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Catalyst-Free Depolymerization of Methanol-Fractionated Kraft Lignin to Aromatic Monomers in Supercritical Methanol

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Abstract: Lignin is considered a renewable source for the production of valuable aromatic chemicals and liquid fuel. Solvent depolymerization of lignin is a fruitful strategy for the valorization of lignin. However, Kraft lignin is highly prone to produce char (a by-product) during the hydrothermal depolymerization process due to its poor solubility in organic solvents. Therefore, the minimization of char formation remains challenging. The purpose of the present study was to fractionate Kraft lignin in methanol to obtain low-molecular-weight fractions that could be further depolymerized in supercritical methanol to produce aromatic monomers and to suppress char formation. The results showed that the use of methanol-soluble lignin achieved a bio-oil yield of 45.04% and a char yield of 39.6% at 280 °C for 2 h compared to 28.57% and 57.73%, respectively, when using raw Kraft lignin. Elemental analysis revealed a high heating value of 30.13 MJ kg^{-1} and a sulfur content of only 0.09% for the bio-oil derived from methanol-soluble lignin. The methanol extraction process reduced the oxygen content and increased the hydrogen and carbon contents in the modified lignin and bio-oil, indicating that the extracted lignin fraction had an enhanced deoxygenation capability and a higher energy content. These findings highlight the potential of methanol-soluble Kraft lignin as a valuable resource for sustainable energy production and the production of aromatic compounds.

Keywords: Kraft lignin; methanol-soluble lignin; hydrothermal liquefaction; bio-oil; phenolic monomer

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1. Introduction

To address the global issue of energy resource scarcity, there has been a strong recent focus on the development of eco-friendly production methods for energy, fuel, and chemicals [1]. Given the rising demand for sustainable options in the face of potential fossil fuel depletion and environmental pollution arising from fossil fuel combustion, a large volume of research has investigated the use of lignocellulose, which contains lignin, cellulose, and hemicellulose, as a promising renewable biomass resource. The lignin structure is capable of holding a variety of renewable aromatic compounds, which can be used in bulk and fine chemical production [2]. Notably, among various kinds of lignins, Kraft lignin and its derivatives have experienced steady market growth, reaching USD 599 million, with a projection of USD 704 million by 2022 [3]. However, despite an annual global production of 70 million metric tons from Kraft pulp mills, Kraft lignin is primarily used as a low-value fuel in recovery boilers. This is because the use of lignin as a sustainable source of aromatic chemicals is limited by the inherent difficulty of depolymerizing Kraft lignin to produce selective phenolic monomers [4].

So far, various depolymerization methods, including pyrolysis, liquefaction, gasification, hydrogenolysis, and oxidative cracking, have been explored to generate valuable products from lignin [5]. In particular, the use of hydrothermal liquefaction (HTL) has recently gained particular research interest to convert waste biomass to value-added products [6–10]. HTL and related techniques such as solvothermal methods can effectively depolymerize biomass under mild conditions [11,12], boosting the yield of oil and reducing char formation [13]. The choice of solvent in HTL (e.g., methanol or ethanol) can also influence product yields by improving the solubility and potential hydrocarbon production [14,15]. Kumar et al. [16] reported that solvents provide hydrogen for the catalytic process while mitigating safety concerns associated with the handling of gaseous hydrogen. Hydrogen-donor solvents, such as methanol, ethanol, formic acid, etc., can serve as internal hydrogen sources. The application of supercritical methanol has garnered significant attention due to its unique physicochemical properties that facilitate the efficient breakdown of lignin's complex structure. Operating above its critical temperature and pressure, supercritical methanol not only enhances the solubility of lignin but also acts as a potent hydrogen donor, promoting the cleavage of ether linkages and yielding a diverse array of phenolic compounds. Mankar et al. [17] investigated the production of aromatic compounds from Kraft lignin using a Pt/HZSM-23 catalyst in supercritical methanol (scMeOH), achieving an 87.3% lignin conversion and yielding 65.1% bio-oil, being primarily composed of aromatics. In another report, Wu et al. [18] achieved an 87.62% lignin conversion in a methanol–water system at 260 °C and 3 MPa N_2 for 4 h, with a monophenol yield of 42.25%. In contrast, scMeOH showed much lower monomeric yields (3.3–7.8 wt%) and higher solid residue yields (26–31 wt%) compared to those from a subcritical water (subH_2O) system, where monomeric yields ranged from 6.2 to 17.9 wt% and solid residue yields were 16–17 wt%. Hidajat et al. [19] found similar results when treating Kraft lignin in methanol, reporting monomeric yields of 3.3–7.8 wt% and solid residue yields of about 26–31 wt% at 330 °C for 30 min. Lignin depolymerization is complicated by char formation because reactive components can lead to insolubilization through cross-linking reactions [20]. Noble metal catalysts (Pt, Pd, and Ru) have been used for lignin depolymerization and the suppression of char formation due to their high performances under reductive conditions [21,22]. However, the catalytic transformation of lignin into defined aromatics remains difficult due to its resilient and amorphous nature [23], while the use of base/acid or metal catalysts can lead to repolymerization, environmental pollution, and complicated post-treatment processes [24]. Thus, it is important to develop a more environmentally, benign, and sustainable technology using a metal-free medium to accelerate free radical formation without the need for additional catalysts.

Researchers have employed a diverse range of physical, chemical, and biological methods to degrade or modify lignin, with the aim of reducing its molecular weight and expanding its range of potential applications [25,26]. In particular, solvent-fractionated lignin exhibits a simpler and more uniform molecular structure and a higher number of active functional groups, making it highly promising for use in electrode materials, fine chemicals, and pharmaceuticals [27–30]. Solvent-fractionated lignin that is rich in phenolic hydroxyls and exhibits bioactive characteristics is also suitable for use in energy storage applications and antibacterial materials [31]. Considering the various advantages of lignin fractionation in solvents, Goldmann et al. [32] studied the solubility and fractionation of commercially available Indulin AT Kraft lignin in ethanol–water mixtures and measured the molar mass and phenolic hydroxyl group content in the resulting lignin fractions. Dastpak et al. [33] investigated six different organic solvents as potential solubilizing agents for lignin and found that both organosolv lignin (OL) and Kraft lignin (KL) demonstrated high solubility despite significant differences in their functional group contents and average molecular weights. Drame et al. [34] evaluated the solubility of Kraft lignin in organic solvents and observed that lignin solubility correlated with the hydrogen-bonding Hansen parameter and the branching levels of the solvents. They also found that the behavior of the solubilized lignins was influenced more by the production process of the lignins than by the solvents used for their solubilization. Ribeiro et al. [35] further explored the impact of solvents on lignin solubility, noting that solvent fractionation resulted in more homogeneous lignin cuts, enhancing the potential for lignin applications across a broader range of industries. Araujo et al. [36] used five different solvents—namely ethyl acetate, methyl ethyl ketone, methanol, acetone, and dioxane–water—for the fractionation of Kraft lignin. They observed that the fractionated Kraft lignin has a lower molar mass and higher heating value as compared to the raw Kraft lignin. In another study, Duval et al. [37] tested three classes of solvents, including alcohols, esters, and ketones, for the fractionation of Kraft lignin. Saito et al. [38] isolated an MeOH-soluble fraction of softwood Kraft lignin with the use of a methanol solvent and extensively investigated the fundamental changes in the MeOH-soluble fraction of lignin, such as its molecular weight, glass transition temperature (T_g), and other chemical properties. Their findings indicated that the MeOH-soluble fraction of lignin had a higher low-molecular-weight content compared to raw softwood Kraft lignin coupled with a lower T_g of 117 °C. Although the MeOH-soluble fraction of Kraft lignin has previously been separated and reported, further investigation of depolymerizing this fraction to produce significant aromatic monomers has not been conducted.

