



Catalytic hydrothermal liquefaction of alkali lignin at low temperature: Effect of acid and base catalysts on phenolic monomers production

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Abstract

Developing efficient process and technologies for the conversion of lignin into valuable functional chemicals is an important aspect of the biorefinery concept. In this study, the effect of low-cost base catalyst (NaOH, KOH, K_2CO_3 and Na_2CO_3) and acid catalyst formic acid (FA) was examined for the effective depolymerization of lignin into monomers of phenolic compounds at low temperatures (140, 160 and 180 °C). Also, different reaction residence time (30, 60 and 120 min.), catalyst amounts have been varied to optimize the liquefaction reaction conditions. In the case of non-catalytic experiments, maximum bio-oil yield (14.2 wt.%) was obtained at 160 °C for 30 min. reaction time. With K_2CO_3 catalysts, maximum bio-oil yield of 26.0 wt.% was observed, whereas in case of formic acid (FA) catalyst lignin depolymerization is very effective as it produced maximum bio-oil yield of 78.0 wt.%. Bio-oils were characterized using GC–MS, FT-IR, NMR analytical methods. Bio-oil analysis showed that it contained higher amount of phenolic monomers after lignin depolymerization. Higher amount of vanillin (41.9%) and isovanillin (44.9%) was found without catalyst and with FA liquefaction reaction. However with base catalyst, dibutyl phthalate (28.8%) was observed as the major compound in lignin depolymerization derived bio-oil. Solid residue analysis shows that base and acid catalyst depolymerized lignin in different ways by breaking of C–O and C–C bonds.

Keywords Alkali lignin · Low temperature · Base catalyst · Acid catalyst · Phenolic compounds

1 Introduction

Lignin is one of the most important polymers of lignocellulosic biomass and is majorly made up of aromatic compounds. Lignin constitutes 15–35% of lignocellulosic biomass along with cellulose (40–50%), and hemicellulose (15–30%) [1, 2]. In pulp and paper industry and ethanol industry, cellulose and hemicellulose components of lignocellulosic biomasses are utilized and lignin is produced as a by-product. Lignin has been utilized as a low-cost energy source in boiler to generate heat, though it can be a source of high-value aromatic compounds [2, 3]. Lignin can be depolymerized into valuable products, which could increase the

profitability of the overall biorefinery and make it economically viable [3, 4].

Over the past few decades, researchers are trying to convert lignin into aromatic monomers as a supplement for fossil fuel derived aromatic chemicals [1, 3, 4]. Various thermo-chemical methods have been investigated to depolymerize lignin into low molecular weight aromatics. These include thermal chemical cracking [2, 4], catalytic reduction (hydrogenolysis) [2, 3], hydrolysis [5], catalytic oxidation [1]. Additionally, lignin has been hydrolytically depolymerized by acid, alkaline [4–6], and supercritical water [2, 7] or ethanol [3]. Lignin could be valorized by liquefaction with or without the addition of catalysts, namely through hydrodeoxygenation and aqueous phase reforming [7]. In pulp and paper industry, lignin separation is done by soda pulping process. Homogeneous base NaOH is used for lignin liquefaction at temperatures of 140–170 °C and this black liquor lignin contains impurities of NaOH and Na_2CO_3 before purification. Liquefaction of lignin in water is an economic and environment friendly process as water acts as a solvent as well as catalyst and reactant. Roberts et al. [7] studied the liquefaction of lignin with NaOH as a catalyst at

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300 °C and 25 Mpa pressure. They found that the concentration of base catalyst influenced the products yield. Maximum bio-oil (23 wt.%) was observed with 4 wt.% NaOH catalyst. They concluded that with increase of base catalyst amount from 2 to 4%, the bio-oil as well as the monomer compounds increased. Toledano et al. [8] studied liquefaction of lignin with two different base catalysts (KOH and NaOH). They found that the strength of the base catalyst influenced the lignin depolymerization and maximum bio-oil yield was observed with NaOH (19.7%) catalyst rather than KOH (13%) catalyst. Further, Chaudhary et al. [9] investigated lignin liquefaction with Na₂CO₃, NaOH and CsOH catalysts at 250 °C for 1-h reaction time. Maximum bio-oil yield (34%) was found with Na₂CO₃ weak base catalyst while liquefaction with strong base NaOH and CsOH was seen to produce low bio-oil yield. Besides the base catalyst, homogeneous acid catalyst is also used for lignin depolymerization [10]. Formic acid is the majorly used acid catalyst for lignin depolymerization as it acts as an in situ hydrogen donor solvent or hydrogen source for many reactions [3, 4]. Bengoechea et al. [3] studied the formic acid-assisted lignin depolymerization with catalyst (NiMo). They found that formic acid increased the bio-oil yield as compared to molecular hydrogen or isopropanol. They suggested that formic acid produced H₂ and CO₂ which was more efficient than molecular hydrogen. Kristianto et al. [11] examined the lignin depolymerization in the presence of Ru/C catalyst in formic acid medium at higher temperatures of 250–350 °C. Results showed that with the use of formic acid, bio-oil yield increased and with the catalyst, oxygen reduction was significant in bio-oil. The molecular weight characterization showed that the bio-oil contained monomeric phenols.

Researchers have carried out lignin depolymerization with base catalyst at higher temperatures in the range of 250–350 °C and produced more number of compounds with less selectivity. Hence to decrease the number of compounds and increase the selectivity, it is necessary to understand the lignin depolymerization at lower temperatures. This study for lignin depolymerization has been carried out at low temperature (140–180 °C) and with base catalysts (NaOH, KOH, Na₂CO₃ and K₂CO₃) and formic acid (FA) catalyst in water solvent system. Different reaction temperatures, time, catalyst and catalyst amount were screened to understand the products yield and its characterization. The obtained products were characterized with the help of GC–MS, NMR, and FT-IR analyses.

