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Renewable gasoline-range aromatics and hydrogen-enriched fuel gas from biomass via catalytic microwave-induced pyrolysis

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A novel pathway was investigated to produce gasoline-range aromatics and hydrogen-enriched fuel gas by microwave-induced pyrolysis of cellulose integrated with packed-bed catalysis in the presence of solid phase catalyst. The employed catalyst was well-promoted ZSM-5 after the couplings of hydrothermal and calcined treatments, completely converting volatile vapors derived from microwave pyrolysis into aromatics and non-condensable gases. A central composite experimental design (CCD) was employed to investigate the effects of catalytic temperature and inverse weight hourly space velocity (WHSV)⁻¹ on the pyrolysis-oils composition. It was observed that the chemical compounds of the upgraded bio-oils from catalytic microwave pyrolysis of cellulose were aromatic hydrocarbons, phenols, and aromatic oxygenates. Aromatic hydrocarbons accounted for the largest selectivity of these compounds were in the range from 82.93 to 96.60% in bio-oils depending on alterations of catalytic conditions. Up to 48.56% selectivity towards aromatics in the upgraded bio-oil belongs to gasoline-range aromatics at the mild condition. The maximum selectivity of aromatic hydrocarbons (96.60%) was gained at packed-bed temperature of 500 °C and WHSV⁻¹ of 0.067 h. Gaseous results show that hydrogen was the dominant composition, occupying approximately 40 vol.%. The high amounts of gasoline-range aromatics and valuable hydrogen is attributed to the technologies of microwave-assisted pyrolysis and ex-situ catalysis. These findings from this study pave a new route for biorefinery industries to produce developed products (aromatics and hydrogen-rich gas) through microwave-induced technologies.

1. Introduction

Growing concerns about global climate change and rapid depleting fossil-based petroleum sources have spurred interest in the utilization of renewable resources for fuels and high value-added chemicals.¹ Cellulose-based carbohydrates are the ubiquitous compounds, which have been realized to manufacture biofuels such as bioethanol instead of petroleum fuels derived from fossil sources. Although bioethanol produced from cellulosic biomass has already been added in automotive engines for improving the combustion, the low energy density (2/3 of gasoline) makes it impossible completely replace petroleum-derived gasoline.² In contrast, renewable gasoline-range aromatics rather than ethanol will be drop-in replacements for petroleum gasoline if current technological innovations contribute to competitive production costs.²

Aromatics have numerous industrial applications, and can be used as fuels additives for octane enhancement or chemical precursors for a variety of plastics and solvents.³ The demand for aromatics exceeds 200 billion lbs/year with a total market of close to \$100 billion in 2010 and compound annual growth rates from 3.1-5.4% (Chemicals Economic Handbook). Aromatics are crucial components of gasoline and fuel oils, up to 85% aromatics are dominant in Kuwaiti gasoline.⁴ Current aromatics are exclusively derived from petroleum sources. Thus discovering a green route to convert renewable resources into

aromatics will pave a new avenue towards renewable resources utilization.

Numerous attempts have been made to substitute petroleum-based aromatics; catalytic fast pyrolysis (CFP) of biomass-derived carbohydrates (e.g. cellulose) is a potential process used for converting biomass into aromatics.⁵⁻¹⁰ However, these conventional techniques were usually conducted with the harsh condition such as high consumption of energy, elevated reaction temperature, and high loading of catalysts, resulting in infeasible commercialization in biorefineries comparing with commercial formulations based on petroleum derived aromatics. Therefore the production of green aromatics from renewable biomass resources calls for an ideal technology with an efficient solid-phase catalyst to make the process economically feasible under a mild, environmentally friendly reaction condition. Instead, microwave-assisted pyrolysis technology has been proven to be one of the most promising methods for enhancing and accelerating chemical reactions due to effective heat transfer through microwave irradiation.¹¹ In comparison with traditional pyrolysis, microwave-induced pyrolysis encloses the potentials of fast and selective heating, easy control of reaction conditions, low reaction temperatures and energy requirements.^{12, 13}

Aforementioned studies were mainly engaged in the topics of production of green aromatics in the presence of ZSM-5

zeolite without any treatments. In fact, moderate treatments can be employed to tailor zeolite properties for modifications of porosity and acidity, which is essential for improving product selectivity and the quality of the bio-oil.¹⁴ Groen et al claimed that hydrothermal treatment is usually conducted to adjust the acidity of ZSM-5 zeolite and improve its stability.¹⁵ The extra-framework aluminum species derived from hydrothermal treatment also act as Lewis acid centers and improve certain catalytic activities.¹⁶ Furthermore, upon removal of the water inside the zeolite pores by calcination at elevated temperature, strong electrostatic fields are built up.¹⁶ Under the condition of the electrostatic fields, remaining water molecules dissociate into a proton bounding to Brønsted acid sites and an OH group. Thereupon mild hydrothermal and calcined conditions can favor the generation of catalytic sites specific efficiency.

