



Short Communication

Additives initiate selective production of chemicals from biomass pyrolysis



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HIGHLIGHTS

- A new method that involved the injection of additives into biomass pyrolysis was introduced.
- By this method, high selectivities of chemicals were obtained under low pyrolysis temperature.
- One high value-added chemical (2,3-dihydrobenzofuran) was obtained with high selectivity.

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ABSTRACT

To improve chemicals selectivity under low temperature, a new method that involves the injection of additives into biomass pyrolysis is introduced. This method allows biomass pyrolysis to achieve high selectivity to chemicals under low temperature (300 °C), while nothing was obtained in typical pyrolysis under 300 °C. However, by using the new method, the first liquid drop emerged at the interval between 140 °C and 240 °C. Adding methanol to mushroom scrap pyrolysis obtained high selectivity to acetic acid (98.33%), while adding ethyl acetate gained selectivity to methanol (65.77%) in bagasse pyrolysis and to acetone (72.51%) in corncob pyrolysis. Apart from basic chemicals, one high value-added chemical (2,3-dihydrobenzofuran) was also detected, which obtained the highest selectivity (10.33%) in corncob pyrolysis through the addition of ethyl acetate. Comparison of HZSM-5 and CaCO₃ catalysis showed that benzene emerged in the liquid because of the larger degree of cracking and hydrodeoxygenation over HZSM-5.

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1. Introduction

Over the past several decades, chemicals have been mainly produced via petroleum-based methods. However, with the depletion of petroleum, finding new synthesis routes from sustainable resources is necessary. In this regard, the conversion of biomass into chemicals, which might become a highly promising process in the future, has been a concern worldwide (Dutta et al., 2012; Qi et al., 2006). The main components of biomass, cellulose, hemi-cellulose, and lignin (Juan et al., 2011; David et al., 2013) form an extraordinarily complex structure that can be converted into various substances. The high oxygen content (Graça et al., 2013; Hu et al., 2012; Bu et al., 2012) creates a potential product that contains a series of furans, phenols, alcohols, and so on. Thus, efficiently improving the selectivities to specific chemicals has become an urgent challenge.

Pyrolysis has become a common method in biomass conversion. Compared with other methods such as degradation and fermentation, pyrolysis is popular because of its simple operation and convenience in serialization production. However, the bio-oil obtained through pyrolysis is difficult to use directly as fuel because of its poor quality. Thus, catalytic pyrolysis (David et al., 2012; Joseph et al., 2010) is proposed to upgrade bio-oil and zeolites, which are considered as the most common catalysts. HZSM-5 was used in green algae pyrolysis in which 25.8 wt.% yield of aromatic hydrocarbons was achieved compared with 0.9 wt.% without catalyst (Suchithra et al., 2012). Catalytic upgrading of pyrolysis vapors using zeolites is a potentially promising method of removing oxygen from organic compounds and converting them to hydrocarbons (Richard and Stefan, 2010). However, some valuable oxy-compounds are lost because of excessive cracking and deoxygenation. Thus, other types of catalyst, such as metallic oxides (Wang et al., 2010a,b) and carbonates (Rutkowski, 2011), are applied in the pyrolysis. Compared with zeolites, the selectivity of phenols and alcohols is higher over alkaline catalysts (Wang

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et al., 2010a,b) for biomass pyrolysis. However, the aforementioned pyrolysis processes require high temperature (>500 °C) and the selectivity to single chemical is at a low level (typically <10%).

In this study, a new method was introduced to selectively produce chemicals. Ethyl acetate (EA), methanol (Me) and acetone (AC) are purged in the pyrolysis process, which is catalyzed over HZSM-5 and CaCO₃. The additives can not only decrease the temperature of liquid product, but can also improve the selectivity to a single chemical. The abundant products are Me, AC, and acetic acid (AA), which are basic chemical raw materials. A valuable chemical—2,3-dihydrobenzofuran (DHB), which has not been reported in biomass pyrolysis, is obtained as the secondary major product via this new method.

2. Methods

2.1. Materials

Three biomass feedstocks were selected for pyrolysis, namely, mushroom scrap, bagasse, and corncob. Mushroom scrap cannot be reused because it is the foster residue of mushroom growth. Bagasse and corncob, abundant in many countries, are the residues of squeezed sugarcane and harvested corn, respectively. These feedstocks were easily acquired because they are widely distributed in many provinces in China at low prices.

