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Supercritical water depolymerization of black liquor, refining and comprehensive analysis of products including biopolyols

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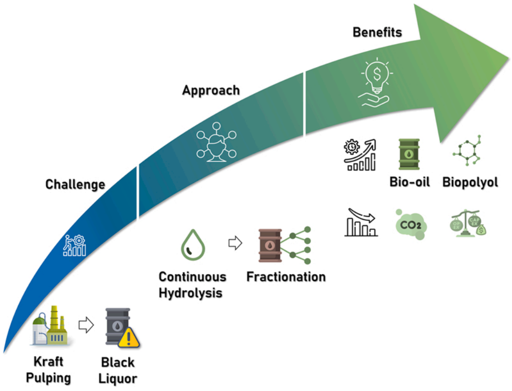
HIGHLIGHTS

- Black liquor depolymerization in SCW produces biopolyols.
- Hydrothermal treatment provided 77% w/w bio-oil yield in 0.4 sec.
- Monomer yield found 30% w/w more in the depolymerized black liquor compared to raw black liquor.
- Inorganics could be reused in pulping process by integrating to its process cycle.
- Aromatic monomers; guaiacol and syringol were produced during the process.

GRAPHICAL ABSTRACT



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ABSTRACT

Black liquor (BL) has valuable lignin and its derived compounds, which can be used for many purposes, such as polyol synthesis. Herein, we reveal polyols presence in depolymerized black liquor (DBL) and propose a fast and scalable approach to increase the yield of this fraction. Hydrothermal treatment (HTL) of black liquor (385°C, 26 MPa) was performed in a custom designed supercritical water (SCW) pilot-plant with rapid reaction times of around 0.4 s. Ash-free, total ethyl acetate extracted bio-oil yield was found 77% w/w. In addition to the contribution of the detailed fractionation methods, this study highlights continuous operation (>1 hour), and short reaction times (~0.4 s) of raw black liquor in SCW to produce biopolyols and aromatic bio-oil.

1. Introduction

Approximately, 170 MT of black liquor is produced annually from pulp & paper industry on a dry basis [1,2], whereas the lignin production is estimated to be between 50 and 70 MT worldwide [3]. Unfortunately, only around 2% of this lignin is utilized as high-value chemicals. The remaining lignin is usually burned as low-value fuel to balance the economics of the plant by creating thermal energy. [4]. The undervalued black liquor can be utilized as a feedstock that would enable industrial application for bio-oil production in a biorefinery. This

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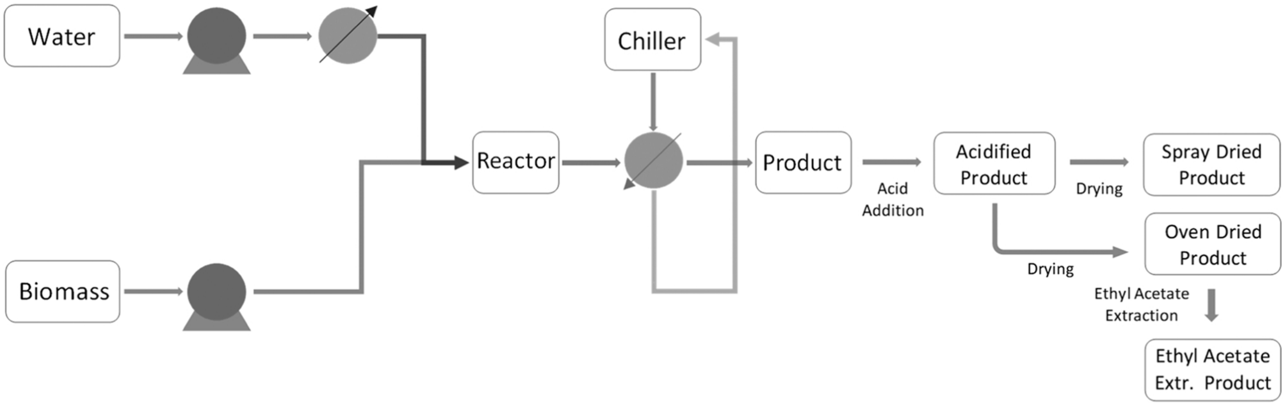

Fig. 1. Simplified block flow diagram of the TRL5 supercritical water depolymerization pilot plant and post-processing steps.

would provide plenty of benefits; (i) the raw material (black liquor) is already present within the pulp and paper facility, which eliminates transportation costs and emissions [1], (ii) the byproducts like cellulose, hemicellulose, mono-, di-, and oligomeric lignin fragments can be used for various purposes such as functionalized materials production [3,5], (iii) pulping chemicals can serve as potential catalysts [2,6], (iv) diversifying pulp mill economics with another product reduces their sensitivity to pulp prices [1], and (v) the capital and operational costs of the new hydrothermal treatment (HTL) unit will be compensated by high temperature steam production and the recovery of pulping chemicals, providing a more feasible approach [1].

Over the last decade, kraft lignin has gained significant importance among researchers for its potential to replace fossil fuel-derived aromatic compounds [4,7–9]. Lignin is a distinctly complex 3D heteropolymer that confers mechanical rigidity to plants through the incorporation of phenylpropanoid units that include methoxy groups, such as syringyl (S-unit), guaiacyl (G-unit), and p-hydroxyphenyl (H-unit) units. It is composed of an abundance of C-O-C (4-O-5, α-O-4, β-O-4) and C-C (5–5, β-β, β-1, β-5) bonds and is intricately linked to cellulose and hemicellulose, rendering its conversion complex. Therefore, the fractionation of lignocellulosic biomass by using various pretreatment methods is essential [10–13]. Predominantly, these methods operate through the cleavage of C-O-C (β-O-4) linkages due to their lower bond dissociation energy (BDE) (between 218 and 314 kJ/mol), compared to the relatively stronger C-C bonds of greater BDE (~384 kJ/mol). This cleavage results in recondensation reactions that modify the structure of lignin, producing what is known as technical lignin [10–13]. Depolymerization of both isolated and native lignin have been extensively researched and it was found that native lignin depolymerization gives around seven times greater monomer yields [4,13]. The existing literature on this topic can be categorized into four main groups: (i) reductive [14–17], (ii) oxidative [18,19], (iii) base- and acid-catalyzed [20–23], and (iv) solvolytic and thermal depolymerization [24,25]. All approaches have specific advantages and disadvantages, which are already discussed in some papers [4,26]. The most promising technology is the reductive catalytic depolymerization and its derivative technologies due to reaching almost complete theoretical monomer yield of lignin used [4,26]. Yet, their common characteristics of long reaction times, the requirement for organic solvents, and low flow rates are major hurdles to overcome to facilitate industrial scale-up [16]. Although for native lignin applications it is favorable and profitable, these technologies do not offer an advantageous solution to the black liquor and lignin produced by traditional biorefineries. Additionally, except SCW gasification studies [27], there are only few research focused on black liquor liquefaction studies in the literature [2,6].

In our laboratory, a custom-designed continuous pilot plant was developed to carry out rapid reactions (<1 sec) using supercritical water mediums. The plant possesses unique properties for hydrothermal processes such as instantaneous heating and cooling [28,29]. This efficient thermal management helps to prevent biomass degradation and char-like formations. The device that is used for this study allows a more precise and accurate control of the reaction time, avoiding repolymerization reactions according to the desired conditions [28]. Supercritical water was selected as the medium since it is environmentally friendly, low-cost, abundant, and does not cause contamination [30]. Taking advantage of the enhanced mass transfer and reaction kinetics in supercritical medium allows to intensify the process and work at rapid reaction times [31].

In this study, black liquor obtained from a commercial pulp & paper company is used without any pretreatment in a supercritical water (SCW) depolymerization process. The reaction conditions used in this study were 385°C, 260 bar, and 0.4 s. The product was subjected to different refining methods for optimization purposes to separate the bio-oil fraction and determine the aromatics and biopolyols present in this fraction. Several characterization techniques were used to understand the product characteristics and the potential use of these novel fractions. This approach presents a good opportunity because it uses the intrinsic pulping chemicals as catalysts, there is no need for drying or separating lignin, skips logistics by directly using black liquor, and benefits from the degradation compounds from lignin in black liquor.

2. Materials and methods

2.1. Materials

Black Liquor was provided by Ence Energía & Celulosa (Pontevedra, Spain). Chemicals used in analysis; ethyl acetate (99%), acetone (99%), sulfuric acid (72% & 96%), sodium hydroxide pellets (98%) were purchased from PanReac. N,O-Bis(trimethylsilyl)trifluoro-acetamide (BSTFA – 99%) and pyridine (99%) were purchased from Merck. The standards used for the gas chromatography calibration were all purchased from Sigma-Aldrich: guaiacol (≥99%), syringol (98%), vanillin (99%), acetosyringone (97%), acetovanillone (98%), and syringaldehyde (97%). Milli-Q grade water was used in the analyses.

