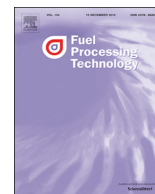




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Research article

Zeolite catalysts screening for production of phenolic bio-oils with high contents of monomeric aromatics/phenolics from hydrolysis lignin via catalytic fast pyrolysis

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ABSTRACT

In this work, zeolite catalysts, widely used catalysts for effectively cracking of organics into highly deoxygenated and hydrocarbon-rich compounds, were screened for their performance in catalytic fast pyrolysis (CFP) of hydrolysis lignin (HL) in a drop-tube fixed bed reactor at temperatures of 400, 450, and 500 °C. Five commercial zeolite catalysts including zeolite X, Zeolite Y (CBV-100, CBV-600, and CBV-780) and ZSM-5 (CBV-8014) were screened, and ZSM-5 exhibited the best performance for converting hydrolysis lignin to monomeric aromatics/phenolics. It was demonstrated that the catalyst total acidity and the Bronsted acid sites play a key role in cracking and deoxygenation of the pyrolysis vapors towards the monomeric aromatic/phenolic hydrocarbons. CFP of HL under the best conditions (450 °C, ZSM-5 catalysts), produced bio-oil at 57.4 wt% yield, and a high yield of monomeric aromatics/phenolics (being 0.11 g/g-HL).

1. Introduction

Increasing energy consumption and depleting petroleum resources combined with environmental concerns about greenhouse gas emissions (GHG) are making it vital to find sustainable sources for liquid fuels and chemicals [1,2]. Lignocellulosic biomass is accounted as a promising resource for energy and chemicals owing to its renewability, high carbon content and abundancy. Lignin is a by-product generated in large amount in pulping and cellulosic ethanol industries. Lignin is a natural macro-molecule containing multiple alkylphenol units, which can be converted to aromatics/phenolics for fuels and chemicals through bio-/thermo-chemical conversions [3].

Fast pyrolysis is a typical thermochemical technology for direct conversion of lignocellulosic biomass into liquid bio-oils for fuels and chemicals, which by far the only industrially realized technology [4]. The foremost technical challenge of fast pyrolysis comes from the lack of commercial application of pyrolysis oils as they are of a lower heating value, only about 50% of that of petroleum, and a pyrolysis oil has poor instability caused by its high oxygen content, high acidity, and hence corrosive. Pyrolysis oils due to these detrimental properties, without expensive upgrading, are unsuitable to be used as a fuel or incorporated into petroleum. Presence of a catalyst in fast pyrolysis,

also called catalytic fast pyrolysis (CFP), can produce upgraded bio-oils with a lower oxygen content, lower acidity/corrosivity and higher heating values, etc. Many catalyst have been investigated, including microporous, mesoporous, and macroporous catalysts (ZSM-5, MCM-41, CaO) [5–8]. Generally zeolites have been commonly used as catalysts for CFP of lignocellulosic biomass due to its high acidity or low Si/Al ratios, being effective for cracking of the vapor during the pyrolysis process to produce low molar mass bio-oils [9,10]. At a high pyrolysis temperature (such as 500–800 °C), the acidic dehydroxylation, demethoxyl reactions would reduce the content of oxygen containing compound with functional groups (–OH and –OCH₃) to yield more BTX. More importantly, the ability of shape selectively of the catalyst, by the characteristic of similar size between porous structure and molecular diameter of single ring aromatics, about 6 Å. Therefore, zeolite has strong ability to increase the content of monomeric aromatics/phenolics in CFP of lignocellulosic materials at medium temperatures (400–500 °C) [11–13].

