



## Full Length Article

# Bio-oil production from sequential two-step catalytic fast microwave-assisted biomass pyrolysis



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## H I G H L I G H T S

- Sequential two-step catalytic fast microwave-assisted pyrolysis of corn stover was studied.
- The pyrolysis and catalytic cracking and upgrading processes can be flexibly and independently controlled.
- High selectivity of aromatic hydrocarbons was obtained by small catalyst loading.
- HZSM-5 catalyst has good stability in the catalytic upgrading process.

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## A B S T R A C T

A sequential two-step fast microwave-assisted pyrolysis (fMAP) for high quality bio-oil production was investigated. In the process, fMAP was followed by catalytic cracking and upgrading using a packed bed catalyst reactor with HZSM-5 as the catalyst. Effects of pyrolysis temperature, catalyst loading, and catalyst bed temperature on the product distribution were investigated. Results showed that maximum bio-oil and aromatic hydrocarbons yields were obtained when pyrolysis temperature reached 550 °C. With the increase in the catalyst loading, the bio-oil yield decreased linearly while the aromatic hydrocarbons yield increased. The catalyst bed temperature also has a significant effect on the product chemical profiles. The aromatic hydrocarbons proportion of the bio-oil was found to increase with increasing catalyst bed temperature and reached its maximum of 26.20% at 425 °C. In addition, coke yield increased with increasing catalyst to biomass ratio and decreasing catalyst bed temperature.

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## 1. Introduction

Biomass is considered as an alternative feedstock for liquid bio-fuel due to its abundance and renewable nature [1–3]. Pyrolysis has been around for several decades. In the process, biomass is exposed to high temperature (450–600 °C) at a high heating rate in an inert atmosphere, and is converted into a liquid known as bio-oil, and bio-char and non-condensable gases. However, bio-oil is a complex mixture of chemical compounds, such as acids, alcohols, esters, sugars, phenols, and furans [4,5]. Its direct use as an alternative to conventional fuels is limited due to its poor quality, such as high water content, poor thermal stability, high oxygen

content and corrosiveness [6]. The high amount of oxygenated compounds renders the bio-oil only half of the heating value of the petroleum fuel equivalents.

The properties of bio-oil produced from biomass pyrolysis are affected by a number of factors including heating characteristics. Bio-oil crude may be catalytically upgraded to high quality fuels. Microwave-assisted pyrolysis employs microwave heating, which offers relatively uniform internal heating of feedstock particles [7–10]. A fast microwave heating method employing microwave absorbents was recently developed [11–13], making fast microwave assisted pyrolysis (fMAP) possible. The present study was to evaluate a sequential two-step catalytic pyrolysis and upgrading method for improving the quality of bio-oil from fMAP of corn stover.

Catalytic fast pyrolysis is a key approach for removing the oxygenated components in order to upgrade bio-oil to improve the

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bio-oil quality and stability. Up to now, most studies in the literature have been focused on one-step catalytic fast pyrolysis where the catalysts are mixed with the feedstock in the pyrolysis reactor. A two-step process, where the upgrading catalyst is separate from the pyrolysis vicinity, has been studied to a less degree. The major disadvantages of the one-step process include fixed cracking and catalytic upgrading temperature, and high coke formation on the catalyst causing the rapid catalyst deactivation, etc. These advantages can be overcome by using the two-step process. Zhang et al. from our lab investigated two-step fast microwave-assisted pyrolysis [14], in which the catalyst bed was placed right above the microwave absorbent inside microwave cavity. In this kind of set-up, there is no need for separate heating for pyrolysis and catalytic upgrading and the pyrolysis temperature and upgrading temperature were assumed the same. Since the optimal temperature for pyrolysis and catalytic upgrading may often differ, there would be advantages if the temperature of two processes could be controlled independently. In the present study, the catalyst bed is placed between the pyrolysis and condensation process outside of the microwave cavity. The advantages of this new two-step catalytic fMAP include not only providing the ability to control the cracking and catalytic upgrading independently for optimum pyrolysis condition and catalytic upgrading conditions but also allowing the bio-char to be removed to avoid contaminating the catalyst, and to be easily separated and collected as the valuable byproduct. In addition, the catalysts life can be significantly extended, and can be recycled and regenerated more easily, therefore reducing the cost. Gungor et al. [15] compared one-step and two-step catalytic fast pyrolysis of pine bark on a semi-batch fixed bed reactor using ReUS-Y catalyst. They reported that oxygen content was found to be reduced in the two-step pyrolysis but not in the one-step pyrolysis. Wang et al. [16] investigated the two-step (ex situ) catalytic pyrolysis of biomass of Douglas fir sawdust pellets on a microwave-assisted reactor with Zn/ZSM-5 catalyst and found that product yield and bio-oil composition were significantly affected by catalyst bed temperature and  $(WHSV)^{-1}$ . Recently, many catalysts [17–19] were screened and analyzed, such as soluble inorganics, metal oxides, microporous materials and mesoporous materials [20], and HZSM-5 has been most extensively studied due to its shape selectivity for aromatic hydrocarbons [21,22]. Due to the three-dimensional structure of HZSM-5 with intermediate pore size ( $0.54 \times 0.56$  nm), only the small molecules are allowed to enter into the micropores and folded to aromatic hydrocarbons.

