Integration of biomass catalytic pyrolysis and methane aromatization over Mo/HZSM-5 catalysts

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Abstract

The development of an effective process to convert bio-oil into intermediate platforms that are compatible with the existing refinery infrastructure is highly needed. To overcome the high cost of hydrogen consumption in conventional bio-oil upgrading processes, this paper reports a novel process that converts three major biomass constituents (cellulose, hemicellulose and lignin) directly into liquid fuels via pyrolysis in the presence of methane over molybdenum impregnated HZSM-5 catalysts. The carbon yield of total aromatics from lignin increased from 12.80 to 15.13 % when pyrolysis atmosphere switched from helium to methane in the presence of HZSM-5 support. However, methane was not effective in improving the aromatics yield from cellulose and hemicellulose in the presence of Mo-modified HZSM-5 catalysts. The molybdenum impregnated catalyst was found to promote deoxygenation of lignin-derived phenols. The carbon yield of polyaromatics from lignin was 5.47 % in the presence of HZSM-5 support under methane, compared to 2.61 % that obtained in the presence of Mo₂C/HZSM-5.

Keywords: *biomass catalytic pyrolysis; methane aromatization; aromatic hydrocarbons; bifunctional catalysts; biofuels*

1. Introduction

Lignocellulose biomass is the only carbon-based renewable resource that has the potential to alleviate our dependence on fossil fuels and mitigate global warming and other environmental issues associated with the use of fossil fuels [1]. Fast pyrolysis has been considered to be a promising and sustainable route to convert solid biomass into liquid fuel. In pyrolysis, biomass is rapidly decomposed into vapors, aerosols and solid char thermochemically under an inert atmosphere in a mild temperature range (400~600 °C), followed by a rapid condensation to recover a liquid product, which is 60-75 wt % of the biomass feed [2-4]. Bio-oil can be combusted directly as a fuel in a burner for power generation, or used in engines or turbines [5]. Bio-oil can also be further upgraded to transportation fuels and chemicals that are currently produced by petroleum refineries [5-7]. However, bio-oil suffers from several negative attributes associated with its high oxygen content, such as low energy content, high viscosity, corrosiveness, thermal instability, and immiscibility with petroleum fuels. These negative attributes of bio-oil pose significant challenges to the facilities in refineries and end users for effectively utilizing bio-oil in existing infrastructure [8,9]. Therefore, there is a critical need for developing methods to enhance bio-oil properties.

One of the most common bio-oil upgrading techniques is deoxygenation. Most deoxygenation methods require heterogeneous catalysts to initiate reactions such as dehydration, decarboxylation, decarbonylation and hydrodeoxygenation, that convert the raw bio-oil into a deoxygenated product [10]. However, these upgrading processes typically require high pressure of hydrogen and consist of multiple steps that increase process complexity and cost. Therefore, catalytic fast pyrolysis (CFP), which combines biomass pyrolysis and catalytic upgrading in a single reactor system, has emerged as a more efficient and economical process [6,11]. Extensive

studies have been conducted to improve the yield of targeted petroleum chemicals (e.g. benzene, toluene, ethylbenzene and xylenes, collectively known as BTEX) using zeolite catalysts [12-19]. The selectivity of these petrochemicals during CFP increased with increasing feed H/C_{eff} ratio, which is defined in eq. (1), where H, C, and O are the mole percentages of hydrogen, carbon and oxygen, respectively, in the feed [10,11,20]. In addition, catalyst deactivation rate decreased with increasing H/C_{eff} ratio [11].

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

The H/C_{eff} ratio of biomass varies from 0 to 0.3 making it not suitable for production of petrochemicals due to rapid deactivation of zeolites [11]. To correct for the low H/C_{eff} , a hydrogen-rich donor can be co-fed into the reactor with the biomass to increase the overall H/C_{eff} ratio of the feed. A number of studies [11,21,22] have demonstrated that co-feeding alcohols such as methanol and propanol can significantly improve the petrochemicals yields due to a synergistic effect of alcohols and pyrolysis vapors.

Methane, the major component of natural gas, can be an ideal hydrogen donor for CFP of biomass for petrochemicals production due to its low cost and high H/C_{eff} of 4. Typically, conversion of methane into higher hydrocarbons requires multiple steps: first, methane is converted into synthesis gases (H_2 and CO) via steam reforming or partial oxidation, and then further converted into hydrocarbon fuels and chemicals via Fischer-Tropsch (FT) synthesis. This reaction route is highly energy intensive due to the need for high reaction temperature and pressures. Furthermore, FT products have wide chain lengths that require further cracking and aromatization [23]. Therefore, one-step methane dehydroaromatization methodologies that utilize metal modified HZSM-5 catalysts for the production of selected aromatic hydrocarbons have been the focus of recent studies [23-26]. The reaction mechanism for methane

