

ARTICLE

Transformation of Biomass into Aromatics with Zeolite Catalysts

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Biomass is a nature renewable resource which can be used for the production of high value chemicals and bio-fuels. In the present work, the transformation of sawdust into aromatics such as benzene, toluene and xylenes was investigated over a series of zeolite catalysts (NaZSM-5, HZSM-5, ReY and HY catalysts). Among the tested catalysts, the HZSM-5 catalyst shows the highest activity for the production of aromatics. The yield and carbon selectivity of aromatics reached about 26.5% and 62.5C-mol%, respectively over the HZSM-5 catalyst under the optimal condition of $T=450\text{ }^{\circ}\text{C}$, $f(\text{N}_2)=300\text{ cm}^3/\text{min}$, and catalyst/lignin ratio of 2. The effects of the reaction conditions including temperature, gas flow rate, and catalyst/sawdust ratio on the production of aromatics were investigated in detail and the formation of aromatics from lignocellulosic biomass was also addressed.

Key words: Biomass, Aromatics, Zeolite catalysts, Catalytic pyrolysis

I. INTRODUCTION

Recently, the increase in high attention to environment problems and the limited petroleum resources has led to an increased interest in the alternative routes for the production of bio-fuels and chemicals using biomass as feedstocks [1–6]. As the only renewable carbon resource on the earth, various plant components of lignocellulosic biomass, have been proven to produce bio-fuels and chemicals [6, 7]. Liquid bio-fuels and chemicals produced from lignocellulosic biomass can significantly reduce our dependence on foreign oil, reduce greenhouse gas emissions, and improve national security.

The lignocellulosic biomass is mainly composed of three components, lignin, cellulose and hemicelluloses. Cellulose consists of long linear fibrils of β -(1,4)-glucopyranoside chains and hemicelluloses is branched polysaccharides composed of 1,4-linked β -D-hexosyl residues. The linkages in the structure of lignin, which is biosynthetically produced by copolymerization of three phenylpropane monomers (coniferyl alcohol, sinapyl alcohol and coumaryl alcohol), include β -O-4, 5-5, β -5, 4-O-5, β -1, dibenzodioxocin, and β - β linkages, of which the β -O-4 linkage is dominant, consisting of more than half of the linkage structures of lignin [1–3, 8–10]. The pyrolysis and catalytic pyrolysis of biomass are two important routes to produce the aromatics [11–13]. Con-

ventional rapid pyrolysis of biomass is a thermal chemical process in the absence of air, at reaction temperatures ranging from 450 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ and the residence time less than 1–5 s, forming organic liquid, solid char/coke and gaseous products [14–16]. The liquid products (generally named as bio-oil or bio-crude) is generally unstable, acidic, corrosive, viscous, and has high moisture content [17–19]. Therefore, it needs to further upgrade to meet conventional fuels.

The catalytic pyrolysis of biomass is an appropriate process to convert biomass into bio-fuels. The products of the catalytic pyrolysis from the biomass contain a wide range of the compounds, such as aromatic hydrocarbons, phenols, acids, furans, ketones, naphthalenes, and others [8, 20–26]. Catalyst is one of the key factors in biomass catalytic pyrolysis, which has a distinct affect on the yield and selectivity of the target products. The conversion of the biomass into aromatics can go through the reactions such as dehydration, decarboxylation, decarbonylation, hydrogen transfer, alkylation, isomerization and aromatization [1, 10]. The reactions occur inside the zeolite catalysts (ZSM-5, Y-zeolite, Al-MCM-22, Beta zeolite, H-USY, SPA and Al-MSU) depending on structural characteristics of the catalyst, including the presence and strength of acid sites and framework [1, 23, 27–39]. The reaction temperature is another key factor in biomass pyrolysis [40, 41]. The thermal degradation of the three main components of biomass (lignin, cellulose, and hemicellulose) leads to different type products. Lignin decomposes mainly into various phenolic compounds during pyrolysis [42], while the cellulose and hemicellulose yield more aldehydes, ketones, acids, esters, and alcohols.

