



Research Paper

Dialysis and column chromatography for biomass pyrolysis liquids separation

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ABSTRACT

In the current study, a novel approach for separating value-added chemicals from pine wood residues' pyrolysis liquids (bio-oil) was effectively carried out. It combined two separation techniques used for the first time in this field: dialysis with water, methanol and acetone, and column chromatography with Amberlite™ XAD7 resin. This strategy made it possible to separate bio-oil into four fractions: (1) pyrolytic lignin, which can be utilized in the synthesis of resins, foams, electrodes, asphalt, etc. (2) acid-rich fraction, with particular relevance to the chemical industry, (3) antioxidant fraction, containing phenolic compounds, with a lot of interest for pharmaceutical and nutraceutical industry, and (4) a final fraction containing the most non-polar chemicals from bio-oil. Thus, it was possible to develop a process that allows the obtention of bioproducts from woody biomass, a residue obtained in significant quantities in the management of non-profitable forests, making a step forward within the context of circular economy and bioeconomy.

1. Introduction

Lignocellulosic biomass residues are obtained in big amounts in the management of forests (Sultana and Kumar, 2011). They offer a promising platform for the obtention of fine chemicals but its intrinsic recalcitrant nature and resistance to degradation make it a difficult feedstock to work with. In this context, different thermochemical treatments have been developed for processing lignocellulosic biomass like combustion, gasification, pyrolysis and liquefaction (Bédué, 2013). One of the most efficient and promising treatments is pyrolysis, a highly efficient process with good environmental performance characteristics (Tang et al., 2022; Xia et al., 2023). There are different types of pyrolysis, depending on the operation conditions, which can be classified into: slow, intermediate and fast. In Spain, pyrolysis is used in industries mainly for tyre recycling and urban waste management, but not much attention has been given to woody biomass pyrolysis (Anthony, 2022; Bioenergy International, 2020). Some of the main advantages of pyrolysis are its capacity to enhance energy density and chemical variety of the initial feedstock reducing transport and handling costs at a relatively low cost and with the possibility of performing it in remote locations (Puy et al., 2011; Zafar, 2021). It consists of the thermal decomposition of matter in the absence of oxygen at high temperatures, around 500 °C,

and at lower temperatures, around 200–300 °C it is called torrefaction (Moldoveanu, 2021). Three products are obtained during the pyrolysis of wood: bio-oil (BO) (liquid fraction), char (solid fraction) and gas, mainly composed of CO₂, CO, H₂ and CH₄ (Costa et al., 2022). The ratio of BO:char:gas obtained, depends on the feedstock, type of reactor and the conditions used, like temperature, heating rate, pressure, etc. (Bédué, 2013). Char, also called biochar, is a highly carbonized solid residue with a porous structure obtained (Wang et al., 2022). It can be used as a fuel for energy production or a functional material for soil amendments, carbon fertilizers to improve the water retention of the soil, CO₂ capture, water purification, etc. (Güleç et al., 2022) BO is formed by the condensable gases produced during the pyrolysis process and it contains water (usually between 15 and 30 wt%), oxygenated aliphatic and aromatic compounds (Yin et al., 2013). Its appearance is a dark brown, viscous liquid with a barbecue smell. It is the chemically richest fraction obtained and it contains a great variety of value-added chemicals that can be isolated with biorefinery techniques and integrated into the economy, promoting a bio and circular economy. The main applications of pyrolysis liquids have been as a liquid fuel to substitute fuel oil or to produce commodity chemicals (Bridgwater et al., 1999). However, bio-oil cannot be used directly as a fuel due to its chemical instability and acidity and hydrotreatment is necessary (Han et al., 2019). BO contains

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between hundreds to thousands of compounds coming from the depolymerization of woody biomass building blocks: hemicellulose, cellulose and lignin (see Fig. 1) (Han et al., 2019; Vispute, 2011). The main monomeric products obtained from the degradation of the first two biopolymers are water and light-oxygenated compounds such as carboxylic acids, ketones, alcohols, furan derivatives, cyclopentenones, simple sugars, etc. These chemicals can be used as platform molecules in the chemical industry (Itabaiana Junior et al., 2020; Shrotri et al., 2017), as food additives for food industries and in pharmaceutical industries (Ryssel et al., 2009).

Also, oligomeric products are obtained, forming a water-soluble heavy fraction of bio-oil difficult to characterise (Rover et al., 2014; Wang et al., 2015). It mainly contains anhydrosugars from cellulose

depolymerization reactions like levoglucosan, levoglucosenone, cello-biosan, oligomeric hybrids from the combination of cellulose and lignin degradation products and other species difficult to identify (Han et al., 2019; Stankovikj et al., 2017). The degradation of lignin gives place to aromatic compounds such as phenols, polyphenols, phenoxy species, benzene, benzene derivatives, etc. (Anca-Couce, 2016; Wang et al., 2021a). These chemicals have attracted great interest in pharmaceutical and nutraceutical industries thanks to their antioxidant properties, which can act against free radicals, protecting the body against oxidative stress (Rice-Evans et al., 1997). Some of them can also be used for flavouring and fragrances (Fache et al., 2016) and for the synthesis of phenol-formaldehyde resins (Gardziella and Mueller, 1990). Apart from this monomeric species, an important oligomeric fraction is obtained,

