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# Liquefactions of peat in supercritical water with a novel iron catalyst

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ABSTRACT

Raw iron ore has been investigated for use as a catalyst in direct liquefaction of peat into bio-crude by supercritical water treatment. The liquefaction treatments were conducted at temperatures from 350 °C to 500 °C for a residence time from 10 min to 4 h. The supercritical water treatment of peat with the iron ore generally resulted in 19–40 wt% yield of heavy oil (HO) that has a higher heating value (HHV) of 30–37 MJ/kg. An increase in the operating temperature generally increased gas yield and decreased oil and char yields, while a maximum HO formation was observed at around 400 °C. At 400 °C for a residence time of 2 h, the addition of the raw iron ore in the operation produced HO at a very high yield of about 40 wt%, nearly doubling that of the treatment without catalyst. An increase of water-to-peat ratio led to enhanced formation of HO products, accompanied by a decrease in gas or char yield. The optimal reaction time appeared to be 2 h for the maximum HO production, and a longer residence time than 2 h generally led to a decrease in HO yield but an increase in gas yield. Compared with the raw iron ore, its $H_2$-reduced form and two synthesized iron-based catalysts (FeOOH and $Fe_2O_3$) all showed a lower activity for HO production. Some conventional biomass liquefaction catalysts (i.e., KOH, $FeCl_3$ and $FeSO_4$) showed negligible or even negative effects on the HO yield, while these catalysts were found very active for promoting the gas yields and hydrogen formation.

## 1. Introduction

Recently, renewable energy has received great attention due to the declining fossil fuel reserves and the increased concerns over greenhouse gas emissions. Biomass is one of the promising options for generating renewable energy. Bio-oil or bio-crude produced from fast pyrolysis or direct liquefaction of biomass can be a potential substitute for petroleum. Fast pyrolysis, operated at a rapid heating rate in an inert medium to a high temperature up to 1000 °C, can produce bio-oil at a yield of 40–70% [1–3]. The bio-oil products from fast pyrolysis contain high contents of water and oxygen, leading to relatively low heating values (~20 MJ/kg). In contrast, biomass direct liquefaction processes produce liquid oil products (normally referred as bio-crude) of a greater heating value (30–35 MJ/kg) than that of a pyrolysis bio-oil. Biomass direct liquefaction processes, operated under a high pressure but at a mild temperature (200–400 °C), usually employ organic solvents (such as alcohols, tetralin) and catalysts [4,5].

Water is likely the most “green” and environmentally benign solvent. Hot-compressed water exhibits very different properties from those of ambient liquid water: a lower dielectric constant, fewer and weaker hydrogen-bond, a higher isothermal compressibility and an enhanced solubility for organic compounds than ambient liquid water [6], which make it a promising reaction medium for biomass conversions. More importantly, employing hot-compressed water as the reaction medium in a biomass conversion process will eliminate the energy costly operation of dewatering/drying of biomass feedstock, which would enable direct use of wet biomass feedstocks, such as residues from fermentation, municipal sewage sludge and industrial waste water sludge and animal manures, and wet-harvested peat. More recently, near-critical or supercritical water (SCW), highly compressed water at above its critical temperature of 374 °C and critical pressure of 22 MPa as the reaction medium or reactant, has attracted increased attention for various biomass conversion processes, including gasification and liquefaction. Supercritical water has unique ability to dissolve materials not normally soluble in either ambient liquid water or steam and has complete miscibility with the liquid/vapour products from the processes, providing a single-phase environment for reactions that would otherwise occur in a multiphase system under conventional conditions [6]. A pioneer work was reported by Appell et al. [7], where a variety of lignocellulosic materials were efficiently converted to oily products in water at around 350 °C. Minowa et al. [8] obtained heavy oil (with calorific values of around 30 MJ/kg) at a yield of 21–36 wt% from a variety of biomass residues in hot-compressed water at 300 °C and around 10 MPa with $Na_2CO_3$ as catalyst. Qu et al. [9] obtained liquid organic products (including water insoluble oil and water soluble organic products) at a total yield of 30–35 wt% by direct liquefaction of

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*Cunninghamia lanceolata* in water at 280–360 °C for 10–30 min. Alkaline solutions, e.g., $Na_2CO_3$, $K_2CO_3$, KOH, $Ca(OH)_2$, $Ba(OH)_2$, $FeSO_4$, RbOH and CsOH, have been widely employed as catalysts in the biomass direct-liquefaction processes to suppress the formation of char and to enhance the yield of liquid products [10–12].