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Recently, we studied the selective production of light olefins from the catalytic pyrolysis of biomass and bio-oil, and synthesis of bio-fuels through the oligomer of light olefins [43, 44]. Production of aromatics such as benzene, toluene and xylenes from the renewable biomass can provide the fraction of the vehicle fuels as well as basic feedstocks for the petrochemical industry. These aromatics also serve as the most important intermediates for the production of fiber, rubber, dyestuff, coatings and pesticide [1–3]. In this work, we investigate the conversion of sawdust as a typical lignocellulosic biomass into aromatics over the different zeolitic catalysts under various reaction conditions, expecting to achieve the maximization yield of the target aromatic hydrocarbons. This conversion may potentially provide a useful approach for the production of aromatics using the renewable biomass.

II. EXPERIMENTS

A. Feedstocks

The sawdust was obtained from Anhui Yineng Bio-energy Co. Ltd. (Hefei, China). The biomass sample was crushed and sieved to obtain particle sizes 0.2–0.3 mm. Dried sawdust consists of 46.2wt% carbon, 47.3wt% oxygen, 6.02wt% hydrogen, and 0.48wt% nitrogen, measured by an elemental analyzer (Vario EL-III, Elementar, Germany). Analytical reagents such as ethanol, acetone benzene, toluene, xylenes, and phenol were purchased from Sinopharm Chemical Reagent Company Limited in China (Shanghai, China).

B. Catalysts and characterization

The quartz sand was purchased from Sinopharm Chemical Reagent Company Limited in China (Shanghai, China), and the zeolites (Na-ZSM-5, ReY, and HY-zeolite) were supplied by Nankai University catalyst Co., Ltd. (Tianjin, China). The HZSM-5 zeolite was prepared by conversion of the sodium form to the protonated form via the NH_4^+ exchange procedure. All catalysts were calcined in nitrogen atmosphere at 550 °C for 4 h prior to use. The elemental contents of these catalysts were measured by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Atomscan Advantage, Thermo Jarrell Ash Corporation, USA). The catalysts were investigated by BET (Brunauer-Emmett-Teller surface area) and NH_3 -TPD (temperature programmed desorption of ammonia) analyses. The N_2 adsorption/desorption isotherms of the catalysts were measured at –196 °C using the COULTER SA 3100 analyzer. For the NH_3 -TPD tests, the catalysts were dried in vacuum oven for 12 h prior to test. Then the catalyst samples were heated to 500 °C under helium flow (ultrahigh purity, 100 mL/min) for

2 h. The adsorption of ammonia was carried out at 120 °C for 1 h. After the catalysts were flushed with He at 120 °C for 1 h to remove the unabsorbed ammonia, the programmed-desorption of NH_3 was run from 120 °C to 700 °C with a heating rate of 10 °C/min. Gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou China) were used to measure the desorbed ammonia with a thermal conductivity detector (TCD).

C. Experimental procedures

The production of aromatics from the catalytic pyrolysis of the sawdust was carried out in a tube reactor (inner diameter: 33 mm, length: 480 mm) under atmospheric pressure [43, 44]. This system consists of a biomass feeder, a gas meter, a heater and temperature controller, two condensers and an on-line gas analyzer. Before each experiment, the reactor was flushed with nitrogen with a flow rate of 300 cm^3/min for 2 h at room temperature to exclude air, and then heated to the setup temperature by the carborudum heater with a programmed temperature controller (10 °C/min). The dried sawdust particle (sizes 0.2–0.3 mm) was mixed with the catalyst (40–80 mesh) at different weight ratio, and then was fed into the reactor by the feeder. Gas products were collected with the gas bags and analyzed by a gas chromatograph (GC-SP6890, Shandong Lunan Ruihong Chemical Instrument Co., Ltd., Tengzhou, China) with two detectors. H_2 , CO , CH_4 , and CO_2 were separated on TDX-01 column, and analyzed by TCD (thermal conductivity detector). The gas hydrocarbons products were analyzed by FID (flame ionization detector). The liquid products (oil and water) in each test were collected by two liquid nitrogen/ethanol bath condensers and then weighed to obtain the mass of liquid products. The main components of the organic liquid products were analyzed by GC-MS (Thermo Trace GC/ISQ MS, USA). The total carbon contents in the liquid products were measured by a Vario EL III elemental analyzer. Water content was analyzed by a moisture analyzer (Model ZSD-1, Shanghai, China). For GC-MS analysis, the main components such as benzene, toluene, xylenes, phenols, and other organic products were determined by the calibrated GC-MS peak area with the standard samples. The solid coke was measured by the TGA analysis (Q5000IR thermogravimetric analyzer, USA) after the reactor was cooled to room temperature in a N_2 flow. The yield (Y_1 (%)) of a specific product and selectivity (S_A (C-mol%)) were calculated as follows [43, 44],