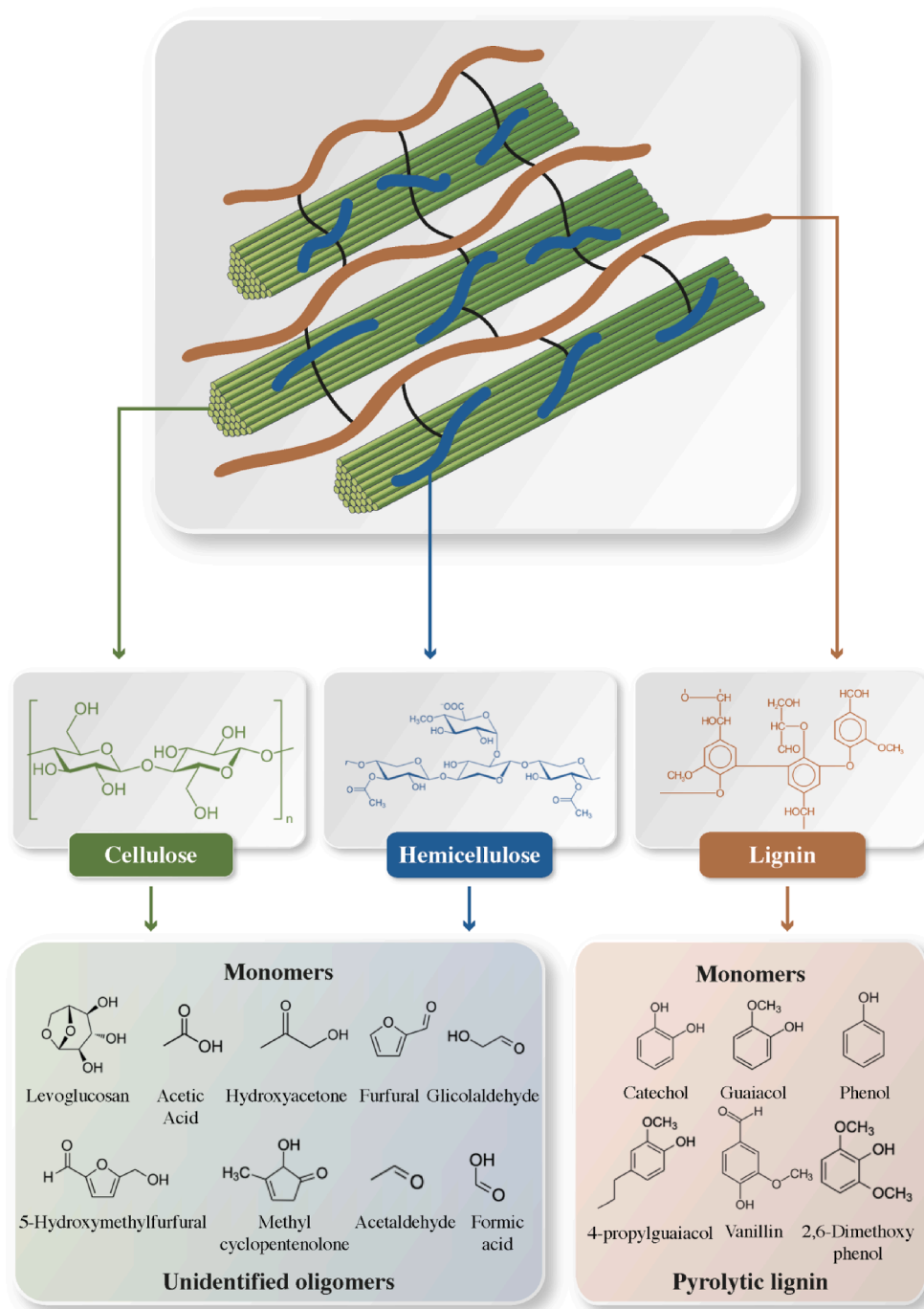


Fig. 1. Major typical components of BO from the pyrolysis of lignocellulosic biomass.

also called pyrolytic lignin (PL) (Charon et al., 2015). PL is formed by lignin oligomers with relatively high molecular weight, and it can make up to 40 wt% of BO (Xu and Ferdosian, 2017). It is insoluble in water, viscous and reactive, causing instability problems in bio-oil (Matos et al., 2021). Thus, it is necessary to remove it from BO. Nevertheless, PL should not be considered as a residue, because it has a lot of potential applications in diverse fields: as a fuel, in the synthesis of resins, such as phenol–formaldehyde resins, epoxy resins, in the synthesis of polyurethane foams (Figueirêdo et al., 2022), as a pitch for asphalt or electrodes, etc. (Zhang et al., 2021).

Therefore, BO coming from wood pyrolysis is a complex liquid fraction in kinetic equilibrium formed by a continuous aqueous phase containing monomeric species and water-soluble oligomers and a discontinuous phase containing the water-insoluble oligomers (PL) (Mohan et al., 2006).

It is of vital importance to create a methodology integrating refining techniques to separate high-value chemicals from BO, achieving the obtention of bioproducts from a renewable source: woody biomass, and diminishing the current dependence on fossil fuels (Cherubini, 2010). With this purpose in mind, diverse authors have attempted to create a separation process of bio-oil, focusing usually on one type of chemical family. The most common technique used is liquid–liquid extraction with organic solvents or basic aqueous solutions to extract phenolic compounds from BO (del Pozo et al., 2018; Mantilla et al., 2015; Wei et al., 2014). The use of supercritical solvents like CO₂, ionic liquids and deep eutectic solvents has also been described by several authors to extract phenolics. Nevertheless, the economic costs of these techniques difficult their implementation (Cesari et al., 2019; Maqbool et al., 2017; Yao et al., 2018). Distillation is another technique that has been proposed in different articles, but the thermal instability of BO limits its application and forces the use of reduced pressure conditions either with vacuum distillation or with molecular distillation (Mora et al., 2022; Nam et al., 2016; Wang et al., 2021b; Wang et al., 2009; Zheng and Wei, 2011). Distillation procedures usually focus on the obtention of low molecular weight compounds from BO in the distilled fraction, such as small carboxylic acids, ketones, furans and some phenols (Wang et al., 2009). Column chromatography is another technique that some authors have used to tackle the problem. They have usually made use of silica gel or alumina as stationary phases and organic solvents like ethyl acetate, cyclohexane or ethanol for the mobile phase (Han et al., 2021; Zeng et al., 2011). It has proved useful for relatively simple samples where compounds are separated according to their polarity. Nevertheless, it is not well suited for complex bio-oils, because it cannot offer an efficient separation due to the high number of different compounds present in the sample and the resin can be altered. There exist other techniques to separate complex mixtures that have not been described yet for the separation of BO. One of them is dialysis, which is based on the separation of molecules according to their molecular weight through a semipermeable membrane, made of cellulose, modified cellulose or a synthetic polymer, with a particular porous size (Ninfa et al., 2009). The compounds diffuse from the original sample (concentrated solution) to a lower-concentrated solution, the dialysate. It is typically used in biochemistry to separate large macromolecules like proteins, DNA and polysaccharides from other small molecules such as salts, dyes, etc. (Berg, 2007) It can also be used for separating colloidal solutions, where particles of colloidal size are dispersed in a continuous phase of different composition, allowing the obtention of a colloid-free solution (Everett, 1972). This is the case of BO, which can be conceived as a colloidal solution. In this way, dialysis offers a promising and unique type of separation in BO, that cannot be achieved with other techniques.

