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Assessment of the Production of Value-Added Chemical Compounds from Sewage Sludge Pyrolysis Liquids

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A procedure to analyze sewage sludge (SS) pyrolysis liquids based on solvent fractionation has been developed. Pyrolysis liquids are separated into three different fractions: heptane soluble (Hep-sol), dichloromethane soluble (DCM-sol), and hydrochloric acid soluble (HCl-sol). Diverse techniques (GC-MS, UPLC-TOF-MS) were employed to qualitatively and quantitatively analyze liquid fractions to assess the potential production of value-added chemicals. Aliphatic hydrocarbons, aliphatic nitriles, and steroids were mostly separated in the Hep-sol fraction, phenols and fatty acids in the DCM-sol fraction, and carboxylic acids and amides in the HCl-sol fraction. The largest production was obtained for ammonia (10–14 kg per tonne of SS) and α-olefins (8–9 kg per tonne of SS). The potential production of some of these value-added chemicals from SS pyrolysis liquid was compared with their current European production. In the case of α-olefins, 16 % of their European production could be achieved by SS pyrolysis.

Introduction

Due to worldwide development and increasingly strict environmental and water protection legislation, the production of sewage sludge (SS) has been growing during recent years and it is expected to continue rising in the years ahead.[1] Some of the practices applied in the past to deal with SS are landfill and agriculture usage. Nowadays, SS landfilling is not applied and is even banned in many countries due to its space requirements and environmental hazards. Although agriculture is still the most usual route of management applied to SS in many countries, it is declining due to social controversy, to the harmful species that SS contains (heavy metals, pathogens, and persistent organic pollutants), and also to agricultural land surface necessities surrounding the wastewater treatment plant.

Thermochemical treatments, such as pyrolysis and gasification, are promising techniques for managing this waste, since they can valorize it while, at the same time, significantly reduce its volume.[2] Pyrolysis is a thermochemical treatment performed in the absence or near absence of oxygen. This reaction can be focused mainly on the production of a solid, namely, char, or a liquid product. The production of char for use as low-smoking charcoal in indoor cooking was the first use of this reaction.

To maximize the yield of the liquid product, it is necessary to carry out the pyrolysis reaction at high heating rates (above 1000 $^{\circ}C\,s^{-1}$), at moderate temperatures (500 °C), and with short residence times of the vapors at high temperature, which is commonly known as fast pyrolysis.[3] Pyrolysis liquids obtained from lignocellulosic biomass have promising applications as fuels and as a source of valuable chemical products. They can be applied directly as fuels in boilers if they fulfill the quality standards required (ASTM D7544-12),[4] but, due to the poor properties derived from their high oxygen content, they cannot be used in transport applications without being upgraded.[5]

Many of the compounds derived from the pyrolysis of the main building blocks of lignocellulosic biomass (cellulose, hemicellulose, and lignin) are chemicals of interest for industry.[3] Recently, numerous research works have focused on the production, separation, or application of valuable chemical products obtained by means of biomass fast pyrolysis.[3,4] Some platform chemicals known to be obtained from the fast pyrolysis of biomass include levoglucosan and levoglucosanone from cellulose, acetic acid mainly from hemicellulose,

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furfural and hydroxyacetaldehyde from both cellulose and hemicellulose, and mono- and oligomeric phenols from lignin. Other chemicals, such as aromatics and light olefins,[5] other anhydrosugars, or light oxygenates,[4e,6] can be obtained in greater proportions by selecting certain operational conditions or by the incorporation of a catalyst into the process. In recent years, different authors have developed studies with the aim of enhancing the yield of holocellulose-derived compounds, such as levoglucosan. The combination of acid washing and acid impregnation of the biomass[4a,b] has been studied with this aim. It has also been proven that the presence of lignin increases the yield of levoglucosan.[4g] Many efforts have been devoted to the production, separation, and application of phenols obtained from the thermochemical processing of biomass.[4c,i] In some cases, chemicals obtained by pyrolysis have been commercialized for many years. For example, acetic acid has been produced on a large scale from the condensates recovered during charcoal production. Hydroxyacetaldehyde has also been produced by means of the pyrolysis of biomass and commercialized as a food additive.[7]

Some of these compounds can also be obtained from the pyrolysis of SS.[8] Other chemicals have also been obtained by means of SS pyrolysis, for example, a phenolic fraction that has been successfully used as a biodiesel antioxidant additive,[12] triacetonamine[13] or 5,5-dimethylhydantoin.[14]

In addition to polysaccharides, SS is also composed of lipids and proteins,[8,9] and a considerable proportion of ash, reaching nearly 50 % by mass when the SS has been digested.[10] Pyrolysis of SS for liquid production has been extensively studied during the last two decades,[2] although most work has focused more on the application of the liquid product as a fuel than on its application as a source of chemical products. Regarding fuels, especially significant studies are those that focus on the transformation of the lipid fraction of SS into hydrocarbons,[11] since this fraction of the liquid could become a cofeed for the petroleum refinery industry.

However, the high nitrogen content of SS, which is mainly present in the form of proteins and pyridine,[15] hinders the application of the liquid as a fuel. Nevertheless, the production of nitrogen-containing organic compounds and other nitrogen-rich organic materials could also be a great opportunity for the use of SS. Nowadays, most nitrogen-containing organic chemicals are synthesized from organic compounds derived from petroleum and ammonia. Recently, Xu et al. studied the production of renewable N-heterocycles from biomass by a thermocatalytic conversion and ammonization process over ZSM-5.[16] However, it would be even more sustainable to produce N-heterocycles by using nitrogen from residues rather than that from ammonia produced by the fixation of stable atmospheric nitrogen. Few studies have dealt with the production of nitrogen-containing compounds from SS pyrolysis liquids. Cao et al. proposed a method to fractionate and to identify by GC-MS the organic nitrogen species present in SS bio-oil,[17] highlighting for example the detection of long-chain aliphatic nitriles (LCANs), which are used in numerous industries.

To assess interest in the value-added chemical products that could be obtained from SS pyrolysis, it is of the utmost importance to know qualitatively and quantitatively the composition of the liquid product to the greatest possible degree. In this way, future research could aim to maximize some of these products, to separate them from the rest of the matrix, and to identify useful applications. The composition of these liquids has been studied by numerous authors by using different analytical techniques: GC-MS,[9,14,17,18] FTIR spectroscopy,[18f,19] and ^{1}H NMR spectroscopy.[20] Because the study of the composition is a difficult task due to numerous compounds with such different properties, some authors have examined the composition of the liquids in greater depth thanks to the fractionation of samples by means of column chromatography,[13,17] fractional distillation,[18h] or solvent fractionation.[21] However, there remain compounds, such as the heaviest and most polar, that require advanced analytical techniques, such as HPLC-TOF-MS and HPLC-FTIR, for their determination.[17]

Moreover, to evaluate interest in each of the compounds or families of compounds, it is necessary to determine quantitatively the presence of each of them. However, the quantitative determination of bio-oil components remains a tedious analytical procedure, largely due to the requirement for multiple calibrations of a plethora of chemicals.[4c] As with most other complex materials, the vast majority of papers focus on semiquantitative analysis of bio-oil, or on the more detailed analysis of a single component/group of components.[4c] Only a small number of studies show quantitative data of the composition of SS pyrolysis liquid.[17,18g,22] Sánchez et al. determined quantitatively the mass proportion of 50 organic compounds in SS pyrolysis liquids obtained at four temperatures (350, 450, 550, and 950 °C).[18g] In spite of the vast number of standards used for the calibration, the mass percentage of samples determined varied between 21 and 41 %,[18g] possibly due to the presence of compounds unsuitable for analysis by GC. Cao et al. studied only the mass proportion of organic nitrogen species, which accounted for almost 6 % by mass of the bio-oil.[17]

The main goal of this work is to assess the presence of valuable chemical products in SS pyrolysis liquid obtained under different operational conditions. The effects of the use of an atmosphere that simulates the recirculation of the pyrolysis noncondensable gases and the in situ catalytic treatment of vapors over γ-alumina are studied. According to researchers from the U.S. Department of Agriculture, the use of a mixture of nitrogen and product gas recirculated as a fluidizing agent enables similar deoxygenation of lignocellulosic pyrolysis liquids to that obtained by means of the catalytic cracking of bio-oil over zeolites.[23] Although this does not occur in the case of the pyrolysis liquid from pennycress press cake, which is a proteinaceous biomass,[23] the use of this fluidizing agent is promising because the heating value of the pyrolysis gas could be significantly increased. On the other hand, the study of the effect of the use of γ-alumina is interesting because it has an important influence on the physicochemical properties of the SS pyrolysis liquids.[11f] To assess the production of value-added chemicals, the composition of SS pyrolysis liquid is studied qualitatively and quantitatively by means of different analytical techniques: GC-MS and UPLC-TOF-MS. A fractionation procedure combining different methods, such as solvent fractionation with inorganic and organic solvents and solid-phase extraction, is applied to facilitate subsequent analysis, but also to separate possible fractions of value-added chemical compounds. At the same time, it is considered which products are of greatest interest in terms of their level of production, their price, and also taking into account if they are produced industrially from nonrenewable resources. Lastly, on the basis of available scientific literature on pyrolysis, the origin and most favorable pyrolysis operational conditions for their production are discussed.

Results and Discussion

Yields and elemental composition of pyrolysis liquid samples

Pyrolysis under different operational conditions has been conducted herein: conventional pyrolysis with nitrogen as a fluidizing agent (N2), pyrolysis with a synthetic gas mixture with the composition of the pyrolysis gas product as a fluidizing agent (REC), and pyrolysis with the synthetic gas as a fluidizing agent combined with the in situ catalytic cracking of vapors over γ-alumina (REC_CAT). The pyrolysis liquids obtained under the operational conditions studied are heterogeneous and separate into different phases. The pyrolysis liquid from the noncatalytic experiments (N2 and REC) has three phases, a light organic phase (LOP), a heavy organic phase (HOP), and an aqueous phase (AP), whereas the pyrolysis liquid from the catalytic experiment (REC_CAT) has only one organic (OP) and one AP. These results agree with those presented in previous works,[11e,f] so the use of the synthetic gas that simulates the recirculation of noncondensable pyrolysis gas does not affect phase separation. The yields, water contents, and elemental analyses of the different phases are shown in Table 1.

The different values of water content and elemental composition of the phases also indicate a different chemical composition of the liquid phases. The LOP obtained in the experiments performed without catalyst seems to have a marked nonpolar character, followed by the OP obtained in the catalytic treatment (REC_CAT), which only had a water content of around 2% by mass. Lastly, the HOPs, which were only obtained in the noncatalytic experiments (N2 and REC), were the most polar OPs and had the highest content in heteroatoms. The high water content of the APs and their pH values, between 9 and 10, indicate a chemical composition rich in basic nitrogen-containing compounds. According to Cao et al. there is a significant proportion of water-soluble organic nitrogen compounds in SS pyrolysis liquids.[8]

Chemical fractionation of the OPs

As shown in Table 1, the water content of the different OPs (LOP N2, HOP N2, LOP REC, HOP REC, OP REC_CAT) does not exceed 15% by mass in any case. Most of the other compounds that constitute these phases will be organic compounds, although some ammonia, solubilized in the moisture of the HOPs and OP from the catalytic treatment, could also be found. Figure 1 shows the mass distribution of the organic compounds of these phases among the different fractions: heptane soluble (Hep-sol) and DCM-KOH-sol + DCM-sol (determined by means of GC-FID analyses; DCM-KOH-sol = dichloromethane from the cleaning of the heptane fraction with KOH, DCM-sol = dichloromethane soluble), hydrochloric acid soluble (HCl-sol) phase treated by solid-phase extraction (HCl-SPE) and insoluble compounds (determined by weight after solvent evaporation), and a fraction of unknown compounds (determined by difference).

As observed in Figure 1, the mass percentage of organic compounds of the sample characterized by the developed

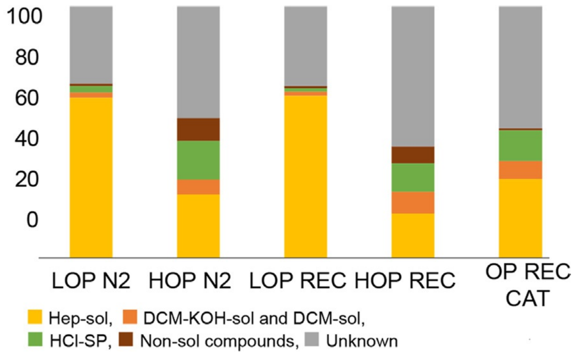

Figure 1. Mass percentage of the fractions extracted from the OPs (dry basis).

