Microwave-assisted catalytic fast pyrolysis of spent edible mushroom substrate for bio-oil production using surface modified zeolite catalyst

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ABSTRACT

In order to minimize coke yield and improve hydrocarbon production during microwave-assisted catalytic fast pyrolysis of spent edible mushroom substrate, ZSM-5 zeolite catalyst is modified with pre-coking treatment, chemical vapor deposition of SiO₂, and ethylene diamine tetraacetic acid (EDTA) chemical modification method, respectively (labeled PC-ZSM-5, SiO₂-ZSM-5 and EDTA-ZSM-5). Experimental results show that all the modification methods result in a loss of external acid sites of ZSM-5. Among the three modified catalysts, the

maximum oil fraction yield and the minimum coke yield are obtained with SiO₂-ZSM-5. The relative content of hydrocarbons in oil fraction increases in the following order: SiO₂-ZSM-5 > EDTA-ZSM-5 > PC-ZSM-5 > original ZSM-5. Moreover, SiO₂-ZSM-5 shows the highest relative contents of toluene and xylene, whereas original ZSM-5 produces the lowest ones. Besides, the selectivity of benzene in aromatics follows the order of original ZSM-5 > EDTA-ZSM-5 > PC-ZSM-5 > SiO₂-ZSM-5, while the selectivity of toluene + xylene presents the opposite trend.

Keywords:

Microwave heating

Spent edible mushroom substrate

Zeolite catalyst

Surface modification

1. Introduction

Energy sustainability, environmental issues, and the security of national energy supplies are the major driving forces in developing alternatives for fossil-based raw materials and energy. In this regard, solid biomass, the only carbon neutral renewable resource, has been researched widely for its direct conversion into liquid fuels (hereinafter “bio-oil”) [1,2]. Spent edible mushroom substrate (SEMS) is the waste derived from edible mushroom farms during cultivation and harvesting period, which can be used as biomass feedstock, soil amendment and fertilizer [3,4]. The common components in SEMS comprise corn cob, wood chip and cottonseed hull, and SEMS

consists of considerable quantities of cellulose, hemicellulose and lignin like other biomasses. Therefore, SEMS is a good biomass candidate and can be very important as well. Nowadays, Chinese edible mushroom industry has achieved a very rapid development, and some mushrooms can grow up very fast on the waste biomass under very limited sunlight, thus leading to the production of a large amount of SEMS. As the largest edible mushroom production country, the total amount of SEMS reached more than 8 million tons per annum in China [5]. These large quantities of SEMS exceed the amount that is being used in agricultural application. Nowadays, the main methods for treatment and disposal of excessive SEMS mainly include dumping, incineration and anaerobic digestion. However, they all can cause secondary environmental problems and have become less acceptable [6,7].

To date, catalytic fast pyrolysis (CFP) technology, which employs fast pyrolysis process and acidic catalysts, is one of the most promising methods to achieve high-quality bio-oil from biomass and has been receiving increasing attention [8,9]. However, it should be emphasized that few researches are focused on the CFP of SEMS. In all acidic catalysts, ZSM-5 zeolite has exhibited an excellent performance for removing oxygenates and producing hydrocarbons during biomass CFP process [10]. Unfortunately, the addition of ZSM-5 also results in the formation of coke on its surface, with a consequence of rapid catalyst deactivation and a decrease in the yield of targeted hydrocarbons. In ZSM-5-catalyzed biomass CFP reactions, some oxygenates with bulky molecule cannot enter the internal intracrystalline pores of ZSM-5 zeolite and will polymerize and form coke on the external surface [11,12].

