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Low-Temperature Hydrothermal Treatment of Biomass: Effect of Reaction Parameters on Products and Boiling Point Distributions

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　　　　Low-temperature hydrothermal treatment of waste biomass (sawdust) was performed using an autoclave at various temperatures of 180, 250, and 280 °C for 15 min and 60 min. The oil product was obtained from both liquid and solid portions of reaction products from the autoclave, and the composition of oil products was investigated separately. At high reaction temperature, i.e., 250 °C and 280 °C, the longer reaction time led to decreased oil yield; at low reaction temperature (180 °C), the oil yield was found to increase with the increase of reaction time. The oil1 (extracted from the liquid portion) consists of low-boiling-point compounds, whereas oil2 (extracted from the solid portion) contained both low- and high-boiling-point oxygenated hydrocarbons. Ca(OH)$_2$ was found to be effective on liquefaction of biomass in terms of both oil yield and composition. The volatility distribution of oxygenated hydrocarbons in oil1 and oil2 was studied by using a C-NP gram which can be used as a tool for characterizing biomass-derived oil products.

Introduction

Biomass may become more important both as an energy source and as a chemical feedstock in the 21st century. Production of oxygenated hydrocarbons from biomass and use as a chemical or fuel has made consideration of alternative renewable sources important. Current biomass resources from industrial waste wood are mainly in the form of sawdust, agricultural residue, pulp process wastes, and so on. Thermochemical conversion of wood yields three products, i.e., liquid (consisting of oil and water), solid (biochar), and gas. There have been many reports on utilizing waste biomass to produce liquid fuel or chemical feedstock,[1] H$_2$, and medium-heating-value gas,[2] as a carbon for solid fuel[3] or for other applications such as catalyst support.[4] Among various liquefaction processes of lignocellulosic materials, pyrolysis has been studied widely. Aguado et al.[5] studied the pyrolysis of sawdust in a conical spouted bed reactor in the temperature range 350 to 700 °C, and they reported that maximum yield of liquid was obtained at 450 °C. Vacuum pyrolysis of lignin

derived from steam-exploded wood yielded 42.7% oil at 465 °C and below 2 kPa absolute pressure.[6] Roy and co-workers also carried out production of carboxylic acid from wood,[7] and catalytic gasification of the aqueous byproduct from vacuum pyrolysis of biomass.[8] Panigrahi et al.[9] studied production of syn gas and high-heating-value (Btu) gas fuel from the pyrolysis of biomass-derived oil and experimental and kinetic studies on pyrolysis of lignins.[10] Karaosmanoglu et al.[11] studied slow pyrolysis of the straw and stalk of the rapeseed plant in a tubular reactor under the conditions of static atmosphere, in the temperature range 350–650 °C. The maximum oil yield (about 18%) was obtained at 650 °C at 30 °C/min heating rate.[11] Besides slow pyrolysis, fast pyrolysis of biomass has also been studied. Recently, Oasmaa et al.[12] have highlighted fast pyrolysis of forestry residue. Product distribution and oil quality were discussed in detail. Analytical pyrolysis of biomass is useful to understand degradation behaviors of various types of biomass. Jakab et al.[13] studied the thermal decomposition of three lignosulfonates, three sodium salts of a spruce milled wood lignin (MWL) and a

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mixture, and MWL and NaCl by thermogravimetry/mass spectrometry. The TG curves and the evolution profiles of degradation products showed that the lignosulfonate cations play an important role in the decomposition. Characterization of sulfur-free lignins of an organosolv pulping and a spruce milled wood lignin (MWL) was carried out by using pyrolysis gas chromatography/mass spectrometry.[14] Analytical pyrolysis of the organosolv lignins and MWL yielded compounds such as phenol, guaiacol and guaicol derivatives, eugenol, etc. Chemical conversion of biomass has been carried out by using different solvents such as ethylene glycol,[15] tetralin,[16] and methanol.[17] Hydrothermal process has become an important process in the chemical conversion of biomass[18-20] as water is a unique, and environmentally benign solvent. Kruse et al.[21] studied the degradation of biomass in water in the ranges of 330-410 °C and 30-50 Mpa and at 15 min reaction time. Identified compounds were phenols, furfurals, acids, and aldehydes.[21] Formation of organic acids during the hydrolysis and oxidation of several wastes in sub- and supercritical water was studied by Calvo et al.[22] They reported that under hydrolytic conditions, 70% of the initial total carbon remained as the liquid. The use of excess oxygen showed 95% conversion to the gaseous product.[22] The main objective of the present study is to investigate the possibility of low-temperature hydrothermal liquefaction of biomass, the effect of reaction temperature and reaction time, identification of oxygenated hydrocarbons from solid and liquid portion independently, and boiling point distribution of hydrocarbons (C-NP gram) obtained from liquid and solid extraction. In addition, we attempted to see the effect of Ca(OH)$_2$ on the yield of liquid products during the hydrothermal treatment and composition of liquid products from catalytic treatment.

Experimental Section

Materials. The biomass (sawdust) used in this study was obtained from Yonebayashi Milling Co., Ishikawa prefecture, Japan, and the composition and properties of biomass was given in Table 1. Elemental analysis and calorific value was obtained from an outside analysis center. Ash content was measured by TGA analysis (TGA-51 SHIMADZU). The biomass (sawdust) was used as received. The solvents, including acetone and ether, were purchased from Wako Chemicals, Japan, and used as received.