In this work the use of separation techniques like dialysis and column chromatography are proposed to separate high-value compounds from BO, focusing especially on monomeric compounds, coming either from the degradation of lignin, cellulose and hemicellulose, and PL. The process consists of first dialysis of BO, where small chemicals are separated from the larger oligomeric fractions like water-soluble oligomers

and PL. The second part consists of a separation with column chromatography using a different strategy than the common ones, where the stationary phase is usually silica gel or alumina. In this work, Amberlite™ XAD7 resin is used. This resin has been typically used for the fractionation of fulvic acids (Bellera et al., 2015; Lopez-Sangil and Rovira, 2013), which are organic acids with a phenolic structure that come from the humic fraction of soil. Amberlite™ XAD7 resin has a macroreticular structure and is composed of a non-ionic aliphatic acrylic polymer (Zimehl et al., 1996). When protonated it has the capability of adsorbing non-polar and slightly polar compounds which can be later eluted when a basic solution of NaOH is passed through de resin. Therefore, this resin has the ability to separate bio-oil into different fractions with different chemical compositions, allowing the separation not only of one type of chemical component but of chemical families. With this methodology, it was expected to separate several families of value-added chemicals from bio-oil with the minimum use of reagents and the minimum alterations to the resin thanks to the previous dialysis step.

2. Materials and methods

2.1. Materials

2.1.1. Bio-oils

The bio-oils used were produced elsewhere from Aleppo Pine wood from Catalan Mediterranean forests (Mora et al., 2022). Two-staged pyrolysis (TSP) was used to produce bio-oil because it was established in previous articles that it results in the obtainment of less chemically complex bio-oils (Hernando et al., 2021; Mora et al., 2022). The two temperatures used in the TSP for the BO production were 300 and 500 °C, resulting in the obtention of three different fractions of bio-oil (Mora et al., 2022):

(1) Aqueous phase (AP) bio-oil obtained at 300 °C, also called BO TSP AP 300. (2) Aqueous phase bio-oil obtained at 500 °C, also called BO TSP AP 500. These two bio-oils concentrated most of the compounds coming from the degradation of cellulose and hemicellulose, like acetic acid, furan derivatives, sugars, alcohols, ketones, etc. (3) Non-aqueous phase (NAP) bio-oil obtained at 500 °C, also called BO TSP NAP 500. This bio-oil was composed mainly of lignin decomposition products such as phenols, polyphenols, benzene derivatives, naphthalene derivatives, etc. These three bio-oils were the ones used for the elaboration of this article.

2.1.2. Reagents

To perform the dialysis of BO, the dialysis membrane used was Spectra/Por™ 3 with a MWCO of 3500 Da from the brand Spectrum™. The resin used in the column chromatography was Amberlite® XAD7 from Sigma Aldrich. All chemicals used in the experiments were commercially available from Sigma Aldrich and were used without further purification: Methanol (≥99.8 %), Acetone (≥99.5 %), Sodium hydroxide pellets (≥98%), Hydrochloric acid (37 wt% in H₂O) and H₃PO₄ (≥85 %). Seven external standards, all purchased from Sigma Aldrich, were used for the GC–MS quantification: Acetic Acid (≥99.7 %), Furfural (≥99 %), Levoglucosan (≥99 %), Vanillin (≥99.0 %), Phenol (≥99.0 %), Catechol (≥99 %), and 4-Propylguaiaicol (≥99.0 %).

2.2. Dialysis and column chromatography

The strategy for the separation of chemical compounds from BO consisted of first dialysis followed by column chromatography of the dialyzed liquid.

BO was placed inside a dialysis bag of 13 cm × 5 cm and it was submerged in the solvent for 24 h, which was agitated with a stirring magnet (see Fig. 2). BO AP 300 and BO AP 500 20 were placed directly into the bag and BO NAP 500 was diluted 1:4 with acetone and placed inside the bag.

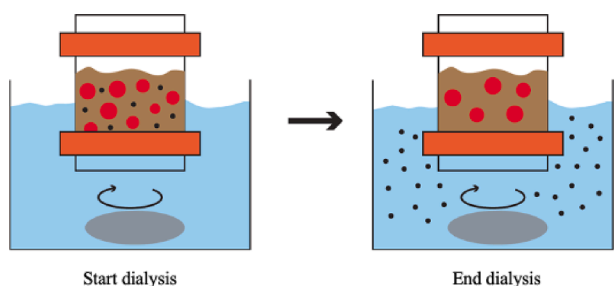


Fig. 2. Dialysis bag technique: Small molecules diffuse outside the dialysis bag through the semi-permeable membrane while colloids and macromolecules remain inside.