$$Y_1 = \frac{x_1}{x_{\text{fed}}} \times 100\% \quad (1)$$

$$S_A = \frac{x_a}{x_A} \times 100\% \quad (2)$$

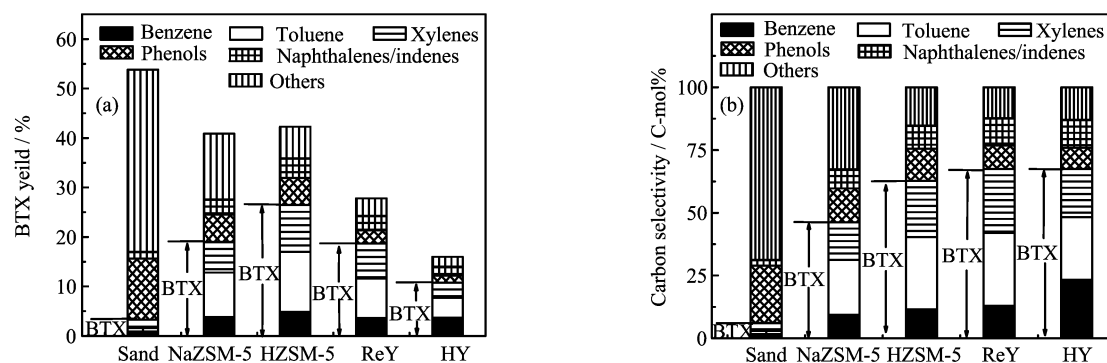


FIG. 1 (a) The BTX yield derived from catalytic depolymerization of sawdust using different catalysts. (b) The selectivity of products derived from catalytic depolymerization of sawdust using different catalysts. Reaction conditions: $T=450\text{ }^{\circ}\text{C}$, $f(\text{N}_2)=300\text{ cm}^3/\text{min}$, and catalyst/sawdust ratio of 2.

TABLE I Main characteristics parameters of the catalysts used in this work*.

Catalyst	Si/Al	$S_{\text{BET}}/(\text{m}^2/\text{g})$	$V_p/(\text{cm}^3/\text{g})$	Total acid/ $(\mu\text{mol}/\text{g}_{\text{cat.}})$	Pore size/ $(\text{nm}\times\text{nm})$
NaZSM-5	25	400	0.24	390.0	0.53×0.56 , 0.51×0.55
HZSM-5	25	282.4	0.20	580.6	0.53×0.56 , 0.51×0.55
HY	6	620.0	0.40	2206.3	0.74×0.74
Re-Y	5	532.6	0.37	712.8	0.74×0.74
SiO_2	∞	0.20	0.00042	20.5	

* Si/Al: the ratio of silicon to aluminum in the zeolites, V_p : pore volume. The values are averages of three trials and standard deviations were less than 10.5%.

where x_1 and x_{fed} are carbon moles in a produce and fed in, respectively, x_a and x_A are carbon moles in an aromatic product and aromatics. Each datum was the mean values based on three tests.