Pyrolysis at temperatures of 400–700 °C with four types of lignin, including alkali lignin, organosolv lignin, milled wood lignin, and klason lignin, were studied by Wang et al. [14], where it was reported that the content of phenolic compounds reached the maximum yield at 600 °C, and pyrolysis of alkaline and klason lignins produced more

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phenols at lower temperatures by breakage of ether bonds in lignin structure. In another study by Heo et al. [15], fast pyrolysis of rice husk at temperatures 400 °C–550 °C was investigated. They reported that the best pyrolysis temperature was 450 °C, leading to the highest bio-oil and phenolic compounds production. Catalytic fast pyrolysis of miscanthus for production of aromatics and phenolics was also investigated by Park et al. [16], and it was reported that 450 °C was the best temperature with and without catalyst (HZSM-5) with respect to bio-oil production as well as phenolic compounds production. In addition, fast pyrolysis of waste furniture sawdust in fluidized bed for bio-oil production at temperatures ranging from 400 °C to 550 °C was studied by Heo et al. [17]. They reported that the highest bio-oil was achieved at 450 °C, where a high concentration of phenolic compounds was also confirmed by GC–MS. In a study by Stefanidis et al. [18] different commercial catalysts (zirconia, titania, alumina, zeolite, etc.) were screened in a fixed bed reactor for CFP of wood biomass. Although each catalyst displayed various degrees of catalytic effects, high surface area alumina catalysts with strong Lewis acidity displayed the highest selectivity towards hydrocarbons formation but resulted in a lower yield of oil products, zirconia/titania produced higher yields of oil products than alumina, and ZSM-5 with high surface area displayed moderate selectivity towards hydrocarbons and moderate oil yields. In another study by Yu et al. [19] CFP of lignin with four different zeolite catalysts of various pore sizes was investigated to determine the role of shape selectivity of zeolites, where it was found that ZSM-5 produced the highest yield of aromatics. Al-MCM-41, Al-MCM-48, HZSM-5 and mesoporous MFI zeolite (ZSM-5) were studied for upgrading the pyrolysis vapor-phase from CFP of miscanthus [20]. In this literature work, it was shown that mesoporous Al-MCM-41 and Al-MCM-48 had better performance in terms of oxygen reduction than the microporous HZSM-5, and mesoporous catalysts can present higher acidity that could assist the removal of oxygenates and the production of phenolics. In another work by Du et al. [21] CFP of microalgae was carried out over various zeolites (H-Y, H-Beta, and HZSM-5). They demonstrated that all the three zeolite catalysts increased the aromatic yields and HZSM-5 was the most effective with the yield 18.13%. Also, they investigated the effects of Si/Al ratio by using HZSM-5 of 30, 80, and 280 Si/Al ratios. In their research, HZSM-5 with Si/Al ratio of 80 and moderate acidity achieved the best aromatic yield. Their results are inconsistent with that reported by Park et al. [20]. The selectivity of five different ZSM-5 catalysts with different Si/Al ratios (23–280) towards production of aromatics was studied by Engtrakul et al. [22], and this study demonstrated that the overall acidity of the catalyst was directly correlated with aromatic yields. Similar results were reported by Zheng et al. [23] in their investigation of CFP of lignin over HZSM-5 of different Si/Al ratios. Whereas, a work by Custodis et al. [24] showed that the selectivity of mesoporous catalysts (Al-MCM-41, Al-SBA-15, and Al-MSU-J) towards to aromatics formation in CFP of lignin was hard to be correlated to solely on acidity of the catalysts. In summary, there are still inconsistent findings on the effects of catalysts acidity on the aromatic products' selectivity, more comprehensive studies are required to correlating the product yields with the catalysts' acidity and the type of acid sites.

Low-boiling point aromatic/phenolic compounds that can be potential used for bio-fuels, fuel additives or chemicals. GC–MS serve as a useful instrument to quantitatively analyze the concentrations of low-boiling point aromatics/phenolics, e.g., monomeric aromatics/phenolics from CFP of lignin. The main objective of this work was to screen some commercial zeolite catalysts with various (Si/Al) molar ratios including zeolite X (1), Zeolite Y (5.1, 5.2, and 80) and ZSM-5 (80) for their performance in CFP of hydrolysis lignin (HL) for the production of bio-oils with high contents of monomeric aromatics/phenolics.