Unfortunately, gas from catalytic fast pyrolysis was usually paid less attention by current researches.¹⁷⁻²⁰ The major constituents in the gaseous products including hydrogen, carbon monoxide, methane, and other light hydrocarbons can be viewed as significant reactants in a majority of refinery processes to produce energy and liquid fuels. Costly hydrogen as one of vital co-products can also be supplied for hydrotreating of aromatics to produce jet fuels. Accordingly, hydrogen-rich gas products from catalytic pyrolysis should be considered to reach the goal for price-competitive renewable aromatics. Nonetheless, there has not been a successfully attempt to produce high-concentration aromatics integrated with hydrogen-enriched fuel gas from catalytic microwave assisted pyrolysis of cellulosic biomass. Herein, this study aims to fill this knowledge gap and investigate the production of green aromatics and hydrogen-enriched fuel gas by catalytic microwave pyrolysis of cellulosic biomass under distinct reaction conditions including catalytic temperature and inverse weight hourly space velocity (WHSV)⁻¹. Well-promoted ZSM-5 via mild hydrothermal and calcined treatments was first used as a catalyst for aromatics and hydrogen-rich gas production in the process of microwave-mediated pyrolysis.

2. Experimental

2.1. Materials

The cellulose (CAS number 9004-34-6) was purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). Cellulose was in the form of microcrystalline powders and particle sizes of cellulose were averaged at 50 μm . Parent ZSM-5($\text{SiO}_2/\text{Al}_2\text{O}_3$ Mole Ratio: 50) was purchased from Zeolyst International, USA.

2.2. Catalyst preparation

In order to determine the optimum catalyst, various treatments upon ZSM-5 were conducted and compared to the parent ZSM-5. The activity of parent ZSM-5 was improved by suffering either hydrothermal or calcined treatment. In this regard, hydrothermal treatment was used to modify the parent ZSM-5 catalyst. Under the gentle stirring, parent ZSM-5 powder was added into deionized water (mass ratio=1) at 60 $^\circ\text{C}$. After addition, the mixture was kept on stirring for 2 h under this condition. The slurry was then dried at 105 $^\circ\text{C}$ till constant weight. The sequential process was the catalyst calcination: parent ZSM-5 or ZSM-5 treated was calcined at 550 $^\circ\text{C}$ for 5 h in a muffle furnace. The catalysts were partially pelletized and sieved to 20 – 40 mesh. Individual properties of catalysts from various treatments were listed in Table 2.

2.3. Catalytic microwave pyrolysis and analysis

Fig. S1 shows the schematic diagram of the microwave-assisted pyrolysis system integrated with catalysis process. Detailed procedures of microwave pyrolysis system were described in our previous studies.^{21,22} The feedstock was air dried at 105 $^\circ\text{C}$ for 24 h to remove the physically bound moisture, prior to conducting the experiments. Fixed loading of cellulose (20g) loaded in a 500 mL quartz flask was placed inside the Sineo MAS-II batch microwave oven (Shanghai, China) by a constant microwave power setting (700 W). 0.05g activated carbon powder was used as the absorber for the microwave-assisted pyrolysis of cellulose. All reactions of microwave pyrolysis

Table 1 Experimental design and product yield distribution

Run ^a	Catalytic Temperature ($^\circ\text{C}$)	WHSV ⁻¹ (h)	Yield (wt.%)			
			Bio-oil	Gas	Char	Coke
C-1	300	0.100	31.55	49.21	16.12	3.12
C-2	300	0.050	33.25	48.14	15.78	2.83
C-3	450	0.100	31.27	51.28	16.07	1.38
C-4	450	0.050	33.41	49.48	15.98	1.13
C-5	269	0.067	34.77	46.01	15.95	3.27
C-6	375	0.067	33.12	49.14	16.04	1.70
C-7	375	0.067	33.11	48.83	16.32	1.74
C-8	375	0.067	32.93	49.49	15.78	1.80
C-9	375	0.126	30.35	52.35	15.65	2.16
C-10	375	0.067	33.04	49.71	15.60	1.65
C-11	481	0.067	30.65	52.73	15.63	0.99
C-12	375	0.067	33.19	49.03	16.04	1.74
C-13	375	0.045	35.20	47.51	15.97	1.32
C-14	500	0.067	30.42	53.06	15.78	0.74
C-15	375	0.054	34.75	48.25	15.46	1.54
C-16	-	-	36.18	46.89	16.93	-

^a C-1 to C-13 was conducted based on central composite design; C-14 and C-15 were added as the controls; C-16 is the control in the absence of catalyst.

