



Production and separation of value-added compounds from pine wood using pyrolysis and biorefinery techniques

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ARTICLE INFO

Keywords:

Alkaline extraction
Bio-oil
Biorefinery
Two-Stage Pyrolysis
Vacuum distillation
Value-added compounds

ABSTRACT

Value-added compounds were obtained from pine wood bio-oil, converting it into a renewable source for several chemicals: acids (acetic acid), sugars (levoglucosan), furan derivatives (furfural) and phenolics (catechol, phenol, 4-propylguaiaicol, vanillin). To achieve this, firstly a comparison of a direct pyrolysis at 500 °C versus a two-staged pyrolysis (300 °C and 500 °C) was made. It was determined that a two-staged pyrolysis ensue in the obtainment of less complex liquid fractions since it concentrates families of compounds in different phases of bio-oil, facilitating their subsequent separation. Secondly, two methodologies (A and B) were designed to establish a procedure for separating the various chemical groups present in bio-oil. Methodology A consisted of a first vacuum distillation followed by an extraction process that combined an alkaline extraction and a simple extraction with ethyl acetate. Methodology B consisted of a first extraction with triethylamine and ethyl acetate followed by a vacuum distillation and an extraction with hot water. The results showed that methodology A was better for the separation of chemical compounds from bio-oil, obtaining one fraction with the carboxylic acid content and furan derivatives, a second fraction containing the phenolic compounds and a third fraction enriched with the sugar content.

1. Introduction

Given the need in our actual society to substitute the use of fossil fuels, new renewable feedstock and energy sources are being investigated. One promising alternative is bio-oil [1] (BO), a liquid fuel and a chemical raw material derived from the pyrolysis of biomass, which not only poses a green alternative to non-renewable energies, but also raises the possibilities to find organic waste management solutions, making a step forward within the context of circular economy and bioeconomy [2]. Pyrolysis consists of the thermal decomposition of lignocellulosic matter in the absence of oxygen at elevated temperatures (usually between 250 and 700 °C) giving place to three products: BO (liquid phase), char (solid phase) and gas [3]. It can be classified into slow, intermediate or fast pyrolysis, depending on the operating conditions, particularly heating rate and vapor residence time. The heating rate increases from slow to fast pyrolysis, while the vapor residence time decreases, going from seconds for fast pyrolysis to minutes for intermediate and days for slow pyrolysis [4]. Each type offers different product distributions, in decreasing order the BO yield obtained for each one is: fast, intermediate, slow. Intermediate pyrolysis is the one which was used in this study because as opposed to fast pyrolysis, the BO obtained

presents phase separation (aqueous phase (AP) and non-aqueous phase (NAP)) whereas for fast pyrolysis usually only one phase is formed [5,6]. This is important because it facilitates the later separation of compounds. These different pyrolysis modes can be performed in several reactors like a fluidized bed reactor, fixed-bed reactor, ablative, cyclone reactor, etc., being the Auger reactor the best suited one for intermediate pyrolysis [7]. Some authors have studied the influence of performing a two-staged pyrolysis of lignocellulosic biomass instead of direct pyrolysis at only one temperature [8,9]. This operation consists of performing a first torrefaction at lower temperatures, usually at 200–350 °C, followed by a pyrolysis of the char obtained at a higher temperature, usually 500–600 °C. The idea behind this procedure is to concentrate the different families of chemicals in different liquid fractions. In spite of the attractive potential of two-staged pyrolysis (TSP), there are not so many studies related to it. Some authors found that the composition of the bio-oils obtained in this type of procedure were not different enough to consider the process successful [10], on the other side, other authors found that it was possible to obtain wood bio-oils with very different chemical compositions, where the products coming from cellulose and hemicellulose were concentrated in the aqueous fraction, while products coming from lignin degradation were concentrated in

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the organic fraction [8].

The composition of BO depends on the type of biomass used and the pyrolysis conditions (type of reactor, temperature, use of catalysts, etc.), but there are some main organic compounds that are always present in this complex mixture, due to the decomposition of the large polymeric structures of cellulose, hemicellulose and lignin. During the pyrolytic process, the first biopolymers to break into smaller fragments at temperatures around 200–300 °C are cellulose and hemicellulose giving place to anhydrosugars, furans, carboxylic acids and other light oxygenated compounds [11,12]. Lignin exhibits a broader degradation range, between 250 and 500 °C, giving place to aromatic aldehydes, phenols and polyphenols [13–15].

In Table 1, some of the main families of chemicals present in BO are shown, together with the most relevant compounds of each one and their potential application in industry.

BO has a very complex composition. To be able to use it as a source for the obtaining of value-added chemicals the development of a separation system that could be integrated into a biorefinery is needed [26,27]. Several authors have studied the separation of specific compounds from BO with different techniques. One of the most common separation strategies to separate the compounds of BO is liquid-liquid extraction. This comprises different types of extractions, like simple extractions with organic solvents, reactive liquid-liquid extraction, switchable hydrophilicity solvent extraction, etc. [28] Organic solvent extraction is one of the most common strategies. This technique is based on the higher affinity of some compounds towards some solvents, which results in a phase transfer that allows the selective separation of those. The BO compounds that have attracted most of the interest are the phenolics.

To separate the phenolic fraction of BO, several authors have studied liquid-liquid extractions with different organic solvents like toluene [29,30], ethyl acetate [30–32] and dichloromethane [30,33]. Other organic solvents have also been studied like hexane [33], octane and hexadecane [34]. It has been found that the best extraction yields of phenolics are obtained when using polar organic solvents, and the best suited one is ethyl acetate, which is also an environmentally safe solvent compatible for agri-food and nutraceutical uses [35].

To separate phenolic compounds, the use of sodium hydroxide has also been employed by several authors, to make a reactive extraction and obtain phenolates that can be transferred into an aqueous phase [30,36].

Studies to recover the acidic fraction of BO are also present in the current literature. They mainly focus on the recovery of acetic acid, which is the main acid found in BO. Trioctylamine and tridodecylamine have been employed to recover the acidic content from BO via a reactive extraction between the long-chain tertiary amine and the acids [37]. Other strategies have made use of calcium oxide and quaternary ammonium anion-exchange resins to react with the organic acids and separate them from the BO [38].