Experimental Procedure. Hydrothermal liquefaction experiments were conducted in a 200 mL TaS-02-HC type
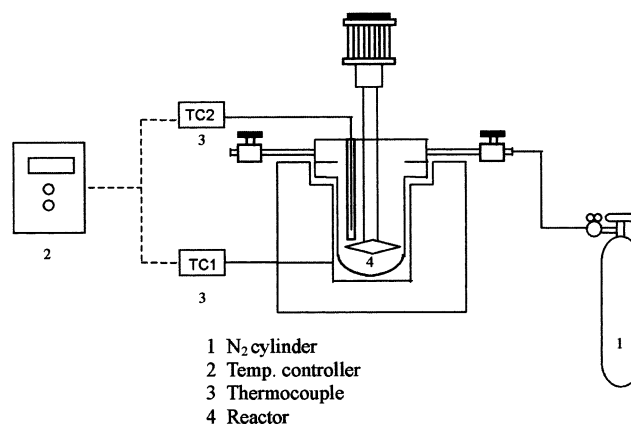
Figure 1. Schematic experimental setup of the autoclave for the hydrothermal treatment of biomass

Table 1. Composition and Properties of Biomass

biomass	moisture, wt %	ash content, wt % (d.b)	calorific value, cal/g (d.b)	carbon, wt % (d.b)	hydrogen, wt % (d.b)
sawdust	32.5	0.5	3270	50.7	6.2

d.b: dry basis

autoclave at 180 °C, 250 °C, and 280 °C for 15 min and 60 min. In a typical hydrothermal liquefaction experiment, the reactor was loaded with 5 g (based on dry basis) of sawdust with 30 mL of ion-exchanged water. In a catalytic experiment, 30 mL of Ca(OH)$_2$ (0.0243 M) solution was used as a solvent instead of water. Ca(OH)$_2$ solution was prepared taking into consideration Ca(OH)$_2$ solubility in 100 mL water (Solubility of Ca(OH)$_2$ in 100 mL of H$_2$O is 0.18 g).[23] Then the reactor was purged five times with nitrogen to remove the inside air. Reactants were agitated vertically at $\cong$ 60 cycles/min using a stirrer as shown in Figure 1. The temperature was then raised to the desired levels at a heating rate of 3 °C/min and kept for 15 min and 60 min for all the temperatures used in the present investigation. After the reaction time, the reactor was cooled to room temperature by a fan. The gaseous products were vented. The procedures for separation and extraction of reaction products are presented in Scheme 1. Solid and liquid products were separated by filtration under vacuum for 5 min. During filtration, 100 mL ion-exchanged water was used for washing solid products. The liquid was acidified with HCl (1.7 M) to pH 1-2. This solution was extracted with an equal quantity of diethyl ether. 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 called oil1. Solid products were extracted with acetone 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 called oil2. The acetone-insoluble fraction was dried at 105 °C and then weighed; it was called solid (biochar).

Analysis of Liquid Products. Both oil1 and oil2 were analyzed by a gas chromatograph equipped with a mass selective detector. [GC-MS; HP 5973; column, HP-1; cross-linked methyl siloxane, 25 × 0.32 mm × 0.17 μm; temperature program, 40 °C (hold 10 min) → 300 °C (rate 5 °C/min) hold for 10 min.]

Results and Discussion

The Effect of Temperature on Oil Yield and Boiling Point Distribution. Hydrothermal liquefaction of biomass was carried out at temperatures of 180 °C, 250 °C, and 280 °C for 15 min and 60 min.

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Table 2. Results on the Effect of Temperature and Reaction Time on the Yield of Various Products (standard deviations on conversion products: ±0.5%)

run no. (reaction temperature and time)	conversion,[a] wt %	Oil			gas,[d] wt %	residue,[e] wt %	others,[f] wt %
		Oil1,[b] wt %	Oil2,[c] wt %	total oil, wt %			
1 (180 °C−15min)	26.7	0.8	2.9	3.7	1.7	73.3	21.3
2 (180 °C−60min)	30.6	0.7	4.6	5.3	2.2	69.4	23.1
3 (250 °C−15min)	56.8	1.4	6.2	7.6	4.2	43.2	45.0
4 (250 °C−60min)	56.4	1.0	5.4	6.4	6.0	43.6	44.0
5 (280 °C−15min)	58.0	1.3	7.2	8.5	9.4	42.0	40.1
6 (280 °C−60min)	58.9	1.2	5.4	6.6	14.0	41.1	38.3
7 (280 °C−15min)	56.8	3.4	5.9	9.3	11.9	43.2	35.6

0.0243 M Ca(OH)$_2$ soln.

[a] See Appendix, eq 1. [b] See Appendix, eq 2. [c] See Appendix, eq 3. [d] See Appendix, eq 4. [e] See Appendix, eq 5. [f] See Appendix, eq 6.