Table 1. Yields, water contents, and elemental analyses of the different phases of the pyrolysis liquids.

Content	N2			REC			REC_CAT	
	LOP N2	HOP N2	AP N2	LOP REC	HOP REC	AP REC	OP REC_CAT	AP REC_CAT
yield [% by mass over SS feed]	0.5	12.9	25.2	1.9	9.8	28.5	10.8	21.4
water [% by mass]	0	14.8	74.3	0	8.3	75.3	2.1	74.5
C [% by mass]	80.0	60.7	9.95	77.6	61.2	9.30	66.6	6.09
H [% by mass]	11.4	7.81	7.72	11.9	7.52	8.13	8.02	8.50
N [% by mass]	1.39	9.29	5.03	1.09	8.22	5.32	7.23	5.14
S [% by mass]	0.51	1.88	0.568	0.979	2.06	0.552	1.38	0.311
O (% by mass) by difference	6.7	20.3	76.7	8.5	21.0	76.7	16.8	80.0

method is around 70% for the LOPs and around 50% for the HOPs and OP from the catalytic treatment. In light of the distribution among the solvents, the use of synthetic gas that simulates the recirculation of pyrolysis gas as a fluidizing agent does not affect the solubility of the compounds of the LOPs in different solvents. The distribution of compounds of the HOPs among the different fractions obtained by the fractionation scheme differs slightly. The proportions of the Hep-sol and HCl-SPE fractions in the N2 experiment are higher than those in the REC experiment. However, a higher proportion of DCM-soluble compounds is obtained in the REC experiment. These two HOPs contain the highest proportion of insoluble compounds, which could be formed in gas-phase polymerization reactions, although this proportion is lower for REC than that for the N2 experiment. The LOPs contain a high proportion (around 65% by mass) of Hep-sol compounds and barely contain DCM-sol compounds (DCM-KOH + DCM-sol) or basic N-containing compounds (HCl-SPE). The high proportion in Hep-sol compounds would confirm the marked nonpolar character deduced from the elemental compositions and water contents. The percentage of Hep-sol compounds in the HOPs is less than half those of the LOPs. However, the proportions of HCl-SPE and DCM-KOH + DCM-sol fractions are significantly higher than those of the LOPs. The mass percentages of HCl-SPE (in dry basis) are around 12–15%, which could justify the high nitrogen content of the HOPs. With regard to the quantification of different fractions in the OP, these have mass percentages between those obtained for the LOPs and those obtained for the HOPs. This could be because the catalytic pyrolysis of SS only yields one OP, which could bring together many of the compounds present in LOPs and HOPs obtained from non-catalytic pyrolysis.

Chemical fractionation of the APs

Table 2 shows the mass percentages of the major components of the APs and the mass percentages of the fractions extracted from them after analysis following the fractionation scheme.

As shown in Table 2, the major component of the APs is water, with a content of around 75% by mass. Apart from water, these APs show a significant presence of ammonia (see Table 2). During the pyrolysis of SS, the decomposition of inorganic nitrogen below 300 °C and the deamination of amine compounds between 300 and 500 °C produces NH_3.[2,28] Herein, the highest ammonia content of the APs was achieved in the experiment with the catalytic treatment of vapors over γ-Al_2O_3, although the use of an atmosphere that simulates the recirculation of pyrolysis noncondensable gas also seems to promote NH_3 generation. As regards this trend, Liu et al. found that the catalytic pyrolysis of amino acids over ZSM-5, an acidic catalyst similar to γ-Al_2O_3, significantly enhanced denitrogenation, transforming most of the nitrogen into ammonia.[29] If the fractionation scheme developed is applied to these APs, no Hep-sol fractions are extracted from these samples. However, these APs contain DCM-sol and HCl-SPE compounds. The mass percentage of the DCM-sol fraction is very low (around 1%) and does not seem to be significantly affected by the operational conditions studied. A higher mass proportion of HCl-SPE compounds was expected to be contained in these APs. The proportion of these HCl-SPE fractions has been determined by weight difference after solvent (acetonitrile) evaporation and it is thought that some light basic N-containing compounds could be lost during this evaporation. As noted in the Experimental Section, the HCl-SPE fractions should contain basic N-containing compounds, which are supposed to be concentrated in the APs. Because these HCl-SPE fractions reached values of around 12–15% in the HOP, it was expected that the compounds extracted in these fractions would be heavier than those present in the APs. Both the use of an atmosphere that simulates the recirculation of pyrolysis gases and the catalytic treatment of vapors seem to decrease the proportion of the HCl-SPE fraction in the APs. This is the opposite trend to that observed for the ammonia content, although, according to our supposition of the loss of the lighter basic N-containing compounds during solvent evaporation, the proportions of HCl-SPE fraction extracted in the APs should follow the same trend as that of the ammonia content.

Table 2. Mass percentages of the main components and fractions extracted from the APs.

Component [%]	N2	REC	REC_CAT
water	75.0	75.3	74.5
NH_3	3.96	4.50	6.50
DCM-sol	1.2	1.1	0.84
HCl-SPE	2.5	1.1	0.2
unknown	17.2	17.8	17.8

Composition of the fractions extracted by the solvent fractionation scheme

Composition of the Hep-sol fractions

All compounds identified and quantified in the Hep-sol fractions extracted from the OPs (LOP N2, LOP REC, HOP N2, HOP REC, OP REC_CAT) are reported in Tables S3–S7 in the Supporting Information. The 30 most abundant compounds are shown in Table 3 and ranked according to their mass proportions (ppm) in these OPs. These compounds have been classified into the following chemical families: paraffins, olefins, aromatic hydrocarbons, other aliphatic compounds, aliphatic nitriles, aromatic compounds with nitrogen (most of them aromatic nitriles), polycyclic aromatic hydrocarbons, heterocyclic aromatic compounds with nitrogen, steroids, and unidentified compounds. The mass percentage of these families in the Hep-sol fractions extracted from the OPs (LOP N2, LOP REC, HOP N2, HOP REC, OP REC_CAT) are shown in Figure 2.

Table 3. Compounds identified in the Hep-sol fractions with higher mass proportions [ppm] in the corresponding OP.[a]

LOP N2		LOP REC		HOP N2		HOP REC		OP REC_CAT	
compound	ppm	compound	ppm	compound	ppm	compound	ppm	compound	ppm
1-undecene	2.4×10^{4}	1-undecene	2.4×10^{4}	9-nonadecene	8.3×10^{3}	1-undecene	8.0×10^{3}	toluene	1.1×10^{4}
1-pentadecene	2.2×10^{4}	1-tetradecene	2.0×10^{4}	BCB	7.4×10^{3}	toluene	6.6×10^{3}	1-dodecene	1.0×10^{4}
1-tetradecene	2.1×10^{4}	1-tridecene	2.0×10^{4}	toluene	7.2×10^{3}	BCB	6.0×10^{3}	1-undecene	9.1×10^{3}
1-tridecene	2.1×10^{4}	(5α)-cholest-3-ene	2.0×10^{4}	1-tridecene	7.1×10^{3}	1-dodecene	5.9×10^{3}	decane	8.9×10^{3}
1-dodecene	2.1×10^{4}	1-dodecene	1.9×10^{4}	1-dodecene	6.8×10^{3}	1-decene	5.8×10^{3}	9-eicosyne	7.9×10^{3}
1-hexadecene	1.9×10^{4}	1-hexadecene	1.8×10^{4}	1-undecene	6.7×10^{3}	9-nonadecene	5.5×10^{3}	6-tridecene	7.2×10^{3}
pentadecano	1.7×10^{4}	(5β)-cholest-2-ene	1.7×10^{4}	1-hexadecene	6.6×10^{3}	1-tetradecene	5.3×10^{3}	1-tetradecene	7.0×10^{3}
1-decene	1.6×10^{4}	1-pentadecene	1.7×10^{4}	1-tetradecene	6.3×10^{3}	decane	4.7×10^{3}	1-decene	6.8×10^{3}
tridecane	1.3×10^{4}	1-decene	1.7×10^{4}	1-decene	6.2×10^{3}	1-hexadecene	4.6×10^{3}	BCB	6.5×10^{3}
(5α)-cholest-3-ene	1.3×10^{4}	pentadecane	1.4×10^{4}	1-pentadecene	6.0×10^{3}	1-nonene	4.1×10^{3}	hexane, 2,4-dimethyl-	6.2×10^{3}
1-octodecene	1.2×10^{4}	tridecane	1.2×10^{4}	decane	5.6×10^{3}	1-tridecene	4.0×10^{3}	1-nonene	6.0×10^{3}
heptadecane	1.1×10^{4}	9-nonadecene	1.1×10^{4}	indole	5.6×10^{3}	1-pentadecene	4.0×10^{3}	tridecane	5.9×10^{3}
9-nonadecene	1.1×10^{4}	heptadecane	1.0×10^{4}	tridecane	5.4×10^{3}	(5α)-cholest-3-ene	3.8×10^{3}	indole	5.6×10^{3}
(5β)-cholest-2-ene	9.8×10^{3}	1-octodecene	1.0×10^{4}	1-octodecene	5.2×10^{3}	1-heptadecene	3.4×10^{3}	hexadecene	5.1×10^{3}
1-nonene	9.8×10^{3}	1-nonene	9.8×10^{3}	benzyl nitrile	4.9×10^{3}	benzyl nitrile	3.3×10^{3}	benzyl nitrile	4.8×10^{3}
heptadecene	9.8×10^{3}	8-heptadecene	8.8×10^{3}	hexane, 2,6-dimethyl-	4.4×10^{3}	indole	3.3×10^{3}	hexadecanenitrile	4.7×10^{3}
BCB	9.4×10^{3}	BCB	7.9×10^{3}	1-heptadecene	4.3×10^{3}	(5β)-cholest-2-ene	3.1×10^{3}	pentadecane	4.3×10^{3}
hexadecane	9.2×10^{3}	hexadecane	7.8×10^{3}	pentadecane	3.9×10^{3}	hexane, 2,4-dimethyl-	3.1×10^{3}	1-pentadecene	4.2×10^{3}
toluene	8.7×10^{3}	1-heptadecene	7.3×10^{3}	benzenepropanenitrile	3.7×10^{3}	pentadecane	3.1×10^{3}	benzenepropanenitrile	4.0×10^{3}
1-heptadecene	8.3×10^{3}	cholest-4-ene	7.0×10^{3}	1-nonene	3.7×10^{3}	3-octadecene	3.0×10^{3}	naphthalene, 2-methyl-	3.6×10^{3}
tetradecane	7.9×10^{3}	tetradecane	6.7×10^{3}	heptadecane	3.2×10^{3}	heptadecane	2.8×10^{3}	*o*-xylene	3.4×10^{3}
7-tetradecene	7.4×10^{3}	toluene	6.7×10^{3}	7-tetradecene	2.9×10^{3}	tridecane	2.4×10^{3}	heptadecane	3.3×10^{3}
dodecane	7.2×10^{3}	*n*-tridecene	6.6×10^{3}	hexadecane	2.9×10^{3}	benzenepropanenitrile	2.1×10^{3}	dodecane	3.3×10^{3}
undecane	5.5×10^{3}	dodecane	6.4×10^{3}	octodecane	2.8×10^{3}	pentadecane, 8-methylene-	1.8×10^{3}	1-octadecene	3.1×10^{3}
decane	5.5×10^{3}	cholest-2-ene	5.6×10^{3}	benzene, (1-pentylheptyl)-	2.3×10^{3}	*n*-tridecene	1.8×10^{3}	ethylbenzene	3.0×10^{3}
n-tetradecene	5.2×10^{3}	decane	5.5×10^{3}	7-tridecene	2.3×10^{3}	benzene, (1-pentylheptyl)-	1.7×10^{3}	benzene, (1-pentylheptyl)-	2.8×10^{3}
pentadecane, 8-methylene-	5.1×10^{3}	pentadecane, 8-methylene-	5.0×10^{3}	long aliphatic nitrile	2.0×10^{3}	dodecane	1.7×10^{3}	long aliphatic nitrile	2.8×10^{3}
tridecane, 2-methyl	5.0×10^{3}	undecane	4.9×10^{3}	9-eicosyne	1.9×10^{3}	hexadecane	1.7×10^{3}	tridecane	2.4×10^{3}
octodecane	5.0×10^{3}	dodecane, 2-methyl	4.8×10^{3}	tetradecane	1.9×10^{3}	tetradecane	1.6×10^{3}	benzenepropanenitrile	2.1×10^{3}
indole	4.7×10^{3}	7-tetradecene	4.7×10^{3}	pentadecane, 8-methylene-	1.9×10^{3}	ethylbenzene	1.6×10^{3}	pentadecane, 8-methylene-	1.8×10^{3}

[a] BCB = benzocyclobutene.

