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Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products

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Abstract

Catalytic hydrothermal treatment of wood biomass was performed at 280 °C for 15 min in the presence of alkaline solutions (NaOH, Na_2CO_3, KOH and K_2CO_3). Oil products were extracted from both liquid and solid portion by different solvents and analyzed individually. The effect of base solutions on the yield of oil products and composition of oils obtained at different stages were discussed in detail. Based on the conversion and yield of liquid products, the catalytic activity can be ranked as follows: $K_2CO_3 > KOH > Na_2CO_3 > NaOH$. In thermal run, the yield of solid residue was about 42% whereas it was 4.0% in the presence of K_2CO_3. Catalytic hydrothermal treatment of biomass produced mainly phenolic compounds. In thermal run, furan derivatives were observed whereas these compounds could not be observed in catalytic runs. The volatility distribution of hydrocarbons (ether extract) was characterized by using C-NP gram and it showed that the majority of hydrocarbons for all runs including thermal were distributed boiling point range of n-C_{11}. The products from hydrothermal treatment of wood biomass were analyzed using GC–MS, ^{1}H NMR, ^{13}C NMR, TOC and ion chromatograph.

Keywords: Biomass; Hydrothermal process; Phenolic compounds; Volatility distribution

1. Introduction

Biomass is a term for all organic material that stems from plants including algae, trees and crops [1]. The conversion of biomass, which represents a renewable and alternative energy source for production of fuels and/or chemicals, is receiving indeed increasing attention in all over the world. In the last century, energy sources were 30% petroleum, 23% natural gas, 22% coal, 6% nuclear, and 19% renewable [2]. The era of a chemical industry based on fossil resources (i.e., mineral oil, gas and coal) will gradually come to an end in the course of the 21st century, as the stocks of fossil resources are finite [3]. Under these circumstances, renewable forms of energy and organic raw material from conversion of biomass are becoming indeed of importance. Under the umbrella of thermo-chemical conversion of biomass [4–6], degradation of biomass in the presence of water [7–10] or solvents [11,12] have been studied widely. A textbook on the fundamentals of thermo chemical biomass conversion by different methods including alkaline treatment was discussed [13]. Direct liquefaction of wood by alkali and alkaline earth salts [14], effect of pressure, temperature, holding time and wood/catalyst/water ratio on oil yield [15], effect of variety of wood on yields and properties of heavy oils [16], effect of addition of 2-propanol [17] and liquid fuel production from woody biomass by direct liquefaction was reviewed [18]. The liquid products collected in the form of heavy oils and the conversions are based on the carbon and hydrogen recovery [14–18]. The summary on developments in direct thermo

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chemical liquefaction of biomass: 1983–1990 is a joint effort from the working group of the international energy agency (IEA) and bioenergy activity on direct liquefaction of biomass and they concluded that the further development is still required for the upgrading process for the production of hydrocarbons from the primary oils [19]. Ba et al. reported the properties of bio-oils obtained by vacuum pyrolysis of softwood bark and characterization of water-soluble and water-insoluble fractions [20], which is an important area for the upgrading the pyrolysis products, the major portion of cellulose and part of water soluble hydrocarbon content will goes to the water soluble portion. Jakab et al. [21] carried out the thermal decomposition of wood and cellulose in the presence of solvent vapors. They reported that the product distribution from decomposition of cellulose was strongly affected by the solvents. In methanol, pyran derivatives dominate besides levoglucosan and glycolaldehyde, whereas the relative abundance of 2-furalaldehyde and 5-(hydroxymethyl)-2-fural aldehyde increased in the presence of water [21]. It was found that the use of bases, alkaline salts, and neutral salts aids the decomposition of lignocellulosic materials [22–24]. Park et al. [24] studied the pyroylsis and oxidation of cellulose in a continuous-feed and -flow reactor in the presence of NaCl. They reported that cellulose in the presence of NaCl showed higher decomposition of levoglucosan and more rapid conversion of heavier initial products to CO_2.

Miller et al. [25] studied the depolymerization of lignin and its model compound by KOH in supercritical methanol or ethanol in a batch microreactor using bases. They concluded that strong bases gave superior conversion and that combinations of bases gave both positive and negative synergistic effect [25]. Most of the previous studies related to biomass liquefaction have been focused on the effect of base solutions on oil yields. However, they did not give any detailed information about the effect of various base solutions on compounds in oil products and their boiling point distributions obtained from different portions. Although separation and extraction procedure is the heart of biomass liquefaction (in water or solvent), there are few studies, which concerned an effective separation and extraction procedure to recover oil products but at different experimental conditions [12,25]. Recently, we have reported the effect of temperature and reaction time on the low-temperature hydrothermal treatment of wood biomass and effect of $Ca(OH)_2$ [0.0243 M] on degradation products [9].

In the present investigation, the hydrothermal treatment of wood biomass at 280 °C for 15 min in the presence of alkaline solutions (NaOH, Na_2CO_3, KOH, and K_2CO_3) was presented. After hydrothermal treatment of wood biomass, an extensive separation and extraction procedure was applied to recover oil products from different portions. The effects of base solutions on oil products and compounds in oils in three different cuts were discussed in detail. Analyses such as total organic carbon (TOC) content for water phase, GC–MS for oil products, ^{1}H NMR and ^{13}C NMR for acetone-soluble hydrocarbons were carried out. In final, the volatility distribution of hydrocarbons (ether extract) was carried out.

