Two-step fast microwave-assisted pyrolysis of biomass for bio-oil production using microwave absorbent and HZSM-5 catalyst

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ABSTRACT

A novel technology of two-step fast microwave-assisted pyrolysis (fMAP) of corn stover for bio-oil production was investigated in the presence of microwave absorbent (SiC) and HZSM-5 catalyst. Effects of fMAP temperature and catalyst-to-biomass ratio on bio-oil yield and chemical components were examined. The results showed that this technology, employing microwave, microwave absorbent and HZSM-5 catalyst, was effective and promising for biomass fast pyrolysis. The fMAP temperature of 500°C was considered the optimum condition for maximum yield and best quality of bio-oil. Besides, the bio-oil yield decreased linearly and the chemical components in bio-oil were improved sequentially with the increase of catalyst-to-biomass ratio from 1:100 to 1:20. The elemental compositions of bio-char were also determined. Additionally, compared to one-step fMAP process, two-step fMAP could promote the bio-oil quality with a smaller catalyst-to-biomass ratio.

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Introduction

Within the past 2 decades, massive consumption of traditional fossil fuels has caused serious issues risking the energy security, global climate and human health (Zhang et al., 2015a; Wang et al., 2013). As a carbon neutral renewable energy source, lignocellulosic biomass can be directly transformed into liquid biofuels (commonly termed as "bio-oil") *via* pyrolysis (Ren et al., 2012; Aho et al., 2010; Czernik and Bridgwater, 2004), thus substituting petroleum based fuels and alleviating the dependency of fossil fuels. However, the direct fuel application of raw bio-oil is restricted by its adverse properties, such as its high oxygen content, low pH value, poor thermal stability, bad combustion behavior and so forth (Ye et al., 2014; Jiang et al., 2011; Yu et al., 2007). Increase the relative content of hydrocarbons and decrease that of oxygenated organic compounds (oxygenates) in bio-oil in the presence of different catalysts, *i.e.* zeolites, is seen as a new promising method to upgrade the raw bio-oil. Currently, dozens of microporous, mesoporous and macroporous catalysts have been researched (Zhou et al., 2014; Imran et al., 2014; Pstrowska et al., 2014; Milina et al., 2014), and it has been confirmed that the use of HZSM-5 zeolite catalyst can accomplish the significant removal of oxygenates (Du et al., 2013; Shao et al., 2013). The 3-dimensional intersecting pore structure of HZSM-5 catalyst contains straight and sinusoidal channels with diameters of 0.51–0.56 nm, which is suitable for the formation of hydrocarbons (especially aromatic hydrocarbons) (Carlson et al., 2009; Zhang et al., 2014). Therefore, HZSM-5 catalyst has a remarkable shape-selective effect on the production of hydrocarbons.

As a relatively new heating method, microwave irradiation can directly convert the electromagnetic energy into heat at the

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molecular level and lead to fast and uniform internal heating for material particles (Sobhy and Chaouki, 2010). Compared to conventional heating method, where heat is transferred from the external surface to the inside core of material particles, microwave heating provides many advantages (Wang et al., 2012). In recent study, Ruan and his co-workers have successfully used this emerging microwave-assisted pyrolysis (MAP) technique for biomass catalytic fast pyrolysis (CFP) to produce bio-oil (Du et al., 2013; Yu et al., 2007; Ren et al., 2012; Wang et al., 2012).

However, it should be emphasized that several minutes are usually required for biomass materials to be heated to the desired CFP temperature with direct microwave irradiation, so this process belongs to the intermediate rate pyrolysis category rather than instantaneous pyrolysis category on this condition (Borges et al., 2014). Therefore, the conventional MAP technique is not beneficial for high bio-oil yield and quality, and the main challenge is to increase the heating rate. It has been reported that some carbon materials, such as charcoal or activated carbon, can be easily heated using microwaves because of their excellent absorption property for microwaves (Menéndez et al., 2010; Du et al., 2011). Use of these microwave absorbents can significantly enhance the heating rate. When biomass is fed onto the heated microwave absorbents in a microwave reactor, it will be heated through two heating mechanisms simultaneously: (1) the direct microwave irradiation; (2) the thermal conduction from heated microwave absorbents (Borges et al., 2014). As a result, fast microwave-assisted pyrolysis (fMAP) conditions will be achieved, and biomass can be instantaneously heated to the desired CFP temperature with this novel heating technique.