However, there are not many articles yet in the current literature that describe an integrated methodology that allows the separation not only

of one family of compounds but from several chemical families of compounds from BO. Some authors that have attempted to do it, have made use of sequential organic solvent extraction with water, chloroform and ethyl acetate to separate into different fractions the acidic content, the sugar content and the rest of the compounds (phenolics, alcohols, furan and ketones) [39]. Methods combining organic solvent extraction and multi-step pH adjustments have also been developed to separate the chemical components of BO, obtaining a phenolic fraction and an acid enriched fraction.

Another common technique in the refining industry is distillation, which is one of the most promising separation technologies for BO due to its complex composition, however the thermal instability of BO poses some problems, like coking or polymerization reactions during the distillation process [40,41]. For this reason it is important to perform the distillation in vacuum conditions, to be able to operate at lower temperatures avoiding overheating problems and obtaining higher separation efficiencies [42]. Other studies have also made use of other more complex separation techniques like column chromatography [38], molecular distillation [43], supercritical carbon dioxide extraction [44], polymeric nanofiltration and reverse osmosis membranes [45], etc. Nevertheless, they have found that techniques involving the use of resins and membranes are not suitable for the separation of BO due to the blocking of the pores. On the other side, techniques involving the use of supercritical fluids and molecular distillation are not easily accessible due to their expensiveness.

Contrary to current approaches for bio-oil refining, where usually only one separation technique is used and only one chemical family is separated, the present study presents two new different methodologies that integrate for the first time different techniques: vacuum distillation, liquid-liquid extraction, reactive liquid-liquid extraction with sodium hydroxide and with TOA, allowing the separation of different families of compounds into different fractions, facilitating its refining and use.

The present work was divided in two different parts to achieve the goal of separating value-added compounds from bio-oil. In the first part, two production methodologies were compared: a direct pyrolysis at 500 °C versus a two-staged pyrolysis, where a first pyrolysis at 300 °C was performed followed by a successive pyrolysis at 500 °C of the char obtained. With this staged configuration, it was expected to separate at 300 °C the compounds coming from the degradation of cellulose and hemicellulose and at 500 °C the ones coming from the degradation of lignin [46], achieving this way a first separation step during the production of BO and facilitating the later separation of compounds. In the second part, two methodologies for separating the value-added compounds listed in Table 1 from BO into different fractions were designed, considering the principles of green chemistry and the economic feasibility of the procedures, making the future scaling-up possible. To separate valuable fractions from crude BO several techniques were used, including vacuum distillation [42,47], reactive liquid extractions with sodium hydroxide [30,36] and trioctylamine [37], and simple extractions with water or organic solvents like ethyl acetate [32].

Table 1
Value-added compounds of bio-oil and their importance for industry.

Compound of interest	Application in industry
Carboxylic acids (acetic acid)	Found in great amounts in BO and used in the fabrication of numerous industrial and pharmaceutical products (for example, in the synthesis of vinyl acetate [16], cellulose acetate [17], as a food additive [18], as an antiseptic for medical applications [19], etc.). This renewable source of acetic acid could pose an alternative to the nowadays most common process for its production, the carbonylation of methanol, a procedure that requires the use of fossil fuels, such as natural gas, coal and light products of petroleum [20].
Sugars (levoglucosan)	Levoglucosan is an anhydrosugar present in great amounts with high economic value and with an interest in the chemical and food industries due to their promising applications as a chemical platform [21].
Furan derivatives (furfural)	Furfural is an aromatic aldehyde derived from furan that has a lot of applications for petroleum refining, synthetic resins, furan derivatives production, etc. [22].
Phenolic compounds (4-propylguaiaicol, vanillin, catechol)	Phenolic compounds comprise a wide variety of chemicals: phenol, polyphenols like catechol, methoxyphenols like 4-propylguaiaicol, aromatic aldehydes like vanillin, etc. These compounds have a lot of interest in the cosmetic, pharmaceutical, nutraceutical, chemical and food industries due to their use as antioxidants [23], flavouring and fragrance agents (vanillin) [24], reagents for the synthesis of phenolic resins (phenol) [25], etc.

2. Materials and methods

2.1. Materials

The feedstock used to produce BO was Aleppo Pine wood from Catalan Mediterranean forests. The biomass was ground to 1–2 cm long and 2–3 mm wide to obtain a splinter size that could be fed into the reactor.

All chemicals used in the experiments were commercially available and were used without further purification: Ethyl acetate ($\geq 99.8\%$) and diethyl ether ($\geq 99.5\%$) from Panreac, sodium hydroxide pellets ($\geq 98\%$), hydrochloric acid (37 wt% in H_2O) trifluoroacetic acid ($\geq 99.0\%$), methanol ($\geq 99.8\%$) and trioctylamine ($\geq 92.5\%$) from Sigma Aldrich. Seven external standards, all purchased from Sigma Aldrich, were used for the GC–MS quantification: Acetic Acid ($\geq 99.7\%$), Furfural ($\geq 99\%$), Levoglucosan ($\geq 99\%$), Vanillin ($\geq 99.0\%$), Phenol ($\geq 99.0\%$), Catechol ($\geq 99\%$), and 4-Propylguaiaicol ($\geq 99.0\%$).

2.2. Bio-oil production

Two different types of pyrolysis reactors were used to produce BO: a lab-scale fixed bed reactor with a capacity of 30 g of biomass [48] and a pilot plant with an auger reactor [49] with a capacity of 3 Kg/h for woody biomass [50,51]. With the fixed bed reactor, two different intermediate pyrolysis were carried out, a direct at 500 °C and a TSP (1st step at 300 °C followed by a 2nd step at 500 °C), to compare the chemical composition of the bio-oils obtained. With the auger reactor, only the TSP was performed, because according to previous studies, this is the best configuration for separating the chemical compounds in different fractions [8]. For this reason, the separation procedures explained in the following sections were only performed with the bio-oils obtained from the TSP with the auger reactor. These BOs, because they were produced with an intermediate pyrolysis, showed different phases: one aqueous phase (AP) for the BO obtained at 300 °C and one aqueous phase and a non-aqueous phase (NAP) for the BO obtained at 500 °C.

2.3. Separation procedures

Two different separation procedures were designed for the obtainment of value-added compounds from BO, combining different separation techniques like liquid-liquid extractions, reactive liquid extractions and vacuum distillation. The instrumentation used to perform the extractions was a rotary mixer Model LD 79 from Labinco to shake the solvents and a separating funnel to separate the immiscible phases. The analytical balance used was from Mettler Toledo and the pH meter used was a 716 DMS Titrino with an electrode of LiCl in ethanol. For the vacuum distillation, a fractionating column and a Polytetrafluoroethylene Diaphragm Vacuum Pump from Fisherbrand™ was used and the necessary laboratory glassware.

