Production of Bio-Crude from Forestry Waste by Hydro-Liquefaction in Sub-/Super-Critical Methanol

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Hydro-liquefaction of a woody biomass (birch powder) in sub-/super-critical methanol without and with catalysts was investigated with an autoclave reactor at temperatures of 473–673 K and an initial pressure of hydrogen varying from 2.0 to 10.0 MPa. The liquid products were separated into water soluble oil and heavy oil (as bio-crude) by extraction with water and acetone. Without catalyst, the yields of heavy oil and water soluble oil were in the ranges of 2.4–25.5 wt % and 1.2–17.0 wt %, respectively, depending strongly on reaction temperature, reaction time, and initial pressure of hydrogen. The optimum temperature for the production of heavy oil and water soluble oil was found to be at around 623 K, whereas a longer residence time and a lower initial H_2 pressure were found to be favorite conditions for the oil production. Addition of a basic catalyst, such as NaOH, K_2CO_3, and Rb_2CO_3, could significantly promote biomass conversion and increase yields of oily products in the treatments at temperatures less than 573 K. The yield of heavy oil attained about 30 wt % for the liquefaction operation in the presence of 5 wt % Rb_2CO_3 at 573 K and 2 MPa of H_2 for 60 min. The obtained heavy oil products consisted of a high concentration of phenol derivatives, esters, and benzene derivatives, and they also contained a higher concentration of carbon, a much lower concentration of oxygen, and a significantly increased heating value (>30 MJ/kg) when compared with the raw woody biomass. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 807–819, 2009

Keywords: bio-crude, hydro-liquefaction, woody biomass, sub-critical methanol, super-critical methanol, catalysts

Introduction

In the last century, the world has been heavily relying on fossil fuels for energy and chemical production, whereas the fossil resources are declining. Moreover, there is an increasing concerns over the environmental issues (such as greenhouse gas emission and global warming) associated with the use of fossil fuels. It is thus of strategically significance to explore alternatives to fossil resources for both energy and chemical production. Among all the potential alternatives to fossil resources, biomass such as wood, woodwaste (sawdust and woodfibre-based sludge from pulp/paper mills), forestry residues (limbs, bark, tree tops), energy crops, and agricultural residues (wheat/rice straws and corn waste) can be a promising one because not only it represents an immense energy source (the global annual biomass production is about 6–8 times that the world energy consumption) but it is renewable.[1,2] Although biomass resources are renewable, carbon-neutral, and remarkably massive in amount, they are very bulky and difficult to transport, handle, and store. Therefore, appropriate biomass conversion technologies are required to convert them into gas, liquid fuels, or other valuable chemicals. Biomass conversion technologies may be classified into two major categories: bio-chemical processes and thermo-chemical processes. Typical bio-chemical processes are anaerobic digestion of organic materials for production of biogas, and fermentation of sugar and starch crops and lignocellulosic materials to produce ethanol. Key

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thermo-chemical processes include direct combustion or co-firing (with coal), gasification combined with gas turbines for power generation, or gasification combined with various catalytic processes for production of synthetic fuels (e.g., methanol and high quality diesel), pyrolysis and direct liquefaction processes for production of bio-oil or bio-crude. Fast pyrolysis is so far the only industrially realized technology for production of bio-oils from biomass. However, pyrolysis oils consist of high oxygen/water contents and hence lower caloric value (20–25 MJ/kg, only about half of that of petroleum), and they are strongly acidic and corrosive. Superior to the pyrolysis technology (operating at a mild pressure of 0.1–0.5 MPa but a high temperature >500°C), direct liquefaction technology with a suitable solvent (water or organics) and catalyst, which is normally operating at <400°C but a high pressure of 5–20 MPa, has the potential for producing liquid oils (also called bio-crude) with much higher caloric values.[3,4] After further treatment and upgrading, the obtained bio-crude can be a potential substitute for petroleum for the production of fuels and a range of chemicals such as phenols, aldehydes, and organic acids, etc.

Supercritical fluids have found applications for the chemical conversion of lignocellulosic materials due to their unique properties, for example, they possess unique transport properties (gas-like diffusivity and liquid-like density) and have complete miscibility with the liquid/vapor products from the processes, providing a single-phase environment for reactions that would otherwise occur in a multiphase system under conventional conditions.[5] In particular, supercritical fluids have the ability to dissolve materials not normally soluble in either liquid or gaseous phase of the solvent, and hence to promote the gasification/liquefaction reactions.[4] Supercritical water treatment has been studied by many researchers for biomass liquefaction.[6–10] However, the drawbacks of utilizing water as the solvent for liquefaction of coal or biomass include the following aspects: lower yields of the water-insoluble oil product (with a greater heating value) when compared with those of water-soluble product (with a lower heating value), and higher oxygen content in the liquefied products, resulting in low heating values for the liquid products.[11]

To enhance the yields of liquid oil products with reduced oxygen contents (hence a greater heating value), sub-/supercritical alcohols have been tested for liquefaction of lignocellulosic materials.[4,12–20] Because these alcohols have critical temperatures and pressures lower than water, much milder reaction conditions can be used. Another advantages of using alcohols as the solvent for biomass liquefaction is that these alcohols were expected to readily dissolve relatively high molecular weight products derived from cellulose, hemicelluloses, and lignin due to their lower dielectric constants when compared with that of water.[3] Among all the alcohols, ethanol and methanol have been widely used for biomass liquefaction. Miller et al.[21] studied the depolymerization of Kraft and organosolv-derived lignins in supercritical methanol or ethanol in the presence of KOH, when high conversions were realized, with only 7% ether insoluble material remaining after treating organosolv lignin in KOH/ethanol at 290°C. Cemek and Kucuk[20] reported the liquid yields of 44.4 wt % and 43.3 wt % in liquefaction of Verbascum stalk at 573 K with supercritical methanol and ethanol, respectively. The conversion was rapid, reaching the maximum value within 10–15 min. To enhance liquid yields further and to obtain liquid products with lower oxygen contents, supply of hydrogen during liquefaction has been proved to be effective.[22] In a previous work by Xu et al.,[4] hydro-liquefaction of a woody biomass (Jack pine powder) was studied in sub-/super-critical fluid of ethanol without and with iron-based catalysts (5 wt % FeS or $FeSO_4$), when a very high liquid yield at 63% was obtained in the operation at 623 K for 40 min with the presence of $FeSO_4$ and H_2 of an initial pressure of 5.0 MPa.

Among all the supercritical organic solvents for biomass liquefaction, methanol appears to be more promising with respect to its lower cost compared with other alcohols or other organic solvents. Besides, methanol can be synthesized from hydrogen and carbon monoxide derived from biomass, thus it can be a renewable solvent just like ethanol. Minami et al.[12] investigated decomposition of lignin in supercritical methanol and indicated that the condensed linkages of lignin (e.g., 5-5 and β-1 linkages) were stable during the treatment with supercritical methanol, whereas the β-ether and α-ether linkages were rapidly cleaved. Minami and Saka[13,14] have reported that 90% of beech wood was successfully decomposed in supercritical methanol and the optimal conditions for the chemical conversion of woods in supercritical methanol were at 350°C/43 MPa. In the present work, birch powder was liquefied in sub-/super-critical fluid of methanol at temperatures of 473–673 K with and without catalyst under hydrogen atmosphere of an initial pressure varying from 2.0 to 10.0 MPa.

Experimental

Materials

The birch wood (as a hardwood) sample used in this study was obtained from a local lumber mill (Northern Wood). After undergoing size-reduction by a chipper, the lumber was ground with a Wiley mill and screened. Particles smaller than 20 mesh (~0.8 mm) were used for the experiments. The wood powder was dried in an oven at 105°C in air for 24 h before use. The proximate and ultimate analysis results of the birch sample and the chemical compositions of the ash from the wood sample are given in Table 1.