Therefore, the present study focused on fractionating commercially available Kraft lignin in methanol and further depolymerizing it into valuable phenolic compounds. Moreover, the impact of the reaction time and temperature on the yield of bio-oil, char, and phenolic compounds were also carefully investigated. The separated MeOH-soluble lignin was characterized via Fourier-transform infrared spectroscopy (FT-IR) and elemental analysis, while the produced bio-oil was assessed using gas chromatograph–mass spectrometry (GC-MS), FT-IR, and elemental analyses.

2. Materials and Methods

2.1. Materials

Kraft lignin from pine wood was procured from Sigma-Aldrich, Saint Louis, MO, USA (CAS no. 8068-05-1; product no. 370959). Pine wood was selected as the lignin source because of its relevance to industrial processes and widespread availability. The chemicals and solvents employed in the study, including MeOH (≥98%) and ethyl acetate ($CH_3COOC_2H_5$), were also obtained from Sigma-Aldrich (USA, ≥99.5%). All chemicals and solvents were utilized as received without undergoing additional purification steps.

2.2. Lignin Extraction

The process used to isolate the MeOH-soluble fraction from the Kraft lignin is presented in Figure 1. The Kraft lignin was first mixed with MeOH at a solid-to-liquid ratio of 1:30 and constantly stirred for 3 h. About 60.27% of the Kraft lignin was soluble in methanol. The MeOH-soluble Kraft lignin was then separated from the insoluble fraction using filter paper. The separated MeOH-soluble lignin was subsequently dried in an oven overnight to produce a solid residue, which was then crushed into a fine powder. The powdered lignin was stored at room temperature for subsequent analysis.

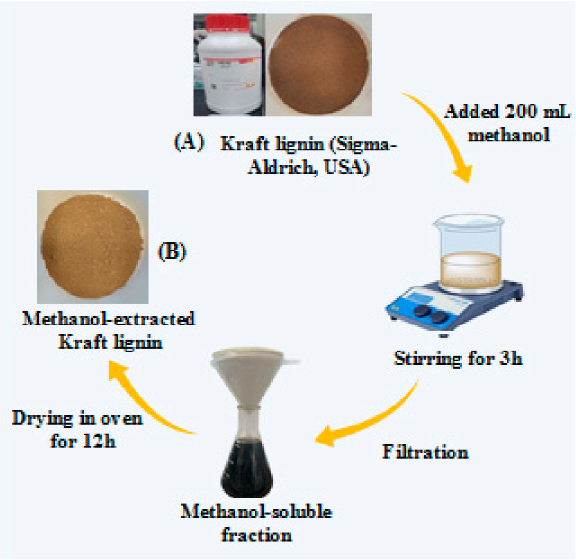


Figure 1. Preparation of methanol-soluble lignin from raw Kraft lignin.

2.3. Lignin Depolymerization

The experimental process was conducted in a 150 mL batch reactor (Hastelloy-C-276; HR-8300, Hanwoul Engineering, Gunpo-City, Republic of Korea) equipped with a reactor controller (Parr 4848). In the initial phase of each experiment, 2.0 g of MeOH-extracted Kraft lignin and 90 mL of MeOH were loaded into the reactor (Figure 2). The reactor was sealed and purged with N_2. The reactor was heated to a predetermined reaction temperature at a controlled rate of 10 °C min^{-1} using an electric furnace. The reactor was maintained at the designated temperature for a specified reaction duration. Once the reaction period had ended, the reactor was cooled to room temperature using an ice–water bath. The reactor was then vented and the reaction product collected. The product was washed through a filter with MeOH, with the liquid portion collected. The solid residue, which consisted of unreacted lignin and char components, was washed several times with tetrahydrofuran (THF). The THF-soluble products (filtrate) was then rotary evaporated to obtain the unreacted lignin, while the THF-insoluble products (char) was oven dried at 110 °C and then weighed. The liquid portion was evaporated using a rotary evaporator at a reduced pressure and 60 °C to remove the methanol solvent and produce bio-oil, which appeared as a brown liquid. The bio-oil was then weighed and collected for subsequent analysis. The yields of the bio-oil, char, unreacted lignin, and gas were determined using Equations (1)–(4), respectively:

$$\text{Yield}_{\text{bio-oil}}\ (\text{wt\%}) = (\text{Weight}_{\text{bio-oil}}/\text{Weight}_{\text{lignin}}) \times 100\% \quad (1)$$

$$\text{Yield}_{\text{char}}\ (\text{wt\%}) = (\text{Weight}_{\text{THF insoluble residue}}/\text{Weight}_{\text{lignin}}) \times 100\% \quad (2)$$

$$\text{Yield}_{\text{unreacted lignin}}\ (\text{wt\%}) = (\text{Weight}_{\text{THF soluble products}}/\text{Weight}_{\text{lignin}}) \times 100\% \quad (3)$$

$$\text{Yield}_{\text{gas}}\ (\text{wt\%}) = 100 - (\text{Yield}_{\text{bio-oil}} + \text{Yield}_{\text{char}} + \text{Yield}_{\text{unreacted lignin}}) \quad (4)$$