Table 2 Textural and acid properties of the ZSM-5 zeolites^a

Catalyst properties	A	B	C	D	E	F	G
BET surface area (m ² /g)	386.9	379.6	382.7	405.6	400.5	396.2	306.3
Pore (17 < dp/Å < 3000) volume (cm ³ /g)	0.078	0.082	0.080	0.091	0.107	0.097	0.063
Pore (17 < dp/Å < 3000) surface area (m ² /g)	55.3	47.9	49.0	77.6	85.4	74.1	52.1
Mesopore size (20 < dp/Å < 500) distribution (%)	98.47	97.41	97.67	98.44	98.95	98.80	70.23
Average pore size ²³	5.7	6.9	6.5	4.7	5.0	5.2	4.6

^a A: parent ZSM-5; B: hydrothermally treated ZSM-5 (Powder); C: hydrothermally treated ZSM-5 (Pellet); D: calcined ZSM-5 (Powder); E: hydrothermally treated and calcined ZSM-5 (Powder); F: hydrothermally treated and calcined ZSM-5 (Pellet); G: spent F at 500 °C with WHSV⁻¹ of 0.067 h.

were conducted at the temperature of 480 °C for 10 min. The pyrolysis volatile vapors from the flask passed through a packed bed catalysis reactor which was filled with catalyst. The packed-bed reactor customized is constructed of quartz and externally heated by a heating tape. A thermocouple was introduced between the reactor and the heating tape to measure catalytic temperature. The separate heating regimes ensured that distinctly separate temperatures in the microwave oven and packed-bed reactor were maintained.

Elemental analysis (C, H and N) of cellulose, char, and coke deposited on spent catalysts was conducted using a 2400 Series II CHN/O Elemental Analyzer (PerkinElmer, USA). Oxygen content was calculated by difference.

The textural properties of the catalyst were determined by means of N₂ adsorption–desorption (Micromeritics TriStar II 3020 Automatic Physisorption Analyzer). Fresh catalysts were degassed in vacuum at 300 °C for 1 h. Spent catalysts were degassed at 150 °C under vacuum for 2 h. The Brunauer–Emmett–Teller equation was applied to calculate the specific surface area using adsorption data at $p/p_0 = 0.05–0.25$. The pore volume was evaluated by using the Barrett–Joyner–Halenda (BJH) method.

The acidity of the catalyst was measured by temperature-programmed desorption (TPD) of ammonia with a Micromeritics AutoChem II 2920 Chemisorption Analyzer equipped with a PFEIFFER mass spectrometer. Fresh catalysts were saturated with NH₃ at room temperature in a flow of 10% NH₃ in nitrogen. After NH₃ saturation the weakly bound NH₃ was desorbed prior to the measurement at 120 °C for 1 h with a He flow rate of 25 ml/min. The desorption curve was then attained at a heating ramp of 10 °C/min from 120 °C to 550 °C at a He flow rate of 25 ml/min.

The chemical composition of the bio-oils was characterized and qualified by Agilent 7890A GC-MS (GC-MS; GC, Agilent 7890A; MS, Agilent 5975C) with a DB-5 capillary column. The GC was first programmed to heat to 45 °C for 3 min followed by heating to 300 °C at a rate of 10 °C/min. The injection sample size was 1 µL. The flow rate of the carrier gas (helium) was 0.6 mL/min. The ion source temperature was 230 °C for the mass selective detector. Compounds were identified by comparing the spectral data with that in the NIST Mass Spectral library. The area percent of compounds obtained from GC/MS results was utilized to predict products selectivity.

The moisture content in the bio-oils was determined by a Karl Fischer (KF) compact titrator (V20 Compact Volumetric KF Titrator, Mettler-Toledo).

The gaseous product was collected in a 1 L Tedlar gas bag and then offline analyzed by an INFICON 3000 Micro-GC (INFICON Inc., Santa Clara, CA, USA) system with a thermal

conductivity detector (TCD). A standard gas mixture consisting of H₂, N₂, CH₄, CO, CO₂, C₂H₄, C₂H₆, and C₃H₆ was used to calibrate the yield of non-condensable gas. Alkanes and olefins (>C₄) were either not detected or negligible in this research.

2.4. Experimental methods and data processing

A central composite experimental design (CCD) was employed to optimize the process conditions and product yields distribution (Table 1). The catalytic temperature (X_1 , °C) and inverse weight hourly space velocity, WHSV⁻¹ (X_2 , h), were chosen as independent variables. WHSV⁻¹ is defined as the mass of catalyst used in the packed-bed reactor divided by the mass flow rate of pyrolysis volatile vapors. In this experiment, the mass of catalyst related to reactant to catalyst ratio varied from 4.54 to 12.58 g, while the mass flow rate was kept constant. The WHSV⁻¹ and packed-bed temperature ranged from 0.045 to 0.126 h, 269 to 481 °C, respectively.

The coke mass was determined by the difference before and after catalytic pyrolysis. The weight of non-condensable gas was calculated using the following equation:

$$\text{Weight of gas} = \text{initial cellulose mass} - \text{liquid mass} - \text{char mass} - \text{coke mass}$$

The liquid, gas, coke, and coke yields were calculated by their corresponding masses divided by the initial reactant mass.