As observed in Figure 2 and in Table 3, olefins were the most abundant compounds in the Hep-sol fractions extracted from different OPs obtained under any of the operational conditions studied. Moreover, most of the olefins identified were α-olefins; those from C9 to C18 were the most abundant (see Table 3). Aliphatic and aromatic hydrocarbons also had significant mass percentages in the fractions. Chromatographic analyses of the Hep-sol fractions extracted revealed a wide variety of aromatic hydrocarbons (e.g., toluene, ethylbenzene, styrene, BCB), linear alkyl benzenes from C10 to C17 (e.g., such as benzene, (1-pentylheptyl)-), and other benzenes mono-, bi-, or tri-substituted with short alkyl chains (e.g., 1,2,3-trimethylbenzene). The mass percentages of aliphatic hydrocarbons were higher than those of aromatic hydrocarbons, except for the Hep-sol fraction extracted from the catalytic experiment (OP REC_CAT). The presence of polycyclic aromatic hydrocarbons was also greater in the Hep-sol fraction from the OP REC_CAT experiment. As a consequence, it seems that the in situ catalytic cracking of the SS pyrolysis vapors over γ-Al_2O_3 favors aromatization reactions, yielding higher mass percentages of aromatic and polycyclic aromatic hydrocarbons. Around 2% by mass of the compounds identified in the Hep-sol fractions were nitrogen heterocyclic aromatic compounds, such as 1*H*-indole and quinoline. The aliphatic nitriles and the aromatic compounds with nitrogen, most of them aromatic nitriles, were also present in the extracted Hep-sol fractions due to the low polarity of this functional group and its nonbasic character. Most of the aliphatic nitriles were long aliphatic ones from C14 to C20 and the aromatic nitriles with the higher mass concentrations in these fractions were benzonitrile and benzenepropanenitrile. The mass percentages of these two families were higher when the catalytic treatment of the pyrolysis vapors was performed. All Hep-sol fractions extracted from different OPs contained steroids, such as (5α)-cholest-3-ene and (5β)-cholest-2-ene, although the catalytic treatment of the SS pyrolysis vapors caused a significant decrease in their mass percentages. Similar effects of the catalytic treatment were reported when the composition of the OPs was analyzed semiquantitatively by percentage area.[11f]

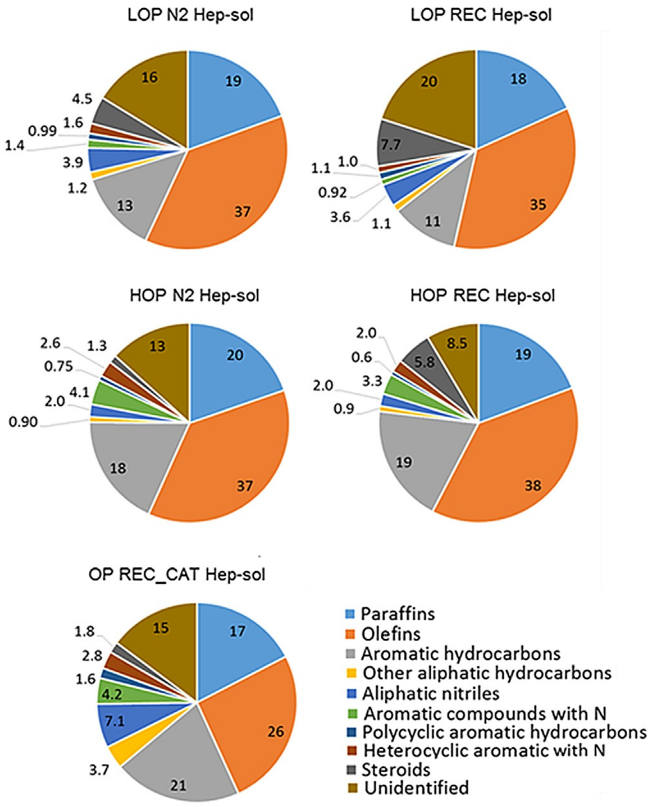

Figure 2. Mass percentage of the chemical families in the Hep-sol fractions extracted from the OPs.

For the effect of the use of a fluidizing agent that simulates the recirculation of noncondensable pyrolysis products, the most significant difference is the higher proportion of steroids in the Hep-sol fractions extracted from the two OPs obtained in this experiment. Steroids come directly from their devolatilization from SS, so that the higher proportion of steroids in these fractions would indicate that the use of a recirculation atmosphere disfavored the cracking of steroids in secondary reactions.

Composition of the DCM-sol fractions

All compounds identified and quantified in the DCM fractions (DCM-KOH-sol + DCM-sol) extracted from all of the different phases obtained (LOP N2, HOP N2, AP N2, LOP REC, HOP REC, AP REC, OP REC_CAT, AP REC_CAT) are given in Tables S8–S15 in the Supporting Information. The 10 most abundant compounds are listed in Tables 4–6 and ranked according to their mass proportions in the pyrolysis liquid phases analyzed. These compounds have been classified into the following chemical families: phenols, fatty acids, aromatic compounds with oxygen, aromatic nitriles, N-heterocyclic aromatic compounds, and nonaromatic compounds with heteroatoms (N, O, and/or S; see Figure 3). As can be seen in Tables S8 to S15 in the Supporting Information, the mass percentages of identified compounds in the DCM fractions of these samples vary from 68 to 94 %.

Fatty acids and phenols are the most abundant compounds in the DCM fractions. A substantial variety of chemical families have been obtained in HOPs from the N2 and REC experiments and in OP from the REC_CAT experiment. Unlike the case of the Hep-sol fractions, the mass percentage of each chemical family extracted in the DCM fractions depends strongly on the sample. The most abundant fatty acids detected in these fractions were penta-, hexa-, and octadecanoic acids. The high presence of pentadecanoic acid, an odd-numbered carbon acid, stands out in comparison with its proportion in the extractives, since the extractives contain mainly even-numbered carbon fatty acids from C14 to C18, of which octadecanoic acid is the most abundant. In general, 4-methylphenol and phenol are the most abundant phenols in these samples.

Composition of the HCl-SPE fractions

As noted above, the HCl-SPE fractions could not be successfully analyzed by GC-MS. The quantitative determination of the HCl-SPE fraction components was not possible in this work. However, the HCl-SPE fraction compositions could resemble those of the APs, and thus, the semiquantitative composition of these APs is presented in this section. Additional-

Table 4. Most abundant compounds identified in the DCM fractions extracted from the different liquid phases obtained in the N2 experiment.

N2 LOP		N2 HOP		N2 AP	
compound	ppm	Compound	ppm	compound	ppm
heptanoic acid	2.2×10^3	4-methyl-phenol	8.1×10^3	butanoic acid, 3-methyl-	2.1×10^3
toluene	1.9×10^3	phenol	5.5×10^3	heptanoic acid	1.7×10^3
1-octadecanol	1.5×10^3	indole	2.8×10^3	azetidine, 1-acetyl-2-methyl	1.3×10^3
pentadecanoic acid	1.4×10^3	nonanoic acid	2.7×10^3	1-octadecanol	1.1×10^3
decanoic acid	1.3×10^3	1*H*-indole, 3-methyl-	2.0×10^3	hexanoic acid	1.0×10^3
phenol	1.2×10^3	benzoylformic acid	2.0×10^3	pentadecanoic acid	9.7×10^2
azetidine, 1-acetyl-2-methyl	1.1×10^3	hexadecanoic acid	2.0×10^3	1,2-benzenedicarboxylic acid, bis(2-methyl propyl ester)	5.8×10^2
2-thiazolidinone, 3-(1-methylethyl)-4-methyl-	9.9×10^3	benzoic acid	1.9×10^3	4-methylphenol	3.8×10^2
benzoic acid	8.1×10^2	azetidine, 1-acetyl-2-methyl	1.8×10^3	phenol	2.4×10^2
2-methylphenol	7.1×10^2	dodecanoic acid	1.6×10^3	catechol	1.2×10^2

Table 5. Most abundant compounds identified in the DCM fractions extracted from different liquid phases obtained in the REC experiment.

LOP REC		HOP REC		AP REC	
compound	ppm	compound	ppm	compound	ppm
butanoic acid, 2-methyl-	1.7×10^{3}	4-methyl-phenol	9.2×10^{3}	butanoic acid, 2-methyl-	2.4×10^{3}
pentadecanoic acid	1.5×10^{3}	octadecanoic acid	8.0×10^{3}	heptanoic acid	1.9×10^{3}
4-methyl-phenol	1.4×10^{3}	phenol	5.8×10^{3}	azetidine, 1-acetyl-2methyl	1.5×10^{3}
1-octadecanol	1.4×10^{3}	indole	5.3×10^{3}	hexanoic acid	1.1×10^{3}
azetidine, 1-acetyl-2methyl	1.3×10^{3}	hexadecanoic acid	4.0×10^{3}	pentadecanoic acid	5.8×10^{2}
benzoic acid	1.2×10^{3}	benzoic acid	2.6×10^{3}	1-octadecanol	5.6×10^{2}
phenol	1.1×10^{3}	nonanoic acid	2.6×10^{3}	1,2-benzenedicarboxylic acid, bis(2-methyl propyl ester)	3.6×10^{2}
heptanoic acid	5.0×10^{2}	1h-indole, 3-methyl-	2.6×10^{3}	4-methyl-phenol	3.2×10^{2}
nonanoic acid	4.9×10^{2}	oleic acid derivate	2.1×10^{3}	phenol	1.7×10^{2}
hexadecanoic acid	4.9×10^{2}	pentadecanoic acid	1.8×10^{3}	2-methylphenol	1.2×10^{2}

Table 6. Most abundant compounds identified in the DCM fractions extracted from different liquid phases obtained in the REC_CAT experiment.

OP REC_CAT		AP REC_CAT	
compound	ppm	Compound	ppm
4-methyl-phenol	1.0×10^{4}	1-octadecanol	1.74×10^{3}
phenol	8.6×10^{3}	heptanoic acid	1.70×10^{3}
2-methylphenol	2.8×10^{3}	pentadecanoic acid	1.50×10^{3}
4-ethylphenol	2.1×10^{3}	azetidine, 1-acetyl-2-methyl	1.28×10^{3}
phenol, 2,6-dimethyl-	2.0×10^{3}	butanoic acid, 2-methyl-	6.05×10^{2}
benzyl nitrile	1.9×10^{3}	1,2-benzenedicarboxylic acid, bis(2-methyl propyl ester)	4.34×10^{2}
benzoic acid	1.8×10^{3}	phenol	1.36×10^{2}
1*H*-indole, 3-methyl-	1.8×10^{3}	2-methylphenol	1.19×10^{2}
1-octadecanol	1.8×10^{3}	4-methylphenol	99.3
nonanoic acid	1.7×10^{3}		

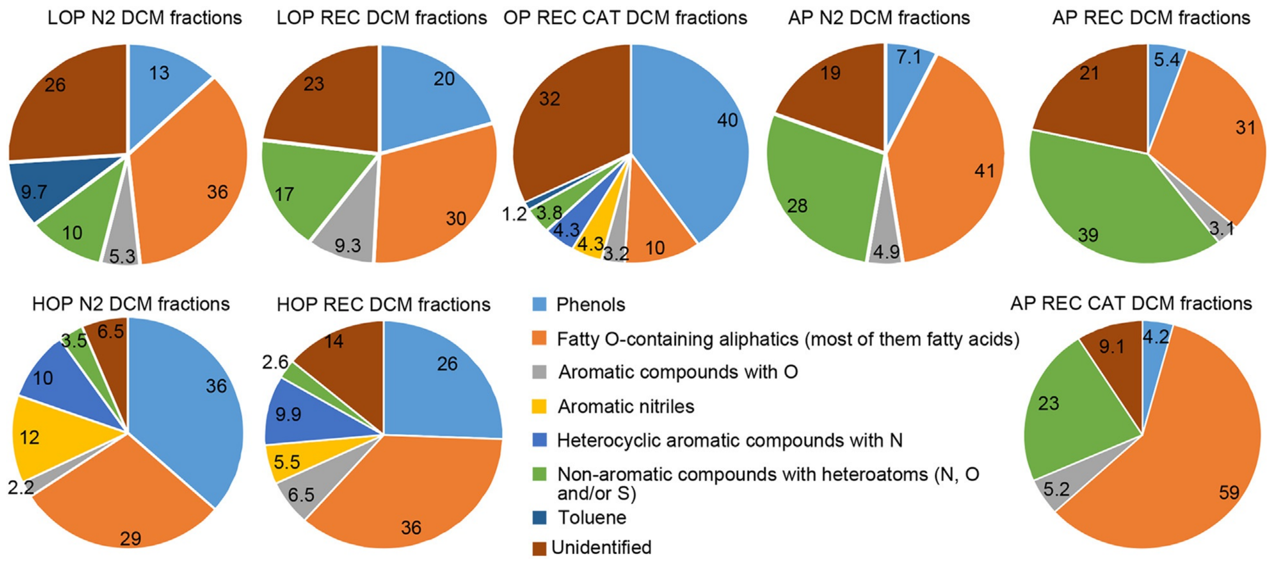

Figure 3. Mass percentage of the chemical families in the DCM fractions extracted from the liquid phases.

ly, the composition of the HCl-SPE fraction extracted from HOP from the N2 experiment has been analyzed by UPLC-MS-QTOF to identify compounds of high molecular weight contained in this fraction.