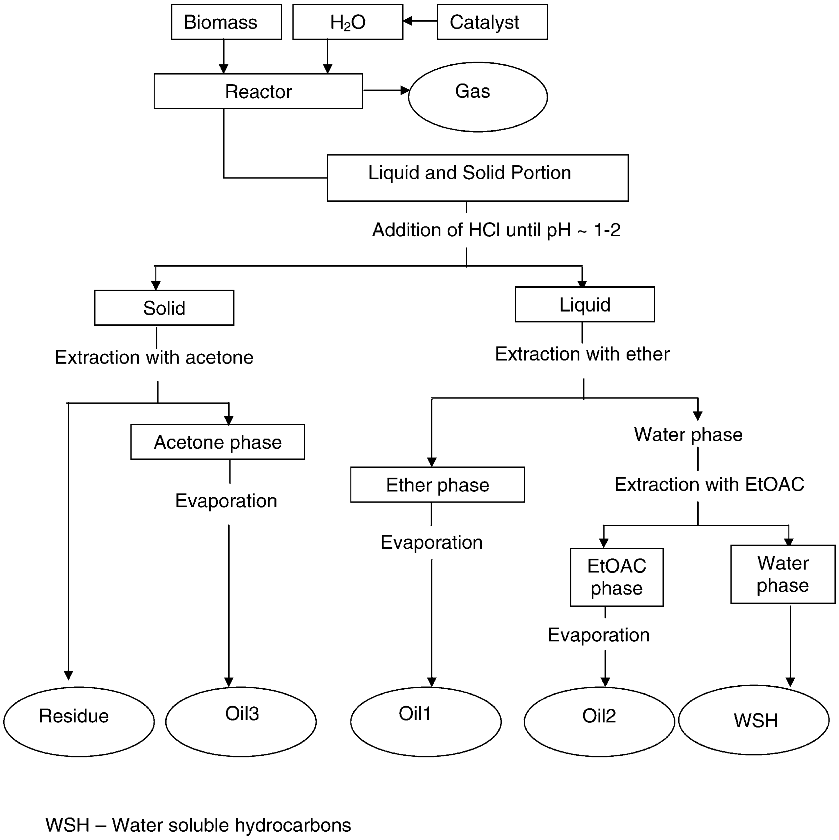
2. Experimental

2.1. Materials

The wood biomass (sawdust) from pine wood was softwood and obtained from Yonebayashi Milling Co., Ishikawa Prefecture, Japan and used as received. Elemental analysis (dry base) and calorific value was obtained from an outside analysis center and they are C (50.7 wt.%), H (6.2 wt.%), O (42.6 wt.%—by difference), ash content (0.5 wt.%), moisture (32.5 wt.%) and calorific value (3270 cal/g). Ash content was measured by TGA analysis (TGA-51; Shimadzu). The solvents (acetone, ether, ethyl acetate) and bases (NaOH, Na_2CO_3, KOH, and K_2CO_3) were purchased from Wako Chemicals, Japan and used as received.

2.2. Apparatus and experimental procedure

Hydrothermal liquefaction experiments were conducted in a 200 ml TaS-02-HC type autoclave at 280 °C for 15 min using solutions (0.94 M) of NaOH, Na_2CO_3, KOH and K_2CO_3. In a typical catalytic hydrothermal liquefaction experiment, the reactor was loaded with 5 g (dry basis) of wood biomass and 30 ml of 0.94 M alkaline solutions (NaOH, Na_2CO_3, KOH and K_2CO_3). In thermal run, the reactor was loaded with 5 g of wood biomass (dry basis) and 30 ml of ion-exchanged water. Then the reactor was purged five times with nitrogen to remove the inside air. Reactants were agitated vertically at 60 ≅ cycles/min using stirrer as shown in [26]. The temperature was then raised up to 280 °C at heating rate of 3 °C/min and kept for 15 min at 280 °C. After reaction, the reactor was cooled down to the room temperature by fan. The procedure for separation and extraction of reaction products are presented in Scheme 1. The gaseous products were vented. The solid and liquid products were rinsed from the autoclave with ion-exchanged water, then acidified to pH ~ 1–2 with HCl (1.7 M) covered and kept in the refrigerator overnight (12 h). Solid and liquid products were separated by filtration under vacuum for 15 min. During filtration, 100 ml of ion-exchanged water were used for washing solid products. The liquid portion was extracted with equal quantity of diethyl ether (600 ml). The etheral solution thus obtained was dried over anhydrous sodium sulfate, filtered and evaporated in a rotary evaporator at room temperature. Upon removal of diethyl ether, this fraction was weighed and designated as oil1. The water phase was further extracted with equal quantity of ethyl acetate (200 ml). The ethyl acetate solution thus obtained was dried over anhydrous sodium sulfate. Upon removal of ethyl acetate under reduced pressure, this fraction was weighed and designated as oil2. After extrac-



Scheme 1. Separation and extraction procedure.

tion, the remaining water phase contained the water-soluble hydrocarbons.

Solid products were extracted with acetone (150 ml) in a Soxhlet extraction apparatus until the solvent in the thimble became colorless (about 20 h). After removal of the acetone under reduced pressure in a rotary evaporator, this fraction was weighed and designated as oil3. Acetone insoluble fraction was dried at 105 °C then weighed, called as solid residue (biochar).

2.3. *Analysis of liquid products*

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-LA400. $CDCl_3$ (for thermal run) and C_3D_6O (for catalytic run) were used as solvent. The amount of cations in water phase was determined using an ion chromatograph (DIONEX;IC25). A TOC analyzer (Shimadzu; TOC-500) was used to measure the total organic carbon content (TOC) in water phase. Oils including oil1–oil3 obtained from low-temperature hydrothermal liquefaction of wood biomass were analyzed by gas chromatograph equipped with a mass selective detector and the detailed analytical conditions can be found elsewhere [26]. The gaseous products collected in a sealed Teflon bag were analyzed by a gas chromatograph equipped with a thermal conductivity detector (GC-TCD: Shimadzu; GC-8A).