3. Results and discussion

3.1. Optimization of catalyst

Various treatments upon ZSM-5, compared to the parent ZSM-5, were shown in Table 2. BET surface area, pore volume, and pore surface area were significantly improved by the combined treatments. Furthermore, ZSM-5 promoted by means of the combined treatments resulted in the generation of secondary porosity (mesoporosity) in the ZSM-5 zeolite matrix. The average pore size of the modified ZSM-5 (Entry-F in Table 2) is 5.2 nm, which is very close to naphthalene diameter (5.5 nm), therefore aromatics are prone to be adsorbed in the pores.²⁴ Because the overall acid amounts can be inferred from the relative peak areas of the NH₃ desorption curves; it can be found that the acidity are similar (Fig. S2). For the catalysts modified by hydrothermal treatment, the maximum of the peak shifted towards low temperatures, which accompanied with a decrease in percentage of strong acid sites; while catalysts solely treated by calcination performed same acidity. Hence, optimal ZSM-5 used in the catalytic reaction was modified by the combined treatments and then pelletized and sieved to 20–40 mesh.

3.2. Product yields

The product yield distributions are summarized as a function of catalytic temperature and inverse weigh hourly space velocity (WHSV^{-1}) in Table 1. It was found that the yields of bio-oil and gas were in the range from 30.42 to 36.18 wt.% versus 46.01 to 53.06 wt.% respectively, showing inverse trends owing to catalytic conditions. The water content of most obtained bio-oils was around 10 wt.%, based on cellulose loading. Results indicate that catalytic temperature had significant effects on both yields of bio-oil and gas. The yield of bio-oil declined with the increase of the catalytic temperature, while the yield of gas increased with the similar increasing tendency of catalytic temperature. It is worth noting that the product yields were also affected by WHSV^{-1} . Increasing WHSV^{-1} contributed to improving the yield of gas, whereas the yield of bio-oil gradually decreased. The optimal condition for maximum bio-oils yield was presented to be a catalytic temperature of 269 °C and WHSV^{-1} of 0.067 h. By contrast, the maximum gas yield was predicted at 500 °C and WHSV^{-1} of 0.067 h. When pyrolysis without catalyst, the bio-oil yield went up to 36.18 wt.% as gas yield simultaneously decreased to 46.89 wt.%. Similar phenomenon was observed by other studies as a result of catalytic temperature and WHSV^{-1} affecting product (bio-oil, gas) yields.^{22, 25}

Solid carbonaceous residue (char and coke) from degraded and catalytic processes can be distinguished due to the ex-situ catalysis. The char yield remained virtually constant at 16 wt.%, suggesting that cellulose loaded in the microwave oven was almost decomposed to volatile compounds. Given the coke deposited on the catalyst resulting in decrease of the active sites and micropores blockage,²⁶ the carbonaceous compounds were a crucial element to be taken into consideration in the study of formation mechanism when zeolites are employed as catalysts. The coke deposition yields as a function of catalytic temperature and WHSV^{-1} is also depicted in Table 1, varying from 0.74 to 3.27 wt.%. As expected, the minor coke deposition was affected by short residence times set at 10 mins, which abated the formation of coke precursors. Formation and deposition of coke was attenuated as the catalytic temperature was increased, declining to below 1 wt.%. It was noticeable that spent ZSM-5 derived from catalytic process at 500 °C still showed high BET surface area, pore volume, and pore surface area (Table 2). Results imply that elevated temperature promoted the cracking reaction of pyrolytic volatiles on the catalyst towards small molecules. Rather, as more catalysts were loaded, more retention time of catalysis will be provided for pyrolytic volatiles to form more polycyclic aromatics, easily generating coke on the catalyst.

3.3 Analysis of the bio-oils

3.3.1. Chemical composition of bio-oils

In order to further understand the chemical reaction of catalytic microwave pyrolysis of cellulose to maximize aromatics content, the chemical compositions of bio-oils were identified and partially quantified by GC/MS. It was observed that the chemical compounds of the upgraded bio-oils from catalytic microwave pyrolysis of cellulose were aromatic hydrocarbons, phenols, and aromatic oxygenates. Aromatic hydrocarbons accounted for the largest selectivity of these compounds were in the range from 82.93 to 96.60% in bio-oils depending on alterations of catalytic conditions. The maximum selectivity of aromatic hydrocarbons (96.60%) was received at packed-bed temperature of 500 °C and WHSV^{-1} of 0.067 h as described in the experiment of Run C-14. Phenols in the

upgraded bio-oils were from 2.51 to 13.41% followed by aromatic oxygenates with an identical tendency from 0.53 to 3.66%. Compared with the optimal result with fresh catalyst at 500 °C and WHSV^{-1} of 0.067 h, spent catalyst reused under this condition still displayed fairly decent catalytic performance, achieving 67.43% aromatic hydrocarbons together with 9.40% phenols (see Fig. S3).