aromatization with metal zeolites is believed to occur in two steps as indicated in Figure 1. Initially, methane reacts to form intermediate radicals such as CH_x ($x < 4$), $\text{H}\cdot$, C_2H_y^+ ($y = 3, 5$) on metal sites, and then these radicals oligomerize into olefins or aromatics on the acidic sites of the zeolite [23,27]. Thermodynamic analysis [23] showed an increasing trend for coke deposition as the methane conversion increases. Hence, deposition of carbon on the catalyst is thought to be a key challenge in methane aromatization. To overcome catalyst deactivation due to the carbon deposition, oxygenates (e.g. CO , CO_2 , O_2 , and NO) were co-fed during the methane aromatization process [28-30]. Several studies also investigated the impacts of co-feeding oxygenates and coals in methane aromatization. By co-feeding methane with CO_2 , acetic acid and formic acid mixtures onto a $\text{Mo}/\text{HZSM-5}$ catalyst, Bedard et al. [31] and concluded that methane dehydroaromatization was highly dependent on thermodynamic equilibrium, while the addition of oxygenates had no effect on the net rate of benzene synthesis. Jin et al. [32] conducted coal pyrolysis over $\text{Mo}/\text{HZSM-5}$ catalyst under methane and hydrogen atmosphere, and found that the total liquid yield under methane atmosphere was significantly higher than that under hydrogen atmosphere. Liu and Wang et al. [33,34] found that by integrating coal pyrolysis with CO_2 reforming of methane, the liquid yield increased by 0.6 and 0.8 times as compared to the liquid yield obtained by coal pyrolysis under nitrogen and hydrogen, respectively. Additionally, by using deuterated methane CD_4 , they concluded that the free radicals released from coal cracking were stabilized by the intermediates, such as CH_x ($x < 4$), $\text{H}\cdot$ and C_2H_y^+ ($y = 3, 5$) produced from CO_2 reforming of methane. Song and He et al [35-38] demonstrated upgrading of biomass with different varieties, bitumen, sludge and solid waste through a so-called methanolysis at a temperature range of 300-600 °C in presence of Ag or/and Zn modified HZSM-5 catalysts, and it was observed that the introduction of methane not only increased the

bio-oil yield but also significantly improved its fuel properties in terms of higher H/C ratio, lower O/C ratio and lower acidity.

The hypothesis of this study was that catalytic deoxygenation of biomass-derived vapors and methane aromatization can be combined to maximize the yield of hydrocarbons. However, before studying reaction mechanisms of aromatics production through co-pyrolysis of biomass and methane over HZSM-5 catalyst, it was imperative to understand the behavior of the three major biomass components (i.e. cellulose, hemicellulose and lignin) and their individual contributions to the targeted hydrocarbons. The reaction pathways for each of these components during CFP have been well studied [13,16,39,40]. Carlson et al. [13] developed a four-step reaction pathway for conversion of cellulose into aromatics over HZSM-5 catalysts. In the first step, cellulose thermally decomposes into anhydrous sugars and other oxygenates. Second step involves dehydration of the anhydrous sugars to form furans in presence of catalyst. In the third step, furans convert into olefins inside the acid pores of zeolite through a series of decarboxylation, dehydration and decarbonylation reactions. Finally, the olefins oligomerize into aromatics. A similar reaction mechanism [41] was proposed for hemicellulose, and furans were thought to be the common intermediates derived from thermal degradation of hemicellulose and cellulose. Mullen et al. [16] hypothesized that lignin depolymerizes into small olefins that can repolymerize into aromatics over HZSM-5 catalysts. Phenol was found to be the end product of deoxygenation of lignin-derived monomers, and could not be further reduced into oxygen-free aromatics because of rapid catalyst coking due to diffusion into catalyst channels. However, the impacts of methane on the pyrolysis reaction pathways of cellulose, hemicellulose and lignin are not available in literature.

The objective of this study was to investigate pyrolysis of cellulose, hemicellulose and lignin (major biomass constituents) over two Mo-modified HZSM-5 catalysts ($\text{MoO}_3/\text{HZSM-5}$ and $\text{Mo}_2\text{C}/\text{HZSM-5}$) in methane atmosphere. MoO_3 and Mo_2C were selected as the Mo species because they have shown difference in reactivity towards methane activation[42].

2. Materials and methods

2.1 Biomass model components

Avicel PH 105 Cellulose (FMC Biopolymer, Philadelphia), beech wood xylan (Sigma Aldrich, St. Louis) and Kraft lignin (Sigma Aldrich, St. Louis) were used as models of cellulose, hemicellulose and lignin, respectively. All the biomass models were used as received without any further treatment. Results of elemental analysis of the feedstock are listed in Table 1.