Hydro-liquefaction

The liquefaction experiments were conducted with a stainless steel autoclave. The stainless steel autoclave (Parr Instrument Company, model 4740; Heater model: 4921) had an

Table 1. Proximate and Ultimate Analyses of the Birch Wood Sample and Its Mineral Elemental Compositions

Proximate Analysis, wt % (d.b.*)				Ultimate Analysis, wt % (d.b.*)				
VM	FC	Ash		C	H	N	S	O†
78.5	21.0	0.50		46.9	6.0	0.1	0.1	46.4
Major mineral elements in the sample, ppmw (d.b.)‡								
Na	K	Mg	Ca	Mn	Fe	Zn	Al	Si
18	429	307	1585	131	37	39	19	5

*On a dry basis.
‡Determined by ICP-AES.
†By difference.

effective volume of 75 ml with a pressure vessel of 1 inch I.D. and 5.6 inches inside depth. The birch powder, the catalyst (if needed), and the methanol solvent were weighed into the reactor in sequence. In a typical run, 4 g of the dried woody biomass sample was weighed into the reactor, followed by adding catalyst (if required) in an amount of 5 wt % (w/w) of the woody biomass sample, and then 20 g reagent-grade methanol was added. The catalysts used in this work were NaOH, K_2CO_3, and Rb_2CO_3. The air inside the reactor was displaced with ultrahigh purity hydrogen by repetitive operation of vacuuming and H_2-charging. Then, the reactor was sealed and pressurized to the predetermined hydrogen pressure (between 2.0 and 10 MPa). The autoclave was heated at about 10°C/min by an external electric heater to the desired temperature. As soon as the desired temperature was reached, the reactor was maintained at the temperature for a specified length of time for reaction. During the reaction, the pressure of the reactor was recorded in an interval of 10 min. After the desired reaction time had elapsed, the electric heater was removed from the reactor, and the reactor was cooled down to ambient temperature quickly with an electric fan and a wet cloth towel. Two to three duplicate runs were conducted for most of the experimental conditions and the relative errors for the liquefaction yields between the runs under the same conditions were ensured within 5% of the reported value of yields.

Separation of reaction products

Once the reactor was cooled to room temperature, the gas inside was collected in a gas cylinder, and was analyzed by GC-TCD. The total amount of gaseous product including CO, CO_2, and C_1–C_3 hydrocarbon species were denoted as "Gas" hereafter. The solid/liquid products were rinsed completely from the reactor with reagent-grade acetone. The resulted suspension was filtered under vacuum through a preweighed Whatman No.5 filter paper to recover the solid products (methanol and acetone insoluble). The recovered solids with the filter paper were dried for at least 2 h in the oven at 105°C before weighing. The filtrate was evaporated under reduced pressure at 50°C to remove the solvents (acetone, methanol). After completely removing the solvents, the mixture of heavy oil (denoted as "HO" hereafter), water soluble oil (denoted as "WSO" hereafter), and pyrolytic water formed in the hydro-liquefaction process were weighed. This was followed by the addition of 50 ml of distilled water. The resulting mixture was sonicated for 40 min to allow the WSO dissolve into the water phase completely. After sonication, the resulted suspension was filtered to separate the water phase containing water soluble oil from heavy oil (retained by the filter paper). The obtained water-soluble oil solution was evaporated under reduced pressure at 80–90°C to remove water. It should, however, be noted that the method adopted in this work for the separation and quantification of the water soluble organic products would yield some errors due to the loss in the fraction of low boiling-point organics during the evaporation process. As a matter of fact, the efficient separation of water from water soluble organic compounds is a challenge due to the relatively high boiling point for water. Evaporating water under reduced pressure is so far the most widely adopted method by many researchers for quantifying the yields of the water soluble organic products. As such, the products of pyrolytic water and light ends (with low boiling points) were unrecoverable due to the loss in the evaporation process. The HO retained on the filter paper was rinsed with acetone to collect in an evaporation flask, and then was evaporated under reduced pressure at 50°C to completely remove acetone. The resulted WSO and HO were weighed, and then recovered to sample vials with 10 ml regent-grade acetone. In this work, the yields of Gas, WSO, HO, and Char products were calculated to the dry organic matters (i.e., on a dry and ash/catalyst-free basis). There is a challenge in quantifying the yield of Char on a dry and ash/catalyst-free basis due to that fact that different catalyst compounds added have different solubility in the solvents. The recovered solid residue might consist of coke/char, ash, and catalyst (if added) depending on the solubility of the catalyst compound in methanol/acetone solvents. For simplification, we assumed all the catalyst compounds were retained in the solid residues, and hence, the Char yields were corrected by excluding the catalyst amount and the ash from the weight of the solid residues after drying. Although the above simplification would inevitably lead to some errors because there was a partition of the catalyst compound in the solid residue and the solvents/liquid products, the overall influence on the product yield calculation shall be minimum because the addition of each catalyst was only in an amount of 5 wt % (w/w) of the woody biomass sample. In addition, the extent of biomass conversion during the treatment was evaluated by "biomass conversion," a conversion based on the disappearance of the dry organic matter of the biomass solids.

Characterization

The compositions of gaseous products were determined using an Agilent 3000 Micro-GC equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors. The elemental compositions (C, H, and N) of Char, and HO and WSO were determined with a CEC (SCP) 240-XA elemental analyzer. The composition of oxygen (O) was estimated by difference, assuming negligible content of sulfur (S) in the products. The HO products were also analyzed by a gas chromatograph equipped with a mass selective detector [Varian 1200 Quadrupole GC/MS (EI), Varian CP-3800 GC equipped with VF-5 ms column (5% phenyl 95% dimethylpolysiloxane, 30 m × 0.25 mm × 0.25 μm); temperature program: 40°C (hold 2 min) → 190°C (12°C/min) → 290°C (8°C/min, hold 20 min)]. Compounds in heavy oil were identified by means of the NIST 98 MS library with the 2002 update. Nonthermal chromatographic techniques such as HPLC may be used to characterize the WSO products in future work. To examine the evolution of the crystalline forms in the wood samples and the dispersion states of the catalyst components (if added), X-ray diffraction (XRD) measurements were carried out by using Ni-filtered Cu-Kα radiation with a Philips PW 1050-3710 Diffractometer.

Results and Discussion

Influence of initial H_2 pressure

Figure 1 shows the product yields for the treatment at 200 and 300°C for a fixed length of reaction time (30 min),

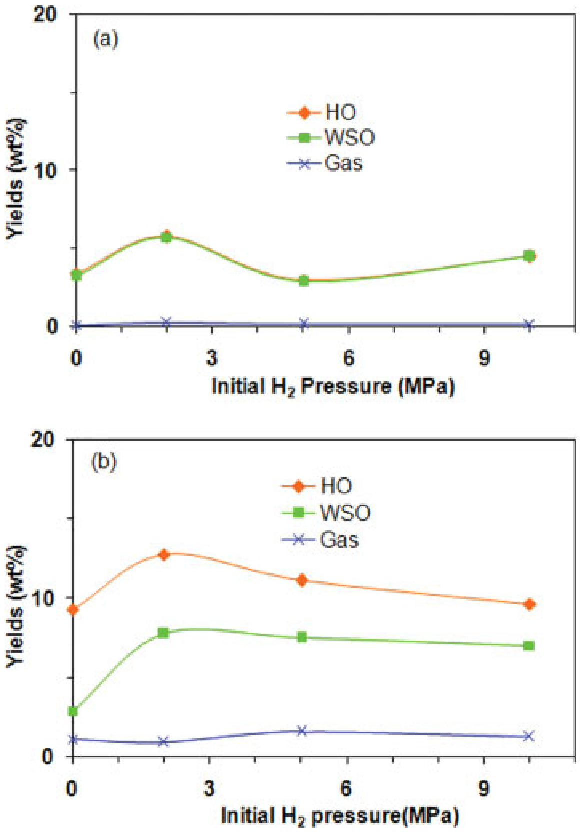

Figure 1. Yields of products as function of initial H_2 pressure in hydro-liquefaction of birch powder in methanol at 200°C (a) and 300°C (b).