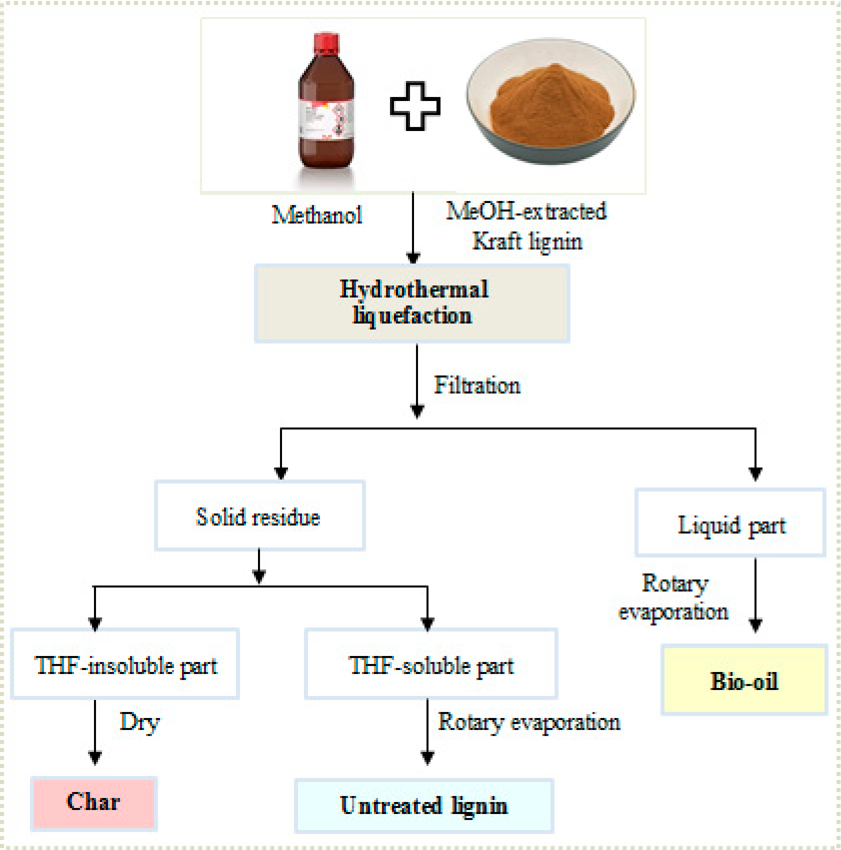


Figure 2. Lignin depolymerization and bio-oil separation processes.

The experimentation process was repeated three times for each trial, and the average value is presented.

2.4. Product Analyses

The bio-oil was qualitatively and quantitatively analyzed using GC-MS (Agilent 6890, Santa Clara, CA, USA) equipped with an HP-5MS capillary column (30 m × 0.25 µm × 0.25 mm). High-purity helium (He) was employed as the carrier gas (flow rate: 1 mL min^{-1}). The column temperature was held at 40 °C for 2 min, followed by an increase to 170 °C at a heating rate of 10 °C min^{-1}, where it was held for 5 min. The temperature was then increased again to 300 °C at a heating rate of 10 °C min^{-1} and was held for an additional 2 min. The individual components in the bio-oils were identified by comparing their GC-MS spectra and retention times with the reference compounds cataloged in the mass spectral library of the National Institute of Standards and Technology. Selective phenolic compounds (phenol, guaiacol, 4-methyl guaiacol, 4-ethyl guaiacol, 4-propyl guaiacol, eugenol, vanillin, acetovanillone, isoeugenol, and homovanillic acid) were quantified using an external calibration method. Their yields were determined using Equation (5):

$$\text{Yield of monomer (wt\%)} = (\text{Weight of the specific monomer}/\text{Total weight of the lignin sample}) \times 100 \tag{5}$$

FT-IR analysis used a 400 FT-IR spectrometer (PerkinElmer, Waltham, MA, USA) operating at a resolution of 1 cm^{-1} across a wavelength range of 500–4000 cm^{-1}. Elemental analyses of the feed Kraft lignin, MeOH-soluble lignin, and bio-oil were conducted using a Vario MACRO cube analyzer (Hanau, Germany). The carbon (C), hydrogen (H), and nitrogen (N) contents of the lignin and lignin-derived bio-oil were determined using an elemental analyzer, with the O content calculated as the resulting difference. The high heating value (HHV), which is used to assess the potential energy yield from a material, of the Kraft lignin and lignin oil was calculated by considering the elemental composition, including C, H, N, sulfur (S), and O, according to the DIN 51900 standard shown in Equation (6) [4]:

$$\text{HHV (MJ kg}^{-1}) = [(34 \times C) + (124.3 \times H) + (6.3 \times N) + (19.3 \times S) - (9.8 \times O)]/100 \tag{6}$$

3. Results and Discussion

3.1. Characterization of MeOH-Soluble Lignin and Raw Kraft Lignin

The FT-IR spectra presented in Figure 3 show notable differences between the raw Kraft lignin and the MeOH-soluble lignin derived from MeOH treatment. The peak at 3382 cm^{-1}, corresponding to hydroxyl groups (O–H) from aliphatic and aromatic compounds, exhibited a lower intensity in the MeOH-soluble lignin compared to the raw Kraft lignin. This reduction represents a decrease in the hydroxyl groups in the MeOH-soluble fraction. The presence of C–H bonds in the methyl and methylene groups was indicated by the presence of peaks at 2940 cm^{-1}, and the decrease in their intensity in the MeOH-soluble lignin was indicated by a weakening of C–H bonds during the MeOH extraction process.

A carbonyl peak was also observed at 1662 cm^{-1}, corresponding to the stretching of the C=O functional group in the lignin side chain conjugated with aromatic compounds. Aromatic features were represented by peaks at 1590 cm^{-1} and 1510 cm^{-1}, reflecting aromatic skeletal vibration and ring stretching [39,40]. Additionally, the peak at 1452 cm^{-1}, indicating C–H deformation, had a lower intensity in the MeOH-soluble lignin, suggesting that the aromatic nature of lignin remains intact following MeOH treatment. The peak at 1370 cm^{-1}, representing the phenolic hydroxyl group, had a higher intensity in the raw Kraft lignin, revealing a difference in the phenolic hydroxyl content between the two samples. This is corroborated by the decrease in the intensity of the peak at 1130 cm^{-1} [41]. Structural units such as guaiacyl units were represented by peaks at 1269 cm^{-1} and 853 cm^{-1}, with a corresponding peak at 1215 cm^{-1} indicating guaiacyl rings. The lower intensity of the latter peak for MeOH-soluble lignin suggests a reduction in the G unit content during extraction. Similarly, the peak at 1029 cm^{-1}, which was associated with C-O-C stretching [42], decreased in intensity in the MeOH-soluble lignin. Collectively, these FT-IR results indicate that MeOH treatment had an impact on the hydroxyl content, C-H bonds, carbonyl groups, aromatic structure, phenolic hydroxyl content, and specific structural units such as guaiacyl units.

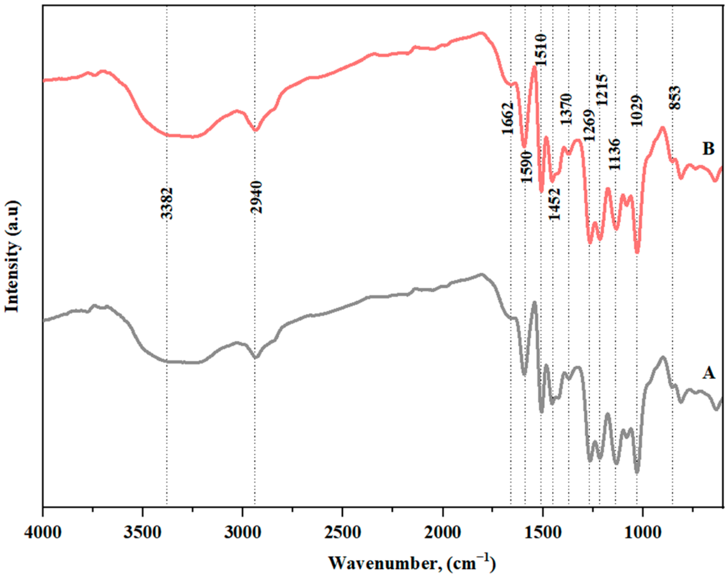


Figure 3. FT-IR analysis of (A) raw Kraft lignin and (B) methanol-soluble Kraft lignin.

