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Fractional Catalytic Pyrolysis of Hybrid Poplar Wood

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Fractional catalytic pyrolysis is a selective in situ conversion of biopolymers into desired products. Fractional catalytic pyrolysis was used to convert the lignin fraction of hybrid poplar wood into high yields of cresols and phenols while the carbohydrate fraction was selectively converted into gaseous products. Ground air-dried biomass was fractionally pyrolyzed at 450−500 °C in a 2-in fluidized bed reactor. The total liquid, gas, and char/coke yields were 33%, 53%, and 12.5%, respectively. The low viscosity liquid products consisted of almost pure phenolics with minor carbohydrate decomposition products. The major liquid components were phenol, cresols, methyl substituted phenols, and small fractions of indene and substituted naphthalenes. The carbon and oxygen contents and high heating value (HHV) of the oil were 71%, 21%, and 30.5 MJ/kg, respectively. About 90 wt % of the gaseous products was carbon monoxide and carbon dioxide, and the rest was a mixture of hydrocarbons.

1. Introduction

Conventional rapid pyrolysis (RP) of biomass is a thermal treatment process in the absence of air, which produces char, liquid, and gaseous products.[1–14] In these processes, the pyrolysis temperatures range from 450 to 600 °C and vapor residence times are less than 1−5 s. In the RP process, liquid production is maximized at the expense of gaseous and solid products. The liquid product (bio-oil or biocrude) is generally unstable, acidic, corrosive, viscous, and has high moisture content.[15–18] The poor stability of biocrude oils is attributed to the char and alkali metals in the oil, which catalyze secondary reactions during storage.[17] However, if the hot pyrolysis vapors are filtered to reduce the char content before condensation, the stability of the oil is improved considerably.[18]

Biocrude oils are complex mixtures of carbohydrate and lignin thermal decomposition products, which cannot be used for most biobased products and fuel applications except after considerable secondary processing. Secondary processing such as catalytic upgrading,[19–26] liquid−liquid extraction,[27–29] or gasification[30–35] increases the cost of the final product and makes it less economically competitive relative to fossil derived products.

Catalytic studies of biomass pyrolysis products have focused on upgrading of pyrolysis oils (post pyrolysis catalysis) to higher value products,[19–26] but most of these studies reported low yields of hydrocarbons, high coke/char yields, and rapid deactivation of the catalysts. Other catalytic studies of whole biomass feedstocks focused on gasification to synthesis gas,[30–35] but fractional pyrolysis has not been reported in published literature.

Biomass feedstocks are composed of structural (lignin, cellulose, and hemicellulose) and nonstructural (extractives) components, which have distinct chemical properties. It is conceivable to selectively convert the biomass constituents to a defined slate of chemicals and separate these products in situ (fractional pyrolysis) without necessarily going through secondary extraction and upgrading processes. Fractional pyrolysis is defined as a selective in situ conversion of biopolymers to desired products. The goal of this research is to selectively convert biomass components in situ into suitable products using suitable catalysts, thus eliminating potential secondary processing steps. In this paper, we report the fractional catalytic conversion of the carbohydrate components of hybrid poplar wood into gaseous products and depolymerization of lignin into phenol, cresols, and catechols.