Scheme 1. Separation Procedure
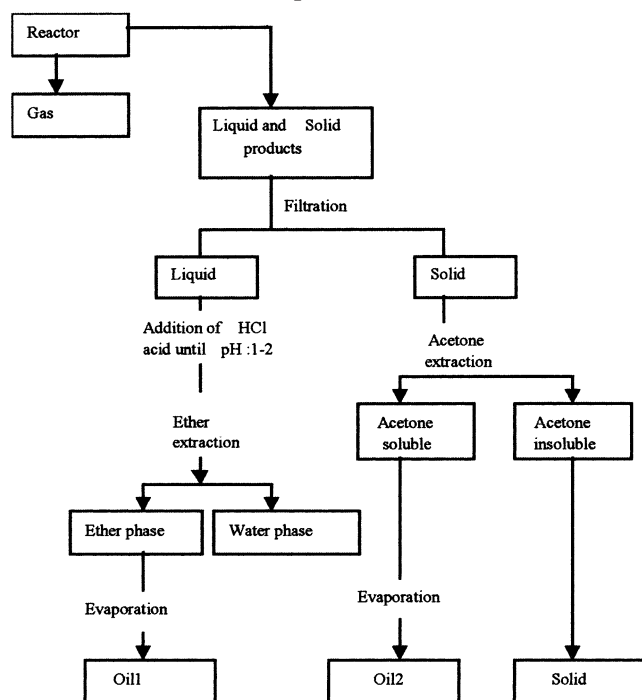
Experimental conditions, conversion, and yields are shown in Table 2. In hydrothermal liquefaction experiments, temperature affected both product composition and yield of products. The low reaction temperature and time were 180 °C for 15 min, the conversion of sawdust was 26.7 wt %, and the total oil yield was found to be 3.7 wt %. Studies in the literature on the conversion of biomass were carried out at elevated temperatures such as s 450−900 °C,[24] 350−700 °C,[5] and 350−650 °C.[11] With an increase in the temperature from 180 °C (15 min) to 250 °C (15 min), total oil yield was increased from 3.7 to 7.6 wt %. Further increase in the temperature to 280 °C (15 min) led to an increase in total oil yield from 7.6 to 8.5 wt %. The increase of reaction temperature from 180 °C (60 min) to 250 °C (60 min) and 280 °C (60 min) increased the conversion of biomass from 30.6 wt % to 56.4 wt % and 58.9 wt %, respectively. There is no appreciable increase in the conversion of biomass with the increase of temperature from 250 °C to 280 °C. The water-soluble hydrocarbons (others in Table 2) were the highest (45%) at the temperature of 250 °C for 15 min. The effect may be caused by decomposition of hemicellulose and cellulose. It is known that the dry weight of plants is typically composed of 50 to 80 wt % of the polymeric carbohydrate and cellulose along with structural materials. The decomposition of cellulose produces highly water-soluble products. The noncatalytic decomposition of cellulose in near-critical water was carried out by Sakaki et al.[25] They reported that cellulose was rapidly decomposed to water-solubles (WS), and the WS were further decomposed after the WS yield reached nearly 80 wt %.

GC-MS analysis of oil1 and oil2 was performed, and the composition of the oils is presented in Table 3 and Table 4, respectively, with an increase in their retention time. The main difference between oil1 and oil2 was found to be the presence of lower-boiling-point compounds in oil1 and low- and high-boiling-point hydrocarbons in oil2. The major hydrocarbons in both oil1 and oil2 (in all runs) are phenolic compounds. Wood chemistry shows that lignin has phenylpropane units, which are a highly rich source of phenolic compounds. Formation of phenolic compounds is considered as decomposition of lignin. In oil1, 1,2-benzenediol was observed in run3 to run7. Klein studied the pyrolysis of guaiacol (2-methoxy phenol) at 350 °C, and it yielded mainly catechol (1,2-benzenediol), methane, phenol, and carbon monoxide.[26] It is considered that in oil1, initially 2-methoxy phenol was formed and decomposed to form 1,2-benzenediol. In another study, the effect of biomass/water ratio on product and boiling point distribution revealed that only sawdust without water liquefaction at 280 °C for 15 min yielded more benzenediol derivatives than in the presence of water in both oil1 and oil2.[27] The presence of water hindered the formation of benzenediol derivatives.

Steroids are important natural products and are used for pharmaceutical applications.[28] Sitosterol is a predominant component of tall oil sterols, which has been recognized as a substrate in fermentation to steroid precursors. These intermediates are commercially important and are used in the synthesis of spirolactone, hydrocortisones, and steroid hormones. 4-Hydroxyandrostene-3,17-dione is a C$_{19}$ which has been synthesized for breast cancer therapy.[28] β-Sitosterol was observed in oil2 from all runs. This compound was not observed in oil1 as it is extracted from the liquid portion, and oil2 was extracted from solid. Hardwood extractives

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Table 3. Identification of Compounds in Oil1 by GC-MS Analysis