To perform the dialysis on BO different solvents were used: water and methanol (MeOH) for BO AP 300 and BO AP 500, and water and acetone for BO NAP 500. In Fig. 3a, the dialysis strategy used for the sample of BO AP 300 is shown. The first dialysis with water was performed, where the water was changed thrice. The first two aqueous solutions (AQS) obtained were mixed, resulting in the solution called AQS1_AP300, and the third one, AQS2_AP300, was analysed separately. Then the solvent for dialysis was changed to methanol and the solution obtained was called MES_AP300. For BO AP 500 the dialysis strategy was very similar to BO AP 300 (see Fig. 3b) but the dialysis water was only changed twice, because it was observed that it was enough, and the AQS were mixed to form AQS1_AP500. Then the solvent for dialysis was changed to methanol and the solution obtained was called MES_AP500. Finally for BO NAP 500 the procedure performed was a bit different (see

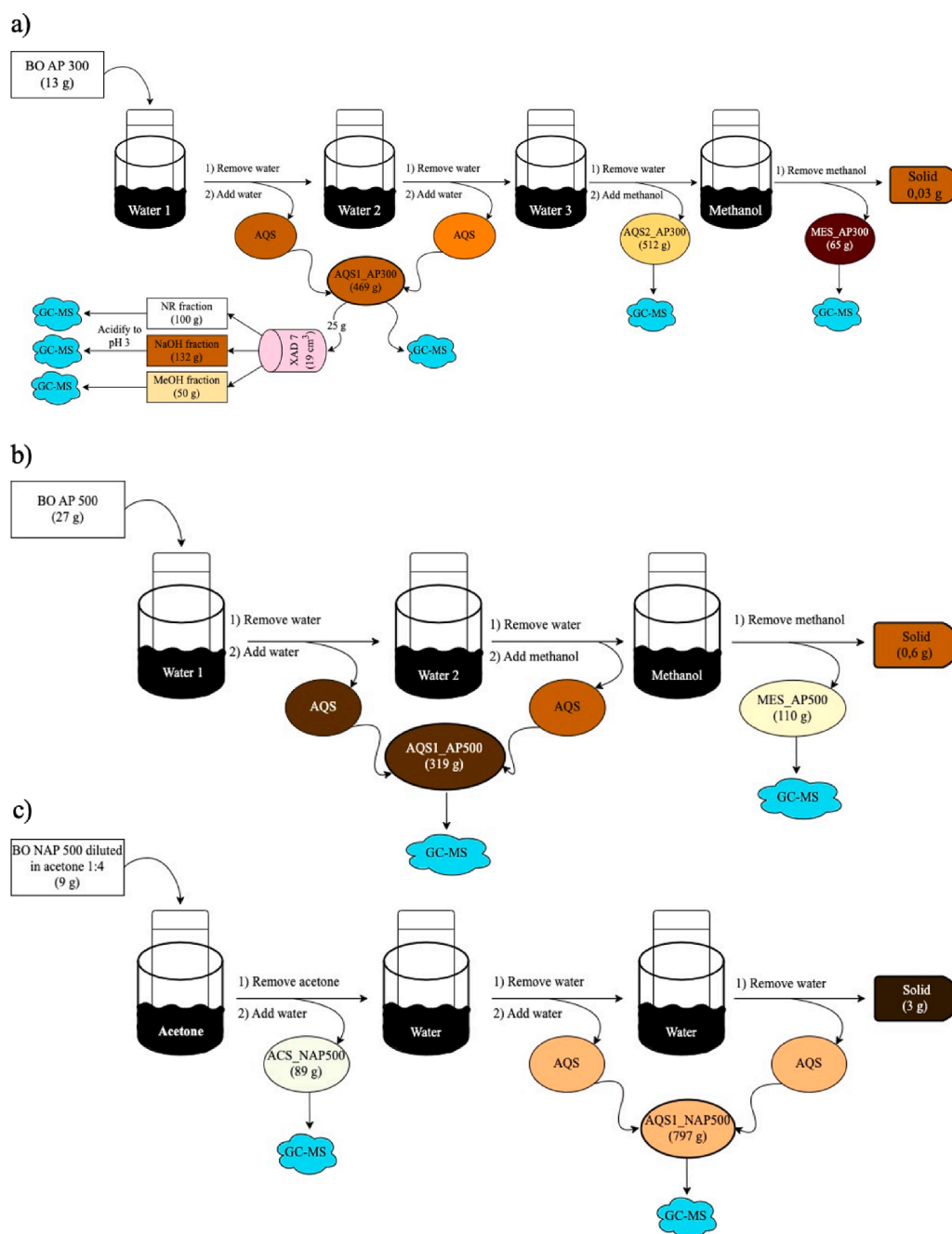


Fig. 3. Separation methodologies using dialysis and column chromatography for (a) BO AP 300 (b) BO AP 500 (c) BO NAP 500. The colours used for labelling the solutions represent their real colour.

Fig. 3c). Because of the high viscosity of BO NAP 500 it was necessary to perform a dilution 1:4 with acetone before placing it inside the dialysis bag. The first solvent used to dialyze was acetone, and the resulting solution was called ACS_NAP 500. Finally, two more dialysis steps with water were performed and the AQS were mixed to form AQS1_NAP500.

AQS1_AP300 was further separated with Amberlite™ XAD7 resin using column chromatography separation (see Fig. 3a). A 2 cm diameter column was filled to a height of 6 cm with the hydrated resin, so the volume of XAD7 used was 19 cm³. The procedure for separating into different fractions the dialyzed liquid with the resin XAD7 was the following: (1) Cleaning of the resin with NaOH 0,1 M, water and HCl 0,1 M; (2) Sample aliquot was passed through the column and distilled water was added to ensure all the compounds that were not retained in the column were eluted, the collected liquid was called the non-retained fraction (NR fraction); (3) NaOH 0,1 M was added to elute part of the retained compounds in the resin and in the end distilled water was added to make sure the column was free from NaOH, the collected liquid was called the NaOH fraction; (4) Methanol was added to elute compounds that were retained in the column but not eluted with NaOH, the collected liquid was called the MeOH fraction.

2.3. Analytical methods

2.3.1. pH

The pH of the bio-oils was measured with the pH meter HI9124N using the electrode HI1049B for non-aqueous solutions from Hanna Instruments.