2.2. Supercritical water pilot plant and depolymerization

A detailed description of the pilot plant used in this study can be found in previous work by our research group [29], and a simplified block flow diagram (BFD) of the pilot plant is presented in Fig. 1. The black liquor (BL) slurry is pumped directly to the reactor at room temperature. As soon as the BL slurry mixes with the supercritical water at the reactor entrance, the BL is instantaneously heated to the desired temperature. The hydrothermal treatment starts at that moment. The plant operates with different reaction times (<1 s to 1 minute) by changing the reactor dimensions. A notable feature of the plant is the Sudden Expansion Micro Reactor (SEMR), which is rapidly decompressed at the outlet by a letdown valve. The sudden depressurization through a control valve, based on the Joule-Thomson effect, allows an instantaneous cooling from supercritical water conditions to approximately 150 ± 10°C, while the pressure drops to ~5 ± 2 bar. These conditions are sufficiently low to ensure that degradation reactions are instantaneously halted or minimized. Furthermore, a subsequent heat exchanger is employed to further reduce the temperature of the products to ambient levels [29]. The desired reaction times are achieved by adjusting the reactor length, inner diameter, or flow rates of the streams.

Black liquor was subjected to hydrothermal treatment in supercritical water at 385 ± 1°C and 260 ± 5 bar. Experiments were conducted in triplicates, each with a steady state operation time of 1 hour. The reaction time inside the reactor ranged between 0.36 s and 0.40 s. The flow rates for the SCW and biomass were set at 15.0 kg/h and 7.5 kg/h, respectively. The BL stream was diluted with water to achieve a slurry concentration of 20% w/w total solids (TS) due to the high solids content in black liquor.

2.3. Solids analysis and downstream processing

The products obtained from the hydrothermal processing were analyzed gravimetrically to conduct a mass balance. First, a dissolved solids analysis (DS) was applied to both raw black liquor (BL) and depolymerized black liquor (DBL) obtained after the process. The DS analysis is a gravimetric technique that allows the determination of water-soluble material in a liquid sample. These results allowed us to evaluate the effect of the hydrothermal process on the amount of the water-soluble fraction [32]. The samples (DBL and BL) were acidified to different pH levels by adjusting sulfuric acid amounts. After acidification, the samples were centrifuged, and the dissolved solids (DS) and suspended solids (SS) fractions were separated. The suspended solids fraction was further washed with pH 2 water to completely remove the DS from the SS phase. The final material was dried in an oven at 105ºC, and dry matter weights for both DS and SS were logged against the measured pH values. This technique was used to understand the amount of suspended solids (SS), dissolved solids, and total solids (TS) generated at different values of pH. This solids analysis method is given in Figure S1.

A comparison between different refining methods was performed using two different approaches. A simplified scheme of these separation methods can be found in Figure S2. In procedure A, after acidification of the BL or DBL to different pH levels, the sample was subjected to direct drying (Oven Drying or Freeze Drying). Subsequently, an ethyl acetate extraction was applied to the dried material, which was then separated by centrifugation. The ethyl acetate-extracted fraction was labeled as EtAc Extracted, whereas the water-extracted fraction was labeled as Water Extracted, and the remaining sample was called Insoluble. Oven Drying was performed at 105°C, while freeze drying was conducted at −55°C and 20 mbar.

In procedure B (*fractionation method*), a fractionation procedure was conducted for detailed separation. Once acidification was completed, instead of using a direct drying method, phase separation was performed by centrifugation. After decanting the DS from the SS, the SS fraction was washed three more times with pH 2 water, and the liquid part was combined with the DS. The ratio of pH 2 water to solids was 1:1. Ethyl acetate extraction was then performed on both fractions, resulting in four different fractions being obtained. At the end of this process, four different fractions were collected: Ethyl Acetate-Soluble in Dissolved Solids (DS-EA), Water-Soluble in Dissolved Solids (DS-W), Ethyl Acetate-Soluble in Suspended Solids (SS-EA), and Insoluble Suspended Solids (SS-Insol.). The organic solvent was removed using a rotary evaporator for the DS-EA fraction. The water bath was set to 50°C, and evaporation was carried out under a vacuum pressure of 350 mbar. After evaporation, the material was further dried in an oven at 50°C. Characterization of other materials (SS-EA, DS-W, SS-Insol.) was beyond the scope of this study.

2.4. Depolymerized black liquor performance evaluation

After the fundamental solids analysis, four different types of samples, along with one blank sample, were designated for further in-depth characterization to evaluate the process performance. These are named as follows: Black Liquor (BL) as the raw material (blank sample), Depolymerized BL (DBL) as the product from the pilot plant, Oven Dried product (OD), Spray Dried product (SD), and Ethyl Acetate soluble (EA) product. Oven Dried and Spray Dried products were obtained by following acidification of DBL and direct drying (oven or spray drying) steps. Product OD was ball milled after drying. Ball milling of the OD product was performed using a Retsch PM 100 for 4 hours. Since freeze-drying extraction results were not promising at lower pH compared to the *fractionation method*, and spray drying process is much faster than freeze-drying, spray drying is included in this part of the research. As the SD particles were uniform, with an average particle size of 10 microns, no further grinding operation was necessary. The spray drying inlet air temperature was set to 160°C, and the product exit temperature was 85°C, while the flow rate was 1.5 kg/h. OD and SD samples were selected to check the effects of particle size and temperature on the chemical composition of the materials. The ethyl acetate-extracted product was produced by subsequent ethyl acetate extraction applied to the OD product. The ethyl acetate-extracted fraction from DBL essentially consists of lignin depolymerized products of black liquor, including monomers and oligomers (containing biopolyols), plus possible repolymerization of oligomers and monomers produced after the depolymerization of black liquor in SCW. A simplified BFD including the post-processing steps to obtain the designated products for further characterization can be found in Fig. 1. A study that focuses specifically on the repolymerization reactions carried out by our previous group member can be found in the literature [33].

The characterization techniques applied to the samples are described below:

The chemical composition of these five samples was determined using the Laboratory Analytical Procedure (LAP) from the National Renewable Energy Laboratory (NREL). Moisture content, acid-soluble and insoluble lignin, carbohydrates, and ash content were determined using methods from NREL [32,34–36]. Acid Soluble Lignin amount was determined for the raw material and the product profiles by using UV-Vis Spectroscopy. The absorbance was recorded at 205 nm, and absorptivity coefficient used was 110 L g^{-1} cm^{-1} [35].

Elemental Analysis of the materials was carried out using a Leco CS-225 Elemental C-S Analyzer to determine the hydrogen, carbon, nitrogen, and sulfur content. The balance of the remaining parts was considered as oxygen and inorganics.

Fourier Transform Infrared (FTIR) characterization of the materials was performed using a Bruker Tensor 27 equipped with a universal attenuated total reflectance accessory with internal diamond crystal lens. The operating range was between 4000 and 400 cm^{-1}, and each spectrum was a mean of 64 single scans.

Thermogravimetric Analysis was conducted using a Mettler Toledo TGA/SDTA RSI Analyzer. Approximately 5 mg of the sample was heated at a rate of 10 °C/min under a nitrogen atmosphere with a flow of 50 mL/min. The temperature started at 30°C and increased to 900°C. The temperature was held constant at 900°C under a nitrogen flow for 10 minutes with the same flow rate.

DS-EA fraction precipitated at different pH levels analyzed and quantified by using an Agilent 7820 GC gas chromatograph with a quadrupole mass spectrometer detector (5978A-Agilent Tech., USA). As the monomer-focused method all the samples were prepared by dissolving them in acetone prior to analysis. The separation was done with a low bleed, non-polar capillary Agilent HP-5 ms column, 30 m x 0.25 mm×0.25 μm. Helium was used as a carrier gas, and the injection

