



# Continuous pyrolysis and catalytic upgrading of corncob hydrolysis residue in the combined system of auger reactor and downstream fixed-bed reactor



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## ARTICLE INFO

### Article history:

Received 23 December 2015

Received in revised form 18 May 2016

Accepted 20 May 2016

### Keywords:

Pyrolysis

Ex situ catalysis

Bio-oil upgrading

HZSM-5

Mono-phenols and aromatics

## ABSTRACT

Continuous pyrolysis of corncob hydrolysis residue, coupled with ex situ catalytic upgrading of the pyrolysis vapor, was investigated in the combined system of an auger reactor and a downstream fixed-bed reactor. The effect of the zeolite catalyst, USY (ultrastable Y) and HZSM-5 (Si/Al = 25, 38) and catalytic temperature on the raw bio-oil upgrading were discussed. The results showed the strong acidity of porous zeolite was essential for catalytic deoxygenation during upgrading pyrolysis vapor. HZSM-5 (25), with the strong acidity and acidic sites, had favored the deoxygenation conversion of carbonyl/carboxyl-containing oxygenates in the pyrolysis vapor, which decreased its content to 2.3 area% via the GC–MS analysis of the upgraded bio-oil. Mono-phenols (phenol and alkylphenols) were enhanced to 53.2 area% over HZSM-5 (25), as compared with that of 17.3 area% during non-catalysis process. The addition of ex situ catalytic upgrading had improved the quality of organic bio-oil at the expense of its yield. Coke formation on the strong acidic sites by condensation of intermediates is detrimental to organic bio-oil yield. The increase of catalysis temperature at the fixed-bed reactor decreased oxygenate compounds to 7.1 area%, 2.3 area% and 1.9 area% at 450 °C, 550 °C and 650 °C, respectively, with 0.75 s of vapor residence time. The TG/DTG/DSC characterization of the used HZSM-5 (25) implied that the coke had deposited on the surface of HZSM-5 (25), which could be removed by combustion to recover its activity.

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## 1. Introduction

Bio-oil, derived from fast pyrolysis of waste lignocellulose, is a promising alternative to fossil fuels due to the high bio-oil yield in the range of ~60–95 wt.% at low costs, depending on the feedstock composition [1]. This process has especial advantage for whole utilization of lignocellulosic biomass [2]. However, direct utilization of raw bio-oil as transportation fuel and value-added chemicals (phenols, aromatic hydrocarbons, furans, etc.) is still challenging, due to its lower heating value, immiscibility with hydrocarbon fuels, instability and corrosiveness [3]. Most of these undesirable properties could be attributed to the oxygen-rich components in raw bio-oils (acids, ketones, aldehydes, furans, sugars, phenols, etc.) [4,5].

Upgrading technologies of raw bio-oil before, during and after pyrolysis, have been the research focus in the late 30 years,

including hydrodeoxygenation, catalytic cracking, emulsification, steam reforming, reactive distillation [6,7]. Biomass, pretreated with H<sub>2</sub>SO<sub>4</sub> and co-feeding with the other feedstock that has high hydrogen to carbon ratio such as methanol, plastic and tyre, has been investigated to improve bio-oil quality [8–10]. The type of pyrolysis/upgrading reactor and reaction conditions could also contribute to bio-oil component adjustment [11–13]. Auger reactor was attractive due to the low carrier gas flow, no need of heat carrier and flexibility to large biomass particle, compared with fluidized bed reactor [14].

Another important approach for the removal of oxygenates and degrading of heavy compounds, dimeric to tetrameric phenolic lignin fragments, is by in situ/ex situ catalysis of pyrolysis vapor [15,16]. A cascade system, made of meso-H-ZSM-5, Ga/meso-HZSM-5 and Cu/SiO<sub>2</sub> in a multi-zone reactor, was reported for upgrading of palm kernel shell pyrolysis vapors with high aromatics yield (15.05 wt.%) [17]. Microporous zeolites (HZSM-5, Beta, Y, et al.), mesoporous M41S/aluminosilicates (Al-MCM-41 and SBA-15) and metal oxides/sulfides have been documented in previous works [16,18].

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Among them, HZSM-5 was widely used for reducing oxygenate amount by deoxygenation, attributed to its Brønsted acid sites and vertically intersection channels of  $\sim 0.55$  nm [19,20]. However formation of undesirable polycyclic aromatic hydrocarbons (PAHs) and coke was observed during upgrading biomass-derived oxygenates, due to the competing reactions of re-polymerization and light aromatic compound formation on the strong acid sites of HZSM-5 [11,21]. Modified HZSM-5, including metal addition and Si/Al ratio adjustment, has been tested to improve the yield to aromatics and phenolics [22,23]. The acidity and pore structure of HZSM-5 were reported to affect product distribution during catalytic upgrading [24]. Yet the detailed relationship between catalyst properties and product distributions is still unknown.

The composition of three main constituents (cellulose, hemicellulose and lignin) in biomass feedstock was another variable that affects bio-oil production, which undergo different depolymerization pathways. The pyrolysis mechanism and radical interactions during pyrolysis and upgrading are currently contradictory, even by using model compounds [2,10]. While it is commonly accepted that the increase of aromatics is obtained during lignin pyrolysis, resulting from its lignin polymer of methoxylated phenyl propyl [25]. Compared with cellulose and hemicellulose, lignin-rich feedstock is a general waste material and has not yet been commercialized for industrial application.