2.2 Catalysts preparation

ZSM-5 zeolites (Si to Al molar ratio of 30 and nominal surface area of $425 \text{ m}^2/\text{g}$) in the ammonium (Alfa Aesar Company, VA 20191, USA) were calcined in the air at 550°C for 4 hrs to make protonated form of HZSM-5. The precursor for Mo was $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Sigma Aldrich, St. Louis, USA), and was purified by recrystallization from water. The Mo species were impregnated on the HZSM-5 support using wet impregnation method. 1 g of HZSM-5 support was degassed under vacuum for 24 hrs and then was impregnated with a solution containing ammonium heptamolybdate (3.5 wt %) and ammonia (1.4 wt %) for 16 hrs at room temperature. Ammonia was added to prevent the ammonium heptamolybdate from precipitating within the HZSM-5 to form molybdic acid. After 16 hrs, the mixture was centrifuged to separate the solid. The supernatant liquid was then decanted and the centrifuge tubes were placed in a -25°C freezer for 5 hrs to freeze the liquid within the pores of the zeolite. The samples were then freeze-dried on a lyophilizer for 24 hrs. The resulting powder was then calcined in air at 550°C for 4 hrs to

yield MoO₃/HZSM-5. The synthesis of Mo₂C/HZSM-5 catalyst followed the same procedure as MoO₃/HZSM-5 but used a different precursor solution as described by Wang et al [43]. This precursor solution contained the same concentrations of ammonia heptamolybdate and ammonia but also contained 3.8 % by weight of hexamethylenetetramine (HMT). Unlike the MoO₃/HZSM-5, the Mo₂C/HZSM-5 was calcined at 700 °C for 2 hrs in a flow of helium.

2.3 Catalysts characterization

Powder X-ray diffraction (XRD, Bruker D8-A25-ADVANCE diffractometer) was used to characterize the crystallinity of the metal impregnated catalysts. The test was performed using Cu K α radiation at 40 kV and 100 mA at a continuous scanning at step size of 0.02°, 0.5 s per step over a scanning range from 5° to 70° (2 θ). Data analysis was carried out with MDI Jade 6.5 software.

The pore structures of metal impregnated catalysts were determined by isothermal nitrogen adsorption at 77 K using a surface area analyzer (Autosorb-1C, Quantachrome, Boynton Beach, FL, USA). Prior to the analysis, catalysts were degassed at 300 °C for 12 hrs. The surface area was calculated according to Brunauer-Emmett-Teller (BET) theory. External surface area, micropore area, and pore volume were derived using a t-plot method [44]. The amount of Mo in the catalysts was measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; ThermoScientific, Waltham, MA, USA).

The surface morphology was characterized by scanning electron microscope (SEM; FEI Quanta 600, Hillsboro, OR, USA). To measure the metal dispersion on the catalysts, energy dispersive X-ray spectroscopy (EDS; Evex EDS, Belle Mead, NJ, USA) with X-ray dot mapping was used.

2.4 Pyrolysis-GC-MS

Catalytic pyrolysis experiments were carried out in a commercial micro pyrolyzer (Pyroprobe model 5200, CDS Analytical Inc., Oxford, PA). The detailed experimental procedure has been described in a previous study [45]. About 0.3 mg of biomass model samples and 3 mg of catalysts were loaded into a quartz tube and separated into two layers with quartz wool. The samples were heated to 700 °C at a filament heating rate of 1000 °C/s and then held at that temperature for 90 s. The volatiles produced were analyzed with a gas chromatography/mass spectrometry (Agilent 7890GC/5975MS) system connected to the pyroprobe by a transfer line. The chromatographic separation was performed using a DB-5 capillary column (30 mL×0.32mm I.D., 0.25 µm film thickness). The GC oven was held at 40 °C for 4 min, and then increased to 280 °C at a ramping rate of 5 °C/min and held for 20 min. The injector temperature was kept at 250 °C, and the split ratio was set to 30:1. Helium (purity: 99.99%) was used as the carrier gas at a flow rate of 1 mL/min.

The compounds were identified by comparing the peaks with National Institute of Standards and Technology (NIST) mass spectral library. Quantification of targeted compounds was performed by calibrating with known concentrations of working standards into GC/MS. The carbon yield and aromatics selectivity was calculated using eq. (2) and (3).

$$\text{Carbon yield} = \frac{\text{Moles of carbon in specific species}}{\text{Moles of carbon in biomass models}} \quad (2)$$

$$\text{Aromatics selectivity} = \frac{\text{Moles of carbon in specific aromatic species}}{\text{Moles of carbon in all quantified aromatic species}} \quad (3)$$

2.5 Experimental design

A full factorial experimental design was used with three independent parameters: two pyrolysis atmospheres (helium and methane), three biomass components (cellulose, hemicellulose and lignin) and three impregnated metal precursor (None, MoO₃ and Mo₂C). All

the experiments were run in triplicate. The average and standard deviation were used to compare carbon yields and selectivity.

