Industrial Crops & Products 113 (2018) 157–166

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Efficient hydro-liquefaction of woody biomass over ionic liquid nickel based catalyst

Qingyin Li[a,b], Dong Liu[b], Linhua Song[c], Xulian Hou[d], Chongchong Wu[a], Zifeng Yan[b,*]

[a] Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive, NW, Calgary, Alberta T2N 1N4, Canada
[b] State Key Laboratory of Heavy Oil Processing, PetroChina Key Laboratory of Catalysis, China University of Petroleum, Qingdao 266580, China
[c] College of Science, China University of Petroleum, Qingdao 266580, China
[d] China Petroleum Engineering Co., Ltd., Beijing Company, China

ARTICLE INFO

Keywords:
Hydro-liquefaction
Bio-oil
Ionic liquid
Biomass
Sawdust

ABSTRACT

The effective hydro-liquefaction process of sawdust is proposed over different ionic liquid Ni-based catalysts at 320 °C. This study investigated the relationship between ionic liquid composition and catalytic performance. The maximum sawdust conversion of 83.11% and liquid yield of 52.38% were achieved over the catalytic system including nickel chloride and 1-butyl-3-methyllimidazolium bromide ([Bmim]Br), suggesting that the anion in ionic liquid played an vital role on the sawdust hydro-liquefaction. The defined impact index was provided to further evaluate the liquefaction performance using ionic liquid Ni-based catalyst. The largest impact index obtained from [Bmim]Br/$NiCl_2$ was in agreement with its excellent catalytic liquefaction performance. The analysis of ionic liquid Ni-based catalyst indicated the coordination interaction between ionic liquid and nickel chloride, which would be favorable to feedstock conversion and improve the bio-oil quality.

According to the component distribution, the introduced ionic liquid Ni-based catalytic system was beneficial to sawdust cracking, resulting in the increased amount of smaller compounds. Additionally, the oil compositions highly depended on the employed type of ionic liquid.

1. Introduction

To solve energy crisis and environmental deterioration caused by unrestrained exploitation of fossil energies, biomass, as one of the most abundant and renewable resources, has gained growing attentions (Zacher et al., 2014; Zhang et al., 2012). The lignocellulosic biomass can be converted into bio-fuels through main thermo-chemical technologies including gasification, pyrolysis, and liquefaction (Demirbas and Balat, 2006; Bridgwater, 2012; Liu et al., 2012). Recently, the biomass liquefaction in supercritical ethanol has been comprehensively investigated (Xu and Etcheverry, 2008; Chumpoo and Prasassarakich, 2010). The studies exhibited some potential advantages such as excellent solubility, low corrosivity, and hydrogen donation ability (Brand et al., 2013).

Many researches concerning biomass liquefaction in supercritical ethanol mainly focused on effect of parameters on the reaction behavior of raw materials. According to the previous literature, the utilized catalyst was one of most significant variables to enhance bio-oil yield and improve quality, and thus many efforts were made to explore the catalytic performance on the biomass conversion (Perego and Bianchi, 2010; Alonso et al., 2010). Due to the negligible vapor pressure, high thermally stability, and strong dissolution ability, ionic liquid has been widely employed in liquefaction of biomss for bio-oil or valuable chemicals (Pârvulescu and Hardacre, 2007; Zhao et al., 2007). Lu et al. found that an acidic ionic liquid 1-carboxypropyl-3-methyl imidazolium chloride was considered as an effective catalyst for the conversion of carbohydrates into 5-hydroxymethylfurfural (Hu et al., 2013). Li et al. reported that the concentrated fructose afforded 5-hydroxymethylfurfural with a high yield in the combination of ionic liquid and microwave irradiation without catalyst (Li et al., 2011). Lu and his co-workers reported that the acidic ionic liquid [Bsmim]HSO_4 exhibited a good performance on the liquefaction of sawdust (Lu et al., 2013). In particular, with the addition of ionic liquid, the hydrogen structure in lignocellulose would be disrupted, and then interaction among the biomass components were highly weakened, resulting in the improved degradation of raw material (Mäki-Arvela et al., 2010).

Additionally, efficient conversion of lignocellulosic biomass was carried out in the ionic liquid-metal ion system. Zhang et al. have reported that the addition of $AlCl_3$ in the 1-butyl-3-methylimidazolium chloride facilitated the conversion of woody biomass into furfural (Zhang et al., 2013). Chinnappan et al. demonstrated that sucrose and glucose could be converted effectively to 5-hydroxymethylfurfural in

* Corresponding author.
E-mail address: zfyancat@upc.edu.cn (Z. Yan).

https://doi.org/10.1016/j.indcrop.2018.01.033
Received 30 June 2017; Received in revised form 9 December 2017; Accepted 13 January 2018

the presence of pyridinium based dicationic ionic liquid ($[C_{10}(EPy)_2]$ $2Br^-$) and chromium chloride (Chinnappan et al., 2015). In view of biomass hydro-liquefaction, Ni-based catalyst is suggested to enhance raw material conversion and highly improve the bio-oil quality (Grilc et al., 2014). Therefore, the Ni-based catalyst ($NiCl_2$) in the ionic liquid was utilized as the catalytic system for biomass hydro-liquefaction. On the one hand, the metal chloride had a coordination interaction with ionic liquid, and higher catalytic activity was expected, which could promote the biomass conversion effectively (Hines et al., 2008). On the other hand, the presence of ionic liquid could destroy the network structure of raw material, and then the biomass reaction could be highly improved.