A newly developed sequential two-step catalytic fast microwave-assisted pyrolysis of biomass through a packed-bed HZSM-5 catalyst for high quality bio-oil production was researched. The effects of pyrolysis temperature, catalyst loading and catalyst bed temperature on product yields and chemical properties were analyzed. The relevant optimized conditions for high aromatic hydrocarbons production were determined. In addition, X-ray Diffraction (XRD) analysis was conducted on the fresh, spent and regenerated HZSM-5 catalyst samples to examine their stability during-catalytic upgrading process.

## 2. Materials and methods

### 2.1. Materials

Corn stover, which was obtained from local farm field in Saint Paul, Minnesota, USA, was used as feedstock. Prior to experiments, feedstock was dried in air and pulverized mechanically and sieved to less than 2 mm before pyrolysis. Proximate analysis of corn stover (wt.%, on dry basis) was 3.90 wt.% moisture, 3.45 wt.% ash, 90.95 wt.% volatile matter and 1.70 wt.% fixed carbon. Elemental

analysis of corn stover (wt.%, on dry basis) was 44.91 wt.% C, 6.00 wt.% H, 1.58 wt.% N and 44.07 wt.% O (by difference). Based on the previous study from our lab [23], composition analysis of corn stover (wt.%, on dry ash-free basis) was 37 wt.% cellulose, 27 wt.% hemicellulose, 18 wt.% lignin and 18 wt.% extractives.

Zeolite powders (Si/Al = 80, Surface Area =  $425\text{m}^2/\text{g}$ ) used in this study were obtained from Zeolyst International (Conshohocken, PA). Prior to use, ZSM-5 catalyst was calcined at  $500^\circ\text{C}$  in air for 5 h to make it become hydrogen form HZSM-5.

### 2.2. Sequential Two-Step catalytic fMAP system

Microwave oven (MAX, CEM Corporation) was operated with power of 750 W and a frequency of 2450 MHz. Pyrolysis process and catalytic process arranged in tandem, both of which can be independently controlled in temperature. The schematic diagram of sequential two-step catalytic microwave-assisted pyrolysis system is shown in Fig. 1. The experimental apparatus is composed of: (1) biomass feeder; (2) biomass feedstock; (3) quartz connector; (4) oven; (5) control panel; (6) quartz reactor; (7) SiC bed; (8) thermocouple (K-type); (9) heater; (10) catalyst bed; (11) quartz wool; (12) outlet quartz connectors; (13) liquid fraction collectors; (14) condenser; (15) connection for vacuum pump.

Experiments in three sections were conducted in this study. The aim of the first section was to determine the effect of pyrolysis temperature on two-step catalytic fMAP product distribution and selectivity. At the fixed catalyst bed temperature and loading, pyrolysis was carried out at different temperature severities  $450^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $550^\circ\text{C}$ ,  $600^\circ\text{C}$  and  $650^\circ\text{C}$  respectively. After the optimum pyrolysis temperature was determined, the effects of catalyst bed temperature and catalyst loading on product distribution and selectivity were investigated at the optimum