3. Results and discussion

3.1 Catalysts characterization

The phases present in HZSM-5 and Mo modified HZSM-5 catalysts were determined by XRD technique as shown in Figure. 2. The main diffraction peaks of HZSM-5 were present at $2\theta=7.96^\circ$ (011), 8.87° (200), 23.11° (051), 23.96° (033), and 24.43° (313) and matched those reported in typical zeolite structure [46,47]. The XRD patterns of $\text{MoO}_3/\text{HZSM-5}$ and $\text{Mo}_2\text{C}/\text{HZSM-5}$ were similar to that of HZSM-5 indicating that the crystal structure of HZSM-5 was retained after impregnating with Mo species. However, no Mo-containing crystalline phases were observed in the patterns of the metal modified catalysts. This may be attributed to either low loading of Mo, as shown in the ICP (Table 3), or formation of amorphous or highly nanocrystalline phase. The relative degree of crystallinity of the catalysts, the ratio of integrated peak areas of the samples over that of reference sample in the range of $2\theta=22.5$ to 25° , was calculated according to ASTM standard D5758-01 [48]. For this study, three major diffraction peaks at the positions of 23.11° (051), 23.96° (033), and 24.43° (313) were used to determine the degree of crystallinity. HZSM-5 support was used as the reference sample, since it exhibited the highest intensities at these positions. Table 2 summarizes the crystallinity and the average crystallite size obtained from the major diffraction peaks of all three catalysts. Crystallinities of both Mo-modified catalysts were lower than that of the HZSM-5 support. The decrease of crystallinity was probably due to the dispersion of Mo species in the support.

The catalysts porous structure, BET surface area, pore volume and average pore size as determined from nitrogen isothermal adsorption at 77 K are shown in Figure. 3 and Table 3. All

the catalysts showed a steep increase of adsorbed volume of nitrogen at low relative pressure (less than 10^{-3}) followed by a flatter increase, indicating that adsorption occurred mainly on micropores. The nitrogen isotherms of HZSM-5 support and $\text{MoO}_3/\text{HZSM-5}$ were type IV in the Brunauer classification, corresponding to the narrow hysteresis loop at $p/p_0=0.5\sim 0.9$ (shown on the isotherm plot, Fig. 3). However, the $\text{Mo}_2\text{C}/\text{HZSM-5}$ exhibited a type I isotherm with no observable hysteresis loop in its adsorption isotherm. BET surface area ($480\text{ m}^2/\text{g}$) of HZSM-5 support was higher than the nominal specific surface area ($425\text{ m}^2/\text{g}$) provided by the manufacturer (Table 3), which is probably due to calcination. Micropore area accounted for up to 70 % of total surface area in both the HZSM-5 support and the Mo-modified catalysts, and this further confirmed the dominance of micropores in all of the catalysts. The incorporation of Mo species led to a slight decrease in the BET surface area and micropore volume of $\text{MoO}_3/\text{HZSM-5}$ and $\text{Mo}_2\text{C}/\text{HZSM-5}$. The decrease in BET area and micropore volume can be attributed to deposition of the Mo species within the channels of the HZSM-5 support.

The morphologies of HZSM-5 support and the Mo-modified catalysts are shown in Figure. 4. The HZSM-5 support was an agglomeration of cubic or spherical particles within sizes ranging from 38.3 to 185.2 nm (Fig. 4 (a, d)). The standard cubic or spherical crystals that were clearly observed in HZSM-5 are difficult to identify in the microstructure of $\text{MoO}_3/\text{HZSM-5}$ (Fig. 4(b)) and $\text{Mo}_2\text{C}/\text{HZSM-5}$ (Fig. 4(c)). Both of these catalysts exhibited compact clusters that were made up of crystals with irregular geometrical profile. The images obtained from X-ray mapping (Fig. 5) show that the major elements, such as Mo, Si, and Al in the Mo-modified catalysts were dispersed uniformly throughout the imaged microstructures. The EDS results (Table 4) indicate that both $\text{MoO}_3/\text{HZSM-5}$ and $\text{Mo}_2\text{C}/\text{HZSM-5}$ had similar Mo content.

3.2 Catalyst activity tests

The products from catalytic pyrolysis of cellulose, hemicellulose and lignin in the presence of HZSM-5 supported catalysts were mostly aromatic hydrocarbons (all products listed in Table 5). These products were grouped into (a) simple aromatics, such as BTEX, (b) benzene derivatives, such as alkybenzene, indanes and indenenes, and (c) polyaromatics, such as naphthalenes and phenanthrene and (d) oxygenates, such as phenols and methoxyphenols. There was no difference in the compounds from cellulose and hemicellulose since they were both polysaccharides. Simple phenols were the only oxygenates detectable in the products of cellulose and hemicellulose. Methoxyphenols (e.g. 2-methylphenol, creosol, etc.) and catechol were only identified in the products derived from lignin. It was observed that the major bio-oil compounds detected in the pyrolysis products of cellulose/hemicellulose/lignin under inert atmosphere also existed in the pyrolysis product of that under methane atmosphere, but there were noticeable changes in relative concentration of these compounds.