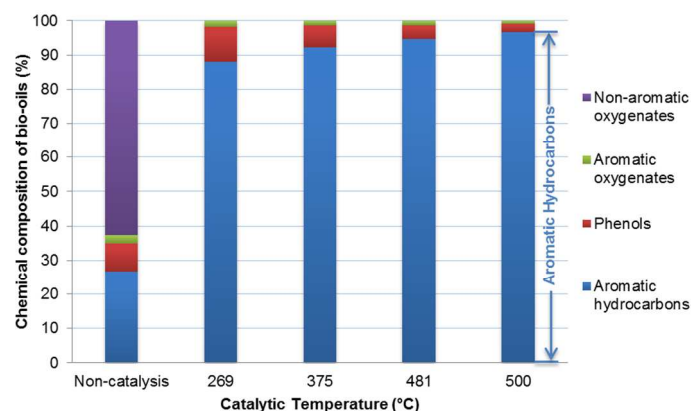


Fig.1 Chemical composition of bio-oils on the base of catalytic temperature at the same WHSV^{-1} of 0.067 h.

3.3.2. The effects of catalytic temperature on the chemical composition of bio-oils

Fig. 1 shows representative results of bio-oils regarding the chemical compounds on the base of catalytic temperature at the same WHSV^{-1} of 0.067 h. In comparison with the bio-oil obtained by non-catalytic pyrolysis of cellulose, the amount of aromatic hydrocarbons in bio-oils derived from catalytic microwave pyrolysis significantly increased. It can be seen that aromatic hydrocarbons were in the range from 88.07% at 269 °C to 96.60% as catalytic temperature increased to 500 °C, implying that a high catalytic temperature favored high selectivity of aromatic hydrocarbons. Aromatic hydrocarbons obtained were predominantly comprised of toluene, xylenes, trimethylbenzenes, indane, indene, naphthalene, and their derivatives. Up to 48.56% selectivity of gasoline-range aromatics (mono-ring aromatic hydrocarbons) were dominant in upgraded bio-oil at the mild condition of 269 °C, indicating a decreased trend as the catalytic temperature increased. Among gasoline-range aromatics, xylenes are the petrochemical intermediates to synthesize fibers, plasticizers and resins, for which there is an urgent market demand in petrochemical industry.²⁷ On the contrary, it is noted that a total selectivity (39.52 - 49.83%) of naphthalene and methyl substituted naphthalene, such as methylnaphthalene and dimethylnaphthalene, were received along with the increment of catalytic temperature from 269 to 500 °C. As reported previously for the formation of mesopores in the modified ZSM-5 catalysts by the treatment and the interconnection of the 10-membered ring pores, the pores can provide enough volume for aromatization and hydrogen transfer reactions. The active sites located at these areas may serve as the reaction sites for the generation of the double-ring aromatic hydrocarbons. Such high selectivity of naphthalene and its derivatives can be hydrotreated to cyclic alkanes with the addition of hydrogen from the process of catalytic microwave pyrolysis. Therefore they can be considered as the precursors of jet and rocket fuels in the aviation field.

The carbon yield of aromatic hydrocarbons as a function of catalytic temperature at WHSV^{-1} of 0.067 h was summarized in Table S1. Over 20 wt.% aromatics were obtained under catalytic conditions, which is similar to other studies.²⁸ It is well known that oxygenates were converted into aromatic hydrocarbons through a

series of decarbonylation, decarboxylation, dehydration, and oligomerization reactions, rejecting the oxygen content in the form of CO₂, CO, H₂O.^{5, 29} To investigate quantitatively these deoxygenated pathways during the catalytic pyrolysis, oxygenated product distribution on the basis of catalytic temperature was demonstrated in Table S2. It was found that decarboxylation and dehydration were the dominant deoxygenated reactions in the catalytic process.

Phenols are vital synthetic materials in chemical industries for synthesizing PF resin, medicines and so forth.³⁰ A maximum selectivity of phenols (10.26%) including phenol, methyl phenol, and ethyl phenols was gained at the catalytic temperature of 269 °C; whereas aromatic hydrocarbons showed the lowest selectivity at this condition. These results indicate that high catalytic temperature favored the scission of hydroxyl group from phenyl to form aromatic hydrocarbons. It is also noteworthy that the rest contents of upgraded bio-oils were aromatic oxygenates, mainly consisting of benzofuran and its derivatives which can be converted into synthetic resins used in manufacturing and adhesives for food packaging.