2. Materials and methods

2.1. Materials

The hydrolysis lignin (HL) used in this study was provided by FPIinnovations, and it was the residual from the TMP Bio™ process for production of mixed sugars (xylose and fructose) from Aspen wood [18]. The HL is not soluble in any solvent as it contains 50–60 wt% lignin balanced by the residual cellulose and hemicellulose. The molecular weight of the HL could not be based on the ultimate analysis of the HL, it contains 49.76 wt% carbon, 6.45 wt% hydrogen, 0.33 wt% nitrogen, and 43.46 wt% oxygen (by difference), all on a dry basis. The proximate analysis of the HL (dry basis) was 82.20 wt% volatile matter, 16.04 wt% fixed carbon and 1.76 wt% ash. Four zeolites including ZSM-5 (CBV 8014 in ammonium form) and zeolite Y (CBV-100 in sodium form, and CBV-600/CBV-780 in hydrogen form), were all purchased from Zeolyst International (Conshohocken, PA). The zeolite X powder with Si/Al molar ratio of 1.0 and particle size of > 45 μm was purchased from Sigma-Aldrich (USA) with CSA 1318-02-1. ACS reagent-grade acetone, purchased from Caledon Laboratory Chemicals (ON, Canada), was used as the reactor rising/washing solvent for product separation.

2.2. Catalyst characterization

The properties of the five commercial zeolite catalysts are listed later in Table 1, in which some characterization properties are obtained from the supplier. In order to prevent losses in the fixed catalyst bed pyrolysis reactor, all zeolite powders were pelletized by pressure pelletizer (about 10 tons), and after crushing, the fraction sieved between 20 and 40 mesh was used for the experiments. The regeneration of the used catalysts was performed by calcining the acetone-washed spent catalysts in a muffle furnace at 450 °C in air for 4 h. The crystalline structure of the fresh/spent ZSM-5 catalyst was characterized by X-ray diffraction (XRD) on a Rigaku-MiniFlex powder diffractometer (Woodland, USA), using Cu-K_α (λ = 1.54059 Å) over the 2θ range of 10°–70° with step width of 0.02°. Textural properties of the fresh/spent catalysts were measured by N₂ isothermal adsorption at 77 K (NOVA 1200e surface area and pore size analyzer). The specific surface area was calculated using Brunauer-Emmett-Teller (BET) method. Total pore volume was estimated using the volume of N₂ gas adsorbed at a relative pressure (P/P⁰) of 0.99. Density functional theory (DFT) was used to calculate the pore size distribution based on N₂ desorption isotherm.

The total acidity of the zeolite catalysts was measured by NH₃-Temperature Program Desorption (NH₃-TPD), carried out on a Quantachrome ChemBET Pulsar TPR/TPD automated chemisorption analyzer. In a typical experiment, about 0.1 g of the sample was pretreated at 300 °C for 1 h under a flow of helium (99.9%, 120 cm³ min⁻¹). After pretreatment, the sample was saturated with anhydrous ammonia at 100 °C for 10 min and subsequently flushed with He at the same temperature to remove any physisorbed ammonia. Then, TPD analysis was carried out by heating the sample in helium from

Table 1
The properties of the 5 commercial zeolite catalysts.

Catalyst	SiO ₂ /Al ₂ O ₃ mole ratio	Cation form	Na ₂ O weight %	Unit cell size, nm	Surface area, m ² /g	Total pore, cm ³ /g	Average pore size, nm
Zeolite X	1.0	Sodium	n.a. ^a	n.a.	1.5	0.01	12
Zeolite Y	5.1	Sodium	13	2.47	900	n.a.	n.a.
Zeolite Y	5.2	Hydrogen	0.2	2.44	660	n.a.	n.a.
Zeolite Y	80	Hydrogen	0.03	2.42	780	n.a.	n.a.
ZSM-5	80	Ammonium	0.05	n.a.	425	0.25	1.3

^a Not analyzed or not available.

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