Other reaction conditions: Without catalyst; Reaction time of 30 min; Solvent-to-Biomass ratio of 5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

whereas the initial pressure of H_2 was varied at different levels, that is, 0.0 MPa, 2.0 MPa, 5.0 MPa, and 10.0 MPa. It shall be noted that in the tests of 0.0 MPa H_2, the reactor was pressurized with 2.0 MPa ultra-pure N_2 (instead of H_2) to avoid boiling of the reactor content during the heating-up process. Because the critical temperature is 239°C for the methanol solvent, the liquefaction operations at 200 and 300°C represent the sub-critical and super-critical conditions, respectively. It is clearly shown in the Figure that at 300°C as the initial pressure of H_2 increased from 0.0 MPa to 2.0 MPa, both WSO and HO yields increased sharply. However, although the initial pressure of H_2 increased further from 2.0 MPa to 10.0 MPa, both WSO and HO yields leveled off with slightly decreased values. In general, with the presence of H_2 in the liquefaction system, hydro-cracking reactions may occur to help break down the long chains of cellulose, hemi-cellulose, and lignin (by cleavage of the aryl ether linkages in lignin[23]) forming intermediates which are the precursors for the liquid products. The cellulose/hemi-cellulose-derived intermediates may be stabilized by H_2 or hydrogen free radical ($H^\bullet$) to yield WSO products (carbohydrates, carboxylic acids, and aldehydes), whereas the lignin-derived intermediates, mostly the aromatic free radicals ($Ar^\bullet$), may be stabilized rapidly by H_2 or hydrogen free radical ($H^\bullet$) to form HO products.[24] With a higher initial pressure of H_2 in the reaction system, generally higher yields of the liquid oil products may be expected, as observed in a previous study by Xu and Etcheverry,[4] which is consistent with the observation in this work as the initial pressure of H_2 increased from 0.0 MPa to 2.0 MPa. However, although the initial pressure of H_2 increased further to above 2.0 MPa, slightly different results were observed in this study as shown in Figure 1, where both WSO and HO yields leveled off at the initial pressure of H_2 of above 2 MPa. This difference may be attributed to different reactors used in reactions. For the work of Xu and Etcheverry, a fast-heated microreactor with an effective volume of 14 ml was used, whereas in the present study, an autoclave reactor with an effective volume of 75 ml was used. The microreactor was heated in fluidized sand bath, which could reach the specified temperature in very short time. Although the autoclave was heated to the desired temperature (200–400°C) at the rate of ~10°C/min, which means 20–40 min to reach the reaction temperature. The reported time commenced from the point when the desired temperature was reached, which means the actual residence time for the biomass was longer in the autoclave reactor that in the microreactor for a same reported reaction time. The difference in heating rates between these two types of reactors could result in different oil yields and compositions at the same reaction conditions (temperature and time, hydrogen pressure, etc.). Another big difference between the two types of reactors lies in the fact that the microreactor was supported on a mechanical shaker (set at 100 rpm), whereas the autoclave in present study was nonstirred. When compared with the well-shaken and fast-heated microreactor, the nonstirred autoclave reactor used in this work was operated under relatively less favorable heat and mass transfer conditions, leading to a lower hydrogen diffusion efficiency in the reaction medium in this work, which would hence explain the liquefaction efficiencies leveled off at the initial pressure of H_2 of above 2 MPa. Another possible explanation for the experimental results as shown in Figure 1, that is, both WSO and HO yields decreased slightly with increasing H_2 pressure, might be that a higher H_2 pressure would enhance the hydro-de-oxygenation reaction (to form water) of the oil products in supercritical methanol, which would lead to reduced yields of oil products.[25] As the main objective of the present study was to produce bio-crude (heavy oil) from woodwaste, the remaining liquefaction operations were all carried out in H_2 of an initial pressure of 2.0 MPa.

Influence of residence time

Figure 2 shows the yields of liquefaction products at 200°C and 300°C for different lengths of reaction time ranging from 10 min to 480 min. As clearly shown in the Figure, the WSO, HO, and Gas yields as well as the biomass conversion (revealed by the char yield) for both temperatures all follow the similar trend: increasing almost monotonically with reaction time. For instance, with supercritical methanol at 300°C, the biomass conversion climbed from 25% for 10 min to 40% for 60 min, and to 82% for 480 min. In the meanwhile, the WSO and HO yields increased from 3% and 10% for 10 min, to 6% and 18% for 60 min, and to 18% and 26% for 480 min, respectively. As such, it may be concluded

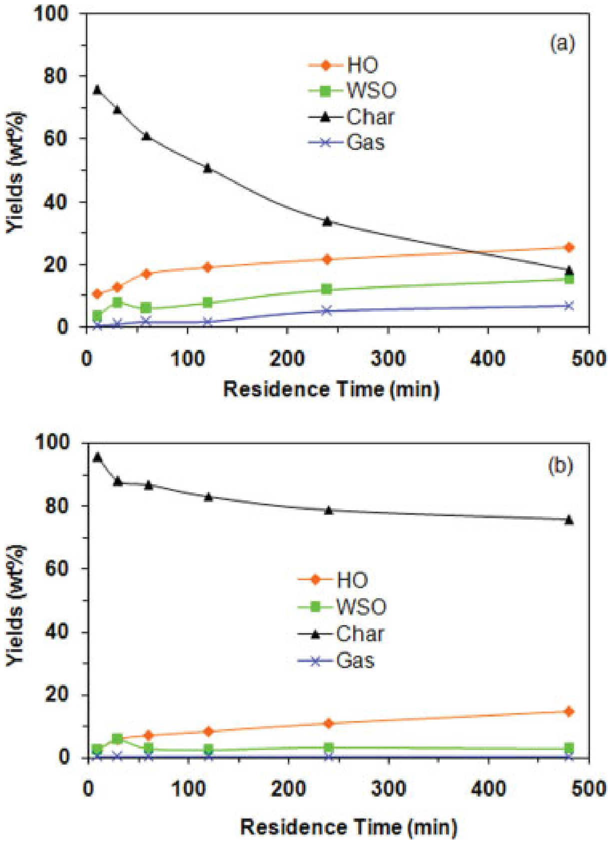

Figure 2. Yields of products as function of residence time in hydro-liquefaction of birch powder in methanol at 200°C (a) and 300°C (b).

Other reaction conditions: Without catalyst; Initial H_2 pressure of 2 MPa; Solvent-to-Biomass ratio of 5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

that a longer residence time is a favorable condition for producing liquid oils (WSO and HO) from biomass in sub-/super-critical methanol, which is consistent with an earlier work by the authors' group on liquefaction of softwood biomass in supercritical ethanol.[4] The above observations however differ from some previous work on liquefaction of biomass in hot-compressed or sub-/super-critical water,[26,27] where a declining HO yield and a climbing char yield was observed with increasing residence time due to condensation of the heavy oil products to form char/coke by condensation and dehydration reactions. The above comparison between alcohols and water may suggest that sub-/super-critical alcohols could be a more advantageous solvent over hot-compressed water for biomass liquefaction due to their superior performance in preventing condensation of the heavy oil products to form coke/char. The above superior performance of an alcohol solvent to water is likely due to the fact that supercritical alcohol can readily dissolve the liquid intermediates/products derived from cellulose, hemicelluloses, and lignin, leading to reduced concentrations of these unstable compounds, and hence retard their condensation and dehydration reactions.

