101456.
- [10] M. Rosental, T. Fröhlich, A. Lieblich, Life cycle assessment of carbon capture and utilization for the production of large volume organic chemicals, *Front. Clim.* 2 (2020) 9.
- [11] D. Milani, A. Kiani, N. Haque, S. Giddey, P. Feron, Green pathways for urea synthesis: A review from Australia's perspective, *Sustain. Chem. Clim. Action* 1 (2022), 100008.
- [12] F. Petrakopoulou, G. Tsatsaronis, Can carbon dioxide capture and storage from power plants reduce the environmental impact of electricity generation? *Energy Fuels* 28 (8) (2014) 5327–5338.
- [13] F. Petrakopoulou, G. Tsatsaronis, T. Morosuk, Assessment of a power plant with CO₂ capture using an advanced exergoenvironmental analysis, *J. Energy Resour. Technol.* 136 (2) (2014).
- [14] J.G. de Paula do Rosário, R. Salvador, M.V. Barros, C.M. Piekarski, L.M. da Luz, A. C. de Francisco, A Review on Multi-criteria Decision Analysis in the Life Cycle Assessment of Electricity Generation Systems, in: W. Leal Filho, P.R. Borges de Brito, F. Frankenberger (Eds.), *International Business, Trade and Institutional Sustainability*, Springer International Publishing, Cham, 2020, pp. 575–590.
- [15] F. Petrakopoulou, D. Iribarren, J. Dufour, Life-cycle performance of natural gas power plants with pre-combustion CO₂ capture, in: *Greenhouse Gases: Science and Technology*, 5, 2015, pp. 268–276.
- [16] E. Batuecas, T. Tommasi, F. Battista, V. Negro, G. Sonetti, P. Viotti, D. Fino, G. Mancini, Life Cycle Assessment of waste disposal from olive oil production: Anaerobic digestion and conventional disposal on soil, *J. Environ. Manag.* 237 (2019) 94–102.
- [17] H. Guzmán, F. Salomone, E. Batuecas, T. Tommasi, N. Russo, S. Bensaid, S. Hernández, How to make sustainable CO₂ conversion to Methanol: Thermocatalytic versus electrocatalytic technology, *Chem. Eng. J.* 417 (2021), 127973.
- [18] M. Nowrouzi, H. Abyar, H. Younesi, E. Khaki, Life cycle environmental and economic assessment of highly efficient carbon-based CO₂ adsorbents: A comparative study, *J. CO₂ Util.* 47 (2021), 101491.
- [19] T. Cordero-Lanzac, A. Ramirez, M. Cruz-Fernandez, H.-J. Zander, F. Joensen, S. Woolass, A. Meiswinkel, P. Styring, J. Gascon, U. Olsbye, A CO₂ valorization plant to produce light hydrocarbons: Kinetic model, process design and life cycle assessment, *J. CO₂ Util.* 67 (2023), 102337.
- [20] J.F. Torres, F. Petrakopoulou, A. Closer, Look at the environmental impact of solar and wind energy, *Glob. Challenges* 6 (8) (2022) 2200016.
- [21] T.Td Cruz, J.A. Perrella Balestieri, J.M. de Toledo Silva, M.R.N. Vilanova, O. J. Oliveira, I. Ávila, Life cycle assessment of carbon capture and storage/ utilization: From current state to future research directions and opportunities, *Int. J. Greenh. Gas. Control* 108 (2021), 103309.
- [22] F. Petrakopoulou, G. Tsatsaronis, T. Morosuk, C. Paitazoglou, Environmental evaluation of a power plant using conventional and advanced exergy-based methods, *Energy* 45 (1) (2012) 23–30.
- [23] F. Petrakopoulou, A. Boyano, M. Cabrera, G. Tsatsaronis, Exergoeconomic and exergoenvironmental analyses of a combined cycle power plant with chemical looping technology, *Int. J. Greenh. Gas. Control* 5 (3) (2011) 475–482.
- [24] Y. He, L. Zhu, J. Fan, L. Li, G. Liu, Life cycle assessment of CO₂ emission reduction potential of carbon capture and utilization for liquid fuel and power cogeneration, *Fuel Process. Technol.* 221 (2021), 106924.

- [25] R. Aldaco, I. Butnar, M. Margallo, J. Laso, M. Rumayor, A. Dominguez-Ramos, A. Irabien, P.E. Dodds, Bringing value to the chemical industry from capture, storage and use of CO₂: A dynamic LCA of formic acid production, *Sci. Total Environ.* 663 (2019) 738–753.
- [26] E. Yoo, U. Lee, G. Zang, P. Sun, A. Elgowainy, M. Wang, Incremental approach for the life-cycle greenhouse gas analysis of carbon capture and utilization, *J. CO₂ Util.* 65 (2022), 102212.
- [27] X. Zhang, B. Singh, X. He, T. Gundersen, L. Deng, S. Zhang, Post-combustion carbon capture technologies: Energetic analysis and life cycle assessment, *Int. J. Greenh. Gas. Control* 27 (2014) 289–298.
- [28] R.M. Cuéllar-Franca, A. Azapagic, Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts, *J. CO₂ Util.* 9 (2015) 82–102.
- [29] M. Rosental, T. Fröhlich, A. Liebich, Life cycle assessment of carbon capture and utilization for the production of large volume organic chemicals, *Front. Clim.* 2 (9) (2020).