3.2. Effects of the Reaction Temperature and Time on the Product Yields

The reaction temperature affects the yield of lignin depolymerization products during the HTL process [43]. Under supercritical conditions, alcohols have several advantages for lignin depolymerization, such as a high lignin solubility, heat transfer, and dispersion capacity, and alcohol self-conversion is also facilitated [44]. To optimize the reaction temperature and achieve higher depolymerization yields in supercritical MeOH, HTL was conducted for 2 h at temperatures of 260, 280, 300, and 320 °C in the present study. Figure 4 shows that the yields of bio-oil and char were strongly dependent on the reaction temperature, with considerable changes observed between 260 and 300 °C. At 260 °C, the yields of bio-oil and unreacted lignin were 38.03 wt% and 13.80 wt%, with a char yield of 34.37 wt%.

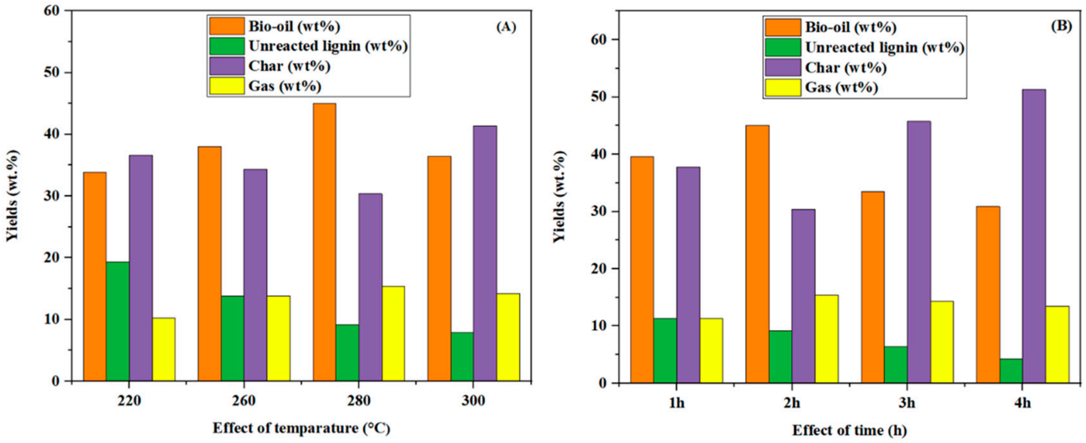


Figure 4. Yields of depolymerized products obtained after hydrothermal liquefaction of methanol-soluble Kraft lignin in supercritical methanol under different (**A**) temperatures and (**B**) reaction times.

When the temperature was increased from 220 to 280 °C, the bio-oil yield rose to 45.04 wt%, while the yields of char and unreacted lignin decreased to 30.38 wt% and

9.22 wt%, respectively (Figure 4A). This increase in the bio-oil yield with a rise in the temperature can be ascribed to the fact that a high temperature (more than 220 °C) could provide the sufficient energy to cleave the β-O-4 linkages in lignin, which resulted in a higher degree of lignin depolymerization [45]. At a lower hydrotreatment temperature (<280 °C), only weaker bonds within the lignin network, such as alkyl ether bonds, are cleaved, leading to the formation of larger lignin fragments [46]. These larger polymeric fragments are prone to repolymerization, which results in a high char yield (36.63 wt%) at 260 °C, due to the formation of insoluble solid products. However, as the hydrotreatment temperature increases, we observe a decrease in char residue, indicating the inhibition of repolymerization reactions. This inhibition may be due to the saturation of free radicals by the hydrogen generated during the depolymerization of lignin, which impedes their ability to recombine and form solid char [47]. Furthermore, the increase in reaction temperature accelerates various reactions, including hydrogenolysis, hydrodeoxygenation, hydrogenation, and decarboxylation, which collectively enhance bio-oil yields. However, increasing the temperature to 300 °C reduced the bio-oil production (36.46 wt%) and increased the percentage of char (41.40 wt%). A further increase in temperature to 320 °C reduced the bio-oil yield further (32.22 wt%) while increasing the char yield (47.75 wt%). This decrease in bio-oil production was most likely due to the intermediate products in the reaction medium undergoing more repolymerization and condensation at higher temperatures, resulting in an increase in char formation [48]. In a previous study, Azadi et al. [31] also reported that secondary repolymerization reactions yielded high amounts of solid residue at higher temperatures.

The reaction time is also an important factor for high lignin conversion rates and the production of bio-oil with desired properties [49,50]. Therefore, we have examined the effect of time on the yield of MeOH-soluble depolymerized lignin products at 280 °C, and the results are shown in Figure 4B. At the initial time of 1 h, the yields of bio-oil and char were 39.54 wt% and 37.74 wt%, respectively, which indicated that lignin depolymerization was insignificant at a low reaction time. An increase in the reaction time from 1 h to 2 h increased the yield of bio-oil from 39.54 to 45.04 wt% and decreased the char yield from 37.74 to 30.38 wt%. Increasing the reaction time further to 3 h and 4 h decreased the bio-oil yields to 33.5 and 30.87 wt%, respectively, with a corresponding increase in the char yields (45.74 wt% and 51.36 wt%). The higher char levels could be due to cross-linking reactions, which become more common as the reaction time increases [51].

For comparison, the depolymerization of raw Kraft lignin was also conducted at 280 °C for 2 h, and the results are displayed in Figure 5. A significant difference in the product yields between Kraft lignin and MeOH-soluble lignin was observed. For Kraft lignin, the yields of bio-oil and char were 28.57 wt% and 53.98 wt%, respectively, while for the MeOH-soluble lignin, the yield of bio-oil increased to 45.04 wt%, and the char yield decreased to 30.38 wt%.

In the case of MeOH-soluble lignin, the increase in the bio-oil yield was possibly due to their higher solubility in methanol solvent as compared to the raw Kraft lignin (which is more susceptible to char formation). Moreover, this observed difference in the product yields can be attributed to differences in the chemical composition and structural properties of the feedstocks. MeOH-soluble lignin likely contains components that are more readily convertible into bio-oil because they are more easily extractable or more amenable to liquefaction. Furthermore, the decrease in the char yield with MeOH-soluble lignin indicates the more efficient conversion of lignin into liquid products via more extensive depolymerization and conversion into bio-oil. Overall, these findings illustrate that the selection of the lignin feedstock is important for lignin valorization processes. In this respect, MeOH-soluble lignin offers advantages in terms of its bio-oil yield and phenolic monomers production.

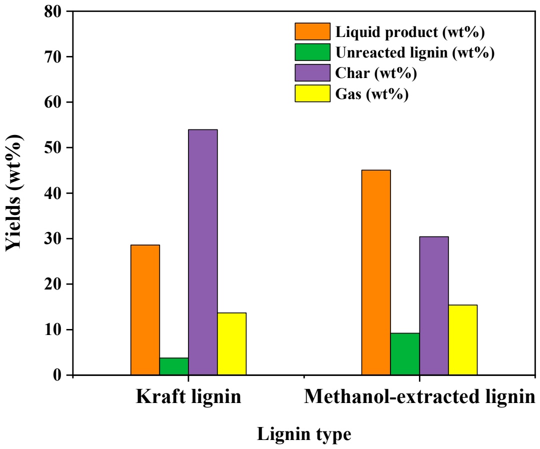


Figure 5. Yields of depolymerized products obtained after hydrothermal liquefaction of raw Kraft lignin and methanol-soluble Kraft lignin in supercritical methanol at 280 °C after 2 h.