No.	R.T., min	Name of Compound	Run1	Run2	Run3	Run4	Run5	Run6	Run7
1	2.04	2-Furancarboxaldehyde	+	+	+	+	+	+	+
2	3.270	2-Cyclopenten-1-one, 2-methyl				+	+	+	+
3	3.492	Ethanone, 1-(2-furanyl)-			+	+	+	+	+
4	3.718	2,5-Hexanedione				+	+	+	+
5	4.932	2-Furancarboxaldehyde, 5-methyl	+	+	+	+	+	+	+
6	7.047	Phenol				+	+	+	+
7	7.544	2-Cyclopenten-1-one, 2-hydroxy-3-methyl				+		+	+
8	7.881	1,2-Cyclopentanedione, 3-methyl				+			
9	8.971	3,4-Dimethyl-2-hydroxycyclopent-2-en-1-one						+	+
10	9.621	Phenol, 2-methoxy	+	+	+	+	+	+	+
11	10.14	Phenol, 3-methyl or Phenol, 4-methyl	+	+	+	+	+	+	+
12	11.496	2-Furancarboxylic acid	+						
13	13.729	Phenol, 2-methoxy, 4-methyl			+	+	+		+
14	14.426	2-Furancarboxaldehyde, 5-(hydroxymethyl)-		+	+				
15	14.657	1,2-Benzenediol			+	+	+	+	+
16	15.443	Phenol, 4-ethyl, 2-methoxy				+	+	+	+
17	16.939	1,2-Benzenediol, 4-methyl						+	+
18	18.162	Vanillin	+	+	+	+		+	+
19	18.239	1,3-Benzenediol, 4,5-dimethyl							+
20	20.326	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-			+			+	+
21	21.456	Butylated hydroxytoluene	+	+	+		+	+	+
22	23.083	Benzoic acid, 4-hydroxy-3-methoxy-		+	+	+			
23	24.5	Benzeneaceticacid, 4-hydroxy-3-methoxy		+			+	+	+
24	40.24	Bis(2-ethylhexyl) phthalate		+					
25	41.044	6H-Dibenzo[b,d]pyran-6-one, 7,9-dihydroxy-3-methoxy-1-methyl	+						
26	44.411	Benzaldehyde, 2,4-dihydroxy	+						

(1−5 wt % dry wood) contain mainly fatty acid esters (fats and waxes) and sterols. Softwood extractives (1−4 wt % dry wood) consist of neutral compounds (hydrocarbons, fatty acids, fatty alcohols, sterol, triterpenyl alcohols, and triglycerides) and resin acids.[12] In run1 (180 °C for 15 min), two streoids named α-estradiol and cholest-14-ene, (5-α) was also observed in oil2. In both oil1 and oil2, 2-furancarboxyaldehyde was observed for all runs (except in oil2 from run1 and run2).

Jakab et al.[29] studied thermal decomposition of wood and cellulose in the presence of solvent vapors. They reported that the product distribution 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-furalaldehyde increased in the presence of water. Wood is composed of mainly cellulose, hemicellulose, lignin, and extractives. Formation of 2-furancarboxaldehyde and 5-methyl-2-furancarboxaldehyde from hydroliquefaction of biomass is in good agreement with this previous report.[29]

The composition of biomass-derived oil is a very complex mixture. Murata et al. discussed the representation of volatility (boiling point) distribution of plastic-derived oils with a C-NP (C stands for carbon and NP stands for normal paraffin) gram.[30] In the present investigation we have used GC-MS analysis data and presented the boiling point distribution of biomass-derived oils, i.e., oil1 and oil2, to understand the composition of hydrocarbons obtained from the liquid and solid portions of reaction products. Briefly, the NP gram is a carbon number distribution of hydrocarbons derived from the gas-chromatogram on the basis of boiling points of a series of normal paraffins. We can find out the peak positions of a series of normal paraffins on a gas chromatogram of the liquid product obtained by thermal degradation of polymers by using PE-derived oil which contains a series of normal paraffins and used as a index material. The NP gram is made by plotting the weight fraction of hydrocarbons, which are located within the range of retention values of two successive normal paraffins, C_{n-1} and C_n, against the carbon number, *n*. Since the carbon number, *n*, corresponds to the boiling point range of a certain group of hydrocarbons, the NP gram actually represents a volatility distribution of the liquid product. The quantitative analysis along with the volatility distribution of liquid products (oil1 and oil2) was done with C-NP. In a recent study, Branca et al.[31] carried out GC/MS characterization of liquids obtained from pyrolysis of wood in the heating temperature range 600−900 K. They used GC-MS data for both qualitative and quantitative analysis. Although reaction conditions in their study[31] (minimum temperature: 327 °C, pyrolysis) and our present study (maximum temperature: 280 °C, hydrothermal) are completely different, the major compounds were similar. In our study, we identified and quantified the compounds by using a C-NP gram from GC-MS data. The C-NP gram of oil1 and oil2 for run1−run6 was presented in Figure 2 and Figure 3, respectively. It can be clearly seen from Figure 2, parts a and b, that the majority of hydrocarbons for oil1 are distributed in the boiling point range of C_{10} to C_{12}, except for 180 °C. At 180 °C, the majority of oxygenated hydrocarbons were in the ranges from C_9 to C_{11} and from C_6 to C_8 for 15 min and 60 min, respectively. Figure 3, parts a and b, shows the C-NP gram of oil2 for run1−run6. In a similar way with oil1, at the lowest temperature the distribution of hydrocarbons was different in oil2 (Figure 3, parts a and b) with other temperatures (250 °C and 280 °C). At 180 °C with a 15 min reaction time, the majority of the hydrocarbons were in the range

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**Table 4. Identification of Compounds in Oil2 by GC-MS Analysis**