In the biomass CFP runs, the non-catalytic fast pyrolysis (non-CFP) reactions will occur at first, leading to the production of thermally cracked products (condensable pyrolysis vapors, noncondensable light gases and bio-char). Then some condensable pyrolysis vapors will diffuse into the internal micropores of HZSM-5 catalyst and be converted into hydrocarbons. Consequently, the quality of bio-oil will be improved. In this study, a two-step fMAP process using microwave absorbent and HZSM-5 catalyst was developed for *in situ* catalytic upgrading of primary biomass pyrolysis vapors. The main purpose of present research is to increase the relative content of hydrocarbons and decrease that of oxygenates in bio-oil. In this study, the effects of key parameters (including reaction temperature and catalyst-to-biomass ratio) on bio-oil production from two-step fMAP process were investigated. Besides, detailed elemental analysis of bio-char was also carried out. In addition, particular emphasis is given to the comparison between one- and two-step fMAP processes.

1. Methods

1.1. Materials and catalyst

Corn stover was used as the biomass feedstock in our two-step fMAP experiments, which was collected from corn crop residual from St. Paul Campus, at the University of Minnesota, Twin Cities, USA. Prior to use, all the biomass samples 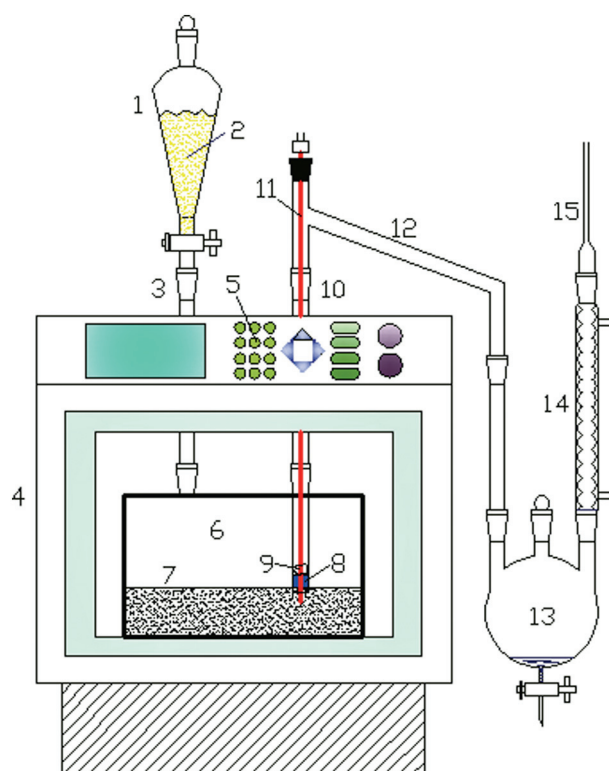were dried (80°C, 24 hr), and smashed to a particle size of 0–0.5 mm in diameter. The proximate analysis of the corn stover (on air-dry basis) was 5.27 wt.% moisture content, 93.00 wt.% volatiles and 2.06 wt.% ash content. The elemental composition of the corn stalk (on dry basis) was 44.013 wt.% carbon, 5.954 wt.% hydrogen, 0.577 wt.% nitrogen and 49.456 wt.% oxygen (by difference). For proximate analysis, moisture content was determined by mass difference after biomass sample was dried at 105°C for 10 hr in a drying oven; volatiles were determined by mass difference after biomass sample was thermally treated at 900°C for 7 min under inert atmosphere; and the ash content was calculated by mass difference after biomass sample was combusted at 815°C. The ultimate analysis was determined using an elemental analyzer (CE-400, Exerter Analytical Inc., USA) according to the operation manual.

The HZSM-5 zeolite catalyst (Si/Al = 50, surface area = 308 m^2/g, particle diameter = 2–5 μm) used in this work was bought from the Catalyst Plant of Nankai University (Tianjin, China).

1.2. Apparatus

Two-step fMAP experiments were conducted in a microwave oven (MAX, CEM Corporation; power: 750 W; frequency: 2450 MHz). The schematic experimental setup, shown in Fig. 1, is composed of: (1) semi-continuous biomass feeder; (2) biomass feedstock; (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 HZSM-5 catalyst mixer; (9) quartz wool; (10) quartz outlet connector (length: 148 mm; diameter: 24.6 mm); (11) thermocouple (K-type) to measure the temperature of (7) and (8); (12) quartz connector; (13) bio-oil collector; (14) condenser; and (15) connection to a vacuum pump to draw the pyrolysis vapors out of quartz reactor. For safety purpose, a microwave detector (MD-2000, Digital Readout) was used to monitor microwave leakage.

