BTMO Catalyzed Hydrothermal Liquefaction of Lignocellulosic Biomass

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ABSTRACT

Binary transition metal oxide (BTMO), (M_1,M_2)-Fe oxide (where M_1 or M_2 = Ni, Zn, Co) nanoparticles were prepared using a soft templating approach and characterized by powder x-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) surface area analyzer. BTMO nanoparticles were investigated as a catalytic material for hydrothermal liquefaction (HTL) of a lignocellulosic biomass with >30 wt% lignin content. An aqueous slurry of a pinewood (10-15 wt% loading) was loaded in a high-temperature high-pressure 300 mL batch reactor and heated to different temperatures of 250 - 300ºC and pressures of 600 - 1500 psi. Following the HTL reaction, the aqueous phase (biocrude) was separated from the biochar residue and analyzed using TOC, HPLC, and GCMS. The bio-oil was extracted from the biochar *via* acetone extraction, which was characterized for higher heating value (HHV) using the elemental analysis.

Keywords: BTMO nanoparticles, hydrothermal liquefaction, pinewood, biocrude, bio-oil.

1 INTRODUCTION

To improve environmental sustainability and energy security, the use of lignocellulosic biomass (LCB) or biomass waste for the production of fuel and value added co-products could be vital[1]. Technologies such as pyrolysis [2], gasification, and hydrothermal liquefaction (HTL)[3, 4] can be employed to achieve the production of fuel and high value co-products. Although commercial scale pyrolysis and gasification systems are available for biomass processing, HTL systems are currently being developed. Lignocellulosic biomass[5] such as pinewood can be liquified at higher temperatures and higher pressures, without any pre-treatment using HTL technology[6]. In order to develop commercial scale HTL system, significant understanding is needed on the techno-economic assessment and life cycle analysis.

In our previous work, we have explored HTL of pinewood[3, 7], wastepaper[8], cardboard[9] and other substrates using homogeneous $Ni(NO_3)_2$ catalyst at 250-300 ºC. After HTL, the aqueous biocrude was found to contain many co-products including C1-C3 acids, phenol and substituted phenols, alcohols, esters, ethers etc. Some of these products can be recovered. Recovered biochar residue was treated with acetone to recover the heavy bio-oil (HBO). Subsequently, the char was converted into nanofiber mat using electrospinning method[10]. Electrospun nanofiber mats were used to fabricate supercapacitors, which exhibited gravimetric capacitance of 37.60 m^2/g at current density of 500 mA/g.

As the catalyst (Ni salt) was water soluble, Ni^{2+} ions could be recovered using ion-exchange resin. As compared to the homogeneous catalytic materials, heterogeneous catalysts will yield different selectivity and yields of fuels and co-products. Few heterogenous catalytic materials[11, 12] have been investigated for the HTL process. Nanocrystalline undoped or doped iron oxide based catalytic materials[13] can be utilized for the HTL process and recovered via magnetic seperation methods. Due to the significantly larger surface area, high chemical stability and higher number of reactive surface sites, the quality of the HTL products such as char, oil, and biocrude can be improved during HTL process. Zhang et al.[14] used various transition metal supported TiO_2 catalysts for the HTL of microalgae at 300 ºC and observed maximum biocrude yield of 48.23%. Plucinski et al.[15] used Zn and Mg doped ferrites as catalysts for HTL of microalgae and observed that the biocrude yield was increased by 13.9%. Although the product yield was enhanced during the catalytic HTL process, some key challenges need to be addressed such as reduction of reactive sites on catalysts due to carbon deposition, sintering, and agglomeration. Binary transition metal iron oxide[16] have higher catalytic sites as compared to single component metal oxides. Hence, in this study, we have synthesized (Co,Ni)- Fe oxide nanoparticles using sol-gel technique and utlized for the hydrothermal liquifaction of pinewood at 300ºC. Products obtained *via* BTMO catalyzed HTL reaction were compared with those obtained with non-catalyzed HTL reaction.

