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Fast microwave-assisted catalytic co-pyrolysis of corn stover and scum for bio-oil production with CaO and HZSM-5 as the catalyst

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HIGHLIGHTS

- Fast microwave-assisted catalytic co-pyrolysis of corn stover and scum was studied.
- Mixed CaO and HZSM-5 catalyst was used to improve the quality of bio-oil.
- Scum can promote the production of bio-oil and aromatic hydrocarbons.
- There was an apparent synergistic effect while the H/C_{eff} ratio exceeds 1.

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ABSTRACT

This study investigated fast microwave-assisted catalytic co-pyrolysis of corn stover and scum for bio-oil production with CaO and HZSM-5 as the catalyst. Effects of reaction temperature, CaO/HZSM-5 ratio, and corn stover/scum ratio on co-pyrolysis product fractional yields and selectivity were investigated. Results showed that co-pyrolysis temperature was selected as 550 °C, which provides the maximum bio-oil and aromatic yields. Mixed CaO and HZSM-5 catalyst with the weight ratio of 1:4 increased the aromatic yield to 35.77 wt.% of feedstock, which was 17% higher than that with HZSM-5 alone. Scum as the hydrogen donor, had a significant synergistic effect with corn stover to promote the production of bio-oil and aromatic hydrocarbons when the H/C_{eff} value exceeded 1. The maximum yield of aromatic hydrocarbons (29.3 wt.%) were obtained when the optimal corn stover to scum ratio was 1:2.

1. Introduction

Fast pyrolysis is a promising technology, which converts the lignocellulosic biomass to liquid valuable fuels such as bio-oil. This technology has been extensively studied in the past decades. As an alternative to conventional fuels, bio-oil still has limited use as a fuel due to its high water content, high viscosity, high oxygen content, chemical instability and corrosiveness (Bridgwater, 2012; Dickerson and Soria, 2013; Mohan et al., 2006). Some of these issues were addressed by using high heating rate in pyrolysis process (fast pyrolysis). One of the fast pyrolysis processes is fast microwave-assisted pyrolysis (fMAP) in which the biomass can be instantaneously heated to the desired temperature. Fast microwave-assisted catalytic pyrolysis technology has already been successfully used in bio-oil production (Borges et al., 2014; Xie et al., 2014). Microwave assisted heating has many advantages over other heating methods, including uniform internal heating for materials particles, ease of operation and maintenance, energy saving and cleaner products because there is no vigorous agitation and carrier gas.

In addition to increasing heating rate to facilitate fast pyrolysis, an increasing number of methods have been investigated and developed for upgrading bio-oil to higher quality and stability. Catalytic fast pyrolysis technology is one of the most prevailing methods for in-situ bio-oil upgrading. Of the hundreds of catalysts that have been tested and analyzed, HZSM-5 zeolite was found to be the most effective due to its deoxygenating capacity and shape-selectivity for aromatics (Czernik and Bridgwater, 2004). However, HZSM-5 can cause formation of coke due to the polymerization of large oxygenates on the surface of the catalyst resulting in its deactivation (Carlson et al., 2010; Vitolo et al., 2001). On the other hand, CaO is a catalyst used for cracking heavy compounds into several light oxygenated compounds (Lu et al., 2010b; Veses et al., 2014),

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which can in turn be converted to aromatics on HZSM-5 catalyst. Thus, combining CaO and HZSM-5 is a potential way to improve the quality of bio-oil by reducing coke formation during pyrolysis.

Furthermore, to improve the quality of the bio-oil, co-pyrolysis of biomass and materials containing higher hydrogen contents can be considered. Zhang et al. (2015b) conducted catalytic pyrolysis of black-liquor by co-feeding with polystyrene in a fluidized bed reactor and obtained the maximum aromatic yield of 55.3%. In addition, previous studies by Martinez et al. (2014) and Cao et al. (2009) showed that co-pyrolysis of biomass and waste tires could increase the bio-oil yield and quality. In the present study, scum from municipal wastewater treatment plant was used as a hydrogen donor in the co-pyrolysis of corn stover and scum. Scum is the floatable solids skimmed off from the surface of the sedimentation process in wastewater treatment plants, and contains fats, oil, grease, and plastics (Spellman, 2014) which are high in hydrocarbons. Therefore, scum can serve as an excellent hydrogen donor in pyrolysis of lignocellulosics. Utilization of scum in co-pyrolysis is a potential solution to current scum disposal methods which are faced with many economic and environmental challenges (Anderson et al., 2015; Bi et al., 2015).

In this study, co-pyrolysis of corn stover and scum with CaO and HZSM-5 as the catalysts was investigated. The synergistic effect of scum and corn stover on bio-oil yield and selectivity was evaluated. The effects of temperature, CaO/HZSM-5 ratio, corn stover/scum ratio on the product fractional yields and chemical and physical properties were analyzed.