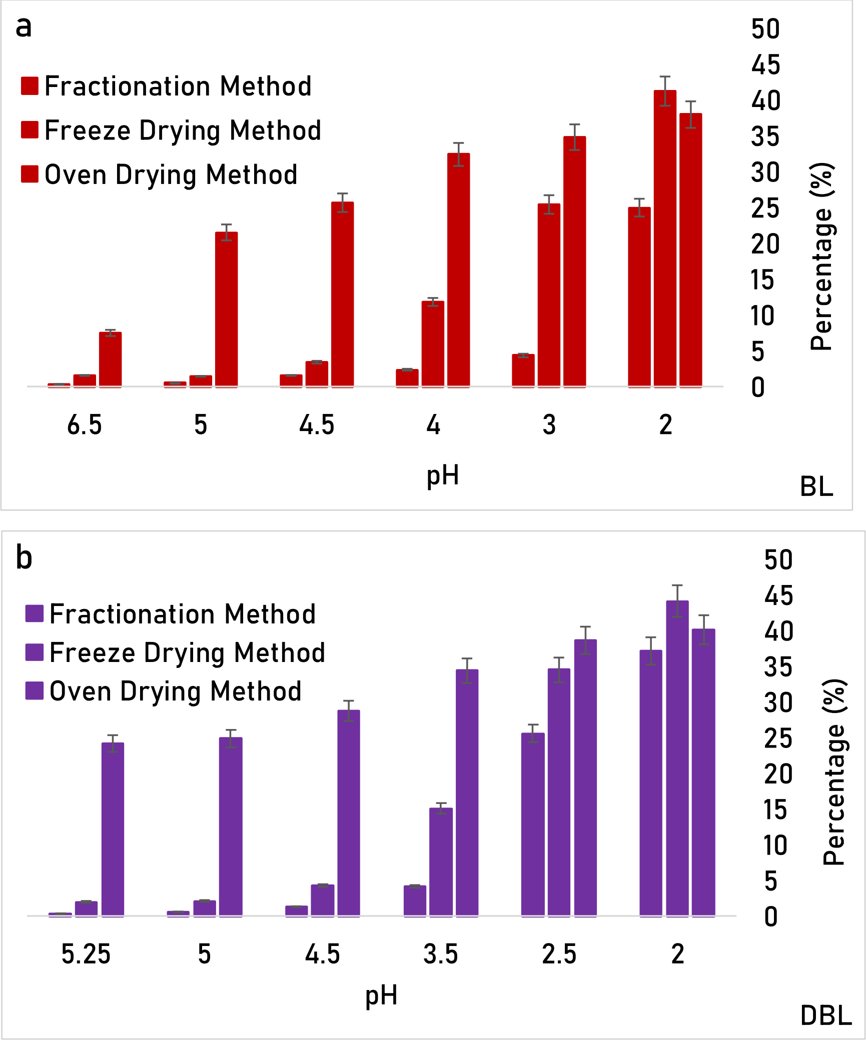

Fig. 2. Yield comparison of ethyl acetate extracted fraction for different separation methods at different pH values; (a) BL and (b) DBL.

was in splitless mode. The temperature program of the oven started at 32°C and held for 10 min; then it was raised to 52°C by an increment rate of 2 °C/min, kept for 2 min; then to 65°C at 2 °C/min with 2 min holding time was followed; then increased to 93°C by 4 °C/min rate, which held for 2 min; followed by a raise to 230°C at 2 °C/min and kept for 3 min; lastly to 300°C at a rate of 15 °C/min and kept for 3 min. Solvent delay program was set to 4 minutes to keep acetone away from sending to MS detector. The compounds identification was done by both validating from NIST library by comparing *m/z* values and the retention times. This method was used to identify the monomers and is a modified version of a previous study performed by our group [37]. Biopolyols and oligomers of the depolymerized black liquor DS-EA fraction were analyzed using a derivatization method which will be called oligomer-focused method. 10 mg/mL lignin oil (LO) solution was prepared in acetone, and a 10:1:2 (v:v:v) mixture (LO:Pyridine:BSTFA) was heated for 20 minutes at 45°C before injection to GC-MS. N,O-Bis(trimethylsilyl)trifluoroacetamide with 1% trimethylchlorosilane (BSTFA) was used as the silylating agent. The oven was started at 150°C and increased at a rate of 4 °C/min until 300°C and held for 18 min. TMS-derivatized oligomers were determined using a 2.5:1 split ratio, and a solvent delay of 15 minutes, to avoid detector overload with an excess of monomers.

Gel Permeation Chromatography (GPC) was performed to check the molecular weight distribution of the selected samples qualitatively. Samples were prepared for GPC by using their dried versions at the end of each process. The samples were dissolved in 1% w/v LiBr in DMSO, and the concentrations were set for 1 mg/mL. Phenomenex Phenogel 5 μ 10^3 Å GPC column with a size of 350 ×7.8 mm was used for the analysis. The column temperature was set to 35ºC, DMSO was the carrier solvent at a flow rate of 0.8 mL/min. The eluents were analyzed using a UV-DAD detector at a wavelength of 254 nm.

Sugar and derivative analyses were performed using high-performance liquid chromatography (HPLC). The column used during the analyses was a Shodex SH-1011 column, with sulfuric acid (0.01 N) as the mobile phase at a flow rate of 0.8 mL/min. A Waters 2414 RI Detector was used for component detection. The NREL Protocol for carbohydrate determination was followed for HPLC analysis.

3. Results and discussion

3.1. *Refining methods*

Different methods were tested to find an easy and quick separation method to make a product ready for industrial use or processing. The primary objective was to minimize time and cost to create an efficient method.

BL and DBL were refined according to the procedures A and B described above. The ethyl acetate-extracted fractions from both procedures are compared in Fig. 2. Both procedures show that the highest yield of ethyl acetate fraction is obtained at pH 2. Also, it was observed

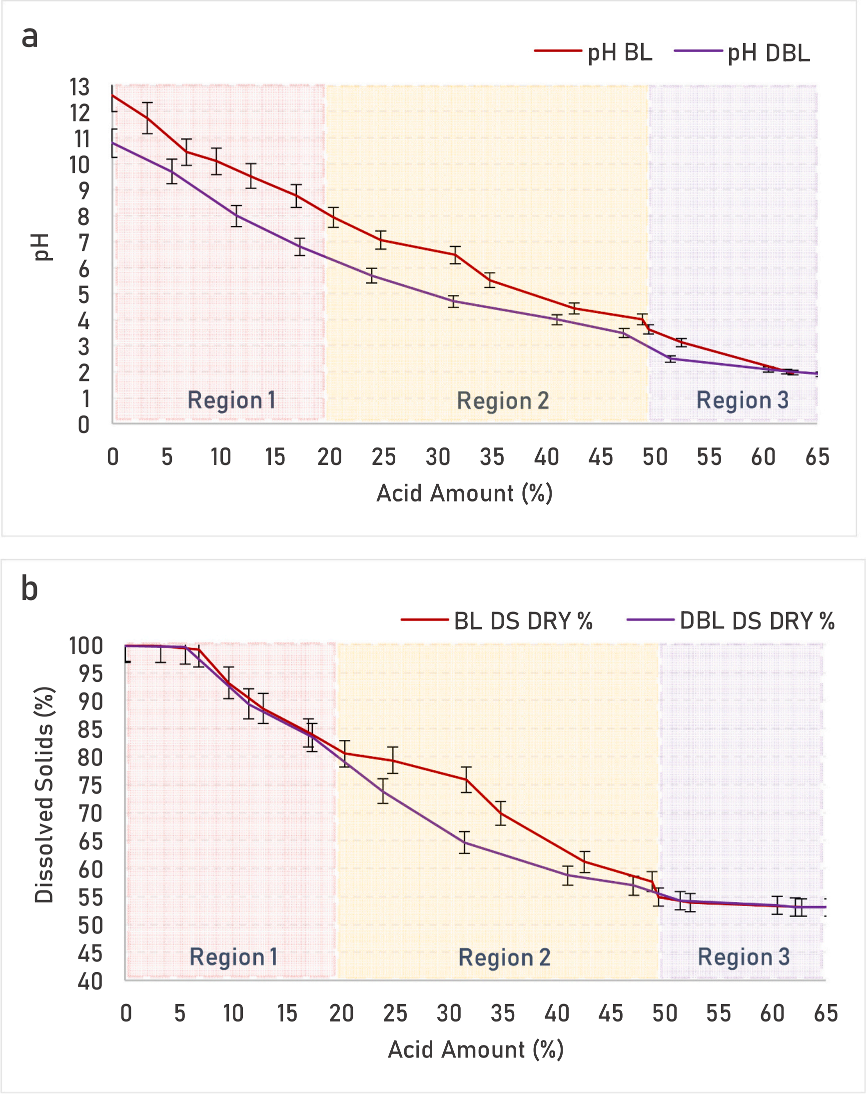

Fig. 3. Effect of pH and acid added during acidification on dissolved & suspended solids; (a) BL and (b) DBL.

that the yield increases as the pH drops. Remarkable differences were observed for the ethyl acetate-extracted fractions between procedure A (drying) and procedure B (not drying). Using the oven drying method, the maximum ethyl acetate-extracted fraction yields was 25% for BL and 37% for DBL. However, the oven drying method yielded less than 5% ethyl-acetate extract at pH values higher than 2.5. This was observed for both BL and DBL. A similar behavior was observed for the freeze-drying method above pH 4 for BL and pH 3.5 for DBL. The *fractionation method* showed higher extraction performance compared to the oven and freeze-drying methods at lower pH values. The oven drying method seems to "encapsulate" smaller fractions of lignin that would be soluble in EA. Additionally, the freeze-dried samples were easier to extract than the oven-dried ones. This is likely related to better particle formation and less agglomeration during the freeze-drying method. Black Liquor ethyl acetate-extracted bio-oil yield was found to be 25% for oven drying, 41% for freeze-drying, and 38% for the *fractionation method*, whereas for depolymerized black liquor, the yields were 37% for oven drying, 44% for freeze-drying, and 40% for the *fractionation method*. Experimental error of these results was less than 6%. These results show that the drying of the samples as they come from the reactor will not affect the availability of the bio-oil fraction (extracted with ethyl-acetate). However, it was seen that the drying technique could affect that bio-oil availability. The combination of oven drying and milling yielded less bio-oil than the samples produced from freeze drying. Industry could expect depolymerized black liquor products as dried samples, but drying should be done in a way to prevent macro agglomeration of the material.