3. Results and discussion

3.1. *Product distribution*

Catalytic low-temperature hydrothermal treatment of wood biomass was carried out at 280 °C for 15 min in the presence of various base solutions (NaOH, Na_2CO_3, KOH, and K_2CO_3). Reaction conditions were standardized at 280 °C for 15 min based on preliminary experiments and results [19,26]. Table 1 shows the product distribution from degradation of wood biomass. Base solutions have found an important effect on the degradation of wood biomass in terms of both oil yield and conversion. In thermal run, the yield of oil1 was 1.3 wt.% whereas it was almost from 6 to 12 times greater with various base solutions. Oil1, oil2 was viscous liquid at room temperature and whereas oil3 was tarry. The yields of oil products ranged from 10.0 to 16.7 wt.%. In this context the term “oil products” was defined to be ether and ethyl acetate-soluble fraction. Among various base catalysts, K_2CO_3 gave the highest oil products (the total of oil1 and oil2, 16.7 wt.%). By considering the yield of oil products and conversion, the order of catalysts activity can be ranked as follows: $K_2CO_3 > KOH > Na_2CO_3 > NaOH$. It can be concluded that alkaline salts are more effective than the corresponding hydroxides. This may come from one possible reason, which is alkaline salts react with water

Table 1
Product distribution from catalytic hydrothermal treatment of wood biomass at 280 °C for 15 min

Run no.	Solution (0.94 M 30 ml)	Conversion[a] (wt.%)	Oil				Gas[b] (wt.%)	Residue[c] (wt.%)	WSH[d] (wt.%)
			Oil1[e] (wt.%)	Oil2[f] (wt.%)	Oil3[g] (wt.%)	Total (wt.%)			
1	Water	58.3	1.3	0.1	7.2[h]	8.6	9.7	41.7	40.0
2	NaOH	86.0	8.0	2.0	12.4[h]	22.4	12.0	14.0	51.6
3	Na_2CO_3	88.5	8.5	1.7	12.8[h]	23.0	11.5	11.5	54.0
4	KOH	91.4	11.8	2.3	14.6[h]	28.7	11.8	8.6	50.9
5	K_2CO_3	96.0	15.2	1.5	17.0[h]	33.7	11.0	4.0	51.3

[a] See Eq. (A.1).
[b] See Eq. (A.5).
[c] See Eq. (A.6).
[d] See Eq. (A.7).
[e] See Eq. (A.2).
[f] See Eq. (A.3).
[g] See Eq. (A.4).
[h] Tarry compounds.

and form their bases and bicarbonates. Bicarbonates may act as secondary catalysts. The low-temperature (280 °C for 15 min) hydrothermal treatment of biomass using K_2CO_3 yielded 96% conversion. Extensive investigations on the liquefaction of wood by alkali and alkaline earth salts with the effect of water, catalyst, pressure, type of biomass, solvent etc were performed by Ogi and coworkers [14–18]. Due to the differences in the separation of products and definitions of conversions, the present investigations cannot be compared. In their scheme [17], the oil products were collected at one stage as heavy oil products (dark brown fluid or viscous material) and conversions were based on the recovery of carbon and nitrogen. However, in the present investigations the oil1 and oil2 was not the heavy (as can be seen in Tables 3 and 4) and conversions were based on the whole raw material. In a recent study, Sinag et al. [27] carried out the hydropyroylsis of glucose in supercritical water in the presence of K_2CO_3. They reported that the use of K_2CO_3 increased both H_2 and phenol yield. Although their experimental conditions (gasification at 450–550 °C) and our experimental conditions (liquefaction at 280 °C) are completely different, it can be concluded that, K_2CO_3 is effective base catalyst for decomposition of biomass not only for gasification [27] but also for liquefaction. In catalytic runs, the yield of oil2 was between 1.5 and 2.3%. Oil3 was the highest (17%) in case of K_2CO_3. The use of base catalysts has increased gas yields slightly. There is no appreciable change in the yields of gaseous products with various base catalysts used in this study. The compositions of gaseous products were CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6 and major being CO_2 for all runs. Others in Table 1 contain water-soluble hydrocarbons and some looses. Wood consists of mainly lignin, cellulose, hemicellulose and extractives. Water-soluble products were formed by decomposition of hemicellulose and cellulose. It is known that the dry weight of plants is typically composed of 50–80 wt.% of the polymeric carbohydrate and cellulose along with structural materials. The non-catalytic decomposition of cellulose in near-critical water was carried out by Sakaki et al. [28]. They reported that cellulose was rapidly decomposed to water solubles (WSS), and the WS was further decomposed after the WS yield reached nearly 80 wt.%. Fig. 1 shows the total organic carbon (TOC) content in water phase. It can be clearly seen that from Fig. 1, TOC content was found higher in catalytic runs than that of thermal case. TOC content was the highest (16% on a carbon basis of raw material) in case of K_2CO_3 whereas it was the lowest in case of NaOH. In a similar way with oil products, TOC content was higher in case of carbonates than the corresponding hydroxides. The content of TOC is might be due to the presence of glucopyranose (1,4:3,6-dianhydro-α-D-glucopyranose, 1,6-anhydro-β-D-glucopyranose) and benzenediol and their derivatives (3-methyl-1,2-benzenediol, 4-methyl-1,2-benzenediol, 4-ethyl-1,2-benzenediol, etc.) as they are easily soluble in water [20].

The cations in water phase were shown in Table 2. Besides Na^+ and K^+, Mg^{2+}, Ca^{2+}, ions were observed in all runs. NH_4^+ was also observed in cases of thermal, KOH, and K_2CO_3 whereas this ion could not be observed in case of NaOH and Na_2CO_3. The formation of these ions can be explained depending on the nature of wood biomass.

Here we report the main differences between catalytic and thermal runs, which observed during experiments. In thermal case, solid products stuck on the autoclave surface that was

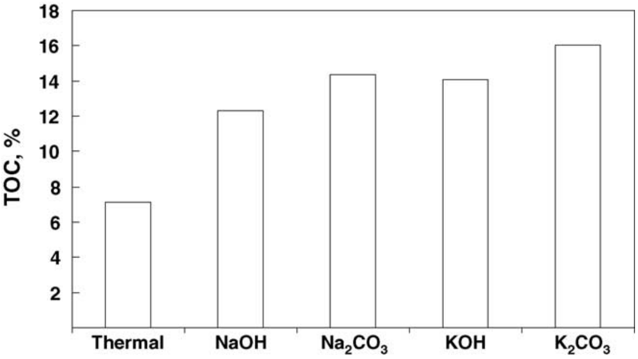


Fig. 1. Total organic carbon (TOC) content of water phase in thermal and catalytic runs.