2.3.2. GC–MS analysis

The composition of BO was analysed with GC/MS using standards of acetic acid, furfural, phenol, vanillin, catechol, 4-propylguaiaicol and furfural for a quantitative determination. The chromatographic method was adapted from previous experience (Artigues et al., 2014; del Pozo et al., 2021a, 2021b, 2020, 2018; Mora et al., 2022). 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 the 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 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 H₃PO₄. The aqueous phases of bio-oil were injected without previous dilution, but the non-aqueous phases were diluted 1:18 with acetone.

2.3.3. Ft-IR

The solid obtained in the separation with dialysis was characterized with the FT-IR spectrometer Bruker Tensor 27 IR. It has a spectral range of 7,500 to 370 cm⁻¹ with standard KBr beam splitter and a resolution better than 1 cm⁻¹. Spectra were recorded with the Attenuated Total Reflectance (ATR) mode.

3. Results and discussion

3.1. Dialysis

3.1.1. General characterisation

When dialysis was performed on the three samples of BO, the aqueous solutions obtained had an acid pH of around 3. This was due to the presence of acetic acid in BO, a small molecule that diffuses outside the dialysis membrane. For BO AP 300 and BO AP 500 the first aqueous solution obtained had a brownish colour due to the presence of phenolic compounds that diffuse through the semipermeable membrane outside of the dialysis bag (see Fig. 7a). In both cases, the second solution had a lighter colour because most of the compounds were already obtained in

the first fraction. It was observed that almost no colouration was obtained in the third dialysis with water for BO AP 300 (AQS2_AP300), for this reason when dialysis of the BO AP 500 was performed, the third change of the dialysis water was eliminated.

Dialysis of BO NAP 500 was performed under a slightly different approach since the solvent used was first acetone and second water. To the naked eye, no apparent diffusion of BO was observed with acetone, because the solution remained colourless. On the other side, in the following dialysis with water, the aqueous phase obtained did have a brown colour, coming from the transfer of phenolic compounds.

After dialysis was finished a solid fraction remained inside the dialysis bag, which is mainly constituted of PL. The solid obtained was brown, and the amounts obtained were the following ones: 2.15 mg solid/g BO AP 300, 20.40 mg solid/g BO AP 500 and 323.56 mg solid/g BO NAP 500. It was observed that a higher amount of PL was obtained at 500 °C than at 300 °C, that is because the lignin polymer decomposes at higher temperatures than cellulose (Wang et al., 2021a).

3.1.2. GC–MS

3.1.2.1. BO AP 300 and BO AP 500. In Fig. 4a) the comparison of the GC–MS spectra of AQS1_AP300 and AQS2_AP300 is shown. It is observed that almost no compounds are obtained in the second solution, for this reason, in the following dialysis procedures with BO AP 500 and BO NAP 500 the third water addition which gives place to AQS2_AP300 is not performed. The principal compounds that are found in AQS1_AP 300 are carboxylic acids (acetic acid, formic acid, etc.), ketones (mainly hydroxyacetone), alcohols (e.g. 1-propanol), furan derivatives (furfural, 5-hydroxymethylfurfural, etc.), phenolic compounds (phenol, methoxyphenols, methyl and ethyl phenols, etc.), quinolines (e.g. 2,4-dimethylquinoline) and sugars (mainly levoglucosan, anhydro-mannosan).

In Fig. 4b) the spectra of MES AP300 can be seen. The abundance of the peaks is much lower than for AQS1_AP300 but different compounds non-polar compounds are observed because they have a greater affinity for methanol than for water. Some of these chemicals are benzene, ethyl benzenes, methyl benzenes, phenolics like some ethyl methyl phenols, naphthalenes, anthracenes, long-chain alkanes like eicosane, etc.

A semi-quantitative analysis was also performed with seven external standards (see Fig. 5). These standard chemicals used are some of the most interesting of BO due to the high amounts present in bio-oil and their relevance for chemical, pharmaceutical and nutraceutical industries.

For BO AP 300, the results showed that six out of seven compounds analysed, acetic acid, furfural, phenol, catechol, 4-propylguaiaicol and vanillin, were mostly found in AQS1_AP300, therefore it would only be necessary to perform a two-step dialysis with water since almost no amount was found neither in AQS2_AP300 or MES AP300. Levoglucosan was not found in great amounts in AQS1_AP300 nor in the other fractions. Since its size is small enough to cross the dialysis membrane, this indicates that it probably forms interactions with water-soluble oligomers preventing it from diffusing outside of the dialysis bag (Han et al., 2019).

The results obtained for BO AP 500 were very similar to BO AP 300. In Fig. 5, the results from the semi-quantitative analysis with GC–MS are depicted. All compounds were mostly obtained in AQS1_AP500, even though 4-propylguaiaicol, which is the less polar compound of the studied ones, was found in important amounts in MES AP500.

3.1.2.2. Bo NAP 500. On the GC–MS spectra of the acetone fraction ACS_NAP 500 it was seen that some compounds did cross the dialysis membrane outside of the bag, especially compounds like benzene, methyl benzenes, ethyl benzenes, styrene, naphthalene derivatives, phenanthrene derivatives, etc. Nevertheless, the most interesting compounds from bio-oil were found in the aqueous phase AQS1_NAP500. This was also observed in Fig. 5 where it was seen that the target