69 Actually, it is the internal acid sites of ZSM-5 that have catalytic effect to favor
70 hydrocarbon production, while the external acid sites produce coke. In order to retard
71 coke formation and promote hydrocarbon production, it is necessary to eliminate the
72 external acid sites of ZSM-5 but meanwhile keep the internal acid sites. Recently, we
73 selectively passivated the external acid sites of ZSM-5 catalyst by means of
74 pre-coking treatment, chemical vapor deposition of inert silica ($\text{SiO}_2\text{-CVD}$), and
75 EDTA chemical modification method (referred as PC-ZSM-5, $\text{SiO}_2\text{-ZSM-5}$ and
76 EDTA-ZSM-5) [13-15]. As pre-coking modified catalyst, PC-ZSM-5 already has
77 some coke deposited on its external surface, thus reducing its external acid sites and
78 improving the external acidity and activity. As a result, appropriate pre-coking can
79 reduce coke yield and promote the production of target products. For $\text{SiO}_2\text{-ZSM-5}$,
80 the modifying precursor used is tetra-ethyl-orthosilicate (TEOS). As a large-molecule
81 compound, TEOS molecule cannot enter the narrow intracrystalline void space of
82 ZSM-5. Consequently, only external acid sites of ZSM-5 can be deposited by SiO_2 via
83 thermal decomposition of TEOS, while the acid sites on the internal surface are not
84 influenced. In this paper, we hypothesize that external surface silanization of ZSM-5
85 will retard coke formation and promote catalytic effect. On the other hand, external
86 acid sites of ZSM-5 are closely related to the framework aluminums on the outer
87 surface. Therefore, in order to promote the anti-coking property of ZSM-5, EDTA
88 chemical modification method can be applied to remove the outer framework
89 aluminums. As a bulky compound, molecular structure of EDTA is incapable of
90 entering into the internal channels of ZSM-5, so the external acid sites will be

removed selectively by EDTA during modification, whereas the internal acid sites will be kept intact. Compared to the parent ZSM-5, all these surface modified catalysts showed a better shape-selective effect for the formation of hydrocarbons in biomass CFP process.

Microwave-assisted catalytic fast pyrolysis (MACFP) is a relatively novel technique by heating biomass and catalyst with microwave irradiation. MACFP offers many advantages over conventional heating process, including internal fast and uniform heating of large-size particles, no need for particle grinding, agitation or fluidization, instantaneous response for rapid start-up and shut down, ease of control, and energy cost saving. Recently, MACFP technique has been successfully applied to processing biomass and produce bio-oil [16-18].

In this work, MACFP of SEMS for bio-oil production over different surface modified ZSM-5 catalyst (PC-ZSM-5, SiO₂-ZSM-5 and EDTA-ZSM-5) was carried out in a microwave chamber. The catalytic characteristics of these catalysts for production distribution, chemical compositions in oil fraction and aromatic production were studied and compared. The flow chart for the whole experimental procedure is shown in Fig. 1.

2. Experimental

2.1 Materials

SEMS was achieved from an edible mushroom farm in the city of Nanjing of

Jiangsu Province, China. Prior to experiment, all the SEMS samples were dried at 105 °C for 24 h, and pulverized and grinded mechanically to a particle size of 0-0.5 mm in diameter. The proximate analysis of SEMS (on air-dry basis) was 9.22 wt.% moisture, 64.16 wt.% volatile, 12.94 wt.% ash, and 13.68 wt.% fixed carbon. The elemental composition of SEMS (on dry, ash-free basis) was 39.47 wt.% carbon, 5.24 wt.% hydrogen, 54.62 wt.% oxygen, 0.56 wt.% nitrogen and 0.11 wt.% sulfur. The component analysis of SEMS (on dry basis) was 30.83 wt.% cellulose, 24.39 wt.% hemi-cellulose, and 20.43 wt.% lignin.

The ZSM-5 zeolite catalyst (Si/Al=50, surface area=308 m²/g, particle diameter = 2-5 μm) in the hydrogen form used in this experiment was purchased from the Catalyst Plant of Nankai University, Tianjin, China. Methanol (analytical grade chemical) and the silicon alkoxide TEOS (analytical grade chemical) were purchased from Aladdin Company, EDTA-2Na (AR, EDTA chemical modification reagent) was obtained from Nanjing Chemical Reagent Co. Ltd., and 1,3,5-tri-iso-propyl-benzene (1,3,5-TIPB, analytical grade chemical) was bought from Sigma-Aldrich Corporation.