3.3. Bio-Oil Characterization

3.3.1. GC-MS Analysis of Bio-Oils

A GC-MS analysis of the bio-oils obtained from the depolymerization of MeOH-soluble lignin and raw Kraft lignin was conducted to identify their components. The primary compounds present in bio-oils, such as guaiacol, 4-methylguaicol, 4-ethhyguaiacol, vanillin, isoeugenol, acetovanillone, and homovanillic acid, are of significant interest due to their potential uses in various applications, including those related to pharmaceuticals, flavors, fragrances, and biofuels. In the present study, phenolic compounds were dominant; this was in accordance with the composition of lignin, which is primarily composed of guaiacyl and phenylpropane units [52]. The presence of these phenolic compounds indicated the successful depolymerization of lignin into smaller, value-added molecules under the employed reaction conditions. Table 1 summarizes the effect of the reaction temperature on the yields of the individual compounds. It was found that the yields of guaiacol (14.91%), methyl guaiacol (5.97%), acetovanillone (1.9%), 1,2-benzene diol-4-methyl (2.06%), and 2,6-dimethoxyphenol (8.70%) were higher at 260 °C, while isoeugenol (4.31%), 4-methoxy-3-(methoxymethyl) phenol (8.93%), and homovanillic acid (6.78%) were more abundant at higher temperatures, such as 280 °C.

Table 1. Yields of major compounds (by relative % peak area) obtained from methanol-soluble lignin depolymerization at different temperatures after a reaction time of 2 h.

RT (min)	Compound	Wt% of Dry Lignin			
		260 °C	280 °C	300 °C	320 °C
13.19	Guaiacol	14.91	7.95	14.79	15.71
16.25	4-methylguaicol	1.02	1.93	4.33	6.83
17.57	2-methoxy-4-vinylphenol	-	-	0.76	2.28
18.67	4-ethylguaiacol	3.15	5.41	10.46	10.46
20.79	Eugenol	-	0.75	0.73	0.93
21.04	4-proylguaiacol	-	0.88	1.86	5.76
21.86	Vanillin	5.76	2.53	0.52	0.80
21.94	Methyl guaiacol	5.97	2.08	-	-
23.14	Isoeugenol	4.22	4.31	2.60	0.50
24.05	Acetovanillone	1.90	1.68	1.21	-

Table 1. *Cont.*

RT (min)	Compound	Wt% of Dry Lignin			
		260 °C	**280 °C**	**300 °C**	**320 °C**
24.81	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)	3.50	3.28	1.56	-
26.29	Benzene acetic acid, 4-hydroxy-3-methoxy	1.63	2.98	2.35	-
26.58	Ethyl vanillate	-	-	0.57	0.90
27.82	Homovanillic acid	5.13	6.78	5.26	4.01
38.47	1,2-benzene diol-4-methyl	2.06	1.76	1.08	0.98
41.08	Gibberellin	1.45	2.02	1.99	1.68
42.15	4,5-Dimethoxy-2-hydroxyacetophenone	2.32	2.70	2.00	1.17
42.32	Dimethyl 2,3-bis(phenylethynyl)fumarate	1.34	1.95	1.66	0.87
42.79	4,5-Dihydroxy-3,6,7-trimethoxyflavone	1.40	1.64	1.60	1.73
42.91	Naphthalene, 1-methyl	20.64	20.65	25.45	27.76
43.65	2,6-Dimethoxyphenol	8.70	8.00	7.13	4.27
44.51	4-Propylguaiacol	-	1.05	0.77	-
46.73	Syringol	0.63	2.90	1.27	0.45
47.75	4-Methoxy-3-(methoxymethyl)phenol	8.93	11.62	3.64	-

Table 2 presents the influence of the reaction time on compound yields at a constant temperature of 280 °C. The data suggest that a prolonged reaction time led to lower yields for some compounds, which were potentially the result of additional side reactions or degradation pathways. However, the yields of other compounds remained relatively stable across different reaction times, highlighting the complex kinetics of compound formation and degradation during lignin depolymerization.

Table 2. Yields of major compounds (by relative % peak area) obtained from methanol-soluble lignin depolymerization with different reaction times at 280 °C.

RT (min)	Compound	Wt% of Dry Lignin			
		1 h	**2 h**	**3 h**	**4 h**
13.19	Guaiacol	6.98	7.95	5.67	15.86
16.25	4-Methylguaicol	1.37	1.93	1.42	3.52
18.67	4-Ethylguaiacol	3.75	5.41	4.65	9.64
20.79	Eugenol	0.76	0.75	-	-
21.04	4-Propylguaiacol	0.58	0.88	-	1.72
21.86	Vanillin	3.56	2.53	-	-
21.94	Methyl guaiacol	3.23	2.08	-	-
23.14	Isoeugenol	5.05	4.31	2.42	2.55
24.05	Acetovanillone	2.03	1.68	1.88	1.62
24.81	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)	2.89	3.28	2.84	1.64
26.29	Benzene acetic acid, 4-hydroxy-3-methoxy	3.39	2.98	2.47	2.03
27.82	Homovanillic acid	6.72	6.78	7.78	6.49
38.47	1,2-Benzene diol-4-methyl	1.69	1.76	1.73	1.51
41.08	Gibberellin	1.60	2.02	2.92	2.41
42.15	4,5-Dimethoxy-2-hydroxyacetophenone	2.42	2.71	3.35	2.80
42.32	Dimethyl 2,3-bis(phenylethynyl)fumarate	1.38	1.95	2.18	1.92
42.79	4,5-Dihydroxy-3,6,7-trimethoxyflavone	1.48	1.64	2.22	1.83
42.91	Naphthalene, 1-methyl	19.85	20.65	36.99	27.3
43.65	2,6-Dimethoxyphenol	7.35	8.00	11.30	8.42
44.51	2-Methoxy-4-vinyl pheno	0.923	1.05	1.303	0.89
46.73	Syringol	2.612	2.891	-	-
47.75	4-Methoxy-3-(methoxymethyl)phenol	11.06	11.62	6.542	3.63

In Figure 6, the yields of different phenolic compounds are compared between raw lignin and MeOH-soluble lignin under the same depolymerization conditions. The results indicate that lignin solubility had a significant impact on the yield of phenolic compounds. It is, thus, important to understand the optimal conditions for the maximum yield of target compounds in order to optimize lignin depolymerization processes and enhance the efficiency and selectivity of bio-oil production.