Composition of the APs determined by GC-MS

The 30 most abundant compounds (in percentage area) identified by GC-MS in the APs of the pyrolysis liquids obtained are shown in Table 7. All compounds identified are listed in Tables S16–S18 in the Supporting Information. Figure 4 shows the percentage area of the chemical families identified in the APs; the most characteristic ones are short linear and branched carboxylic acids, heterocyclic nonaromatic amides; N-heterocyclic aromatic compounds; linear or branched short amides; short aliphatic and aromatic nitriles; short aliphatic nitriles; phenols; and other compounds that seem to come from biological structures, such as peptides, pentoses, and riboses.

Many short linear and branched carboxylic acids have been detected in these samples. None of these carboxylic acids present additional functional groups, such as hydroxyl groups. As observed in Figure 4, the lowest percentage area of short aliphatic carboxylic acids (C_2–C_8) was obtained in the REC_CAT experiment and the highest in the experiment performed with an atmosphere that simulated the recirculation of pyrolysis noncondensable gases, which occurred with the fatty acids extracted in the DCM fractions. The percentage areas of the aromatic carboxylic acids determined in these APs follow the same trends as these short aliphatic hydrocarbons.

The proportion of N-heterocyclic nonaromatic compounds decreases with the use of catalyst, while the proportion of N-heterocyclic aromatic compounds increases, probably due to the enhancement of unsaturated bonds thanks to the use of catalyst. However, the increase in the percentage area of the N-heterocyclic aromatic compounds is much sharper than the decrease in the percentage of nonaromatic ones, so there must be another mechanism to justify the significant increase. The in situ catalytic cracking of vapors over γ-alumina has a negative effect on the percentage area of amides and a positive one on the proportion of aliphatic and aromatic nitriles. As discussed in the following sections, the formation of nitriles through the reaction of fatty acids with ammonia is favored by the catalytic cracking of vapors over γ-Al_2O_3. In this reaction, amides appear as intermediates that end up as nitriles by means of a dehydration reaction. This reaction mechanism would be supported by the compounds identified in these samples, since the proportion of short carboxylic acids and short alkyl amides decreases in the REC_CAT experiment, while the proportion of short aliphatic nitriles increases. In the same way, the ratio of aromatic nitriles

Table 7. Most abundant compounds identified in the APs ranked according to their percentage area determined by GC-MS analyses.

N2		REC		REC_CAT	
compound	Area [%]	compound	Area [%]	compound	Area [%]
acetic acid	12	acetic acid	16	acetic acid	6.6
2,4-imidazolidinedione, 5-methyl-	9.2	2,4-imidazolidinedione, 5-methyl-	8.6	2,4-imidazolidinedione, 5,5-dimethyl-	5.7
5-isopropyl-2,4-imidazolidinedione	5.1	acetamide	5.8	acetonitrile	5.5
acetamide	4.9	propanoic acid	4.1	1*H*-imidazole, 2-methyl-	4.1
propanoic acid	3.7	5-isopropyl-2,4-imidazolidinedione	3.9	2-pyrrolidinone	3.9
hexanoic acid, 2-methyl-	3.5	hexanoic acid, 2-methyl-	3.7	2(1*H*)-pyridinone	3.6
acetonitrile	3.0	2-pyrrolidinone	2.8	1*H*-imidazole, 1,2-dimethyl-	3.1
2-pyrrolidinone	2.5	acetonitrile	2.3	2,4-imidazolidinedione, 5-ethyl-5-methyl-	2.9
5-ethylhydantoin	2.3	2,4-imidazolidinedione, 5,5-dimethyl-	2.2	3-pyridinol	2.5
2,4-imidazolidinedione, 5,5-dimetyl-	1.9	5-ethylhydantoin	1.9	2,4-imidazolidinedione, 5-methyl-	2.3
2-butanone, (2-ethoxyethyl)methylhydrazone	1.8	3-pyridinol	1.7	1*H*-imidazole, 4-methyl-	2.3
butanoic acid	1.8	2,5-pyrrolidinedione	1.6	3-aminopyridine	2.2
3-pyridinol	1.6	1,2,4-triazine-3,5(2*H*,4*H*)dione	1.6	1*H*-imidazole	2.0
2,4-imidazolidinedione, 5-(2-methylpropyl)-, (*S*)-	1.4	benzenecarboxylic acid	1.3	propanoic acid	1.9
2(1*H*)-pyridinone	1.4	propanoic acid, 2-methyl-	1.3	acetamide	1.9
2,5-pyrrolidinedione	1.4	butanoic acid	1.3	2(3*H*)-naphthalenone, 4,4*a*,5,6,7,8-hexahydro-1-methoxy-	1.8
formamide, *N*-methyl-*N*-4-[1-(pyrrolidinyl)-2-butynyl]-	1.2	2,4-imidazolidinedione, 5-ethyl-5-methyl-	1.2	dec-9-en-6-oxo-1-ylamide	1.7
propanoic acid, 2-methyl-	1.2	2,4-imidazolidinedione, 5-(2-methylpropyl)-, (*S*)-	1.2	hexanoic acid, 2-methyl-	1.6
benzenecarboxylic acid	1.1	hexanoic acid	1.2	5-isopropyl-2,4-imidazolidinedione	1.5
2-piperidinone	1.0	1*H*-imidazole, 4-methyl-	1.1	2-aminopyridine	1.5
hexanoic acid	1.0	*N*,*N*′-dimethyltrimethylenethiourea	1.1	2(1*H*)-pyridone, 6-methyl-	1.4
2,4-imidazolidinedione, 5-ethyl-5-methyl-	1.0	pentanoic acid, 4-methyl-	1.0	2(1*H*)-pyridinone, 3-methyl-	1.4
pyridine	0.98	2-piperidinone	0.99	2-piperidinone	1.3
1*H*-pyrazole, 4-methyl-	0.98	1*H*-imidazole	0.91	acetamide, *N*-methyl-	1.3
butanamide, 3-methyl-	0.98	isocrotonic acid	0.90	pyrrole	1.1
uridine, 5-methyl-	0.96	butanamide, 3-methyl-	0.89	1*H*-imidazole, 2-ethyl-	1.1
pentanoic acid, 4-methyl-	0.94	cyclohexane, 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethyl-	0.89	2,5-pyrrolidinedione	1.1
1*H*-imidazole, 2-methyl-	0.91	benzenepropanoic acid	0.85	pyridine	1.1
phenol	0.85	benzeneacetic acid	0.85	1*H*-imidazole, 2-ethyl-	1.0

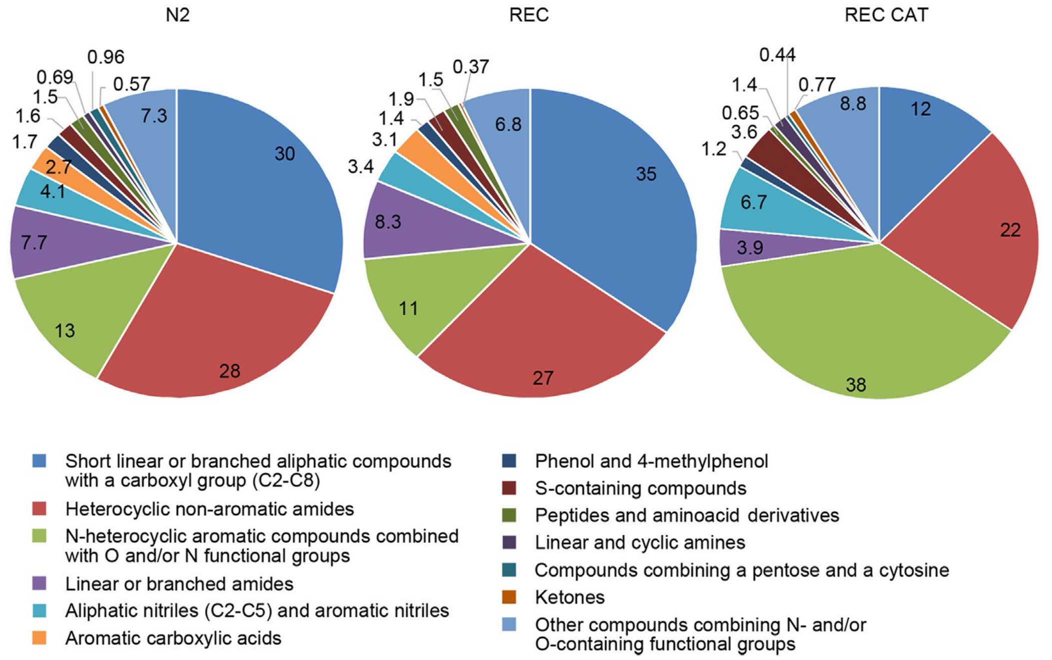

Figure 4. Percentage area of the chemical families in the APs.

obtained in the experiments performed without catalyst (N2 and REC) was significantly lower than that obtained in the catalytic experiment (REC_CAT).

Composition of the HCL-SPE fractions determined by UPLC-MS-QTOF

UPLC-MS-QTOF has been used to identify the compounds of high molecular weight present in the HCl-SPE fraction separated from HOP from the conventional pyrolysis experiment, N2. The compounds identified by UPLC-MS-QTOF are pentylimidazole, hexylimidazole, trimethoxybenzene, heptylimidazole, octylimidazole, nonylimidazole, *n*-hexyl-5-oxododecamide, octocrylene, dietildodecamide, and oleamide.

The families of compounds identified are mainly alkyl imidazoles and fatty acid amides (FAAs).

The FAAs identified in this fraction could have different origins, for example, the pyrolysis of microbial cells yields amides.[17] Linear amides could also come from the primary decomposition of proteins or from amines in amino acids, which react with carboxylic acids and then produce amides and water.[30] Because FAAs are also present in living organisms, they could even come from the direct devolatilization of SS.[31] In our experiments, amides seem to be generated in reactions between fatty acids and ammonia. Moreover, the dehydration of these amides would probably yield nitriles. This mechanism would be supported by the presence of ammonia, fatty and short carboxylic acids, and the corresponding amides and nitriles. According to Alvarez et al., the yield of amides reached a maximum at a pyrolysis temperature of 500 °C.[32] At higher temperatures, amides could undergo cyclization reactions, yielding pyrroles, and also dehydration reactions, yielding nitriles. As shown in Table 7 and Tables S16–S18 in the Supporting Information, the APs of SS pyrolysis liquids contain pyrrole and pyrrole derivatives, such as 2-pyrrolidinone or 2,5-pyrrolidinedione.

Imidazole and its derivatives are aromatic heterocyclic compounds present in several natural products, such as histamine, histidine, or purine.[31] According to Tian et al., heterocyclic compounds could probably come from the pyrolysis of pyrrolic and pyridinic species.[15a] The proteins first decompose to form amines, which are intermediates for the formation of heterocyclic compounds and nitriles during secondary cracking reactions.[15a]

Building blocks of SS yielding pyrolysis liquid compounds

Apart from the pyrolysis operational conditions, the raw material has a profound effect on the composition of the liquid product. Table 8 provides a summary of the SS building block or blocks from which the different pyrolysis products are derived. Some pyrolysis liquid products are assumed to come from the reaction between primary pyrolysis products of two different building blocks. Some considerations could be made in light of these results. For example, levoglucosan, levoglucosanone, furfural, or other sugar monomers were not obtained in any of the fractions, despite the presence of carbohydrates in the raw material. The absence of anhydrosugars could be caused by the high proportion of ash, especially alkaline and alkaline-earth metallic species, in the raw material.[33] Typical carbohydrate pyrolysis products that have been detected in SS bio-oil are short carboxylic acids and ketones. On the other hand, it is interesting to note that there are some value-added chemicals, such as α-olefins or N-containing compounds, which can only be obtained from materi-

Table 8. SS building blocks and derived pyrolysis products.