2.2 Modification of ZSM-5

In this experiment, PC-ZSM-5 was achieved by pre-coking of fresh ZSM-5 via methanol to olefin (MTO) reaction: ZSM-5 catalyst was pre-coked in a laboratory-scale tubular reactor with an inner diameter of 15 mm and a length of 1000 mm, externally heated by an electric heater. Before pre-coking, 0.5 g ZSM-5 catalyst was placed in a heated section in the reactor. Methanol was fed into the reactor, and

then evaporated and passed through the ZSM-5 catalyst layer at 450 °C with a constant rate of 30 ml/h, leading to the MTO reactions and thus, some coke was formed on the external surface of ZSM-5. Besides, nitrogen gas with a constant rate of 300 ml/min was introduced into the reactor and served as the carrier gas. The treatment time was 2 h. After modification, PC-ZSM-5 catalyst was dried at 120 °C for 1 h and then collected carefully. In this paper, the pre-coking percentage of PC-ZSM-5 is 2.4%.

SiO₂-ZSM-5 samples were attained by SiO₂-CVD modification, which is described as follows: 0.5 g ZSM-5 catalyst was modified for silylation in above-mentioned reactor. A 1.0 wt.% TEOS solution in 50:50 (v/v) methanol and toluene was introduced into the reactor, and then evaporated and passed through the ZSM-5 catalyst layer at 250 °C with a constant rate of 10 ml/h. Hydrogen flow with a constant rate of 50 ml/min was introduced into the reactor and played as the carrier gas at the same time. The treatment time was 2 h. After modification, ZSM-5 catalyst was calcined at 550 °C for 10 h in air for the degradation of TEOS into SiO₂. In this paper, the SiO₂ deposited amounts of SiO₂-ZSM-5 is 2.5%.

EDTA-ZSM-5 samples were obtained by EDTA chemical modification, which is described as below: 0.33 mol/L EDTA solution and parent ZSM-5 catalyst were fully mixed at 80 °C water bath for 2 h with a liquid to solid mass ratio of 10:1. Then the achieved mixture slurry went through vacuum filtration with deionized water washing until the pH of the filtrate became 7.0. At last, the modified samples were dried at 120 °C for 2 h and then combusted at 500 °C for 4 h to remove EDTA residues.

157

158 *2.3 Determination of external acid sites*

159 The extent of inactivation of the external acid sites of modified ZSM-5 samples
160 was evaluated through catalytic cracking of 1,3,5-TIPB in a fixed bed, which was
161 described elsewhere [11].

162

163 *2.4 Apparatus*

164 The tests of SEMS MACFP were carried out in a microwave oven (MAX, CEM
165 Corporation) with a power of 750 W and a frequency of 2450 MHz. A schematic of
166 the experimental setup is shown in Fig. 2. During the experiment, SiC particles
167 (particle size: 30-grit) were used as the microwave absorbent, whose temperature
168 could increase very quickly when microwave was absorbed by them. Five hundred
169 grams of SiC particles were first placed into the quartz reactor to form a microwave
170 absorbent bed, which was then put into the cavity of the microwave oven. After the
171 quartz inlet and outlet tubes were connected, 0.25 g ZSM-5 catalyst and some SiC
172 particles were fully physically mixed and placed into the bottom of quartz outlet
173 connector to form a second fixed bed, which was used for the upgrading of primary
174 pyrolysis vapors. The microwave oven was turned on for heating process. When the
175 temperature of the first and second fixed beds ((7) and (8)) reached the desired
176 temperature (500 °C), 5 g SEMS was introduced into the reactor semi-continually
177 through the SEMS feeder and pyrolysis reactions occurred once SEMS was dropped
178 onto the hot SiC bed (7). Then the primary pyrolysis vapors were upgraded when they

passed through the fixed bed (8). A pulse width modulation (PWM) control was used to keep the microwave oven on and off every 15 s to maintain the desired reaction temperature of (7) and (8). The vacuum degree of the experimental system was kept at 250 mm Hg to maintain an inert atmosphere in the reactor. Each experiment ran 45 min. For safety purpose, a microwave detector (MD-2000, Digital Readout) was used to monitor microwave leakage.