III. RESULTS AND DISCUSSION

A. Catalyst characterization

The main properties of a series of zeolite catalysts (NaZSM-5, HZSM-5, ReY and HY catalysts) used in this work are summarized in Table I. The HZSM-5 zeolite was prepared by conversion of the sodium form (NaZSM-5) to the protonated form via an NH_4^+ exchange procedure, followed by calcination at $550\text{ }^{\circ}\text{C}$ for 4 h. Both HZSM-5 and NaZSM-5 had typical MFI (Mobil fifth) structure with the same pore size ($0.53\text{ nm}\times 0.56\text{ nm}$). The Si/Al ratios for HZSM-5 and NaZSM-5 were about 25. After the ion exchange procedure, the BET surface area (S_{BET}) for HZSM-5 was decreased to $282.4\text{ m}^2/\text{g}$, as compared with the value of NaZSM-5 ($400\text{ m}^2/\text{g}$). Especially, the total acid sites of the HZSM-5, estimated by the NH_3 -TPD tests, was about $580.6\text{ }\mu\text{mol}/(\text{g}_{\text{cat.}})$, which was much higher than that of NaZSM-5 ($390.0\text{ }\mu\text{mol}/(\text{g}_{\text{cat.}})$). In addition, two Y-type zeolites of HY and ReY had a larger pore size of $0.74\text{ nm}\times 0.74\text{ nm}$ than that of ZSM-5. The total acids of the HY and ReY catalysts were about 2206.3 and

$712.8\text{ }\mu\text{mol}/(\text{g}_{\text{cat.}})$, respectively. Quartz sand (SiO_2) with a very low acidity was used as the control experiments.

B. Catalyst screening

The comparative tests of the transformation of sawdust into aromatics were performed using four different zeolite catalysts (NaZSM-5, HZSM-5, ReY, and HY) and quartz sand. As shown in Fig.1, the main products observed in the pyrolysis of sawdust with quartz sand were oxygenated organic compounds including substituted phenolics, acids, furans, alcohols, aldehydes, ketones and other heavier oxygenates. Only small amount of aromatics were formed in the pyrolysis of sawdust.

However, the formation of aromatics (especially BTX) was notably enhanced as the zeolite catalysts were used (Fig.1(a)). The yields of aromatics from catalytic cracking of sawdust with different zeolites decreased in the following order: HZSM-5>NaZSM-5>ReY-zeolite>HY-zeolite. The BTX selectivities over HZSM-5, NaZSM-5, ReY and HY were 62.8C-mol%, 46.3C-mol%, 67.5C-mol%, and 67.5C-mol%, respectively under the typical reaction condition: $T=450\text{ }^{\circ}\text{C}$, $f(\text{N}_2)=300\text{ cm}^3/\text{min}$ and catalyst/sawdust ratio of 2 (Fig.1(b)). Among the tested catalysts, HZSM-5 gives the maximum carbon yield of 26.5% with a high BTX selectivity of 62.8C-mol%. The

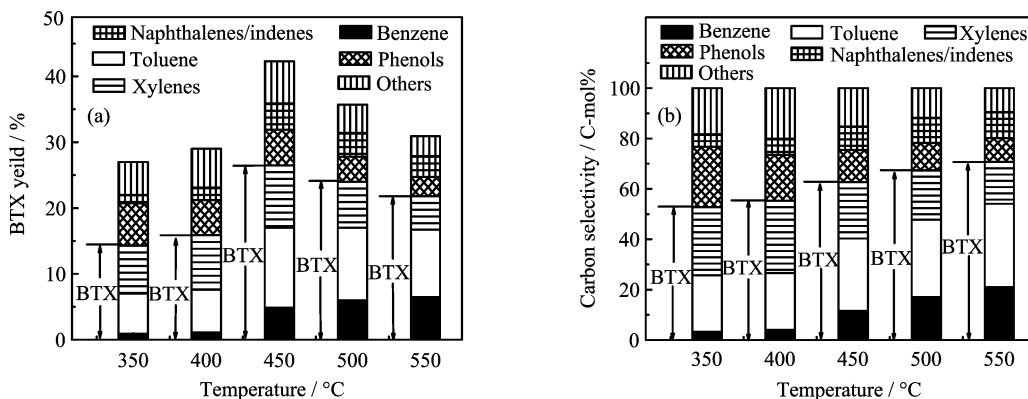


FIG. 2 (a) The yield of BTX on depolymerization of sawdust over the HZSM-5 catalyst. (b) The selectivity of the products on depolymerization of sawdust over the HZSM-5 catalyst. Reaction conditions: $T=350\text{--}550\text{ }^{\circ}\text{C}$, $f(\text{N}_2)=300\text{ cm}^3/\text{min}$, and catalyst/sawdust ratio of 2.