2.3.1. Methodology A

Separation methodology A can be seen in Fig. 1, where the process followed and the expected compounds to be separated from BO are shown. It involved on one side the distillation of the aqueous phases (AP) in vacuum conditions, with the intention to distillate the carboxylic acids found in bio-oil, which is mainly acetic acid. On the other side the non-aqueous phase of bio-oil (NAP) and the undistilled fraction from the distillation of the bio-oil AP were subjected to an alkaline extraction with an aqueous solution of NaOH 4 M and diethyl ether, followed by an acidification and extraction with ethyl acetate. On the reactive extraction with sodium hydroxide the medium was basic enough ($pH > 12$) to deprotonate the polyphenols which have a pK_a around 10–12 and transfer them to the aqueous phase, separating them from other compounds without acid-base properties, for e.g. naphthalene and benzene derivatives. The following step involved a liquid-liquid extraction with ethyl acetate, followed by an acidification with HCl 4 M to pH 7.0 to protonate the polyphenols and transfer them to the organic phase and

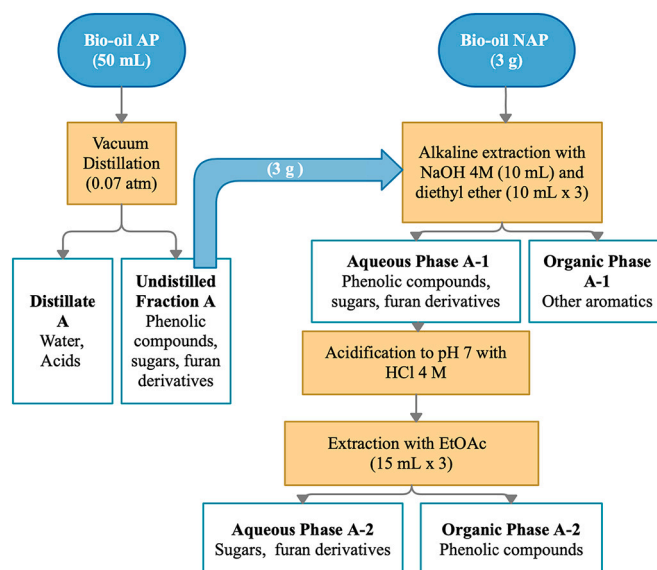


Fig. 1. Separation Methodology A for the aqueous phase (AP) of bio-oil and the non-aqueous phase (NAP) of bio-oil.

maintain the organic acids deprotonated in the aqueous phase (pK_a acetic acid = 4.7). Both organic solvents used in the procedure (diethyl ether and ethyl acetate) can be recovered by distillation.

2.3.2. Methodology B

Methodology B was designed to propose a separation that avoids possible degradation problems of thermally sensitive compounds, for e.g. sugars, that could appear in Methodology A because of the distillation. In this separation process (see Fig. 2) an extraction with trioctylamine (TOA) and ethyl acetate (EtOAc) was carried out, transferring the acid content into the ethyl acetate phase thanks to the formation of an ionic pair [37]. The use of TOA during this extraction is necessary to

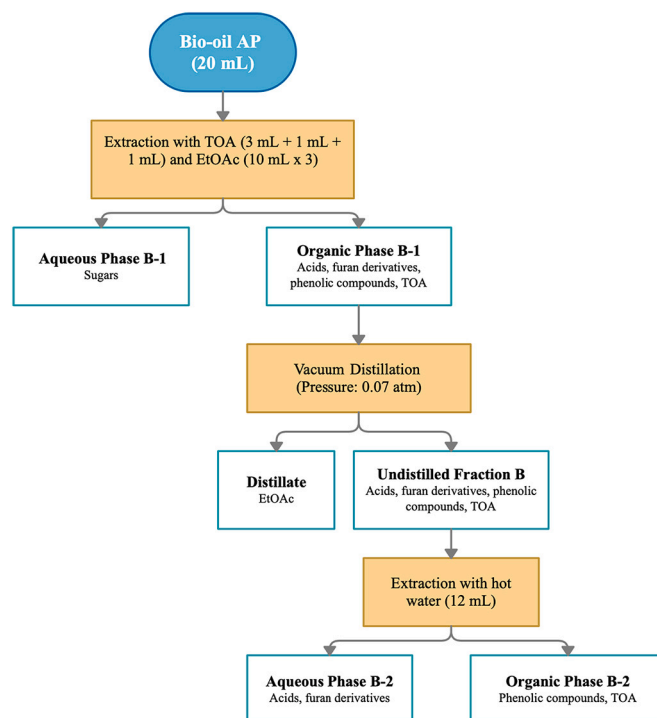


Fig. 2. Separation methodology B for the aqueous phase (AP) of bio-oil.

concentrate the acids, mostly acetic acid, into the organic phase since it is soluble in both water and ethyl acetate. The next step of the procedure was a vacuum distillation to remove the solvent (EtOAc: bp 77 °C at 1 atm; bp 0 °C at 0.07 atm), leaving the remaining fraction still liquid thanks to the presence of TOA which acts as a solvent. Finally, to separate the acids from the phenolic compounds in the undistilled fraction, an extraction with water at 90 °C was performed, breaking the bond between the acid and TOA. This methodology was only conducted with the aqueous phase of the BO obtained in the pyrolysis at 300 °C because it is the fraction with the highest acid content [8,52], therefore it is ideal to evaluate the efficiency of the separation with TOA.

2.4. Analytical methods

2.4.1. Biomass characterisation

The water content of the biomass was analysed with the Moisture Analyzer HB43-S from Mettler Toledo. The elemental composition of the biomass was determined with a Carlo Erba-1108 analyzer. This technique provides the content of C, H, N and S of the sample and it is based on the complete oxidation of the sample at 1000 °C in an atmosphere of pure oxygen and the analysis of the different products resulting from the combustion.

2.4.2. Bio-oil characterisation

2.4.2.1. pH and density. The pH of BO was measured with the pH meter 716 DMS Titrimo using an electrode of LiCl in ethanol, which can be used for a wide range of samples including non-aqueous solutions. The density of bio-oil was measured using an analytical balance from Mettler Toledo and a micro pipette from Labnet.