2.5 Products analysis

After each experiment, the solid residue (coke and char) was cooled to room temperature. The spent ZSM-5 samples were collected carefully and dried at 120 °C for 1 h. Then the dried samples were put into a muffle furnace for combustion (650 °C, 2 h) so that the coke yield could be determined. Besides, the char yield was calculated by the weigh difference of the quartz reactor with and without char. The bio-oil (oil fraction and water) yield was determined by the weigh difference of the bio-oil collector before and after each experiment, while the gas yield was determined by difference according to mass balance ($\text{Gas yield} = 100\% - \text{Coke yield} - \text{Char yield} - \text{Bio-oil yield}$). The water content in bio-oil was determined using the method of Karl Fischer Titration. The yield of oil fraction in bio-oil was determined by difference ($\text{Oil fraction yield} = \text{Total bio-oil yield} - \text{Water content in bio-oil} \times \text{Total bio-oil yield}$). Each experiment was repeated at least twice under the same conditions, and their average values were calculated and used for discussion.

The chemical compositions in oil fraction were identified with a gas

chromatography / mass spectrometer (GC/MS) instrument (7890A/5975C, Agilent). High-purity helium was used as carrier gas (1.2 mL/min). The oven temperature was 40 °C, which was held for 3 min initially and then increased to 290 °C with a heating rate of 5 °C/min. It was held at 290 °C for 5 min. The GC/MS injector temperature of 250 °C and detector temperature of 230 °C were held. The GC separation was carried out using a capillary column named HP-5 MS. A split ratio of 1:10 was used with the injection size of 1 µL. The chromatographic peaks were discriminated and analyzed by means of the National Institute of Standards and Technology (NIST) mass spectral data library. Relative content of each component in the bio-oil was determined by calculating its chromatographic area percentage.

3. Results and discussion

3.1 Porosity and acidity characteristics of ZSM-5 catalysts

Porosity characteristics of original and modified ZSM-5 samples were determined by N₂-adsorption analysis, and the BET equation was used for the calculation of surface area. The results are listed in Fig. 3(a) and (b). As can be seen, all the modification treatment gave rise to a loss of BET surface area and pore size of ZSM-5 samples in contrast with original catalyst. The results showed reductions of 6.32, 6.01 and 5.99% in the BET surface area of ZSM-5 samples after pre-coking, SiO₂-CVD and EDTA chemical modification treatment, respectively.

In this study, catalytic cracking of 1,3,5-TIPB was performed to investigate the

extent of inactivation of the external acid sites of original and modified ZSM-5, and Fig. 3(c) presents the conversion efficiencies of 1,3,5-TIPB over different ZSM-5 samples. It could be found that all the pre-coking, SiO₂-CVD and EDTA chemical modification treatment resulted in a decrease in the conversion efficiency of 1,3,5-TIPB. This illuminates that all these surface modification methods can selectively eliminate the outer acid sites of ZSM-5 catalyst.

3.2 Product yields

The product distribution of catalytic fast pyrolysis of SEMS over original and modified ZSM-5 catalysts in the MACFP reactor is shown in Fig. 4. In this paper, microwave assisted non-catalytic fast pyrolysis (non-MACFP) of SEMS was also conducted at 500 °C. In contrast with non-MACFP process, MACFP process resulted in a decrease in the yield of oil fraction and increase in the yields of water and gas. ZSM-5 samples have a 3-dimensional intersecting pore structure with 10-membered rings of straight 0.53×0.56 nm channels and sinusoidal 0.51×0.55 nm channels, and the intersection cavity of ZSM-5 is 0.9 nm. When the primary pyrolysis vapors passed through the ZSM-5 catalyst layer, they were adsorbed by ZSM-5 catalyst first, and then several reactions occurred inside the small pore size, internal structure and internal volume including dehydration, decarboxylation, isomerization and decarbonylation, thereby removing oxygen as water and light gas (CO, CO₂ and other light non-condensable gases) [19]. As the result, the use of different ZSM-5 catalyst can reduce the yield of oil fraction and increase the yields of water and gas.