3.2.1 Catalytic pyrolysis of cellulose

Aromatic hydrocarbons were found to be the major products derived from cellulose, whereas the oxygenates were trivial (Table 6). The total carbon yield of aromatics varied across different HZSM-5 supported catalysts, with a low of $16.63 \pm 2.09\%$ for $\text{MoO}_3/\text{HZSM-5}$ under inert atmosphere and a maximum of $35.00 \pm 4.37\%$ for HZSM-5 under inert atmosphere (Table 6). Tukey's multiple comparison showed that pyrolysis atmosphere (helium and methane) had no significant effect on the yield of individual aromatic groups and total aromatic hydrocarbons. ANNOVA analysis revealed that the performance of the three HZSM-5 supported catalysts was different. $\text{MoO}_3/\text{HZSM-5}$ yielded the lowest amount of aromatic hydrocarbons, whereas HZSM-5 support yielded the highest amount of aromatics. However, the difference between HZSM-5 support and $\text{Mo}_2\text{C}/\text{HZSM-5}$ was not significant.

The tornado plot in Figure 6 shows the aromatics selectivity of products, namely benzene, toluene, ethylbenzene, *p/o*-Xylene, benzene derivatives and polyaromatics from cellulose under helium and methane atmospheres. It can be seen that all HZSM-5 supported catalysts have high selectivity (up to 70%) towards BTEX. Among all the aromatics, the selectivity for toluene was the highest for all of the catalysts, with a maximum of 32.87% with MoO₃/HZSM-5 under helium. The pyrolysis environment did not have significant impact on the selectivity for aromatic. However, the impacts of Mo impregnation on aromatics selectivity were noticeable. With MoO₃/HZSM-5, the selectivity for polyaromatics significantly decreased, whereas selectivities for the benzene and toluene increased significantly as compared for the other two HZSM-5 supported catalysts. Polyaromatics are commonly viewed as indicators for coke formation that may lead to catalyst deactivation during catalytic fast pyrolysis. By comparing aromatics yield and selectivity, it can be concluded that HZSM-5 deactivated during impregnation with MoO₃. Generally, there are three common reasons to account for catalyst deactivation: (1) poisoning of active sites by catalyst coking; (2) blockage of pores by catalyst coking; (3) reduction in number/strength of active sites [42]. In this case, MoO₃/HZSM-5 showed the lowest selectivity towards polyaromatics, indicating low tendency towards coking. Therefore, the low catalytic reactivity of MoO₃/HZSM-5 could be attributed to the reduction in acidity of HZSM-5 support during impregnation. To verify this assumption, the MoO₃/HZSM-5 catalyst was treated with a solution of nitric acid followed by calcination. After acidification, the catalytic reactivity restored (data not shown).

3.2.2 Catalytic pyrolysis of hemicellulose

The product yield from catalytic pyrolysis of hemicellulose is shown in Table 7. The total aromatics yield from hemicellulose was significantly lower than that from cellulose. For instance,

the carbon yield of total aromatics from cellulose and hemicellulose in the presence of HZSM-5 under helium was 35.00 ± 4.37 and $19.48 \pm 1.26\%$, respectively. These values are in good agreement with those reported in the literature [49]. Although both cellulose and hemicellulose are carbohydrates, hemicellulose is thermally less stable than cellulose. Therefore, the cracking of hemicellulose in the presence of a zeolite is easier than that of cellulose. This can be confirmed from the high yield of gaseous products from the catalytic pyrolysis of hemicellulose reported in other studies [49,50]. Similar to the results of cellulose, methane shows no significant effects in improving the yield of aromatics of hemicellulose.

The selectivity of aromatic products from catalytic pyrolysis of hemicellulose is shown in Figure 7. All of the HZSM-5 supported catalysts yielded product compositions with the selectivity of BTEX up to 70%. The maximum BTEX selectivity of 79.14% was achieved when $\text{MoO}_3/\text{HZSM-5}$ was used under methane environment. Cellulose and hemicellulose yielded similar selectivities for toluene, ethylbenzene and polyaromatics. Variations are noticeable in the yields of benzene, xylene and benzene derivatives from cellulose and hemicellulose. The selectivity of benzene and benzene derivatives was lower for hemicellulose than that for cellulose. However, the selectivity for xylene showed opposite trend. For example, benzene selectivity dropped from 17.58 to 14.41%, xylene selectivity increased from 17.67 to 23.01%, and benzene derivatives selectivity decreased from 12.29 to 11.36% when hemicellulose was used instead of cellulose. The introduction of methane had an impact on the formation of some of the aromatic compounds. As shown in Figure 7, the benzene selectivity under methane was slightly higher than that under helium, and this difference was significant ($p < 0.05$) with $\text{MoO}_3/\text{HZSM-5}$ and $\text{Mo}_2\text{C}/\text{HZMS-5}$ as the catalysts. In contrast, the selectivity of benzene derivatives under methane was slightly lower than that under helium, and the difference was

significant with HZSM-5 and MoO₃/HZSM-5 catalysts. The impacts of impregnated Mo species on formation of aromatics for hemicellulose were similar to that observed for cellulose. No significant differences in aromatic yields were observed between HZSM-5 support and Mo₂C/HZSM-5. However, MoO₃/HZSM-5 did yield more toluene and benzene and less polyaromatics than the HZSM-5 and Mo₂C/HZSM-5 catalysts.

