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Two-stage ex-situ catalytic pyrolysis of lignocellulose for the production of gasoline-range chemicals

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ABSTRACT

The appropriate system is needed to produce a scalable and economically viable renewable energy from biomass. The objective of this study is to improve the quality of bio-oil, in terms of Organic Liquid Product (OLP), water content, acidity, favourable fractions, as well as gasoline-range chemicals. The influence of a staged layered catalyst system consists of a mesoporous catalyst, Al-MCM-41, and a microporous catalyst, HZSM-5, on the bio-oil quality was investigated. Additionally, the effect of reaction temperatures in the range of 400–600 °C with the optimum staged catalyst system on the catalytic pyrolysis product was analysed. The experiments of lignocellulosic biomass pyrolysis and catalytic pyrolysis were performed using a fixed bed reactor equipped with oil condensers and a gas collection sample bag. The quality of bio-oil produced from the thermal pyrolysis of lignocellulosic biomass, catalytic pyrolysis with single catalysts, catalytic pyrolysis with the staged catalyst system, as well as catalytic pyrolysis with mixed catalyst system was studied. The results show that Al-MCM-41 with HZSM-5 in the staged catalyst system enhanced the production of favourable compounds: hydrocarbons, phenols, furans, and alcohols. The favourable compounds yield that boosted 5.25–6.43% of that with single HZSM-5 catalyst was produced with HZSM-5:Al-MCM-41 mass ratio of 3:1 and 7:1. The pyrolysis and catalysis temperature of 500 °C with HZSM-5:Al-MCM-41 ratio of 3:1 obtained the optimum quality of bio-oil with 11.08 wt.% of OLP, 76.20% of favourable fractions, 41.97 wt.% of water content, low TAN of 43.01 mg-KOH/g, high deoxygenation, as well as high gasoline-range production of 97.89%.

1. Introduction

The world energy consumption is projected to grow by 56% between 2010 and 2040 [1]. Despite the various energy carriers, the liquid hydrocarbon still appears to be the primary form of transportation fuel [2]. Thus, the production of liquid fuels from renewable resources is widely recognized as a potential future solution to the increase in energy demands worldwide [3].

Biomass is considered as one of the available sources of carbon-based materials, chemicals, and fuels since it is abundant and represents the cheapest carbon source [4]. However, due to its complex composition [5], the direct use of biomass (e.g. lignocellulose material) as a chemical feedstock faces problems [6]. Therefore, appropriate technologies have been widely investigated to produce a scalable and economically viable renewable energy.

The liquid fuel can be obtained from biomass through thermo-chemical methods, such as pyrolysis [7] where biomass is decomposed at high temperatures in the absence of oxygen. Besides the liquid phase, known as pyrolysis oil or bio-oil, the pyrolysis results in a solid phase called char and non-condensable gases [8]. The emerging variant of this process, namely the fast pyrolysis process, is characterized by the use of a controlled temperature of around 500 °C, a high heating rate, and a short vapour residence time [9]. The main drawback of a biomass pyrolysis is the high content of water and organic compounds with undesirable properties which lead to low heating values, corrosiveness, and instabilities, often called aging, of the resulting oil [10].

Upgrading the bio-oil can be achieved by introducing catalysts in the pyrolysis process, which can either be done in-situ or ex-situ. Catalytic fast pyrolysis of biomass has been carried out by many researchers since the production of hydrocarbon fuels from biomass is potentially economically attractive [11]. Recent reviews summarize the works [4,12–14].

Among the zeolite catalyst, the most prominent catalyst to produce aromatic hydrocarbons and lighter fractions with a high activity in deoxygenation is an HZSM-5 catalyst. Jae et al. [15] reported that medium pores zeolite, ZSM-5, with pore sizes in the range of 5.2–5.9 Å, led to the highest aromatic yield and the least amount of coke for the conversion of glucose to aromatics in a pyro-probe reactor. However,

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due to the large molecular size of lignin-derived oxygenates which is considerably larger than the ZSM-5 pore size, the oxygenates cannot enter the pores of ZSM-5 and form coke on its surface. According to an investigation by Yu et al. [16], the large-molecule oxygenates can enter the pores of zeolites when the zeolite was thermally distorted at 650 °C, which enlarged the pore size of zeolite by 2.5–3.4 Å.

The mesoporous catalyst, Al-MCM-41, which has larger pore size than ZSM-5, in the range of 30–40 Å [6,17–20], has the ability to crack large molecules, to be less prone to deactivation, and to give higher yields of OLP which contains aliphatic hydrocarbons. In addition, the Al-MCM-41 appears to eliminate completely levoglucosan [2,6,21–23].

Each mentioned catalysts, HZSM-5 and Al-MCM-41, have high potential in converting biomass into desirable chemicals with high selectivity and yield as well as low coke formation. It is possible to improve or alter the OLP composition through a cascade system of the mesoporous and microporous catalyst. There have been several studies in the literature reporting the bio-oil upgrading through a cascade system of catalysts.

Marker et al. [24] recovered 30 wt.% of gasoline and 8 wt.% of diesel from catalytic hydrocracking of lignin with combined zeolite and amorphous silica-alumina catalyst at a temperature between 340 and 435 °C under a pressure about 3.4 MPa to about 12 MPa. In the Fluid Catalytic Cracking (FCC) process, zeolite Y and silica-alumina (SiO_2-Al_2O_3) are utilized to produce a high gasoline yield.