During the experiments, SiC particles (particle size: 0–0.6 mm) were used as the microwave absorbent. 500 g of SiC particles were placed in the quartz reactor to form a layer of microwave absorbent bed. Then the quartz reactor was put into the cavity of the microwave oven. After connecting the quartz inlet and outlet tubes, some SiC particles and HZSM-5 catalyst were fully mixed and put into the bottom of quartz outlet connector to form another fixed bed. This fixed bed was expected to upgrade primary pyrolysis vapors. Then the microwave oven was turned on for heating processing. When the first and second fixed beds ((7) and (8)) were heated to the desired temperature, 5 g corn stover was introduced onto the hot SiC bed (7) semi-continually through the biomass feeder. Pyrolysis reactions occurred in the quartz reactor and the primary pyrolysis vapors were upgraded when they passed through the fixed bed (8). In this set of experiments, the pyrolysis temperature and upgrading temperature were exactly the same. A pulse width modulation control was applied to keep the microwave oven on and off every 15 sec to maintain the desired reaction temperature of (7) and (8). The vacuum degree of the experimental system was kept at

Fig. 1 – Schematic diagram of two-step fast microwave-assisted pyrolysis (fMAP) experimental setup. (1) semi-continuous biomass feeder; (2) biomass feedstock; (3) quartz inlet connector; (4) microwave oven; (5) microwave control panel; (6) quartz reactor with two necks; (7) microwave absorbent (SiC) bed; (8) fixed bed with SiC and HZSM-5 catalyst mixer; (9) quartz wool; (10) quartz outlet connector; (11) thermocouple (K-type) 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. fMAP: fast microwave-assisted pyrolysis.

250 mm Hg to maintain an inert atmosphere in the reactor. Each experiment ran 45 min. At the end of each experiment, the solid residue was cooled to room temperature, and its yield was calculated by the weight difference of the quartz reactor and outlet connector with and without solid residue. The bio-oil yield was determined by the weight difference of the bio-oil collector before and after each experiment, while the gas yield was determined by difference according to mass balance. Each experiment was repeated at least twice under the same conditions to confirm the reproducibility and avoid experimental uncertainly, and the standard deviation values were calculated.

1.3. Product analysis

The chemical compositions of bio-oil were identified using a gas chromatography/mass spectrometer (GC/MS) instrument (7890A/5975C, Agilent, USA). High-purity helium was employed as the 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 mass spectral data library. Relative content of each component in the bio-oil was determined by calculating its chromatographic area percentage.