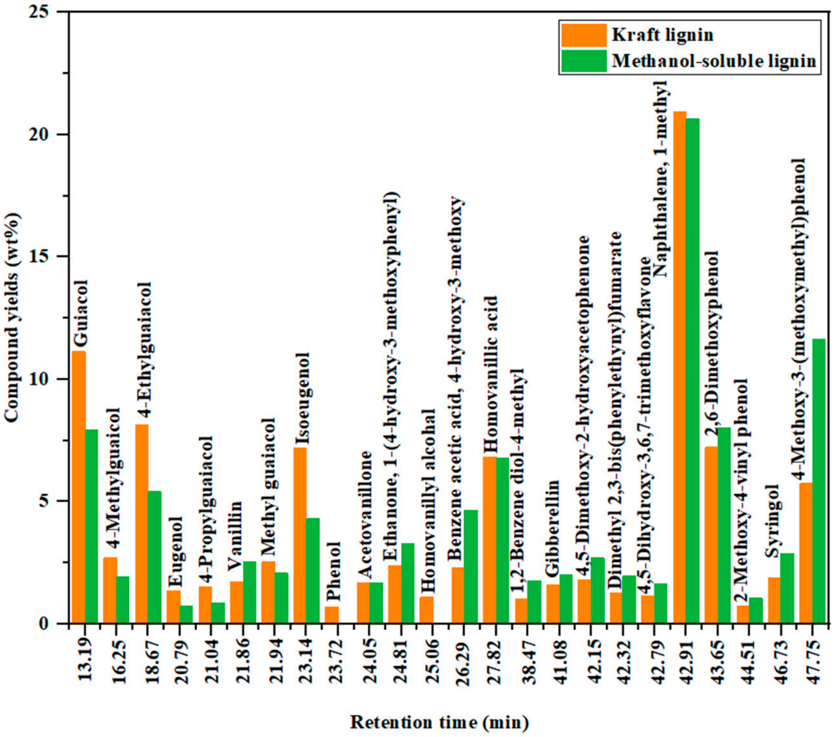


Figure 6. Yields of major compounds obtained from raw Kraft lignin and methanol-soluble lignin depolymerization at 280 °C after 2 h.

3.3.2. FT-IR Analysis of the Bio-Oils

FT-IR analysis was conducted to investigate the structural changes that occurred in MeOH-soluble lignin at different depolymerization temperatures (Figure 7A) and reaction times (Figure 7B). The FT-IR spectra and summary of the characteristic peaks (Figure 7A and Table 3, respectively) suggest that bio-oils obtained under all liquefaction conditions had similar functional group band assignments (e.g., carbonyl, methyl, methylene, and carboxyl), although with varying peak intensities. The broad absorption peak observed at around 3092 cm^{-1} to 3627 cm^{-1} was attributed to the stretching vibrations of intermolecular bonded hydroxyl groups, while the moderate absorption peaks between 2851 cm^{-1} and 2934 cm^{-1} corresponded to the C–H stretching vibrations of methyl and methylene groups. The intensity of these bands increased with the depolymerization temperature and reaction time.

The highest peak intensities were observed for bio-oil obtained at 280 °C after 2 h. These results indicate that MeOH-soluble lignin was effectively depolymerized into various types of alkyl-substituted phenolic compounds under these reaction conditions. The stretching vibrations at 1715 cm^{-1} were ascribed to the carbonyl group in non-conjugated ketone, carbonyl, and ester groups. This peak had a lower intensity at 280 °C and 2 h than under other conditions, indicating a decrease in the concentration of compounds containing carbonyl groups, such as ketones, aldehydes, or esters. The sharp peaks at 1606 and 1508 cm^{-1} were identified as C–H stretching in aromatic rings. The intensity of these bands was higher in the bio-oil obtained at 280 °C and 2 h. The bands observed at 1253, 1141, and 1110 cm^{-1} were due to the stretching vibration of C–O bonds attached to the guaiacyl ring, while the peak at 1029 cm^{-1} was related to the C–O vibrations in ether, acid, or ester groups. In addition, the intensities of the peaks at around 804 and 743 cm^{-1} were found to increase in the bio-oil obtained at 280 °C and 2 h, indicating a higher content of para-substituted aromatic monomers in the bio-oil.

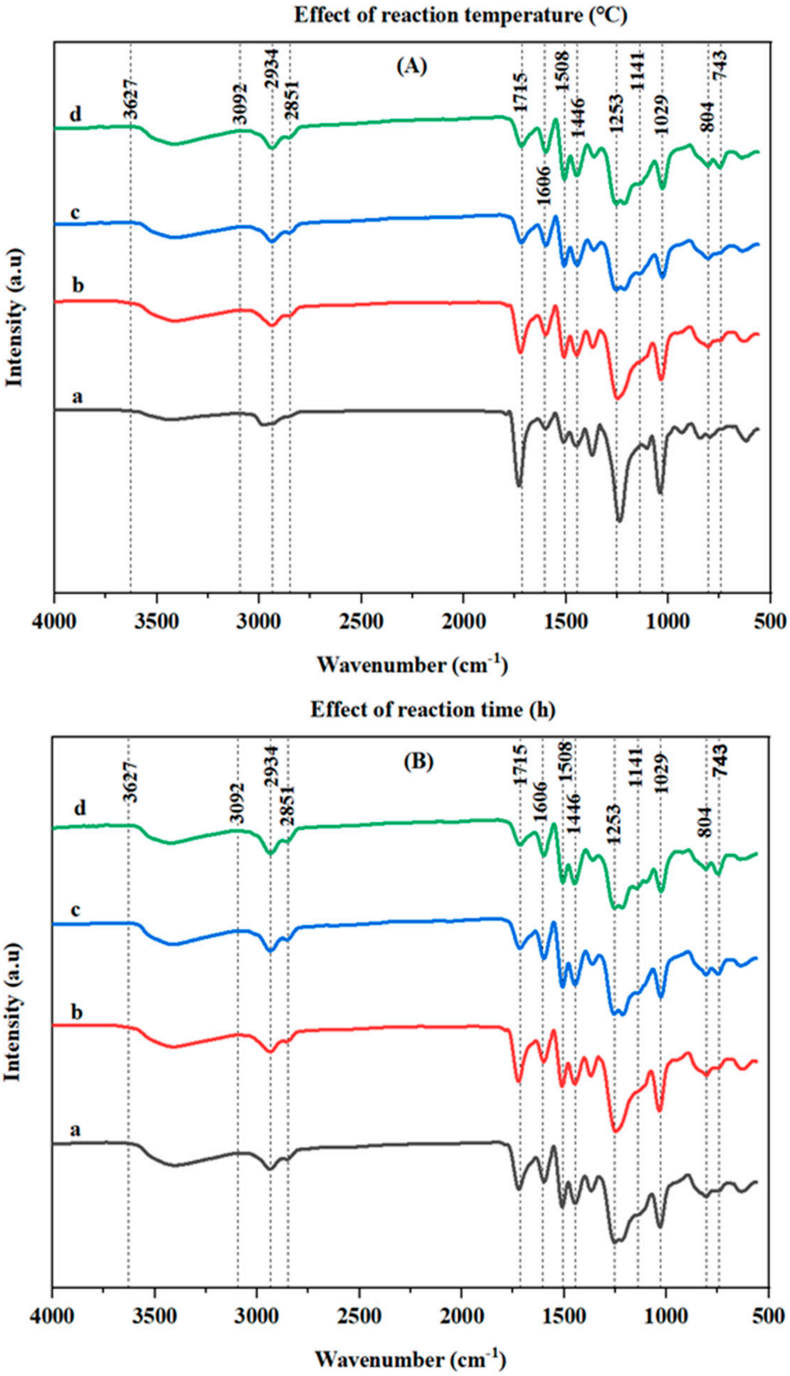


Figure 7. (**A**) FT-IR analysis of bio-oil obtained from methanol-soluble Kraft lignin with a reaction time of 2 h and temperatures of (a) 260 °C, (b) 280 °C, (c) 300 °C, and (d) 320 °C. (**B**) FT-IR analysis of bio-oil obtained from methanol-soluble Kraft lignin at a temperature of 280 °C and reaction times of (a) 1 h, (b) 2 h, (c) 3 h, and (d) 4 h.

