

In-situ catalytic upgrading of biomass pyrolysis vapor: Co-feeding with methanol in a multi-zone fixed bed reactor



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ABSTRACT

The in-situ catalytic upgrading of the biomass pyrolysis vapor and its mixture with methanol were conducted in a fixed bed multi-zone reactor. The steps were comprised; thermally converting the biomass in the pyrolysis reactor, passing its vapor in contact with the HZSM-5 zeolite catalyst in the presence of methanol vapor, and transformation of the resulting upgraded pyrolysis vapor into the liquid product. The biomass pyrolysis and catalytic pyrolysis vapor upgrading were performed at 500 °C. The highly valuable chemicals production was a function of the hydrogen to carbon effective ratio (H/C_{eff}) of the feed. This ratio was regulated by changing the relative amount of biomass and methanol. More aromatic hydrocarbons (50.02 wt.%) and less coke deposition on the catalyst (1.3 wt.%) were yielded from the biomass, when methanol was co-fed to the catalytic pyrolysis process ($H/C_{\text{eff}} = 1.35$). In this contribution, the deposited coke on the catalyst was profoundly investigated. The coke, with high contents of oxo-aromatics and aromatic compounds, was generated by polymerization of biomass lignin derived components activated by catalyst acid sites.

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1. Introduction

Environmental concerns caused by using fossil fuels, increasing of global energy demand, oil price rising and shortage of petroleum resources motivated the development of alternative energy sources for the production of renewable liquid fuels [1,2]. Lignocellulosic biomass has been considered as a promising alternative energy source, as it is renewable, CO₂ neutral, and has the potential to participate in secure energy supply. Thermal conversion of the biomass can play an important role to produce materials that can replace fossil fuels [3]. Pyrolysis is one of the most important pathways for the biomass conversion into the bio-oil (chemicals and fuels). The bio-oil, a dark brown liquid, is generally acidic and has high oxygen and water content [4].

The presence of the oxygenated compounds caused most of the deficiencies of the bio-oil, such as its high corrosiveness, immiscibility with petroleum fuels, low heating value, and instability under prolonged transportation and storage conditions [1,4]. Over the last twenty years, there have been dozens of investigations focused on the biomass and its derived feedstock catalytic conversion with acidic zeolite catalysts, such as Mordenite, Y, Beta and

HZSM-5. They were studied as candidate catalysts for the biomass pyrolysis. Among them, HZSM-5 was the most important zeolite investigated and was found to considerably change the composition of the bio-oils by both increasing the aromatic species and producing gasoline like components and simultaneously reducing the amounts of oxygenated compounds through deoxygenation reactions [5,6]. Formation of large amount of coke and consequently rapid zeolite catalyst deactivation is the main problem for the biomass thermal conversion with zeolites.

A parameter named the hydrogen to carbon effective ratio (H/C_{eff}) has been defined by Chen et al. [7]. This parameter, which is shown in Eq. (1), can be utilized to compare the relative amount of hydrogen available in various feeds and to describe if a feed can be economically converted into hydrocarbons using zeolite catalysts according to the amount of hydrogen, carbon and oxygen in the feed. In Eq. (1), H, O and C are the moles of hydrogen, oxygen and carbon in the feed, respectively.

$$H/C_{\text{eff}} = \frac{H-2O}{C} \quad (1)$$

Chen et al. [7] showed that feedstocks with hydrogen to carbon effective ratio (H/C_{eff}) less than 1 were difficult to upgrade over a HZSM-5 catalyst due to its quick deactivation. The H/C_{eff} ratio of petroleum based feedstocks varies from 1 to 2, whereas that of the biomass feeds are only from 0 to 0.3. Therefore, the biomass

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contained hydrogen deficient molecules, and approaches for the biomass and its derived feedstocks transformation must consider their H/C_{eff} ratio.

Chang and Silvestri [8] stated that hydrogen deficient oxygenated compounds could be successfully converted on HZSM-5 zeolite catalyst if co-fed with an adequate amount of hydrogen rich chemicals such as methanol. In the other research, Melligan et al. [9,10] showed major improvement in the biomass pyrolysis vapor by using hydrogen as carrier gas over Ni-HZSM-5 and Ni-MCM-41 catalysts. Ni loading to the catalysts caused acid sites enhancement and consequently increased decarboxylation, dehydration, and cracking reactions. Therefore, the yield of the aromatic hydrocarbons was increased. Recently Zhang et al. [5] showed that the thermal conversion of the biomass derived feedstocks to petrochemicals over zeolite catalysts was a function of the H/C_{eff} ratio of the feedstock. This suggested that the petrochemicals yield would be enhanced, while it was co-fed with a feedstock owing a high H/C_{eff} ratio.

Methanol has shown to produce high yield of hydrocarbons, when processed over zeolite catalysts [11,12]. In addition, it is usually recommended as an appropriate co-processing component due to its high H/C_{eff} ratio of 2. Therefore, methanol can be co-fed with biomass to enhance the overall hydrogen to carbon effective ratio of the feed. Fig. 1 indicates the overall reaction chemistry of the biomass derived feedstocks cofed with methanol over the HZSM-5 catalyst.