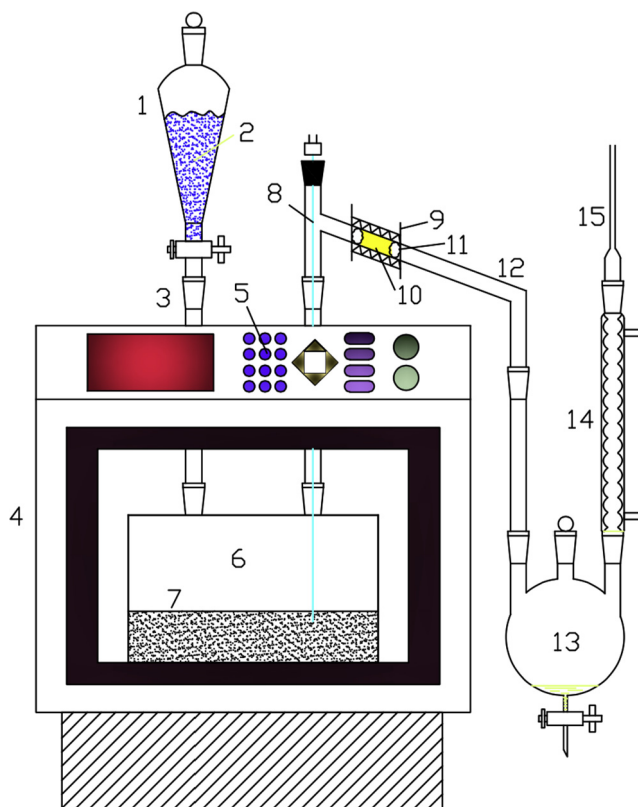


Fig. 1. Schematic diagram of sequential two-step catalytic microwave-assisted pyrolysis system.

temperature achieved in Section 2 and 3, respectively. Prior to the pyrolysis, the reactor was vacuumed for 15 min and the vacuum was kept during the whole process at 100 mmHg to eliminate the influence of oxygen. A blank pyrolysis test without using catalyst was conducted.

For a typical run, 500 g silicon carbide (size: 30 grit) was used in the reactor as absorbent of the microwave. SiC can be easily heated due to its excellent absorptive capacity of the microwave. The desired temperature was reached instantaneously due to the heat transfer from SiC particles bed heated by microwave. The catalyst bed temperature was controlled by the heater. When the temperature of reactor and catalyst reached the set point, the sample was fed onto the heated SiC bed. To maintain a stabilized temperature of microwave absorbent bed, the microwave oven was manually turned on or off. The biomass was pyrolyzed in the pyrolysis reactor and the pyrolysis vapors were upgraded in the catalyst bed reactor. Quartz wool was used to support the catalyst and remove the unreacted char and mineral components prior to exposing pyrolysis vapors to the upgrading catalyst. After the pyrolysis vapor went through the catalyst reactor and travelled to the condensers, its condensable components were condensed into liquid form which is collected as bio-oil. The solid residue (char & coke) was cooled to room temperature. A sieve was used to separate the char and SiC by difference of particle sizes. The weight of char was determined by weight difference of quartz reactor before and after experiments. The coke was calculated by the difference of catalyst bed weights before and after catalysis. The bio-oil and solid residue yields were calculated using their actual weight, and the gas yield was computed using the following equation (Gas yield = 100% – Char yield – Coke yield – Bio-oil yield). Microwave leakage was monitored by a type MD-2000 microwave detector (Digital Readout) for safety purpose. The experiments were repeated twice.

### 2.3. Bio-oil characterization

Chemical composition of bio-oil was determined using Agilent 7890-5975C GC/MS with a HP-5 MS capillary column at 30 m × 0.32 mm and 0.25 μm thickness. The oven temperature was held at 50 °C for 2 min. After that, at heating rate of 5 °C/min, it was increased to 260 °C and maintained at 260 °C for 5 min. The injector temperature was 290 °C, and the injector size was 1 μL with a split ratio of 1:10. The flow rate of the carrier gas (helium) was 1.2 mL/min. By comparison of the mass spectra and library data of National Institute of Standards and Technology (NIST), the organic compounds were identified. Because bio-oil has a large number of compounds, the calibration was not carried out. A semi-quantitative method was adopted by calculating the peak area percentage of gas chromatogram to determine the each compound distribution. An external standard method was used for the quantification of 8 major components in the bio-oil. The five-point calibration curve with the  $R^2$  above 0.99 was established using the standard solutions. The content of each compound in the bio-oil sample could be determined graphically.

An elemental analyzer (Type CE-440, Exeter Analytical Inc., MA) was used to determine elemental composition of the corn stover and organic liquid phase. The higher heating value (HHV) was calculated using the equation [24].

Water content was determined by Karl-Fischer titration.

