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ScienceDirect

Energy Procedia 105 (2017) 557 – 561

Energy Procedia

The 8th International Conference on Applied Energy – ICAE2016

Catalytic consequences of micropore topology on biomass pyrolysis vapors over shape selective zeolites

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Abstract

Research on utilization of abundant rice residue for valuable bioenergy products is still not explored completely. A simple, robust, cheap and one step fast pyrolysis reactor is still a key demand for production of bioenergy products, i.e. high quality bio-oil and bio char. Bio-oil produced from fast pyrolysis has poor quality (e.g. acidic and highly oxygenated). Catalytic fast pyrolysis using zeolites in the fast pyrolysis process effectively reduce the oxygen content (no H_2 required). In this paper, zeolites having a variety of pore size and shape (small pore: SAPO-34 (0.56), Ferriertite (20), medium pore: ZSM-5 (23), MCM-22 (20), ITQ-2 (20) and large pore zeolite Mordenite (20) were tested in a drop type fixed-bed pyrolyzer. The catalytic deoxygenation is conducted at 450 °C at the catalyst/biomass ratio of 0.1. Zeolite catalysts, its pore size and shape could influence largely on deoxygenation. Small pore zeolites did not produce aromatics while medium pore zeolites formed higher amount of aromatics. ZSM-5 and ITQ-2 zeolites were especially efficient for the higher deoxygenation of biomass pyrolysis vapors due to better pore dimension and higher acidity.

Keywords: Biomass; Zeolites; Characterization; Pyrolysis oil; Fixed bed pyrolyzer; Deoxygenation

1. Introduction

Increasing environmental risks and reduction of fossil fuels are the main concerns for renewable energy resources. Biomass is a major renewable energy product that can be used as alternative to various recent energy production sources[2][3]. Lignocelluloses biomass is a second generation biomass that can replace crude oil in factories for production of transportation fuel. Rice husk is a highly produced agricultural biomass in areas like India, Malaysia, China, and Brunei that are rich in rice production[4][5].Rice production in Malaysia is about 0.7% of the total biomass production of which paddy residue production has increased up to 7 million tons per year by 2020 so it can be used for as a source of bio-oil[6][7]. Textile processing is an energy intensive process having 5 – 8 kg of steam consumption per kg of output. Cost of producing the same one ton of steam with rice husk is 72% cheaper when compared with furnace oil and 35% cheaper than natural gas. There are two ways for conversion of biomass to biofuel (i) Thermo-chemical conversion process (ii) bio-chemical conversion. Thermo-chemical process involves pyrolysis, gasification, liquefaction, carbonization, combustion and co-firing. Pyrolysis is a starting point of all reactions as it involves the formation of products with zero oxygen concentration[8][9][10].The products of pyrolysis are solid(bio-char), liquid(bio- oil) and gas. The bio-oil cannot be used directly because it is highly unstable and has complex composition.

doi:10.1016/j.egypro.2017.03.356

Gaseous product has low yield and has complex process conditions of purification and separation for large scale applications. High water and oxygen contents (15-30)wt% and (35-60)wt% respectively[13][14]. The reason for high oxygen content as previously described is the due to the presence of oxygenated groups that forms the low heating value fuels. The use of gaseous products of biomass and their upgardation using zeolite is a better and low cost alternative to reduce the effect of these oxygenated compounds[15][16].

Zeolites are microporous alumino silicate structured materials. The particular structure of zeolite depends on synthesis condition synthesis gel composition, temperature, pH and also use of surface directing agents[17]. As a result of specific pore size diameter particularly in the range of 100-800m^2/g, zeolites can adsorb large molecules on the surface and molecules can penetrate through this microporous structure. This special structure of zeolites provide them with two special characteristics shape selectivity and acidity that are useful for required application[18].

This paper aims to study the catalytic fast pyrolysis process of rice husk using zeolites. The research on utilization of bioenergy from rice residue has not been completely exploited. Moreover catalytic fast pyrolysis process using rice residues via suitable reactor is still a key challenge for researchers for production of bio-oil and bio-char. In this work, synthesized and commercial zeolites based on their pore topology were tested and evaluated their performance in biomass pyrolysis process for the production of bio-oil and bio-char.

2. Materials & Methods

2.1. Feedstock & Zeolites

Rice husk was obtained locally. The sample was grinded sieved upto (100>p>355 µm) and dried in electrical oven for 24 h at 105 °C to reduce the moisture content. Low pore zeolites (SAPO-34 & Ferrierite), medium pore zeolites (ZSM-5, MCM-22 & ITQ-2) and large pore zeolites (Mordenite) were used to catalytic fast pyrolysis process of rice husk. Ferrierite, ZSM-5 and Mordenite of Si/Al ratio 30 were the commercial zeolites and purchased from Zeolyst. The SAPO-34 zeolite was synthesized by following the method described in the literature [17]. The layered zeolite structure, MCM-22 and the delaminated aluminosilicate, ITQ-2, at Si/Al ratio of 30 were synthesized from layered zeolite precursor, MCM-22 (P), using the similar method described in the literature [16].

2.2. Catalytic fast pyrolysis

The schematic diagram of the pyrolyzer is shown in Figure 1. The amount of rice husk was 10 g for all experimental runs. Fast pyrolysis experiments were conducted in the in-bed mixing mode. In the in-bed mixing mode, biomass and catalyst are premixed and subjected to the pyrolyzer. After the desired pyrolysis temperature, the biomass (non-catalytic) or biomass/catalyst mixture (catalytic) was dropped into the fast pyrolysis zone and held at that temperature for 10 min until no significant release of gas was observed. In order to exploit the impact of catalyst, the biomass-catalyst mixed sample was pyrolyzed at 450 °C with catalyst/biomass ratio of 0.1. The Pyrolysis oil's yield was considered equal to the gain in the mass of the ice-trap divided by the mas of biomass used. The change in weight of the pyrolyzer before and after the experiment divide by the mass of biomass is equal to the yield of the solid. The yield of the non-condensable gases was calculated by applying overall material balance. All the experiments were performed three times. The gas compositions from fast pyrolysis and catalytic fast pyrolysis were analysed in a SHIMADZU GC-8A gas chromatograph with a TCD detector.

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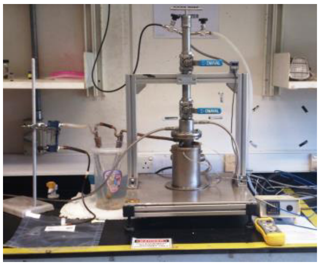

Fig. 1. Drop type fixed-bed pyrolyzer.