SS building block	Derived SS pyrolysis liquid products
protein-based components	phenols, heterocyclic nonaromatic amides, N-heterocyclic aromatic compounds, linear or branched short amides, compounds combining a pentose and a cytosine
lipids	fatty acids, paraffins, olefins
carbohydrates	short-chain carboxylic acids, ketones
protein + lipids	fatty nitriles
protein + carbohydrates	short aliphatic amides and nitriles

als that contain lipids and proteins, respectively. Fatty nitriles could be obtained by means of the pyrolysis of a material containing both proteins and lipids. In the same way, secondary reactions of the primary pyrolysis products obtained from carbohydrates and proteins allow short aliphatic amides and nitriles to be obtained.

Value-added chemicals in the SS pyrolysis liquids

Value-added chemical products

The possible production of value-added chemical compounds extracted from the SS pyrolysis liquids and their production per tonne of pyrolyzed SS are shown in Table 9.

Aliphatic hydrocarbons

Different operational conditions have caused small differences in the yield of each of the possible value-added compounds identified in the Hep-sol fractions. For example, it seems that both the use of simulated recirculation gas as the fluidizing agent and the catalytic treatment of pyrolysis vapors yield lower amounts of paraffins and olefins. Similar results have been found for the production of n-paraffins. Paraffins and olefins may originate from the direct devolatilization of SS[9] and from the pyrolysis of other components of SS, such as fatty acids,[34] triglycerides,[11b,35] and steroids.[36]

Interestingly, the production of α-olefins seems to be influenced by the operational conditions studied. The lowest yield of α-olefins has been obtained in the experiment performed by using the gas that simulates the recirculation of pyrolysis noncondensable gases to the reactor. However, the highest production of α-olefins was obtained in the experiment that combined both the use of the recirculation gas as a fluidizing agent and the catalytic treatment of pyrolysis vapors over γ-alumina. The main products obtained in the pyrolysis of fatty acids and triglycerides were n-paraffins and α-olefins.[37] The increase in the production of α-olefins by means of the catalytic cracking of pyrolysis vapors over γ-alumina has been highlighted by other authors.[38] According to these authors, the decomposition of the triglycerides occurs through two mechanisms that are favored by the bonding of a carbonyl oxygen to an acid site on the alumina catalyst. The results obtained in this work indicate a negative effect of the recirculation atmosphere on the production of α-olefins, which could be compensated for by the positive effect of catalytic cracking over γ-alumina, resulting in the highest yield of α-olefins in the REC_CAT experiment. With regard to the effect of other operational conditions, Sánchez et al. observed that the increase in pyrolysis temperature resulted in a decrease in the yield of n-paraffins and α-olefins.[18g]

Table 9. Production of the value-added chemical compounds quantified in the pyrolysis liquids.

Value-added chemical compound	Yield [kg t^{-1} SS]		
	N2	REC	REC_CAT
paraffins + olefins	17	16	14
α-olefins	8.6	7.8	8.9
n-paraffins	4.5	4.0	3.5
aromatic hydrocarbons	5.5	4.3	6.9
toluene	0.98	0.77	1.30
ethylbenzene	0.23	0.20	0.33
xylene	0.37	0.37	0.82
α-methylstyrene	0.17	0.16	0.16
BCB	1.0	0.74	0.70
long linear alkyl benzenes	0.59	0.38	0.65
short alkyl benzenes	1.7	1.4	2.2
long aliphatic nitriles	0.7	0.7	1.5
aromatic nitriles	1.9	1.0	1.7
indole and derivatives	1.4	1.2	1.1
quinoline	0.00	0.04	0.15
phenol	0.78	0.64	0.96
phenol and derivatives	2.6	2.2	3.2
fatty acids	2.9	3.7	1.3
ammonia	10	13	14

Nowadays, linear α-olefins (LAOs) are valuable chemical compounds. The utility of LAOs is due to their reactivity thanks to the position of the double bond. The main applications of these chemicals depend on the chain length and are summarized in Table 10. Their current production is based on nonrenewable sources mainly by ethylene oligomerization. Moreover, it is worth emphasizing that these compounds cannot be obtained directly by pyrolysis of lipid-free biomass, such as lignocellulosic biomass. Their production in 2009 in Europe was 566 kt and they cost \$1200–2100 per tonne in 2010, depending on the carbon chain lengths.[39] Currently, the production of LAOs by ethylene oligomerization does not generate a single product, but a range of even-numbered carbon chains from C_4 to $>C_{30}$.[39] They also contain small amounts of other branched and internal olefin isomers and paraffin impurities.[39] However, they can be purified and fractionated into specific carbon chain length fractions.[39] There are also methods to separate olefins from paraffins.[40] Nevertheless, there are no studies on the specific separation of this family of compounds from pyrolysis liquids.

Aromatic hydrocarbons

Aromatic hydrocarbons are generated in secondary reactions, since SS does not contain this family of compounds.

Table 10. Principal applications of LAOs by chain length.[39]

Chain length	Application
C_6–C_{10}	plasticizer alcohols
C_{10}–C_{12}	poly-α-olefins and other additives for lubricants, amine oxides, and amines
C_{10}–C_{16}	detergent alcohols, nonionics, and oil field chemicals
C_{16}–C_{18}	oil field chemicals, lube oil additives, and surfactants
C_{20}–C_{30+}	oil field chemicals and wax replacement

The lowest production of this chemical family was obtained in the REC experiment. The use of an atmosphere that simulates the recirculation of pyrolysis gas inhibits secondary pyrolysis reactions, in which aromatic hydrocarbons are generated. As expected, the use of catalyst favored aromatization reactions and the highest yield of aromatic hydrocarbons was obtained in the REC_CAT experiment. Similar effects of the utilization of γ-alumina on the presence of aromatic hydrocarbons in the SS pyrolysis liquid were found when the liquid composition was analyzed semiquantitatively by percentage area.[11f] Other researchers found the same effect when performing fast microwave-assisted catalytic pyrolysis of SS with HZSM-5; an acid catalyst similar to γ-alumina.[41] With regard to the effect of other operational conditions, many researchers have concluded that their proportion in pyrolysis liquids increases with temperature thanks to their formation through a Diels–Alder mechanism.[9,18b,22,42] Toluene and other benzene derivatives found in these SS pyrolysis liquids may originate from the pyrolysis of some SS components, such as amino acids (phenylalanine or tyrosine[43]) and polysaccharides.[44]

Some compounds found within the aromatic hydrocarbons, such as toluene, ethylbenzene, and xylenes, can be considered value-added chemical compounds because they are widely used in the large-volume organic chemical industry.[45] The production of these compounds, similar to that of aromatic hydrocarbons, reached its highest value in the REC_CAT experiment. Toluene is mainly used as a solvent in cleaning agents, adhesives, or paints; as a fuel additive; in the manufacture of cosmetics, dyes, explosives, or polymers; or to obtain benzene, xylene, and phenol. Ethylbenzene is a very important intermediate in the synthesis of styrene, which is a precursor to polystyrene. Xylenes are mainly used as solvents, and *p*-xylene is also used to produce terephthalic acid (TPA) and dimethyl terephthalate; both are precursors of polyethylene terephthalate (PET).[45] The industrial production of these chemicals is also based on nonrenewable sources. Most BTEX (benzene, toluene, ethylbenzene, and xylenes) production comes from refinery reformates and steam cracker pyrolysis gasoline (pygas),[45] and they are usually co-produced. With the aim of producing these chemicals by means of the pyrolysis of lignocellulosic biomass by using modified HZSM-5 zeolites, Vispute et al. reported yields of aromatics about 20 wt% (carbon basis).[5] The mass percentage of aromatic hydrocarbons in the Hep-sol fractions ranged from 11 to 20% by mass (see Figure 2). There are industrial processes to separate aromatics from aliphatic hydrocarbons for concentrations higher than 20% by mass of aromatics. Commercial liquid–liquid extraction methods are used for their separation when the concentration is between 20 and 65% by mass. Extractive and azeotropic distillation are applied for the range from 65 to 90% by mass and for concentrations higher than 90% by mass, respectively. However, there are no large-scale separation processes for lower concentrations of aromatic hydrocarbons,[45] although there are some experimental works about the separation of aromatics in lower concentrations by using ionic liquids,[24,46] adsorption,[47] or pervaporative separation with membranes.[48]

Apart from these aromatic hydrocarbons used in the large-volume organic chemical industry, other benzene derivatives that can be considered as value-added chemicals, such as BCB, have been identified in the Hep-sol fractions extracted from the organic samples. The highest production of BCB was obtained in the conventional pyrolysis experiment N2. BCB has the ability to isomerize to form *o*-xylylene under thermal activation, although BCB is more stable than *o*-xylylene, which easily undergoes Diels–Alder reactions.[49] BCB is of special interest thanks to its unique molecular structure and polymeric properties,[50] which are useful for the production of several materials, such as biocompatible polymers, fibers, coatings, and films for microelectronics or high-performance polymers.[51] The use of BCB requires a high degree of purity, so separation from the heptane fraction and purification is necessary. There is a patent for the purification of BCB from a mixture of cyclobutenoarenes and aromatic impurities,[52] but no work has been performed to separate this compound from pyrolysis liquids.

The aromatic hydrocarbons found in the samples contain other value-added chemicals, for example, long linear alkyl benzenes and benzenes mono-, bi- or tri-substituted with short alkyl chains, such as propyl benzene or 1,2,3-trimethylbenzene.

Long linear alkyl benzenes are used in the production of a family of surfactants, namely, linear alkyl sulfonates (LAS), which are commonly used in detergents and are therefore usually present in wastewater. In the process of wastewater purification by activated sludge, LAS are degraded to their long alkyl chain homologues and external isomers; the long alkyl chain homologues are preferably sorbed onto the particulate matter,[53] which later ends up in the SS. Therefore, long linear alkyl benzenes could originate from the direct devolatilization of SS. This fact would not justify the higher production obtained in the experiment performed with the catalytic treatment of vapors. Moreover, SS extractives showed a much lower proportion of long linear alkyl benzenes. Thus, it is thought that the sulfonate group in LAS is fixed by the acid site of the catalyst and long, linear, alkyl benzene would be obtained by the scission of this sulfonate group.

Short, linear alkyl benzenes, such as 1,3,5-trimethylbenzene, benzene 1-ethenyl-2-methyl, propylbenzene, or benzenebutyl, have been found in the Hep-sol fractions. The highest production of these compounds was obtained in the

REC_CAT experiment because, as noted previously, the use of catalyst favored aromatization reactions. These compounds could be used, for example, as fuel additives, since aromatic hydrocarbons increased the octane number of gasoline.

Aliphatic nitriles

LCANS have been identified in the OPs obtained under the three operational conditions studied (N2, REC, REC_CAT), reaching their largest production in the experiment performed with the catalytic treatment of pyrolysis vapors. LCANs could come from the reaction of fatty acids with ammonia, via the amide intermediate, since both fatty acids and ammonia are produced during SS pyrolysis. This reaction could be confirmed by the fact that the oils had nitriles with a carbon number distribution similar to that of fatty acids. However, there should also be another mechanism or this reaction should be combined with the cracking of the alkyl chain, since the samples contain both odd- and even-carbon-numbered nitriles and even-carbon-numbered fatty acids are mostly present in nature, and consequently, in SS. The catalytic experiment could lead to a higher production of nitriles because the reactions of the fatty acids with ammonia could be favored by bonding of the carbonyl oxygen of the fatty acid to an acid site of γ-alumina. On the other hand, the reaction atmosphere does not have any significant effect on the production of this chemical family. With regard to the effect of other operational conditions, Huang et al. determined that the yield of aliphatic nitriles decreased with increasing pyrolysis temperature from 400 to 700 °C, at the expense of increasing the yield of aromatic nitriles.[22]

LCANs are valuable chemicals, mainly used as plasticizers, rubber softeners, oil additives in lubricants, and as chemical intermediates to produce insecticides and amines.[30] Cao et al. achieved the analytical separation of LCANs from the rest of the SS pyrolysis liquid by using a column packed with silica gel 10 % ethyl acetate in *n*-hexane as the eluent.[17]

Aromatic nitriles and N-heterocyclic aromatic compounds

Both families of N-containing aromatic compounds are common products in the pyrolysis of SS. Benzyl nitrile and benzyl propanenitrile were the aromatic nitriles identified in these samples, whereas the compounds belonging to the aromatic heterocyclic family were indole and 3-methyl-1*H*-indole. All of these value-added chemicals mainly extracted in the Hep-sol fractions were also detected in some of the DCM-sol fractions because they were distributed among the solvents used in the fractionation scheme. Therefore, the yields to these chemicals over SS shown in Table 9 are the result of the sum of the yields of each of them extracted in the two fractions (Hep-sol and DCM-KOH-sol + DCM-sol). The lowest production of these compounds was obtained in the REC experiment, which was performed with the fluidizing agent that simulated the recirculation of noncondensable pyrolysis gases. These compounds are generated in gas-phase secondary reactions of primary pyrolysis products, so that the use of an atmosphere that simulates the recirculation of noncondensable gases seems to disfavor this kind of reaction.