2.4.2.2. GC-MS analysis. The composition of BO was analysed with GC/MS using standards of acetic acid, furfural, phenol, vanillin, catechol, 4-propylguaiacol and furfural for a quantitative determination. The chromatographic method was adapted from previous experience [53–57]. The instrument used was an HP 6890 Series II GC System Chromatograph with a mass spectrometry electron impact ionization detector HP5973 from Agilent Technologies. The separation was made in a Zebron ZB-5 capillary column (30 m × 0.25 mm × 0.25 µm) from Phenomenex, using Helium as carrier gas, an injector temperature of 300 °C and a maximum column temperature of 360 °C. To analyse with GC-MS the different fractions obtained an acidification to pH 3 was

necessary, in order to have all the species protonated (including acetic acid). The acidification of the aqueous phase was carried out with a solution of HCl 4 M and the acidification of the organic phases of ethyl acetate and diethyl ether was performed with trifluoroacetic acid (TFA). The aqueous phases of bio-oil were injected without previous dilution, but the non-aqueous phases were diluted 1:10 with methanol.

2.4.2.3. HPLC-UV/Vis analysis. Bio-oils were analysed by HPLC coupled to an UV/Vis detector because the heavier compounds present in BO are not detectable with GC-MS [58]. The instrument used was an 1200RR Chromatograph with a DAD detector from Agilent Technologies. The column used was a Luna Omega C18 100A (150 m × 4.6 mm, 5 µm) from Phenomenex, using two mobile phases (0.1% HCOOH in water and CH₃OH). The aqueous phases of bio-oil were injected without previous dilution, but the non-aqueous phases were diluted 1:10 with methanol.

3. Results and discussion

3.1. Biomass characterisation

The water content of the biomass was 7.2 ± 0.3 wt% and the elemental analysis showed that it was composed of 46.3 wt% of carbon, 6.3 wt% of hydrogen (the hydrogen content includes the hydrogen from the water content), 0.2 wt% of nitrogen and 47.2 wt% of oxygen (calculated by difference). Therefore, the results were coherent with the composition of lignocellulosic biomass and the number of elements that could form potentially hazardous compounds during the pyrolysis, like nitrogen [59] or sulphur [60] were not significant.

3.2. Bio-oil characterisation

Bio-oil resulting from intermediate pyrolysis conditions is usually composed of two phases [61], an aqueous phase (AP), that concentrates most of the hydrophilic thermochemical products that mainly come from the degradation of cellulose and hemicellulose, and a non-aqueous phase (NAP), that concentrates most of the hydrophobic compounds derived from the degradation of lignin. The bio-oil obtained, in the first step of the two-staged pyrolysis, at 300 °C only showed one aqueous phase and bio-oils produced at 500 °C exhibited two phases, one aqueous phase (AP) and a non-aqueous phase (NAP), that were easily separated via decantation (see Fig. 3).

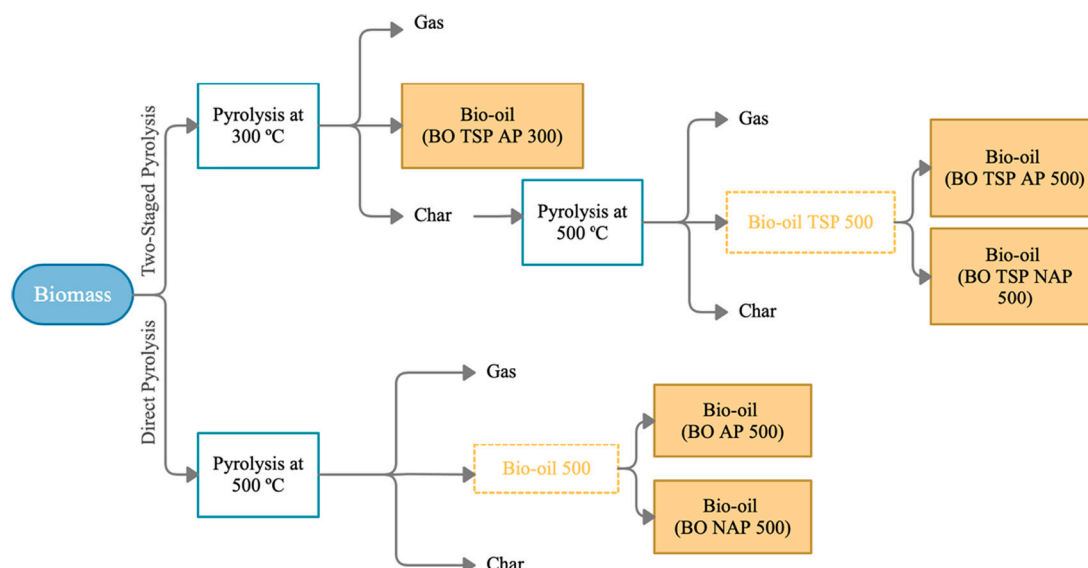


Fig. 3. Bio-oils and phases obtained in the two-staged pyrolysis and in the direct pyrolysis.



Fig. 4. From left to right: BO TSP AP 300, BO TSP AP 500 and BO TSP NAP 500.

All the produced bio-oils were acidic due to the presence of organic acids, especially acetic acid, exhibiting a pH range of 3.2–3.6 and a density range of 1.05–1.06 g/mL for the aqueous phases of BOs and 1.1 g/mL for the non-aqueous phases of BOs.

As it can be observed in Fig. 4, aqueous phases had a brownish colour while non-aqueous phases exhibited a black colour and higher density. Also, the brown colour was lighter for the BO obtained in the TSP at 300 °C and darker for the BOs obtained in the TSP at 500 °C.

The chemical composition of the bio-oils obtained was determined with GC–MS. It was seen that for all the bio-oils, the aqueous phases had a relatively similar composition, exhibiting a high content of acetic acid and levoglucosan. Other compounds that were also found were ketones, like propanone and cyclopentenone derivatives, furan derivatives and aldehydes. Also, phenolic compounds were found in the aqueous phases due to the early degradation of lignin. Nevertheless, these compounds were especially concentrated in the non-aqueous phases, where several benzene, naphthalene and phenol derivatives were found. This coincides with previous literature where the procedures of intermediate pyrolysis are described resulting in the obtainment of an aqueous phase of bio-oil (also called light fraction) that concentrates the light oxygenated compounds and a non-aqueous phase (also called heavy fraction) where phenolic and heavier compounds are concentrated [62].