Table 2
The amount of cations in water phase from low-temperature hydrothermal treatment of wood biomass at 280 °C for 15 min

Cation	Thermal (g)	NaOH (g)	Na_2CO_3 (g)	KOH (g)	K_2CO_3 (g)
Na^+	6.47×10^{-6}	0.6484	1.3007	8.0×10^{-6}	4.74×10^{-4}
K^+	6.02×10^{-5}	5.76×10^{-3}	3.63×10^{-3}	1.0998	2.1997
Mg^{2+}	2.48×10^{-6}	1.91×10^{-4}	3.76×10^{-4}	2.1×10^{-6}	4.74×10^{-4}
Ca^{2+}	2.48×10^{-5}	2.68×10^{-3}	3.63×10^{-3}	2.52×10^{-3}	9.48×10^{-4}
NH_4^+	1.99×10^{-6}	n.d.	n.d.	6.3×10^{-4}	4.4×10^{-4}

n.d.: not detected.

necessary to scrape to take solid whereas in all catalytic runs dark black liquid with small amount of solid was recovered from the autoclave. With regard to the bases, the experimental observations and results suggested a role of the alkali solutions used in this study inhibited the formation of char. It can be clearly seen that in catalytic case, the solid residue (biochar) was less compared to the thermal run. In thermal run, the yield of solid residue was about 42% whereas it was 4.0% in the presence of K_2CO_3. Minowa et al. [22] studied the liquefaction of cellulose in hot compressed water in the presence of Na_2CO_3. They reported that the use of Na_2CO_3 for liquefaction of cellulose decreased the formation of char and favored the formation of oil. Our results are in good agreement with this previous report [22].

Another important experimental observation is related to separation procedure in catalytic runs. In our preliminary experiments, we added the HCl after the filtration step. However, complete separation of liquid and solid portion could

Table 3
Identification of compounds in oil1 by GC–MS analysis

No.	RT (min)	Name of compound	Area (%)				
			None	NaOH	Na_2CO_3	KOH	K_2CO_3
1	1.025	Acetic acid	–	2.58	4.05	2.83	4.19
2	1.645	Propanoic acid	0.88	0.98	1.77	–	0.67
3	2.04	2-Furancarboxaldehyde	12.46	–	–	–	–
4	3.27	2-methyl-2-cyclopenten-1-one	0.74		–	–	–
5	3.492	1-(2-Furanyl)-ethanone	1.06	–	–	–	–
6	3.718	2,5-Hexanedione	1.38	–	–	–	–
7	4.932	5-Methyl-2-furancarboxaldehyde	5.15	–	–	–	–
8	7.047	Phenol	1.55	–	–	–	–
9	7.544	2-Hydroxy-3-methyl-2-cyclopenten-1-one	5.65	–	–	–	–
10	9.621	2-Methoxy-phenol	13.30	43.85	48.99	34.04	27.49
11	10.14	4-Methyl-phenol	24.19	1.95	1.39	–	–
12	11.716	1,2-Dimethoxy-benzene	–	–	1.26	1.74	1.80
13	12.974	4-Methyl-2-methoxy-phenol	2.53	13.08	4.06	8.15	3.77
14	14.657	1,2-Benzenediol	3.42	3.05	1.26	2.85	6.46
15	15.443	4-Ethyl-2-methoxy-phenol	3.85	5.32	3.25	9.32	18.66
16	17.192	4-Methyl-1,2-benzenediol	–	2.91	2.14	4.30	11.51
17	17.92	4-Propyl-2-methoxy-phenol	–	–	–	1.34	–
18	18.239	4,5-Dimethyl-1,3-benzenediol	–	1.35	2.71	2.16	2.72
19	19.138	4-Ethyl-1,3-benzenediol	–	2.44	0.49	1.34	4.53
20	19.725	2,3-Dimethylhydroquinone	–	–	1.50	2.16	1.73
21	20.767	1-(4-Hydroxy-3-methoxyphenyl)-ethanone	–	–	0.61	0.62	1.57
22	21.456	Butylated hydroxytoluene	5.07	2.45	2.46	3.96	2.99
23	21.788	1-Hydroxy-3-(4-hydroxy-3-methoxy phenyl)-2-propanone	–	0.28	0.56	–	–
24	24.5	4-Hydroxy-3-methoxy-benzeneacetic acid	7.82	–	–	–	–
Total area (%)			89.05	80.24	76.50	74.81	88.09

Table 4
Identification of compounds in oil2 by GC–MS analysis

No.	RT (min)	Name of compound	Area (%)				
			Thermal	NaOH	Na_2CO_3	KOH	K_2CO_3
1	3.04	Butyrolactone	–	10.41	5.29	10.08	4.75
2	10.185	3-Hydroxy-2-pentanone	–	47.43	43.06	49.42	40.87
3	11.378	3-Methoxy-1-propene	25.75	22.15	24.53	15.5	23.87
4	12.01	4-*oxo*-Pentanoic acid	31.95	–	–	–	–
5	13.84	5-Ethyldihydro-2(3H)-furanone	10.57	–	–	–	–
Total area (%)			68.27	79.99	72.88	75.00	69.49

not be managed in catalytic runs. The addition of HCl after the reaction and keeping in refrigerator led to complete separation of liquid and solid products in the present study.