Table 3. FT-IR spectra of Kraft lignin and bio-oils obtained under different reaction conditions.

Wavenumber (cm^{-1})	Characteristics
3092 to 3627	O–H groups
2934	C–H (aliphatic and aromatic groups)
2851	C–H (methoxy groups)
1715	C=O in unconjugated ketone, carbonyl, and ester groups)
1606	Aromatic ring (C=C) vibrations
1508	Aromatic ring (C=C) vibrations
1253, 1141, and 1110	G ring and C–O vibrations
1029	C–O vibrations in ether, acid, or ester groups
804 and 743	Para-substituted aromatic rings

3.3.3. Elemental Analysis

The results of the elemental composition analysis for the raw Kraft lignin, MeOH-soluble Kraft lignin, and the bio-oil resulting from lignin depolymerization are presented in Table 4. It can be seen that methanol extraction resulted in a slight increase in the S content in the modified lignin, potentially due to the selective removal of certain components (such as lignin sulfonate and sulfides compounds) during the extraction.

Table 4. Elemental analysis of Kraft lignin and bio-oils.

Entry	Sample	Elemental Composition (%)					HHV (MJ/kg) *
		C (%)	H (%)	O (%)	N (%)	S (%)	
1	Kraft lignin	60.83	5.80	31.09	0.77	1.52	25.19
2	Methanol-soluble lignin	63.31	6.20	27.52	1.04	1.94	26.98
3	Kraft lignin bio-oil [1]	68.03	7.16	23.81	0.32	0.67	29.85
4	Methanol-soluble lignin bio-oil [2]	64.69	6.34	27.55	0.51	0.91	27.38
5	Methanol-soluble lignin bio-oil [3]	68.04	6.76	23.03	0.43	1.75	29.64
6	Methanol-soluble lignin bio-oil [4]	67.98	7.52	24.12	0.29	0.09	30.13
7	Methanol-soluble lignin bio-oil [5]	68.88	7.20	22.84	0.31	0.77	30.30

[1] Reaction conditions = 2.0 g Kraft lignin and 90 mL methanol, 280 °C for 2 h. [2] Reaction conditions = 2.0 g methanol-soluble Kraft lignin and 90 mL methanol, 260 °C for 2 h. [3] Reaction conditions = 2.0 g methanol-soluble Kraft lignin and 90 mL methanol, 280 °C for 1 h. [4] Reaction conditions = 2.0 g methanol-soluble Kraft lignin and 90 mL methanol, 280 °C for 2 h. [5] Reaction conditions = 2.0 g methanol-soluble Kraft lignin and 90 mL methanol, 280 °C for 4 h. * HHV ($MJ\ kg^{-1}$) = $[(34 \times C) + (124.3 \times H) + (6.3 \times N) + (19.3 \times S) - (9.8 \times O)]/100$.

The raw Kraft lignin had an elemental composition of 60.83% C, 5.8% H, and 31.09% O. Subsequent methanol extraction led to a decrease in the O content, accompanied by increases in H and C in the modified lignin and bio-oil obtained under optimal conditions. These findings were corroborated using GC-MS analysis, indicating a significant decrease in guaiacols and syringol with a high O content in bio-oil derived from MeOH-soluble lignin under optimal conditions compared to bio-oil derived from raw Kraft lignin. Notably, bio-oil obtained from HTL at 280 °C over 4 h exhibited the highest C content (68.88%) and the lowest O content (22.84%), indicating a superior deoxygenation capability compared to other processing conditions. However, the bio-oil obtained from treatment at 280 °C and 2 h had the lowest S content among the tested conditions. The HHV of raw Kraft lignin was 25.18 MJ kg^{-1}, increasing to 26.97 MJ kg^{-1} for the MeOH-soluble fraction, suggesting a higher energy content following MeOH treatment. Moreover, the bio-oil obtained from MeOH-soluble lignin at 280 °C and 2 h had a high HHV of 30.13 MJ kg^{-1}, with an S content of only 0.09%, surpassing the HHV of the bio-oil derived from raw Kraft lignin under the same conditions (29.85 MJ kg^{-1}). Importantly, no significant change was observed in the HHV at higher reaction times.

Figure 8A presents the O/C and H/C ratios for raw Kraft lignin, MeOH-soluble lignin, and the bio-oil fractions, while Figure 8B displays the S/C and H/C ratios. The O/C and H/C ratios for raw Kraft lignin were 0.511 and 0.095, respectively. The O/C ratio for

MeOH-soluble lignin was lower at 0.491, while the H/C ratio increased to 0.097. After 2 h of depolymerization at 280 °C, the O/C ratio for the raw Kraft lignin was 0.457 and the H/C ratio was 0.105.