To further evaluate the liquefaction behavior from ionic liquid Ni-based catalyst, a novel impact index was defined with tetralin employed as the chemical probe. Generally, tetralin was considered as the excellent hydrogen donor for biomass conversion (Beauchet et al., 2011). In the closed reaction system, the ionic liquid in the catalytic system would promote the feedstock conversion, and increase the amount of produced intermediates. Therefore, these fragments could greatly affect the hydrogen-donating ability of tetralin. On the other hand, the presence of ionic liquid had an influence on the solvent effect, and thus altered the liquefaction performance of lignocellulose, which definitely affect the tetralin conversion during the process. According to the above discussion, a new impact index was put forward to explore the impact of ionic liquid Ni-based catalyst on the lignocellulose liquefaction.

According to the previous work, sawdust and its three sub-components hydro-liquefaction were investigated with [Bmim]Cl and $NiCl_2$ as the catalytic system (Liu et al., 2015). However, the influence of ionic liquid in the catalytic system on the liquefaction behavior was seldom reported. Besides, the formed transition metal complex between nickel chloride and ionic liquid should be described in detail. The aim of this work was to determine the catalytic performance of various ionic liquids in nickel chloride on the liquefaction performance of sawdust. Additionally, the defined new index was used as a reference to further evaluate the ionic liquid Ni-based catalyst influence in the reaction system. The chemical composition of bio-oil derived from the optimal condition were analyzed by Fourier transform infrared (FTIR), gas chromatography-mass spectrometry (GC–MS), elemental analysis (EA), and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The ionic liquid nickel catalyst was characterized by FTIR, ^1H nuclear magnetic resonance (^1H NMR) and electron spray ionization-mass spectrometry (ESI-MS), respectively.

2. Experimental section

2.1. Material and methods

The sawdust was obtained from wood processing industry in Qingdao, China. The raw material was firstly washed and dried in an oven at 378 K overnight. Subsequently, the desired sample with 60 meshes was achieved through the pretreatment of crushing and sieving. The ionic liquids including [Bmim]Br, [Bmim]Cl, and [Emim]Cl were synthesized according to the reported procedures (Burrell et al., 2007; Holbrey et al., 2001). Additionally, $[Bmim]BF_4$ was supplied from Sigma-Aldrich without further purification. All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. The lab-made high-pressure autoclave was depicted in Supplementary Fig. S1.

As illustrated in Table 1, the chemical compositions of tested sample were determined based on Van Soet method (Carrier et al., 2011). The elemental components were measured via a Vario EL III elemental analyzer. The oxygen content was evaluated from mass balance closure without regard to inorganics contained in the feedstock. The Higher Heating Value was estimated from the elemental results, and calculated by the formula described in the literature (Huang et al., 2013). Additionally, the elemental compositions and HHV were analyzed based on a dry and ahs-free basis.

$$\text{HHV (MJ/kg)} = 338.2\,\text{wt.\%(C)} + 1442.8(\text{wt.\%(H)} - \text{wt.\%(O)}/8) \quad (1)$$

2.2. Experimental procedures and product separation

In each catalytic run, 1 g sawdust, 10 mL ethanol, 300 μg/g Ni-based catalyst ($NiCl_2$) and a certain amount of ionic liquid was placed into the autoclave, and then the ethanol solution was stirred to make it mixed evenly. The reactor was purged with hydrogen and then elevated to 4.0 MPa initial pressure. Subsequently, it was heated up to the required temperature and maintained for the desired time. Finally, the reaction was quenched immediately with cooling water. The procedure for separation of liquefaction products was described previously (Liu et al., 2015). To explore the product distributions, the yields of bio-oil and conversion were defined based on the Eqs. (2)–(3). Especially, the obtained raw oil surely contained the employed catalyst. However, the remaining ionic liquid was not taken into consideration in the mass balance due to its small amount. It should be noted that the gaseous yield included yield of volatile components, produced water and gas.

$$Yield\ of\ bio\text{-}oil = \frac{Weight\ of\ bio\text{-}oil}{Weight\ of\ sawdust} \times 100\% \quad (2)$$

$$Conversion = \frac{Weight\ of\ sawdust - Weight\ of\ residue}{Weight\ of\ sawdust} \times 100\% \quad (3)$$

All the product yields were calculated on the tested sample. Beside, each experiment was duplicated three times under identical conditions to ensure the accuracy of data. The results were dispersed within 4% standard derivation and the calculated mean value was analyzed to investigate the catalytic performance on the sawdust hydro-liquefaction.

2.3. Characterizations

The analysis of nickel species in ionic liquid was performed through FTIR, ESI-MS, and ^1H NMR, respectively. The ^1H NMR spectrum was acquired from a Bruker Avance III 500 MHz NMR spectrometer with 500 MHz resonance frequency. ESI-MS analysis was conducted using an Agilent 6300 mass spectrometry.

The functional group distribution was determined using a Nicolet 6700 FT-IR spectrometer. The chemical composition of bio-oil was characterized via a GC–MS system from ThermoFisher with a DB-35MS column (30 m × 0.25 mm × 0.25 μm). The dominant components detected in the liquid product were identified by a NIST mass spectral database.

The compositional analysis of bio-oils was conducted using a 9.4 T FT-ICR MS instrument (Bruker Apex-Ultra) equipped with ESI. The negative mode was operated with the source voltage of 3.0 KV and the

Table 1
Chemical and elemental compositions of sawdust.

Elemental composition/wt.%				Chemical composition/wt.%				
C	H	N	O[a]	Cellulose	Hemicellulose	Lignin	Extractives	Ash
47.68	6.30	0.45	45.57	48.27	19.50	19.80	11.40	0.97

[a] Caculated by difference.