2 Materials and methods

Alkali lignin (AL) used in this study was purchased from Sigma-Aldrich. Alkali lignin was extracted from rice straw biomass. All catalysts NaOH (98.5%), KOH (98%), K₂CO₃ (98%) and Na₂CO₃ (99.5%) and formic acid (FA, 96%) and

solvents (ethyl acetate, 99%) were purchased from Fischer Scientific. Double distilled water used in the reaction was prepared in the laboratory.

2.1 Experimental procedures

Alkali lignin (AL) depolymerization experiments were conducted in a pressure tube reactor (20 mL). In the reaction, 0.5 g alkali lignin and water solvent (ratio 1:10) was taken and then the required amount of catalyst (NaOH/KOH/K₂CO₃/Na₂CO₃/formic acid) was added in the reactor. Reaction was carried out in the atmospheric pressure of air. After that, the reactor was heated by using oil bath to the desired temperature (140, 160 and 180 °C) and maintained for different reaction holding times (30, 60, 90 and 120 min). After the completion of the reaction, reactor was cooled using tap water to room temperature of 25 °C. The gas was vented out from the reactor. For the base catalytic reaction, 2N HCl was added into the solution until the pH of the solution became acidic (pH = 2). However in case of formic acid reaction, bio-oil was extracted directly by adding ethyl acetate solvent. The bio-oil was separated from the solid residue (bio-residue) by using ethyl acetate solvent followed by filtration. Ethyl acetate solvent was removed from the bio-oil by using rotary evaporator under reduced pressure at 50 °C. After that, the bio-oil was kept in oven at 80 °C for 3 h to ensure complete removal of the solvent. Bio-residue was dried at 105 °C overnight. All reactions were carried out in duplicates, and the average values have been taken for calculations and reported.

$$\text{Bio - oil yield (wt.\%)} = \frac{\text{Weight of Bio - oil}}{\text{Weight of Lignin feed}} \times 100$$

$$\text{Bio - residue yield (wt.\%)} = \frac{\text{Weight of Solid residue}}{\text{Weight of Lignin feed}} \times 100$$

$$\text{Others - yield (wt.\%)} = 100 - (\text{Bio - oil yield} + \text{bio - residue yield})$$

2.2 Characterization methods

Thermogravimetric analysis of alkali lignin (AL) was performed on a DTG 60 unit (Shimadzu, Japan). Nitrogen gas (99.998%) flow of 20 mL/min was used, and the sample was heated from room temperature to 900 °C at a heating rate of 10 °C/min. Elemental analysis such as C, H, N and S of alkali lignin was performed on an Elementar vario microcube unit while O was calculated by difference. Proximate analysis of alkali lignin was carried out by using oven and muffle furnace. For the calculation of moisture content, lignin was kept for 5 h at 105 °C and also kept in muffle furnace for 2–3 min. at 900 °C for volatile matter estimation.

Ash content of lignin was found by keeping the sample at 575 °C for 3 h. The functional groups on the surface of AL, bio-oil and bio-residue were qualitatively measured in a spectrum range of 400 cm⁻¹ to 4000 cm⁻¹ using Fourier transform infrared spectroscopy (Perkin Elmer FT-IR spectrometer). Functional protons in the bio-oil were characterized by NMR on a Bruker Avance 500 Plus instrument using DMSO-D₆ as solvent. The chemical composition of the bio-oil samples was characterized using a gas chromatography/mass spectrometry (GC/MS, Agilent Technology, 7890B) equipped with an HP-5 column. Helium (99.999%) was used as the carrier gas at a flow rate of 1 mL min⁻¹ in an HP-1 column (25 m×0.32 mm×0.17 μm). The obtained bio-oil was dissolved in acetone solvent. The column was heated from 50 °C to 280 °C at a heating rate of 5 °C min⁻¹, and it was held for 5 min. 0.4 μL bio-oil was injected in split less mode.

3 Results and discussions

3.1 Alkali lignin characterization

The ultimate and proximate analyses of alkali lignin are given in Table 1. Ultimate analysis showed that lignin is composed of 60% carbon (C) and 29.3% oxygen (O). Hydrogen (H), nitrogen (N) and sulfur (S) content were low at 7.8, 0.2 and 2.9%, respectively. The result of proximate analysis showed that lignin contained 88.0% volatile content and 4.2% fixed carbon. Moisture and ash content were found to be 6.2 and 2.6%, respectively.

Thermal decomposition of lignin showed a total of 72.5 wt.% loss within 25 to 900 °C temperature range (Fig. 1). It occurred in three stages as shown in Fig. 1. In the first stage, only 3.8 wt.% loss was obtained in between 25 and 120 °C due to removal of moisture or drying of lignin. Maximum weight loss (55 wt.%) was found between 120 and 550 °C. It was due to the devolatilization reaction and breakage of various functional groups such as phenolic hydroxyl, carbonyl and benzyl hydroxyl present in the complex structure of lignin [1, 2]. This stage is mainly responsible for the conversion of lignin in to liquid products. Third stage of TGA curve showed 13.7 wt.% loss that indicated the breaking of

Table 1 Ultimate and Proximate analyses of Alkali lignin (wt.%, dry basis)

Ultimate analysis		Proximate analysis	
C	60.0	Moisture	6.2
H	7.8	Ash content	2.6
O	29.1	Volatile matter	88.0
N	0.2	Fixed carbon	4.2
S	2.9		

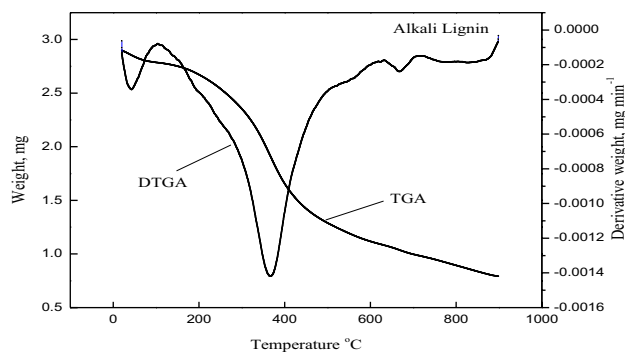


Fig. 1 TGA/DTG thermogram of Alkali lignin

aromatic or poly aromatic units of lignin and led their conversion into bio-char [12, 13].