Influence of reaction temperature

Effects of temperature on the liquefaction product yields can be shown from Figure 3, where the results were obtained from the experimental runs at various temperatures ranging from 200 (sub-critical) to 400°C (supercritical), while under the same remaining conditions (2.0 MPa H_2, solvent-to-biomass ratio of 5:1, residence time of 30 min, and without catalyst). As clearly shown from the figure, the operation temperature significantly affected the biomass conversion process in hot-compressed methanol: The biomass conversion and the gas yield increased continuously as the temperature increased from 200 to 400°C, suggesting an enhanced decomposition of biomass and gas formation at a higher temperature. These effects were found to be more evident as temperature was above 300°C. The gas yield climbed rapidly from 1 wt % at 300°C to 12 wt % at 400°C, accompanied by a drastic decrease in Char yield from 70% at 300°C to as low as 16 wt % at 400°C. Over the tested temperature range (200–400°C), the yields of liquid products generally increased with increasing temperature, while the formation of HO and WSO attained a maximum yield of 20 wt % and 17 wt %, respectively, at about 350°C. As the operation temperature further increased to 400°C, the HO yield decreased to 16 wt %, and the WSO yield reduced to 13 wt %. It might be concluded that 350°C is the optimum operating temperature for hydro-liquefaction of birch powder in methanol. Similar experiment results were obtained by Minami et al.[13] in liquefaction of Japanese beech and Japanese cedar in supercritical methanol, and by Xu and Etcheverry[4] in lique-

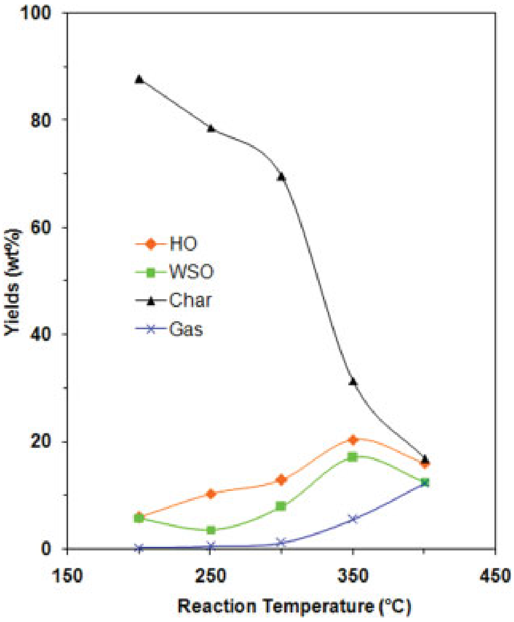

Figure 3. Yields of products as function of reaction temperature in hydro-liquefaction of birch powder in methanol without catalyst at various temperatures.

Reaction conditions: Without catalyst; Reaction time of 30 min; Solvent-to-Biomass ratio of 5; Initial H_2 pressure of 2 MPa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

faction of a pine wood in ethanol. These previous studies have both demonstrated that 350°C appeared to be the optimal treatment temperature for liquefaction of woody biomass in supercritical alcohols. For the production of liquid oils from biomass by direct liquefaction using supercritical alcohols, a too high operation temperature is not preferred, not only because thermal cracking of alcohols may occur at 370°–380°C,[17] but also because of the remarkably enhanced cracking/condensation/dehydration reactions of the oil intermediates and products at a high temperature. The greatly enhanced cracking/condensation/dehydration reactions of the oil intermediates/products in the process would result in a significantly higher gas yield as evidenced in Figure 3, formation of amorphous carbon as evidenced later by the XRD observation in Figure 8, and a greater formation of pyrolytic water. Unfortunately, the products of water and light ends (with low boiling points) were unrecoverable in this study due to the loss in the evaporation process for recovering the WSO and HO products, and thus the formation of pyrolytic water was unable to be quantified directly. Nevertheless, the total amount of pyrolytic water and light ends could be calculated indirectly from the mass balance in the operation. Based on the data given in Figure 3, the calculations showed the total amount of pyrolytic water and light ends was as high as 46 wt % at 400°C, when compared with only 10 wt % at 300°C, suggesting greatly promoted dehydration and cracking reactions of the oil intermediates/products at a high temperature, as proposed above.

In addition to the liquid and total gas yields as discussed above in Figure 3, yields of various gas species during the liquefaction operations at different temperatures are given in Figure 4. Generally, the yields of all gas species increased with temperature due to the enhanced cracking and pyrolysis reactions. In the operations at a temperature lower than 300°C, the dominant species was CO_2 without significant formation of other species. The formation of CO_2 at low treatment temperatures is more likely a result of thermal cleavage of carboxyl group in the lignocellulosic structure by the following decarboxylation reactions:

$$\mathrm{R{-}C(O)OH} \ \text{or}\ \mathrm{R{-}C(O)O{-}R'} \leftrightarrow \mathrm{R{-}H} + \mathrm{CO_2} \ \text{or}\ \mathrm{R{-}R'} + \mathrm{CO_2} \qquad (1)$$

where, the R and R' stand for any possible functional groups derived from the lignocellulosic materials, such as alkyl, phenyl, and hydroxyl groups. As temperature increased further to above 300°C, as shown in Figure 4, the dominant species became CO, followed by CO_2, CH_4, and $(C_2 + C_3)$ species. The reason that the formation of CO_2 was overtaken by CO at a higher reaction temperature is believed to be mainly related to the following carbon gasification reaction:

$$\mathrm{C} + \mathrm{CO_2} \rightarrow 2\mathrm{CO} \qquad \Delta H = 172\ \mathrm{kJ/mol} \qquad (2)$$

The above reaction is endothermic, and hence, it is thermodynamically favorable at a higher reaction temperature, leading to favorable conversion of CO_2 to CO. The methane and $C_2 + C_3$ (ethylene, ethane, and propane) began to form in the process at above 350°C, and the yield of methane increased dramatically from 0.07 mmol/g at 350°C to 0.43 mmol/g at 400°C, which is likely due to the methanation reaction as follows:

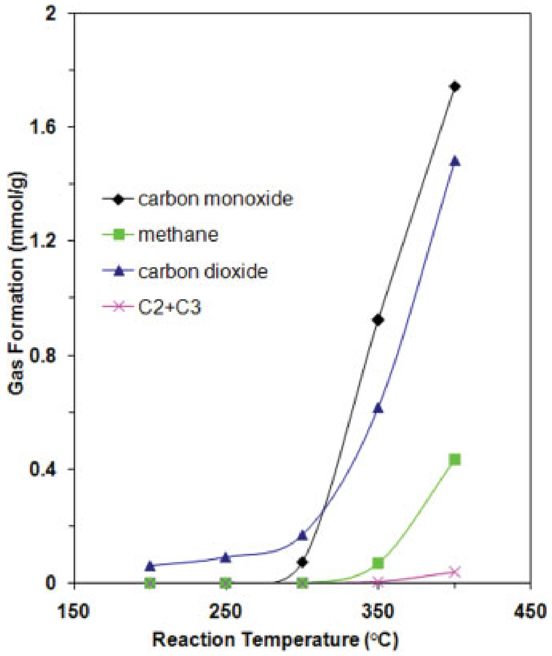

Figure 4. Yields of compositions of gases as function of reaction temperature in hydro-liquefaction of birch powder in methanol without catalyst at various temperatures.

Reaction conditions: Without catalyst; Reaction time of 30 min; Solvent-to-Biomass ratio of 5; Initial H_2 pressure of 2 MPa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$3\mathrm{H_2} + \mathrm{CO} \rightarrow \mathrm{CH_4} + \mathrm{H_2O}\ (\mathrm{g}) \qquad \Delta H = -206\,\mathrm{kJ/mol} \qquad (3)$$

H_2 might also form in the liquefaction process, but it was unable to quantify its yield because H_2 was used as the pressurizing gas and a reactant for the hydro-liquefaction process.