3.2.2 Catalytic pyrolysis of lignin

The carbon yields of catalytic pyrolysis products from lignin are shown in Table 8. The total carbon yields of lignin were even lower than those of hemicellulose. Therefore, the rank order of three biomass constituents in terms of yielding aromatics was cellulose>hemicellulose>lignin, which is consistent with other results reported [49,50]. Also, it should be noted that the oxygenate yield from lignin was significantly higher than that from either cellulose or hemicellulose. Lignin is primarily depolymerized into phenolic compounds during pyrolysis. The low reactivity of these phenols in HZMS-5 is responsible for the high yield of oxygenates from lignin [16,49]. Methane slightly increased the yield of BTEX, polyaromatics and total aromatics but the change was not statistically significant. MoO₃/HZSM-5 had the lowest aromatics yield among all three catalysts. This could be due to deactivation during catalyst impregnation as discussed above.

The tornado plot in Figure 8 shows the aromatic selectivity of products from lignin. The selectivity of polyaromatics from lignin was the highest among biomass components. The maximum polyaromatics selectivity from lignin reached up to 36% in the presence of HZMS-5, while the selectivity was only 20% from cellulose and hemicellulose. This variation could also be attributed to the conversion of the lignin-derived phenols into polyaromatics and coke through polycondensation in the channel of HZSM-5 [49]. Effect of methane was only significant on the

selectivity of benzene and benzene derivatives with HZSM-5. However, the carbon yields of lignin-derived BTEX and polyaromatics under methane were higher (but not significant) than those under Helium. Also, impregnation with the Mo species significantly changed the selectivity of aromatics (Fig. 8). In general, the presence of Mo increased selectivity of BTEX and decreased selectivity of polyaromatics. Transition metals such as Ni, Co, and Mo have shown to catalyze deoxygenation of phenolic compounds to form aromatics leading to their widespread use in hydrodeoxygenation (HDO) of bio-oil compounds [10,51,52]. Rather than ending up as polyaromatics and coke in the channels of HZSM-5, lignin-derived phenolic compounds may have incorporated into the active sites of the Mo species, where hydroxy and methoxy groups, possibly, directly stripped from the aromatic rings. Zheng et al [53] demonstrated that $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$ exhibited a high selectivity of monocyclic aromatics and an extremely low selectivity of polyaromatics (2.2%) from lignin. In the current study, Mo impregnated HZSM-5 acted as a bifunctional catalyst: Mo species provided active sites for deoxygenation and the Lewis and Bronsted acid sites in HZSM-5 were responsible for the aromatization of lignin-derived olefins. The increase in BTEX selectivity and decrease in polyaromatics could be the synergistic result of these two mechanisms.

3.2.4 Role of methane and reaction network

As discussed above, methane significantly increased aromatic hydrocarbon yield from lignin but did not significant effect the aromatic hydrocarbon yield from cellulose and hemicellulose. Even with only HZSM-5 support, the carbon yield of aromatics obtained with methane was higher than that obtained under helium (Table 8). These results imply that methane can incorporate into lignin derived phenols directly and form aromatics through HDO without being activated on the active sites on Mo species. Lignin-derived intermediates, such as

guaiacols and phenols can be converted into aromatics through a series of reactions like dehydration, demethylation and transalkylation that occur in the HDO process [41]. These reactions are promoted under a hydrogen-rich environment, possibly provided by reforming of methane with water that evolved from lignin degradation. The reaction pathway on conversion of lignin over HZSM-5 supported catalysts under methane is summarized in Figure 9. However, to validate this reaction pathway and further understand the reaction mechanisms, an isotope labeling study using deuterated methane (CD_4) or ^{13}C containing biomass model compound as the feed is needed. The fact that the yield of aromatic compound from carbohydrates was not very sensitive to reaction atmosphere, suggest that the Mo-based catalysts might not have activated methane efficiently.

4. Conclusions

This study investigated catalytic pyrolysis of three biomass constituents (cellulose, hemicellulose and lignin) under both helium and methane atmospheres in the presence of HZSM-5 and HZSM-5 supported molybdenum-based catalysts. Cellulose contributed most to the production of aromatic hydrocarbons followed by hemicellulose and lignin. The introduction of methane enhanced hydrodeoxygenation of lignin-derived phenols leading to increased aromatics yield in presence of HZSM-5 zeolites. The carbon yield of total aromatics from lignin increased from 12.8 to 15.13 % when pyrolysis atmosphere changed from helium to methane in presence of HZSM-5 support. However, in contrast to our expectation, methane was not effective in improving the aromatics yield from cellulose and hemicellulose. The active sites provided by Mo species facilitated the deoxygenation of lignin-derived phenols and thus inhibited the production of polyaromatics and coke.