3.2 Products yield

3.2.1 Effect of temperature and reaction time

Lignin depolymerization was studied at three different temperatures, viz. 140, 160 and 180 °C and the results are illustrated in Fig. 2. The results are consistent with the previous research which states that reaction temperature has a significant influence on the lignin degradation and bio-oil yield [14–16]. At a low reaction temperature of 140 °C, only 5 wt.% bio-oil was obtained and as the reaction temperature increased to 160 °C, the bio-oil yield also increased to 14.2 wt. %. The increase in depolymerization of lignin with increase in reaction temperature can be attributed to the endothermic nature of the reaction, which is favored at higher temperature. However, as the temperature was further increased to 180 °C, the bio-oil yield dropped down to 12.4 wt.% and gaseous product yield increased to 43.6 wt.%. This is due to the enhanced cracking of the compounds into smaller molecules (non-condensable gases) at higher temperature [15, 16]. With increase in reaction temperature, the

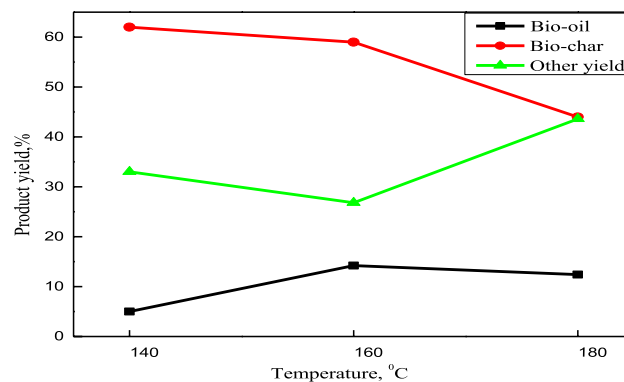


Fig. 2 Effects of reaction temperature on products yield

other yield significantly increased. Maximum other yield (43.6 wt.%) was found in case of higher temperature reaction (AW-180). It demonstrated that higher temperature efficiently decomposed the lignin; however the decomposed product goes in other fraction. The reduction of bio-residue yield at higher temperature may indicate higher decomposition into products or reduced repolymerization reaction or condensation reaction [15]. Thus on the basis of bio-oil yield, reaction temperature of 160 °C was found to be optimum for effective lignin depolymerization.

The other aim was to understand the effect of holding time on lignin depolymerization. Lignin depolymerization was carried out for 30, 60, 90 and 120 min using water as solvent at 160 °C. Our results as shown in Fig. 3 demonstrated that the bio-oil yield decreased from 14.2 to 6.0 wt. % as the holding time was increased from 30 to 120 min. Maximum bio-oil (14.2 wt. %) and low bio-residue yield (59.0 wt. %) was observed at 30 min holding time. With increase in reaction time, bio-residue yield increased indicating increased repolymerization at longer residence time [17]. Hence, results suggested that lower reaction holding time is suitable for lignin depolymerization as also observed by other research groups [15].

3.2.2 Effect of base catalyst

Under optimized reaction conditions at 160 °C and 30 min reaction holding time, various base catalysts (0.2 g), viz. KOH, NaOH, K_2CO_3 and Na_2CO_3 were used for alkali lignin depolymerization. It can be seen from Fig. 4 that the type of base influenced the lignin degradation. Several researchers studied homogeneous base catalytic lignin degradation at higher temperature range of 200 to 350 °C and higher pressure [8, 9, 18]. However, this study examined the base catalytic depolymerization at low temperature (160 °C) and atmospheric pressure of air. Maximum bio-oil yield (26.0 wt.%) was obtained with K_2CO_3 catalyst with lowest yield of bio-residue (62.0%). Approximately similar yield