Influence of solvent-to-biomass ratio

Solvent-to-biomass ratio has been found as an important factor to influence biomass liquefaction in hot-compressed or supercritical water,[27,28] where interestingly an decreased water-to-biomass ratio generally led to increased yields of heavy oil and char but a decreased yield of water soluble oil. For the operations with a smaller water-to-biomass ratio, a higher biomass concentration or a lower water concentration prevailed throughout the whole process, which might thus restrict the solvolysis/hydrolysis/hydration of the lignocellulosic solids, leading to a smaller yield of WSO and a higher yield of solid residue or Char. On the other hand, it is likely that a high biomass concentration or a low water concentration promoted the dehydration reactions of the WSO intermediates/products and the depolymerization/cracking of the lignocellulosic solids leading to a greater yield of HO. For the biomass liquefaction operations in this study using methanol and hydrogen, different from the previous work (using water and an inert atmosphere), it is thus necessary to exam-

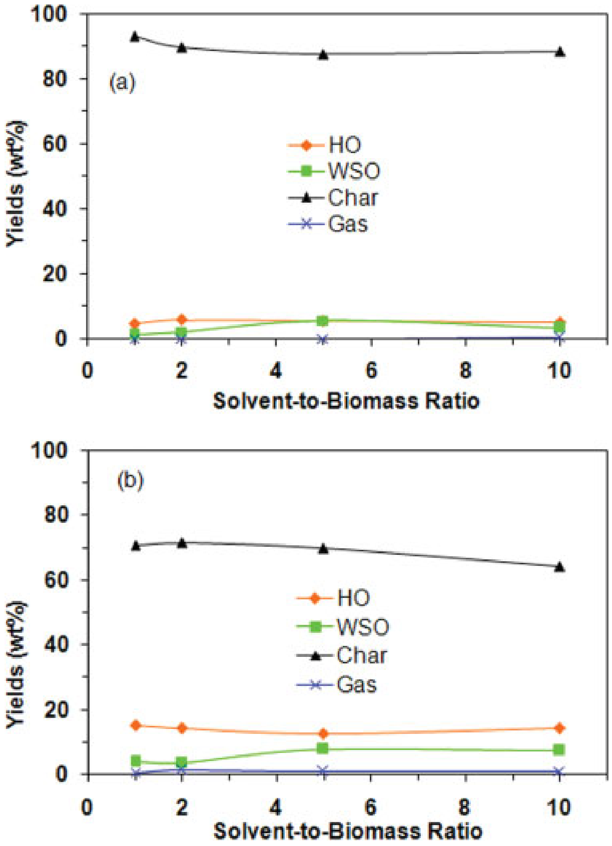

Figure 5. Yields of products as function of solvent-to-biomass ratio in hydro-liquefaction of birch powder in methanol at 200°C (a) and 300°C (b).

Other reaction conditions: Without catalyst; Reaction time of 30 min; Initial H_2 Pressure of 2 MPa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ine the influence of solvent-to-biomass ratio. Effects of solvent-to-biomass ratio were investigated by conducting the liquefaction experiments for a reaction time of 30 min at 200°C and 300°C at various initial solvent-to-biomass ratios of 1, 2, 5, and 10. The results of product yields are illustrated in Figure 5. As clearly shown from the Figure, a higher WSO yield was observed at an increased solvent-to-biomass ratio, similar as that observed previously in the liquefaction of biomass with hot-compressed water.[27,28] In contrast, however, at both temperatures the solvent-to-biomass ratio did not show a significant influence on the liquefaction product yields except for the WSO yield, suggesting that in the present hydro-liquefaction process, solvent-to-biomass ratio was not a dominating factor affecting biomass conversion, when compared with other factors such as hydrogen pressure, residence time, and temperature as discussed earlier. The above result may be due to the unique solvolysis and transport properties of sub-/super-critical methanol, providing complete miscibility with the liquid/vapor products from the processes and a single-phase environment for reactions, thus minimizing the barrier of mass transfer that would otherwise be significant for a multiphase system.[5]

Effects of catalysts

Alkali metal compounds, for example, Na_2CO_3, NaOH, K_2CO_3, KOH, RbOH, and CsOH, etc., have been widely used as catalysts in direct-liquefaction of agricultural/forest biomass to suppress the formation of char and to enhance the yield of liquid products.[29–31] A comparison of the yields of WSO and HO in hydro-liquefaction of birch powder in methanol for 60 min under H_2 of an initial pressure of 2.0 MPa with and without catalyst (NaOH, K_2CO_3, and Rb_2CO_3) is given in Figures 6a,b. At a temperature between 200°C and 300°C, the yields of both oils were significantly improved by the use of all the catalysts. For all catalysts, their effects on HO formation were found to be more evident at a higher temperature, attaining a maximum at 300°C. As clearly shown in Figure 6, Rb_2CO_3 and K_2CO_3 were more effective than NaOH for enhancing the yields of either WSO or HO. At 300°C, the HO yield reached about 30 wt % with the presence of Rb_2CO_3 or K_2CO_3, almost double that of the operation without catalyst or with NaOH. However, as temperature increased to above 300°C the catalytic effects of all catalysts decreased significantly, and surprisingly the yields of both WSO and HO for the operations in the presence of all catalysts fell down to a level below that without catalyst. For instance, at 350°C, the HO yield decreased to 15 wt % and 11 wt % with the presence of Rb_2CO_3 and K_2CO_3, respectively, when compared with 17 wt % without catalyst. Some reasons to account for these adverse effects of the catalysts on the yields of liquid products at 350°C shall be discussed. A comparison of the gas yield in the hydro-liquefaction operations with and without catalyst, as given in Figure 6c, describes the roles of the catalysts at a high temperature. When compared with the runs without catalyst, all runs with the presence the catalyst generated a much higher gas yield in particular when the temperature was higher than 300°C. At 350°C, the gas yield was increased remarkably from 6 wt % (without catalyst) to 15–18 wt % (with NaOH, K_2CO_3 or Rb_2CO_3). The formation of gas products in the operations with and without catalyst increased monotonically with increasing temperature, a trend that is different from those for WSO and HO products as shown in Figures 6a and 6b. Comparing Figures 6c with 6a and 6b for temperatures >300°C, we may find that a remarkably increased gas formation due to the presence of the catalyst is accompanied by a drastic reduction in HO yield. This observation may suggest that the cracking reactions of HO products, thermodynamically favorable at a higher temperature, be catalyzed by the added catalysts, leading to a greatly reduced HO yield and a significantly enhanced gas formation, as evidenced by Figures 6b,c.

On the other hand, the effects of different catalysts on biomass conversion can be shown in Figure 6d, where a comparison of the biomass conversion in hydro-liquefaction of birch powder in methanol with and without catalysts is given. When compared with the operations without catalysts, the addition of all catalysts was effective for promoting biomass conversion at all temperatures in the range of 200–350°C, whereas the effects were found to be the most evident at 300°C and the effects remarkably dropped as the temperature increased to above 300°C, similar as those observed for HO yields in Figure 6b. At 300°C, the biomass conversion

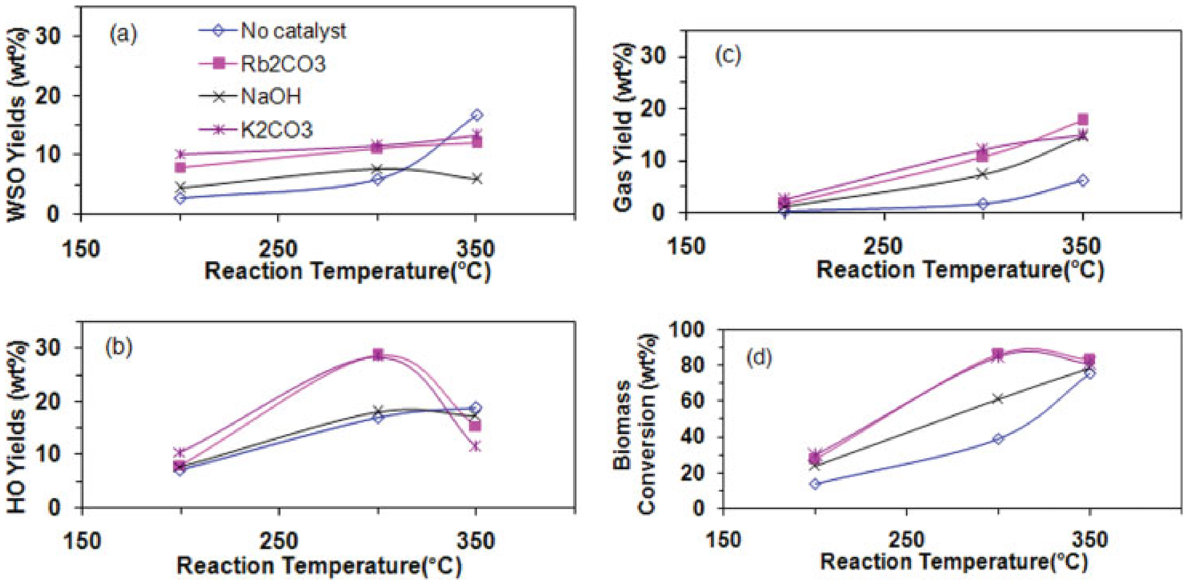

Figure 6. Effects of catalysts on yields of WSO (a), HO (b), Gas(c), and biomass conversion (d) in hydro-liquefaction of birch powder in methanol (solvent-to-biomass ratio of 5) at various temperatures for 60 min under H_2 of an initial pressure of 2.0 MPa.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was increased remarkably from 39% (no catalyst) to 85% (with K_2CO_3 or Rb_2CO_3), whereas the use of the catalysts resulted in only a small increase in biomass conversion at 350°C. The declining activities for the catalysts on biomass conversion at a temperature higher than 300°C may be accounted for by the condensation/cracking reactions of WSO and HO products as discussed above. The catalyzed condensation and cracking reactions of the oil products at a high temperature $>$ 300°C would lead to a remarked decrease in HO yield, a significantly enhanced gas formation and an increase in coke/carbon formation (which might thus result in a reduced value of biomass conversion), as evidenced by the Figures 6b through 6d. Another possible reason for the declining activities for the catalysts on biomass