3.2. Composition of oil1

C-MS analysis of oil1–oil3 was performed and the identified compounds in the oils were presented in Tables 3–5, respectively, with increasing their retention time. The results of chromatographic areas (percentage of total area) belong to the identified compounds and the similar presentation was also used by other researchers [35]. The difference to 100% represented the area of unidentified compounds. As can be seen from Table 4, 3- or 4-methyl-phenol, 2-furancarboxaldehyde, 2-methoxy-phenol were major compounds in thermal run. However, in catalytic runs, 2-furancarboxaldehyde could not be observed and 3-methyl or 4-methyl-phenol were observed in cases of NaOH, Na_2CO_3 and found minor compound. The total ion chromatogram (up to retention time of 25 min) of oil1 obtained from thermal and catalytic (K_2CO_3) is presented in Fig. 2. Peak numbers in Fig. 2 corresponds to compound numbers in Table 3. As can be seen from Fig. 2, peaks belonged to 2-furancarboxaldehyde (peak no. 3) and 3-methyl-phenol (peak no. 11) were observed in thermal run whereas these compounds could not be observed in case of K_2CO_3. It can be clearly seen both from Table 3 and Fig. 2, the compounds such as 2-furancarboxaldehyde, 2-methyl-2-cyclopenten-1-one, 1-(2-furanyl)-ethanone, 2,5-hexanedione, 5-methyl-2-furancarboxaldehyde, phenol, 2-hydroxy-3-methyl-2-cyclopenten-1-one, 4-hydroxy-3-methoxy-benzeneacetic acid were observed in thermal case. However, these compounds were not observed in case of K_2CO_3 and other catalytic runs. In catalytic run, acetic acid and propanoic acid were observed whereas in thermal run only propanoic acid was observed. The peak of acetic acid is overlapping with solvent peak (ether). The main difference between thermal and catalytic runs was

Table 5
Identification of compounds in oil3 from thermal run by GC–MS analysis

No.	RT (min)	Name of compound	Area (thermal) (%)
1	2.04	2-Furancarboxaldehyde	5.37
2	3.27	2-Methyl-2-cyclopenten-1-one	0.36
3	3.492	1-(2-Furanyl)-ethanone	0.39
4	3.718	2,5-Hexanedione	0.36
5	4.932	5-Methyl-2-furancarboxaldehyde	3.34
6	7.047	Phenol	0.48
7	7.544	2-Hydroxy-3-methyl-2-cyclopenten-1-one	0.48
8	7.809	3,4,4-Trimethyl-2-cyclopenten-1-one	0.35
9	9.621	2-Methoxy-phenol	7.70
10	10.14	3-Methyl-phenol or 4-methyl-phenol	18.32
11	12.974	4-Methyl-2-methoxy-phenol	2.21
12	15.443	4-Ethyl-2-methoxy-phenol	2.57
13	17.795	2′,4′-Dihydroxypropiohenone	1.11
14	18.162	Vanillin	0.84
15	19.775	Eugenol	6.22
16	24.5	4-Hydroxy-3-methoxy-bezeneaceticacid	0.85
17	30.584	(15-Alpha, 9-alpha, 10-beta)-kaur-15-ene	0.75
18	31.187	Hexadecanoic acid	0.44
19	32.444	6,6,9-Trimethyl-3-propyl-6H-dibenzo[*b*,*d*]pyran-1-ol	2.86
20	33.134	1-Hydroxy-3,5,6-trimethoxy-9H-xanthen-9-one	0.44
21	34.444	3,5,7-Trihydroxy-2-(4-hydroxy)-4H-1-benzopyran-4-one	0.56
22	35.233	Hemigossypol	0.64
23	36.16	4-Hydroxy-3-methoxy-benzeneaceticacid-methyl ester	3.62
24	36.631	4-Hexanoylresorcinol	1.36
25	38.433	2(1H)-phenanthrenone,3,4,4a,9,10,10a-hexahydro-6-hydroxy-1,1,4a-trimethyl)-, (4aS-*trans*)-	1.18
26	40.235	Diosooctyl ester-1,2-Benzenedicarboxylic acid	1.18
27	40.699	9(1H)-phenanthrenone,2,3,4,4a,10,10a-hexahydro-6-hydroxy-1,1,4a-trimethyl-7-(1-methylethyl)-, (4aS-*trans*)-	2.99
28	41.044	7,9-Dihydroxy-3-methoxy-1-methyl-6H-dibenzo[*b*,*d*]pyran-6-one	2.58
29	41.427	6,7-Dimethoxy-3′-phenyl-spiro[benzofuran-2(3H),2′-oxiran]-3-one	0.66
30	44.033	3-Acetyl-7,8-dimethoxy-2-methyl-1H-naptho[2,1-b]pyran-1-one	7.53
31	44.411	2,4-Dihydroxy-benzaldehyde	0.66
32	49.79	Betasitosterol	0.96
Total area (%)			79.36

found to be the presence of benzenediol derivatives such as 4-methyl-1,2-benzenediol, 4,5-dimethyl-1,3-benzenediol and 4-ethyl-1,3-benzenediol in catalytic runs. However, in thermal case only 1,2-benzenediol was observed. Klein studied the pyroylsis of guaiacol (2-methoxy-phenol) at 350 °C and it yielded mainly catechol (1,2-benzenediol), methane, phenol and carbon monoxide [29]. It is considered that in oil1, initially 2-methoxy-phenol was formed and decomposed to form 1,2-benzenediol. Compared to thermal run, the use of base solutions increased the amount of 2-methoxy-phenol (Table 3). The area percent of 2-methoxy-phenol was higher in the presence of NaOH and Na_2CO_3 than that of KOH and K_2CO_3 (Table 3). In contrast to thermal run, 4-methyl-phenol was low in case of NaOH and Na_2CO_3 and it could not be observed in KOH and K_2CO_3. Lignin in wood is both physically and chemically bonded to constituent polysaccharides (cellulose, hemicellulose, etc.) forming a complex three-dimensional network that contains acetal, α-phenyl-β-ether, phenyl-β-glucosidic and hydrogen bonds [30]. The majority of hydrocarbons in oil1 were phenol and benzenediol derivatives in catalytic runs. Breaking of β-aryl and benzoylether bonds in lignin produced phenolic compounds and further decomposition of phenolic compounds produced benzendiol derivatives. Thermochemical conversion of wood yields three products, i.e., liquid (consisting of oil and water), solid (biochar), and gas. The yield of these products including phenolic compounds from lignin depend on the experimental conditions which include, the configuration of lignin in wood, solvent, reaction temperature, reaction time, solvent/biomass ratio, type of reactor and so on. Jegers and Klein [31] studied the influence of reaction time and temperature on the phenolic compounds of the pyrolytic oils from kraft lignin, milled-wood lignin, and pine wood. Pyroylsis of kraft lignin and kraft lignin with tetralin, at 400 °C showed that guaiacol (2-methoxy-phenol) was produced in high yields at short reaction times. Catechol (1,2-benzenediol) yield was high at long reaction time in case of Kraft lignin with tetralin, whereas it was produced in high yields at short reaction time by pyrolysis of Kraft lignin without using tetralin. The amount of guaiacol was changed depending on the type of biomass [31]. In a recent study, Kruse et al. [32] carried out biomass gasification in supercritical water and discussed the influence of the dry matter content and the formation of phenols. They reported that the yield of phenols increases drastically with the dry matter content in a continuous stirred tank reactor and decreases in the batch reactor [32]. Beside phenol and benzendiol derivatives, 2,3-dimethylhydroquinone and 1-(4-hydroxy-3-methoxyphenyl)-ethanone was observed in oil1 in catalytic runs except in case of NaOH.