For MACFP process, PC-ZSM-5, SiO₂-ZSM-5 and EDTA-ZSM-5 led to a decrease in the yields of coke and oil fraction and increase in the yields of water and gas compared to original ZSM-5. As mentioned above, all these three surface modification methods can selectively eliminate the external acid sites of ZSM-5 catalyst. Consequently, coke formation was restrained through pre-coking, SiO₂-CVD and EDTA chemical modification treatment, thus decreasing the coke yield. On the other hand, the removal of external acid sites and decrease of coke yield could improve catalyst life and promote catalytic reactions. In this regard, more primary product vapors could diffuse into the internal pores of ZSM-5 and be converted, producing more water and light gas. Therefore, the yield of oil fraction decreased and the yields of water and gas increased over modified ZSM-5 samples.

Among PC-ZSM-5, SiO₂-ZSM-5 and EDTA-ZSM-5, the maximum yields of oil fraction was obtained with SiO₂-ZSM-5 catalyst, which is 16.0%. On the other hand, the yield of coke is shown the minimum value (2.2%) with SiO₂-ZSM-5. MACFP of SEMS with PC-ZSM-5 produced the lowest yield of oil fraction (14.8%) and the highest yield of coke (3.0%). The yield of oil fraction decreases and the yield of coke increases in the following order: SiO₂-ZSM-5 > EDTA-ZSM-5 > PC-ZSM-5. This result shows that SiO₂-CVD performs best to minimize coke yield among all the there modification methods.

3.3 Chemical compositions of oil fraction

The chemical compositions of oil fraction determined by GC/MS could be

classified into different chemical families: aliphatic hydrocarbons, aromatic hydrocarbons, oxygen-containing aliphatic compounds, oxygen-containing aromatic compounds and others (nitrogen-containing compounds and unidentified compounds). [Fig. 5\(a\)](#) shows the relative contents of different chemical families of oil fraction. It was found that there were almost no hydrocarbons in the oil fraction from non-MACFP of SEMS (the relative contents of aliphatic hydrocarbons and aromatic hydrocarbons in the oil fraction were only 0.468% and 0.471%, respectively), and the oil fraction mainly consisted of oxygenates. On the other hand, as could be seen, the addition of different ZSM-5 samples gave rise to a significant increase in the relative contents of aliphatic hydrocarbons and aromatic hydrocarbons and decrease in the relative contents of oxygen-containing aliphatic compounds and oxygen-containing aromatic compounds. Series catalytic deoxygenation reactions could occur inside the internal structure of catalyst when ZSM-5 was used in the experiment, accomplishing the removal of oxygenated organic compounds and favoring the formation of hydrocarbons in the pyrolysis vapors. As a result, the relative contents of aliphatic hydrocarbons, aromatic hydrocarbons and total hydrocarbons increased and the relative contents of oxygen-containing aliphatic compounds, oxygen-containing aromatic compounds and total oxygenates decreased over different ZSM-5 catalysts in this study.

Besides, it was clear that more oxygenates in oil fraction were converted into hydrocarbons by surface modified ZSM-5 comparing with original ZSM-5 (see [Fig. 5\(b\)](#)). The relative content of hydrocarbons increases in the following order:

SiO₂-ZSM-5 > EDTA-ZSM-5 > PC-ZSM-5 > original ZSM-5. For original ZAM-5 sample without surface modification, coke could be generated easily, leading to the blockage of pore opening and the prevention of subsequent catalytic deoxygenation reactions. For PC-ZSM-5, SiO₂-ZSM-5 and EDTA-ZSM-5, surface modification treatment process resulted in the inactivation or removal of outer acid sites, thus reducing the coke yield and improving the pore opening blockage. Consequently, these three catalysts showed better catalytic performance than oroginal ZSM-5. Moreover, these results also indicate that SiO₂-ZSM-5 has the highest cracking and deoxygenating characteristics.