2. Methods

2.1. Materials

The feedstocks used were corn stover and scum. Corn stover (provided by Agricultural Utilization Research Institute, Waseca, Minnesota, USA) was air dried and mechanically pulverized and sieved to less than 2 mm. Scum was obtained from the Metropolitan Wastewater Treatment Plant, Saint Paul, Minnesota, USA. Prior to use, the solid scum samples were melted in water bath at 70 °C for 4 h and filtered through a 100-micron polyester mesh filter bag to remove large solid particles. The elemental compositions of corn stover and scum are listed in Table 1. The elemental analysis was performed with elemental an analyzer (CE-440, Exerter Analytical Inc., MA).

2.2. Catalyst

CaO was purchased from Sigma–Aldrich Corporation. Ammonium form ZSM-5 (Si/Al = 80, Surface Area = 425 m^2/g) was obtained from Zeolyst International (Conshohocken, PA, USA). Prior to use, the ZSM-5 was activated to its hydrogen form HZSM-5 in a muffle furnace at 500 °C in air for 5 h.

2.3. Experimental procedure

The schematic diagram of microwave-assisted catalytic co-pyrolysis system is shown in Fig. 1. Microwave oven (MAX, CEM Corporation) was used with a constant power input of 750 W at a frequency of 2450 MHz. The system has been described elsewhere (Xie et al., 2014). In this study, experiments were carried out in three sections. The aim of the first section was to determine the effect of reaction temperature on co-pyrolysis product fractional yields and selectivity. Co-pyrolysis was conducted at temperatures of 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. After the optimal temperature was determined, the effects of CaO to HZSM-5 ratio and corn stover to scum ratio on product fractional yields and selectivity were studied at the optimal temperature in Section 2 and 3, respectively. A blank pyrolysis test without using CaO/HZSM-5 was conducted. Prior to the pyrolysis, the system was vacuumed at 100 mmHg for 15 min to eliminate the influence of air. The vacuum was maintained during the entire experiment.

For a typical run, 500 g SiC particles (30 grit) were used as the microwave adsorbent. SiC was used due to its unique absorptive capacity of the microwave. Because of the thermal conduction from heated SiC particles, the desired temperature was reached instantaneously. The sample was prepared by physically mixing corn stover, scum and catalyst according to a certain ratio. The ratio of biomass (corn stover + scum) to catalyst (CaO + HZSM-5) was constant at 1:1, with the total weight of 30 g for each run. When the temperature reached the set point, the well-mixed sample was introduced onto the heated SiC in the microwave reactor. The microwave oven was turned on or off manually to maintain a stable temperature of the SiC bed. When the pyrolysis vapor traveled to the condensers, the condensable volatiles were converted to liquid form and collected as bio-oil fraction. The solid residue was cooled to room temperature and collected after each experiment as biochar fraction. The char and SiC can be separated easily using the sieve because of different particle sizes. The weight of char can be calculated by weight difference of quartz reactor with and without char. The bio-oil and biochar yields were calculated using their actual weight, while the gas fraction yield was calculated by difference based on the mass balance. For safety purpose, a microwave detector (MD-2000, Digital Readout) was used to monitor microwave leakage. The experiments were repeated twice.

2.4. Pyrolysis products characterization

Chemical composition of bio-oil was analyzed using Agilent 7890-5975C gas chromatography/mass spectrometer (GC/MS). The column used was a HP-5 MS at 30 m × 0.32 mm and 0.25 μm thickness. The oven temperature was programmed to be held at 50 °C for 2 min and then increased to 260 °C at a rate of 5 °C/min, and held at 260 °C for 5 min. The injector temperature was 290 °C, and the injector size was 1 μL with a split ratio of 1:10. Helium was used as the carrier gas at a flow rate of 1.2 mL/min. The compounds were identified by comparing their mass spectra with those from the National Institute of Standards and Technology (NIST) mass spectral data library. Calibration was not carried out due to the large number of compounds in the pyrolysis bio-oil. A semi-quantitative method was used to determine the relative proportion of each compound in the bio-oil by calculating the chromatographic area percentage. The volatile compounds that were detected by GC–MS were the main components of the bio-oil.

2.5. Evaluation method

In our work, the overall yields of different chemical groups were analyzed and discussed. The overall yield of relative content was defined and calculated as follows:

$$Y_E = Y_{\text{Bio-oil}} \times Y_{\text{chemical group}} \quad (1)$$

Table 1
Elemental compositions of corn stover and scum.

Compound	Elemental analysis (wt.% dry basis)				
	C	H	N	O[a]	Ash
Corn stover	44.91	6.00	1.58	44.07	3.45
Scum	65.77	11.50	1.05	17.77	3.91

[a] Calculated by difference, O(%) = 100–C–H–N–ash.