Benzonitrile, benzonitrile-4-methyl, and benzenepropanenitrile were some of the aromatic nitriles found in the liquids. Their production was not evidently higher in any of the operational conditions studied, although the lowest yield was obtained in the REC experiment. These aromatic nitriles could come from the reaction between carboxylic aromatic acids and ammonia, which are both present in SS pyrolysis products. According to other researchers who studied the pyrolysis of this amino acid at temperatures near to that used herein, benzonitrile-4-methyl could also originate from the pyrolysis of the amino acid proline.[54]

Indole and its derivatives could be obtained from the pyrolysis of amino acids such as asparagine, proline, histidine, and tryptophan.[44,54] In the case of asparagine, indole and methylindole may be obtained by means of the formation of the intermediate succinimide, which, under pyrolysis conditions, is likely to be oxidized to form more unsaturated compounds, such as indole and methylindole.[54] Quinoline was only detected in experiments performed with the recirculated atmosphere, achieving the largest production in the experiment with vapors treated catalytically with γ-alumina. Other authors detected the presence of quinoline in bio-oil from the pyrolysis of amino acids such as lysine, leucine, tryptophan, and phenylalanine.[54] Quinoline is also a value-added chemical that can be used as a solvent; in the manufacture of dyes; and as a feedstock in the production of other specialty chemicals, such as drugs or agrochemicals. The N-containing chemicals, especially N-heterocycles, such as pyrroles, pyridines, and indoles, are widely used in the pharmaceutical, agrochemical, and dye industry. Due to their special properties, they are also used in new molecular materials for electronic, optic, or transmission applications.[16] More than one billion dollars' worth of N-heterocycles are produced every year, including 10 000 t pyrroles per year ($\$25\,000\ t^{-1}$); 200 000 t pyridines per year ($\$5000\ t^{-1}$), and 10 000 t indoles per year ($\$20\,000\ t^{-1}$).[16]

Phenols

Phenols are one of the main families of compounds identified and quantified in the DCM fractions. The main phenols identified are phenol, methyl phenols (*ortho*-, *meta*-, and *para*-cresol), and 4-ethylphenol. Phenol and its alkyl derivatives may originate from the pyrolysis of tyrosine-containing peptides and proteins.[43,44] According to the results obtained (see Table 9), the highest production of phenols was obtained in the REC_CAT experiment. The catalytic cracking of the pyrolysis vapors over γ-alumina could promote the production of methyl phenols due to the greater cracking of the protein-derived pyrolysis products. Moreover, in general, phenols are not easily deoxygenated over a moderate acid catalyst,[55] such as HZSM-5,[55,56] so that once formed they would not be significantly reduced by the effect of the catalytic treatment. Phenol is mainly industrially produced by the cumene hydroperoxide process, from nonrenewable benzene and propylene.[57] Other methyl phenols, such as 4-methylphenol (*p*-cresol), are also produced in industry from raw materials, for example, toluene, obtained mainly from nonrenewable sources. Phenols are reported to be valuable chemicals, reaching a market volume of 9000000 t per year and a price of €1400 per tonne. They have antioxidant, germicidal, and antidiarrheal properties, and can be used as intermediates to produce pharmaceutical products or specialty polymers.[58] Moreover, phenols from biomass pyrolysis liquid are commonly used in the production of phenol formaldehyde resins; an important type of adhesive used in the production of wood-based panels with superior water resistance.[59] The production and price of phenol formaldehyde resins are 2300000 t per year and €150 per tonne, respectively.[60] Several works have been performed to produce and isolate phenolic-rich fractions from biomass pyrolysis liquids, and the methods employed vary from solvent extraction or column chromatography to distillation.[4c,i,58,61] For example, some of these researchers have performed the pyrolysis of sawdust at 480–520 °C and have obtained 55 % by mass of dry pyrolysis oil with a phenolic content of around 20–25 %.[4i] The antioxidant properties of phenols contained in SS pyrolysis liquids have been used to improve the oxidation stability of biodiesel.[12]

Fatty acids

Apart from phenols, fatty acids are the other major chemical family in the DCM fractions extracted from the SS pyrolysis liquid phases. These acids come from their direct devolatilization from SS, since SS extractives have a high content of these compounds. The production of fatty acids reached its lower value in the catalytic experiment. The reaction of fatty acids is promoted by the use of γ-alumina due to the bonding of the carbonyl oxygen to a Lewis acid site on the γ-alumina catalyst. As noted previously, the main products obtained from the reaction of fatty acids would be α-olefins and fatty nitriles, which could come from the reaction between fatty acids and ammonia and the subsequent dehydration reaction of the intermediate fatty amide. The highest production of fatty acids was obtained in the experiment that simulated the recirculation of the noncondensable pyrolysis vapors. This result could be related to the high concentration of CO_2 in the reaction atmosphere, since CO_2 would inhibit the decarboxylation of fatty acids.

Fatty acids are also of interest for industry. Their price is around €1500 per tonne.[60] Unlike the other value-added chemicals discussed herein, fatty acids are currently produced in industry from triglycerides, which are a renewable source. Hydrolysis of triglycerides gives fatty acids, with glycerin as a byproduct. Fatty acids and their derivatives are used in the production process of a great variety of products, such as biodiesel, soap, synthetic organic detergents, rubber compounding, synthetic rubber polymerization, paints, varnishes, surface coatings, insecticides, disinfectants, and germicides.[62] Distillation is the most common process used to separate fatty acids. Mixed fatty acids are purified with simple distillation and fatty acids are also separated according to chain length by fractional distillation. Chain lengths that differ by two carbon atoms are easily separated.[63] Blends of fatty acids are usually used to optimize the properties in the production of soap and detergents.[64] Apart from distillation methods, there are other less frequently used methods to separate individual fatty acids, such as crystallization, adsorption, or partition with solvents.[65]

Ammonia

Ammonia, which is mainly concentrated in the APs, is the major specific value-added chemical produced in these SS pyrolysis experiments (see Table 9). Ammonia is one of the most highly produced inorganic chemicals in the world in terms of volume, with a global production of 137 Mt in 2012. Ammonia is used as a reagent in the production of a wide variety of products, such as fertilizers, explosives, or other N-containing chemicals.[66] Although its industrial production process is very well known and firmly established, the production of NH_3 from N-containing residues would offer a renewable source for this chemical that could contribute to the solution of global environmental problems posed by the destabilization of the biogeochemical nitrogen cycle.[67]

Acetic acid and short carboxylic acids

Acetic acid represents the largest percentage area in the chromatographic analyses performed on the three APs. Acetic acid is considered to be a large-volume organic chemical. It is mainly used in the production of vinyl acetate monomer (VAM), which can be polymerized to form poly(vinyl acetate). Acetic acid is also used in the production of acetic anhydride, acetate esters, and as a solvent in the production of TPA. The latter is used as a feedstock for the manufacture of PET. These chemicals can be used in the manufacture of plastics, detergents, paints, rubbers, or solvents.[4j,68] Recently, a scheme has been proposed by Lian et al. to produce lipids with *Cryptococcus curvatus* from the carboxylic acids present in the pyrolytic AP from lignocellulosic biomass.[69] The total production of acetic acid in 2009 was 6.94 million tons with a market price of $600 per ton (2009 level). Acetic acid obtained in the pyrolysis of SS could be generated during the hydrolysis of the acetyl ester groups present in polysaccharides[6b,70] and fatty acids.[44] Today, the main production of this chemical is based on nonrenewable sources, although, as noted in the Introduction, acetic acid from pyrolysis liquids, in the form of pyroligneous acid, has been commercialized for many years. Therefore, the isolation of acetic acid from the pyrolysis liquid may not only create a different renewable source to obtain this chemical, but also make the pyrolysis liquid more economically attractive. There are some studies in the literature on the isolation of acetic acid from pyrolysis bio-oil by means of reactive extractions with tri-*n*-octylamine or supercritical carbon dioxide.[4j,68a,71]

Acetamide

Acetamide may have different origins in SS pyrolysis liquids. For example, it could come from the pyrolysis of microbial cell walls,[72] and also from thermally labile proteins that contain glycine.[44] According to Eudy et al., the N-acetyl group of cell wall amino sugars produced acetamide during pyrolysis.[73] However, in this case, acetamide could also come from the reaction between acetic acid and ammonia. The main uses of acetamide are as a plasticizer and an industrial solvent.[74]

Acetonitrile

Acetonitrile is one of the most commonly used organic solvents. With a high degree of purity, it can be used in pharmaceuticals, as a chromatography solvent, and in DNA testing.[75] Acetonitrile could be formed by the dehydration of acetamide.[31,76]

Imidazolidinedione compounds

Imidazolidinedione compounds are oxygen and N-heterocyclic nonaromatic compounds with ketone groups that have been identified in the pyrolysis of glycine[77] or human hair.[78] It has been suggested that these N-heterocyclic compounds are formed during amino acid pyrolysis.[79] Imidazolidinedione derivatives are considered to be valuable products thanks to their pharmacological, antibacterial, antifungal, antiprotozoal, antimalarial, or anthelmintic properties.[79] They could also be formed from melanoidin compounds, which are generated in the Maillard reaction from reducing sugars and proteins or amino acids.[31] N-Heterocyclic aromatic compounds, such as pyridine, imidazole, and their derivatives, have also been identified in the APs of these liquids. Imidazole derivatives have an important role in the pharmaceutical industry thanks to their polarity and ionizable properties that confer an important role in medicinal chemistry.[80] The recovery and purification of alkyl imidazoles with only one or two carbon atoms in the alkyl substituent has been studied.[81]

Fatty acid amides (FAAs)

FAAs are naturally occurring compounds that possess impactful biological properties and have pharmacological functions.[82] FAAs have also been tested as plasticizers,[83] as antiwear and extreme pressure additives in lubricating oil,[84] and in the production of waterproofing agents and waxes.[85] Cao et al. also identified this kind of species in the pyrolysis bio-oil of SS, and used column chromatography on silica gel to separate a fraction that contained mainly FAAs.[17]

Lastly, octocrylene, which has been identified in the HCl-SPE fraction by UPLC-MS-QTOF, is used as an ingredient in sunscreens and cosmetics.

Organic fractions as valuable products

Hep-sol fractions as a whole valuable fraction

The fractionation scheme applied to the samples has managed to separate a fraction, Hep-sol, that is almost free of nitrogen-containing compounds. Therefore, the nitrogen content in the Hep-sol fractions is lower than those of the original OPs HOP N2 and LOP N2 samples from which the Hep-sol fractions have been extracted (see Tables 1 and 11), achieving nitrogen content reductions of 79.4 and 47.8 %, respectively.

Table 11. Elemental analyses of the Hep-sol fractions extracted from the pyrolysis liquid obtained by conventional pyrolysis (N_2 as a fluidizing agent).