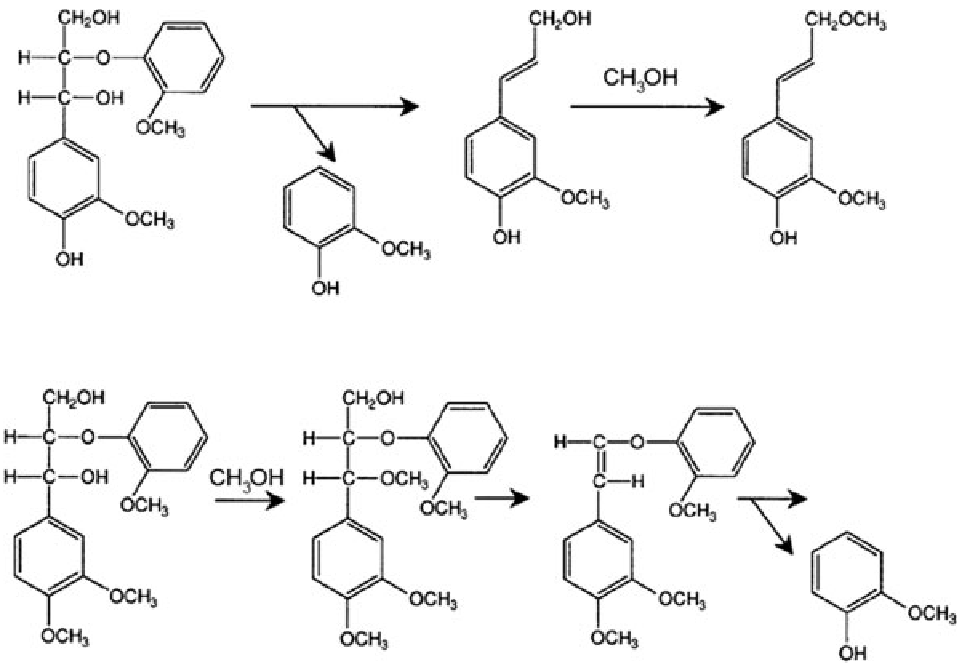

Figure 7. Degradation pathways of phenolic and nonphenolic *β*-*O*-4 lignin model compounds treated in supercritical methanol.[12]

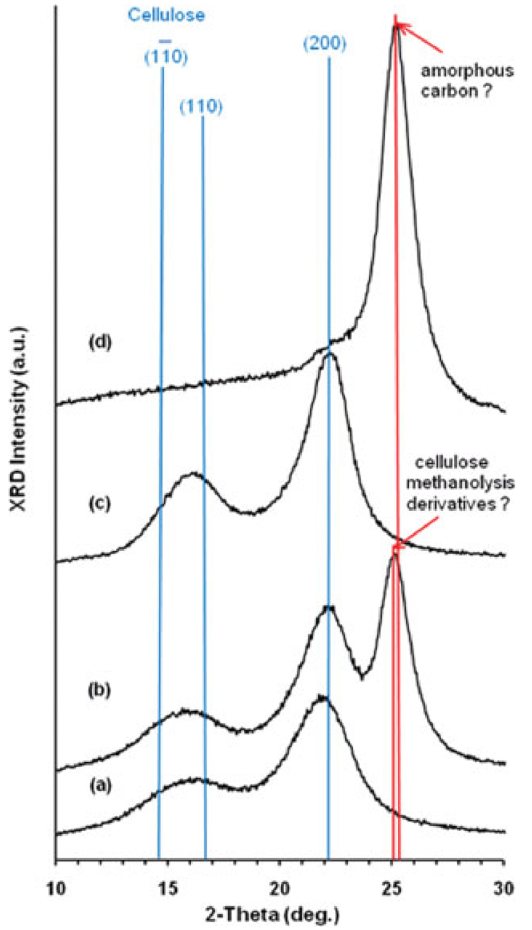

Figure 8. X-ray diffraction patterns of birch powder before and after liquefaction in methanol under H_2 of an initial pressure of 2.0 MPa for 60 min at various temperatures without catalysts.

(a) crude birch powder; (b)treatment at 200°C; (c) treatment at 300°C; (d) treatment at 400°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

conversion at a temperature higher than 300°C might be related to the catalysts thermal degradation, which caused decomposition of the catalyst compounds (K_2CO_3 or Rb_2CO_3) or aggregation of the catalyst molecules (resulting in decreased surface areas of the catalysts). Theoretically, decomposition of K_2CO_3 or Rb_2CO_3 or aggregation of the catalyst molecules, if occurring during the treatment, would be able to verified by the XRD measurements of the resulted chars should different crystalline species (such as K_2O or Rb_2O) or increased crystalline sizes of K_2CO_3 or Rb_2CO_3 be observed. However, no crystalline species ascribed to the catalyst compounds were detected in our XRD measurement, as shown later in Figure 9, most likely because of the low loading amount (5 wt % of the biomass fed) for the catalyst compounds and possibly a high dispersion of the catalyst species on the resulted chars. From the above experiment results, it may be concluded that the optimal conditions for the production of bio-crude from woody biomass by hydro-liquefaction using supercritical methanol are: 300°C and with the presence of Rb_2CO_3 or K_2CO_3 as a catalyst.

Characterizations of the liquid/solid products

Carbon balance was calculated in this study to evaluate the material balance of the liquefaction operations. The carbon compositions of the liquefaction products (HO, WSO, and Char) were analyzed with an elemental analyzer, and the carbon contents in the Gas products were obtained by GC-TCD. We defined the carbon recovery in a liquefaction product by the percentage of the moles of carbon in the product in relation to the moles of carbon in dried birch powder added to the reactor in the liquefaction operation. Some typical results of the carbon recovery in the products of HO, WSO, Char, and Gas and the carbon balance calculated by summing the carbon recovery for all the products are presented in Table 2. As indicated in Table 2, the overall carbon molar conservation fell in a reasonable range of 80–92% in