In 1996, Adjaye et al. [25] investigated the upgrading of biofuels from a rapid thermal processing of maple wood when using silica-alumina and HZSM-5 catalysts in a fixed-bed micro-reactor at a temperature of 370 °C. Their results showed that it is possible to change the hydrocarbon distribution in the Oil Liquid Product (OLP) fraction by physically mixing catalysts with different functionalities. Silica-alumina produced an OLP fraction which mostly of aliphatic hydrocarbons. By gradually increasing the amount of HZSM-5 in the catalyst mixture, the content of OLP gradually changed from predominantly aliphatic to a mixture of aliphatic and aromatic hydrocarbons. When the HZSM-5 content was increased, in the range between 13 and 27 wt.% of the biofuel feed, the yield of OLP was also rose. The main product was aliphatic hydrocarbons (37–77 wt.% of OLP), followed by aromatic hydrocarbons (2–38 wt.% of OLP).

A study by Zhang et al. [26] examined the effect of adding mesoporous and macroporous catalyst (Gamma-Al2O3, CaO, and MCM-41) in the microporous catalyst (LOSA-1) by physically mixing the catalysts for the catalytic pyrolysis of rice stalk in an internally interconnected fluidized bed. Compared to using a single LOSA-1 catalyst, the maximum aromatic and olefin yield of 25.3% was obtained with 10% Gamma-Al_2O_3/90% LOSA-1 [26].

Zhang et al. [27] also point towards improving the aromatics yield by adding meso- and macroporous catalysts (CaO, MgO, and FCC) in a microporous catalyst (ZSM-5). They performed and analysed a catalytic pyrolysis of pine wood with two catalysts using Thermogravimetry-Fourier Transform Infrared Spectroscopy (TG-FTIR) and Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS). The maximum aromatic yield which was 30 wt.% higher than that with pure ZSM-5 was obtained with a biomass/CaO/ZSM-5 mass ratio of 1:4:4 in a separate mode of feedstock, CaO, and ZSM-5 inside a quartz filler tube.

The present study considers using a staged mesoporous and microporous catalyst to enhance the bio-oil quality, as seen in Fig. 1. By employing mesoporous catalyst, Al-MCM-41, and microporous catalyst, HZSM-5, in staged layers, and considering a continuous flow of carrier gas, the pyrolysis vapour is constrained to pass through a layer of catalyst one after another. This system will ensure the large molecule oxygenates will be cracked into small molecule oxygenates through Al-MCM-41 before entering HZSM-5 pores. In case of using physically mixing catalyst, there may be no certain path whether the pyrolysis vapour firstly passes through Al-MCM-41 or directly enters the pores of HZSM-5. A bench-scale experiment using a fixed bed reactor has been carried out to investigate the effect of a staged layered catalyst system on the bio-oil quality in a large scale compared to using Py-GC/MS.

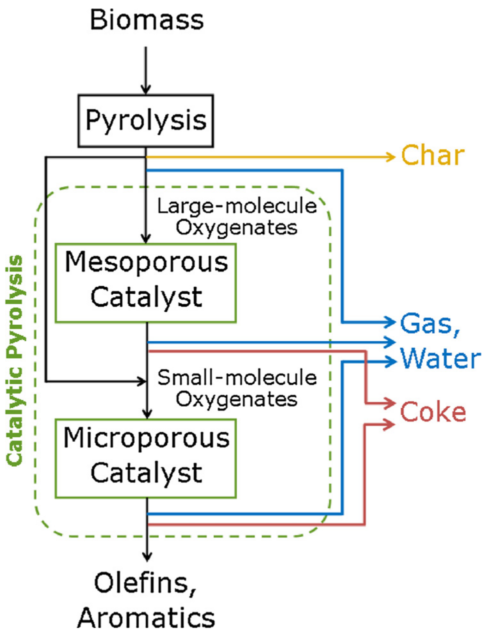

Fig. 1. Catalytic pyrolysis of biomass with mesoporous and microporous catalyst.
(adapted from Zhang et al. [21]).

Recent work by Author et al. [28] obtained positive results on upgrading waste plastics to produce gasoline-range hydrocarbons by using Al-MCM-41 and ZSM-5 zeolite catalysts in a staged layered catalyst system. The results showed that using the staged catalysis a high yield of oil product (83.15 wt.%) was obtained from high-density polyethylene at an Al-MCM-41:ZSM-5 ratio of 1:1. The oil product was highly aromatic (95.85 wt.% of oil) consisting of 97.72 wt.% of gasoline range hydrocarbons. Later in this study, the results revealed that the bio-oil was also in the range of gasoline chemicals.

Accordingly, the objective of this work is to improve the quality of bio-oil, in terms of OLP, water content, acidity, favourable fractions, as well as gasoline-range chemicals, in lignocellulosic biomass catalytic pyrolysis by using staged-catalysts of HZSM-5 and Al-MCM-41. Nevertheless, enhancing the yield of bio-oil was examined. The effect of the physically mixing of the Al-MCM-41 with HZSM-5 zeolite catalyst on the products was also evaluated. Furthermore, the influence of the temperature on the composition of the oils and gases during the staged catalyst pyrolysis of biomass was observed.

2. Materials and methods

2.1. Materials

Lignocellulosic biomass from beech wood was provided by J. Rettenmaier & Söhne GMBH + CO KG, Rosenberg. For the catalytic pyrolysis experiments, the sample had a particle size ranging from 300 μm to 500 μm. Before an experiment, the sample was dried in an oven at 110 °C overnight to reduce the water content [29]. The proximate and ultimate analysis is shown in Table 1.

Catalysts in the powder form of Al-MCM-41 and HZSM-5 were obtained from Nankai University Catalyst Plant in China and Alfa Aesar in Germany, respectively. Prior to catalytic pyrolysis experiments, the catalysts were calcined in a muffle furnace at 550 °C for 15 h and dried in an oven at 110 °C for 12 h.

Table 2 shows the properties of the catalysts.