### 2.4. Catalyst regeneration and characterization

Fresh catalyst, spent (coked) catalysts, and regenerated catalysts were studied using X-ray powder diffraction (XRD). The spent zeolites were regenerated in a muffle oven at 580 °C for 15 h to remove all the coke from the zeolite structure. The X-ray powder

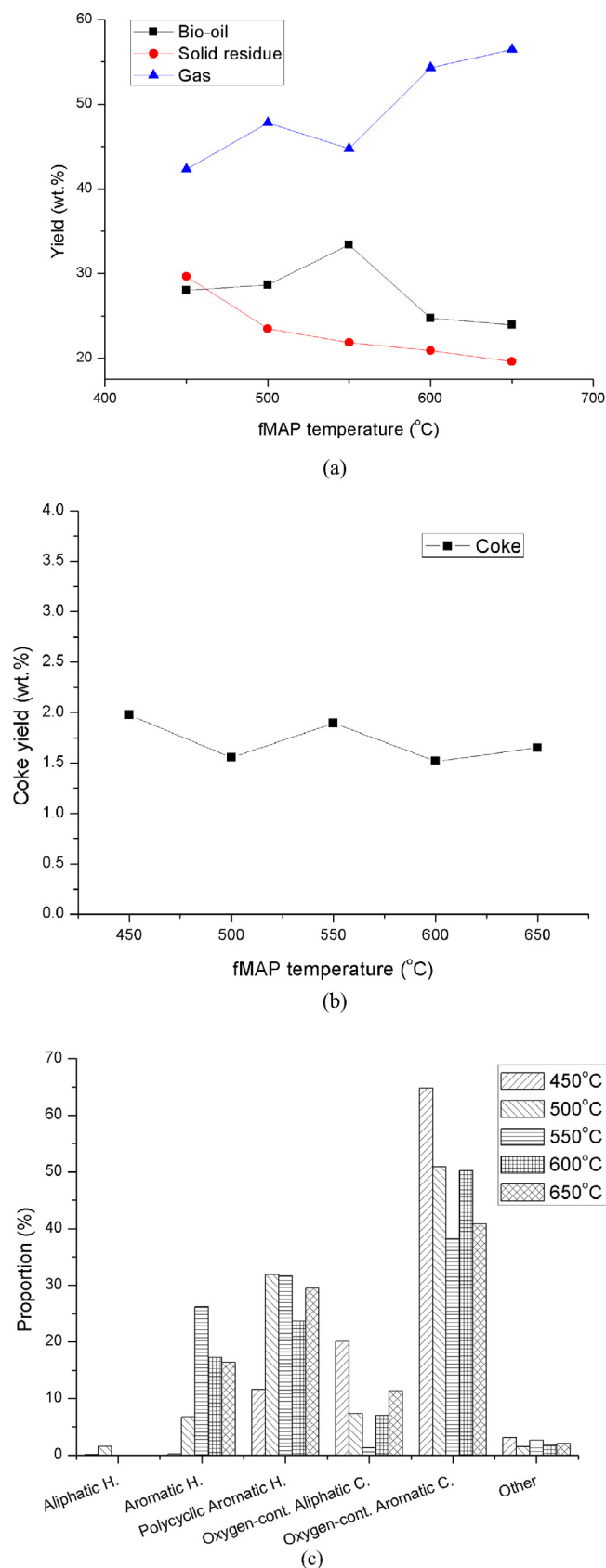
diffraction (XRD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer instrument. A Lynx-eye position sensitive detector was used to allow for a range of scattering angles to be measured simultaneously, increasing signal detection and decreasing scan times. Samples were exposed to a Cu K $\alpha$  radiation (45 kV × 40 mA) over an angular range of 5–60° 2 $\theta$  with a step size of 0.04° and a dwell time of 0.5 s.

## 3. Results and discussion

### 3.1. Effect of pyrolysis temperature on two-step catalytic fMAP

To investigate the effect of pyrolysis temperature on two-step catalytic fMAP, catalyst bed temperature was fixed at 425 °C with constant ratio of catalyst to feed ratio being 1:5, and the fMAP temperatures were 450 °C, 500 °C, 550 °C, 600 °C and 650 °C, respectively. Fig. 2 shows the effect of pyrolysis temperature on two-step catalytic fMAP of corn stover. As shown in Fig. 2(a), pyrolysis temperature significantly influenced the product distribution. The bio-oil yield increased with increasing pyrolysis temperature and reached its maximum of 33.38 wt.% at 550 °C. A decrease in bio-oil yield was observed after 550 °C to 23.97 wt.% at 650 °C. The devolatilization reaction would be promoted by higher temperature, then the strong organic bonds were broken, which is one of the possible reason for the bio-oil yield increasing from 450 °C to 550 °C. However, a decrease in bio-oil yield was observed when the temperature was higher than 550 °C because of the secondary thermal cracking reactions. This can also explain the increase in gas yield when the pyrolysis temperature increased above 550 °C. Besides, the solid residue yield decreased from 29.67 wt.% (450 °C) to 19.6 wt.% (650 °C) with increasing pyrolysis temperature. As shown in Fig. 2(b), the amount of coke deposited on the catalyst was not significantly influenced by the pyrolysis temperature. The coke yields were around 1.7 wt.% at the pyrolysis temperature over the range between 450 °C and 650 °C.