No.	R.T., min	Name of Compounds	Run1	Run2	Run3	Run4	Run5	Run6	Run7
1	2.04	2-Furancarboxaldehyde			+	+	+	+	+
2	3.27	2-Cyclopenten-1-one, 2-methyl					+	+	+
3	3.492	Ethanone, 1-(2-furanyl)-			+		+	+	
4	3.718	2,5-Hexanedione					+		
5	4.932	2-Furancarboxaldehyde, 5-methyl			+	+	+	+	+
6	7.047	Phenol					+		+
7	7.544	2-Cyclopenten-1-one, 2-hydroxy-3-methyl					+		
8	7.809	2-Cyclopenten-1-one, 3,4,4-trimethyl					+		
9	9.621	Phenol, 2-methoxy			+	+	+	+	+
10	10.14	Phenol, 3-methyl or Phenol, 4-methyl	+	+	+	+	+	+	+
11	12.455	Phenol, 2,4-dimethyl							+
12	13.729	Phenol, 2-methoxy, 4-methyl			+	+	+	+	
13	15.443	Phenol, 4-ethyl-2-methoxy			+	+	+	+	+
14	16.501	Ethanone, 1-(3-methoxyphenyl)-		+					
15	17.795	2',4'-Dihydroxypropiohenone					+	+	+
16	18.162	Vanillin	+	+		+	+		
17	18.239	1,3-Benzenediol, 4,5-dimethyl							+
18	19.775	Eugenol	+	+	+	+	+	+	+
19	19.842	Phenol, 2-methoxy-4-(1-propenyl)-				+		+	+
20	20.326	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-				+			
21	24.5	Benzeneacetic acid, 4-hydroxy-3-methoxy	+	+	+	+	+	+	+
22	25.658	Benzene, 1,2-dimethoxy-4-(2-propenyl)-	+						
23	30.379	Dibutyl phthalate	+						
24	30.584	Kaur-15-ene, (15-alpha, 9-alpha, 10-beta)	+				+		
25	31.187	Hexadecanoic acid	+			+	+	+	
26	32.444	6H-Dibenzo[b,d]pyran-1-ol, 6,6,9-trimethyl-3-propyl					+		
27	33.134	9H-Xanthen-9-one, 1-hydroxy-3,5,6-trimethoxy					+	+	
28	34.694	4H-1-Benzopyran-4-one, 3,5,7-trihydroxy-2-[4-hydroxy]					+		
29	35.233	Hemigossypol					+		
30	35.516	Cholest-14-ene, (5-α)-	+						
31	35.716	α-Estradiol	+						
32	36.16	Benzeneaceticacid, 4-hydroxy-3-methoxy, methyl ester					+	+	
33	36.401	Podocarpa-6,8,11,13-tetraen-12-ol, 13-isopropyl-, acetate	+						+
34	36.498	3-Phenanthrenol, 4b,5,6,7,8,8a,9,10-octahydro-4b,8,8-trimethyl-2-(1-methylethyl)-, acetate, (4bS-trans)-	+	+					
35	36.631	4-Hexanoylresorcinol					+		
36	38.433	2(1H)-Phenanthrenone,3,4,4a,9,10,10a-hexahydro-6-hydroxy-1,1,4a-trimethyl-7-(1-methylethyl)-, (4aS-trans)-			+		+		+
37	40.231	Cyclopropanenonanoic acid, 2-[(2-butylcyclopropyl)methyl]-, methyl ester		+					+
38	40.235	1,2-Benzenedicarboxylic acid, diisooctyl ester					+		
39	40.237	Bis(2-ethylhexyl)phthalate						+	
40	40.699	9(1H)-Phenanthrenone,2,3,4,4a,10,10a-hexahydro-6-hydroxy-1,1,4a-trimethyl−7-(1-methylethyl)-, (4aS-Trans)-	+	+	+	+	+	+	+
41	41.044	6H-Dibenzo[b,d]pyran-6-one, 7,9-dihydroxy-3-methoxy-1-methyl	+	+			+		
42	41.085	Estradiol			+				
43	41.106	Podocarpa-6,13-diene, 13-isopropyl-			+	+			
44	41.427	Spiro[benzofuran-2(3H),2'-oxiran]−3-one, 6,7-dimethoxy-3'-phenyl					+	+	
45	41.64	1-Hydroxy-3-n-hexyl-9-methyl-7,8,9,10-tetrahydro-6-dibenzopyrone	+						
46	43.393	4-(1,1-Dimethylallyl)-9-methoxy-7H-furo[3,2-G][1]benzopyran-7-one	+	+					
47	44.033	1H-Naphtho[2,1-b]pyran-1-one, 3-acetyl-7,8-dimethoxy-2-methyl					+	+	
48	44.411	Benzaldehyde, 2,4-dihydroxy	+			+	+		+
49	44.5	1,3-Benzodioxol-5-ol			+				+
50	45.352	Phenanthro[3,2−6]furan-7,11-dione, 1,2,3,4,8,9-hexahydro-4,4,8-trimethyl-, (t)-				+			
51	45.358	9,10-Anthracenedione, 1,5-diethoxy-				+			
52	49.79	β-Sitosterol	+	+	+	+	+	+	+
53	51.125	Stigmast-4-en-3-one	+	+	+				

C_{16} to C_{18} and they are about 31 wt % (Figure 3a). The hydrocarbons were found around 20 wt % at C_{23}, and about 11 wt % at C_{11} at 180 °C with a 15 min reaction time. However, at 280 °C for 15 min, hydrocarbons were distributed as around 9 wt % at C_8, about 42 wt % at