2. Experimental Section

2.1. Feedstocks and Catalyst. The feedstock used for these experiments was hybrid poplar wood that was ground in a Wiley mill (model 4) to pass a 1-mm screen. The ground wood was air-dried at ambient laboratory conditions to equilibrium moisture content, and its moisture content was determined using infrared moisture determination method. The elemental composition of the hybrid poplar wood is shown in Table 1. An ExxonMobil HZSM-5 catalyst was used for the experiments. A 200 g batch of this catalyst was used for the fluidized bed pyrolysis experiments.
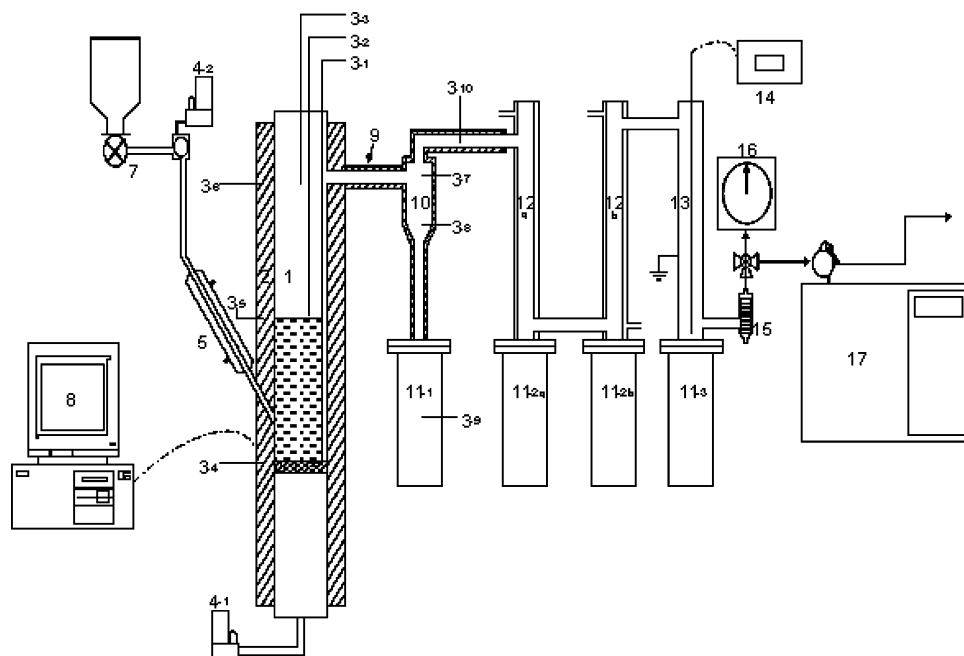
2.2. Fluidized Bed Pyrolysis. The reactor consisted of a 500 mm (2-in.) schedule 40 stainless steel pipe, 500 mm (20.0 in.) high (including a 140-mm (5.5 in.) preheater zone below the gas distribution plate) and equipped with a 100-μm porous metal gas distributor (Figure 1). The fluidizing medium was the above catalyst, and the bed was fluidized with nitrogen. The reactor was externally heated with a three-zone electric furnace. The reactor tube contained a bubbling fluid bed with back mixing of the feed and catalyst. For the noncatalytic rapid pyrolysis (RP) runs, silica sand was substituted for the catalyst.

The biomass was loaded into a feed hopper (batchwise) and conveyed by a twin-screw feeder into an entrainment compartment where high-velocity nitrogen gas entrained the feed and carried it through a jacketed air-cooled feeder tube into the fluidized bed. The pyrolysis temperature was maintained at 500 °C, and the apparent pyrolysis vapor residence time was about 1 s. The apparent residence time of gases and vapors was

Table 1. Elemental Composition of and Calorific Values of Hybrid Poplar Feedstock (Moisture Free Basis)

component	hybrid poplar wood
carbon (%)	49.30 ± 0.29
hydrogen (%)	5.69 ± 0.56
oxygen (%)	44.07 ± 0.97
nitrogen (%)	<0.5
ash (%)	0.94 ± 0.10
sulfur (%)	<0.05
chlorine (ppm)	34
HHV (MJ/kg)	18.4

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Figure 1. Schematic diagram of the bench scale fluidized bed pyrolysis unit: (1) fluidized bed reactor, (2) furnace, (3) thermocouple, (4) mass flow controller, (5) heat exchanger, (6) hopper, (7) sample feeder, (8) computer, (9) heating tape, (10) cyclone, (11) reservoir, (12) condenser, (13) electrostatic precipitator, (14) ac power supply, (15) filter, (16) wet gas meter, and (17) gas chromatograph.

Table 2. Product Yields (Dry Basis) from Various Biomass Feedstocks Using Fractional Catalytic Pyrolysis (FCP) as well as Noncatalytic Pyrolysis (RP) Methods[a]

biomass	total RP liquid (%)	total FCP liquid (%)	char (%)	gas (%)	liquid pH	liquid viscosity at 25 °C (cP)
hybrid poplar wood	n/a	33.6 ± 4.2	12.6 ± 1.1	53.6 ± 5.3	3.45 ± 0.01	147.3 ± 2.4
hybrid poplar wood	63.3 ± 1.3	n/a	12.7 ± 2.0	24.0 ± 1.1	2.82 ± 0.01	798

[a] For the noncatalytic process, the medium was sand.

defined as the free reactor volume (the empty reactor volume minus the volume of hot catalyst) divided by the entering gas flow rate at reactor conditions. A typical run lasted for 2−3 h, and the feed rate was 100 g/h. The feed rate, gas flow rate, and reactor temperature were kept constant during each run.