Table 2

Yields of the bio-oil production. The yields are always referred to initial biomass.

	Yield (wt%)				
	Fixed bed reactor			Auger reactor	
	Direct pyrolysis 500 °C	Two-Staged pyrolysis		Two-Staged pyrolysis	
		1st step 300 °C	2nd step 500 °C	1st step 300 °C	2nd step 500 °C
BO AP	24.2	24.0	17.0	22.5	11.5
BO NAP	3.2	–	4.0	–	2.8
Char	25.2	64.0	25.7	55.2	29.3
Gas	17.8	15.2	17.5	23.2	20.0

3.3. Comparison of bio-oil production methodologies

One of the objectives of this work was to compare two different methodologies for the production of bio-oil regarding the yield and the chemical composition of the fractions obtained. A direct pyrolysis at 500 °C was compared to a more complex procedure, a TSP (first pyrolysis at 300 °C followed by a successive pyrolysis at 500 °C of the char obtained).

3.3.1. Yields

In Table 2 the yields obtained with the different reactors and configurations are depicted. The conversion to BO is quite similar for the three experiments, around 20%, having higher conversion yields in the first step of the TSP and lower yields in the second step.

3.3.2. HPLC-UV/Vis

In Fig. 5 the chromatograms obtained with HPLC-UV/Vis obtained for the bio-oils of the TSP with the auger reactor are depicted. It was seen how BO TSP AP 300 presents most of the peaks in the range of 10–15 min, which belongs to light oxygenated compounds coming from the degradation of cellulose and hemicellulose and some small phenolic compounds coming from the degradation of lignin. On the other side BO TSP NAP 500 mainly presented peaks in the range of 20–25 min, which were not seen in BO TSP AP 300 and correspond to the zone of lignin derived heavier aromatic compounds that are not GC–MS detectable.

3.3.3. GC–MS

The results obtained with GC–MS can be seen on Fig. 6. It was observed that when performing a TSP, the compounds that come from the decomposition of cellulose and hemicellulose (acetic acid, levoglucosan and furfural) are mostly concentrated in the aqueous phases (BO TSP AP 300 and BO TSP AP 500), especially acetic acid and levoglucosan, which are almost not found in BO TSP NAP 500. On the other side compounds that come from the degradation of lignin, like phenol, 4-propylguaiaicol, catechol are mostly concentrated in the fractions obtained in the pyrolysis at 500 °C, especially in the non-aqueous phase (BO TSP

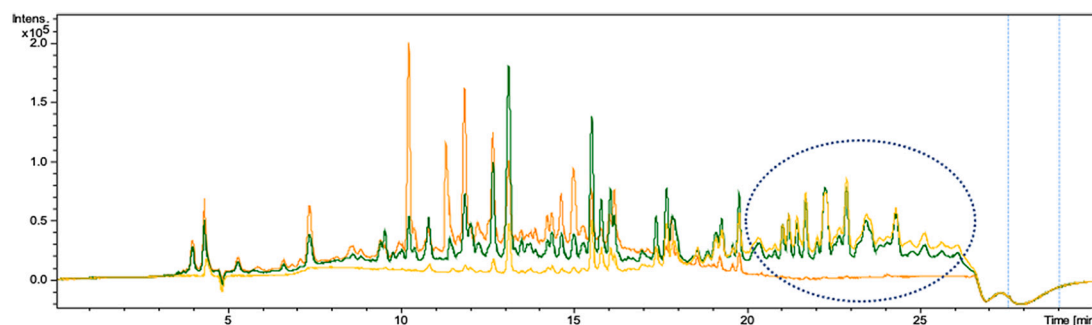


Fig. 5. HPLC-UV/Vis Chromatogram at 190–950 nm of BO TSP AP 300 (orange), BO TSP AP 500 (green) and BO TSP NAP 500 (yellow). All samples were injected directly except for BO TSP NAP 500 which was diluted 1:10. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