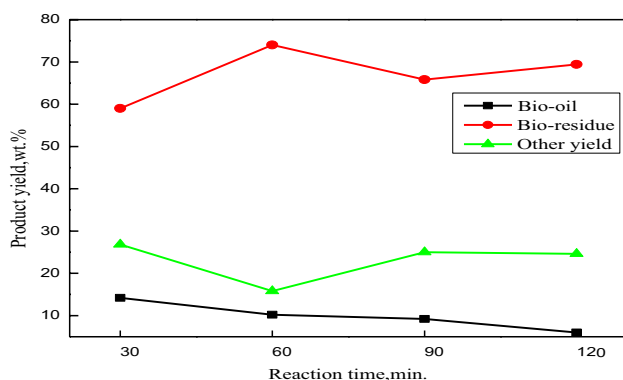


Fig. 3 Effects of reaction time on products yield

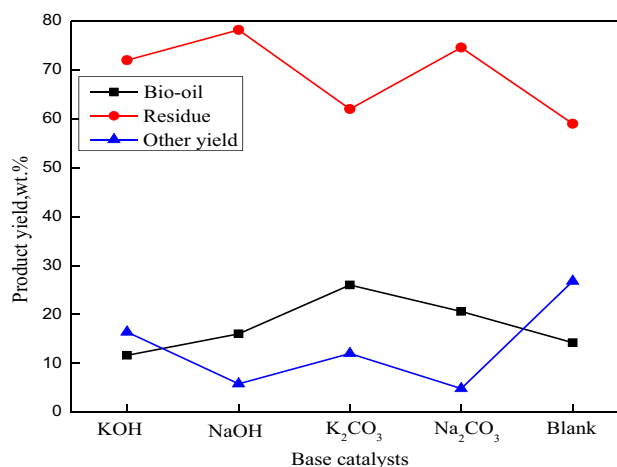


Fig. 4 Effects of different base catalysts on products yield

(27 wt.%) was found by Mahmood et al. [18]; however the reaction was carried out at a higher temperature of 300 °C. Strong bases such as NaOH and KOH produced lower bio-oil yield with higher bio-residue. Weak basic catalyst such as Na_2CO_3 also depolymerized lignin efficiently as compared to strongly basic NaOH and KOH catalyst, but its bio-oil yield was lower than that obtained with K_2CO_3 . K_2CO_3 has lower basicity as compared to KOH and NaOH and in aqueous medium produces K^+ and CO_3^{2-} , which promotes the breaking of ether linkage (C-O linkage) in the lignin during liquefaction. It was thus demonstrated that moderately basic K_2CO_3 was suitable for the low-temperature lignin depolymerization.

Toledano et al. [8] studied liquefaction of lignin with two different bases including KOH and NaOH. They found that the strength of the base catalyst influenced the lignin depolymerization and maximum bio-oil yield was found with NaOH (19.7%) catalyst rather than KOH (13%) catalyst. Further Chaudhary et al. [9] investigated lignin liquefaction with Na_2CO_3 , NaOH and CsOH base catalysts at 250 °C for 1-h reaction time. Maximum bio-oil yield (34%) was found with Na_2CO_3 weak base catalyst while liquefaction with strong base NaOH and CsOH produced low bio-oil yield. Based on this, K_2CO_3 was considered as the best catalyst for lignin depolymerization. Hence it can be seen from the products distributions that not only base catalyst influenced the lignin depolymerization but also lignin sources and types play an important role on products distribution [8, 9].

3.2.3 Effect of catalyst concentration

The effect of quantity of optimized base catalyst on lignin depolymerization was examined by varying the amount of K_2CO_3 , and the results are shown in Fig. 5. It was observed that lower base concentrations yielded higher bio-oil yield.

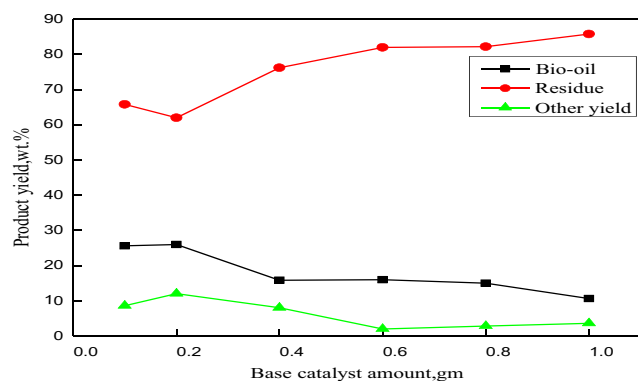


Fig. 5 Effects of different base catalysts amounts on products yield

Maximum bio-oil yield (26 wt.%) was obtained with 0.2 g K_2CO_3 base catalyst with lower bio-residue. However, with changes in base concentration from 0.4 to 0.8 g, the bio-oil yield was approximately constant at 15–16 wt.%. Further increase in the base catalyst amount to 1 g led to minimum bio-oil yield (10.0 wt.%). This indicated that catalyst amount greatly influenced the products yield. On the other hand, the other yield such as aqueous fraction and gas yield was higher with 0.2 g K_2CO_3 catalyst. Bio-residue yields were increasing steadily (62 to 85.8 wt.%) as the catalyst amount increased.

3.2.4 Effect of formic acid on lignin degradation

According to several researchers, presence of hydrogen during the lignin depolymerization reaction enhanced the bio-oil yield as well the bio-oil quality [14, 16]. It has been seen that in situ hydrogen donor solvent such as formic acid could be a promising solvent for lignin depolymerization [17, 19] as compared to external hydrogen. Owing to the in situ hydrogen donating ability of formic acid, the effect of formic acid on lignin depolymerization was studied. Alkali lignin was depolymerized using water/formic acid solvent mixture and at optimized reaction conditions of 30 min holding time and reaction temperature at 160 °C. The amount of formic acid was varied from 0.5 to 8 ml, and these results are shown in Fig. 6. On increasing the amount of formic acid from 0.5 to 8 ml, bio-oil yield increased, *i.e.* from 21 to 78 wt. % and simultaneously the yield of bio-residue decreased. However without FA, the bio-oil yield was significantly lower 14.2 wt.% (Fig. 2). This demonstrates that the addition of FA has a positive effect on lignin depolymerization by breaking the C–O–C bond [16]. Maximum bio-oil yield of 78 wt.% was observed using 8 ml formic acid, but excess use of formic acid would not be feasible for lignin depolymerization as it increases the experimental cost. Maximum bio-residue (75.4 wt. %) was obtained using low concentration (0.2 ml) of formic acid as solvent.