The catalyst and reactor temperatures were measured and controlled by three K-thermocouples inserted into a thermal well dipping into the catalyst bed. One thermocouple spanned the full length of the thermal well, and this was used to measure and control the catalyst bed temperature. The next thermocouple was maintained above the bed height, and the third thermocouple measured the exit temperature of the pyrolysis vapors and gases. The catalyst bed temperature was maintained at 500 °C, but the area above the bed and the exit zone were nominally set at 450 °C to avoid any possible cracking of the pyrolysis products in these zones.

Pyrolysis gases and vapors exiting the reactor passed through a heated hot gas filter unit to separate char/ash and any entrained catalyst. The hot-gas filter temperature was maintained at 400 °C to avoid condensation of the pyrolysis vapors. The pyrolysis gases and vapors were then passed through a condensation train consisting of chilled water condensers, an electrostatic precipitator, and a coalescing filter (all connected in series). The electrostatic precipitator was maintained at 18−20 kV throughout the run. The temperatures, gas flow rates, pressure drop across the reactor, and electrostatic precipitator voltage were controlled and/or monitored using an Omega data acquisition unit. Pressure drop across the hot gas filter was monitored by a pressure gage.

The gas samples were collected in syringes and analyzed after each run. Total gas flow was measured using a rotameter. To ensure good mass closure, the entire setup (excluding the rotameter) was weighed before and after each run. The pyrolysis oils collected from each condenser receiver were kept separate and analyzed by GC/MS, GPC, and ^{13}C NMR. The residual pyrolysis oils on the walls of the condensers were recovered (after weighing the pyrolysis unit) by rinsing the condensers with acetone. The acetone was evaporated under vacuum (40 °C and 61.3 kPa), and the oils recovered. None of the oils recovered from the acetone wash were used for analysis, because there was always some residual acetone associated with this fraction and the potential of losing some volatile components during the operation precludes it from being a representative pyrolysis oil sample.

The char/coke content was determined by weighing the reactor/catalyst and hot gas filter before and after each run, the difference in weight was recorded as char/coke.

2.3. Gas Analysis. The pyrolysis gases were sampled and analyzed on a Shimadzu GC14A. Three packed columns (Porapak N, molecular sieve 5A, and Hysep Q) connected in series were used to analyze the gases. The oven was temperature programmed from 30 to 200 °C at a heating rate of 25 °C/min. The gas chromatogram was processed using Shimadzu CLASS-VP program.

3. Results

3.1. Pyrolysis Products. The material balances for the fractional catalytic pyrolysis (FCP) runs are shown in Table 2. Compared to conventional rapid pyrolysis (RP), the total liquid yields for these runs were very low (33.6 wt %), the gas yields

Table 3. GC/MS Estimated Composition of Pyrolysis Oils[a]

|	FCP oils		RP oils	
compound	ESP oil	condenser oil	whole wood	phenol/neutral fraction
hydroxyacetaldehyde	0	0	46	0
hydroxyacetone	0	0	175	0
ethanedial	0	0	0	0
2-cyclopenten-1-one	194	14	24	35
3-methyl-2-cyclopentene-1-one	41	36	0	0
levoglucosan	0	0	213	0
phenol	373	350	119	222
indan	12	15	0	13
indene	36	43	0	11
2-methyl phenol (o-cresol)	239	234	30	68
4-methyl phenol (p-cresol)	419	387	19	55
2-methoxy phenol (guaiacol)	60	61	29	41
methylbenzofuran	37	44	0	13
2,4-dimethyl phenol	131	128	13	24
dimethyl phenol	201	184	0	17
1,2-dihydroxy benzene (catechol)	213	130	33	191
naphthalene	69	76	12	0
2,4,6-trimethyl phenol	47	45	0	20
1,2-dihydroxy-3-ethyl benzene (3-methyl catechol)	55	67	24	76
dimethyl indene/trimethyl phenol	192	185	0	36
2-methoxy-4-ethyl phenol (4-ethyl guaiacol)	46	47	23	39
2-methyl naphthalene	169	184	0	0
2-ethyl naphthalene	0	0	14	25
cinnamyaldehyde	208	187	0	144
2,6 dimethoxy phenol	113	148	68	92
dimethyl naphthalene	229	221	0	0
2,6 dimethyl-4-methyl phenol	164	152	43	41
1-(4-hydroxy-3-methoxy phenyl) propene	182	181	53	68
syringaldehyde	152	171	213	0
3-methoxy-4-hydroxy cinnamic acid	174	278	0	61

[a] All data are raw area counts ($\times 10^6$), but because the same mass of sample was used, the results could be compared on a relative basis.

were very high (53.6 wt %), but the char/coke yield (12.6 wt %) was similar to the RP char/coke yield.