C_{11} in oil2 (Figure 3a). This clearly shows the effect of temperature on the production of hydrocarbons with a wide range of boiling points. The major difference between oil1 and oil2 was the presence of higher-boiling-point compounds in oil2 (Figure 3, parts a and b) after
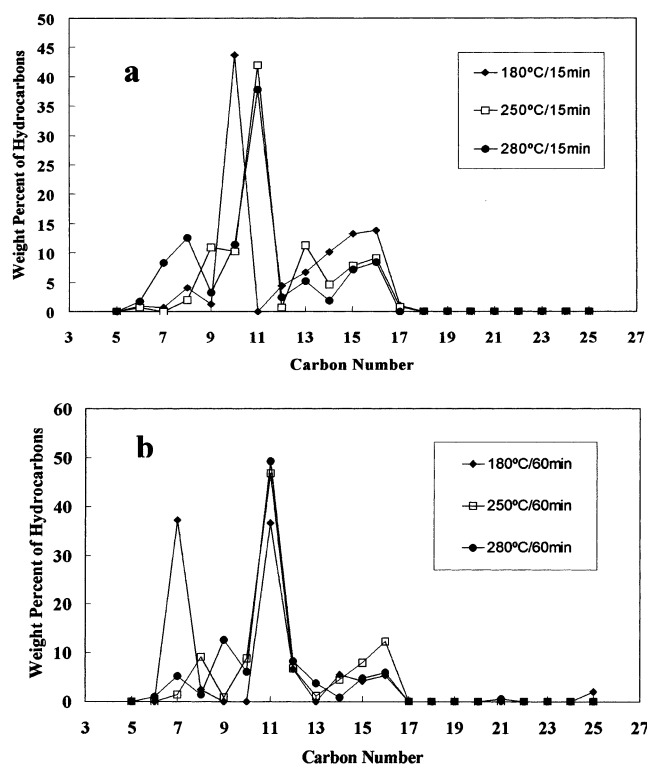
Figure 2. (a) C-NP gram of oil1 at the temperatures of 180 °C, 250 °C, and 280 °C for 15 min. (b) C-NP gram of oil1 at the temperatures of 180 °C, 250 °C, and 280 °C for 60 min.
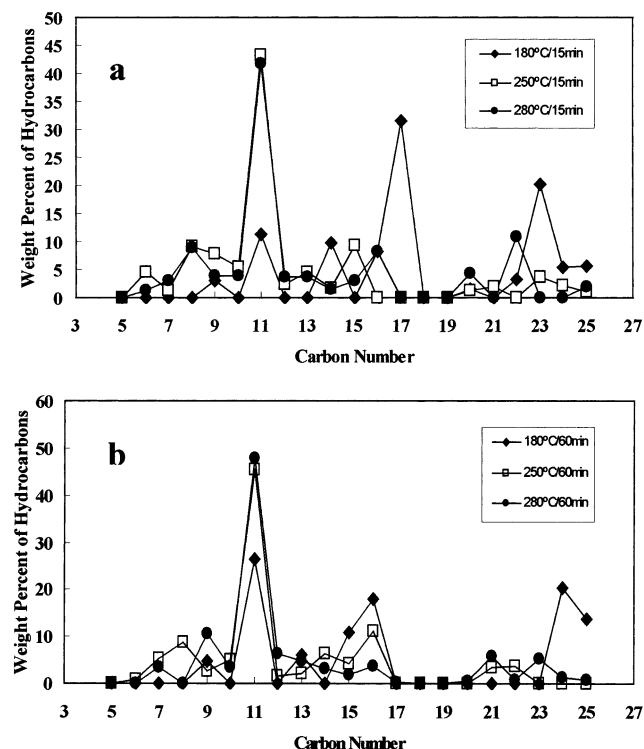
Figure 3. (a) C-NP gram of oil2 at the temperatures of 180 °C, 250 °C, and 280 °C for 15 min. (b) C-NP gram of oil2 at the temperatures of 180 °C, 250 °C, and 280 °C for 60min.

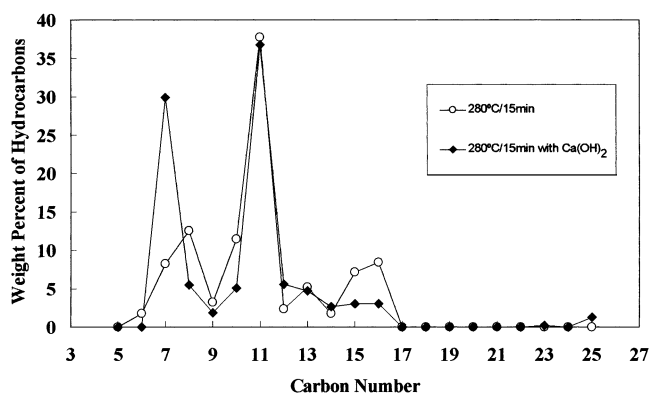C_{17} up to C_{25} hydrocarbons, which are not observed in the C-NP gram of oil1 (Figure 2, parts a and b).