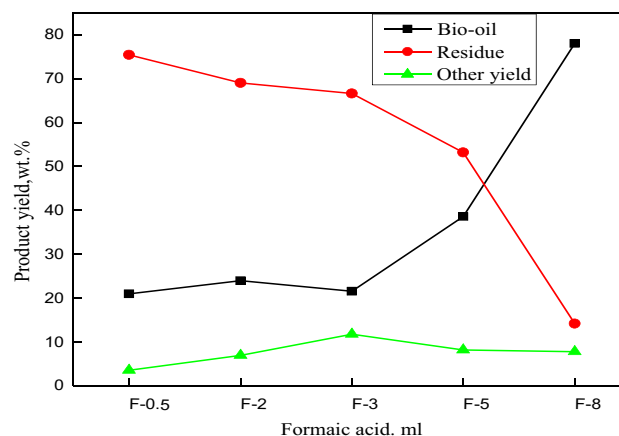


Fig. 6 Effects of formic acid on products yield

3.3 Bio-oil analyses

3.3.1 Molecular composition of bio-oil

The identification of different functional compounds present in the bio-oil was performed using GC–MS. It can be seen from Tables 2 and 3 that the different reaction conditions significantly influenced the bio-oil components. Different types of compounds such as ketone-type, aldehyde-type, carboxyl-type, and hydroxyl-type were plentifully found due to cleavage of different linkages such as ether (C–O–C), carbon–carbon bond (C–C) and side chain of the lignin moieties [2, 20, 21]. In case of non-catalytic reaction, the bio-oil majorly contained compounds such as Vanillin (41.9%), Homovanillic acid (17.3%), 4-Methoxy-4', 5'-methylene dioxybiphenyl-2-carboxylic acid (9.6%), 2-Pentanone, 4-hydroxy-4-methyl (8.9%) and Apocynin (7.1%). However in case of catalytic reaction, the bio-oil showed distinct components. For K_2CO_3 catalytic reaction, bio-oil showed reduced area percentage of vanillin (7.2%) while new compounds were formed such as Dibutyl phthalate (28.8%), Phthalic acid, butyl 2-pentyl ester (12.3%) and 1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester (7.8%). Interestingly with formic acid, lignin depolymerization bio-oil contained different components as compared to the non-catalytic and K_2CO_3 base catalytic bio-oil. Higher area percentage of Benzaldehyde, 3-hydroxy-4-methoxy (Isovanillin) (44.2%), 2-Pentanone, 4-hydroxy-4-methyl- (14.5%) and Phenylacetyl formic acid, 4-hydroxy-3-methoxy (15%) were found. Based on the products analysis, it can be seen that formic acid acts as a catalyst breaking the C–O–C link rather than as the hydrogen donor [21]. Moreover formic acid is involved in the reaction with phenolic monomers forming new compounds (Table 2). Aryl ether bond (C–O) and C α -Car in the lignin polymer structure could be broken easily leading to higher yield of aldehyde or carbonyl compounds [21, 22]. Hence, it can be said that

Table 2 Molecular composition of bio-oil derived from Alkali lignin degradation via HTL at different experimental conditions

Blank			K ₂ CO ₃			Formic acid		
RT	Area,%	Compounds	RT	Area,%	Compounds	RT	Area,%	Compounds
6.7	8.9	2-Pentanone, 4-hydroxy-4-methyl-	14.2	0.8	Phenol, 2-methoxy-	6.7	14.5	2-Pentanone, 4-hydroxy-4-methyl-
20.7	1.0	2H-Inden-2-one, 1,4,5,6,7,7a-hexahydro-7a-methyl-, (S)-	24.2	7.2	Vanillin	14.2	2.4	Phenol, 2-methoxy-
23.9	1.2	1,4-Benzenediol, 2-methoxy-	26.2	1.2	Apocynin	24.2	44.2	Benzaldehyde, 3-hydroxy-4-methoxy-
24.2	41.9	Vanillin	33.9	7.8	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	25.5	0.9	Homovanillyl alcohol
26.2	7.1	Apocynin	34.0	2.7	Phthalic acid, isobutyl 2-pentyl ester	26.2	5.6	Apocynin
27.1	3.5	Homovanillyl alcohol	34.8	2.3	Phthalic acid, isobutyl 2-methylpent-3-yl ester	27.1	3.4	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-
28.3	1.6	.alpha.-Amino-3'-hydroxy-4'-methoxyacetophenone	35.0	28.8	Dibutyl phthalate	28.3	1.1	2,4'-Dihydroxy-3'-methoxyacetophenone
29.6	17.3	Homovanillic acid	35.2	4.3	Phthalic acid, bis(2-pentyl) ester	30.4	15.0	Phenylacetylformic acid, 4-hydroxy-3-methoxy-
32.0	1.2	Benzeneacetic acid, 4-hydroxy-3-methoxy-, methyl ester	35.6	0.8	Phthalic acid, butyl isohexyl ester	33.7	2.5	Phenol, 3-(dimethylamino)-
32.3	1.5	4-Hydroxy-2-methoxycinnamaldehyde	35.70	1.6	Phthalic acid, heptylpentyl ester	35.0	3.5	Dibutyl phthalate
35.0	4.5	Dibutyl phthalate	35.8	3.6	Phthalic acid, butyl isohexyl ester	46.0	1.7	Cobaltocene, 1,2,3,4,5-pentamethyl-
48.7	9.6	4-Methoxy-4',5'-methylene-dioxybiphenyl-2-carboxylic acid	35.9	1.3	Phthalic acid, di(2-methylbutyl) ester	48.7	4.6	Butorphanol
			36.6	12.3	Phthalic acid, butyl 2-pentyl ester			
			36.7	3.5	Phthalic acid, pentyl 2-pentyl ester			
			38.4	1.9	Dibutyl phthalate			