Fraction	Content [%]		
	C	H	N
Hep–sol HOP N2	80.7	11.7	1.91
Hep–sol LOP N2	84.5	12.2	0.73

However, a small amount of organic nonbasic nitrogen-containing compounds (aliphatic and aromatic nitriles, and N-heterocyclic aromatic compounds) is present in the Hep-sol fractions. The presence of these compounds limits the possible use of the Hep-sol fractions as a fuel or for cofeeding in petroleum refineries, since these nitrogen contents are higher than that typical for crude oil. The nitrogen content in crude oil needs to be reduced because nitrogen-containing compounds polymerize easily and inhibit the hydrodesulfurization reaction. The hydrodenitrogenation of pyrolysis liquids from protein-rich biomass has been scarcely studied.[86] In most of the operational conditions studied in these two works, the nitrogen content reduction achieved was lower than 30 %.[86] Only when part of the bio-oil was solubilized with 80 % xylene was complete elimination of nitrogen achieved.[86a] On the other hand, the hydrogen requirements for the removal of nitrogen from N-heterocyclic aromatic compounds are at least more than double those needed for the reduction of other heteroatoms in the pyrolysis liquid compounds.[87]

Most of the nitrogen-containing compounds identified in the Hep-sol fractions are considered as value-added chemicals, so recovering these compounds rather than removing them is preferable because it would allow both a reduction of the nitrogen content and extraction of these value-added nitrogen-containing compounds. Cao et al. developed a method to fractionate and identify the organic species present in bio-oil.[17] These researchers extracted a fraction free from nitrogen-containing compounds and other fractions with different families of nitrogen-containing compounds obtained by means of column chromatography on silica gel with different solvents, including mixed solvents, as eluents. One of the fractions contained mainly LCANs, so this method could be used to separate these kinds of compounds from the Hep-sol fractions. There is also a patent to separate nitrile–hydrocarbon mixtures.[88] The separation of nitrogen-containing compounds in liquids derived from coal liquids and petroleum has also been studied.[89] A possible application of these LCANs could be their hydrogenation to form fatty amines, which are widely used as surfactants. The hydrogenation reaction of the LCANs could be performed once the fatty nitriles were separated or even on the whole Hep-sol fraction, since its subsequent separation from the sample would not be difficult.

The mass yields to Hep-sol compounds over SS fed were calculated by taking into account the yields to the OPs (Table 1) and the total mass proportion of Hep-sol compounds (Tables S3–S7 in the Supporting Information). These are presented in Table 12.

The yields obtained are quite low and would be even lower if the nonbasic *N*-containing compounds were separated from these fractions. The highest yield was obtained in the catalytic experiment, probably because the catalyst caused the loss of heteroatoms in the liquid compounds, and therefore, an increase in the production of compounds containing mainly hydrogen and carbon, which were extracted in the Hep-sol fraction.

DCM fractions as a whole valuable fraction

Because these fractions contain a significant mass proportion of phenols, they could be applied as antioxidant additives, especially the fraction extracted from samples obtained in the REC_CAT experiment, since the proportion of phenols is the highest. The whole OP obtained from SS pyrolysis with catalytic treatment of the vapors over γ-Al_2O_3 has already been successfully tested as an antioxidant additive for biodiesel.[12] The yields of these fractions that can be obtained in each of the experiments per tonne of SS fed are presented in Table 12.

Table 12. Total yield of the Hep-sol and DCM fractions per tonne of SS fed for the different experiments.

Fraction	Yield [kg t^{-1} SS] N2	 REC	 REC_CAT
Hep–sol	30	29	33
DCM–KOH–sol + DCM–sol	10	12	9.7

Assessment of the production of value-added compounds

The maximum possible production of some of these value-added chemicals if all SS produced in Europe annually (10 Mt) were pyrolyzed has been compared with the current European production of these chemicals (Table 13). This possible maximum production has been calculated by using the highest yield obtained among the three sets of experimental conditions used herein. Some of the current European production figures have had to be approximated from data offered by different sources.

The level of production of α-olefins by SS pyrolysis could reach an important percentage of their current European production from petroleum. Other chemicals that could be produced by means of pyrolysis at a reasonably high level are fatty nitriles, *n*-paraffins, short alkyl benzenes, α-methylstyrene, long linear alkyl benzenes, short alkyl benzenes, and acetic acid. According to the data shown in Table 13, the maximum possible production of most of the value-added chemicals is achieved in the REC_CAT experiment. The production of fatty acids by SS pyrolysis appears to be of little interest due to the low percentage of European production. Moreover, the pyrolysis of fatty acid compounds gives interesting products, such as α-olefins and fatty nitriles. From this point of view, the REC_CAT experiment would also be the most interesting, since the conversion of fatty acids is the highest. However, the operational conditions should be optimized even further to achieve the complete conversion of

Table 13. Maximum possible production of various value-added chemicals obtained by SS pyrolysis and comparison with their current European production.

Value-added compounds	Annual European production [kt] (year cited)	Maximum possible annual production by SS pyrolysis [kt] (exptl)	European production [%]
α-olefins	566 (2009), 2666 (2009) (world), [39]	89 (REC_CAT)	16
n-paraffins	≈1000, 3100 (2007) (world), [90]	45 (N2)	4.5
toluene	2635, [45]	13 (REC_CAT)	0.49
ethylbenzene	4881, [45]	3.3 (REC_CAT)	0.068
xylenes	2872, [45]	8.2 (REC_CAT)	0.29
α-methylstyrene	61 (2000), [91]	1.7 (N2)	2.8
long linear alkylbenzene (LAB)[a]	≈400 (1995), 2600 (world) (1995), [92]	6.5 (REC_CAT)	1.6
short alkyl benzenes	490, [45]	22 (REC_CAT)	4.5
fatty acids	≈25 000, [94], 1 000 000 (world), [93]	37 (REC)	0.15
phenol	1819 (2012), [94]	9.6 (REC_CAT)	0.53
phenol and derivatives	9000 (world), [94]	32 (REC_CAT)	0.36
fatty nitriles[b]	300 (world)[95]	15 (REC_CAT)	5.0
ammonia	≈15 000, 137 000 (2012) (world), [96]	140 (REC_CAT)	0.93
acetic acid	≈1041, 6940 (2009) (world), [4j, 97]	39[c] (REC)	3.7

[a] Estimated values from the production of alkylbenzene sulfonates because > 98 % of all LAB are used as intermediates in their production process. [b] Production data for fatty amines because industrially they are mainly obtained by hydrogenation of fatty nitriles. [c] Production estimated from percentage area in the chromatographic analysis of APs.

fatty acids and maximization of the products derived from them.

Conclusions

Quantitative determination of the chemical composition of the pyrolysis liquid from SS is required to assess its potential as a source of valuable chemicals. Because pyrolysis liquid is a mixture of hundreds of compounds, this quantitative determination is very tedious. The present study proposes a procedure based on solvent fractionation with inorganic (HCl) and organic solvents (Hep and DCM) to facilitate the chemical analysis of the liquids. With this method, the pyrolysis liquids were separated into four different fractions: Hep-sol, DCM-sol, HCl-sol, and insoluble fractions. This procedure enabled the determination of the chemical composition to be improved. However, more treatments are required to separate and purify specific chemicals.

The most interesting valuable chemical compounds found in the liquids in terms of their production level, price, or production from nonrenewable resources were ammonia, α-olefins, *n*-paraffins, aromatic hydrocarbons, nitriles, phenol and its derivatives, fatty acids, short carboxylic acids, and indole and its derivatives. α-Olefins, *n*-paraffins, and aliphatic nitriles were separated in the Hep-sol fraction; α-olefins were the most abundant compounds in this fraction. Phenols and fatty acids were mostly concentrated in the DCM-sol fraction and carboxylic acids and amides in the HCl-sol fraction.

α-Olefins were the value-added organic compounds with the highest production from SS (8–9 $\mathrm{kg\,t^{-1}}$ SS). Their current production is based on nonrenewable resources. Pyrolysis as a process to produce α-olefins from renewable sources requires biomass that has lipids in its chemical composition; this is the case with SS. According to the results obtained in this study, about 16% of the European production of α-olefins could be obtained from SS. The production of nitrogen-containing compounds from SS is also of great interest, since most of these compounds are synthesized by nonrenewable resources. Pyrolysis of biomass containing proteins and lipids could be a direct way to produce nitrogen-containing compounds from renewable sources. Ammonia (10–14 $\mathrm{kg\,t^{-1}}$ SS), nitriles (2–3 $\mathrm{kg\,t^{-1}}$ SS), and indole and its derivatives (1–2 $\mathrm{kg\,t^{-1}}$ SS) were the most abundant nitrogen-containing compounds quantified in this work. Fatty acids (1–3 $\mathrm{kg\,t^{-1}}$ SS) can also be produced from SS pyrolysis, by means of direct devolatilization of the lipids present in the SS; however, their production seems to be less interesting because they are already industrially obtained from renewable sources (triglycerides), and also because the percentage of European production that could be generated from SS is only around 0.2%. Other interesting compounds, such as fatty nitriles and α-olefins, could originate from secondary reactions of fatty acids during pyrolysis. Phenol and its derivatives (2–3 $\mathrm{kg\,t^{-1}}$ SS) and aromatic hydrocarbons (4–7 $\mathrm{kg\,t^{-1}}$ SS) are other value-added chemicals that could be obtained from SS. However, these compounds can also be produced to a higher degree by the pyrolysis of other types of biomass, for example, lignocellulosic biomass.

The highest production of value-added chemicals in this study was achieved by pyrolysis under an atmosphere that simulated the recirculation of noncondensable gases with catalytic post-treatment of vapors over γ-Al_2O_3. This catalyst favored the pyrolysis reactions of fatty acids to generate α-olefins, and also the reactions between fatty acids and ammonia to generate fatty nitriles. The recirculation atmosphere seemed to disfavor the production of α-olefins, but this negative effect could be compensated for by catalytic cracking over γ-Al_2O_3. Pyrolysis under a recirculation atmosphere implies a lower cost of the fluidizing agent and a higher heating value of the pyrolysis gas produced. Further studies are required to optimize the SS pyrolysis operating conditions to produce value-added chemicals, specifically α-olefins and nitriles.

Experimental Section

Sewage sludge (SS)

SS used in this work was provided by an urban wastewater treatment plant located in Madrid (Spain). SS was anaerobically digested and thermally dried. Proximate and ultimate analyses, heating value, extractive content, and other properties of these SS samples are reported elsewhere.[24]

The SS extractives were determined by Soxhlet extraction with DCM and after solvent evaporation. Their proportion in the sample was 4.5% by mass. The composition of these extractives was analyzed by GC-MS and is shown in Table S0 in the Supporting Information. The compounds identified belonged mainly to two chemical families: fatty acids and sterols. Apart from these compounds, some aliphatic hydrocarbons and long, linear alkylbenzenes were detected.

SS pyrolysis liquids

SS pyrolysis liquids were obtained in a laboratory-scale fluidized bed plant. Additional information about the components of the experimental plant can be found elsewhere.[11e,25]

The condensable vapors generated in the pyrolysis process were condensed in the liquid recovery system, which consisted of two ice-cooled condensers and an electrostatic precipitator. The electrostatic precipitator provided a potential difference of 10000 V. The liquid fractions collected in the three devices were mixed and placed together in a glass bottle for later analyses. The whole liquid product was not homogeneous and separated into two or three phases, depending on the operational conditions. Phase separation was enhanced by centrifugation for 30 min at 4500 rpm (2038*g*). Samples from the three phases were separated by using a Pasteur pipette for later analysis.

The composition of the SS pyrolysis liquids obtained under different operational conditions was studied herein. The experiments were performed by using a pyrolysis temperature of 530 °C, a ratio gas velocity over minimum fluidization velocity (u/u_{mf}) of 7.8, and a SS diameter size between 250 and 500 μm. The effects of the use of an atmosphere that simulated the recirculation of the pyrolysis noncondensable gases and the in situ catalytic treatment of the vapors over γ-alumina were studied. In brief, three types of experiments were performed: conventional pyrolysis by using nitrogen as a fluidizing agent (N2), pyrolysis by using a synthetic gas mixture with the composition of the pyrolysis gas product as a fluidizing agent (REC), and pyrolysis by using the synthetic gas as a fluidizing agent combined with the in situ catalytic cracking of the vapors over γ-alumina (REC_CAT). High-purity γ-Al_2O_3 (Puralox, Sasol Germany GmbH) was selected as a catalyst for the post-treatment of the hot pyrolysis vapors. Prior to its use as a catalyst, γ-Al_2O_3 was activated by ex situ calcination at 600 °C for 3 h and kept in a desiccator before its use in the secondary catalytic fixed-bed reactor. Further details of its characterization can be found in a previous report.[11e] The composition of the synthetic gas mixture that simulated the recirculation of the pyrolysis gas reflected that obtained in previous works,[25] and is shown in Table 14.

Table 14. Composition of the synthetic gas used as a fluidizing agent.

Compound	Content [vol %]
CO_2	47.50
CO	12.35
H_2	22.80
CH_4	6.65
H_2S	3.80
C_2H_4	0.95
C_2H_6	0.95
N_2	5.00

Chemical characterization of the samples

As noted previously, the objective of this work was to assess the presence of valuable chemical products in the pyrolysis liquid from SS. Therefore, it was desired to develop a fractionation method able to separate almost the whole pyrolysis liquid into fractions that could contain potentially valuable chemical products. It was also sought to establish a versatile method that could be applied to the polar AP and to the two nonpolar OPs. Finally, it was considered that the separation of the liquid phases into different fractions would also facilitate subsequent chromatographic analyses.