The composition of biomass derived oil is quite complex mixture. In the present investigation we have used the GC–MS analysis data and presented the boiling point distribution of biomass derived oil (oil1). Fig. 3 is called C-NP (normal paraffin) gram, which was obtained by plotting the area fraction of individual components against the equivalent carbon number of normal paraffins. The carbon numbers in the abscissa represent the equivalent boiling point (bp) range of normal paraffins. The details about C-NP gram can be found in elsewhere [33,34]. In brief, the NP gram is a carbon number distribution of hydrocarbons derived from the gas chromatogram based on boiling points of a series of normal paraffins. We can find out the peak positions of a series of normal paraffin's on a gas-chromatogram of the

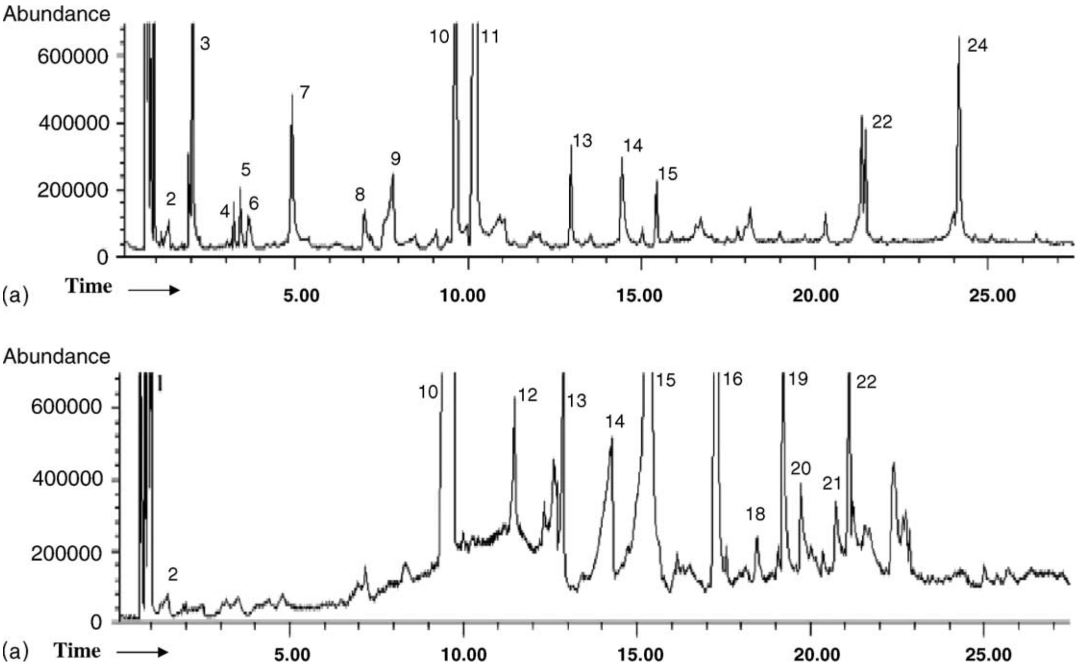


Fig. 2. Comparison of total ion chromatogram of oil1 from: (a) thermal run; (b) catalytic run (K_2CO_3).

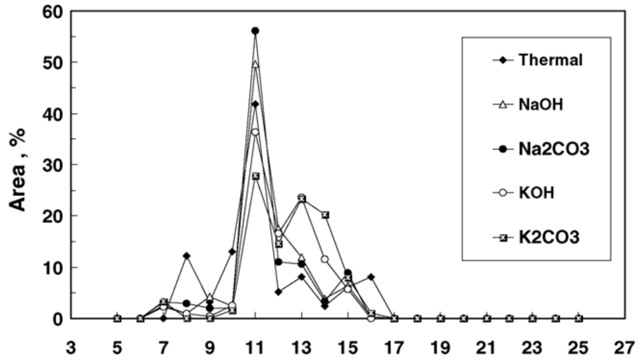


Fig. 3. C-NP gram of oil1 obtained from thermal and catalytic runs at 280 °C for 15 min.