- [30] B. Young, M. Krynock, D. Carlson, T.R. Hawkins, J. Marriott, B. Morelli, M. Jamieson, G. Cooney, T.J. Skone, Comparative environmental life cycle assessment of carbon capture for petroleum refining, ammonia production, and thermoelectric power generation in the United States, *Int. J. Greenh. Gas. Control* 91 (2019), 102821.
- [31] Y. Khojasteh-Salkuyeh, O. Ashrafi, E. Mostafavi, P. Navarri, CO₂ utilization for methanol production; Part I: Process design and life cycle GHG assessment of different pathways, *J. CO₂ Util.* 50 (2021), 101608.
- [32] Z.-Y. Khoo, E.H.Z. Ho, Y. Li, Z. Yeo, J.S.C. Low, J. Bu, L.S.O. Chia, Life cycle assessment of a CO₂ mineralisation technology for carbon capture and utilisation in Singapore, *J. CO₂ Util.* 44 (2021), 101378.
- [33] A. Gaikwad, D. Maga, S. Schlüter, Comparative lifecycle assessment of methanol and urea produced from steel mill gases, *Chem. Ing. Tech.* 94 (10) (2022) 1476–1488.
- [34] L. Shi, L. Liu, B. Yang, G. Sheng, T. Xu, Evaluation of Industrial Urea Energy Consumption (EC) Based on Life Cycle Assessment (LCA), *Sustainability* 12 (9) (2020) 3793.
- [35] D. Milani, S. Nelson, M.T. Luu, M. Aghaei Meybodi, G. Puxty, A. Abbas, Tailored solar field and solvent storage for direct solvent regeneration: A novel approach to solarise carbon capture technology, *Appl. Therm. Eng.* 171 (2020), 115119.
- [36] D.V. Quang, D. Milani, M. Abu, Zahra, A review of potential routes to zero and negative emission technologies via the integration of renewable energies with CO₂ capture processes, *Int. J. Greenh. Gas. Control* 124 (2023), 103862.
- [37] D. Milani, M.T. Luu, Y. Li, S. Nelson, A. Abbas, Techno-Economic Analysis of 'Solar-Powered' Post-Combustion Carbon Capture, *Proceedings of the 15th Greenhouse Gas Control Technologies Conference*, 2021, pp. 15–18.
- [38] M. Dehghanimadvar, R. Shirmohammadi, F. Ahmadi, A. Aslani, K.R. Khalilpour, Mapping the development of various solar thermal technologies with hype cycle analysis, *Sustain. Energy Technol. Assess.* 53 (2022), 102615.
- [39] C.A. Schoeneberger, C.A. McMillan, P. Kurup, S. Akar, R. Margolis, E. Masanet, Solar for industrial process heat: A review of technologies, analysis approaches, and potential applications in the United States, *Energy* 206 (2020), 118083.
- [40] D. Milani, M.T. Luu, Y. Li, S. Nelson, A. Abbas, Solar-powered PCC: An upfront levy for sustainable carbon capture, *Int. J. Greenh. Gas. Control* 115 (2022), 103611.
- [41] L. Wibberley, *Co2 capture using solar thermal energy*, US Patents, 2010.
- [42] F. Parvareh, M. Sharma, A. Qadir, D. Milani, R. Khalilpour, M. Chiesa, A. Abbas, Integration of solar energy in coal-fired power plants retrofitted with carbon capture: a review, *Renew. Sustain. Energy Rev.* 38 (2014) 1029–1044.
- [43] M. Saghafifar, S. Gabra, A critical overview of solar assisted carbon capture systems: Is solar always the solution? *Int. J. Greenh. Gas. Control* 92 (2020), 102852.
- [44] J. Wang, J. Zhao, Y. Wang, S. Deng, T. Sun, K. Li, Application potential of solar-assisted post-combustion carbon capture and storage (CCS) in China: A life cycle approach, *J. Clean. Prod.* 154 (2017) 541–552.
- [45] R. Shirmohammadi, A. Aslani, R. Ghasempour, L.M. Romeo, F. Petrakopoulou, Techno-economic assessment and optimization of a solar-assisted industrial post-combustion CO₂ capture and utilization plant, *Energy Rep.* 7 (2021) 7390–7404.
- [46] R. Shirmohammadi, A. Aslani, R. Ghasempour, L.M. Romeo, F. Petrakopoulou, Exergoenvironmental analysis and thermoeconomic optimization of an industrial post-combustion CO₂ capture and utilization installation, *J. CO₂ Util.* 59 (2022), 101927.
- [47] R. Shirmohammadi, A. Aslani, R. Ghasempour, L.M. Romeo, F. Petrakopoulou, Process design and thermoeconomic evaluation of a CO₂ liquefaction process driven by waste exhaust heat recovery for an industrial CO₂ capture and utilization plant, *J. Therm. Anal. Calorim.* (2021).
- [48] R. Shirmohammadi, A. Aslani, R. Ghasempour, L.M. Romeo, CO₂ utilization via integration of an industrial post-combustion capture process with a urea plant: process modelling and sensitivity, *Anal., Process.* 8 (9) (2020) 1144.
- [49] D.L. Ortiz, E. Batuecas, C.E. Orrego, L.J. Rodríguez, E. Camelin, D. Fino, Sustainable management of peel waste in the small-scale orange juice industries: A Colombian case study, *J. Clean. Prod.* 265 (2020), 121587.