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Characterization of hydrothermal liquefaction products from coconut shell in the presence of selected transition metal chlorides

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ABSTRACT

Subcritical hydrothermal liquefaction (HTL) of coconut shell (CCNS) was carried out in a batch-type reactor at varying temperatures (240, 270, 300, and 330 °C) in the presence of transition metal chlorides ($ZnCl_2$, $CuCl_2$, and $NiCl_2$) under high pressure (~22 MPa) and N_2 atmosphere. The mass balance and properties of essential HTL products including crude-like oil (HTL oil), char, and the water-soluble fraction (WSF) were investigated. Yields of HTL oil increased with rising temperature and the highest yield of 13.9 wt% was obtained at 300 °C. The water content and total acid number (TAN) of HTL oil were in the range of 3.0–9.6% and 98–190 mg KOH/g, respectively. Transition metal chlorides (2.5–10.0% (w/w sample)) were added as catalysts, and HTL oil yield decreased significantly at higher metal doses. The amounts of gas, WSF, and char were diverse by transition metal type. Compared with the physicochemical features of HTL oil without the addition of transition metals, water content increased up to 11.8% (for 10.0% $CuCl_2$), but the TAN decreased. Levulinic acid (LA) and γ-Valerolactone (GVL), main decomposition products of cellulose, were generally detected in HTL oil. HTL oil obtained with $CuCl_2$ had a relatively low GVL yield as well as a high LA yield compared with HTL oil obtained with $ZnCl_2$ and $NiCl_2$. Experiments using a model compound (cellulose) tentatively confirmed that hydrogenation/dehydration of LA into GVL might be disrupted by Cu^{2+} ionized from $CuCl_2$ under acidic hydrothermal conditions.

1. Introduction

Global warming and the abrupt climate shift caused by greenhouse gas emission are largely attributed to the burning of fossil fuels [1]. Thus, it is important to develop alternative energy sources that are plentiful and have high energy resource potential, for example, lignocellulosic biomass. Lignocellulosic biomass can be classified into woody biomass and non-wood materials, such as agricultural crops related to sugar and oil, herbaceous plants, and processing residues. Agricultural residues are the most common and inexpensive non-wood materials. In recent years, conversion of various types of agricultural residues into energy carriers was studied. A typical example is a residue produced from coconut plantations (coconut husks, fiber and shells). These coconut byproducts, especially coconut shells (CCNS), waste materials that cause environmental problems such as air pollution or soil erosion when they are burned or discarded [2]. Identifying their high-value applications for these materials would thus be advantageous on economic and environmental perspectives.

Direct liquefaction of biomass is defined as thermochemical conversion of biomass into crude-like oil using organic solvent such as ethanol [3], ethylene glycol [4], and glycerol [5]. Also, various types of catalyst and ionic liquid as a hydrogen donor are used [5–7]. Among them, hydrothermal liquefaction (HTL) process uses subcritical water as a solvent. Under conditions of overpressure and at temperature up to 374 °C, water exists in liquid phase, but its dielectric constant and the strength of its hydrogen bonds decrease and the concentrations of hydronium and hydroxide ions increase [8]. Subcritical water acts as both a solvent for hydrophobic organics and an acid/base catalyst. Major organic compounds in lignocellulosic biomass, such as cellulose, hemicellulose, and lignin undergo thermal degradation and dissolve in subcritical water. From the process, HTL oil, char (hydrochar), the water-soluble fraction (WSF), and product gas can be obtained. HTL process has the competitiveness in absence of drying process which requires high cost and energy. HTL oil, a target product of the process, has the potential to

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provide bio-transportation fuels and biochemicals since it is made up of various phenolic and cellulose-derived molecules.

Catalytic liquefaction of lignocellulosic biomass initiates deep degradation and decomposition of the components, and numerous studies have explored the effects of catalysts on the HTL process. Alkaline catalysts remarkably extract and interact with lignin polymer, while acid catalysts are prone to cellulose conversion and produce specific compounds (furan, 5-HMF and formic acid) [9]. As alkaline catalysts, potassium salts KOH and K_2CO_3 were used in a study on HTL of water hyacinth [10]. Karagöz et al. [11] performed catalytic liquefaction of pine sawdust with four alkaline solutions (NaOH, Na_2CO_3, KOH, and K_2CO_3). As acid catalysts, HTL of low-input high-diversity mixtures of native grassland perennials was carried out with H_2SO_4 and solid superacid SO_4^{2-}/ZrO_2-Al_2O_3 [12]. NaOH and CaO-ZrO_2 (solid alkali) were used for comparison. This study focused on transition metals for thermochemical conversion of biomass. Transition metal effects on thermogravimetric properties of biomass [13] and its cation form contributes to decompose microcrystalline cellulose to form hydrocarbons [9] and [14]. The catalytic effects of transition metals on pyrolysis and gasification have been studied. But their effects on the HTL process remain unclear. In this paper, catalytic liquefaction of CCNS was performed with transition metal chlorides since it is advantageous to determine catalytic effect of the metals on the liquefaction.