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Figure captions

Fig 1. Reaction mechanisms for methane aromatization [23].

Fig 2. XRD patterns of catalysts.

Fig 3. N₂ isothermal adsorption plot of catalysts.

Fig 4. SEM images of catalysts: (a) HZSM-5, (b) MoO₃/HZSM-5, (c) Mo₂C/HZSM-5, (d) particle size of HZSM-5.

Fig 5. X-ray mapping of elemental composition within the selected microstructure of (a) MoO₃/HZSM-5 and (b) Mo₂C/HZSM-5, Red: Mo; Green: Si; Blue: Al.

Fig 6. Aromatics selectivity of catalytic pyrolysis products of cellulose.

Fig 7. Aromatics selectivity of catalytic pyrolysis products of hemicellulose.

Fig 8. Aromatics selectivity of catalytic pyrolysis products of lignin.

Fig 9. Conversion pathways of lignin with methane.

Table 1 Elemental analysis of the feedstock as received basis.

Feedstock	Elemental analysis (wt. %)			
	C	H	N	O
Cellulose	42.09	6.32	0.18	51.51
Hemicellulose	39.79	6.09	0.22	51.32
Lignin	61.59	5.63	0.89	30.7

Table 2 Relative crystallinity and crystallite sizes of catalysts.

Catalysts	Crystallinity (%)	^a Average crystallite size (nm)
HZSM-5	100	^b 52.7±0.6
MoO ₃ /HZSM-5	92.45	59.9±0.9
Mo ₂ C/HZSM-5	92.74	58.2±0.8

^aAverage crystallite size estimated from the major diffraction peaks at position of 7.96° (011), 8.87° (200), 23.11° (051), 23.96° (033), and 24.43° (313).

^bValue reported as the mean ± estimated standard deviation.

Table 3 BET surface area, pore volume, pore size, and Mo content of the catalysts.

Catalysts	BET surface area (m ² /g)	Micropore area (m ² /g)	External surface area (m ² /g)	Micropore volume (cc/g)	Total volume (cc/g)	Average pore size (nm)	Mo content by ICP (wt %)
Mo ₂ C/H ZSM-5	467	344	122	0.115	0.468	4.03	2.50
MoO ₃ /H ZSM-5	457	334	122	0.113	0.439	3.92	2.43
HZSM-5	479	345	134	0.119	0.448	3.69	N/A

Table 4 Relative contents of Mo, Si and Al within selected microstructure in Figure 5.

Catalysts	Mo (wt. %)	Si (wt. %)	Al (wt. %)
MoO ₃ /HZSM-5	23.56	72.84	3.60
Mo ₂ C/HZSM-5	24.05	71.33	4.63

Table 5 List of compounds identified from catalytic pyrolysis products.

Compound	Category	Cellulose	Hemicellulose	Lignin
Benzene	BTEX	^a *	*	*
Toluene	BTEX	*	*	*
Ethylbenzene	BTEX	*	*	*
Styrene	BTEX	*	*	*
p-Xylene	BTEX	*	*	*
o-Xylene	BTEX	*	*	*
Phenol	Oxygenates	*	*	*
Benzene, 1,2,3-trimethyl-	Benzene derivatives	*	*	*
Indane	Benzene derivatives	*	*	*
Indene	Benzene derivatives	*	*	*
Phenol, 2-methyl-	Oxygenates	*	*	*
p-Cresol	Oxygenates	*	*	*
Phenol, 2-methoxy-	Oxygenates			*
2-Methylindene	Benzene derivatives	*	*	*
1H-indene, 1-methyl-	Benzene derivatives	*	*	*
Naphthalene	Polyaromatics	*	*	*
Creosol	Oxygenates			*
Catechol	Oxygenates			*
Phenol, 4-ethyl-2-methoxy-	Oxygenates			*
Methylnaphthalene	Polyaromatics	*	*	*
2-Methoxy-4-vinylphenol	Oxygenates			*
Dimethylnaphthalene	Polyaromatics	*	*	*
Fluorene	Polyaromatics	*	*	*
Phenanthrene	Polyaromatics	*	*	*
Anthracene, 1-methyl-	Polyaromatics	*	*	*

^aCompounds detected in the catalytic pyrolysis products of individual biomass constituent.

Table 6 Carbon yield from catalytic pyrolysis of cellulose (wt. %) in two reaction atmospheres (He=Helium, Me=Methane)^a.