The Effect of Reaction Time on Oil Yield and Boiling Point Distribution. Not only the temperature but also the reaction time has an important effect on oil yield and boiling point distribution. At the temper-

ature of 180 °C for 15 min, the conversion was 26.7 wt % and total oil yield was found to be 3.7 wt %. At the same temperature, the longer reaction time (60 min) increased both conversion (30.6 wt %) and total oil yield (5.3 wt %). As can be seen from the Table 2, the oil products were extracted both from the liquid and the residue portions after the hydrothermal treatment and designated them as oil1 and as oil2, respectively. In contrast to 180 °C, at 250 °C the longer reaction time (60 min) decreased the total oil yield from 7.6 wt % to 6.4 wt %. This is because the secondary decomposition of oil to the gas has taken place and subsequently the gas yield increased from 4.2 wt % to 6.0 wt %. Minowa et al.[32] studied the decomposition of cellulose and glucose in hot compressed water under catalyst-free conditions. They found that the longer reaction time led to decreased oil yield. At 280 °C for 15 min, the total oil yield was 8.5 wt % and the gas yield was 9.4 wt %. At this temperature with a 60 min holding time, total oil yield decreased to 6.6 wt % (gasification of oil products) and gas yield increased to 14.0%. In oil1 (Table 3) at the temperatures of 180 °C at the longer reaction time, 5-(hydroxymethyl)-2-furan carboxaldehyde, 4-hydroxy-3-methoxybenzoic acid, 4-hydroxy-3-methoxybenzene-acetic acid, and bis(2-ethylyhexyl) phthalate were observed. However, these compounds were not observed at the same temperature for 15 min. In oil2 (Table 4), at 280 °C for 15 min, some compounds such as vanillin, phenol, 2,4-dihydroxybenzaldehyde, etc., were found but these compounds were not observed at the longer reaction time (60 min). It can be concluded that reaction time also has an effect on the type of compounds both in oil1 and oil2 at all temperatures. As can be seen from Figure 2a and Figure 2b, at 180 °C for 15 min, the hydrocarbons in the range C_9 to C_{11} were about 43%, while at the longer reaction time, the hydrocarbons in the ranges C_6 to C_8 and C_{10} to C_{12} were about 37% and 36%, respectively. At 250 °C for both 15 min and 60 min, the majority of hydrocarbons were in the same range (from C_{10} to C_{12}). However, the hydrocarbons are about 9% in C_7 to C_9 at the longer reaction time (Figure 2b), while the hydrocarbons were found to be 2% (Figure 2a) in the same range for 15 min. It is clear that at this temperature, longer reaction time led to crack hydrocarbons in oil1 (Figure 2a,b). At 280 °C, the longer reaction time produced hydrocarbons around 49% in the range C_{10} to C_{12}, 12% in the range C_8 to C_{10}, and 8% in the range C_{11} to C_{13} (Figure 2b). At the same temperature with a 15 min reaction time, the distributions of hydrocarbons were 37% in C_{10} to C_{12}, 11% in C_9 to C_{11}, and 7.2% in C_{14} to C_{16}. It can be clearly seen from Figure 3a,b that the reaction time did not have a remarkable effect on the distribution of hydrocarbons in oil2 at temperatures of 250 °C and 280 °C. The majority of the hydrocarbons were distributed in the range C_{10} to C_{12}. However, at 180 °C with 15 min holding time, the majority of hydrocarbons were 32% in the range C_{16} to C_{18} (Figure 3a). At the longer reaction time, the majority of hydrocarbons were about 26% and distributed between C_{10} and C_{12} (Figure 3b). It can be concluded that the longer reaction time was more pronounced in oil2 at the lowest temperature.

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The Effect of Ca(OH)₂ on Product and Boiling Point Distribution. There has been a plethora of research[33-37] on the efforts to use some catalysts for liquefaction of biomass. Direct liquefaction of wood in a hydrogen donor solvent (tetralin) at 400 °C and 10 Mpa using Co–Mo/γ-Al₂O₃ and Pt/γ-Al₂O₃ was carried out by Araya et al.[33] They reported that lighter organic liquids were obtained in the presence of catalysts. Boocock et al.[34] studied the production of synthetic organic liquids from wood using a modified nickel catalyst. With the use of Raney nickel catalyst at 350 °C with hydrogen pressures of 6.6 Mpa, high hydrogen uptake with concomitant methane formation initially occurred. Base catalysts have been used widely in the degradation of biomass. The degradation of biomass in anhydrous glycerin in the presence of Na_2CO_3 or KOH,[35] co-condensation of NaOH-catalyzed liquefied wood wastes, phenol, and formaldehyde for the production of resol-type adhesives,[36] and also improved alkaline oxidation for production vanillin and syringaldehyde from steam-explosion hardwood lignin[37] were widely reported in the literature. To investigate the catalytic effect of Ca(OH)₂ on product distribution and oil composition, we carried out hydrothermal liquefaction of biomass in the presence of Ca(OH)₂.

A quantity of 30 mL of Ca(OH)₂ [0.0243 M] solution was used in the hydrothermal liquefaction of biomass at 280 °C for 15 min. Compared to hydrothermal liquefaction of sawdust (run5), there is no remarkable change in total conversion. However, the gas yield increased to 11.9% and water-soluble products decreased to 35.6 wt %. The use of Ca(OH)₂ increased the oil yield, and total oil was found to be 9.3 wt %. With hydrothermal treatment in the presence of catalyst (280 °C, 15 min), higher oil1 yield (3.4 wt %) was observed than in the absence of catalyst (1.3 wt %). It is well-known that the use of neutral or alkaline salts such as KCl, NaCl, Na_2CO_3, and K_2CO_3 have an important effect on the decomposition of lignocellulosic materials. Cellulose decomposition in hot compressed water with alkali or nickel catalyst[38] and pyrolysis of wood with alkaline and neutral salts[39] were widely reported in the literature. Not only alkaline or neutral salts[40] but also basic additives or solutions[35] have an important effect on the decomposition of lignocellulosic materials. Compared to hydrothermal liquefaction, in oil1 (Table 3) 3,4-dimethyl-2-hydroxycyclopent-2-en-1-one, 4-methyl-1,2-benzenediol, vanillin, and 4,5-dimethyl-1,3-benzenediol were observed in the catalytic run. In oil2 (Table 4) in the absence of Ca(OH)₂, some compounds such as 1-(2-furanyl)ethanone, hexadecanoic acid, and 6,7-dimethoxy-3′-phenyl-spiro[benzofuran-2(3H),2′-oxiran]-3-one were observed while these compounds could not be observed