Interestingly, the material created emulsions at high pH values, >6.5 for BL, and >5 for DBL. The presence of emulsions made the separation of suspended and dissolved solids less efficient, resulting in lower bio-oil yields. Although the freeze-drying method and the *fractionation method* had similar extraction yields at pH 2, the *fractionation method* was chosen for detailed aromatic component analysis since it outperformed the freeze-drying method at lower pH levels. For example, the extracted fraction from BL by freeze drying is 1%, whereas by the *fractionation method* is ~22% at pH 5. A similar behavior can be observed for DBL, where using freeze drying yields a 2% extraction fraction, while the *fractionation method* yields 25% at pH 5.

3.2. *Effect of pH on solids yield*

The solids yield of BL and DBL after acid precipitation are presented in Fig. 3. The graph 3-a shows the amount of acid (% - g of acid per g dried material) added to the product versus the resulting pH after acid addiction. On the other hand, graph 3-b shows the amount of soluble material (% Dissolved Solids) at different acid additions for both BL and DBL. As depicted in Fig. 3a and b, the pH evolution of BL and DBL differs,

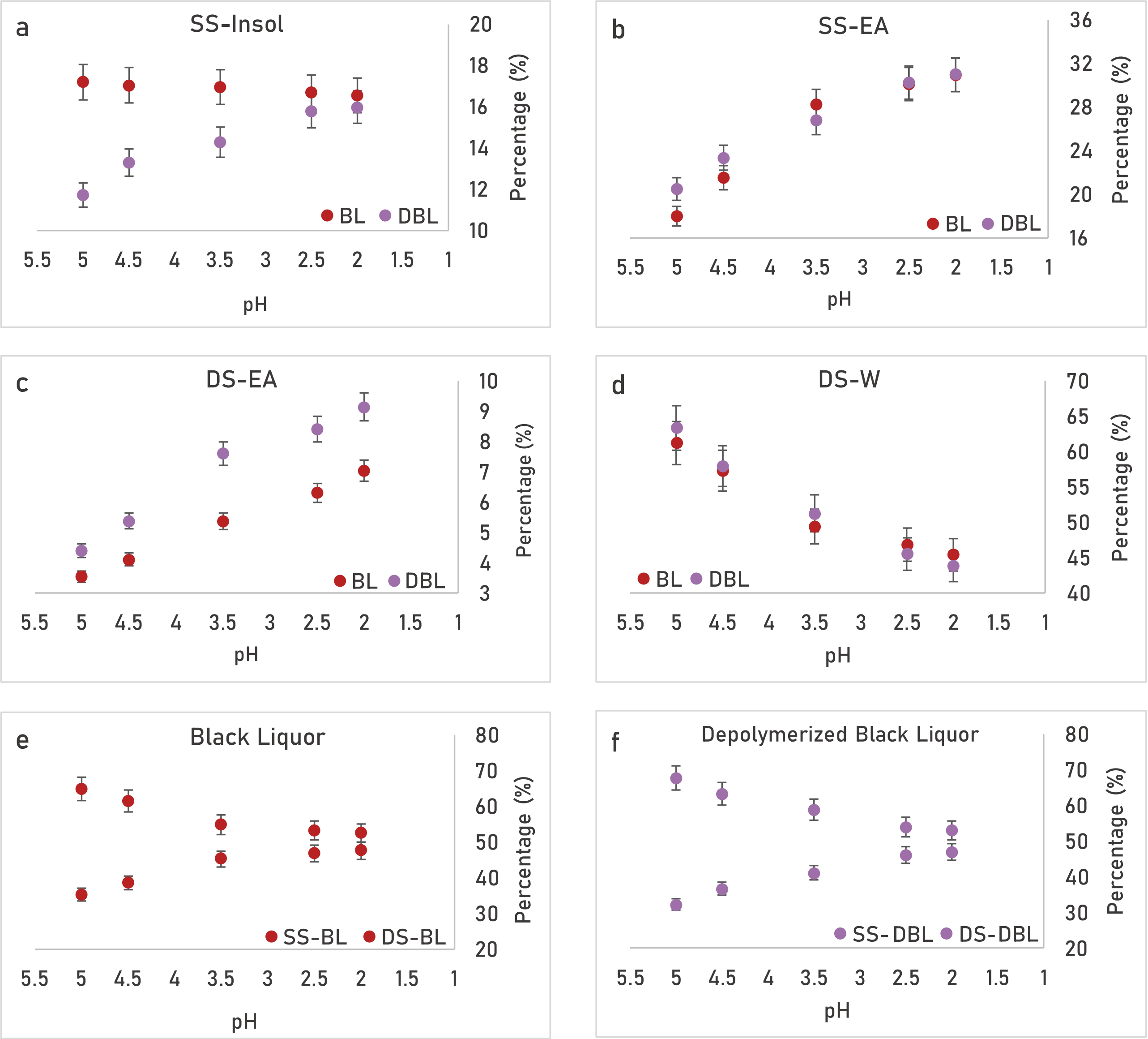

Fig. 4. Comparison of black liquor (BL) and depolymerized black liquor (DBL); (a) insoluble suspended solids, (b) suspended solids in ethyl acetate, (c) dissolved solids in ethyl acetate, (d) dissolved solids in water, (e) suspended (SS) & dissolved solids (DS) of black liquor, (f) suspended (SS) & dissolved solids (DS) of depolymerized black liquor. Percentages are given on a dry basis.

indicating that the consumption of -OH groups before and after the reaction in SCW varies. The evolution of the DS amount with acid addition shows an intriguing difference between BL and DBL. The discussion can be divided into three distinct regions: between 0% and 20% w/w (region 1); 20–50% w/w (region 2); and 50–65% w/w (region 3) acid addition.

In region 1, the DS decreased gradually for both BL and DBL, with no significant difference between them. In region 2, a distinct gap between DBL and BL is observed up to 50% acid addition, which continues until pH ~4. This gap indicates that the DBL requires less acid than BL to precipitate the lignin. Although the overall DS% has a declining trend, the BL acidification experiments showed a slower drop of pH in the region of 20–30%. Precipitation of suspended solids for BL (down to pH 9) and DBL (down to pH 7) was very low due to the low acidity of the medium, which is insufficient to precipitate weakly acidic groups (typically molecules that contain phenols/phenolic groups). Lignin was charged and soluble in the medium. Simply, at this point lignin can be envisioned as an amorphous macromolecule formed by crosslinked microgel coil-like structures [38–40]. The cations used in the kraft pulping processes (Na^+, K^+, etc.) surround the lignin macromolecules, which are negatively charged by phenolic groups. This effect makes lignin soluble in an alkaline medium [41]. As the medium acidifies and hydrogen ion concentration increases, weakly acidic phenolic groups become protonated. There is a point where repulsive and attractive forces reach equilibrium. Thus, the second region represents a transition where repulsive forces become less dominant and attractive forces predominate. In this region, self-aggregation of the lignin molecules was observed for both BL and DBL [41,42]. This aggregation occurs when the pH is close to the acidic strength of phenolic groups (pKa). At the end of this transition region, a substantial amount of lignin molecules precipitates.

The amount of precipitated solids decreased significantly beyond 50% w/w of acid (region 3), and the precipitation became nearly constant between pH 2 – 4. Fig. 3 additionally shows that DBL had a lower initial pH (10.8) than BL (12.6). This is likely due to an increased number of phenolic groups made during the hydrothermal process, causing a decrease in the pH level of the product. A similar observation is reported by Orebom [6]. Ultimately, despite slight differences in formation, both BL and DBL have nearly the same percentage of DS