The concentrations of four main compounds (*p*-xylene, naphthalene, phenol, and furfural) were also quantified by GC/MS. The concentration of *p*-xylene increased from 0.010 g/mL without catalysis to 0.080 g/mL at the catalytic temperature of 269 °C, whilst the highest concentration of naphthalene (0.075 g/mL) was obtained at the catalytic temperature of 500 °C compared with the lowest concentration of 0.019 g/mL in the absence of catalyst. For the concentration of phenol, the maximum was 0.073 g/mL at the catalytic temperature of 269 °C, while the concentration of phenol in raw bio-oil was only 0.038 g/mL. In the catalytic groups, there was no furfural detected in comparison with non-catalytic pyrolysis at the concentration of 0.086 g/mL. Thereafter the furanic compounds which may act as intermediates, diffused into the modified catalyst pores and went through a series of decarbonylation, decarboxylation, dehydration, and oligomerization reactions to form monocyclic aromatics.^{5, 29} This observation is the key point to identify the reaction mechanisms resulting in this high aromatic hydrocarbon selectivity. The actual mechanism of the furans-to-aromatic hydrocarbons (FTAH) process inside the catalyst pores can be proposed according to hydrocarbon pool model as illustrated in Fig. S4. The cooperation of the entrained aromatic component inside the inorganic zeolite framework possibly created a rather unique reaction route. The inorganic zeolite framework acted as the dehydration, oligomerization, aromatization and methylation center for the generation of aromatic hydrocarbons. polymethylbenzenes mainly worked as the entrained aromatic compounds because naphthenic species usually have a high energy barrier.³¹ The crucial reaction mechanism of hydrocarbon pool may be that furans reacted with entrained hydrocarbon species in the catalyst including a series of complicated steps to form the aromatic hydrocarbons and olefinic products during the catalytic cycle.

3.3.3. The effects of WHSV⁻¹ on the chemical composition of bio-oils

The chemical composition of bio-oils from catalytic microwave pyrolysis at 375 °C as a function of WHSV⁻¹ was explained in Fig. 2. Compared with the lowest aromatic hydrocarbons content (26.64%) evolved from pyrolysis without the addition of catalyst, the content increased gradually from 82.93 to 94.24 % with the increase of WHSV⁻¹ from 0.045 to 0.126 h, which is consistent with the similar trend claimed by other researches.^{25, 32} The phenols fraction was fluctuant caused by WHSV⁻¹, which first increased from 8.33% (the control) to 13.41% (WHSV⁻¹ of 0.045 h) and then decreased to 5.33% with the increase of WHSV⁻¹ to 0.126 h. As such, the content of aromatic oxygenates had the same tendency as phenols from 2.35

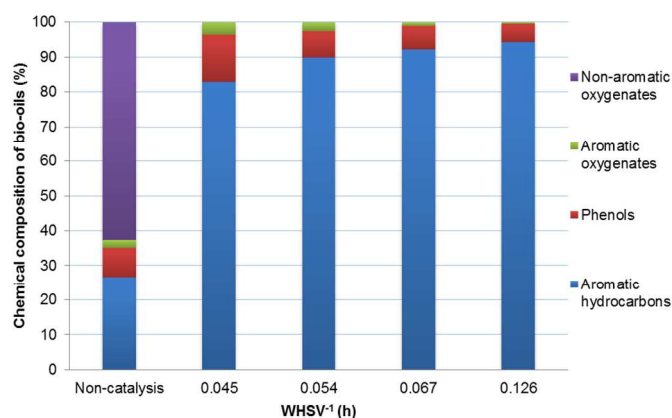


Fig.2 Chemical composition of bio-oils as a function of catalytic temperature at the same temperature of 375 °C.

to 0.53%. In the upgraded bio-oils, there were no any non-aromatic oxygenates detected. It was confirmed that pyrolysis volatiles generated were completely catalyzed online when going through the catalytic reactor. Thus introduction of the catalysts into pyrolysis could convert oxygenated compounds into aromatics and phenols effectively, which is identical to other research.³³

The WHSV⁻¹ also had a significant effect on the species of aromatics. As for the total amount of gasoline range aromatics and double-ring aromatic hydrocarbons, increasing the WHSV⁻¹ contributed to dramatically enhancing the former selectivity from 38.96 to 49.54 % in upgraded bio-oils; while results obtained for the latter content were around 43%. Hence most volatile oxygenates from microwave pyrolysis were converted into mono-cyclic aromatic hydrocarbons, the mono-cyclic aromatic hydrocarbons may not readily react with oxygenates to further form polycyclic aromatic hydrocarbons at this catalytic temperature. It was noted that the concentrations of *p*-xylene and naphthalene increased appreciably from 0.010 g/mL and 0.039 at the control to 0.137 g/mL and 0.069 g/mL at the WHSV⁻¹ of 0.126, respectively; while the concentration of phenol first went up from 0.039 g/mL at the control to 0.087 g/mL and subsequently declined to 0.048 g/mL as WHSV⁻¹ increased from 0.045 to 0.126 h. The variations of the chemical composition in bio-oils affected by the alteration of WHSV⁻¹ were much alike other researches' results.^{5, 34} These outcomes suggest that a higher WHSV⁻¹, which means more active sites were offered to volatile vapors in unit time, resulted in more severe zeolite cracking, oligomerization, aromatization reactions occurs in the pack-bed reactor.