yield of aromatics over the NaZSM-5 catalyst is lower than that over HZSM-5, indicating that increasing the acidity of the catalysts favors the production of aromatics. It was also noticed that the yields of aromatics using the ReY and HY catalysts were obviously lower than the level using the HZSM-5 catalyst. Compared with the HZSM-5 catalyst, the ReY and HY catalysts have much stronger acidity with larger pore sizes (Table I). The excess acid sites and larger pore channels in the ReY and HY catalysts favor to form coke by the polymerization of aromatics, leading to the decrease in the BTX yield.

C. Effect of temperature on transformation of sawdust to aromatics

Figure 2 shows the effect of the temperature on the production of the aromatics from sawdust over the selected HZSM-5 catalyst at $350\text{--}550\text{ }^{\circ}\text{C}$, the flow rate of the carriers gas of $300\text{ cm}^3/\text{min}$ and catalyst/sawdust ratio of 2. The transformation of sawdust to aromatics tended to increase with increasing reaction temperature below $450\text{ }^{\circ}\text{C}$, and the aromatics yield decreased over $450\text{ }^{\circ}\text{C}$ (Fig.2(a)). The maximum BTX yield of 26.5% was obtained at $450\text{ }^{\circ}\text{C}$. The catalytic cracking of biomass generally involves two key steps, biomass depolymerization into the monomers followed by the complex second reactions such as decarbonylation, decarboxylation, dehydration, hydrogen or hydride transfer, cyclization, aromatization and oligomerization reactions. Because both the biomass depolymerization and deoxygenation are the endothermic processes, increasing reaction temperature will favor the production of aromatics. On the other hand, further increasing the temperature from $450\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$ will lead to the second cracking of aromatics, resulting in a significant decrease in BTX carbon yield from 26.5C-mol% to 21.8C-mol%. This explanation is also supported by the fact that the yield of the gaseous products (mainly con-

sisting of CO and CO₂, together with a small amount of CH₄, C₂–C₄ alkanes and C₂=C₄ olefins) increased from 15.8C-mol% to 33.0C-mol% with increasing the temperature from $350\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$.

For the distribution of products (Fig.2(b)), benzene, toluene and xylenes (BTX) were the main aromatic products together with a smaller amount of phenols, C₉⁺ aromatics and other carbon-containing compounds, depending on the reaction temperature. The order of the formation of different aromatics at $450\text{ }^{\circ}\text{C}$, based on their selectivities, was as follows: toluene (28.8C-mol%)>xylenes (22.5C-mol%)>phenols (12.7C-mol%)>benzene (11.5C-mol%)>C₉⁺ aromatics (9.3C-mol%). With increasing reaction temperature, the formation of benzene and toluene significantly increased, accompanied by an obvious decrease in xylenes and phenols aromatics. These changes in the aromatics distribution suggest that higher temperature is favorable to further removal of functional groups from the initial heavier aromatics (for example demethylation of xylenes and dehydroxylation from phenol), resulting in an increase in the formation of benzene and toluene. Moreover, the carbon balance, evaluated by the overall mass yields obtained from the gas, liquid and solid products, was generally between 90% and 105%.

D. Effects of the catalyst/sawdust ratio and carrier gas on cracking of sawdust

Figure 3 present the influence of the catalyst to feed ratio on production of aromatics from sawdust over the HZSM-5 catalyst. When quartz sand was substituted for the catalyst (the catalyst/sawdust ratio=0), the main products observed in the pyrolysis of sawdust were the oxygenated organic compounds including substituted phenolics, acids, furans, alcohols, aldehydes, ketones and other heavier oxygenates. Only small amount of aromatics was formed in the pyrolysis of sawdust over quartz sand. In the presence of the catalyst,