2 EXPERIMENTAL

2.1. Materials

Precursors such as $NiCl_2.6H_2O$, $CoCl_2.6H_2O$ and $FeCl_2.4H_2O$ were purchased from Sigma Aldrich. Absolute ethanol and propylene oxide (reagent grade - 99%) were purchased form Alfa Aesar. Pinewood flour (avg. particle size 150 μm) was obtained from the American Wood Fibers. Acetone, dichloro methane (DCM), and ethyl acetate, (reagent grade) were purchased from Sigma Aldrich. N_2 from a cylinder with high purity (HP grade) was used for the

HTL reactions. Helium (UHP grade) was purchased from Lindweld Inc., Rapid City, SD and used for GCMS analysis.

2.2. Methods

2.2.1. Synthesis of BTMO Nanoparticles

Precursor salts of Ni, Co, and Fe were taken in stoichiometric quantities and dispersed in ethanol (1:2 w/v) *via* sonication until a visually clear solution was obtained. Gelation was achieved by the addition of propylene oxide. The resultant gel was aged for 24 hrs and calcined at 600 °C to form (Co,Ni)-Fe-oxide nanoparticles. Detailed synthesis procedure is shown as a schematic in Figure 1.

2.2.2. Catalytic liquifaction of Lignocellulosic Biomass

Hydrothermal liquifaction (HTL) of lignocellulosic biomass was performed in a 300 mL SS316 PARR reactor rated for 350 °C and 3000 psi. 15 g of dry pinewood flour and 0.75 g of BTMO powder (5 wt% of biomass) were added to 150 mL DI water. After the reactor was sealed and checked for leaks, it was purged with N_2 few times to displace air and then pressurized with N_2 (40 psi). The reactor contents were heated to the set temperature of 300 °C and maintained for 1 hour under continuous stirring at 1300 rpm. At such conditions, the total reactor pressure was observed as 1500 psi. The reactor temperature was maintained using the 4836 Parr PID controller. After the completion of the experiment, the reactor was cooled down to room temperature by circulating cold water through the cooling loop installed inside the reactor. Further details of the mechanical aspects and operation the the PARR reactor were given elsewhere.[3]

2.3. Characterization

Sol-gel derived BTMO powder recovered after the calcination step was characterized for phase purity by the x-ray diffraction using Rigaku Ultima IV x-ray diffractometer (operating conditions- 40 kV, 1.76 kW) in the 2θ range of 10° to 90°. The specific surface area (SSA) and the pore size were determined by using Micromeritics Gemini II – 2375 BET (Brunauer-Emmett-Teller) surface area analyzer. Total phenols in the biocrude obtained after HTL reaction was analyzed Agilent GC–MS/7890 GC system/5975C MSD equipped with Agilent HP-5 ms capillary column consisted 5% phenyl 95% dimethylpolysiloxane (30 m x 250 μm x 0.25 μm), respectively. The total organic carbon (TOC) content in the biocrude was measured using GE Sievers InnovOx laboratory TOC analyzer. Phosphoric acid (6M) and 30% (w/v) sodium persulfate were used as reagent and oxidizer, respectively. C1-C3 acids in the biocrude were analyzed using Shimadzu HPLC equipped with Phenomenex ROA-Organic Acid H+ (8%) LC Column (300 mm x 7.8 mm). Detailed procedures were reported elsewhere [3, 9].

3 RESULTS AND DISCUSSION

### 3.1. Characterization of BTMO Nanoparticles

(Co,Ni)-Fe-oxide nanoparticles were characterized by XRD and the profiles obtained are shown in Figure 1. The 2θ reflections corresponding to 35.54°, 37.16° and 43.19° indicated $CoFe_2O_4$ phase, whereas 30.17°, 57.17°, 62.77°, 74.27°, 79.30°, and 87.03° indicated the phase composition of $Ni_{0.4}Fe_{2.6}O_4$, which is consistent with those reported in the literature [17, 18] and ICDD (International Center for Diffraction Data) [19] pattern. As these peaks were recognized at their respective lattice planes, RIR based quantative analysis was performed to determine the phase fractions using MDI Jade software. Following the analysis, 55.1% of $CoFe_2O_4$ and 44.9% of $Ni_{0.4}Fe_{2.6}O_4$ were observed in the BTMO nanoparticles. Average crystal size calculated using Scherrer's equation [20] and it was found to be 26.33 nm. The specific surface area (SSA) of the (Co,Ni)-Fe-oxide nanoparticles as measured using BET analyzer was found to be 34.39 m^2/g with avg. pore diameter of 15.79 nm and pore volume of 0.136 cm^3/g.

