



# Hydrothermal liquefaction of barks into bio-crude – Effects of species and ash content/composition



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## HIGHLIGHTS

- Bark-containing ash can be efficiently removed by diluted nitric acid treatment.
- Bark conversion and bio-crude yield differ significantly with bark species.
- The K and Ca compounds in bark ash catalyze bark conversion into bio-crude.
- The bio-crude oils are aromatic/phenolic nature and have HHVs of 25.5–38.9 MJ/kg.
- The bark-derived bio-crude oils have lower molecular weights ( $M_w = 800$ –1700).

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## ABSTRACT

Liquefaction of barks of white pine, white spruce and white birch was performed in ethanol–water (50:50, v/v) co-solvents under the initial  $N_2$  pressure of 2.0 MPa at 300 °C for 15 min. It was found that the liquefaction efficiency, in terms of bark conversion and bio-crude yield, varied significantly with bark species and ash content/composition. As far as the bark conversion was concerned, the order follows: white spruce bark (92%) > white birch bark (89%) > white pine bark (68%), which is also in good agreement with the ash content of the barks: white spruce bark (3.07%) > white birch bark (2.68%) > white pine bark (1.07%). Bio-crude yield reduced in the following order: white birch bark (67%) > white spruce bark (58%) >> white pine bark (36%). Effects of ash content on bark liquefaction were investigated by comparing the liquefaction efficiencies between crude bark and de-ashed bark. Deashing pre-treatment of barks in 0.5 M nitric acid efficiently decreased ash content in barks of white pine, white spruce and white birch from 1.07%, 3.07%, 2.68% to 0.67%, 0.33% and 0.32%, respectively. The de-ashing of bark decreased both bark conversion rate and bio-crude yield for all barks, suggesting that the ash of the bark play catalytic roles in the bark liquefaction, which was confirmed by the addition of  $K_2CO_3$  and  $Ca(OH)_2$  into de-ashed barks. The bark-derived bio-crude oils are aromatic/phenolic in nature with HHVs of 25–39 MJ/kg. The obtained bio-crude oils also have relatively lower molecular weights ( $M_n = 320$ –600 g/mol,  $M_w = 800$ –1700 g/mol, PDI = 2.2–2.9), which makes the bio-crude oils promising in the applications for either bio-fuel or as a phenol substitute in bio-phenolic resins.

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## 1. Introduction

Nowadays chemicals and liquid transportation fuels are mainly derived from non-renewable fossil resources (particularly petroleum and natural gas), which has been facing a longstanding challenge due to the rapidly declined reserves and fluctuating prices of crude oil. Thus, to search alternative sources for chemical and fuel production has attracted increasing attention and a lot of research efforts. Direct liquefaction is considered as a promising pathway for the conversion of biomass into liquid fuels and value-added

chemicals. Biomass direct liquefaction technology was reported as early as 1970s and was successfully applied in liquefaction of wood in the presence of water or other organic solvents with or without catalysts. The choice of solvents has a great impact on the yield and chemical composition of bio-oil [1]. Hydrothermal liquefaction of biomass in hot-compressed or sub-/supercritical water at 250–450 °C has been widely studied and the heavy oil obtained from hydrothermal liquefaction (often called bio-crude) mainly contains ketones, phenols, aldehydes, alcohols and carboxylic acids, with a higher heating value (HHV) of ~30 MJ/kg [2]. Feedstock, reaction temperature, reaction time and catalysts are the main parameters affecting bio-crude yield and properties [3]. In hydrothermal liquefaction of cherry wood (rich in cellulose)

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and cypress wood (rich in lignin), cherry wood liquefaction resulted in higher proportion of acetic acid while liquefied cypress wood contained a major proportion of phenolic hydrocarbons and derivatives [4]. Karagoz et al. [5] investigated the effects of feedstock type on bio-oil yield and composition in hydrothermal liquefaction at 280 °C for 15 min, cellulose exhibited the highest conversion, sawdust and rice husk have the similar lower conversion, while lignin showed the lowest conversion rate. However, in terms of bio-oil yield, the order changes to: sawdust > rice husk >> lignin > cellulose. As far as bio-oil chemical compositions were concerned, cellulose liquefaction resulted in more furan derivatives while phenolic compounds were the main products from lignin liquefaction involving demethoxylation, alkylation, hydrolysis and cleavage of  $\beta$ -O-4 ether and C–C linkages [6]. Chemical composition in bio-oils from sawdust and rice husk liquefaction is dominated by phenolic compounds, even though some of furans also exist. Besides, initial pH value is also a great factor affecting products yield and bio-oil composition. Yin et al. [7] liquefied cellulose in water under an original pH value of 3 (acidic), 7 (neutral) and 14 (alkaline) at 275–320 °C for 0–30 min. It was concluded that acidic condition resulted in the highest bio-oil yield, followed by neutral condition, alkaline condition yielded least bio-oil, which can be explained by the acid catalyzed cellulose hydrolysis to generate carbohydrates that are precursors of the bio-oil. For example, acidic condition favors 5-HMF formation while the main compounds in bio-oil produced under alkaline conditions were C2–C5 carboxylic acids. Higher temperature and longer residence time lead to lower bio-oil yield, regardless of the pH value, normally accompanied by an increase in solid residue formation due to the condensation reactions of bio-oils or polymerization between the phenolic bio-oils and HMF. However, the effect of pH on hydrothermal liquefaction varied with feedstock. With lignocellulosic biomass and lignin, a higher pH promotes the biomass conversion and bio-oil yield owing to the catalytic effects of alkali compounds in hydrothermal liquefaction. In one case, heavy oil yield as high as 21–36% was achieved through hydrothermal liquefaction of agricultural and forest residues with the catalysis of  $\text{Na}_2\text{CO}_3$  at 300 °C under 10 MPa for 30 min [8]. For other alkali catalysts such as NaOH,  $\text{Na}_2\text{CO}_3$ , KOH and  $\text{K}_2\text{CO}_3$ , their effects on hydrothermal liquefaction of woody biomass could be ranked as:  $\text{K}_2\text{CO}_3 > \text{KOH} > \text{Na}_2\text{CO}_3 > \text{NaOH}$  [9]. Interestingly, effect of  $\text{K}_2\text{CO}_3$  on heavy oil yield was found to be dependent on lignin content of the feedstock: the lower the lignin content, the weaker the effect [10].