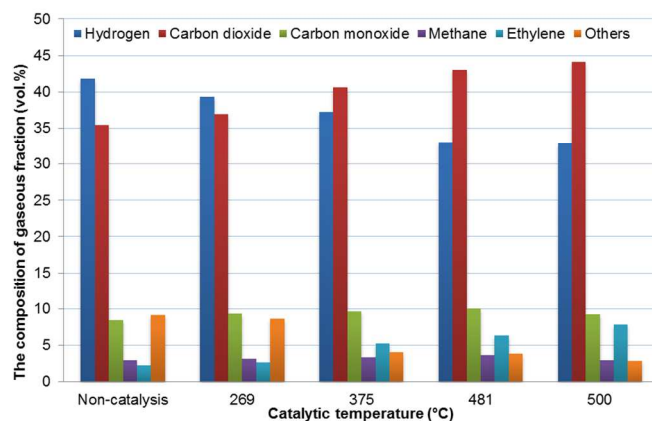


Fig.3 The composition of gaseous fraction with respect of catalytic temperature at the same WHSV⁻¹ (0.067 h)

3.4 Analysis of non-condensable gases

Gas was one of the major co-products of cellulose from packed-bed catalysis integrated with microwave pyrolysis. The composition of the gases were detected and quantified by Micro-GC, which would be helpful to investigate the reaction pathways in the packed bed reactor. The gas yield varied from 46.01 to 53.06 wt.% in comparison with no catalyst loaded in the packed bed reactor observing 46.89 wt.% gas yield as shown in Table 1. The large amount gas should be attributed to the modified catalyst in the process that can facilitate the cracking reaction of volatiles toward small molecules from decomposition of cellulose. The non-condensed gas was mainly comprised of hydrogen, carbon dioxide, carbon monoxide, methane, and light olefins such as ethylene.

The composition of gaseous fraction with respect to catalytic temperature is depicted in Fig. 3. Results indicates that hydrogen was the dominant composition from 41.83 to 32.89 vol.%. It is attributed to the technology of microwave-assisted pyrolysis inducing hot spots where are capable of producing hydrogen-rich fuel gas. Unlike the conventional pattern of pyrolysis with low heating rate, microwave-mediated pyrolysis with a focused and high heating rate can readily induce hot spots inside biomass.¹⁷ This high amount of hydrogen can be supplied for the hydrogenation of aromatics or fuel gas. The concentrations of carbon dioxide, carbon monoxide, and methane gradually went up as the catalytic temperature increased, which verifies that decarbonylation, decarboxylation, and oligomerization reactions on the catalyst were promoted by increasing catalytic temperature. Owing to the reducing characteristics of syngas (H_2 , CO), they could react with oxygen content in pyrolysis volatiles to generate water and CO_2 . More aromatic hydrocarbons obtained at high catalytic temperature as reported previously; hence oxygenated compounds derived from decomposition of cellulose were reduced by the reducing syngas. As the more reducing syngas was consumed, consequently the less reducing syngas was gained, which was consistent with GC results as shown in Fig. 3. CO derived from furans decarbonylation reaction offset the consumption for deoxygenation reaction. Wherefore the content of CO was kept at the higher level from catalytic pyrolysis than parent pyrolysis. High amount of CO_2 not only arose from decarboxylation reaction but also was produced from CO reducing conversion, which was correspondingly increased as catalytic temperature was elevated. As expected, the maximum selectivity of xylenes (12.39%) and toluene (8.77%) in the upgraded oils were received at catalytic temperature of 500 °C, which suggests that the elevated temperature favored the formation of xylenes and toluene. High selectivity of *p*-xylene (12.39%) at 500 °C arises from the removal of strong acid sites in catalysts after hydrothermal treatment suppressing disproportionation, transalkylation, which is in

agreement with the former observation.³⁵

According to the detailed production distributions, The proposed reaction pathway for furfural conversion to xylenes and toluene is described in Fig. 4. It was proposed that furfural initially underwent decarbonylation reaction to form allene (C_3H_4) and CO.³⁶ Since there were no any furfural compounds being detected in the catalytic experiments, they could act as the intermediates to be completely transformed. The allene could go through either aromatization to generate benzene or oligomerization and crackings to form propylene, hydrogen and cyclopentadiene.³⁶ The alkylation of benzene readily occurred under the high temperature condition due to the active feature of benzene. Thus propylene that served as the intermediate compound could react with benzene through alkylation to produce xylenes, toluene and ethylene. Meanwhile, toluene formed could further react with propylene to generate xylenes via alkylation. From the reaction pathway of furfural conversion into xylenes, proportion of ethylene as by-products could be viewed as an index of aromatic formation for catalytic pyrolysis of cellulose. Increasing proportion (2.23 – 7.79 vol.%) of ethylene as a function of catalytic temperature was in accordance with the rising xylenes yield in Fig. 3. Accordingly, the product distribution not only confirms that aromatic hydrocarbon originated from furans derived from cellulose, but also reaffirms the convergence of intermediate products to aromatic hydrocarbons.