liquid product obtained by thermal degradation of polymers by using poly ethylene (PE) derived oil which contain series of normal paraffin's as a index material. NP gram is constructed by plotting the weight fraction of hydrocarbons, which are located within the range of retention values of two successive normal paraffin's, C_{n-1} and C_n, against the carbon number, *n* [33]. The oxygenated hydrocarbons from both thermal and catalytic runs are distributed in the boiling point range of C_7–C_{16}. It can be clearly seen that the majority of hydrocarbons for oil1 in all runs including thermal run are distributed at C_{11}. Among the catalysts tested, Na_2CO_3 produced the highest amount of hydrocarbons at C_{11}, which were about 56%. 2-Methoxy-phenol mainly contributed to increase the hydrocarbons at C_{11}, as 2-methoxy-phenol was major compound in oil1 in case of Na_2CO_3. At C_{11} (174.0–195.8 °C), the hydrocarbons were about 50% in case of NaOH, about 42% in case of thermal, about 36% in case of KOH and about 28% in case of K_2CO_3. It is clear that the use of K_2CO_3 led to form other oxygenated hydrocarbons such as benzenediol derivatives and 4-ethyl-2-methoxy-phenol. Thus, boiling point of the hydrocarbons from K_2CO_3 was distributed about 28% at C_{11}, 15% at C_{12}, 23% at C_{13}, 20% at C_{14}. It is interesting that the hydrocarbons at C_{13} were about 23% in cases of K_2CO_3 and KOH whereas they were about 11% in cases of NaOH and Na_2CO_3. It can be clearly seen that the distribution of hydrocarbons from thermal run had a sharp peak at C_8, which is mainly 2-furancarboxaldehyde.

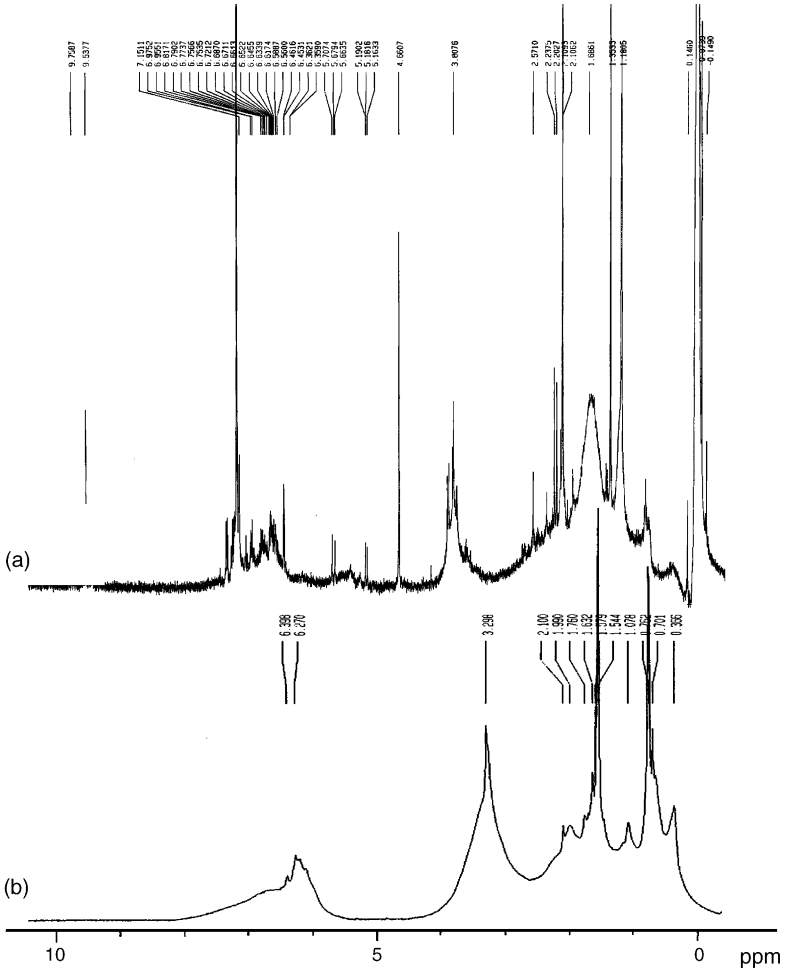


Fig. 4. Comparison of ^{1}H NMR of oil3: (a) thermal run; (b) catalytic run (KOH).

3.3. Composition of oil2 and oil3

Table 4 shows the identified compounds in oil2. As can be seen from Table 4, 3-methoxy-1-propene was observed in all runs. In thermal run 4-*oxo*-pentanoic acid and 5-ethyldihydro-2(3H)-furanone were observed while butyrolactone and 3-hydroxy-2-pentanone were observed in catalytic runs. In all catalytic runs, 3-hydroxy-2-pentanone was major compound.

In thermal case, 32 compounds in oil3 were identified and presented in Table 5. However, in catalytic runs, the compounds, which are 2-methoxy phenol (RT, 5.884 min), 1,2-dimethoxy-benzene (RT, 7.246 min, in case of NaOH this compound was not observed.), 4-methyl-2-methoxy-phenol (RT, 8.398 min), hexadecanoic acid (RT, 26.659 min), octadecanoic acid (RT, 31.525 min) were observed. In thermal case, the compounds, which observed in oil1 (Table 5 from peak nos.1 to 11 and 16), were also observed in oil3. The reason is that these compounds could not pass into liquid portion and remained in the solid portion. The compounds remained in solid portion could be extracted by acetone in a Soxhlet extraction apparatus. The compounds (from peak nos.17 to 32) observed in thermal run were higher-boiling-point compounds. The use of base solutions led to crack of higher-boiling-point compounds and helped to pass the compounds into liquid portion. ^{1}H NMR spectra of oil3 for thermal and catalytic (KOH) was shown in Fig. 4. As can be seen from Fig. 4, ^{1}H NMR of oil3 obtained from thermal and catalytic is quite different. In thermal case, sharp peaks were observed whereas peaks are broadened with a low intensity especially in the aromatic region in catalytic case. This shows that oil3 from catalytic runs consist of tarry compounds. In thermal case, the peaks observed 9.5377 and 9.7587 ppm belonged to aldehyde proton of 2-furancarboxaldehyde and 5-methyl-2-furancarboxaldehyde. The aromatic protons were in the range between 6 and 8 ppm. The sharp peak at 7.117 ppm is mainly due to the aromatic proton in meta position of 3-methyl-phenol. The hydroxylic protons of phenolic compounds are more deshielded than that of alcohol derivatives. The exact position of the O–H signal depends on the extent of hydrogen bonding, and on whether the hydrogen bonding is intermolecular or intramolecular. The extent of intermolecular hydrogen bonding depends on the concentration of the phenolic compounds and this strongly affects the position of the O–H signal. The peaks in the region between 4 and 6 ppm show the O–H signal. The peak at 4.6607 ppm is mainly due to –OH proton of 4-methyl-phenol and 2-methoxy-phenol. The peak at 3.8076 ppm is due to $-OCH_3$ signal of 2-methoxy-phenol, 4-ethyl-2-methoxy-phenol and 4-methyl-2-methoxy-phenol. Alkyl protons were in the range between 0.5 and 3.5 ppm.