In addition, the elemental analysis of bio-char was conducted using the methodology described in by Borges et al. (2014) and Xie et al. (2014).
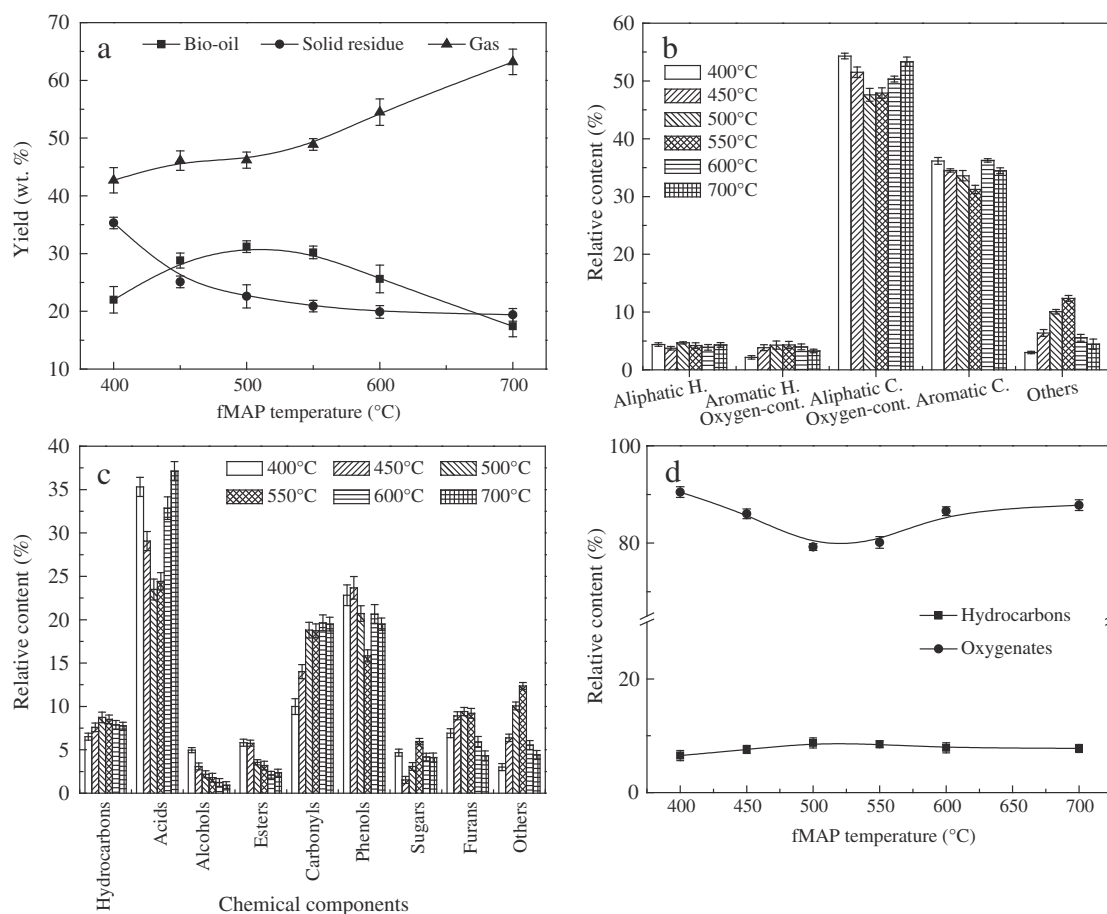
2. Results and discussion

2.1. Effect of fMAP temperature on bio-oil production

The effect of fMAP temperature (including pyrolysis temperature T_1 and upgrading temperature T_2, $T_1 = T_2$) on product distribution was investigated. During this study, the catalyst-to-biomass ratio (m/m) was 1:20, and the fMAP temperatures were 400, 450, 500, 550, 600 and 700°C, respectively. As shown in Fig. 2, it was clearly seen that fMAP temperature had a pronounced influence on the yield and composition of bio-oil from two-step fMAP of corn stover. From Fig. 2a, we could see that the bio-oil yield increased in the first stage, and then decreased after the maximum value of 31.2% was achieved at 500°C, while the gas yield increased dramatically from 42.7% to 63.2% over the ranges of fMAP temperatures studied. Two-step fMAP of corn stover was an

endothermic process. With fMAP temperature increased, higher energy was produced, and then more strong organic bonds were broken (Zhang et al., 2015b). Thus, more corn stover would be pyrolyzed, which was in accordance with the initial increase of bio-oil yield when fMAP temperature increased from 400 to 500°C. The decrease of bio-oil yield beyond 500°C was mostly due to the significant secondary cracking reactions (Encinar et al., 2000). Besides, the yield of solid residue decreased sequentially with increasing fMAP temperature. This was due to the greater primary thermal decomposition of corn stover and secondary thermal decomposition of the solid residue under higher fMAP temperatures (Zhang et al., 2009). These results were in good agreement with literature report (Liu et al., 2014; Zhang et al., 2014). Obviously, the optimal fMAP temperature for maximum bio-oil yield was 500°C.

The bio-oil components were also affected by fMAP temperature. Fig. 2b gives the relative contents of different chemical families (aliphatic hydrocarbons, aromatic hydrocarbons, oxygen-containing aliphatic compounds, oxygen-containing aromatic compounds and others (nitrogen-containing compounds and unidentified compounds)) in the bio-oil from two-step fMAP of corn stover. As could be seen, the relative content of aromatic hydrocarbons first increased to a maximum value at 550°C, and then decreased. It was reported that