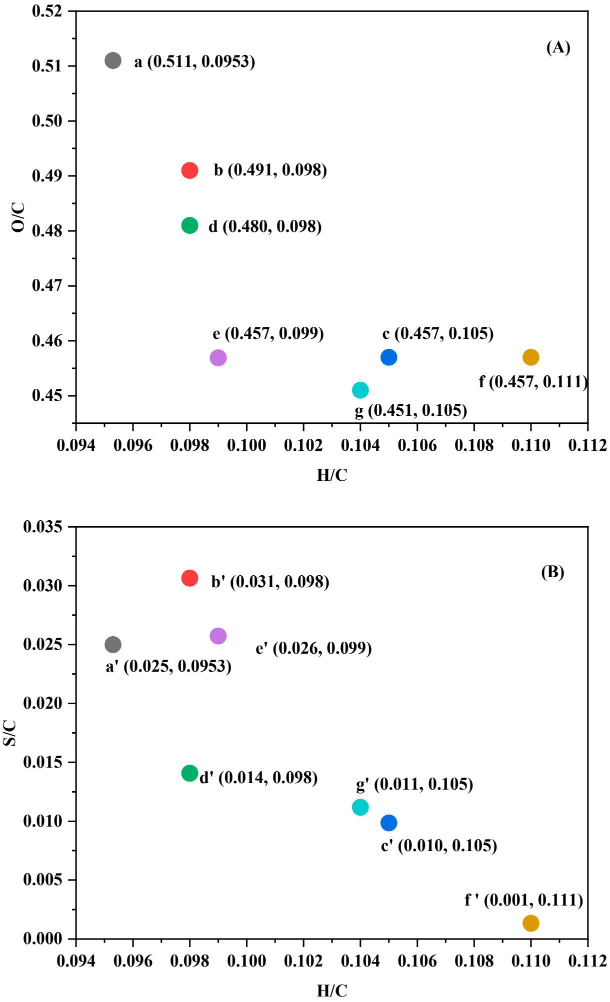
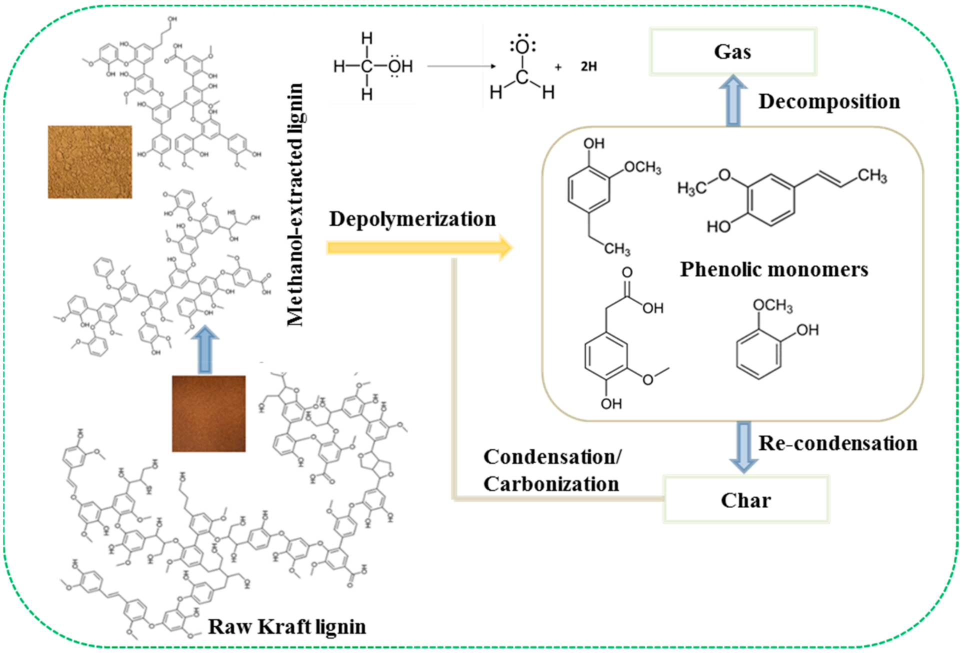


Figure 8. Van Krevelen diagrams of Kraft lignin, methanol-soluble Kraft lignin, and bio-oil. (**A**) O/C vs. H/C and (**B**) S/C vs. H/C ratios for Kraft lignin (a and a′), methanol-soluble Kraft lignin (b and b′), bio-oil obtained from Kraft lignin at 280 °C and 2 h (c and c′), and bio-oil obtained from methanol-soluble Kraft lignin at 260 °C and 2 h (d and d′), 280 °C and 1 h (e and e′), 280 °C and 2 h (f and f′), and 280 °C and 4 h (g and g′).

Under the same reaction conditions, the O/C ratio of the MeOH-soluble lignin fell, but its H/C ratio increased dramatically. This result suggests that MeOH-soluble lignin underwent greater deoxygenation of the depolymerized products and hydrogenation of unsaturated bonds in lignin and lignin-derived depolymerized products. Nielsen et al. [53] reported that the irreversible reaction of MeOH with depolymerized lignin species can inhibit repolymerization and effectively reduce the O content in bio-oil. In another study, Daniel et al. [54] concluded that the presence of S in bio-oil limits its industrial potential. As shown in Figure 8B, the S/C and H/C ratios for the raw Kraft lignin were 0.025 and 0.095, respectively. The S/C ratio increased in the MeOH-soluble lignin, indicating that specific components had been removed selectively during MeOH extraction. However, the S/C ratio dropped significantly to just 0.001 after 2 h of MeOH-soluble lignin depolymerization at 280 °C, representing the production of a more sustainable and environmentally friendly bio-oil.

3.4. Reaction Route and Mechanism

The possible reaction routes involved in lignin depolymerization under supercritical methanol conditions are illustrated in Scheme 1. Rohde et al. [55] reported that MeOH fractionation can successfully extract the low-molecular-weight fraction of Kraft lignin. Under supercritical conditions in HTL, this MeOH-soluble lignin initially decomposes into different reaction intermediates or macromolecular fragments via solvolysis. Singh et al. [56] reported that MeOH acts as a hydrogen donor via formaldehyde formation. The hydrogen released due to the thermal reforming of MeOH leads to the hydrogenolysis of the ether linkages in lignin, resulting in depolymerization and demethoxylation [57]. In another study, Li et al. [58] found that methanol provided hydrogen for the hydrogenolysis of β-O-4 linkages in a non-catalytic reaction, with MeOH transforming into formaldehyde.



Scheme 1. Plausible decomposition pathway for methanol-soluble Kraft lignin in supercritical methanol.

In general, lignin conversion processes involve complex pathways in which the lignin is involved in reactions such as alkylation, deoxygenation, and hydrogenation. Guaiacol, homovanillic acid, eugenol, isoeugenol, and vanillin are key precursors for these transformations. For example, alkylation reactions result in the addition of alkyl groups to phenolic compounds, leading to the formation of derivatives such as 4-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol. Additionally, deoxygenation reactions involve the removal of O atoms from molecules such as homovanillic acid, yielding products such as 4-ethylguaiacol.

4. Conclusions

In this work, the fractionation and depolymerization of commercially abundant Kraft lignin in methanol were investigated. It was observed that the low-molecular-weight fraction of Kraft lignin was successfully extracted in methanol and efficiently depolymerized into phenolic compounds in supercritical methanol. The results showed that there was a significant increase in the bio-oil yield (45.04 wt%) obtained from the depolymerization of the MeOH-soluble fraction at 280 °C over 2 h compared with that for the raw Kraft lignin (28.57 wt%), while the char yield fell by 23.60 wt%. Elemental analysis of the bio-oil revealed an HHV of 30.13 MJ kg^{-1} and a low S content of 0.09% for bio-oil derived from MeOH-soluble lignin, indicating a higher energy content and deoxygenation capability. These results highlight the potential of MeOH-soluble Kraft lignin as a valuable resource for sustainable energy production and the generation of aromatic compounds. This study also demonstrates the effectiveness of MeOH as a supercritical fluid in valorizing Kraft lignin, offering a promising pathway for the use of lignocellulosic biomass in eco-friendly energy and chemical production processes. Furthermore, the ability to utilize this non-soluble fraction as a precursor for energy generation or chemical feedstock aligns with the principles of a circular economy, emphasizing the importance of maximizing resource use and minimizing waste. Future research should focus on developing efficient processes for the valorization of this non-soluble fraction, thereby enhancing the overall sustainability of lignin-based biorefineries.

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