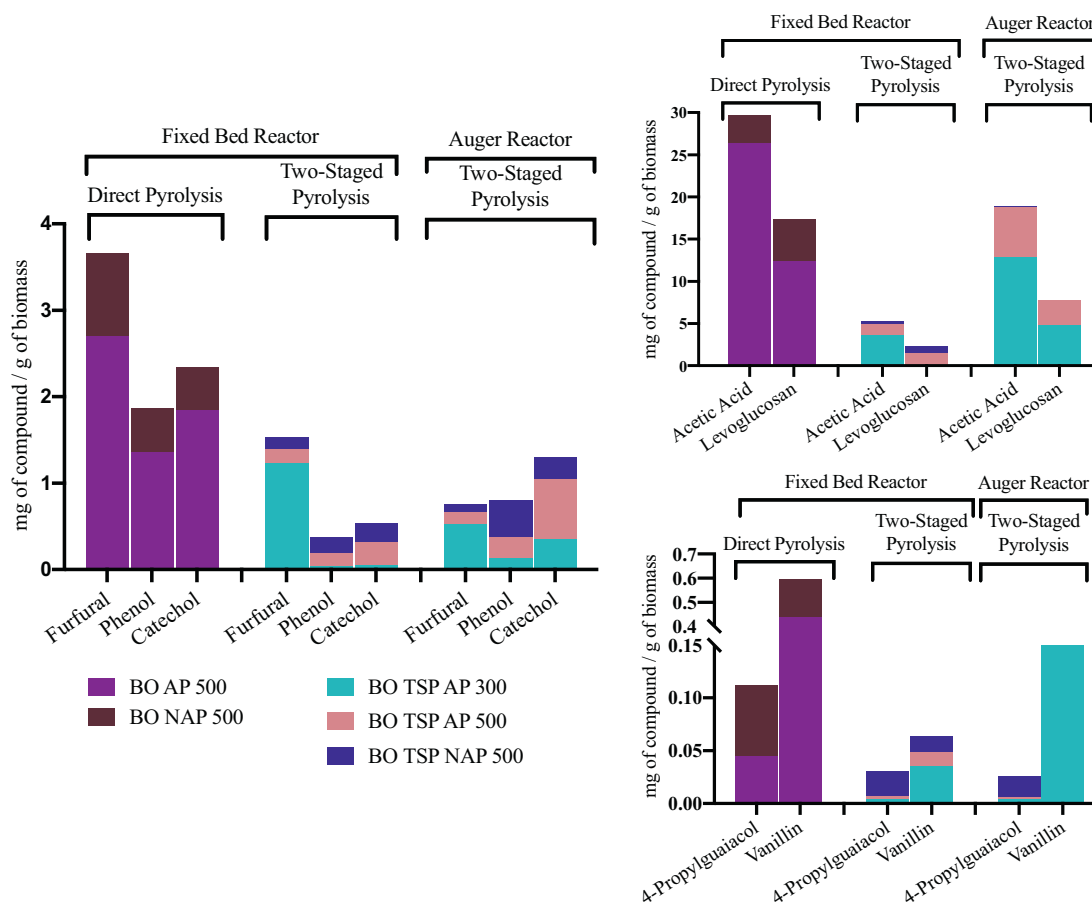


Fig. 6. Mass of compounds obtained with GC-MS for the different bio-oils and phases in the direct and two-staged pyrolysis with the fixed bed and the auger reactor.

NAP 500) except for catechol which is found in a greater amount in the aqueous phase (BO TSP AP 500). Finally, vanillin is only found in the aqueous fraction of the 300 °C pyrolysis since it comes from the degradation of lignin at low temperatures.

When performing a direct pyrolysis at 500 °C, the compounds that come from the degradation of cellulose and hemicellulose (acetic acid, levoglucosan and furfural) even though they are mainly concentrated in the aqueous phase (BO 500 AP) they are also found in smaller amounts in the non-aqueous phase (BO 500 NAP). Compounds that come from the degradation of lignin, like phenol, catechol and vanillin are concentrated in the AP and 4-propylguaiaicol in the NAP.

Comparing the results obtained for the two different processes, it was inferred that a two-staged pyrolysis offers significant advantages in front of a direct pyrolysis regarding the chemical composition of the fractions obtained, despite having lower product yields. Firstly, TSP concentrated almost all the acetic acid, levoglucosan, furfural and vanillin generated during the degradation process in the aqueous phases, making their subsequent separation easier. Secondly, it concentrated most of the phenolic and polyphenolic content in the non-aqueous phase, except for catechol. On the other side, when performing a direct pyrolysis all the compounds were found in both phases (AP and NAP), so no previous separation was achieved.

3.4. Separation methodologies

3.4.1. Separation methodology A

The main objective of the present work was to develop a separation process that allowed the obtainment of value-added compounds from bio-oil (see Table 1). For this reason, two different separation methodologies were designed and evaluated. Methodology A was divided in two

parts: First, a distillation of the aqueous phases of bio-oil (BO TSP AP 300 and BO TSP AP 500) and second, an alkaline extraction, followed by an acidification to pH 7.0 with a final extraction using ethyl acetate. The second part was performed on the non-aqueous phase of bio-oil (BO TSP NAP 500) and on the undistilled fractions of the two aqueous phases. It was expected to distillate the acids (mostly acetic acid) and the water from the BO, since they have the lowest boiling temperatures. Because the chemical composition of the BO TSP AP 300 and BO TSP AP 500 was very similar, the results are only shown for the first one and the results for the second one can be found in the Supporting Information.

The results shown in Fig. 7 demonstrated that when performing a vacuum distillation of the aqueous phases of bio-oil it was possible to obtain almost all the acetic acid in the distillate. Furthermore, it was possible to distil most of the furfural and part of the phenol content. It should be pointed out, that only one distillate fraction was obtained even though a fractionating column was used, so the different compounds of lower boiling temperatures distilled together at 24 °C. It should be also noted that small amounts of 4-propylguaiaicol were also found in the distillate fraction, even though no catechol was found, which has a very similar boiling point. This phenomenon is probably due to the higher interactions of catechol with the matrix because of the presence of one additional OH group in the chemical structure in relation to 4-propylguaiaicol. This could provoke an increase of catechol boiling temperature.

After the distillation of the BO TSP AP 300, the undistilled fraction A was subjected to the extraction procedure as well as the BO TSP NAP 500. It was seen that in the first step of the extraction procedure, where an alkaline extraction with diethyl ether was performed, only the 4-propylguaiaicol was found in small amounts in the Organic Phase A-1 (ether phase). This was probably due to the non-complete deprotonation of the