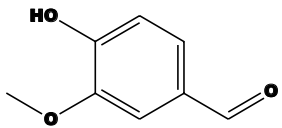
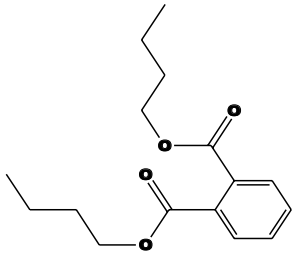
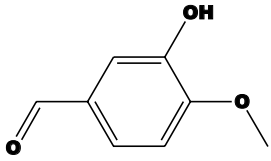
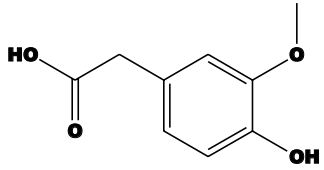
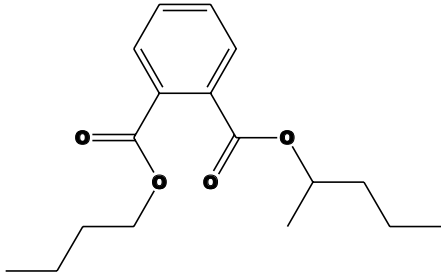
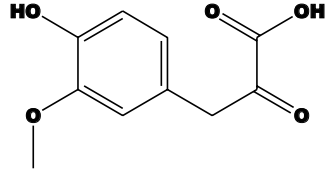
formic acid degraded the lignin by acid-catalyzed reaction. On the other hand, base catalyst K₂CO₃ produced potassium cation and this enhanced the ether bond (C–O–C) cleavage by formation of six-member ring. Although several authors suggested that base catalytic lignin depolymerization reaction required higher temperatures, it was observed that the number of compounds was higher making the compounds separation very complicated. Hence low temperature could be beneficial for the lignin depolymerization with higher selectivity towards the produced compounds. Overall it can be seen that bio-oil majorly consisted of G-type compounds.

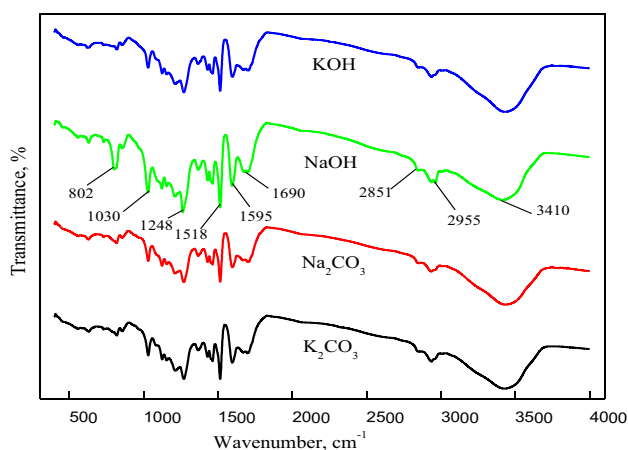
3.3.2 FT-IR analysis of bio-oil

The FT-IR analysis of the bio-oil obtained from the depolymerization of alkali lignin using different types of base catalysts showed various absorption bands of different stretching frequency (Fig. 7). The spectrum of all bio-oils

showed similar trend of absorption bands which were different in their relative intensity. The band observed at 3410 cm⁻¹ indicated the presence of –OH functional group of aliphatic or phenolics. Two absorption bands corresponding to the stretching frequency of 2955 and 2851 cm⁻¹ were attributed to the asymmetric and symmetric bands of –CH₂, respectively. Among both the –CH₂ bands, the asymmetric stretching (2955 cm⁻¹) was found to be more intense in the bio-oil of NaOH as compared to the other. The ketonic groups of bio-oil were observed at 1690 cm⁻¹, whose intensity was also found to be high for NaOH bio-oil. Two bands at 1595 and 1518 cm⁻¹ were found due to C=C stretching of syringyl and guaiacyl aromatic ring. The band appearing at 1248 cm⁻¹ showed the C–O stretching of syringyl, and 1030 cm⁻¹ indicated the C–H deformation of syringyl [1, 23]. In addition, the band observed at 802 cm⁻¹ indicated the presence of para-substituted aromatic compounds [24].

Table 3 Major compounds with chemical structure obtained at different reaction conditions

Compounds observed in higher area%		
Blank reaction (Bio-oil yield-14.2%)	K ₂ CO ₃ , (Bio-oil yield-26.0%)	Formic acid, (Bio-oil yield-78.0%)
 <p>Vanillin</p> <p>GC-MS yield- (area 41.9%)</p>	 <p>Dibutyl phthalate,</p> <p>GC-MS yield-(area 28.8%)</p>	 <p>Isovanillin,</p> <p>GC-MS yield-(area 44.2%)</p>
 <p>Homovanillic acid</p> <p>GC-MS yield-(area 17.3%)</p>	 <p>Phthalic acid, butyl 2-pentyl ester</p> <p>GC-MS yield-(area 12.3%)</p>	 <p>Phenylacetylformic acid, 4-hydroxy-3-methoxy-,</p> <p>GC-MS yield-(area 15.0%)</p>

**Fig. 7** FT-IR spectra of bio-oils obtained with base catalysts

The FT-IR spectra of bio-oils obtained while using different amounts of formic acid (0.5, 2, 3, 5 and 8 ml) are shown in Fig. 8. The spectra showed the following vibration bands at 3440, 2926, 2843, 1709, 1600, 1516, 1260, 853 and 800 cm⁻¹ stretching frequency. The peak at 3440 cm⁻¹ indicated the presence of -OH functional group in bio-oil. The asymmetric and symmetric vibration bands of -CH were found at 2926 and 2843 cm⁻¹, respectively. Higher intensity of these bands was observed in the bio-oil obtained using 5 ml of formic acid, while these bands were absent in the bio-oil of 2 and 8 ml of formic acid. The fundamental vibrational band of ketone was found at 1709 cm⁻¹ in the bio-oil of 0.5, 3 and 5 ml, although unsaturated ketone was seen at 1650 cm⁻¹ in the bio-oil of blank, 2 and 8 ml of formic acid. The syringyl unit of bio-oils showed the stretching frequency of C=C at 1600 and 1516 cm⁻¹. The band obtained at 1260 and 1100 cm⁻¹ indicated the presence of C-O functional group in all bio-oils [25]. The C-H out of plane vibration in positions of 2, 5 and 6 of guaiacyl unit were observed at 800