Fractionation method

As known from previous works,[18g,21] pyrolysis liquid from SS contained a significant fraction of hydrogen- and carbon-rich compounds, such as aliphatic hydrocarbons and steroids, an important proportion of oxygen-containing compounds, such as fatty acids and phenols, and also a significant presence of nitrogen-containing compounds, most of them with a strong basic character, which caused a high pH value of the liquid of around 9 or 10. Taking into account these families of compounds, three different solvents were chosen to develop the extraction method: Hep, DCM, and HCl (1 mol L^{-1}).

An aliquot (≈100 mg) of each phase was weighed and placed in a 13 mL glass vial to which Hep (5 mL) was added. The vial was placed in an ultrasonic bath for 5 min. Then, HCl (5 mL, 1 mol L^{-1}) was added to the vial, which was placed for another 5 min in the ultrasonic bath. Two fractions were obtained: the upper one, which consisted of Hep-sol compounds, and the lower one, which was expected to contain the basic N-containing compounds of the sample solubilized in HCl. From this point, in the same way as previously explained, all extraction steps followed in this procedure were performed by maintaining the samples for 5 min in the ultrasonic bath.

The Hep fraction was separated into another glass vial. This fraction was purified by means of extraction with KOH (5 mL, 1 mol L^{-1}). After that, the remaining Hep fraction was separated and placed in a vial by passing it through a funnel with anhydrous magnesium sulfate to remove traces of water. The KOH fraction was neutralized by adding HCl (10 mL, 1 mol L^{-1}) and the organic compounds it contained were extracted with DCM (5 mL). Finally, the DCM fraction was separated and placed in a vial by passing it through a funnel with anhydrous magnesium sulfate. In this manner, two of the four final fractions were obtained: Hep-sol and DCM-KOH-sol.

Next, the HCl fraction obtained in the first step of this procedure, which remained in the first glass vial in which the sample was placed, was extracted with DCM. Two fractions were obtained and separated: the HCl (HCl-prev) and the DCM (DCM-prev) fractions. To enhance separation, a double extraction was performed by adding DCM (5 mL) to HCl-prev and HCl (5 mL) to DCM-prev. Finally, one DCM and one HCl fraction were obtained in each vial. The two DCM fractions were separated and placed in the same vial by passing them through a funnel with anhydrous magnesium sulfate (DCM-sol). Meanwhile, both HCl fractions were placed in the same vial and neutralized by adding KOH (15 mL) to give the compounds in their original form (neutralized-HCl-sol). The neutralized-HCl-sol fraction was treated by SPE with a Waters cartridge model Oasis HTB. Next, the compounds were eluted from the cartridge with acetonitrile (HCl-SPE). In this manner, the two other fractions in which the liquid was fractionated were obtained: DCM-sol and HCl-SPE. Figure 5 shows the fractionation scheme developed herein. This procedure was used to characterize each of the phases of the pyrolysis liquid.

The results offered by the fractionation method were completed with the water content of the samples determined by Karl-Fisher titration and by the determination of the mass percentage of insoluble compounds in the solvents used. The ammonia content was also determined in the APs by using a volumetric method adapted from APHA standards.[26]

Chemical composition analysis of the Hep-sol and DCM fractions

The chemical composition of the Hep-sol, DCM-KOH-sol, and DCM-sol fractions was analyzed qualitatively and quantitatively by GC-MS (Agilent 7890A) and GC-FID (Agilent 6890A), respectively. A mid-polarity capillary column, Agilent DB17-ms (60 m × 250 μm × 0.25 μm), was used in both chromatographs. A flow of helium at 1 mL min^{-1} (99.999 % purity) was used as a carrier gas. The injector temperature was set at 300 °C. The following temperature program was adopted: oven starting temperature 80 °C held for 5 min, increased to 320 °C at 5 °C min^{-1}, and held for 7 min. The MS detector operated in the full-scan mode between *m/z* 45 and 600 and its working temperature was 320 °C.

In the case of the DCM fractions, derivatization of all samples by means of silylation was performed to identify and quantify some majority compounds, such as fatty acids, through improved chromatographic resolution, as observed in Figure S1 in the Sup-

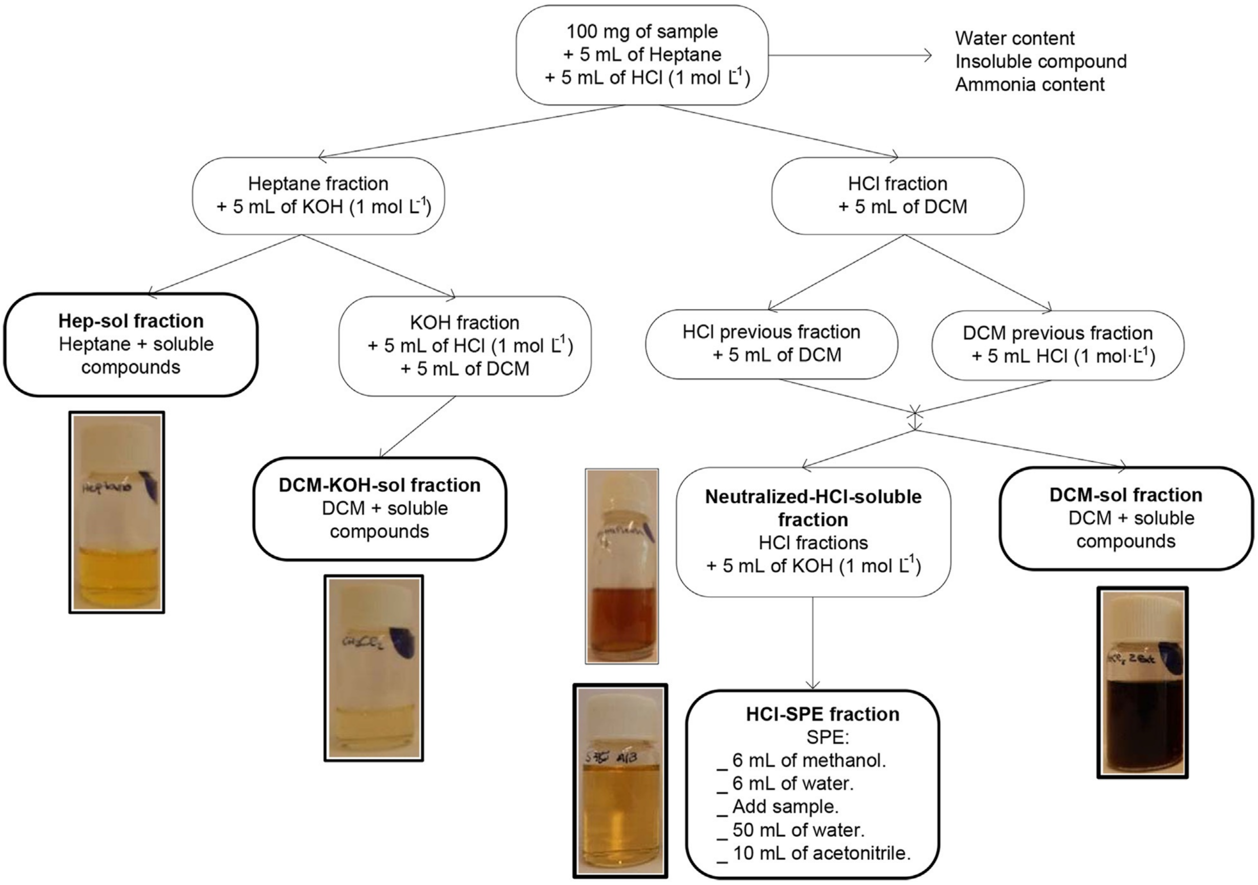

Figure 5. Fractionation scheme developed herein.

porting Information. The silylation reagent used was *N*,*O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) of 99 % purity. The DCM fraction (1.485 mL) and BSTFA (0.2 mL) were added to a 1.5 mL glass vial, which was then heated to 40 °C for 30 min. Identification of the sample compounds was performed by using the automatic search in the NIST library (match probability >80 % for most of the signals).

The compounds identified in the Hep-sol fraction and in the two DCM fractions by GC-MS were identified in the GC-FID chromatogram by calculating the linear retention indexes of each compound in the GC-MS and in the GC-FID. Correspondence of the signals was accepted for linear retention indexes that differed by less than 5 units, and in a few cases by less than 10 units (see Tables S1 and S2 in the Supporting Information). Finally, the compounds present in these three fractions were quantified in the GC-FID by performing specific calibrations with different standards. In the case of the Hep-sol fraction, a calibration curve was created with nine different concentrations of each of the following standards: toluene, *p*-xylene, propylbenzene, indene, benzyl nitrile, naphthalene, benzenepropanenitrile, indole, biphenyl, and phenanthrene. In addition, a calibration curve of six points of diesel was used for the quantification of alkanes and alkenes. For the quantification of the DCM fractions, a calibration was performed with seven different concentrations of each of the following standards: toluene, phenol, 4-methylphenol, 4-ethylphenol, benzyl nitrile, benzylpropanenitrile, indole, and hexadecanoic acid, which were silylated, as explained above. Due to the huge amount of compounds identified in these fractions, it was not possible to obtain and manage standards for all of them. Thus, the response factors of some compounds were considered equal to that of the standard with the most similar chemical structure. Quantification by GC-FID was performed without removing the solvent by evaporation because some compounds of the sample were lost with the solvent, as observed in Figures S2 and S3 in the Supporting Information. The mass proportion of individual compounds in each phase was used to calculate the percentage of samples solubilized in the solvents used (Hep-sol and DCM-KOH-sol + DCM-sol). Moreover, the concentration of each of the compounds determined quantitatively by GC and the yield of the phase obtained in the different experiments were used to calculate the possible production of each chemical over SS fed.

Chemical composition analysis of the HCl-SPE fraction

Basic N-containing species were supposed to be concentrated in the HCl-SPE fraction. However, despite our best efforts, these fractions could not be successfully analyzed by GC-MS. Thus, three strategies were followed: 1) the percentage of HCl-SPE compounds extracted from all phases was determined quantitatively by mass difference after solvent (acetonitrile) evaporation; 2) the composition of the APs was analyzed qualitatively by GC-MS without any fractionation pretreatment because it was thought that these compounds would be most similar to those extracted in the HCl-SPE fraction; and 3) the UPLC-MS-QTOF technique was used to analyze one of the HCl-SPE fractions to check if these phases could contain non-GC-elutable compounds with high molecular weight. Each of these strategies is explained as follows:

1) After the elution of the compounds from the cartridge with acetonitrile, the sample was left in the open air for solvent evaporation and HCl-sol compounds were determined by weight.
2) The composition of the APs was analyzed qualitatively without any fractionation pretreatment by GC-MS (Agilent 7890A). A polar capillary column, HP-FFAP (50 m × 200 μm × 0.3 μm), was used. The carrier gas was 1 mL min^{-1} of helium of 99.999 % purity. The injector temperature was set at 300 °C. The following temperature program was adopted: oven starting temperature 60 °C held for 6 min, increased to 80 °C at a rate of 1.5 °C min^{-1} and held for 5 min, increased to 100 °C at a rate of 3.5 °C min^{-1} and held for 20 min, increased to 200 °C at a rate of 1 °C min^{-1} and held for 5 min, and lastly increased to 240 °C at a rate of 1.8 °C min^{-1} and held for 30 min. The MS detector operated in the full-scan mode between m/z 10 and 500 and its working temperature was 320 °C.
3) As noted above, the chemical composition of the HCl-SPE fraction separated from the HOP N2 was analyzed qualitatively by UPLC-MS-QTOF by the University Analytical Research Group of the Universidad de Zaragoza. A Waters column model Acquity BEH C18 (100 × 2.1 mm and 1.7 μm of particle size) was used in the analyses. The mobile phase was methanol with 0.1 % formic acid (phase A) and water with 0.1 % formic acid (phase B). Chromatography was performed in gradient mode: 30/70 (phase A/phase B) to 100/0 (phase A/phase B) for 9 min. The instrumental parameters were as follows: positive and negative ionization (ESI+ and ESI−), sensitivity mode, capillary at 2.5 kV, sampling cone voltages 30 and 75 V, extraction cone at 4 V, source temperature at 120 °C, desolvation temperature of 450 °C, desolvation gas flow of 700 L h^{-1}. The procedure followed for the identification of the most representative compounds of the sample was performed by using the MassLynx® and MassFragment® software packages. A more detailed explanation can be found elsewhere.[27]

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Keywords: biomass · nitrogen · heterocycles · pyrolysis · renewable resources

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