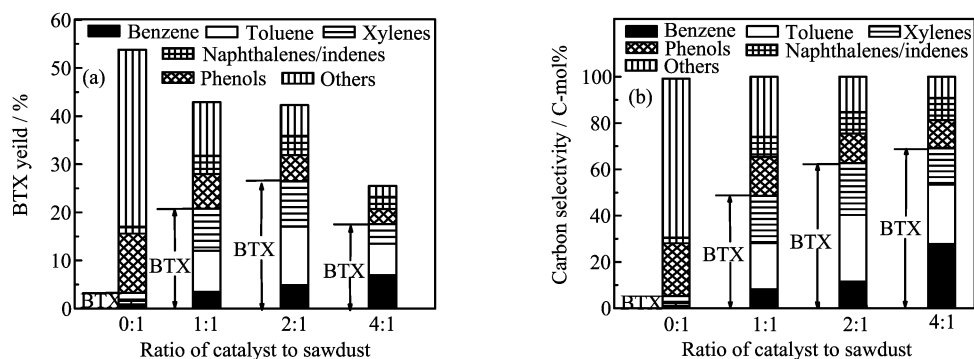


FIG. 3 (a) Effect of the catalyst/sawdust ratio on the yield of BTX derived from catalytic depolymerization of sawdust over HZSM-5. (b) Effect of the catalyst/sawdust ratio on the selectivity of products derived from catalytic depolymerization of sawdust over HZSM-5. Reaction conditions: $T=450\text{ }^{\circ}\text{C}$, $f(\text{N}_2)=300\text{ cm}^3/\text{min}$.

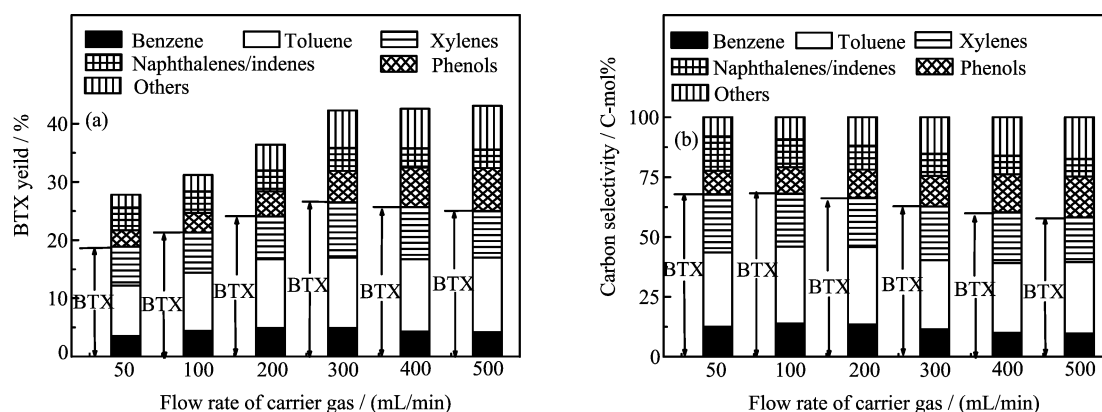


FIG. 4 The influence of carrier gas flow rate on (a) the yield of BTX (b) the selectivity of products from sawdust over HZSM-5. Reaction conditions: $T=450\text{ }^{\circ}\text{C}$ and catalyst/sawdust ratio of 2.

the aromatics yield increased with increasing the catalyst to feed ratio, indicating the catalyst enhances the biomass depolymerization and deoxygenation. With the increase of the catalyst/sawdust ratio from 1:1 to 2:1, the yield of BTX increased from 20.8% to 26.5% (Fig.3(a)), and the BTX selectivity was improved from 48.6C-mol% to 69.2C-mol% (Fig.3(b)). Although the aromatics selectivity showed a positive dependence on the catalyst/lignin ratio, the aromatics yield decreased with further increasing the catalyst/sawdust ratio over 2:1. This implies that the secondary decomposition of aromatics is enhanced at an excess catalyst/feed ratio.