reaction temperature of 500–600°C was conducive to the formation of aromatic hydrocarbons (Zhang et al., 2015a). In contrary, the relative contents of oxygen-containing aliphatic compounds and oxygen-containing aromatic compounds tended to decrease at first and then increase over the range of fMAP temperature studied. Besides, the relative content of aliphatic hydrocarbons fluctuated slightly, while the maximum value was achieved at 500°C. In this paper, the highest relative contents of aliphatic hydrocarbons and aromatic hydrocarbons and the lowest relative contents of oxygen-containing aliphatic compounds and oxygen-containing aromatic compounds were obtained at the fMAP temperature of 500 or 550°C. In detail, the chemical components in bio-oil could be classified into several groups as hydrocarbons, acids, alcohols, esters, carbonyls, phenols, sugars, furans and others. Fig. 2c shows the relative contents of detailed chemical components in bio-oil under different fMAP temperatures. As could be seen, the highest relative content of hydrocarbons was obtained at the fMAP temperature of 500°C. Among all the oxygenates, acids, carbonyls and phenols accounted for the largest share. The relative contents of acids and phenols tended to decrease at first and then increase over the range of fMAP temperature studied, while the relative content of carbonyls increased with the increase of fMAP temperature. As shown in Fig. 2(d), the maximum relative content of hydrocarbons and the minimum

Fig. 2 – Effect of fMAP temperature on bio-oil production from two-step fMAP of corn stover: (a) product distribution; (b) relative contents of different chemical families; (c) relative contents of detailed chemical components; (d) relative contents of hydrocarbons and oxygenates.

relative content of oxygenates were observed at the fMAP temperature of 500°C. As mentioned in the Introduction, deoxygenation of bio-oil could promote the bio-oil quality, and the main purpose of our research is to increase the relative content of hydrocarbons and decrease that of oxygenates in bio-oil. Therefore, the optimal fMAP temperature was 500°C.
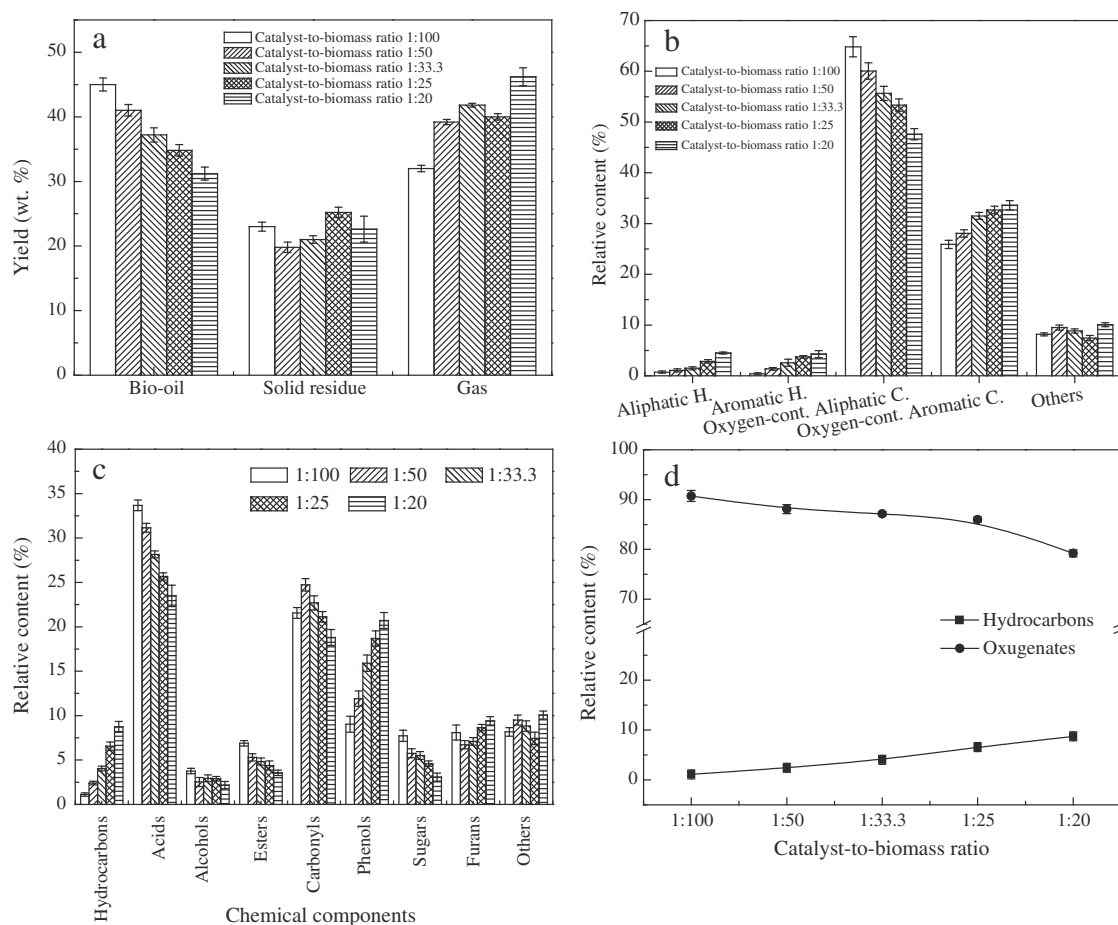
In addition, potential industrial chemical compounds obtained from bio-oil at 500°C included D-limonene (0.66%), benzene (0.60%), toluene (1.04%), xylene (1.19%), indene (0.12%), naphthalene (0.51%), phenol (2.30%), 2,3-dihydro-benzofuran (2.56%) and levoglucosan (2.05%). These price-competitive renewable chemicals could be used as fuels, solvents or precursors for resins and polymers.