Peat, accumulation of partially decayed vegetation matter from wetlands, may not be a truly qualified renewable energy resource due to its lower re-generation rate in relation to biomass, but peat contains only one tenth of the sulfur content of a bituminous coal and virtually no mercury, which is similar to biomass feedstock. Peat can thus be a potential clean fuel as a substitute for ''dirty'' coals. From published literature, however, only very limited research on direct liquefaction of peat can be found [13–15]. Recently, Xu and Donald [14] investigated on upgrading peat into gas and liquid fuels in hot-compressed water with and without catalyst, where an expensive $RuO_2$ catalyst proved to be very active for promoting both oil and gas yields. Zhang et al. [15] reported conversion of peat into oil products using supercritical water with CaO and KOH as catalysts. For further exploration of using wet-harvested peat as an alternative energy resource, it is thus of interest to further study on direct liquefaction of peat in supercritical water by using more efficient and less expensive catalyst(s). The objective of this study is to investigate the feasibility of upgrading peat to liquid fuels (bio-crude) by supercritical water treatment using a locally available iron ore as the catalyst. A raw iron ore normally contains high concentration (>50%) of goethite (FeOOH), magnetite ($Fe_3O_4$) or hematite ($Fe_2O_3$). $Fe_2O_3$ was widely used as a catalyst for tar cracking in biomass gasification [16–19]. It was reported recently that limonite iron ores (FeOOH) could be effective catalysts for coal liquefaction in an organic solvent under a high pressure of $H_2$, and for hot gas cleanup (ammonia removal) [20,21]. No published work was found on the use of raw iron ore for direct liquefaction biomass in supercritical water. In addition to the raw iron ore, its $H_2$-reduced form and synthesized iron-based catalysts including $Fe_2O_3$ and goethite (FeOOH), as well as $FeCl_3$, $FeSO_4$, KOH are also tested for the SCW treatment of peat for bio-crude production.

## 2. Experimental

### 2.1. Materials

The peat sample was supplied from an Ontario-based company (Peat Resources Limited). The peat was ground with a Wiley mill and screened to particles smaller than 50-mesh (~0.3 mm) for the experiments. The powder was dried in an oven at 105 °C in air for 24 h before use. The proximate and ultimate analysis results of the dried peat powder and the compositions of major inorganic elements in the peat sample are given in Table 1.

The primary catalyst tested in this work was raw iron ore obtained from a local mine in Atikokan, Ontario. The iron ore mainly consisted of iron (42 wt%) and silicon (3.1 wt%), where the Fe ions are present in the forms of goethite (FeOOH) and hematite ($Fe_2O_3$), identified by X-ray diffraction, as shown in Fig. 1. For comparison, a reduced iron ore (prepared by hydrogen reduction of the raw iron ore at 500 °C for 4 h) and other two synthesized iron-based catalysts (goethite and hematite) were prepared and used in this research. The synthesized goethite and hematite were produced in the authors' lab in the following procedures: precipitation of $FeCl_3$ with KOH (1 M) solution (both were ACS reagents supplied from Sigma–Aldrich) at room temperature under magnetic stirring, followed by thoroughly washing using distilled water to remove the KCl byproduct and any un-reacted KOH and $FeCl_3$. The filtered paste-like powder was then dried in an oven in air at 105 °C overnight, and was recovered as the synthesized FeOOH. The synthesized hematite ($Fe_2O_3$) was simply prepared by calcining the obtained FeOOH at 500 °C for 5 h. All the iron-based solid catalysts (i.e., the raw iron ore, the reduced iron ore, the synthesized FeOOH and $Fe_2O_3$) were crushed into fine particles of less than 100-mesh (<150 μm) before being used as the catalysts. The XRD spectra for all these iron-based solid catalysts were collected and shown comparatively in Fig. 1. In addition, some conventional catalysts, including potassium hydroxide (KOH), iron(III) chloride ($FeCl_3$) and iron (II) sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$), all ACS. reagents received from Sigma–Aldrich, were also tested in the present work for their catalytic activities for liquefaction of peat in supercritical water.

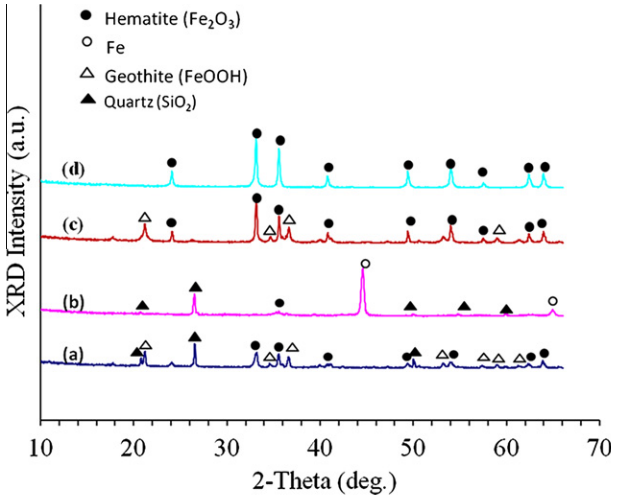

**Fig. 1.** XRD patterns of raw iron ore (a), reduced iron ore (b), synthesized FeOOH (c) and synthesized hematite ($Fe_2O_3$) (d).

### 2.2. Supercritical water liquefaction process and separation of the liquefaction products

The liquefaction experiments were carried out in a 75 ml Parr high-pressure reactor (Parr Instrument, N4740), made of Hastelloy alloy, with maximum working pressure of 6000 psi at 600 °C. In a

**Table 1**
Proximate and ultimate analyses of the peat sample and concentrations of major inorganic elements in the peat.

| Proximate analysis, wt% (db)[a] | | | | Ultimate analysis, wt% (db)[a] | | | | |
|---|---|---|---|---|---|---|---|---|
| VM | FC | Ash | | C | H | N | S | O[b] |
| 65.6 | 29.0 | 5.4 | | 54.7 | 5.5 | 2.1 | 0.2 | 32.1 |
| Major inorganic elements, wt% (db)[c] | | | | | | | | |
| Na | K | Mg | Ca | P | Fe | S | Al | Si |
| <0.1 | <0.1 | 0.1 | 0.8 | 0.1 | 0.6 | 0.1 | 0.3 | 0.1 |

[a] On a dry basis.
[b] By difference.
[c] Determined by ICP-AES.