The bio-oil composition was also affected by pyrolysis temperature. The relative components of bio-oil could be classified into several groups such as aliphatic hydrocarbons, aromatic hydrocarbons, oxygen-containing aliphatic compounds, oxygen-containing aromatic compounds, polycyclic aromatic compounds (PAHs), and others. It can be seen from Fig. 2(c) that increasing pyrolysis temperature from 450 °C to 650 °C increased the aromatic hydrocarbons yield up to 26.20% at 550 °C. When temperature was higher than 550 °C, there was little change in aromatic hydrocarbons yield. As could be seen, there were almost no aliphatic hydrocarbons in this temperature range. Besides, the proportion of oxygen-containing aliphatic compounds and oxygen-containing aromatic compounds decreased at first and then increased in the test temperature severities. The formation of aromatic compounds containing oxygen in most cases were attributed to the polymerization reaction. In addition, the proportion of PAHs slightly decreased from 31.87% (500 °C) to 29.50% (650 °C, including naphthalene, methyl-naphthalene, ethyl-naphthalene and anthracene). It seems changing pyrolysis temperature has little effect on the selectivity for C<sub>10+</sub> aromatics. From the results above, pyrolysis temperature of 500–650 °C was beneficial to aromatic hydrocarbons production. When bio-oil yield and its composition were considered, the optimal temperature for two-step catalytic fMAP of corn stover with HZSM-5 as the catalyst was 550 °C, at which the highest bio-oil yield (33.38 wt.%) and maximum proportion of aromatic compounds (26.20%) were achieved. The potential industrial chemical compounds obtained from bio-oil at 550 °C included toluene (0.70%), xylene (3.73%), indene (5.14%), phenol (4.65%) and naphthalene (15.62%), which are all valuable chemical intermediates for the production of useful chemical products. The



**Fig. 2.** Effect of pyrolysis temperature on two-step catalytic fMAP of corn stover: (a) Product distribution; (b) Coke formation; (c) Bio-oil composition.

optimal temperature of 550 °C was used in the subsequent experiments.