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Figure 4. Comparison of C-NP gram of oil1 obtained from thermal and catalytic run at 280 °C.
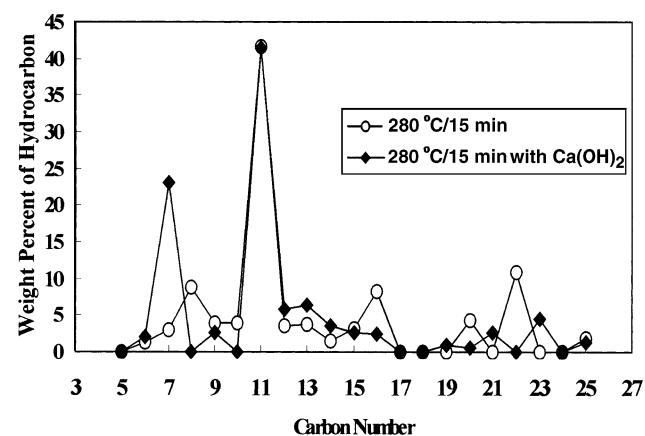
Figure 5. Comparison of C-NP gram of oil2 obtained from thermal and catalytic run at 280 °C.

in the catalytic case. The main big difference was observed in C-NP grams (Figure 4 and Figure 5) between the thermal and the catalytic case. It can be clearly seen from the C-NP gram in oil1 (Figure 4), that the use of Ca(OH)₂ produced the oxygenated hydrocarbons about 30% in C_6 to C_8, whereas it was about 8% in the thermal case. The majority of the hydrocarbons in both the thermal and catalytic cases were distributed in the range C_{10} to C_{12} in both oil1 (Figure 4) and oil2 (Figure 5). While in the thermal case the boiling point distribution of oxygenated hydrocarbons in oil2 (Figure 5) in the range of C_6 to C_8 was about 3.5%, with Ca(OH)₂ it was about 23% in the same range. It might be that the presence of Ca(OH)₂ increased phenolic compounds in both oil1 and oil2. Similar results were reported by Thring et al.[41] They studied alkaline depolymerization of lignin.[41] Lignin was isolated from wood by a solvolytic process using ethylene glycol and then depolymerized at 300 °C for 1 h in a batch reactor by using 1–6% NaOH solutions under a N₂ atmosphere. Highest total phenols yield was obtained with 1–2 wt % NaOH solutions. In the present investigation, we used Ca(OH)₂ as a catalyst and found the dominant effect in terms of product selectivity and quality of oil. Further investigation on the effect of the amount of calcium and other conditions in increasing the yield of liquid products is in progress.

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Conclusions

Hydrothermal liquefaction of biomass was carried out at temperatures of 180 °C, 250 °C, and 280 °C with reaction times 15 min and 60 min and found the effect of temperature and residence time on product and boiling point distribution. The increase of reaction temperature increased the conversion of biomass and total oil yield. The maximum oil was found to be 8.5 wt % at 280 °C for 15 min. In the catalytic case, total oil yield was found to be 9.3 wt %. During the longer reaction times, secondary reactions of oil products occurred and subsequently the yields of oil products were decreased except at the low reaction temperature of 180 °C. The oxygenated hydrocarbons extracted from the solid portion of the reaction gave the high-boiling-point hydrocarbons up to C_{25}; in the case of the liquid portion it was about C_{17}. The low-temperature hydrothermal treatment of biomass produced lower oil yield in comparison to the pyrolysis process. However, the selective conversion of biomass to phenolic compounds for use as chemicals is an interesting option. The major hydrocarbons in both oil1 and oil2 obtained from hydrothermal treatment of biomass were phenolic compounds. $Ca(OH)_2$ increased the oil yield and selectively the phenolic compounds in oil1 and oil2.

Appendix

Equations 1−6 refer to Table 2:

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

$$\text{Oil1 yield (wt \%)} = \frac{W_e}{W_{sawdust}} \times 100 \quad (2)$$

$$\text{Oil2 yield (wt \%)} = \frac{W_a}{W_{sawdust}} \times 100 \quad (3)$$

$$\text{gas yield (wt \%)} = \frac{W_c - W_r}{W_c} \times 100 \quad (4)$$

$$\text{residue yield (wt \%)} = \frac{W_{residue}}{W_{sawdust}} \times 100 \quad (5)$$

others (wt %): $100 - (\text{Oil1} + \text{Oil2} + \text{solid} + \text{gas})$ (6)

where $W_{sawdust}$ = weight of sawdust (dry basis), $W_{residue}$ = weight of residue, W_e = weight of ether-soluble hydrocarbons, W_a = weight of acetone-soluble hydrocarbons, W_c = charged weight (sawdust + water, in catalytic case $Ca(OH)_2$ solution instead of water), and W_r = recovered weight (recovered products). All yields were calculated on a dry basis material.