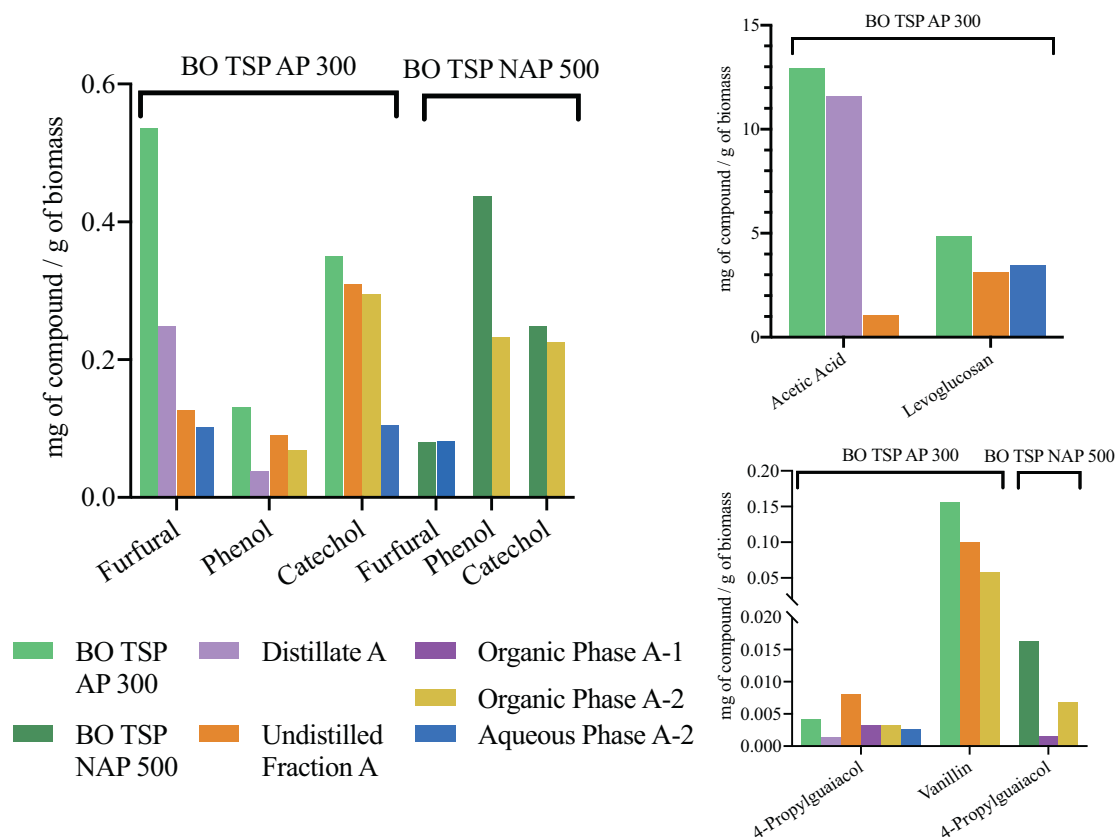


Fig. 7. Distribution of compounds in Methodology A for BO TSP AP 300 and BO TSP NAP 500 (obtained with GC-MS).

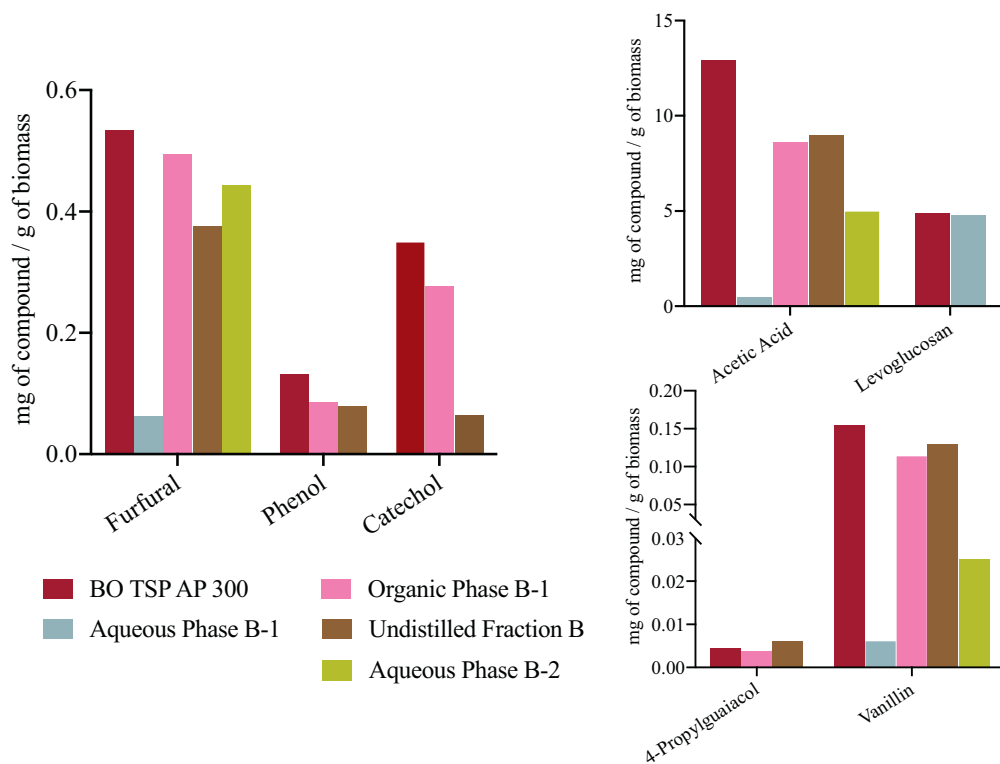


Fig. 8. Distribution of compounds during the extraction process of methodology B for the BO TSP AP 300 (obtained with GC-MS).

phenolic compound and their higher affinity for the organic phase. In the ether phase, the main extracted compounds were benzene, naphthalene, cyclopentene and quinoline derivatives. The results also showed that the phenolic compounds (phenol, catechol, 4-propylguaiaicol and vanillin) were mostly extracted into the Organic Phase A-2 (ethyl acetate phase) as it was expected. Levoglucosan and furfural remained always in the aqueous phases, this was totally expected for the sugar, since the solubility of sugars in organic solvents is very limited. On the other side this was not so predictable for furfural since it is soluble in both ethyl acetate and water.

3.4.2. Separation methodology B

The second separation methodology that was carried out (Methodology B) was mainly focused on the separation of acetic acid and sugars, for this reason it was only applied to the BO TSP 300 AP since it was the bio-oil with a higher content of these compounds.

This methodology offered a contrary approach to the previous one because it involved a first extraction followed by a distillation. The idea behind this procedure was to remove the sugar content from the bio-oil prior to the distillation to avoid the possible degradation of the sugars during the distillation process due to their thermal sensitivity. Since acetic acid is soluble in both water and ethyl acetate, the use of triethylamine (TOA) was needed to extract the acetic acid in the organic phase thanks to the formation of an ionic pair. The results showed in Fig. 8 demonstrated that a first extraction with ethyl acetate and TOA concentrated almost all the acetic acid in Organic Phase B-1 and all the

levoglucosan in Aqueous Phase B-1 successfully. The rest of the components, mainly phenolics, were found mostly in Organic Phase B-1 as it was expected, and only small amounts of furfural and vanillin were found in the Aqueous Phase B-1. The second part of Methodology B involved a vacuum distillation to remove ethyl acetate, which did not distil together with acetic acid as it happened in Methodology A due to the chemical interactions with the TOA. For this reason, a second extraction with hot water was needed to transfer the acetic acid into Aqueous phase B-2. It was seen that most of the acetic acid was extracted into Aqueous phase B-2, but the extraction efficiency could probably be improved with successive extractions. Furfural and vanillin did also transfer to Aqueous phase B-2, leaving phenol, catechol, 4-propylguaiaicol and TOA in Organic phase B-2.

3.4.3. Comparison between separation methodology a and B

The final fractions obtained with each methodology for the different samples (BOs AP and NAP) are summarized in Fig. 9, where the quantities obtained in the different fractions for BO TSP AP 300 and BO TSP NAP 500 are shown. The chemical compounds showed on each fraction are the ones found in greater amounts, but separation processes are never completely efficient, so small amounts of some compounds can be also found in other fractions.