3.3. BTMO Catalyzed HTL of Pinewood

Following the HTL reaction, the aqueous biocrude was seperated from the char using vacuum filtration. Light bio-oil (LBO) component in the biocrude was obtained using DCM extraction using the procedure reported elsewhere [9]. The biocrude obtained after DCM extraction can be either recycled or treated to obtain value added co-products. The remaining solids after the bio-crude seperation were throughly washed with acetone and the heavy bio-oil (HBO) was extracted. The resultant char was sonicated and washed with DI water to remove residual oil components and dried in an oven at 65 °C. About 135 mL of aqueous biocrude was obtained after the HTL reaction. The results obtained are summarized in the Table 1. Higher heating value (HHV) of the biomass and the products derived from the HTL reaction was calculated using Dulong formula [9]. The higher HHV value of LBO and HBO was found to be 27.19 MJ/kg and 31.83 MJ/kg, respectively.

Table 1. Elemental analysis and HHVs of pinewood and products derived after HTL process.

Elements	Pinewood	LBO	HBO
C (wt%)	57.17	63.5	71.95
H (wt%)	6.16	6.78	6.97
N (wt%)	0.22	0.65	1.14
O (wt%)	33.14	29.17	19.85
HHV (MJ/kg)	20.15	27.19	31.83
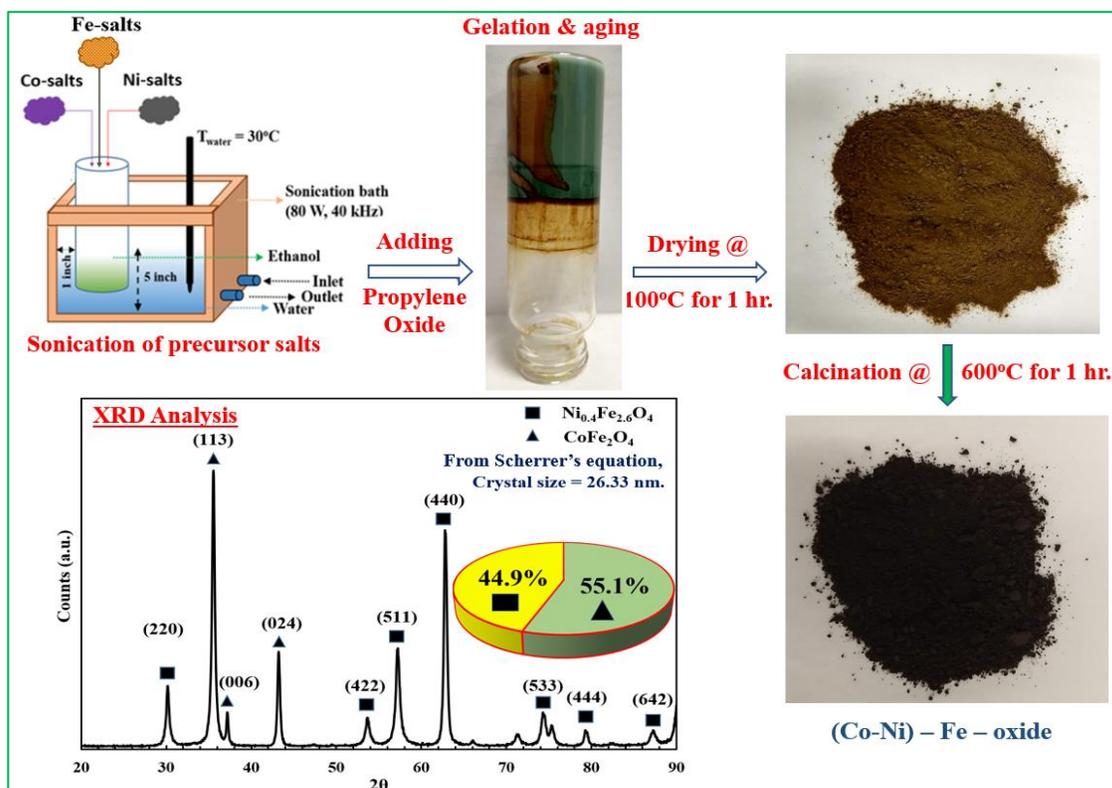
Figure 1. Sol-gel synthesis of BTMO (Co, Ni) - Fe - oxide powdered material and x-ray diffraction analysis.