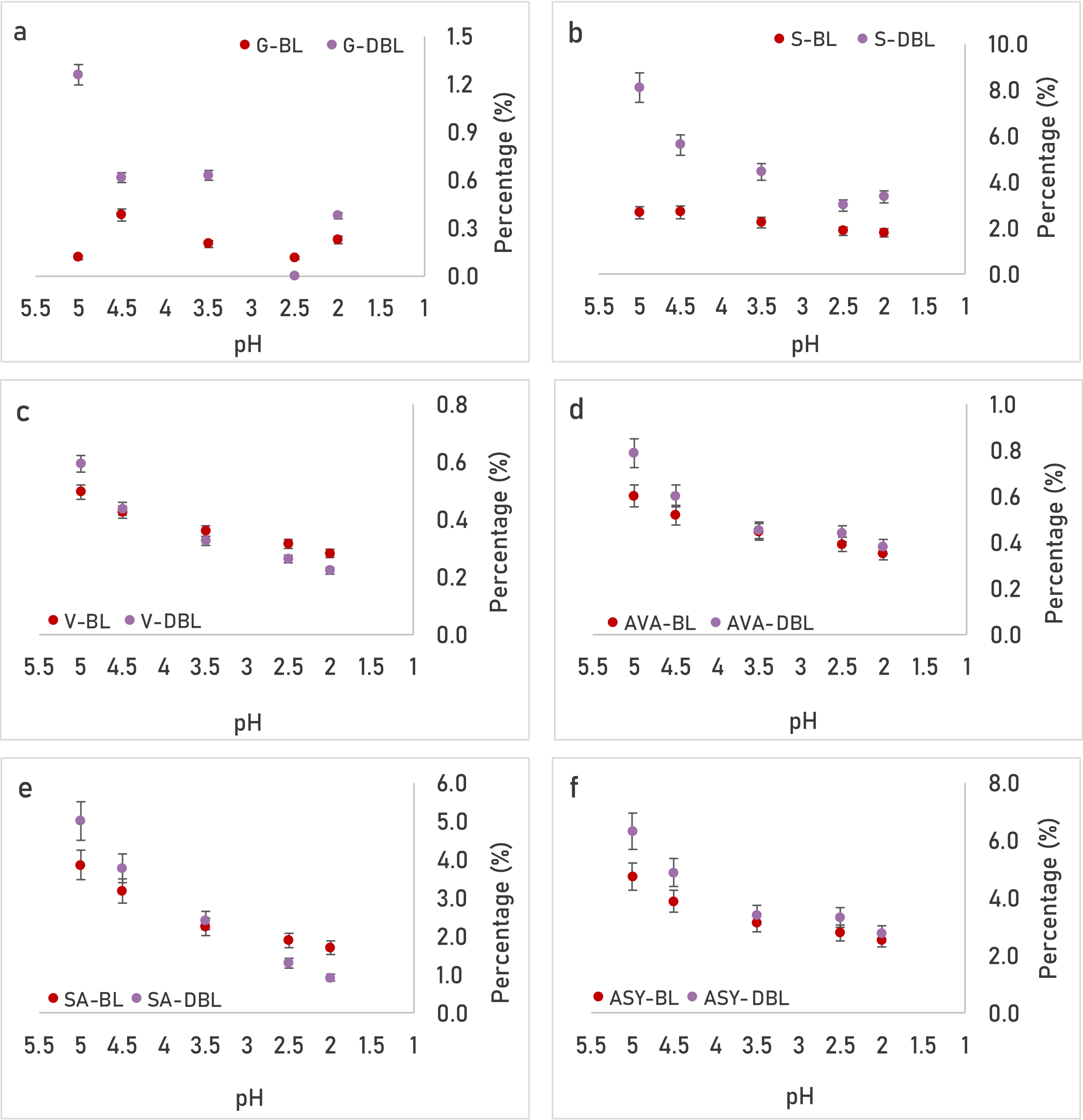

Fig. 5. Distribution of main aromatic monomers percentage; (a) guaiacol, (b) syringol, (c) vanillin, (d) acetovanillone, (e) syringaldehyde, (f) acetosyringone in DS-EA fraction at different pH values that were analyzed by GC-MS.

(~53%) and SS (~47%) around pH 2.

The *fractionation method* (from procedure B) samples of both BL and DBL are evaluated in Fig. 4a-d. The samples were divided into: Insoluble Suspended Solids (SS-Insol.), Suspended Solids in Ethyl Acetate (SS-EA), Dissolved Solids in Ethyl Acetate (DS-EA), and Dissolved Solids in Water (DS-W). Additionally, SS, DS, and TS are depicted in Fig. 4e-f. These yields were obtained without removing the inorganics amount from the calculations in a dry basis compared to the total solids. Details of the calculations can be found in Supporting Information Section 1. The main observations can be summarized as follows:

- The EA insoluble fraction from the suspended solids was consistently higher for BL than DBL. It is noteworthy that BL yielded an insoluble fraction of about 17% regardless of the pH. In contrast, DBL was significantly affected by pH, with the insoluble fraction increasing from 11% to 16% as the pH dropped from 5 to 2. This effect could be related to the presence of smaller lignin fractions in DBL compared to the original BL. These oligomers might be more stable in dissolution or microemulsion due to their smaller molecular size.
- The EA soluble fraction of the suspended solids was similar for DBL and BL. In both cases, the soluble fraction increased when the pH was reduced to 2, reaching a maximum.
- The EA soluble fraction in the DS was increased by the hydrothermal treatment. The DS fraction of the DBL contained about 9% EA soluble compounds, while the BL samples had 7%, which is about a 30% increase compared to the BL (Fig. 4c). The total ethyl acetate-soluble fraction yield was found to be 40% (9% DS-EA + 31% SS-EA) on a dry basis, including ash. Conversely, when the ash content is

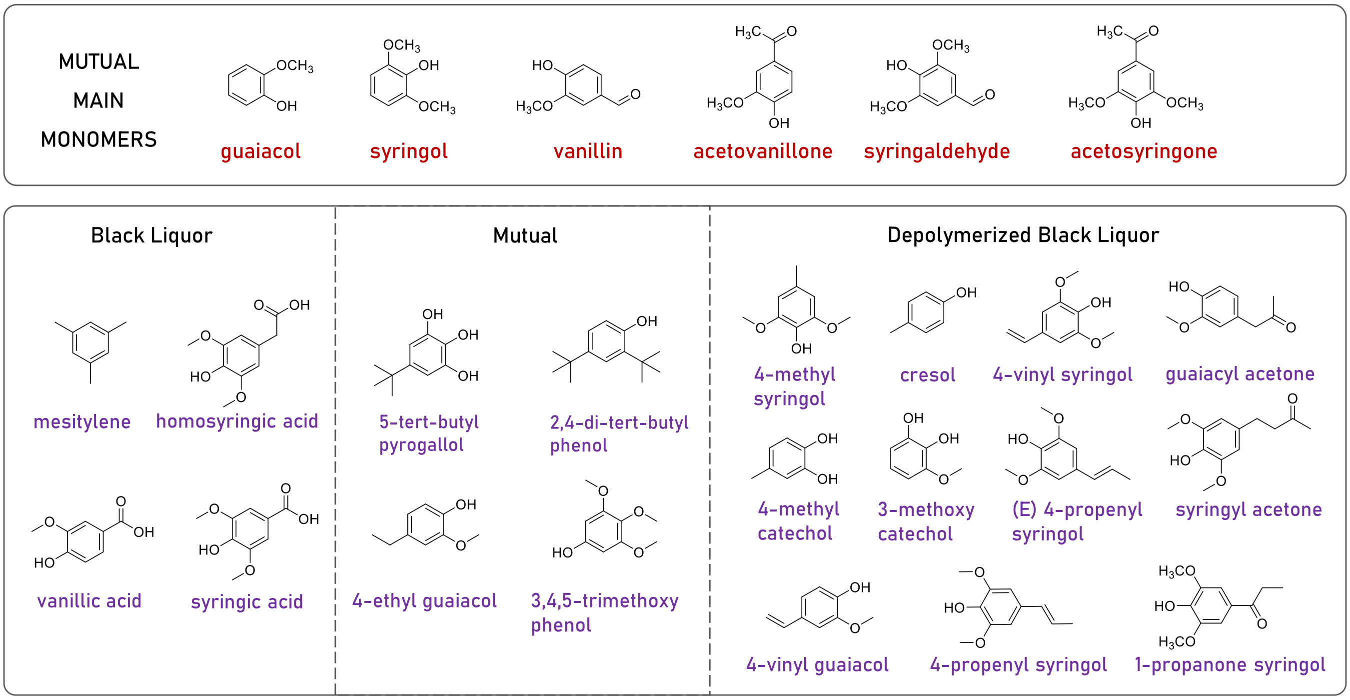

Fig. 6. Difference between black liquor & depolymerized black liquor samples DS-EA fraction identified products by monomer focused GC-MS method.