2.2. Effect of catalyst-to-biomass ratio (m/m) on bio-oil production

Experiments with different catalyst-to-biomass ratios were also carried out. The application of HZSM-5 catalyst in two-step fMAP of corn stover and the effect of catalyst-to-biomass ratio on bio-oil production were investigated. During these experiments, the fMAP temperature was 500°C, and the catalyst-to-biomass ratios were 1:100, 1:50, 1:33.3, 1:25 and 1:20, respectively. Fig. 3 gives the product distribution and

bio-oil composition under distinct catalyst-to-biomass ratios, and the catalyst-to-biomass ratio was observed as an important factor. As shown in Fig. 3a, when catalyst-to-biomass ratio increased from 1:100 to 1:20, the bio-oil yield decreased linearly and the gas yield increased significantly. The 3-dimensional pore system of HZSM-5 zeolite contained 10-membered rings with Z-shaped channels of 0.51 × 0.55 nm and straight channels of 0.53 × 0.56 nm. During the two-step fMAP experiments, the fMAP of corn stover firstly resulted in the production of various intermediate oxygenates (primary pyrolysis vapors), and then all the primary pyrolysis vapors had to pass through the HZSM-5 catalyst layer. When they diffused into the internal pores of HZSM-5 catalyst, some of them were converted into hydrocarbons through a series of deoxygenation reactions through a common intermediate (called "hydrocarbon pool") within the HZSM-5 framework (Scheme 1) (Dahl and Kolble, 1994; Li et al., 2012), thereby removing oxygen as CO, CO_2 and H_2O. These catalytic upgrading reactions would lead to a decrease of product vapors yield and an increase of light gas yield. Consequently, the bio-oil yield decreased and gas yield increased.

The effect of catalyst-to-biomass ratio on different chemical families in bio-oil from two-step fMAP of corn stover is presented in Fig. 3b. It was found that the relative contents of

Fig. 3 – Effect of catalyst-to-biomass ratio on bio-oil production from two-step fMAP of corn stover: (a) product distribution; (b) relative contents of different chemical families; (c) relative contents of detailed chemical components; (d) relative contents of hydrocarbons and oxygenates.

aliphatic hydrocarbons, aromatic hydrocarbons had an apparent increase, while the relative content of oxygen-containing aliphatic compounds decreased in the studied mass ratio range. This result was in good agreement with literature report showing that primary pyrolysis vapors could be deoxygenated and cracked to form hydrocarbons over HZSM-5 catalyst (Du et al., 2013; Carlson et al., 2009; Zhang et al., 2014). On the other hand, significant increase in the relative content of oxygen-containing aromatic compounds was observed with increasing catalyst-to-biomass ratio. Oxygen-containing aromatic compounds were mainly from the pyrolysis of lignin and its derivatives. More HZSM-5 catalyst would result in the catalytic decomposition of more lignin derivatives, thus increasing the relative content of oxygen-containing aromatic compounds. Fig. 3c shows the relative contents of detailed chemical components in bio-oil under different catalyst-biomass ratios. The relative contents of hydrocarbons and phenols increased dramatically and the relative contents of acids, alcohols, esters, carbonyls and sugars tended to decrease significantly with increasing catalyst-biomass ratio. From Fig. 3d, we could find that the relative content of oxygenates decreased gradually with increasing catalyst-biomass ratio. HZSM-5 catalyst could change the bio-oil products. When more HZSM-5 catalyst was used, more primary pyrolysis vapors would diffuse into the pores of HZSM-5 catalyst and be converted into hydrocarbons.
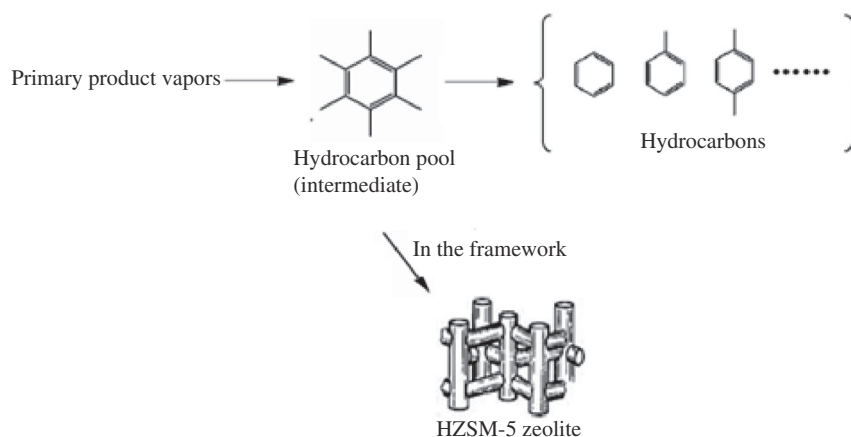
2.3. Analysis of bio-char