We obtained three liquid fractions from the first two condensers and the ESP that were very different from RP oils. The liquid from the first condenser was brown, with extremely low viscosity and flowed freely at room temperature. The liquid from the second condenser was light yellow and also had low viscosity. The composition of the second condenser liquid was 95% water and 5% dissolved organics. The liquids from the ESP and the first condenser were similar in appearance and viscosity and were immiscible with water. However, the RP liquid product was miscible with water. The FCP oils were less viscous that the corresponding RP oils.

Qualitative GC/MS analysis of the liquids from the first condenser and the ESP showed similar chemical composition (Table 3). We estimated that over 95% of the injected liquid eluted from the column. The liquids were very rich in phenolics with minor carbohydrate pyrolysis products. The constituents of the two liquid fractions were mostly phenol, cresols, guaiacol, methyl-substituted phenols, small quantities of indene, and substituted naphthalenes. Neither, benzene, toluene, nor xylenes were detected in any of the products. These results were confirmed by ^{13}C NMR analysis of the liquid products. The GC/MS analysis of the RP whole oil as well as the phenol neutral (PN) fraction extracted from the RP whole oil are also shown in Table 3 to illustrate the differences between the oils. Whereas the FCP and the PN oils had very low carbohydrate decomposition products, the whole oil was very rich in such products. The FCP oils were richer in phenolics compared to the PN fraction of the RP oil.

The ^{13}C NMR spectra of the FCP and RP oils are shown in Figure 2a and b. The signals between 0 and 35 ppm were assigned to aliphatic chains; signals from 60 to 100 ppm were assigned to carbohydrate degradation products,[36] whereas those
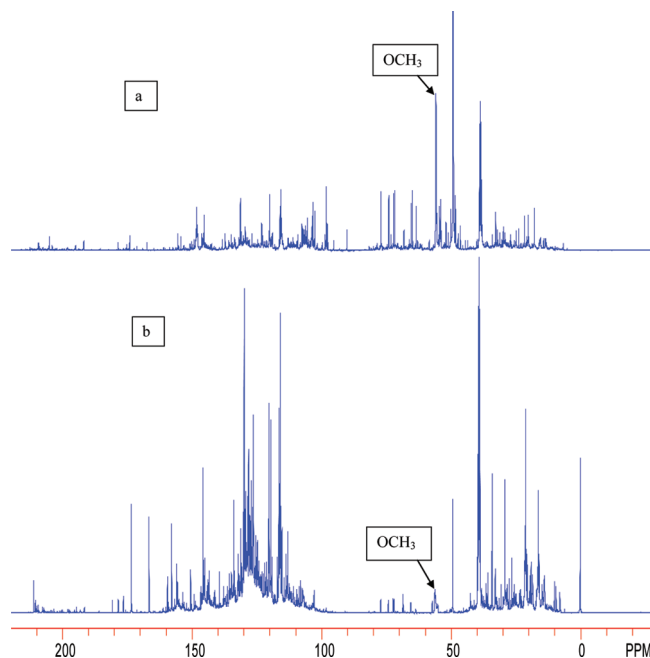
Figure 2. ^{13}C NMR spectra of fractional catalytic pyrolysis and rapid pyrolysis liquid products of hybrid poplar wood: (a) conventional rapid pyrolysis oil spectrum; (b) fractional catalytic pyrolysis oil spectrum.

from 100 to 160 ppm were assigned to lignin or phenolic compounds.[36] The signals at 210 ppm were assigned to carboxylic carbons. It is clear from Figure 2a and b that the FCP oils lost most of their carbohydrate degradation components whereas the RP oil retained all those components.