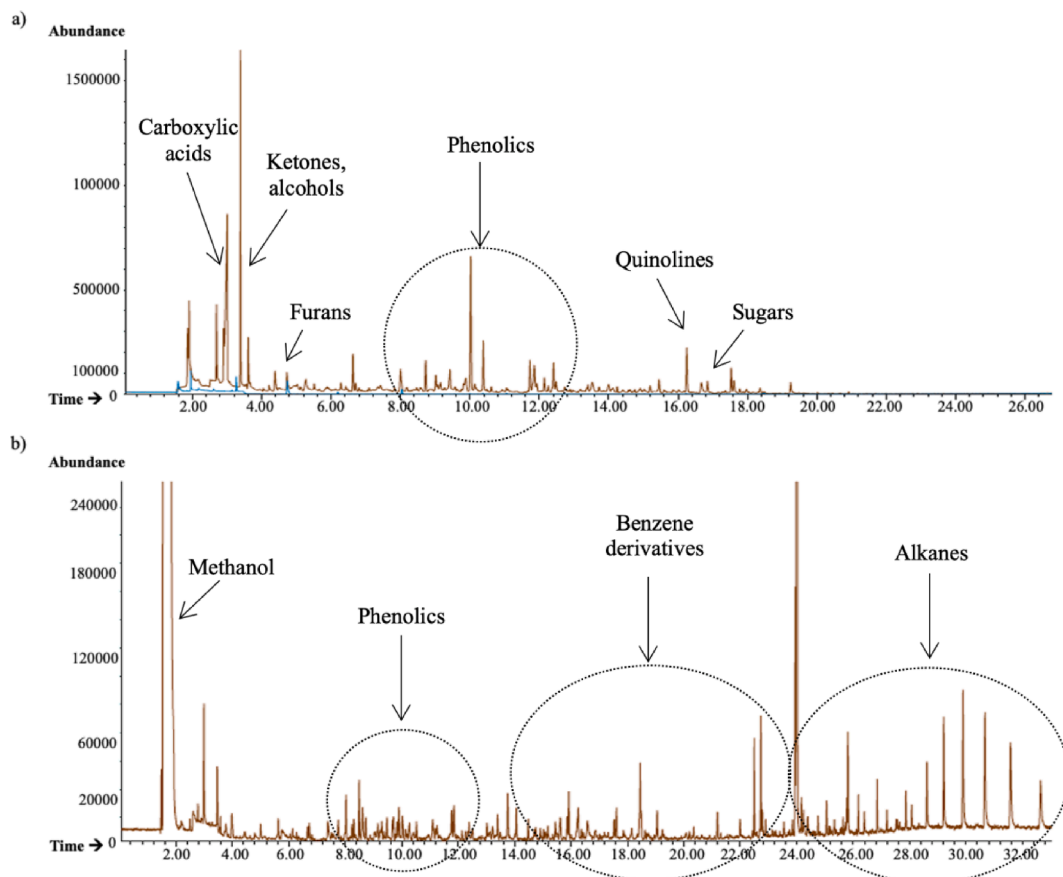


Fig. 4. (A) comparison of the gc-MS spectra of AQS1_AP300 (brown color) and AQS2_AP300 (blue color). (b) GC-MS spectra of MES_AP300.

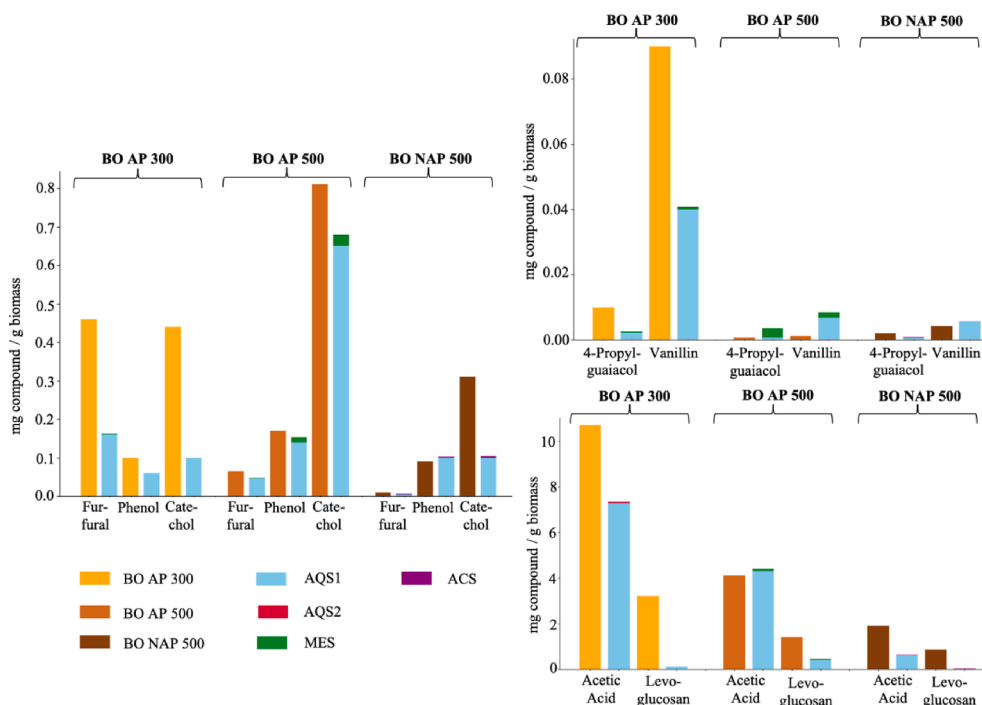


Fig. 5. Semi-quantitative results for GC-MS analysis for the dialysis of BO AP 300, BO AP 500 and BO NAP 500.

compounds were found in the AQS1 not in the ACS, only small amounts of 4-propylguaiacol were found in ACS_NAP 500. Most of the acetic acid, furfural, phenol, catechol, 4-propylguaiacol and vanillin were obtained

in AQS1_NAP500, allowing the separation of these compounds from initial BO inside the dialysis bag. As it was observed with the other samples levoglucosan was not found in considerable amounts in either

fraction.

It can be concluded that dialysis can separate light chemicals of bio-oil from heavy ones. This is very important because it allows on one side the obtention of a simpler liquid fraction containing value-added compounds and on the other side the obtention of PL, a solid which can be used directly as a product itself. Moreover, dialysis can be considered a green technique if the solvents used are considered green solvents or if they can be reused in the procedure.