Alcohols such as methanol and ethanol have lower critical temperatures and pressures than water, and the condition can be milder when supercritical alcohols are used for biomass liquefaction. Liquefaction in compressed methanol was systematically studied by Minami et al. [11–13]. It was suggested that supercritical methanol depolymerizes lignin effectively into the lower molecular weight products through  $\beta$ -ether structure cleavage. The liquefaction efficiency in supercritical methanol strongly depends on biomass types and temperature. For instance, beech wood decomposed to a greater extent than cedar wood at 270 °C; while at 350 °C, both beech and cedar wood decomposed to a great extent. Yamazaki [14] investigated the effects of monohydric alcohol type (methanol, ethanol, 1-propanol, 1butanol, 1-octanol, 1-decanol) on Japanese beech (*Fagus crenata* Blume) liquefaction at 270 °C and 350 °C under the supercritical pressure. It was demonstrated that alcohols of longer alkyl chains tended to liquefy wood faster particularly at 350 °C, but at this temperature, as much as more 90% of wood can be finally liquefied, regardless of the alcohols used. For liquefaction at 270 °C for 10 min, the solid residue amount increased slightly with increasing the alcohol alkyl chain length, but when the reaction time was longer than 10 min, the solid residue decreased with increasing length of alcohol alkyl

chain. Cellulose is much more resistant to the liquefaction in alcohols at 270 °C than hemicellulose and lignin. However, when the temperature was 350 °C, cellulose, hemicellulose and lignin were all readily to be liquefied. According to Yang's study [15] on birch wood liquefaction in methanol at temperature range of 200–400 °C under initial 2.0 MPa  $\text{H}_2$  pressure, a longer residence time and lower initial hydrogen pressure favored the formation of heavy oil containing phenol derivatives, esters and benzene derivatives, and the optimal temperature for heavy oil production was around 350 °C. Also, base catalysts like  $\text{K}_2\text{CO}_3$ ,  $\text{Rb}_2\text{CO}_3$  and NaOH could significantly increase the yield of liquid and gaseous products, even when the temperature was below 300 °C. For the effects of iron based catalysts on Jack pine wood liquefaction conducted sub-/super-critical ethanol, Xu et al. [16] found that without any catalysts, the oil yields were 17–44%, depending on temperature, reaction time and initial pressure, but when  $\text{FeSO}_4$  was applied at 350 °C and 5 MPa  $\text{H}_2$  for 40 min, a bio-oil yield as much as 63% was obtained. Another effective way to promote hydrothermal liquefaction of woody biomass is using co-solvents as liquefying reagents. Water–alcohol co-solvents have been demonstrated to favor biomass liquefaction by reducing the formation of high boiling-point materials or solid residue. The addition of water into methanol or ethanol drastically enhanced wood liquefaction under hot compressed condition [13,17,18] due to the synergistic effects of alcohol (methanol or ethanol) and water on sawdust direct liquefaction, and higher bio-oil yields (65 wt%) and better biomass conversion (95 wt%) at the optimal conditions (300 °C for 15 min) than those from liquefaction in mono-solvent of alcohol (~25 wt% bio-oil yield, and ~42 wt% biomass conversion) or water (40 wt% bio-oil yield, and 70 wt% biomass conversion) were obtained from liquefaction in ethanol–water (50:50, v/v) co-solvents [19].

Bark, which is defined as all the tissues external to and surrounding the vascular cambium, comprises about 9–15% of a typical log by volume or 13–21% on a dry weight basis [20,21]. Mainly derives from pulp and wood industries, the annual bark yield in Canada is estimated to be 17 million  $\text{m}^3$ . However, as the value of bark is quantitatively and qualitatively inferior to that of wood, bark has been treated as a waste from forest industries before 1970s. In Canada, some of bark is used for thermal energy production, but more than half of the bark is incinerated or landfilled [22]. Thus, to find a pathway for utilizing bark (rich in lignin) for value added products (liquid transportation fuels or chemicals such as bio-based phenolic compounds, etc.) is of environmental/economic significance. Different from the correspond wood, bark is well-known to contain much higher content of ash. This ash's main components are base metals that may catalyze the thermochemical conversion. Nevertheless no research has been conducted to elucidate the roles of ash and ash composition in bark liquefaction and the properties of the bio-crude products derived from various barks. This study aims to investigate on the effects of species and ash on products distribution from bark liquefaction and chemical composition of the resulted bio-crude.

## 2. Experimental

### 2.1. Materials

Barks of white pine, white spruce and white birch were kindly provided by a local sawmill in Northwestern Ontario. The barks were firstly air dried, then ground into particles of less than 20 mesh. Elemental content and chemical compositions of the barks were analyzed, as shown in Table 1. Bark de-ashing treatment was conducted through the lixiviation of bark in 0.5 M nitric acid at a bark/nitric acid ratio of 1:20 (g/mL) at room temperature for

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