The elemental compositions of corn stover and bio-char were determined (elemental analysis and inductively coupled plasma - optical emission spectrometry (ICP-OES) multi-element determination)(Table 1). The bio-char was obtained from two-step fMAP under the fMAP temperature of 500°C and catalyst-to-biomass ratio of 1:20. As could be seen, the contents of mineral elements in bio-char were much higher than those in corn stover, indicating that most mineral elements were concentrated and retained in bio-char. The bio-char is valuable by-product, and the main routes for the final use include: (1) Fuel. Bio-char can be used for combustion to produce heat or electricity. (2) Adsorbent. As a porous material, bio-char can be used as an adsorbent. (3) Microwave absorbent. As a carbon material, bio-char can be easily heated using microwaves due to its significant absorption property

for microwaves. (4) Soil amendment. As detected, the contents of Ca, K, P and Mg are relatively high (Ca: 1857.82 mg/kg, K: 1952.63 mg/kg, P: 300.21 mg/kg, Mg: 490.12 mg/kg). As we know, Ca, K, P and Mg are essential elements for plant growth, so the potential utilization way of bio-char is to be applied as soil amendment to improve soil fertility and promote crop yield. However, it is noteworthy that there are still some hazardous heavy metals in bio-char (Cd: 0.12 mg/kg, Cr: 0.22 mg/kg, Pb: 0.11 mg/kg), the bio-char may have negative effect on plant growth, and we will do more researches to evaluate the effect comprehensively in the future.

2.4. Comparison between one-step and two-step fMAP of corn stover

We also conducted experiments to compare the results between one- and two-step fMAP of corn stover. One-step fMAP experiments were also performed in the reactor (6) in the presence of SiC (see Fig. 1). Corn stover and HZSM-5 catalyst were fully mixed and then put into the semi-continuous biomass feeder (1). No HZSM-5 catalysts were placed in the quartz outlet connector. In the case of one-step fMAP experiments, 500 g SiC particles were applied in the quartz reactor to form a layer of microwave absorbent bed. During the experiments, the CFP temperature was set at 500°C. When the temperature of (7) reached the prefixed level, 5 g corn stover and some HZSM-5 catalyst were introduced onto the hot SiC bed semi-continually through the biomass feeder. Other experimental conditions and procedures were similar to those in the two-step fMAP experiments. In order to make sure that the catalyst and biomass were homogeneously mixed together for one-step fMAP, when the catalyst to biomass ratio was 1:20, 0.25 g HZSM-5 catalyst and 0.5 g corn stover were fully mixed first, and then those 0.75 g mixtures were further fully mixed with other 4.5 g corn stover.

As shown in Fig. 4, when the catalyst-to-biomass ratio was 1:20, the bio-oil yield was 31.2% in the case of two-step fMAP, while it was 42.6% in the case of one-step fMAP. In addition, two-step fMAP increased the gas yield. For the general chemical families in bio-oil, two-step fMAP could improve the bio-oil quality as it favored the production of aliphatic hydrocarbons and aromatic hydrocarbons and reduced the relative content of oxygen-containing aliphatic compounds in contrast with one-step fMAP (Fig. 4b).

Primary product vapors

Hydrocarbon pool (intermediate)

Hydrocarbons

In the framework

HZSM-5 zeolite

Scheme 1 – The mechanism of two-step fMAP experiments.