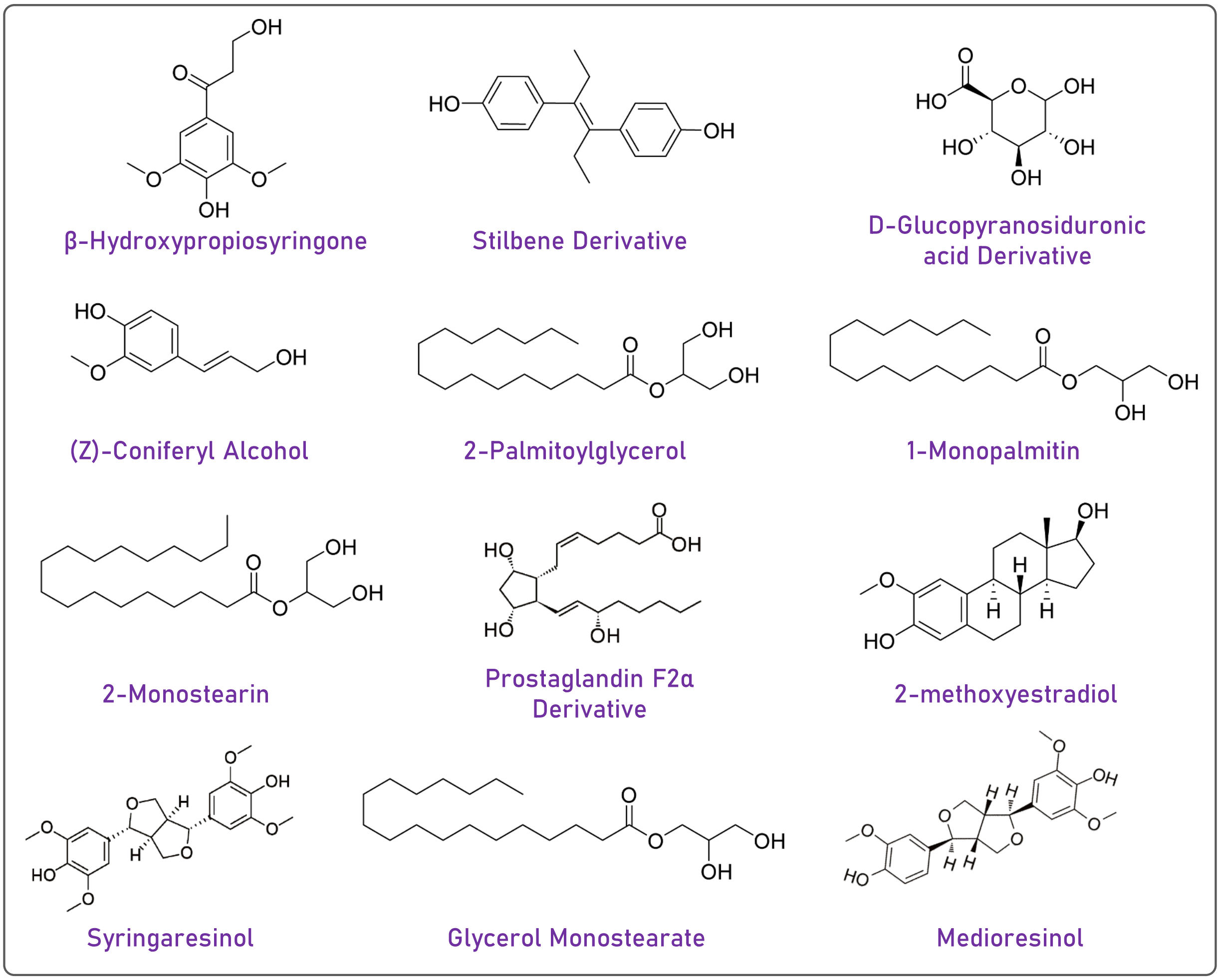

Fig. 7. Identification of depolymerized black liquor DS-EA fraction products by oligomer focused GC-MS method (identified biopolyols).

removed from the calculations, the total ethyl acetate-extracted fraction yield was found to be 77% (17% DS-EA + 60% SS-EA) on a dry basis.

- The EA insoluble fraction in DS (water-soluble) represents the largest fraction since it includes the inorganics from the kraft pulping process. Both DBL and BL exhibited similar results, with pH reduction prompting a decrease in water-soluble material. In this case, the reduction of pH promotes the reduction of water-soluble material. Separating this fraction is crucial for plant economics, as it enables the recycling of inorganics back into the kraft pulping process cycle.

Fig. 4e and f demonstrate that the total solids amount has negligible changes between pH 4 and 2 for both BL and DBL. However, SS and DS did vary with the change in pH. A pH of 2 was determined to be an appropriate level for performing the *fractionation method* since the goal was to recover a greater amount of DS-EA fraction to search for biopolyols in DBL.

3.3. Bio-oil composition

The monomers in the EA fractions were determined by using GC-MS. Comparison of these aromatic monomers at different pH levels can be seen in Fig. 5a-f. Guaiacol (G), Syringol (S), Vanillin (V), Acetovanillone (AVA), Syringaldehyde (SA), and Acetosyringone (ASY) were the main monomers observed in GC-MS analysis. A previous study conducted by our team members, which used lower concentrations of black liquor, monitored the same main aromatic monomers as found in this study, except creosol [43]. According to Fig. 5, generally, the concentration of the monomers decreased as the pH of the samples lowered. However, Fig. 4c demonstrates that DS-EA percentage increases by decreasing pH. This observation indicates that the drop of pH promotes the precipitation of dimers, trimers, and oligomers which are still linked to the metal cations in the DS fraction.

The main difference between DBL and BL was observed in the syringol yields. The syringol concentration in the EA-soluble fraction of DS increased approximately fourfold after hydrothermal treatment. The percentage of monomers in the DS-EA fraction was higher for both DBL and BL at pH 5 than at pH 2. Total quantified aromatic monomer yield, based on the DS-EA fraction, was found to be 8% w/w for DBL and 7% w/w for BL at pH 2, while it was 22% w/w for DBL and 13% w/w for BL at pH 5. The remaining DS-EA fraction consists of higher molecular weight compounds such as dimers, trimers, oligomers and biopolyols.

The differences in the molecules identified by the monomer-focused GC-MS method between black liquor and the depolymerized black liquor DS-EA fraction are shown in Fig. 6. As the dominant raw material of the black liquor used in this study was eucalyptus wood, and eucalyptus is a hardwood, the presence of both guaiacyl (G) and syringyl (S) derived monomers was expected in the GC-MS analysis. Mutual monomers present in both BL & DBL were 2,4-di-tert-butylphenol, 5-tert-butylpyrogallol, 3,4,5-trimethoxyphenol, and 4-ethylguaiacol. Mesitylene, homosyringic acid, vanillic acid, and syringic acid, which were detected in BL were not present in DBL. On the other hand, several low molecular weight aromatics formed after the supercritical water depolymerization of BL can also be seen in Fig. 6. Using the monomer-focused GC-MS method, three different biopolyols (5-tert-butylpyrogallol, 4-methylcatechol, and 3-methoxycatechol) were detected.

The main biopolyols identified after the supercritical water depolymerization of black liquor are shown in Fig. 7. A detailed table of the components identified using the oligomer-focused GC-MS method can be found in Table S1. The identified biopolyols can be categorized into three groups: aromatic polyols, sugar polyols and long-chain fatty acid-derived polyols. Stilbene, D-glucopyranosiduronic acid, and Prostaglandin F2α were found as derivatized versions in DS-EA fraction. For simplicity, in Fig. 7, their backbone (non-derivatized forms) was only given. Interested readers can find the full names of these molecules in Table S1 in Appendix A.

Table 1
Chemical Composition Percentages of the Samples (Dry Basis).

	Klason Lignin	Soluble Lignin	Total Lignin	Ash	Carbs
Black Liquor (BL)	20.5 ± 1.4	11.8 ± 1.2	32.2 ± 1.4	48.9 ± 0.9	<1
Depoylm. BL (DBL)	18.5 ± 2.2	8.0 ± 0.8	26.4 ± 2.9	48.5 ± 1.1	<1
Spray Dried (SD)	19.7 ± 2.4	10.4 ± 0.4	30.1 ± 2.7	60.7 ± 0.8	<1
Oven Dried (OD)	24.3 ± 1.6	6.3 ± 0.6	30.7 ± 1.1	59.8 ± 0.6	<1
EA Extracted (EA)	47.8 ± 2.1	18.9 ± 2.1	66.7 ± 2.1	2.0 ± 0.2	<1

The presence of biopolyols allows us to utilize the DS-EA fraction produced by performing supercritical water depolymerization for various purposes, such as lubricant or polyurethane production [5,44, 45]. Therefore, the next step considered was to conduct a more thorough chemical characterization of five different samples for comparison purposes.

3.4. Characterization of the selected samples

The samples were subjected to chemical composition analysis using NREL Protocols, and the results were summarized in Table 1. The carbohydrate content was found negligible as less than 1% w/w. The ash content of black liquor is quite high, as was presumed, due to the kraft pulping process. After depolymerization in supercritical conditions, the ash content of DBL was observed to be the same as that of BL, suggesting that inorganics did not get stuck in the system. As expected, the ash content of SD and OD were increased due to the sulfuric acid addition during precipitation step. However, the increment of the ash content for OD and SD were only around 25%, which is much lower than the acid amount added for precipitation. This might have been due to gas formation during precipitation [46]. Therefore, some part of the lignin or lignin-derived compounds could have been recovered from the inorganics and contributed to the total lignin calculations, which can explain the slight increment of total lignin in SD and OD products.