3.4 Production of aromatic hydrocarbons

It is worth noting that the pore diameter of ZSM-5 is similar to the dynamics diameter of benzene, toluene and xylene, so the ZSM-5 catalyst has a remarkable shape-selective effect on the production of aromatic hydrocarbons [20]. The primary pyrolytic vapors will diffuse into the internal pores of ZSM-5 when passing through the catalyst layer, and from aromatic hydrocarbons through a common hydrocarbon pool intermediate. The tentative reaction mechanism for the improved selectivity is presented in Fig. 6. Fig. 7(a) shows the relative contents of benzene, toluene, ethylbenzene, xylene (including p, m and o-xylene), indene and polycyclic aromatic hydrocarbons (PAHs) in oil fraction. Obviously, EDTA-ZSM-5 catalyst showed the highest relative content of benzene (3.38%), while PC-ZSM-5 catalyst gave the lowest one (2.34%). On the other hand, SiO₂-ZSM-5 showed the highest relative contents of

toluene and xylene (4.77% and 5.31%, respectively), whereas original ZSM-5 produced the lowest ones (1.99% and 1.81%, respectively). Besides, note that PAHs were carcinogenic toxins, and special attention should be paid to the production of PAHs in this study.

[Fig. 7\(b\)](#) gives the detailed selectivities of aromatic hydrocarbons. The selectivity of benzene + toluene + xylene in aromatic hydrocarbons was more than 90% for all these catalysts. On the other hand, the selectivity of benzene was increased in the following order: original ZSM-5 > EDTA-ZSM-5 > PC-ZSM-5 > SiO₂-ZSM-5, which was between 22.7% (with SiO₂-ZSM-5) and 34.6% (with original ZSM-5) for all these catalysts. However, the selectivity of toluene + xylene presented the opposite trend, which was between 55.4% (with original ZSM-5) and 70.7% (with SiO₂-ZSM-5) for all these catalysts. Besides, the minimum selectivity of PAHs was achieved over SiO₂-ZSM-5 (6.1%). Toluene and xylene mainly come from the alkylation of benzene, and PAHs are generated from the polymerization of monocyclic aromatic hydrocarbons (benzene, toluene and xylene) with oxygenated fragments [\[21\]](#). These results show that SiO₂-ZSM-5 catalyst has a stronger alkylation and less further reaction effects than other catalysts. Moreover, it should be pointed out that PAHs have a lower value than monocyclic aromatic hydrocarbons (benzene, toluene, xylene and so forth). Therefore, SiO₂-ZSM-5 catalyst is better than other catalysts in this case.

4. Conclusion

333

334 CFP of SEMS over different surface modified catalysts was performed in a
335 MACFP reactor. All the modification methods resulted in a loss of external acid sites
336 of ZSM-5 samples. Among the three modified catalysts, the maximum oil fraction
337 yield and minimum coke yield were obtained with SiO₂-ZSM-5. The relative content
338 of hydrocarbons in oil fraction increased in the following order: SiO₂-ZSM-5 >
339 EDTA-ZSM-5 > PC-ZSM-5 > original ZSM-5. Besides, the selectivity of benzene in
340 aromatics increased in the following order: original ZSM-5 > EDTA-ZSM-5 >
341 PC-ZSM-5 > SiO₂-ZSM-5, while the selectivity of toluene + xylene presented the
342 opposite trend.

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354 **References**

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356 [1] H.W. Lei, S.J. Ren, Q. Bu, J. Julson, J. Holladay, R. Ruan, Microwave pyrolysis of distillers
357 dried grain with solubles (DDGS) for biofuel production, *Bioresour. Technol.* 102 (2011)
358 6208.