It should be noted that in catalytic case, the intensity of peaks from GC–MS was low. The reason is that the use of base catalysts led to the formation of significant amount of tar, which was extracted from solid portion by using acetone. Information on molecular structures of tars obtained is only available in terms of analyses in the GC–MS ranges [36]. To confirm the presence of hydrocarbons in oil3, ^{13}C NMR was performed. ^{13}C NMR of oil3 obtained from KOH was shown in Fig. 5. Global characteristic of groups are as follows: Signals in the range 160–185 ppm show carboxylic acid carbon (–COOH), signals in the range 120–160 ppm show aromatic carbons (Ar–), signals in the range 100–160 ppm show C atom bonded $-OCH_3$ group ($-C-OCH_3$) and C atom bonded OH (–C–OH). Signals in the range 0–60 ppm show the alkyl carbons ($-CH_3$, $-CH_2$).

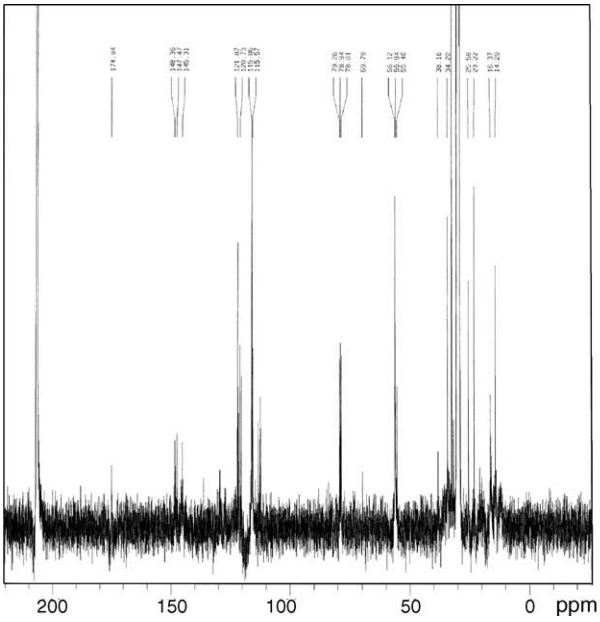


Fig. 5. The representative ^{13}C NMR of oil3 from catalytic run (KOH).

4. Conclusions

This investigation is on the effect of Na and K hydroxides and carbonates on low-temperature hydrothermal treatment of biomass (280 °C for 15 min) products yields and boiling point distributions of oxygenated hydrocarbons. The independent analysis of oil products extracted at various stages led us to see the detailed information on composition and amount of products. The major hydrocarbon was 2-methoxy-phenol in oil1 (ether soluble) from all catalytic runs (NaOH, Na_2CO_3, KOH, K_2CO_3), whereas 3- or 4-methyl-phenol was major hydrocarbon in thermal run. The use of base solutions led to favored the formation of other compounds such as 4-methyl-2-methoxy-phenol, 4-ethyl-2-methoxy-phenol and benzenediol derivatives. Base catalysts increased the water-soluble hydrocarbons and decreased solid residue (biochar). TOC analyses of water phase showed that the base catalysts increased the total organic carbon content. In thermal run furan derivatives were observed whereas these compounds could not be observed in catalytic runs. Oil3 from thermal run contained both low and high boiling point compounds. Catalytic hydrothermal liquefaction of wood biomass mainly produced phenolic compounds the product distribution changed depending on type of base solution.

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Appendix A

Eqs. (A.1)–(A.7) refer to Table 1:

$$\text{conversion (wt.\%)} = \frac{W_{\text{sawdust}} - W_{\text{residue}}}{W_{\text{sawdust}}} \times 100 \tag{A.1}$$

$$\text{oil1 yield (wt.\%)} = \frac{W_{\text{e}}}{W_{\text{sawdust}}} \times 100 \tag{A.2}$$

$$\text{oil2 yield (wt.\%)} = \frac{W_{\text{ea}}}{W_{\text{sawdust}}} \times 100 \tag{A.3}$$

$$\text{oil3 yield (wt.\%)} = \frac{W_{\text{a}}}{W_{\text{sawdust}}} \times 100 \tag{A.4}$$

$$\text{gas yield (wt.\%)} = \frac{W_{\text{c}} - W_{\text{r}}}{W_{\text{c}}} \times 100 \tag{A.5}$$

$$\text{residue yield (wt.\%)} = \frac{W_{\text{residue}}}{W_{\text{sawdust}}} \times 100 \tag{A.6}$$

$$\begin{aligned}\text{WSH and others (wt.\%)} &= 100 - (\text{oil1} + \text{oil2} + \text{oil3} \\ &\quad + \text{solid} + \text{gas})\end{aligned} \tag{A.7}$$

where W_{sawdust} is the weight of sawdust (dry basis), W_{residue} the weight of residue, W_{e} the weight of ether soluble hydrocarbons, W_{ea} the weight of ethyl acetate soluble hydrocarbons, W_{a} the weight of acetone soluble hydrocarbons, W_{c} the charged weight (sawdust + water, in catalytic case 30 ml of alkaline solution instead of water), and W_{r} is the recovered weight (recovered products). All yields were calculated on a dry basis of material.

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