Table 1 shows the difference in total lignin percentages between before the reaction (BL) and after the reaction (DBL) were different (32% w/w vs 26% w/w). The configuration of the pilot plant does not allow checking the gases formed during the reaction. However, it is known that during supercritical water depolymerization of lignin, some gases are being formed. The difference between BL and DBL in terms of total lignin percentages could have been due to gas formation during the process. Another possibility that caused this decrease could be gas formation during precipitation by strong acid. Modification in the structure of the lignin and lignin-derived materials after depolymerization in SCW may have made the compounds in the DBL more prone to gas evolution during precipitation. It is also widely known in industry and literature that extreme gas evolution occurs during precipitation, including CO_2 and H_2S [47]. Yet, this argument should be verified in-depth using other characterization techniques. The total lignin in the EA product was found to be the highest since the aromatic depolymerized fraction was extracted from the complex matrix into the ethyl acetate fraction and became almost completely free of ash.

Elemental analysis results of the selected products are given in Table 2. CHNS elements were analyzed by elemental analyzer, inorganics were determined via ash analysis, and oxygen was estimated as the balance. The maximum error percentage was less than 3% w/w. According to these results, the products can be grouped into three categories. In the first group, the H:C ratio decreased from 1.55 in BL to 1.29 in DBL, indicating that dehydration reactions took place during hydrothermal treatment, which is common for the supercritical water depolymerization of lignin [37]. This suggests that more aromaticity

Table 2
Elemental Analysis of Samples (Dry Basis).

	AVERAGES									
	N	C	H	S	O + Inorg.	Inorg.	HHV (MJ/kg)	LHV (MJ/kg)	H:C	O:C
Black Liquor (BL)	1.51	33.36	4.34	0.00	60.79	48.9	14.47	13.50	1.55	0.27
Depolym. BL (DBL)	1.69	33.02	3.56	0.49	61.25	48.5	13.40	12.61	1.29	0.29
Spray Dried (SD)	1.59	23.79	2.07	0.28	72.27	60.7	8.27	7.81	1.04	0.36
Oven Dried (OD)	1.54	24.41	2.08	1.96	70.01	59.8	8.83	8.36	1.01	0.31
EA Extracted (EA)	1.50	57.56	4.85	0.00	36.09	2	22.22	21.13	1.00	0.44

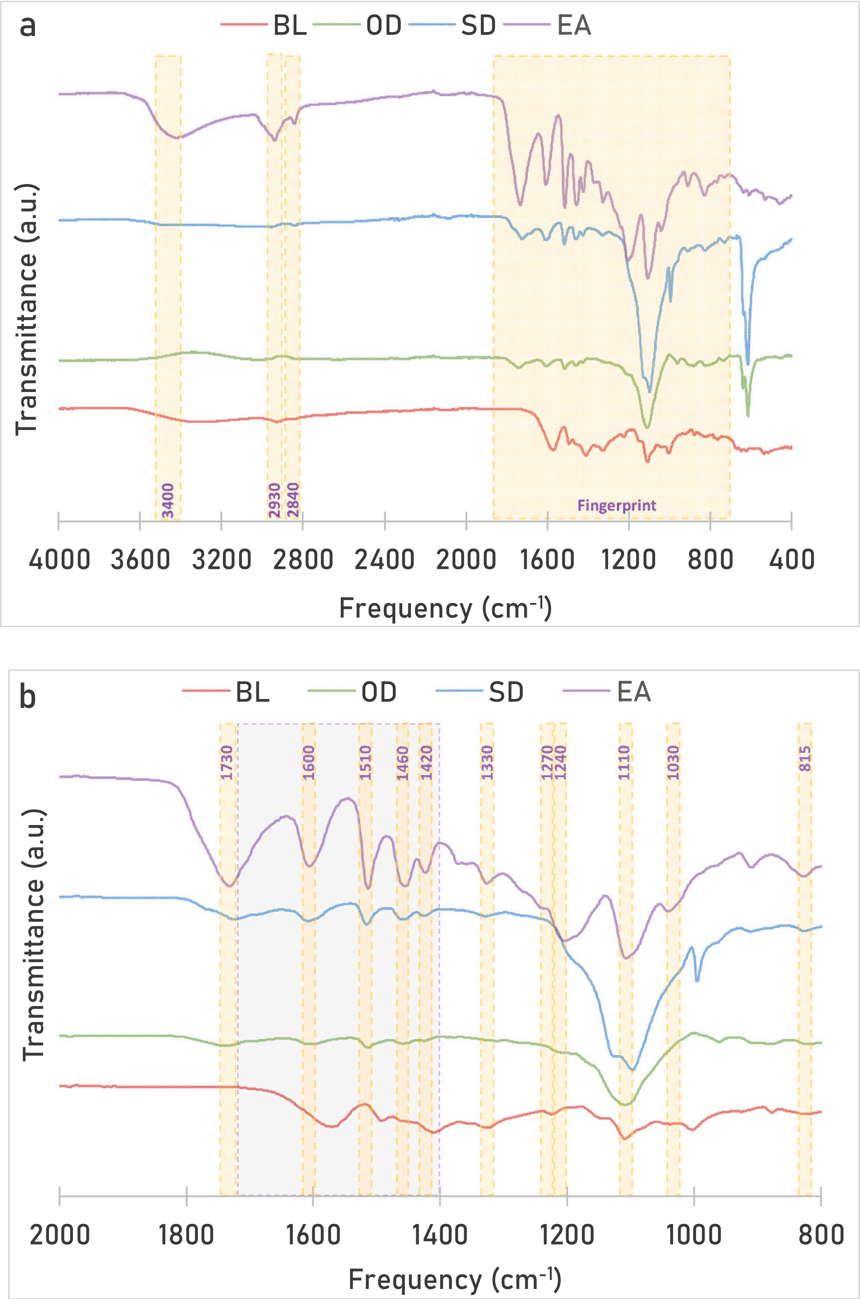

Fig. 8. FTIR Spectra; (a) full spectrum, (b) fingerprint region in detail.

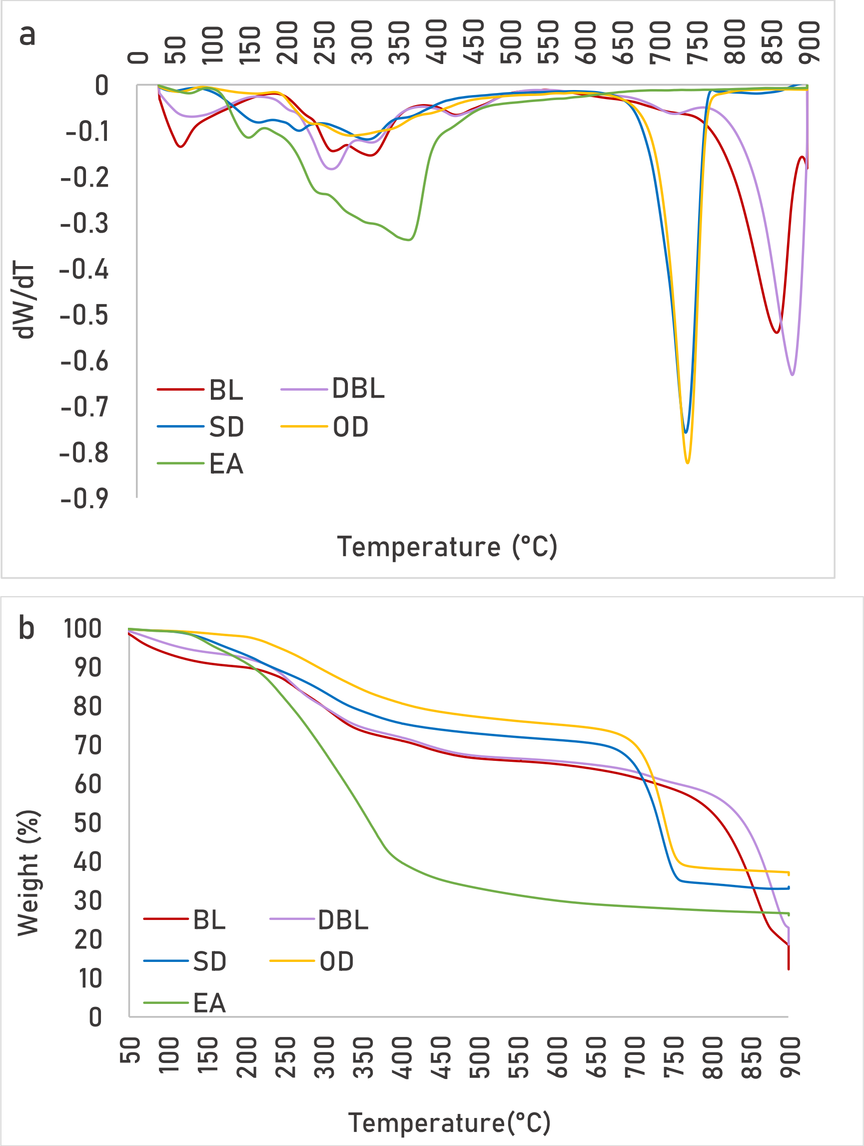

Fig. 9. DTG (a) & TGA (b) diagrams of the samples.

and/or the presence of double bonds in DBL are expected. However, when examining the H:C and O:C ratios together, it appears that demethylation occurred overall. Van Krevelen diagram of elemental analysis results can be found in Figure S7. Another important point is the difference of the components identified by GC-MS in Fig. 6 between BL and DBL. The carboxylic group-containing components present in raw BL disappeared in DBL samples, indicating that decarboxylation occurs during the process. A study by a previous group member also supports the existence of decarboxylation reactions during supercritical water experiments [33]. Nevertheless, the increase in methoxy groups in DBL samples, alongside elemental and GC-MS analysis results, indicates that various types of reactions occur simultaneously. The second group includes SD and OD, and these products have H:C ratios of 1.04 and 1.01, respectively. The last group contains the EA product, which has the lowest H:C ratio of 1.00. The difference between DBL and the second group is only in the acidification and drying of the materials, suggesting that CO_2 was likely released during the drying process. The varying ash content in the products resulted in broad higher heating value (HHV) calculations. The lack of ash content gives an advantage to the EA product, showing an HHV value of 22.2 MJ/kg.