The biomass-derived feedstocks first undergo decarbonylation, decarboxylation and dehydration reactions to produce CO_2 , H_2O , CO as well as intermediate oxygenated compounds and homogeneous coke on the catalyst's surface. In the second stage, these intermediate oxygenated compounds diffuse into the zeolite catalyst pores and produce olefins and aromatics as well as heterogeneous coke through a series of oligomerization, dehydration, decarbonylation and decarboxylation reactions. The formation rate of the aromatic compounds is quite slow compared to the pyrolysis reaction. The coke generation, from polymerization of the pyrolysis vapors' oxygenated molecules, is the considerable competing reaction with the aromatic's formation. The aromatic production reactions continue through a hydrogen pool or a common intermediate within the framework of zeolite. Methanol co-feeding with the biomass probably alters the hydrocarbon pool and enhances the aromatics formation rate [5,13,14].

To the best of our knowledge in-situ catalytic pyrolysis vapor upgrading through its co-feeding with methanol over HZSM-5 zeolite catalyst in a fixed bed reactor has not been reported. The objective in the present study is to investigate the in-situ catalytic pyrolysis vapor upgrading of palm kernel shell (PKS) and its mixture with methanol in a fixed bed multi-zone reactor to study the effects of methanol co-feeding on the improvement of valuable hydrocarbons yield. Further, special attentions has been drawn to reduce catalyst deactivation. This study therefore provides critical insights, as to how the aromatics' yield can be enhanced by co-feeding of PKS with methanol that have a high hydrogen to carbon effective ratio.

2. Materials and methods

2.1. Biomass materials

The palm oil biomass named palm kernel shell (PKS) (Table 1) was obtained from Szetech Engineering Sdn. Bhd. located in Selangor, Malaysia. The sample was crushed using high-speed rotary cutting mill and sieved to desired particle size ($<300\ \mu\text{m}$). Then, the sample was dried at $105\ ^\circ\text{C}$ for 24 h and kept in tightly screw cap plastic bottles. The approximate molecular formula of the biomass was $\text{C}_{4.1}\text{H}_{5.5}\text{O}_{2.7}$.

2.2. Preparation of the catalytic materials

The catalytic materials used for the in-situ biomass pyrolysis vapor experiments were a crystalline HZSM-5 zeolite (Zeolyst CBV5524G, $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio = 50). The catalyst was calcined at $550\ ^\circ\text{C}/12\ \text{h}/\text{air}$ with heating ramp of $3\ ^\circ\text{C}/\text{min}$.

2.3. X-ray Fluorescence (XRF) analysis

The inorganic contents of the catalyst sample was quantified using X-ray Fluorescence (XRF) instrument (PANalytical Axios^{MAX}).

2.4. Scanning electron microscopy (SEM) analysis

The surface nature of the virgin and regenerated catalysts was investigated by SEM (model FEI QUANTA 450 FEG, operating at a 5 kV accelerating voltage and low vacuum) to characterize the

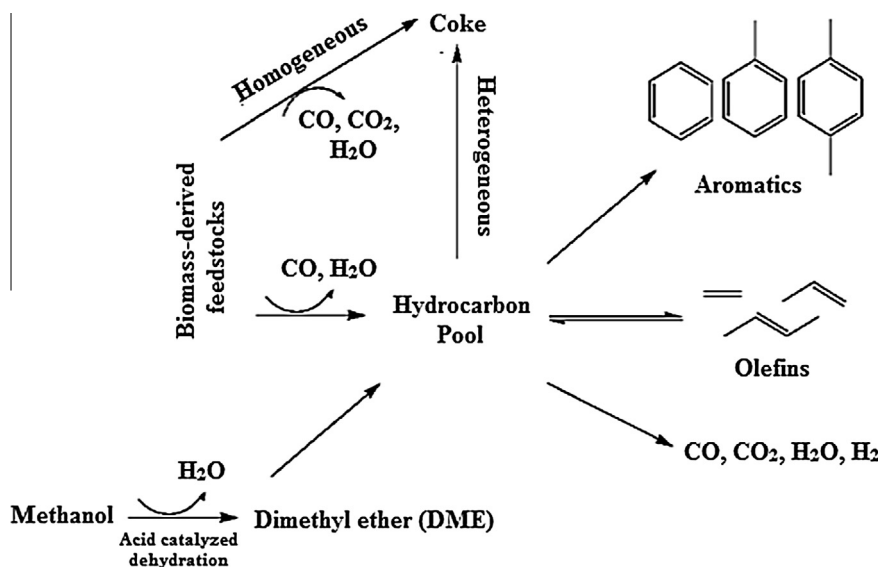


Fig. 1. Overall reaction chemistry for biomass/methanol co-feeding over HZSM-5 zeolite catalyst during pyrolysis/upgrading [5,13,14].

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