### 3.2. Effect of catalyst loading on two-step catalytic fMAP

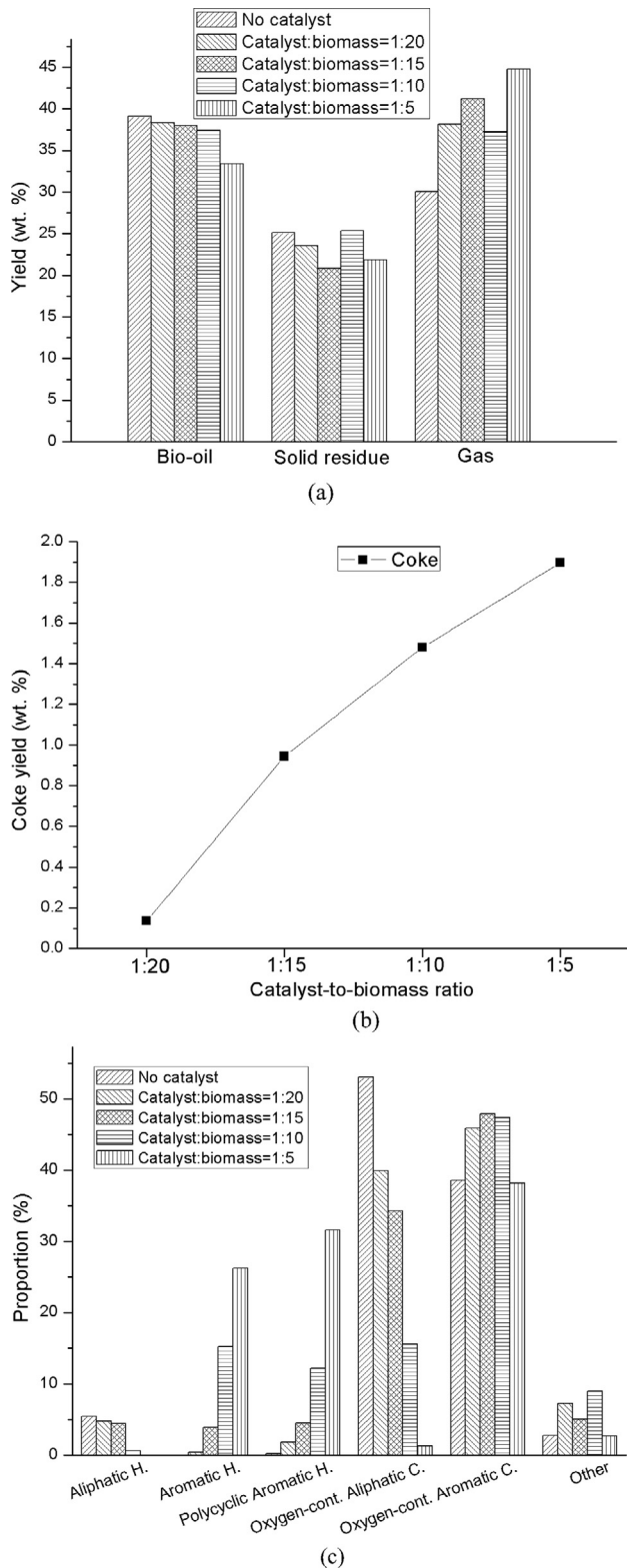
The effect of catalyst loading on two-step catalytic fMAP was carried out in this section. To achieve this aim, the effect of catalyst to biomass ratio on product yields and chemical compositions were investigated. During experiments, the pyrolysis temperature was fixed at 550 °C, and the catalyst to biomass ratios were no catalyst, 1:20, 1:15, 1:10, 1:5, respectively. Fig. 3 shows effect of catalyst loading on two-step catalytic fMAP of corn stover. As shown in Fig. 3(a), the use of catalyst in the second step resulted in a slight decrease in bio-oil yield. In addition, when catalyst to biomass ratio increased from 1:20 to 1:5, the bio-oil yield decreased linearly from 38.31 wt.% to 33.38 wt.% and gas yield increased significantly. This could be explained by the three-dimensional porous structure of the HZSM-5 [25]. When the pyrolysis vapor passed through the internal cavities of the catalyst, the large molecules of it were converted into smaller size of gaseous hydrocarbons, while oxygen was removed as H<sub>2</sub>O, CO and CO<sub>2</sub>, leading to in the increased yield of gas products. Similar results were reported by Seo et al. [26] and Zhang et al. [14]. Also Putun et al. [27] indicated that in two-stage catalytic upgrading of olive residue with three kind of catalyst (natural zeolite, HZSM-5, H-Y) in fixed-bed reactor, the increase in catalyst to biomass ratio resulted in an increase in gas products, especially for the HZSM-5. Fig. 3(b) shows the effect of catalyst to biomass ratio on the coke deposits on the catalyst. As it can be seen from Fig. 3(b), coke yield increased from 0.13 wt.% to 1.90 wt.% with increasing catalyst to biomass ratio. Meng et al. [28] studied the coking behavior for catalytic pyrolysis of heavy oil, and indicated that increasing catalyst-to-feedstock ratio resulted in higher average activation of catalysts while increasing the pyrolysis extent and promoting condensation reactions, leading to a coke yield increase.

The chemical composition was also influenced by catalyst to biomass ratio on the two-step catalytic fMAP. As shown in Fig. 3 (c), the proportion of aliphatic hydrocarbons and oxygen-containing aliphatic compounds decreased with increasing catalyst to biomass ratio. Significant increases in proportion of aromatic hydrocarbons and PAHs were observed over the catalyst to biomass ratios tested. The aromatic hydrocarbons reached maximum value of 26.2% at the catalyst to biomass ratio of 1:5. The possible reaction mechanism is that various oxygenated compounds produced in the catalytic pyrolysis of corn stover, including acid, alcohols, ketones and aldehydes, are intermediates in the production of aromatics [29–31]. When they passed through the internal pores of HZSM-5 catalyst, some of these intermediates were transformed to single-ring aromatic products through a series of oligomerization, decarboxylation, decarbonylation and dehydration reactions. Other aromatics can be obtained through alkylation and isomerization reactions. In addition, single-ring aromatic products may further react with another oxygenate to form PAHs. This is the possible reason for the decreased proportion of oxygen-containing aliphatic compounds. Thus, HZSM-5 has been widely studied due to its shape selectivity for aromatic hydrocarbons [32].