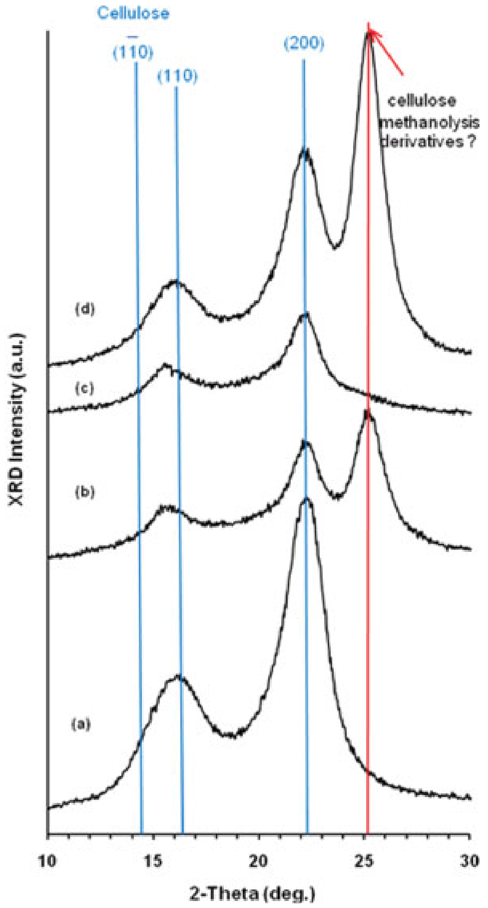

Figure 9. X-ray diffraction patterns of birch powder after liquefaction in methanol under H_2 of an initial pressure of 2.0 MPa at 300°C for 60 min without and with catalysts: (a) without catalyst; (b) with Rb_2CO_3; (c) with K_2CO_3; (d) with NaOH.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 2. Carbon Recovery in the Products Produced by Hydro-Liquefaction of Birch Powder at 300°C and 2.0 MPa H_2 for 60 min with and without Catalyst

Liquefaction Operation	Carbon Recovery in Products (%)				Carbon Balance (%)
	HO	WSO	Char	Gas	
Without catalyst	24.60	6.50	59.83	1.22	92.15
Rb_2CO_3	42.61	12.83	16.21	7.64	79.29
K_2CO_3	43.31	17.55	14.94	8.55	84.35
NaOH	27.05	17.34	41.73	5.33	91.45

all operations, suggesting generally acceptable mass conservation and reliable experiment data. When compared with the hydro-liquefaction operations with a catalyst, better carbon conservation was obtained for the operation without catalyst, when the carbon balance was as good as 92.3%. Relatively poor carbon balance was resulted from the liquefaction operation with Rb_2CO_3 or K_2CO_3. It is more likely due to the loss of some low boiling point light ends during the product separation process involving evaporation. As evidenced earlier in Figure 6, Rb_2CO_3 or K_2CO_3 was a very active catalyst to promote the formation of gas and liquid products during liquefaction of the birch sample, when some low boiling point hydrocarbon compounds might form by decomposition of the lignocellulosic structures and by cracking of the liquid intermediates/products. This may be evidenced by a previous study by Karagoz et al.[30] on liquefaction of a woody biomass in hot-compressed water (280°C for 15 min), where liquid products were found to include C_5–C_6 hydrocarbons of a boiling point ranging from 40°C to 60°C.

Properties of the heavy oil products are of a particular interest in this work. The elemental compositions (C, H, and N) of some typical HO products are presented in Table 3, where the elemental compositions of the crude birch sample are also given for comparison. The oxygen contents of the samples were obtained by difference assuming negligible sulfur content, and the higher heating value (HHV) of each sample was calculated by the Dulong Formula, that is, HHV (MJ/kg) $= 0.3383C + 1.422 (H - O/8)$ where C, H, and O were from the elemental analysis on a dry basis. When compared with the crude birch powder, all HO samples obtained from hydro-liquefaction of the birch powder have much higher contents of carbon and hydrogen, and lower concentrations of oxygen, leading to a significantly increased higher heating value (HHV). The HO products from the operations have a HHV of above 30 MJ/kg in relation to only 16 MJ/kg for the crude birch wood. Accordingly, with the maximum HO yield of about 30 wt % obtained from the treatment in the presence of 5 wt % Rb_2CO_3 or K_2CO_3 as shown in Figure 6, about 60% of the energy of the feedstock was recovered as the heavy oil (bio-crude) products. The result suggests that hydro-liquefaction in methanol with catalysts can be a promising technique (due to its relatively mild temperature conditions) for upgrading of woodwastes of a low-heating value to a liquid bio-crude with a significantly increased heating value. As also shown from the Table, all the bio-crude samples obtained with or without catalyst have very similar values of O/C (0.22–0.27) and H/C (1.2–1.3), both of which are much lower than those of the crude biomass feedstock (0.75 and 1.5, respectively), which may suggest high concentrations of phenolic or hydrocarbon compounds in the heavy oil products, as evidenced by the GC/MS results to be discussed below.

The GC/MS analysis of heavy oil products obtained from the hydro-liquefaction of birch powder in supercritical methanol under an initial pressure of H_2 of 2.0 MPa and 300°C for 30 min (without catalysts) and 60 min (with catalysts) were performed and presented in Table 4. The area % for each compound identified (defined by percentage of the compound's chromatographic area out of the total area) and the total area % for majority of the identified compounds are shown in the Table 4. It can be seen from Table 4 that the high proportions of phenol derivatives, followed by esters and benzene derivatives, such as 2,6-dimethoxy-phenol, 5-tert-butylpyrogallol, 4-hydroxy-4-methyl-2-pentanone, dimethyl ester nonanedioic acid, methyl ester octadecanoic acid, and methyl ester eicosanoic acid were observed in all the HO samples tested, of which the concentrations of first two phenolic compounds were much higher in the samples obtained with catalysts than without catalyst. As shown in the Table, 2,6-dimethoxy-4-(2-propenyl)-phenol, 2-methoxy-4-(1-propenyl)-phenol, and 12-(acetyloxy)-methyl ester 9-octadecenoic acid were the major compounds in heavy oils from the operation without catalyst, whereas most of these compounds were not detected by GC/MS in the HO products from the treatments with catalysts. As well known, the phenolic compounds were originated from the degradation of the lignin component in the lignocellulosic biomass feedstock.[32] Lignin is a natural polymer of three main lignin building blocks (structural monomers), that is, *p*-hydroxy-phenyl-propanol, guaiacyl-propanol, and syringyl-propanol, linked mainly by two types of linkages: condensed linkages (e.g., 5-

Table 3. Elemental Compositions of the Crude Birch Powder and the HO Produced by Hydro-Liquefaction of the Birch Powder at 300°C and 2.0 MPa H_2 for 60 min with and without Catalyst

Sample	Elemental Compositions, wt % (d.b.)*				HHV[‡] (MJ/kg)	O/C (−)	H/C (−)
	C	H	N	O[†]			
Crude birch powder	46.9	6.0	0.1	47.0	16.0	0.75	1.5
HO, no catalyst	68.5	6.7	0.1	24.7	28.3	0.27	1.2
HO, 5 wt % NaOH	71.1	7.6	0.0	21.3	31.0	0.22	1.3
HO, 5 wt % K_2CO_3	72.3	7.0	0.0	20.7	30.7	0.21	1.2
HO, 5 wt % Rb_2CO_3	70.4	7.0	0.0	22.7	29.7	0.24	1.2

*On a dry basis.
[†] By difference and assuming that the sulfur content is negligible.
[‡] Higher heating value (HHV) calculated by the Dulong Formula, that is, HHV (MJ/kg) $= 0.3383C + 1.422 (H - O/8)$.

Table 4. GC/MS Analysis Results for the Heavy Oils Obtained in Hydro-Liquefaction of the Birch Powder in Methanol Under an Initial H_2 Pressure of 2.0 MPa at 300°C for 30 min (without Catalyst) and 60 min (with Catalysts)