3.1.3. Ft-IR

When dialysis was performed, a solid was obtained which remained inside the bag. This solid is mainly composed of the oligomeric fraction coming from the degradation of lignin, also called Pyrolytic Lignin (PL). Its high hydrophobicity and elevated molecular weight prevent it from escaping the dialysis bag into the dialysate. PL has already been well characterized by other authors (Bai et al., 2014; Jiang et al., 2010; Li et al., 2020; Matos et al., 2021; Sammons et al., 2013; Wang et al., 2015). In this study, a FT-IR analysis was carried out to characterise the solid obtained and confirm its PL structure. In Fig. 6, the FT-IR spectra of the solids obtained in the dialysis of bio-oils are depicted and compared to the FT-IR of organosolv lignin. It was appreciated that there are a lot of similarities in the region of typical FT-IR lignin bands: O–H stretching (3421 cm^{-1}), C–H stretching (2937 cm^{-1} and 2840 cm^{-1}), C = O stretching (1700 cm^{-1}), aromatic skeletal vibration + C = O stretching (1600 cm^{-1}), aromatic skeletal vibration (1515 cm^{-1}), C–H deformations methyl and methylene (1460 cm^{-1}), C–O stretching of the guaiacyl ring (1270 cm^{-1}), C–C, C–O, C = O stretching in guaiacyl ring (1215 cm^{-1}), aromatic C–H deformation in the syringil ring (1100 cm^{-1}) and aromatic C–H in-plane deformation (1033 cm^{-1}) (Aljerf and Nadra, 2019). In the FT-IR spectra it was observed that the peak at 1366 cm^{-1} had higher intensity in the solids obtained in the dialysis (PL) than in organosolv lignin. This phenomenon was already observed by (Wang et al., 2015). They noticed that PL, besides conserving the basic structural units of lignin, it also had abundant side chains as indicated by the peak at 1366 cm^{-1} , originated by the aliphatic C–H and phenolic OH stretching. This peak suggested that PL has more aliphatic side chains, carbonyls and unsaturated double bonds than lignin which increases its reactivity. The peaks associated with syringyl and guaiacyl units were

also found in the solids obtained, even though sometimes with lower intensities than in organosolv lignin (e.g. peak at 1100 cm^{-1}). This indicates that even though these groups are still found in the solids obtained, their structure might be a bit affected by the pyrolysis process, a phenomenon already described by several authors (Asmadi et al., 2011; Guizani et al., 2017; Saiz-Jimenez and De Leeuw, 1986). It can be concluded that the solid separated with the dialysis procedure is PL, which has a lignin-like structure, conserving most of the basic structural units of lignin and incorporating an increase in reactive sites. Thus, as it has been described previously in the literature, PL can be used for the synthesis of resins (Effendi et al., 2008), foams (Figueirêdo et al., 2022), asphalts (Zhang et al., 2021), carbon fibres (Qin and Kadla, 2012), etc.

3.2. Column chromatography separation

3.2.1. General characterisation

A column chromatography separation was performed on the dialyzed liquid to further separate the compounds and be able to obtain simpler fractions. Amberlite™ XAD7 was used, a resin that retains non-polar or slightly non-polar compounds. For this reason, it is important that the pH of the sample before passing it through the column is acidic, in order to have the phenolic species protonated and that they can consequently be retained in the resin. To elute the retained compounds, a sodium hydroxide solution was passed through the column, and the slightly non-polar compounds were eluted. To elute the non-polar compounds, it was necessary to use a less polar solvent, like methanol.

Sample AQS1_AP300 was the chosen one to further refine using column chromatography with the resin Amberlite™ XAD7. In Fig. 7b the colouration of each fraction obtained is shown: yellow–brown for the AQS1_AP300, colourless for the NR fraction, yellow–brown for the NaOH fraction due to the presence of phenolic species and yellowish for the MeOH fraction, also due to the presence of some phenolics.

3.2.2. Gc–MS

The three fractions obtained (NR fraction, NaOH fraction and MeOH fraction) were characterized with GC–MS. The detailed identification of compounds from GC–MS chromatograms (see Supporting Information) showed that the chemicals observed in the NR fraction are carboxylic

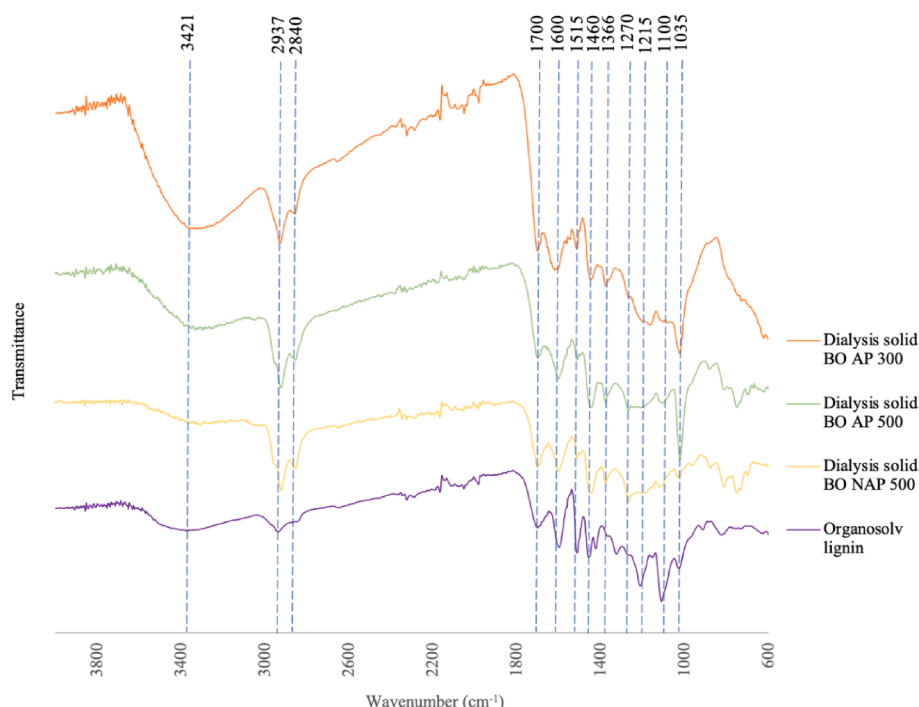


Fig. 6. FT-IR of the solids obtained in the dialysis of BO AP 300, BO AP 500, BO NAP 500 and organosolv lignin.