Considering the two studied separation methodologies it could be determined that both exhibited some advantages and disadvantages. On one side, in Methodology A, the distillation in the first step of the procedure could cause the degradation of some compounds of bio-oil due to

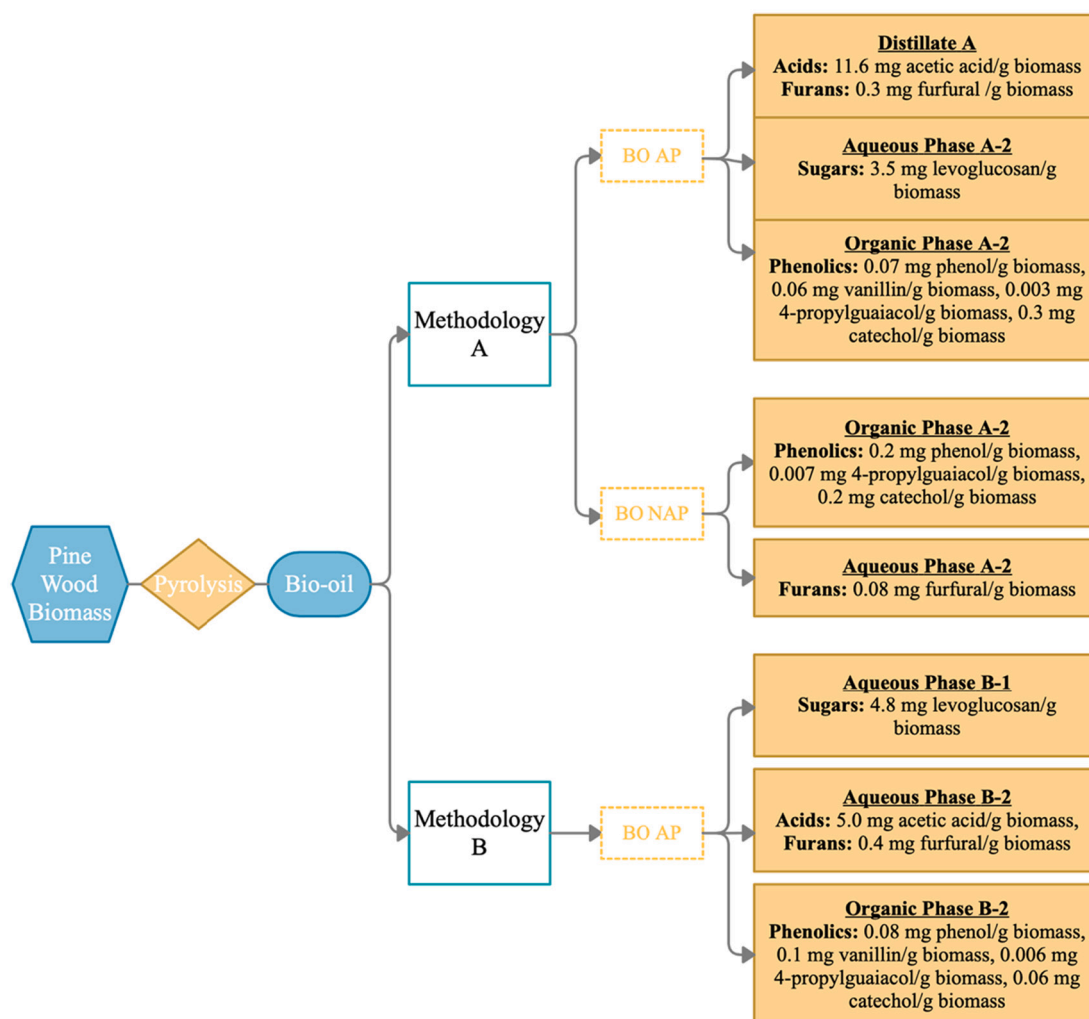


Fig. 9. Final fractions obtained for Methodology A and B. Quantities obtained are shown in mg compound//g biomass for the BO TSP AP 300 and BO TSP NAP 500.

their thermal instability, especially sugars. Also, the need to have to use NaOH and HCl in the procedure introduced an additional number of inorganic ions in the bio-oil that in some cases could pose a problem in its further commercialization as a bioproduct. On the other side Methodology B, posed the challenge of the remaining TOA in the organic phase, which was not possible to remove by means of a distillation because of its high boiling point (365 °C).

Considering the pros and cons of the two studied methodologies, it was concluded that the approach performed in Methodology A offered a more promising groundwork for the separation of value-added compounds from bio-oil. The reason is that it allowed a high recovery of the different compounds in three fractions, one with the acetic acid and the furfural, another with the sugars and a third one with the phenolic content. It also allowed the recovery of the solvents used via distillation and no degradation of the sugars was observed thanks to the use of vacuum conditions.

4. Conclusions

In this work it determined that a two-staged pyrolysis at 300 °C and 500 °C provides less chemically complex liquid fractions (bio-oil) than a direct pyrolysis at 500 °C, making their subsequent separation easier. It was also possible to develop a process (Methodology A) for the separation of value-added compounds from bio-oil, such as phenolics (vanillin, phenol, 4-propylguaiaicol, catechol), furan derivatives (furfural), sugars (levoglucosan) and acids (acetic acid) resulting in the obtainment of three different fractions, one with the acids and furan derivatives, another with the sugars and a third one with the phenolic content. To conclude, in this work, an innovative combination of several separation techniques is proposed, resulting in the obtainment of a biorefinery system that allows the obtainment of fine chemicals from a renewable feedstock. The technologies used for the procedure are also chosen considering sustainability criteria, for this reason distillations are included, and the solvents used are environmentally safe and compatible for agri-food and nutraceutical uses. All this affects directly to the future development of biorefineries, making possible the obtainment of chemical products from biomass, therefore, contributing to circular economy and bioeconomy.

CRedit authorship contribution statement

Mireia Mora: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft. **Esteve Fàbregas:** Writing – review & editing, Supervision. **Francisco Céspedes:** Writing – review & editing, Supervision. **Jordi Bartrolí:** Supervision. **Neus Puy:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was elaborated with the collaboration of the Environmental Research Group from Instituto de Carboquímica, CSIC, Zaragoza, which made possible the production of bio-oils. We would also like to acknowledge the financial support of the LIFE Programme of the European Union for the project LIFE BIOEFFORMED (LIFE 19 ENV/ES/000544) and the support of the MINECO for the project PID2020-

117216RB-100 and the Group of Sensors and Biosensors of the Universitat Autònoma de Barcelona.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuproc.2022.107509>.

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