The main objective of the study was to examine the effects of transition metals on HTL of CCNS. In order to determine the optimal temperature with regard to HTL oil yield, direct liquefaction was carried out at 240–330 °C for 30 min under pure water conditions. Second, catalytic liquefaction was performed at a fixed temperature (that of optimal HTL oil yield) in the presence of three transition metal chlorides, $ZnCl_2$, $CuCl_2$, and $NiCl_2$. Finally, HTL oil products were recovered with CH_2Cl_2 and the physicochemical properties and composition were analyzed.

2. Materials and methods

2.1. Materials

As a raw biomass sample for this study, CCNS from coconut palms (*Cocos nucifera* L.) was used. A cutting mill (PULVERISETTE 19, Fritsch, Germany) was used to cut CCNS down to a size of approximately 0.5 mm. Transition metal chlorides, $CuCl_2$ (97%), $NiCl_2$ (98%), $ZnCl_2$ (reagent grade, ≥98%), and cellulose powder (Avicel® PH-101) were purchased from Sigma-Aldrich Korea (South Korea).

Carbon, hydrogen, and nitrogen in the CCNS sample were analyzed using a CHNS-932 (LECO Corp., Michigan, USA). Holocellulose, lignin, and ash content were analyzed according to National Renewable Energy Laboratory (NREL) standard procedures [15,16]. Inorganic compounds were analyzed via inductively coupled plasma emission spectroscopy (ICP-ES) [17]. Thermogravimetric analysis (TGA) was performed with a Q-5000 IR instrument (TA Instruments, USA). The sample was heated under an inert atmosphere (25 ml/min N_2 flow) at a heating rate of 10 °C/min up to 800 °C. The results of sample analysis are listed in Table 1.

Table 1
Chemical composition and thermal properties of CCNS.

Properties	Value
Elemental analysis (wt%)	
Carbon	49.3 ± 0.5
Hydrogen	4.8 ± 0.5
Nitrogen	0.1 ± 0.1
Oxygen[a]	45.8 ± 1.1
Component analysis (wt%)	
Holocellulose	72.2 ± 0.1
Lignin	28.6 ± 0.4
Extractives	1.2 ± 0.0
Ash	0.5 ± 0.0
Inorganic compound analysis (ppm)	
Aluminum	50
Calcium	150
Iron	100
Magnesium	80
Potassium	1410
Phosphorus	260
Silicon	130
Thermogravimetric analysis	
Volatiles (wt%)	77.0
Char (wt%)	23.0
Temperature at max. degradation rate (°C)	349.9

[a] By difference.

2.2. Subcritical HTL of CCNS

HTL of CCNS was carried out in an autoclave-type batch reactor (Hanwoul Engineering, South Korea). This device includes a furnace that can be heated to 750 °C, a 500 ml stainless steel reactor with a stirrer, and water cooling system. The reactor was loaded with biomass, transition metal chloride, and deionized water at a specific ratio, and then purged for 60 s with N_2 gas to remove the air inside. Reactants were mixed using a stirrer set at 300 rpm. Reactions were performed in duplicate over a temperature range of 240–330 °C and under high pressure conditions up to 22 MPa with a heating rate of 8 °C/min. After the reaction, the reactor was cooled down to 20 °C at a rate of −3 °C/min. Reaction products were washed with methylene chloride and separated with filter paper (Whatman No. 42) to isolate the liquid portion from the mixture. The filtered solid portion was dried and labeled as hydrochar. The liquid portion was then divided into the water phase and the organic phase, which was labeled as HTL oil. Hydrophilic compounds in the water phase were labeled as WSF. Cellulose powder in the presence of transition metals was also used as a model compound for HTL. The reaction temperature was fixed at 300 °C, and other conditions were set to those of CCNS HTL. Product yields were calculated using the following equations:

$$\mathrm{HTLoilyield(wt\%)} = W_{oil}/W_{biomass} \times 100\%$$

$$\mathrm{Hydrocharyield(wt\%)} = W_{char}/W_{biomass} \times 100\%$$

$$\mathrm{Gasyield(wt\%)} = (W_{biomass} + W_{water} - W_{oil} - W_{char} - W_{wp})/(W_{biomass} + W_{water}) \times 100\%$$

$$\mathrm{WSFyield(wt\%)} = 100\% - (\text{The sum of HTL oil, hydrochar, and gas yield})(\mathrm{wt\%})$$

$W_{biomass}$ and W_{water} are the weight of the CCNS and solvent water. W_{oil}, W_{char}, and W_{wp} are the weight of HTL oil, hydrochar, and the water phase, respectively.

2.3. Characterization of HTL oil

The water content of HTL oil was calculated using a 870 KF Titrino plus (Radiometer, Switzerland) with HYDRANAL®-Composite 5 reagent [18]. Total acid number (TAN), which represents the acidity of HTL oil, was determined using a 848 Titrino plus (Radiometer) and a method suggested by Shao and Agblevor [19]. Calorific value of HTL oil was calculated using a Parr 6400 Calorimeter (Parr Instrument Company, USA). GC/MS analysis of HTL oil was performed to identify the chemical compounds in HTL oil. HTL oil (0.5 mg) was diluted with 1 ml acetone