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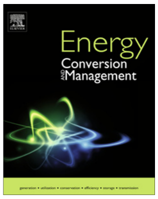

In-situ catalytic upgrading of biomass pyrolysis vapor: Using a cascade system of various catalysts in a multi-zone fixed bed reactor

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ABSTRACT

The in-situ catalytic upgrading of palm kernel shell (PKS) fast pyrolysis vapors was performed over each individual meso-H-ZSM-5, Ga/meso-HZSM-5 and Cu/SiO_2 catalyst or a cascade system of them in a multi-zone fixed bed reactor. The effects of mesoporosity creation into the parent H-ZSM-5 catalyst and also gallium incorporation into mesoporous H-ZSM-5 on the produced bio-oil chemical composition and distribution were studied. Key upgrading reactions for different oxygenated compounds in pyrolysis oil (small oxygenates, lignin derived and sugar derived components), including aldol condensation, alkylation, hydrogenation, aromatization, and deoxygenation were discussed. The catalysts were characterized using SEM, XRF, XRD, N_2 adsorption and NH_3-TPD methods. Furthermore, the produced bio-oils (catalytic and non-catalytic) were analyzed using GC–MS, FTIR, CHNS/O elemental analyzer and Karl Fischer titration. Production of the upgraded bio-oil with lower content of oxygenated compound was the main objective of this investigation. Among different catalysts, meso-H-ZSM-5 zeolite demonstrated a very good activity in aromatization and deoxygenation during the upgrading of pyrolytic vapors, although it decreased the bio-oil yield (32.6 wt.%). The gallium incorporation into the meso-HZSM-5 zeolite increased the bio-oil yield from 32.6 wt.% (meso-HZSM-5) to 35.8 wt.% (using 1.0 wt.% Ga). Furthermore, the aromatics selectivity was enhanced when the appropriate amount of gallium (1.0 wt.%) was introduced. A cascade system of various catalysts comprising meso-HZSM-5, Ga (1.0 wt.%)/meso-HZSM-5 and Cu (5.0 wt.%)/SiO_2 indicated the best performance on aromatics formation (15.05 wt.%) and bio-oil deoxygenation through small oxygenates, lignin derived phenolics and sugar derived compound conversion, respectively.

1. Introduction

Biomass utilization in the energy sector has recently attracted considerable interest across the world. In contrast to the other renewable sources, which their output is preliminary electricity, biomass has the potential to produce various solid, liquid or gaseous energy contents [1]. Biomass thermal conversion can play an important role to yield materials that can partially replace fossil fuels. Fast pyrolysis is one of the known pathways for the biomass conversion into the bio-oil [2]. It is characterized by moderate temperatures (450–600 °C), high heating rates and the pyrolysis products rapid quenching [3]. The formed vapors during biomass pyrolysis condense into liquid product, which is called bio-oil.

Bio-oil produced from the degradation of cellulose, hemicellulose and lignin, three most important biomass building block, is a complex mixture of different oxygenated compounds with broad molecular weight range from 18 to 5000 g/mol [4]. Theses oxygenated compounds with inherent characteristics including high viscosity, high corrosivity, chemical instability and incompatibility with conventional fuels render bio-oil useless as a fuel [2,4]. Various oxygenated compounds in the pyrolysis liquid can be divided into three main families of components [5]: (a) small aldehydes, ketones and acids (like acetol, acetone, acetic acid and etc.); (b) sugar derived compounds such as furfural and levoglucosan; and (c) lignin derived phenolics. The main challenge is not only elimination of oxygen from these components, but also preservation of carbon in the product, with least hydrogen consumption.

Among the various biomass conversion processes, fast pyrolysis coupled with catalytic pyrolysis vapor upgrading before its condensation has been one of the technologically and economically promising thermochemical processes for advanced biofuel production [1]. This process, which has been studied extensively in recent years [2,4,6], has the advantage of inhibiting some of the gum formation and polymerization reactions that generally occur in bio-oil and therefore, greatly reduce its instability [1].

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During biomass pyrolysis and catalytic upgrading, the pyrolysis vapors need to pass through certain stabilizing catalytic processes. In this situation, pyrolysis vapor components undergo several reactions comprising condensation, cracking, dehydration, aromatization, decarboxylation and decarbonylation. Through these reactions, oxygen can be eliminated in the form of $CO_{2,}$ CO and water. The catalysts could be chosen according to the process necessities. As an initial step, to achieve this objective, fundamental knowledge on reaction pathway is necessary. This can be attained through model compound studies. The model compound approach investigations could be employed to produce gasoline range molecules through conversion of small oxygenates (with minimum carbon loss), conversion of lignin-derived phenolics and conversion of sugar-derived compounds using appropriate catalysts.

Catalytic upgrading of the small oxygenated molecules of the biomass pyrolysis vapors can employ appropriate catalysts that either deoxygenate the oxygenated components or utilize the relatively high reactivity of oxygen functionalities (carbonyl, hydroxyl, ketonic and carboxylic groups) to facilitate C—C bond formation reactions, such as aldol condensation of ketones and aldehydes or ketonization of carboxylic acids [7–9]. It means, instead of the oxygen functionalities removal too early, a cascade system of catalysts may facilitate the conditions to take the advantages of their reactivity before trying the deoxygenation. Model compounds investigations showed that zeolites (HZSM-5) and metal oxide catalysts (such as $CeZrO_2$) were effective in catalyzing C—C bond formation reactions, but zeolites indicated a higher selectivity to aromatics [9–11]. For instance, HZSM-5 could selectively convert propanal to C_7—C_9 aromatics through a reaction path that involved successive aldol condensation, followed by cyclization [5,10].