### 3.3. Effect of catalyst bed temperature on two-step catalytic fMAP

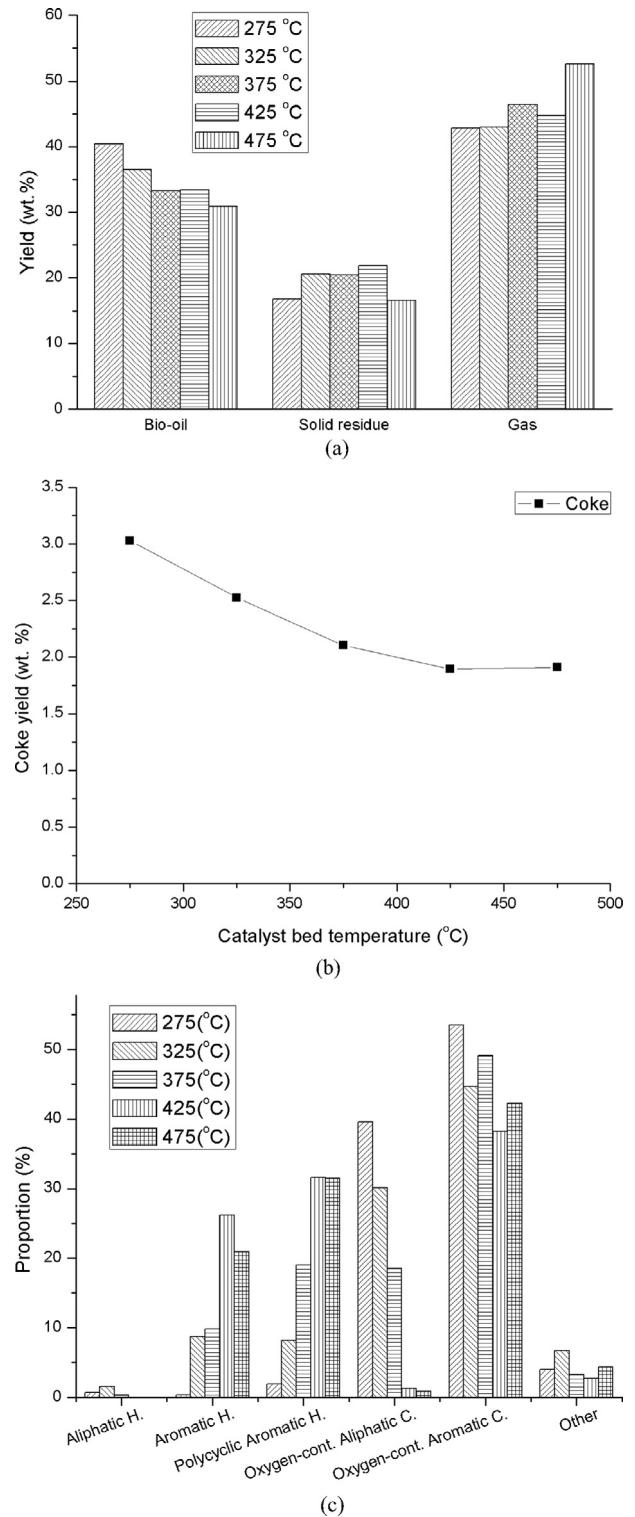
To investigate the effect of catalyst temperature on two-step catalytic fMAP, pyrolysis temperature was fixed at 550 °C with constant ratio of catalyst to feed ratio being 1:5. Catalyst bed temperature of 275 °C, 325 °C, 375 °C, 425 °C and 475 °C were tested. Fig. 4 shows the effect of catalyst bed temperature on two-step catalytic fMAP of corn stover. As shown in Fig. 4(a), the bio-oil yield decreased from 40.38 wt.% (275 °C) to 30.83 wt.% (475 °C), while gas yield increased dramatically from 42.8 wt.% to 52.59 wt.% over the ranges of catalyst bed temperature studied. On the contrary, the solid residue yield did not change obviously. Liu et al. [8]





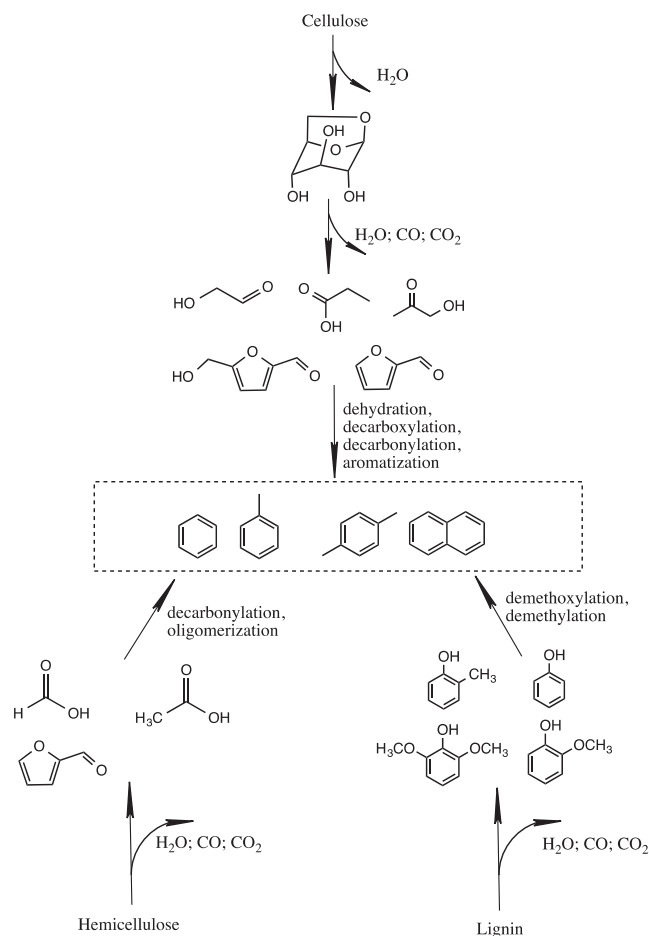
**Fig. 3.** Effect of catalyst loading on two-step catalytic fMAP of corn stover: (a) Product distribution; (b) Coke formation; (c) Bio-oil composition.