In the present work, the combined system, auger pyrolysis reactor and downstream fixed-bed catalytic reactor, was applied for the continuous pyrolysis of corncob hydrolysis residue (denoted as HRC), which is a solid waste in bio-ethanol production process. Auger pyrolyzer could minimize the use of carrier gas and ex situ catalytic upgrading of pyrolysis vapor could avoid the direct contact of bio-char with zeolites. The effect of different zeolites, ultra-stable Y (USY) and HZSM-5 with Si/Al ratio of 25 and 38, was investigated on ex situ catalysis of vapor phase for bio-oil upgrading. Particular attention was paid towards the effect of zeolite structure and its acidity, as well as catalysis temperature and pyrolysis vapor residence time on product distribution in the upgraded bio-oil, especially towards mono-phenols (phenol and alkylphenols) and aromatics. The coke deposition and reusability of HZSM-5 (25) after regeneration were also discussed.

## 2. Experimental

### 2.1. Materials

HRC, donated from Shangdong Longlive Bio-technology Co. Ltd, China, was the residual from acidic hydrolysis of corncob. HRC samples for pyrolysis were dried at 105 °C for 6 h with 9.1% moisture content (ASTM E 871), ground using a high-speed rotary cutting mill and sieved by a vibrating sieve machine to a particle size less than 0.85 mm. The sample was further dried to decrease its moisture content to less than 2.0 wt.% for proximate analysis and ultimate analysis (ash- and moisture-free). Elemental analysis was measured with a Vario EL Analyzer and the amount of oxygen was determined by difference. Proximate determined volatile combustible matter (ASTM D 3175), moisture content (ASTM E 871), ash content (ASTM D 482). Fixed carbon content was calculated by difference. And the results are shown in Table 1.

Lignin content was ca. 60 wt.% (according to the analysis method by National Renewable Energy Laboratory, NREL/TP-510-42681).

Zeolite catalysts of HZSM-5 with Si/Al molar ratio of 25 and 38 (BET: 360.3 m<sup>2</sup>/g, 325.0 m<sup>2</sup>/g; pore volume: 0.27 mL/g, 0.22 mL/g; pore diameter: 0.56 nm, 0.56 nm; denoted as HZSM-5 (25) and HZSM-5 (38), respectively) and USY with Si/Al molar ratio of 5.6 (BET: 470.5 m<sup>2</sup>/g; pore volume: 0.31 mL/g; pore diameter: 0.64 nm) were supplied by Nankai University Catalyst Co. Ltd., China. All zeolites were in cylindrical shape ( $\varphi 5 \times (8-12)$  mm) and calcined in air at 550 °C for 6 h before use.

### 2.2. Catalyst characterization

NH<sub>3</sub>-temperature programmed desorption (NH<sub>3</sub>-TPD) measurement was performed by a TPD apparatus with TCD detector. Each sample (0.2 g) was pretreated at 500 °C for 1 h in He flow, cooled to 120 °C, and then saturated with ammonia flow for 30 min. After purging with He flow for 1 h to remove physisorbed ammonia, the desorption analysis was carried out at a heating rate of 10 °C/min from 100 °C to 600 °C. Thermal analysis curve of the used zeolite catalyst was obtained by STA449PC (Netzsch Instruments) from 40 °C to 900 °C at the heating rate of 20 °C/min.

### 2.3. Pyrolysis and ex situ catalytic upgrading of pyrolysis vapor

Experiments were carried out in an auger reactor and a downstream catalytic reactor, following the procedure described elsewhere [13]. Briefly, HRC was fed into the auger reactor at 20 kg/h as shown in Fig. 1. An auger screw pushed HRC through the hot zone of the reactor at the auger rate of 5 rpm, corresponding to HRC solid residence time of 8 min. A stainless-steel tube (ID: 150 mm; length: 3.0 m) was used to surround the auger screw and heated by a hot blast stove to provide pyrolysis heat by diesel combustion in a burner. The temperature gradient of ca. 100 °C was observed between the wall of the tube and HRC due to the low heat transfer efficiency. And the heating zone was about 2.40 m along the pyrolyzer's axis. Pyrolysis tests were conducted at HRC temperature of 500 °C for efficient HRC depolymerization and high bio-oil yield, according to our previous studies on pine wood pyrolysis and the other literatures [15,17]. The char was collected in a char pot at the end of the auger reactor and weighted. The stainless-steel fixed-bed reactor (ID: 78 mm; length: 1.3 m) was packed by zeolite catalysts of ca. 1.5 kg and heated by an electrical furnace at 450–650 °C. The pyrolysis vapor was sucked into the fixed-bed during ex situ catalysis by a Roots vacuum pump (1.1 kW, maximum capacity of 1.1 Nm<sup>3</sup>/min). A frequency converter of the vacuum pump was used to control sucking vapor flow rate, and thus adjust the residence time of pyrolysis vapor inside the catalytic reactor at 0.25–1.5 s. The liquid fraction, cooled by a condenser and a series of traps, was collected and weighted after upgrading. The coke was calculated by the difference of the catalyst weight before and after upgrading. The non-condensable gas was calculated by difference, which was introduced to the hot blast stove as fuel gas for the burner combustion along with diesel.

**Table 1**  
Proximate and ultimate analysis of HRC.

Proximate analysis (wt.%)				Elementary analysis (wt.%)				
Ash	Volatile matter	Fixed carbon	Moisture	C	H	O	N	S
2.56 ± 0.1	67.1 ± 3.1	28.7 ± 1.4	1.64 ± 0.1	47.6 ± 1.8	5.86 ± 0.1	46.1 ± 1.3	0.25 ± 0.1	0.19 ± 0.1

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