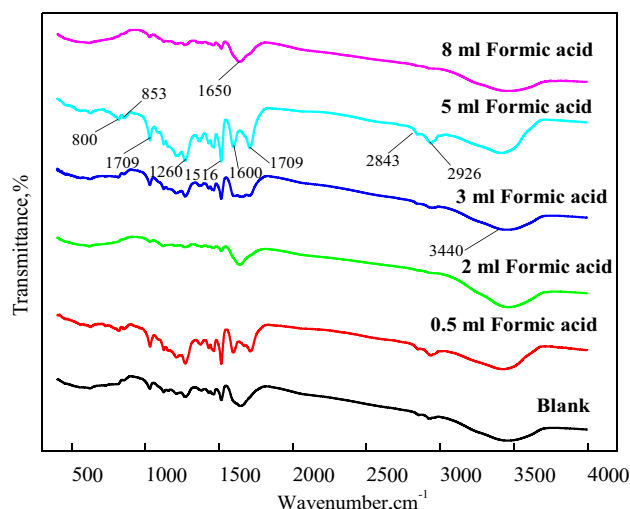


Fig. 8 FT-IR spectra of bio-oils obtained with formic acid catalysts

and 853 cm^{-1} . The FT-IR analysis indicated the presence of aromatic, ether, alcohol, carbonyls in the bio-oils obtained from the depolymerization of alkali lignin using various amounts of formic acid. Therefore, FT-IR analysis results were in good agreement with that of GC–MS indicating the multiple functionalities (aliphatic, aromatic, carbonyl etc.) of compounds present in the bio-oil.

3.3.3 NMR analysis of bio-oil

$^1\text{H-NMR}$ spectra of bio-oils obtained while using the different types of base catalysts provide complementary information to FT-IR analysis and GC–MS analysis. The $^1\text{H-NMR}$ integrated area was divided into various regions such as 0.5–1.5, 1.5–3.0, 3–5, 5–8 and 9–10 ppm on the basis of types of proton present in the bio-oils as shown in Fig. 9. The $^1\text{H-NMR}$ region from 0.5–1.5 ppm indicated the shielded region of aliphatic proton attached to sp^3 hybrid carbon atom or away from any type of hetero atom. In this region, maximum proton percentage (4.99%) was obtained for the blank reaction. The region from 1.5–3.0 ppm represents the aliphatic proton that may be bonded to sp^2 carbon or any hetero atom. The bio-oil obtained using Na_2CO_3 showed the maximum percentage (18.73%) of this type of protons. The next region of $^1\text{H-NMR}$ spectrum from 3.0–5.0 ppm indicates the methoxy proton or methylene proton that joins two aromatic units [1, 23]. All the bio-oils showed higher proton percentage in this region and confirmed the presence of high area percentage of GC–MS compounds having the methoxy group. Maximum percentage of this type of protons (64.52%) was obtained with KOH. In the aromatic region of $^1\text{H-NMR}$ (5–8 ppm), maximum proton percentage (25.5%) was observed in the bio-oil of K_2CO_3 . The down field or deshielded region of $^1\text{H-NMR}$ (8–10 ppm) indicated

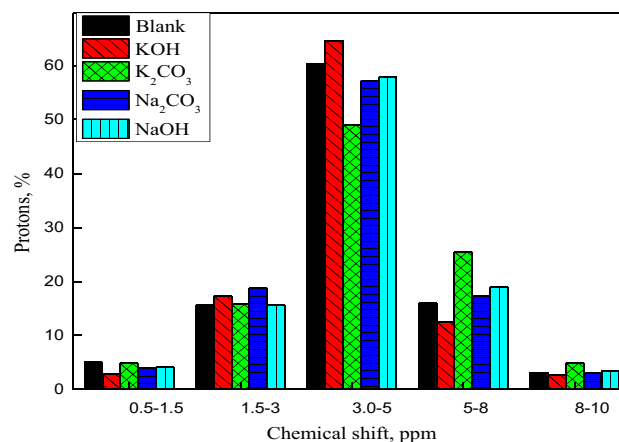


Fig. 9 Proton NMR analysis of bio-oils obtained with base catalysts

the presence of aldehyde protons [23]. All bio-oils had relatively small percentage of this type of proton and maximum (4.9%) was observed with K_2CO_3 .

The $^1\text{H-NMR}$ analysis of bio-oils obtained while using formic acid also showed the presence of different types of protons as shown in Fig. 10. In the up field region of spectrum (0.5–1.5 ppm), maximum percentage of aliphatic proton (7.63%) was observed with 0.5 ml of formic acid, while it was 4.99% in the bio-oil of blank reaction. The aliphatic proton attached to double bond or any hetero atom was observed within the region of 1.5–3.0 ppm. In this region, maximum proton percentage (15.85%) was noted with 5 ml formic acid. Although the bio-oil of blank reaction showed 15.55%, all the remaining bio-oils showed around 8% of this type proton. The proton percentage of methoxy proton (3.0 to 5.0 ppm) increased with increase in the amount of formic acid in the reaction mixture, and reached to its maximum value (76.46%) with 8 ml of formic acid. The aromatic proton was noticed in the region from 5 to 8 ppm. The bio-oil obtained while using 2 ml of formic acid indicated the maximum (18.21%) percentage of aromatic protons. The down