359 [2] T. Dickerson, J. Soria, Catalytic fast pyrolysis: A review, *Energies* 6 (2013) 514.

360 [3] C. Dorado, C.A. Mullen, A.A. Boateng, H-ZSM5 catalyzed co-pyrolysis of biomass and
361 plastics, *ACS Sustainable Chem. Eng.* 2 (2014) 301.

362 [4] F. Abnisa, A. Arami-Niya, W.M.A.W. Daud, J.N. Sahu, I.M. Noor, Utilization of oil palm tree
363 residues to produce bio-oil and bio-char via pyrolysis, *Energ. Convers. Manage.* 76 (2013)
364 1073.

365 [5] H.F. Jiang, Z.Q. Cheng, T.Q. Zhao, M.Z. Liu, M.Y. Zhang, J.N. Li, M.J. Hu, L. Zhang, J.F. Li,
366 Pyrolysis kinetics of spent lark mushroom substrate and characterization of bio-oil obtained
367 from the substrate, *Energ. Convers. Manage.* 88 (2014) 259.

368 [6] K.L. Lau, Y.Y. Tsang, S.W. Chiu, Use of spent mushroom compost to bioremediate
369 PAH-contaminated samples, *Chemosphere* 52 (2003) 1539.

370 [7] X.S. Shi, X.Z. Yuan, Y.P. Wang, S.J. Zeng, Y.L. Qiu, R.B. Guo, L.S. Wang, Modeling of the
371 methane production and pH value during the anaerobic co-digestion of dairy manure and
372 spent mushroom substrate, *Chem. Eng. J.* 244 (2014) 258.

373 [8] D.J. Royse, J.E. Sanchez, Ground wheat straw as a substitute for portions of oak wood chips
374 used in shiitake (*Lentinula edodes*) substrate formulae, *Bioresour. Technol.* 98 (2007) 2137.

375 [9] Y. Xue, A. Kelkar, X.L. Bai, Catalytic co-pyrolysis of biomass and polyethylene in a tandem
376 micropyrolyzer, *Fuel* 166 (2016) 227.

377 [10] B. Zhang, Z.P. Zhong, K. Ding, Y.Y. Cao, Z.C. Liu, Catalytic upgrading of corn stalk fast
378 pyrolysis vapors with fresh and hydrothermally treated HZSM-5 catalysts using Py-GC/MS,
379 *Ind. Eng. Chem. Res.* 53 (2014) 9979.

380 [11] B. Zhang, Z.P. Zhong, Q.L. Xie, P. Chen, R. Ruan, Reducing coke formation in catalytic fast
381 pyrolysis of bio-derived furan with surface modified HZSM-5 catalysts, *RSC Adv.* 5 (2015)
382 56286.