Table 1 – Elemental composition of bio-char.

Elemental composition (wt.%)				Mineral elements (mg/kg)									
	C	H	N		Al	B	Be	Ca	Cd	Co	Cr	Cu	Fe	K
Corn stover	42.68	6.21	1.22	1	25.79	1.24	0.08	354.63	0.04	0.05	0.08	1.59	37.26	608.88
				2	150.48	4.03	0.13	1857.82	0.12	0.10	0.22	5.27	84.25	1952.63
					Li	P	Mg	Mn	Na	Ni	Pb	V	Zn	
Bio-char	47.98	2.87	0.44	1	0.07	95.27	178.22	5.96	0.03	0.19	0.05	0.06	9.81	
				2	0.11	300.21	490.12	35.26	0.07	0.65	0.11	0.15	30.26	

The bio-oil yield and chemical families from one-step fMAP with a catalyst-to-biomass ratio of 1:3 was similar to the results from two-step fMAP with a catalyst-to-biomass ratio of 1:20, which indicated that two-step fMAP process could significantly reduce the catalyst loading. There were two reasons to explain the results. On one hand, for two-step fMAP process, all the primary fMAP vapors would pass through the HZSM-5 catalyst layer and all the vapors would be upgraded. However, for one-step fMAP, some primary fMAP vapors from degradation of solid biomass could not well be in contact with HZSM-5 catalyst. In the case of one-step fMAP process, the surface contact between some fMAP vapors and catalyst particles was not adequate. On the other hand, as we know, HZSM-5 catalyst was in contact with solid biomass/char during one-step process, so some solid biomass/char would be adsorbed on the surface of HZSM-5 catalyst, thus giving rise to the blockage of pore opening and preventing the subsequent shape-selective reactions. Obviously, the deactivation of HZSM-5 catalyst would be caused in the case of one-step fMAP process (Güngör et al., 2012). As a result, two-step fMAP was more effective and promising than one-step fMAP.
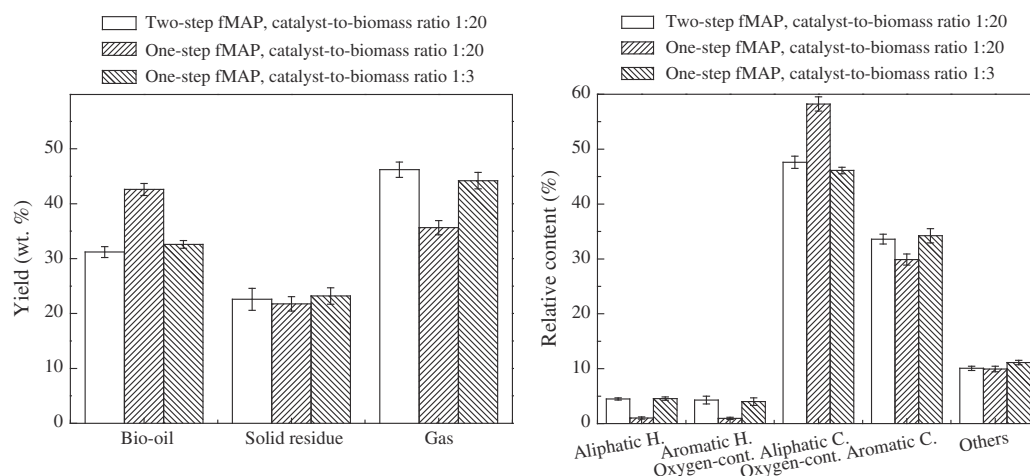
3. Conclusions

This study investigated a novel technology of two-step fMAP of corn stover for bio-oil production using microwave absorbent and HZSM-5 catalyst. Effects of fMAP temperature and catalyst-to-biomass ratio on bio-oil yield and chemical components were examined. The results showed that the optimum fMAP temperature was 500°C, and the increase of catalyst-to-biomass ratio reduced the bio-oil yield and promoted the bio-oil quality. Besides, the elemental compositions of bio-char were also determined. In addition, compared to one-step fMAP, two-step fMAP could reduce the use of HZSM-5 catalyst and improve the bio-oil quality.

Acknowledgments

Fig. 4 – Comparison between one-step and two-step fMAP of corn stover: (a) product distribution; (b) relative contents of different chemical families. fMAP: fast microwave-assisted pyrolysis.

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