Atmosphere, catalyst	Aromatics			Total Aromatic HCs	Oxygenates
	BTEX	Benzene derivatives	Polyaromatics		
He, HZSM-5	23.67±3.19 ^a	4.29±0.43 ^a	7.03±1.28 ^a	35.00±4.37 ^a	0.78±0.11 ^b
Me, HZSM-5	23.70±3.40 ^a	3.72±0.30 ^{a,b}	7.04±0.44 ^a	34.47±3.98 ^a	0.75±0.23 ^b
He, MoO ₃ /HZSM-5	12.30±1.74 ^b	2.15±0.27 ^c	2.18±0.23 ^b	16.63±2.09 ^b	0.86±0.10 ^b
Me, MoO ₃ /HZSM-5	13.33±2.54 ^b	2.48±0.76 ^{b,c}	2.67±0.49 ^b	18.47±3.60 ^b	0.96±0.36 ^b
He, Mo ₂ C/HZSM-5	20.41±4.33 ^a	4.46±1.02 ^a	5.80±0.34 ^a	30.67±5.67 ^a	1.60±0.33 ^a
Me, Mo ₂ C/HZSM-5	17.69±1.26 ^{a,b}	3.56±0.36 ^{a,b}	6.20±0.49 ^a	27.46±1.79 ^a	1.28±0.21 ^{a,b}

^aMeans in the same column with no letter in common are significantly different ($p < 0.05$) from the Tukey's HSD test. The letters (a-c) superscripts refer to the highest estimates to the least.

Table 7 Carbon yield from catalytic pyrolysis of hemicellulose (wt. %) in two reaction atmospheres (He=Helium, Me=Methane)^a.

Atmosphere, catalyst	Aromatics			Total Aromatic HCs	Oxygenates
	BTEX	Benzene derivatives	Polyaromatics		
He, HZSM-5	12.99±0.96 ^a	2.29±0.06 ^a	4.20±0.32 ^a	19.48±1.26 ^a	0.31±0.02 ^a
Me, HZSM-5	12.45±0.51 ^a	1.45±0.08 ^{a,b}	3.95±0.27 ^a	17.84±0.77 ^a	0.25±0.07 ^a
He, MoO ₃ /HZSM-5	7.29±1.05 ^b	1.11±0.30 ^{a,b}	1.25±0.21 ^b	9.65±1.56 ^b	0.35±0.06 ^a
Me, MoO ₃ /HZSM-5	7.47±0.79 ^b	0.79±0.29 ^b	1.22±0.26 ^b	9.48±1.34 ^b	0.24±0.07 ^a
He, Mo ₂ C/HZSM-5	13.00±1.54 ^a	2.21±0.99 ^a	3.90±0.53 ^a	19.10±2.96 ^a	0.74±0.48 ^a
Me, Mo ₂ C/HZSM-5	13.34±1.20 ^a	1.47±0.48 ^{a,b}	3.76±0.54 ^a	18.57±1.82 ^a	0.67±0.64 ^a

^aMeans in the same column with no letter in common are significantly different ($p < 0.05$) by the Tukey's HSD test. The letters (a-b) superscripts refer to the highest estimates to the least.

Table 8 Carbon yield from catalytic pyrolysis of lignin (wt. %) in two reaction atmospheres (He=Helium, Me=Methane)^a.

Atmosphere, catalyst	Aromatics			Total Aromatic HCs	Oxygenates
	BTEX	Benzene derivatives	Polyaromatics		
He, HZSM-5	6.73±0.56 ^{a,b}	1.38±0.17 ^a	4.70±0.90 ^a	12.80±1.59 ^{a,b}	1.40±0.41 ^a
Me, HZSM-5	8.41±0.39 ^a	1.26±0.03 ^a	5.47±0.17 ^a	15.13±0.45 ^a	1.40±0.43 ^a
He, MoO ₃ /HZSM-5	3.34±1.26 ^c	0.49±0.34 ^a	0.67±0.58 ^d	4.50±1.99 ^d	1.19±0.77 ^a
Me, MoO ₃ /HZSM-5	4.60±0.65 ^{b,c}	0.48±0.17 ^a	1.09±0.21 ^{c,d}	6.17±1.03 ^{c,d}	1.35±0.65 ^a
He, Mo ₂ C/HZSM-5	6.31±0.58 ^{a,b}	1.30±0.54 ^a	2.30±0.16 ^{b,c}	9.90±1.20 ^{b,c}	1.70±0.37 ^a
Me, Mo ₂ C/HZSM-5	7.03±1.08 ^a	1.21±0.94 ^a	2.61±0.63 ^b	10.85±2.62 ^{a,b}	1.45±0.74 ^a

^aMeans in the same column with no letter in common are significantly different ($p < 0.05$) by the Tukey's HSD test. The letters (a-d) superscripts refer to the highest estimates to the least.

Fig. 1.

Fig. 2.

Fig. 3.

(a)

(b)

(c)

(d)

Fig. 4.

(a-1)

(b-1)

(a-2)

(b-2)

(a-3)

(b-3)

(a-4)

(b-4)

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.