It is interesting to note the difference in the height of the methoxyl peak at 58 ppm in the ^{13}C NMR spectra of the FCP and RP products. The FCP oils appeared to be less methoxylated

Table 4. Elemental Composition of and Calorific Values of Noncatalyzed Pyrolysis Oil (Bio-oil) and FCP Oils Produced from Hybrid Poplar Feedstock (Moisture Free Basis)

component	noncatalyzed pyrolysis oil (bio-oil)	FCP oil
carbon (%)	60.37 ± 0.41	71.16 ± 1.81
hydrogen (%)	6.67 ± 0.06	6.82 ± 0.14
oxygen (%)	32.94 ± 0.46	21.85 ± 1.95
nitrogen (%)	<0.5	<0.5
ash (%)	<0.09	<0.08
sulfur (%)	<0.05	<0.05
chlorine (ppm)	367	89 ± 41
HHV (MJ/kg)	24.48	30.5

than the RP oils. This suggests that either demethylation or demethoxylation reactions took place during the pyrolysis process.

The elemental composition of the poplar FCP liquid products shown in Table 4 had high carbon (71%) and relatively low oxygen content (22%) compared to the equivalent RP oils. The high heating value (HHV) was consequently high (30.5 MJ/kg) compared to 24 MJ/kg for the RP oil.

Gel permeation chromatography (GPC) of the liquid products showed very low molecular mass distribution of the products. The number average molecular weight (M_n) of the FCP oil from poplar was 160 while the weight average molecular weight (M_w) was 215. The molecular mass distribution of these products were about one-half those reported for phenol/neutral fraction RP oils ($M_n = 290$, $M_w = 440$).[26]

The biomass char/coke yields were similar to those from the RP experiments. These char/coke yields were low compared to those reported for post-RP oil catalysis.[19-26,37] The char and the coke were intricately mixed so we could not distinguish between them. The thermogravimetric analysis method could not distinguish between the coke and the char, and no further analysis was carried out.

The gas yields for the FCP process were high compared to the RP process. The gaseous products were a mixture of C_1-C_4 hydrocarbons, carbon monoxide (CO), and carbon dioxide (CO_2). About 90 wt % of the gaseous products was CO and CO_2, and the rest was a mixture of hydrocarbons (methane, ethane, propane, butane, ethylene, and butane). Three other small peaks were present in the chromatogram, but these were not identified. Butene was the most abundant hydrocarbon and in some cases constituted 30% of the total hydrocarbon products.

3.2. Catalyst Activity. The CO and CO_2 concentrations varied with time during the catalytic pyrolysis. The variation was attributed to catalyst deactivation. In these studies, we monitored the catalyst activity by following the variation in CO and CO_2 composition in the gaseous product mixture. The CO/CO_2 ratio for the FCP process decreased with time and appeared to approach the RP CO/CO_2 ratio (Figure 3). The CO/CO_2 ratio varied from 3.5 to 4.4 during the runs. At the early stages of the run, the ratio was high but gradually decreased with time. In contrast, the CO/CO_2 ratio for RP process was typically 1.3–1.4 and remained almost constant throughout each run. If we assume that this ratio is a true measure of the catalytic activity, then it appears the catalyst was still active after 3 hours run albeit less active than the fresh catalyst. This finding is significant because it provides a simple method for monitoring catalyst activity.

4. Discussion

The char/coke yield for the poplar FCP was about 12.5 wt %, which was similar to what was obtained for the RP processes. Under post-RP catalysis conditions, biomass feedstocks tend
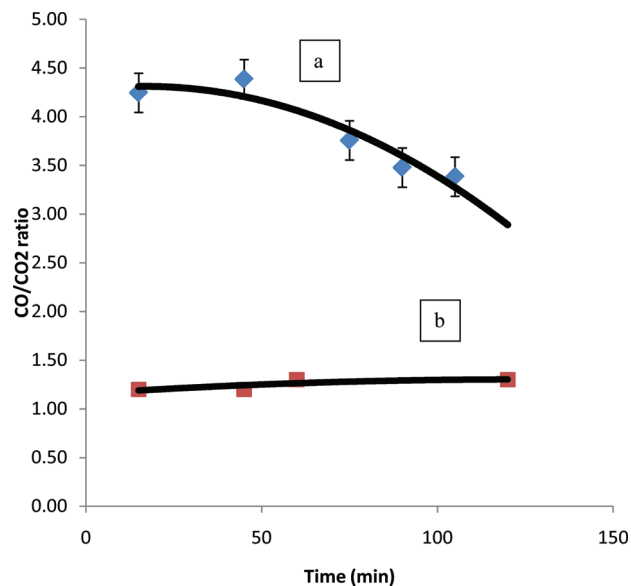
Figure 3. Variation of carbon monoxide and carbon dioxide content during fractional catalytic pyrolysis and conventional rapid pyrolysis of hybrid poplar wood: (a) fractional catalytic pyrolysis; (b) conventional rapid pyrolysis.