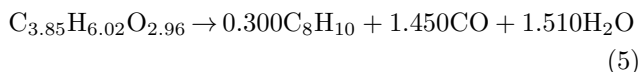
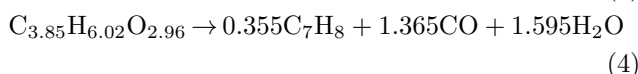
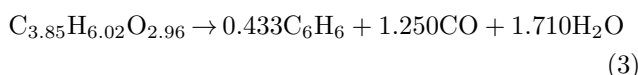
Moreover, the flow rate of carrier gas is also another important factor in the production of the aromatics from biomass. Figure 4 shows the effect of the flow rate of the carrier gas on the yield and selectivity of the products from the sawdust over the HZSM-5 catalyst under the following reaction condition: $450\text{ }^{\circ}\text{C}$, catalyst/sawdust ratio of 2, and the carrier gas flow rate varied from $50\text{ cm}^3/\text{min}$ to $500\text{ cm}^3/\text{min}$. With the increasing of the flow rate of carrier gas from $100\text{ cm}^3/\text{min}$ to $500\text{ cm}^3/\text{min}$, the aromatics yield increased from 24.7% to 32.4% (Fig.4(a)) and BTX selectivity decreased from 68.1C-mol% to 58.2C-mol% (Fig.4(b)). Increasing of

the flow rate of carrier gas will shorten the reaction residence time of biomass in the heating zone of the reactor. The increase in the aromatics yield at a faster flow rate of carrier gas (corresponding to a shorter residence time) is mainly attributed to the decrease in the secondary catalytic pyrolysis of aromatics. For the products distribution, increasing of the flow rate of carrier gas decreased the BTX selectivity, accompanied by the increase in the phenols and other oxygenates. This result indicates that the deoxygenation efficiency is reduced for a shorter reaction residence time.

E. Reaction paths for the conversion of sawdust to aromatics

Biomass mainly consists of three main components, *i.e.*, cellulose, hemicellulose, and lignin. The disruption of the complicated polymers in cellulose, hemicellulose and lignin into smaller subunits is generally an important initial step for the catalytic conversion of lignocellulosic biomass [3, 13, 26, 45,]. These subunits (intermediates) can be further catalytically converted into target hydrocarbon products with a zeolite cata-

lyst [13, 46, 39]. For example, with regarding to the catalytic conversion of lignin, the first step is the pyrolysis of lignin to intermediate (mainly various phenolic compounds), and then these intermediates mainly form aromatic hydrocarbons (*e.g.*, benzenes, toluene, xylene and naphthalenes) via the decarbonylation, decarboxylation, dehydration, and hydrogen or hydride transfer, cyclization, aromatization and oligomerization reactions over the zeolite catalyst. Moreover, the theoretical yields of BTX from the biomass (represented by $C_xH_yO_z$) can be evaluated by the following stoichiometric expressions (Eqs. (3)–(5)), which assumed that biomass was converted BTX, water and CO, in view of that the observed CO content was much more than that of CO₂.



The theoretical yields of benzenes, toluene, xylene for sawdust are about 67.5C-mol%, 64.5C-mol%, 62.3C-mol%, respectively. The highest yield of BTX from sawdust was about 26.5C-mol% over HZSM-5 at 450 °C, the carrier gas flow rate of 300 cm³/min and catalyst/sawdust ratio of 2, corresponding to 64.3% of the theoretical yield. To make clear the transformation of biomass to aromatics, further study on the model compounds is required in the future work.

IV. CONCLUSION

We reported the conversion of sawdust into aromatics such as benzene, toluene, and xylenes (BTX) over the different zeolitic catalysts under various reaction conditions. The highest yields of aromatics and BTX from sawdust reached about 32.4% and 26.5% over HZSM-5 at 450 °C, the carrier gas flow rate of 300 cm³/min and catalyst/sawdust ratio of 2. The BTX selectivity was about 62.8C-mol% under the optimal condition. The acidity and pore size of the zeolite catalysts as well as the reaction parameters have important impacts on the aromatics yield and its selectivity. The catalytic cracking of sawdust involves two key steps, *i.e.*, biomass depolymerization into the monomers followed by the decarbonylation, decarboxylation, dehydration, and hydrogen or hydride transfer, cyclization, aromatization and oligomerization reactions. Production of the aromatics from sawdust can be potentially served as high-valued chemicals and bio-fuels for the petrochemical industry using the renewable biomass resource.

V. ACKNOWLEDGMENTS

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