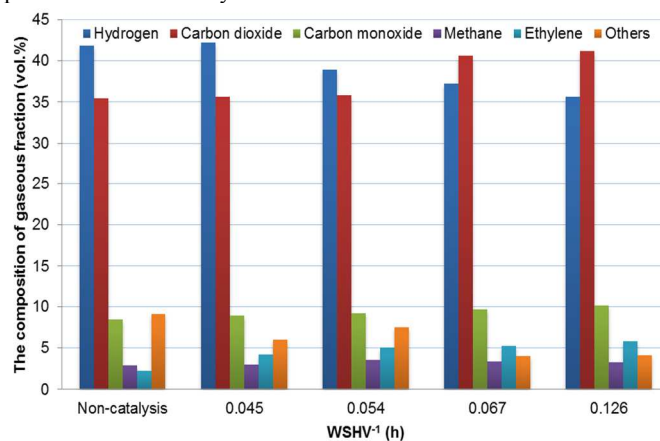


Fig.5 The composition of gaseous fraction as a function of $WHSV^{-1}$ at the same catalytic temperature (375 °C)

The development of the gaseous composition as a function of $WHSV^{-1}$ is illustrated in Fig. 5. The yield of hydrogen was first increased slightly as the catalyst was employed, albeit in a less pronounced way; it was thereafter decreased due to the

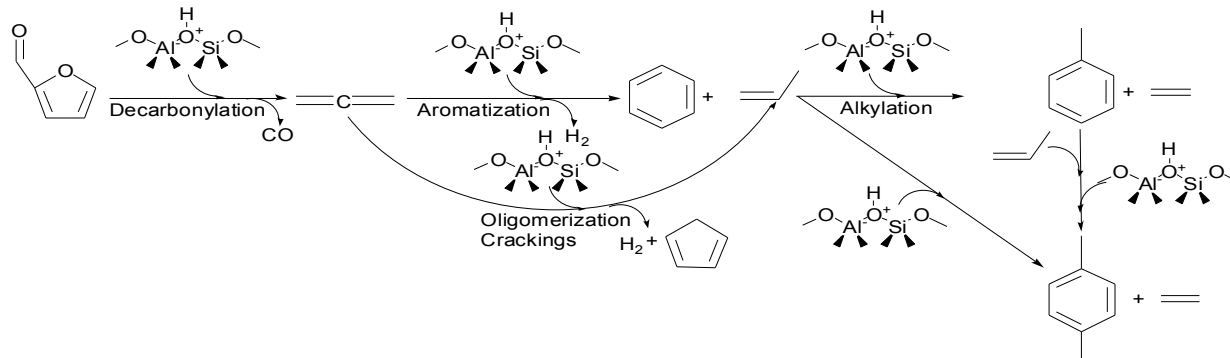


Fig. 4 The proposed reaction pathway for furfural conversion to xylenes and toluene over modified ZSM-5.

hydrogen-consumed reactions dominating the catalytic process. The yield of carbon dioxide was found to increase in the most pronounced way from 35.48 vol.% at the control to 41.15 vol.% at WHSV⁻¹ of 0.126 h, which suggests that more catalyst added in the process accelerated the decarboxylation reaction in the process. With the increasing addition of the catalyst, the amounts of gases with such as ethylene and methane generally increased. These gaseous results imply that in addition to aromatics, catalytic microwave pyrolysis of cellulosic biomass can be tuned to generate hydrogen-enriched fuel gas, which can be used either directly as energy or fuel precursors after upgrading.

4. Conclusions

This study investigated that renewable gasoline-range aromatics and hydrogen-rich fuel gas can be produced from catalytic microwave pyrolysis of cellulose over modified ZSM-5. GC-MS analysis showed aromatic hydrocarbons were the most abundant compounds which were approximately 82.93 – 96.60% in upgraded bio-oils, depending on the catalytic pyrolysis conditions. Over 20 wt.% carbon yield of aromatics were obtained under various catalytic conditions. Decarboxylation and dehydration were the dominant deoxygenated reactions in the catalytic process. The non-condensable gases (46.01 - 53.06 wt.% based on cellulose mass) were mainly composed of hydrogen, carbon dioxide, carbon monoxide, methane. The share of hydrogen was from 41.83 to 32.89 vol.%, which was the dominant composition in the gases fraction. The coke deposition yield varied from 0.74 to 3.27 wt.%; spent catalyst also showed decent catalytic performance due to the quite high BET surface area, pore volume, and pore surface area. Significant quality of bio-oils and flexibility of catalytic microwave mild conditions provide competitive merits compared with conventional methods from petroleum resources. From this perspective it was proved that cellulosic biomass can be used to generate developed products (aromatics and hydrogen-rich gas) through catalytic microwave-induced pyrolysis.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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A pathway for producing renewable gasoline-range aromatics and hydrogen-enriched fuel gas from biomass via catalytic microwave-induced pyrolysis