to produce very high coke yields, which rapidly deactivated the catalyst[19,20,37] within a few minutes of pyrolysis and the post-RP catalysis liquid products usually contained benzene, toluene, xylene, naphthalenes, substituted benzene, and naphthalenic products.[19,20,22] On the contrary, in the FCP process where the biomass was fed into the catalyst bed and there was thorough backmixing of catalyst and biomass, the catalyst was still active after 3 h of pyrolysis, and the product slates were quite different from those reported for post-RP catalysis. Clearly in the FCP process, there appeared to be a selective pyrolysis and gasification of the biomass components. It appeared that the carbohydrate decomposition intermediate products (ions, free radicals, and molecules) had smaller sizes and could enter the HZSM-5 pores and were subsequently converted into gaseous products such as carbon dioxide, carbon monoxide, and C_1-C_4 hydrocarbons. As the catalyst slowly deactivated, it appeared that some carbohydrate pyrolysis products such as hydroxyacetaldehyde, ethanedial, hydroxyacetone, and cyclopeteneone were not cracked, and these condensed with the aqueous phase in the chilled water condenser. Commercial HZSM-5 catalysts are very uniform in their three-dimensional structures, and the pore sizes (5.3×5.6 nm)[38] are large enough for small molecules such as glucose,[39] xylose, and furfural[40] to diffuse into the active sites to react. Studies by Moreau et al.[40] and O'Neill et al.[41] showed that furfural and other carbohydrate decomposition products because of their small size relative to the pore size of HZSM-5 could easily enter the HZSM-5 pores and were subsequently converted into other products. These results are in agreement with our explanation of the FCP mechanism. The importance of the reactant dimensions relative to the catalyst pore size was also investigated for the dehydration of glucose on Y zeolites,[42] the results showed that the pore size played a very important role in the formation of 5-hydroxymethyl furfural, formic acid, coke or oligomerization of the 5-hydroxymethyl furfural.

On the contrary, the lignin pyrolysis products underwent limited gasification reactions and formed the bulk of the liquid products probably because the lignin decomposition intermediate products (radicals, ions, and unstable molecules) were too large to diffuse into the active sites of HZSM-5 catalyst and therefore

were not cracked into gaseous products. Studies by Kumbar et al.[43] and Atoguchi et al.[44] show that guaiacol, catechol, and other substituted phenolic compounds were too large to diffuse into the HZSM-5 pores. These observations are in agreement with our explanations.

The presence of high proportions of cresols and dihydroxy phenols (catechol) suggested that demethylation, demethoxylation, and cleavage of the lignin decomposition products occurred. The presence of methyl and ethyl phenols in the liquid product also suggested that there might have been some alkylation reactions. These reactions probably took place on the exterior surface of the catalyst.

The yield of the liquid products also supported the above explanations. The total liquid yield was only 33.5 wt %, and its water content was 30−40 wt %. This implies that the organic liquid yield was only 18−21 wt %. The total lignin content of hybrid poplar wood is about 22−24 wt %,[45] and thus taking into consideration the demethoxylation reactions and loss of some side chains, the above organic liquid yield appear to be reasonable. Thus, the fractional catalytic pyrolysis process appeared to favor production of phenolic liquids from the lignin fraction of the biomass while converting the carbohydrate fraction into gases.

5. Conclusions

We have demonstrated the concept of fractional pyrolysis of biomass. In this work, we showed that the lignin fraction of the biomass could be effectively converted into phenolic liquids when catalysis and pyrolysis reactions were performed simultaneously. The liquid yields were lower than those from conventional pyrolysis but the char/coke yields for FCP process were similar to those obtained from conventional rapid pyrolysis. The molecular mass distribution of fractional catalytic pyrolysis liquid products were about one-half that obtained for phenol/neutral fraction in a conventional pyrolysis and there appeared to be considerable demethylation and demethoxylation reactions. The variation of the ratio of CO/CO_2 could be potentially used to follow the deactivation of the catalyst.

Acknowledgment

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