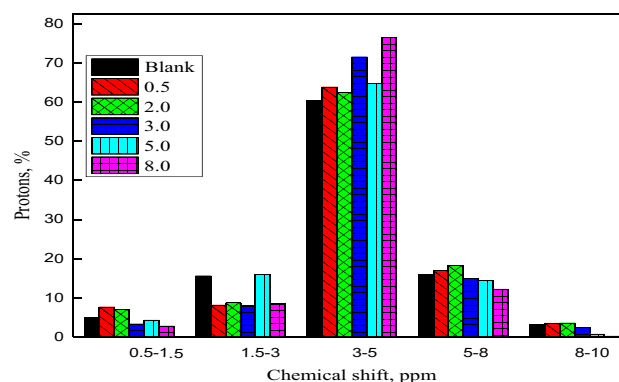


Fig. 10 Proton NMR analysis of bio-oils obtained with formic acid

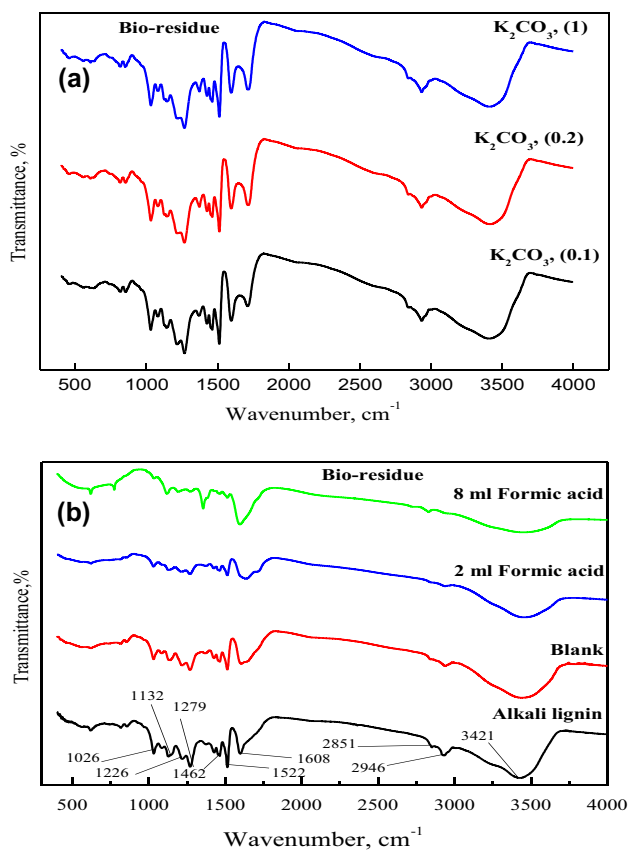


Fig. 11 Bio-residue analysis by FT-IR (a) with base catalysts, (b) with formic acid

field region of $^1\text{H-NMR}$ (8 to 10 ppm) indicated a very less amount of proton percentage of aldehyde type proton. Thus, $^1\text{H-NMR}$ analysis of bio-oils indicated the presence of various types of compounds.

3.4 Bio-residue analysis by FT-IR

The solid residue obtained after the catalytic depolymerization of lignin using different amounts of base catalyst (K_2CO_3) and formic acid were characterized by FT-IR and it is shown as Fig. 11a and b). The absorbance obtained at 2946 and 2851 cm^{-1} due to $-\text{CH}$ stretching is weak in case of solid residue as compared to raw lignin. The peak intensity of these bands in the solid residue obtained while using formic acid was weaker as compared to blank reaction indicating that formic acid stimulated breaking of lignin [26]. However in case of base catalytic depolymerized lignin, residues showed higher intensity as compared to the FA depolymerized residue. Moreover other stretching frequency was also found to have higher intensity as compared to the FA depolymerized residue again implying increased and efficient depolymerization with formic acid. The absorbance observed at 1608, 1522, and 1462 cm^{-1}

indicated absorption corresponding to aromatic nuclei and 1132 and 1026 cm^{-1} were attributed to C-O-C ether bonds of lignin [27]. The intensity of these absorption bands was found to decrease in case of bio-residue. The weakening of absorption bands in bio-residue as compared to raw lignin directly implies the breaking of various linkages present in the raw lignin ($\beta\text{-O-4}$, $\alpha\text{-O-4}$, $\alpha\text{-}\beta$, $\beta\text{-5}$ etc.), and conversion of them in to liquid and gaseous products [24, 26]. Overall the oxygen functionality in the bio-residue decreased and this indicates that dehydration and decarboxylation has happened during the liquefaction of lignin [28, 29].

4 Conclusions

Lignin depolymerization was carried out at low temperatures in the presence of base and acid catalyst. Among the four base catalysts tested, K_2CO_3 was found to be a suitable catalyst for the lignin depolymerization. Acid catalyst such as formic acid also was seen to significantly influence the products yield. Bio-oil yield of 26 wt.% was obtained with base catalyst while with formic acid, the yield was found to be 78 wt.%. It was found that base catalysts influenced the products yield remarkably. The major compounds found were vanillin in non-catalytic reaction, Dibutyl phthalate with K_2CO_3 base catalyst and isovanillin with formic acid depolymerization reaction. Based on the product compositions, it is shown that catalysts efficiently cleaved the ether (C-O-C) and carbon-carbon (C-C) linkages in the lignin which is well in agreement with the analysis of bio-residues.

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Authors contribution Bijoy Biswas contributed to conceptualization, investigation, methodology, and writing—original draft; Avnish Kumar contributed to investigation; Komal Saini contributed to methodology; Shivam Rawat contributed to formal analysis; Ramandeep Kaur contributed to formal analysis; Bhavya B Krishna contributed to writing—review and editing; Thallada Bhaskar contributed to conceptualization, supervision, writing—review and editing.

Declarations

Conflicts of interests 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.

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