In a subsequent stage, selective cleavage of aromatics carbon–oxygen bonds in lignin structure is a crucial goal to unlocking the potential of lignocellulosic biomass to be used for biofuels production. Lignin is very difficult to upgrade due to its complex structure and recalcitrant nature. Moreover, lignin comprises many phenolic moieties, which can deactivate zeolite catalysts [12]. Guaiacol and anisol were selected as model compound of lignin-derived phenolics for the investigations [13–16].

Hydrodeoxygenation of phenol and methyl-substituted phenols in lignin components is a more demanding reaction for bio-oil upgrading. Researchers have disputed if hydrodeoxygenation of phenolic constituents must proceed through phenyl ring hydrogenation followed by water elimination or it can also proceed via direct C—O bond hydrogenolysis without breaking aromatic structure. The latter, seems unfavorable energetically attributed to the C—O bond stabilization. By contrast, some researchers have supported the role of this route based on the observed low concentration of partially saturated or saturated rings in the product. Thus, bifunctional zeolite supported metal catalysts (like Ga/HZSM-5) are basically effective since hydrogenation and dehydrogenation take place on the metal function (Ga), while dehydration can happen on the acid sites [14,17,18]. In contrast to low temperature bio-oil upgrading, that produces saturated rings with high hydrogen consumption, at high temperature, dehydrogenation of the ring is favored and it will conduct to aromatics formation [19].

Among various oxygenated compounds mostly found in bio-oil, furfural could be chosen as a model for sugar derived compounds. Due to the high reactivity of these compounds, they are needed to be catalytically deoxygenated to improve bio-oil storage stability, water solubility, and boiling point range [20]. Furfural potentially is produced both during the cellulose pyrolysis and dehydration of sugars.

Group Ib metals like Cu could catalyze furfural conversion to furfuryl alcohol, but decarbonylation was only performed at high temperature with high metal loading [21]. The furfural hydrodeoxygenation over three different metal catalysts, Ni, Cu and Pd supported on SiO_2 was investigated by Sitthisa et al. [20]. The reactions over silica supported Ni, Cu and Pd catalysts indicated different products distribution in terms of molecular interactions with the metal surface. Furfuryl alcohol was produced over Cu catalyst through hydrogenation of carbonyl group. This was due to preferred adsorption on Cu, $\eta^1(O)$ – aldehyde.

As the outcome of the authors' survey [4] on model compounds to select catalysts and process for in-situ biomass pyrolysis vapor upgrading, Fig. 1 at a glance shows simply the various catalysts' classes suggested for conversion of small oxygenates, lignin derived phenolics and sugar-derived components through condensation, deoxygenation and alkylation reactions. As shown in Fig. 1, zeolite catalysts are prone to accomplish varieties of upgrading reactions including condensation, deoxygenation and alkylation. Deoxygenation can be done by different types of catalysts, comprising zeolites, zeolite supported metals and oxide supported metals. According to our investigations, HZSM-5 selected for aldol condensation of small oxygenates to use the high reactivity of oxygen functionality to yield larger molecules before their oxygen elimination. Further, Ga/HZSM-5 and Cu/SiO_2 were selected for lignin phenolics and sugar-derived components upgrading, respectively. The selected catalysts are active, selective and productive to yield fuel-like components. Based on this aforementioned survey, in-situ atmospheric pyrolysis vapor upgrading with minimum carbon loss and hydrogen consumption can be performed efficiently using a cascade system of selected catalysts in an integrated pyrolysis/upgrading process.

In this study, for the first time, based on the results of the model compound approach researches [4], catalysts and process for palm kernel shell (PKS) fast pyrolysis vapor upgrading were selected to produce bio-oil with lower content of the oxygenated compounds. The model compound approach was employed to select the reaction conditions and catalysts that are active and selective for several classes of pyrolysis vapor upgrading reactions. A multi-zone fixed bed reactor was designed and fabricated to carry out biomass pyrolysis and its vapors upgrading using three distinct beds of catalysts in series (meso-HZSM-5, Ga/meso-HZSM-5 and Cu/SiO_2). The biomass pyrolysis vapors after passing through three fixed bed catalysts (biomass catalytic pyrolysis vapors upgrading) were quenched by two condensers and formed upgraded liquid bio-oil.

Condensation, ketonization and etherization reactions to build longer (fuel molecule) carbon chains from small oxygenates (aldehydes, ketones, acids) were performed by using meso-HZSM-5 zeolite catalyst in the first zone of the reactor. Zeolite supported metal (Ga/meso-HZSM-5) and supported metal catalysts (Cu/SiO_2) were employed for deoxygenation of lignin derived phenolics and sugar-derived compounds in bio-oil in the second and third reactors' zones, respectively. Transalkylation and alkylation by zeolite and zeolite supported metals improved carbon retention. Based on this investigation the selected catalysts were very effective for PKS pyrolysis vapor upgrading in a cascade process.

2. Materials and methods

2.1. Biomass materials

The palm kernel shell (PKS) (Table 1), as one of the palm oil biomasses, was supplied by Szetech Engineering Sdn. Bhd. located in Selangor, Malaysia. The sample was crushed using high-speed rotary cutting mill and sieved to desired particle size (<300 μm). Then, the sample was dried at 105 °C for 24 h and kept in tightly screw cap plastic bottles. The approximate molecular formula of the biomass was $C_{4.1}H_{5.5}O_{2.7}$.