		Area (%)			
RT (min)	Name	None	NaOH	K_2CO_3	Rb_2CO_3
4.882	2-Pentanone, 4-hydroxy-4-methyl-	1.7	5.39	5.76	1.91
11.113	1,2,3-Trimethoxybenzene		4.90	7.45	4.54
11.654	Phenol, 2,6-dimethoxy-	6.77	21.60	23.83	23.97
11.76	Phenol, 2-methoxy-4-propyl-			2.95	2.48
11.763	Phenol, 3,4-dimethoxy-		3.53		
12.092	Benzene, 1,2,3-trimethoxy-5-methyl-		1.14	2.15	1.44
12.582	Octanedioic acid, dimethyl ester		0.91	1.14	1.07
12.688	1,2,4-Trimethoxybenzene		7.41	4.32	4.54
12.778	Phenol, 2-methoxy-4-(1-propenyl)-	7.32			
12.87	Benzaldehyde, 3,4,5-trimethoxy-		2.76	3.75	
12.88	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-				2.4
13.444	5-tert-Butylpyrogallol	3.8	20.05	16.08	13.36
13.598	Nonanedioic acid, dimethyl ester	7	6.58	7.44	7.29
13.683	9H-Carbazol-3-amine, 9-ethyl-			1.26	0.99
13.956	3′,5′-Dimethoxyacetophenone	3.03			
14.227	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	25.84			1.6
14.284	Benzene, 1,1′-propylidenebis-				7.96
14.282	2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester		12.84		
14.295	Benzene, 1-ethyl-3-(phenylmethyl)-			6.52	
14.548	1-Acetyl-4,6,8-trimethylazulene	1.55			
14.644	Isoelemicin		0.21		1.36
14.766	Benzene, 2-acetate-1,3-dimethoxy-5-(1-propenyl)	1.32			
15.01	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	4.65			
16.316	3,4,5-Trimethoxybenzyl methyl ether	4.30			
18.727	Hexadecanoic acid, methyl ester			3.36	3.97
18.788	9-Octadecenoic acid, 12-(acetyloxy)-, methyl ester	6.18			
23.622	9,12-Octadecadienoic acid, methyl ester			2.81	
23.634	10,13-Octadecadienoic acid, methyl ester				2.99
23.885	15-Octadecenoic acid, methyl ester	1.37			
24.496	Octadecanoic acid, methyl ester	7.9	3.26	4.47	5.62
25.846	Hexadecanoic acid, butyl ester	1.80			
26.639	Dodecanoic acid, 2-methyl-	1.60			
28.214	Eicosanoic acid, methyl ester	4.37	2.19	1.19	2.39
29.084	Octadecanoic acid, butyl ester	2.12			
29.64	Heneicosanoic acid, methyl ester	1.28			
30.807	Docosanoic acid, methyl ester	1.7	1.27	0.63	1.15
Total		95.6	94.06	95.11	91.03

5 and β-1 linkages) and ether linkages (e.g., β-*O*-4 and α-*O*-4), whereas the ether linkages are the dominant linkages between the three main lignin building blocks. A previous study by Minami et al.[12] using lignin model compounds indicated that the condensed linkages of lignin are more stable during treatment with supercritical methanol, than the β-ether and α-ether linkages, and degradation pathways of phenolic and nonphenolic β-*O*-4 lignin model compounds treated in supercritical methanol were shown as in Figure 7. Therefore, the phenol derivatives, esters, and benzene derivatives as observed in the HO products are mainly resulted from decomposition/depolymerization of lignin by cleavage of its ether linkages in supercritical methanol. Hardwood (such as birch used in the present study) lignin, which is known to have more ether linkages, is therefore more readily depolymerized and liquefied when compared with softwood lignin.[13]

To examine the evolution of the crystalline forms in the wood samples and the dispersion states of the catalyst compounds, XRD measurements were carried out. Figure 8 illustrates the XRD spectra of the birch wood sawdust before and after liquefaction in methanol under H_2 of an initial pressure of 2.0 MPa at various temperatures ranging from 200°C to 400°C without catalysts. The X-ray diffraction pattern of the crude birch wood may be resolved into three peaks at 2θ of 14.6°, 16.5°, and 22.4°, corresponds to the $(1\bar{1}0)$, (110), and (200) planes of cellulose-I.[22,33,34] After being treated at 200°C in methanol, the three peaks derived from cellulose I weakened, whereas a very strong XRD signal at $2\theta = 25.1^\circ$ was detected, as shown in Figure 8. A similar XRD signal at $2\theta = 25.1^\circ$ was reported in liquefaction of Jack pine wood in ethanol, which was attributed to the diffraction of cellulose acetates with a certain degree of substitution.[4] In the present situation, this strong XRD signal at $2\theta = 25.1^\circ$ might be attributed to the diffraction of cellulose methanolysis derivatives formed by the interaction between cellulose and the methanol solvent. Ishikawa et al.[35] researched the chemical conversion of microcrystalline cellulose (avicel), cotton linter and dissolving softwood pulp in supercritical methanol and found that the main decomposition pathway of cellulose in supercritical methanol starts with methanolysis of cellulose producing methylated cellotriose and methylated cellobiose, which are further converted to methyl α- and β-D-glucosides. Methyl α- and β-D-glucosides are anomerized in supercritical methanol, however, these products may be decomposed further under prolonged treatment to other products such as

5-(Hydroxymethyl) furfural (5-HMF). As shown in the Figure 8, the peak of cellulose methanolysis derivatives disappears when the reaction temperature increased further to 300°C, which likely was resulted from further decomposition of cellulose methanolysis derivatives at this temperature. In the 300°C methanol-treated samples, the dominant X-ray diffraction peaks were observed at 14.6°, 16.0°, and 22.4°, 2θ, typical of cellulose I. It should however be noted that the cellulose I detected at 300°C was more likely the cellulose I_β which has monoclinic two-train crystallite structure, a more disordered form of cellulose I than cellulose I_α that was observed in the crude wood without treatment.[4] As clearly shown in Figure 8, if further increasing the temperature to 400°C, there were strong X-ray diffraction lines at 2θ between 24 and 26° dominating the spectrum. These XRD signals might be attributed to the C(002) diffraction lines of amorphous carbon ($2\theta = 24.4$) and turbostratic carbon ($2\theta = 26.2$), suggesting formation of partially crystallized coke/carbon from the pyrolysis of lignocellulosic matrix or condensation of liquid intermediates/products at high temperatures. Similar observations of crystallization of carbon have been reported in some previous studies on hydrothermal treatment of biomass in near and supercritical water.[31,36]

Figure 9 illustrates the XRD spectra of the birch wood sawdust after liquefaction in methanol under H_2 of an initial pressure of 2.0 MPa at 300°C with and without catalysts (NaOH, K_2CO3, Rb_2CO_3). First, no X-ray diffraction signals attributable to any a catalyst compound were detected in the chars from the treatment with the catalysts, which may suggest an excellent dispersion of the catalyst compound on the corresponding char. After treatment at 300°C in supercritical methanol, for all the operations with and without catalysts, the X-ray diffraction peaks were observed at $2\theta = 14.6°$, 16.0°, 22.4°, typical of cellulose I, whereas these peaks were relatively weaker in the chars from treatments with catalysts than those without catalyst. For the chars from the treatments with Rb_2CO_3 and NaOH, X-ray diffraction peaks of $2\theta = 25.1°$ that might be attributed to the diffraction of cellulose methanolysis derivatives were also observed, as observed in the char after treatment in methanol without catalyst at 200°C (Figure 8).

Conclusions

In this study, high yields of heavy oil of a HHV > 30 MJ/kg were obtained by hydro-liquefaction of birch powder in sub-/super-critical methanol with and without catalyst at temperatures of 200–400°C in hydrogen of an initial pressure of 2.0 MPa. The conclusions may be summarized as follows:

(1) A longer residence time and a lower initial H_2 pressure were found to be favorable conditions for the producing heavy oil products from biomass in sub-/super-critical methanol, while the optimal temperature for the heavy oil production appeared to be at around 350°C.

(2) The addition of a basic catalyst of NaOH, K_2CO_3, or Rb_2CO_3 not only significantly enhanced biomass conversion or suppressed char formation, but greatly increased the yields of liquid and gas products, in particular when the operation temperature was lower than 300°C. When compared with NaOH, K_2CO_3, and Rb_2CO_3 showed higher catalytic activities. The yield of heavy oil attained about 30 wt % for the liquefaction operation in the presence of 5 wt % K_2CO_3 or Rb_2CO_3 at 300°C and 2 MPa of H_2 for 60 min.

(3) Revealed by the GC-MS measurements, phenol derivatives, esters, and benzene derivatives were the dominant compounds detected in the obtained heavy oil products, while their compositions could be altered by catalysts.

(4) The HO products from the operations have a HHV of above 30 MJ/kg in relation to only 16 MJ/kg for the crude birch wood. Hydro-liquefaction in methanol can thus be a promising technique for upgrading of woodwastes of a low-heating value to bio-crude with a significantly increased heating value.

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