- [12] P. Matias, J.M. Lopes, S. Laforge, P. Magnoux, M. Guisnet, F.R. Ribeiro, n-Heptane transformation over a HMCM-22 zeolite: Catalytic role of the pore systems, *Appl. Catal. A - Gen.* 351 (2008) 174.
- [13] B. Zhang, Z.P. Zhong, X.B. Wang, K. Ding, Z.W. Song, Catalytic upgrading of fast pyrolysis biomass vapors over fresh, spent and regenerated ZSM-5 zeolites, *Fuel Process. Technol.* 138 (2015) 430.
- [14] B. Zhang, Z.P. Zhong, P. Chen, R. Ruan, Microwave-assisted catalytic fast pyrolysis of biomass for bio-oil production using chemical vapor deposition modified HZSM-5 catalyst, *Bioresour. Technol.* 197 (2015) 79.
- [15] B. Zhang, Z.P. Zhong, Z.W. Song, K. Ding, P. Chen, R. Ruan, Optimizing anti-coking abilities of zeolites by ethylene diamine tetraacetic acid modification on catalytic fast pyrolysis of corn stalk, *J. Power Sources* 300 (2015) 87.
- [16] F. Yu, S.B. Deng, P. Chen, Y.H. Liu, Y.Q. Wan, A. Olson, D. Kittelson, R. Ruan, Physical and chemical properties of bio-oils from microwave pyrolysis of corn stover, *Appl. Biochem. Biotechnol.* 136-140 (2007) 957.
- [17] S.J. Ren, H.W. Lei, L. Wang, Q. Bu, S.L. Chen, J. Wu, J. Julson, R. Ruan, Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet, *J. Anal. Appl. Pyrol.* 94 (2012) 163.
- [18] Z.Y. Du, X.C. Ma, Y. Li, P. Chen, Y.H. Liu, X.Y. Lin, H.W. Lei, R. Ruan, Production of aromatic hydrocarbons by catalytic pyrolysis of microalgae with zeolites: catalyst screening in a pyroprobe, *Bioresour. Technol.* 139 (2013) 397.
- [19] B. Zhang, Z.P. Zhong, K. Ding, Z.W. Song, Production of aromatic hydrocarbons from catalytic co-pyrolysis of biomass and high density polyethylene: analytical Py-GC/MS study, *Fuel* 139 (2015) 622.
- [20] J. Wang, Z.P. Zhong, K. Ding, Z.Y. Xue, Catalytic fast pyrolysis of mushroom waste to

408 upgraded bio-oil products via pre-coked modified HZSM-5 catalyst, Bioresour. Technol. 212

409 (2016) 6.

410 [21] T.R. Carlson, J. Jae, G.W. Huber, Mechanistic insights from isotopic studies of glucose

411 conversion to aromatics over ZSM-5, ChemCatChem 1 (2009) 107.

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Figure captions

Fig. 1. Flow chart for the whole experimental procedure.

Fig. 2. Schematic diagram of MACFP experimental setup.

Fig. 3. Porosity and acidity characteristics of ZSM-5 catalysts: (a) BET surface area; (b) Pore size; (3) conversion efficiency of 1,3,5-TIPB.

Fig. 4. Product yields.

Fig. 5. Chemical compositions of oil fraction: (a) Relative contents of different chemical families; (b) Relative contents of hydrocarbons and oxygenates.

Fig. 6. Tentative reaction mechanism for the production of aromatic hydrocarbons.

Fig. 7. Production of aromatic hydrocarbons: (a) Relative contents; (b) Selectivities.

Fig. 1. Flow chart for the whole experimental procedure.

Fig. 2. Schematic diagram of MACFP experimental setup. (1) semi-continuous SEMS feeder; (2) SEMS; (3) quartz inlet connector (length: 140 mm & diameter: 24.6 mm); (4) microwave oven; (5) microwave control panel; (6) quartz reactor with two necks (specially made with fused quartz; length: 128 mm & diameter: 127 mm); (7) microwave absorbent (SiC) bed; (8) fixed bed with SiC and ZSM-5 mixer; (9) quartz wool; (10) quartz outlet connector (length: 148 mm & diameter: 24.6 mm); (11) thermocouple to measure the temperature of (7) and (8); (12) quartz connector; (13) bio-oil collector; (14) condenser; (15) connection to a vacuum pump to draw the pyrolysis vapors out of quartz reactor.

(a)

(b)

(c)

Fig. 3. Porosity and acidity characteristics of ZSM-5 catalysts. (a) BET surface area; (b) Pore size; (3) conversion efficiency of 1,3,5-TIPB.

Fig. 4. Product yields.

(a)

(b)

Fig. 5. Chemical compositions of oil fraction. (a) Relative contents of different chemical families; (b) Relative contents of hydrocarbons and oxygenates.

Fig. 6. Tentative reaction mechanism for the production of aromatic hydrocarbons.

(a)

(b)

Fig. 7. Production of aromatic hydrocarbons. (a) Relative contents; (b) Selectivities.

Graphical abstract