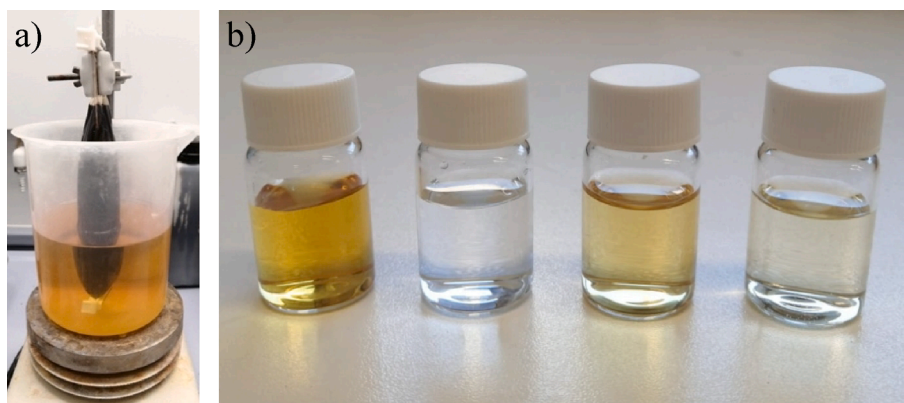


Fig. 7. (A) first dialysis of bo ap 300 with water after 24 h. (B) From left to right: AQ51_AP300, NR fraction, NaOH fraction, MeOH fraction.

acids like acetic acid and formic acid, alcohols and ketones like hydroxyacetone, furan derivatives like furfural and 5-methylfurfural, and sugars like anhydro-mannosan. In the NaOH fraction phenolic compounds were identified, such as guaiacol, vanillin, phenol, etc. Finally, in the MeOH fraction a mixture of non-polar compounds was observed, composed of a wide variety of benzene derivatives (toluene, xylene, cumene), quinolines, long-chain alkanes and also some highly non-polar phenolic species.

In Fig. 8, the semi-quantitative results using seven external standards are shown. It was seen that acetic acid was mostly found in the NR fraction as was expected. Furfural was obtained in both the NR fraction and MeOH fraction. Phenol and vanillin were found in the NaOH fraction as it was expected and 4-propylguaiacol was eluted in the MeOH fraction since it is a less polar compound than the others. Catechol did not quantitatively elute in any of the three fractions, meaning that most of it remained in the resin. Levoglucosan did not appear quantitatively on the NR fraction, which was the expected one, because it was not obtained in an appreciable amount in the AQ51_AP300.

Therefore, the separation with the resin Amberlite™ XAD7 was capable of separating different chemical families of BO in different fractions according to their polarity. Firstly, carboxylic acids, alcohols and ketones were obtained in the NR fraction, secondly, phenolic compounds were obtained in the NaOH fraction and finally, other non-polar compounds such as benzene derivatives and quinolines were obtained in the MeOH fraction. This MeOH fraction is the one with less

interest for bioproducts obtention and can be reutilized in the column chromatography procedure, making the process greener.

4. Conclusions

The novel separation strategy combined dialysis and column chromatography with Amberlite™ XAD7 resin, techniques never used before in this field. It resulted in the obtention of pyrolytic lignin, which can be used for resin synthesis, and acid-rich fraction, which can be further refined and used for chemical and food industries, a fraction rich in antioxidants, key products for nutraceutical and pharmaceutical industries and a fraction with highly non-polar compounds. In this way, it was possible to separate value-added chemicals from the light and heavy fractions of pine wood pyrolysis liquids. Thus, it was possible to transform lignocellulosic biomass, a by-product of the management of unprofitable forests like Mediterranean woodlands, into a renewable feedstock to produce fine chemicals.

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. **Pere Rovira:** Supervision. **Neus Puy:** Writing – review & editing, Supervision, Project administration,

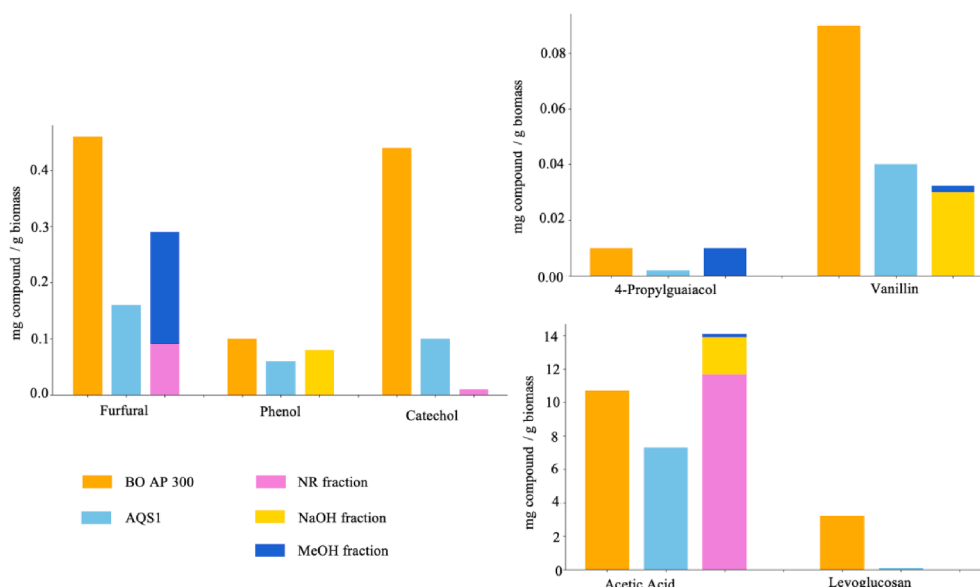


Fig. 8. Column chromatography separation with Amberlite™ XAD7 resin of the fraction AQ51_AP300.

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.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2023.06.005>.

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