The chemical structures of black liquor, and the products were examined by attenuated total reflection FTIR spectroscopy which can be found in Fig. 8. Fig. 8a and b are the spectra obtained by this technique. Total wavenumber range analysis is given in Fig. 8a, whereas a close-up view of fingerprint range analysis can be found in Fig. 8b. The broad band formed by EA-extracted product at 3400 cm^{-1} belongs to the phenolic and/or alcoholic units O-H stretching. Regarding the bands at 2930 and 2840 cm^{-1}, aliphatic groups C-H bonds vibration can be assigned to these bands (-CH_2 groups for 2930 cm^{-1}, and -CH_3 groups for 2840 cm^{-1}). Black liquor 3400 cm^{-1} and 2940 cm^{-1} absorption bands were vaguely recognizable, although the intensity of the bands was very low because of high inorganic content. The fingerprint region of these products started around 1900 cm^{-1}. The stretching of C=O bonds at 1730 cm^{-1} was originated from lignin, and as it can be seen in Fig. 8b, it is visible for all three products except black liquor. The aromatic skeletal vibrations of lignin can be found between 1700 and 1400 cm^{-1} (Fig. 8b - dotted area). The signals observed at 1600 and 1510 cm^{-1} were due to the C-C aromatic skeletal vibrations, while the bands at 1460 and 1420 cm^{-1} were formed by the -CH_2 and -CH_3 groups' C-H deformation, and C-H aromatic ring vibrations, respectively. The bands between 1700 and 1200 cm^{-1} found the highest in ethyl acetate extracted product compared to the other products, that supports the increased aromaticity of the ethyl acetate extracted fraction of the DBL.

The nature of the feedstock brings along some small differences for the bands that can be observed in FTIR in terms of being softwood or hardwood. Since the starting material was eucalyptus, as it was mentioned before, signals that correspond to both syringyl (S units) and guaiacyl units (G units) can be seen in Fig. 8b clearer. The bands at 1270 and 815 cm^{-1} are the typical signals that were well known in the literature which correspond to G units [5]. Considering the S units absorption signals, the bands at 1330 cm^{-1} that were formed from C═O stretching, also a small shoulder of C═O stretching in syringyl units was assigned to 1240 cm^{-1}, and at 1110 cm^{-1} was due to aromatic C-H in plane deformation of S units. Additionally, the small shoulder around 1030 cm^{-1} could be attributed to aromatic ring deformation which is usually more intense for G units compared to S units.

Thermogravimetric analysis (TGA) was performed to study the stability and degradation behavior of the selected products (Fig. 9). As with the elemental analysis, TGA/DTG results can also be divided into three groups. Although the samples were dried before analysis, the BL and DBL samples showed some moisture content up to 100°C. For the other products, the moisture content was less than 1%. The degradation of lignin-derived monomeric compounds generally occurs between 120 and 265°C, in addition to carbohydrate degradation [48,49]. Regarding high boiling point monomeric components, the last degradation zone for lignin was accepted as between 300 and 500°C [50]. BL and DBL started to degrade at around 190°C, and only one peak was observed up to 300°C. Nevertheless, while OD exhibited similar behavior between 120 and 300°C, SD degradation started around 120°C. This supports that SD has a greater amount of lower molecular weight components compared to OD. This could also explain why SD had a higher acid-soluble lignin (ASL) content in its chemical composition according to Table 1. Apart from that, the EA product had the highest degradation among the other products between 120 and 500°C, where lignin degradation ends. Fig. 9 demonstrates that the degradation profiles of BL, DBL, OD, and SD are quite similar between 300 and 500°C. However, their profiles changed above 575°C, the region that is accepted as the end of total carbon removal. Above 575°C, the BL and DBL samples exhibited volatilization at higher temperatures compared to SD and OD. Since BL and DBL were not acidified, large amounts of lignin remained bonded to inorganics as phenolates/carboxylates of sodium or potassium. SD and OD were acidified before their drying processes; however, lignin volatilization did not increase. Nevertheless, they showed a lower volatilization temperature for the degradation of inorganic-metal bonded materials compared to BL and DBL. The inorganic-metal bonded materials' degradation occurred between 675 and 775°C for SD and OD. However, for BL and DBL, this range was between 750 and 900°C. According to studies on the thermal degradation of black liquor, carbon compounds do not completely consume up to 575°C. These studies showed that intermediate alkaline compounds still exist at 900°C. These components can be present as –[CO_2M], –[COM], and –[CM], where M represents sodium (Na), potassium (K), or sulfur (S). During the degradation of these intermediates, CO forms [50]. Hence, it can be said that acidification appears to aid in releasing CO and CO_2 gases from the solution. Moreover, from Fig. 9, it can be understood that carboxylates/phenolates of alkaline metals are still present in SD and OD products.

Another important point to note is the degradation peak shift of DBL compared to BL at temperatures over 750°C. The DBL DTG peak shifted around 50°C compared to BL. This could result from repolymerization reactions during the process. The shift in the DTG diagram may indicate the formation of high molecular weight components bonding with metals present in the mixture. After degradation completed at 900°C, the products were subjected to this temperature for an additional 10 minutes. The BL and DBL products continued to lose weight at this temperature, while other products showed no significant difference. Having alkaline metal-carbon structures still present in the matrix should be the reason for this behavior.

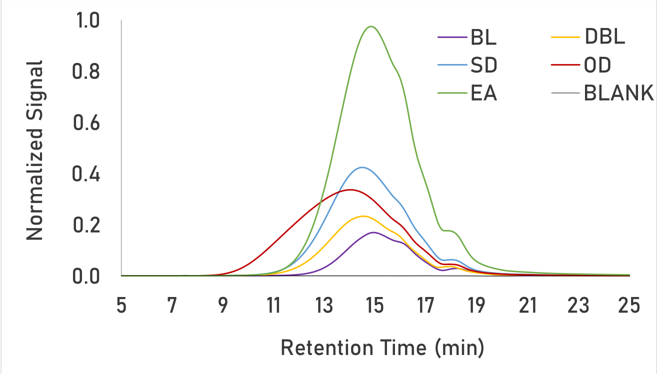

Fig. 10. GPC chromatograms of the samples.

The Gel Permeation Chromatography results graph is presented in Fig. 10. The DBL shifted slightly to a lower residence time compared to black liquor, indicating a greater number of high-molecular-weight components in DBL compared to BL. Among all, the OD sample was the first to show a peak. SD, compared to OD, had a narrower peak, and its highest peak point occurred later than OD, suggesting that SD contains a greater amount of low molecular weight components. According to Gordobil, the drying process and its severity can affect the final lignin product observed. In that study, the difference between 25°C and 55°C drying temperatures of kraft lignin resulted in increased hygroscopicity in the 25°C dried product, and lighter-colored lignin particles were mentioned [51]. Hygroscopicity could be related to the difference in acid-soluble lignin (ASL) amounts between SD and OD, since SD had a lower drying temperature (85°C) compared to OD (105°C). The EA product showed the highest peak abundance compared to other products, as expected, due to having low ash content.

4. Conclusions

It is possible to dry the SCW depolymerized black liquor without losing bio-oil yield. However, the drying technique affects the yields. Spray drying gave better biooils yields than the combination of oven drying and milling. The *fractionation method* was better than the drying methods when separating monomers at high pH. Biopolyol included in the DS-EA fraction yield was found 30% w/w more in DBL. Ash-free total ethyl acetate extracted bio-oil yield found as 77% w/w. Polyols existence in bio-oil enables the production of functionalized materials such as lubricants or polyurethanes by using this fraction directly. This study shows continuous and fast HTL of BL could be a noteworthy option to upgrade traditional pulp & paper refineries in the future.

CRediT authorship contribution statement

Emre Demirkaya: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **María José Cocero:** Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Danilo Cantero:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors do not have any conflicts of interest to declare.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.supflu.2024.106296.

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