Dissolved organic carbon in the aqueous biocrude as analyzed using TOC analyzer was observed as 9830 ppm. From the TOC analysis, the % liquefaction yield [9] was calculated as 40%, whereas for non-catalyzed HTL of pinewood under similar operating conditions, the %liquefaction yield was 34%. This shows that the presence of BTMO nanoparticles resulted in higher liquefaction yield.

The biocrude sample was diluted in 1:10 ratio with DI water and was loaded in the HPLC to measure the C1-C3 acids. As shown in Figure 2, C1-C3 acids were observed as 17 wt% in the biocrude. To measure the phenol concentration, the obtained biocrude sample was diluted with equal volumes of ethyl acetate and mixed for 1 minute using vortex mixer. The resultant mixture was left undisturbed for 15 min. After a two pass solvent extraction, the supernatent was loaded in the GCMS and analyzed for presence of phenols. The overall yield of phenols (based on the area % of total compounds) was found to be 7%. The yields of different products observed with the BTMO catalyzed HTL of pinewood are compared with non-catalytic HTL of pinewood at similar operating conditions. The results for the product yields are summarized in Figure 2. It can be observed that the presence of BTMO nanoparticles have improved the liquefaction yield, and yields of oils, C1-C3 acids, and phenols. It suggest that the surface of BTMO nanoparticles has contributed to higher conversion and selectivity.
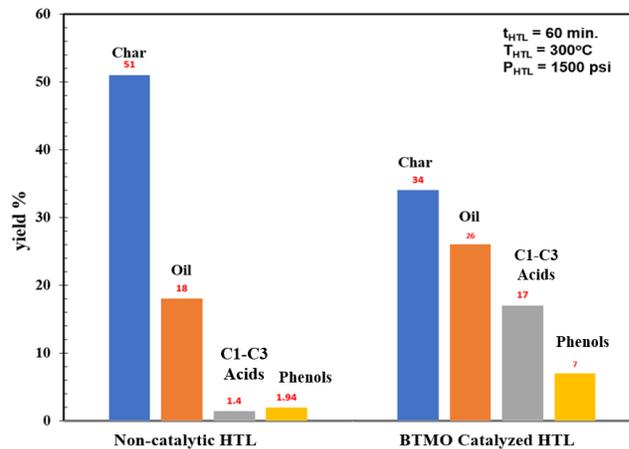
Figure 2. Comparison of the yields of char, total oils, C1-C3 acids, and phenols for non-catalytic and BTMO catalyzed HTL of pinewood.

4   CONCLUSIONS

(Co,Ni)-Fe-oxide nanoparticles were synthesized using sol-gel technique. The powdered x-ray diffraction analysis revealed the mix phase of Ni-Fe oxide and (Co,Ni)-Fe oxide with avg. crystal size of 26.33 nm. BTMO nanoparticles (5 wt%) were used for the HTL of pinewood flour (avg. particle

size 150 μm) at 300 ºC for 1 hour. The yield of different products obtained via BTMO nanoparticles catalyzed HTL reaction was compared with those obtained under non-catalytic HTL reaction condition. Higher liquefaction yield of 40% was observed with BTMO catalyzed reaction, which resulted in the lower char yield. Higher yields of oil, C1-C3 acids and phenols of 26%, 17% and 7%, respectively were observed with the BTMO catalyzed HTL reaction as compared to the non-catalytic HTL of pinewood flour.

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