2.2. Catalytic activity measurements and characterization

The pyrolysis experiments over different catalysts were evaluated in a tubular quartz packed-bed reactor heated by electricity. In each run, a well-mixed mixture of catalyst and feed powder (1:5 mass ratio) (Leng et al., 2013) was placed at the center of the reactor quartz tube (diameter = 25 mm, length = 400 mm), above the layer of quartz wool. Before the reaction, an N₂ flow (40 mL/min, 99.999%, Shanghai) was bubbled into the reactor to eliminate the air. The reactor was heated up to 300 °C at a rate of 50 °C/min, maintained for 0.5 min, and then cooled down at room temperature. The additives (liquid) were continuously injected by a peristaltic pump (Baoding Lead Fluid Tech. Co. Ltd.) at a rate of 0.3 mL/min when the temperature rose to 100 °C (to ensure additives vaporized). The reaction products were collected in a conical flask in an ice–water bath and analyzed via GC out-line (Zhejiang Fuli Analytical Instrument Co. Ltd., 9790) using an AT SE-5 capillary column and an FID detector. Principal component analysis of the liquid products was conducted using GC–MS (ThermoFisher DSQ). The selectivity of chemical was the percentage in liquid, which was calculated from data based on area percentage from GC. The tail gas was excluded from the air.

The results of the GC–MS were analyzed on a ThermoFisher DSQ. The gas chromatography conditions are as follows: HP-5 MS elastic quartz capillary column (30 m × 0.25 mm × 0.25 μm); carrier gas: highly pure He, 1 mL/min; and column temperature: 50–300 °C, 10 °C/min. The mass spectrum conditions are as follows: ET source, 70 eV; filament current: 100 μA; voltage multiplier: 1200 V; and full scan.

3. Results and discussion

First, a series of catalysts, such as HZSM-5, CaCO₃, Na₂CO₃, NaOH, CaO, ZnO, and ZnO–V₂O₅, were screened in the pyrolysis. Those experiments were carried out under a high temperature (500 °C) without additives. The results showed that HZSM-5 had a higher yield to basic chemicals (32.6%) and CaCO₃ was more prone to DHB (12.3%). There was no liquid products under 300 °C

were generated. Second, the influence of eight additives, namely, EA, AC, Me, isopropanol, benzene, chloroform, tetrahydrofuran, and diethyl ether to the yield of chemicals, were investigated. Accordingly, EA, AC, and Me performed better. Then, the experiments of adding three additives into the pyrolysis of three feedstocks over two catalysts were conducted under 300 °C.

3.1. Influence of additives in producing different chemicals in biomass pyrolysis

Fig. 1 shows that Me, EA, and AC were added into mushroom scrap, bagasse, and corncob pyrolysis, which were all catalyzed over CaCO₃ under 300 °C. With these additives, it is found that the selectivity of these chemicals under 300 °C is much higher than that under 500 °C without these additives (Table S1). In the pyrolysis of mushroom scrap, different additives induced the production of different chemicals, which were as follows: Me induced AA (98.33%, selectivity), EA induced AC (75.90%, selectivity), and AC induced Me (94.21%, selectivity). The selectivity to a single chemical via this method was significantly higher than in general catalytic pyrolysis (Zhang et al., 2013). To identify the universality of this new method, bagasse and corncob were also applied, in which most of the results showed high selectivity to chemicals. Although the total selectivity of Me, AC, and AA was lower in bagasse pyrolysis by Me addition and in corncob pyrolysis by EA addition, it was still high enough because the others were scores of chemicals which single chemical had extremely low content (<0.1%). The production of chemicals can be efficiently controlled by injecting different additives into biomass pyrolysis. For example, the principal product was Me in mushroom scrap pyrolysis by AC addition, and it was AC in bagasse and corncob pyrolysis.

Generating some valuable chemicals through this method is significant. DHB (Huang et al., 2013), which was widely used as a drug intermediate, surprisingly emerged in the liquid at such low temperature. DHB selectivity was higher in corncob pyrolysis than in bagasse, no matter what additive was injected, probably because corncob had harder cracking difficulty that impeded DHB degradation (Fig. S1). The addition of EA in corncob pyrolysis showed the best performance of DHB selectivity (10.33%). No DHB was produced in mushroom scrap pyrolysis. Thus, the previous conclusion in which chemicals can be controlled was deduced because of the different biomass structures.

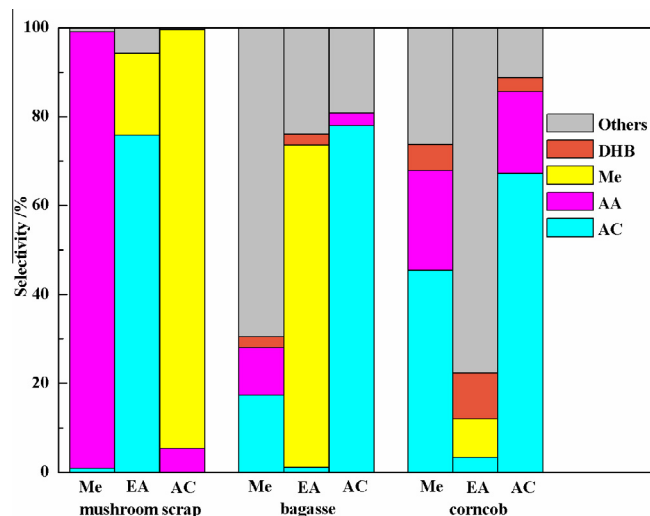


Fig. 1. Selectivities of different additives over CaCO₃ in different biomass pyrolysis.

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