mentioned that use of catalyst in the pyrolysis results in a decrease in bio-oil yield due to the reason that the pyrolysis vapors passed through the catalyst bed, which increased the gas residence time and promoted the secondary thermal cracking. Wang et al. [16] studied the influence of catalyst bed temperature on catalytic



**Fig. 4.** Effect of catalyst bed temperature on two-step catalytic fMAP of corn stover: (a) Product distribution; (b) Coke formation; (c) Bio-oil composition.

pyrolysis of Douglas fir pellets. They concluded that increasing catalyst bed temperatures results in a decrease of the bio-oil yield. The similar results were reported by Putun et al. [27]. Therefore, catalyst bed temperature at 425 °C was considered as the optimum temperature for desirable catalytic upgrading. In addition, Fig. 4(b) shows the effect of catalyst bed temperature on the coke deposits on the catalyst. The coke formation was reduced from 3.03 wt.% to



**Fig. 5.** The possible reaction pathway of sequential two-step catalytic fMAP of lignocellulosic biomass.

1.90 wt.% as the catalyst bed temperature increased from 275 °C to 475 °C. Wang et al. [33] also showed that coke formation was reduced as the catalyst bed temperature was increased from 400 °C to 700 °C.

The effect of catalyst bed temperature on two-step catalytic fMAP on the chemical composition of bio-oil is shown in Fig. 4

(c). It was found that the proportion of aromatics increased with the increased catalyst bed temperature and reached the maximum yield of 26.20% at 425 °C, which was about 5 times as that of the previous study [14]. A decrease in the proportion of aromatic hydrocarbons was observed after 425 °C to 20.93% at 475 °C. It is noted that only 0.33% of aromatic hydrocarbons was obtained at 275 °C which revealed that the catalyst bed did not reach active temperature for the catalyst at this temperature. The bio-oil aromatic hydrocarbons and PAHs proportions for two-step catalytic fMAP were significantly increased in comparison with those of non-catalytic pyrolysis, at the cost of aliphatic hydrocarbons and oxygen-containing compounds. The selectivity for certain aromatic hydrocarbons varied significantly with temperature. Among them, benzene, toluene and xylenes (BTX) were extremely low or were not detected among the monocyclic hydrocarbons at low catalyst temperature, which increased to around 5% (BTX) at 425 °C. In addition, as another high amount of compound, phenols were first increased from 29.55% at 275 °C to 36.59% at 375 °C, and then decreased to 26.63% at 475 °C. The possible reaction pathway of sequential two-step catalytic fMAP of lignocellulosic biomass is shown in Fig. 5 [33,34]. Anhydrosugars are formed from cellulose by dehydration reactions at first step, then these anhydrosugars undergo a series of dehydration, depolymerization, cyclization, fragmentation and aromatization reactions to obtain the aromatics. Due to its lacking of crystallinity and low degree of polymerization, hemicellulose is less thermally stable than cellulose [35]. Even though the reaction mechanism is similar with the cellulose, catalytic pyrolysis of hemicellulose will produce more char and less oil [34]. The phenols were mainly derived from the lignin pyrolysis. The contents of guaiacol-type and syringol-type compounds were decreased when the catalyst temperature above 375 °C. This is probably because the catalyst reached the optimal temperature around 400 °C, which could be beneficial to demethoxylation reaction and demethylation reaction [36]. Overall, the optimal catalyst bed temperature for two-step catalytic fMAP was 425 °C when both yield and composition of bio-oil were considered.

### 3.4. Quantitative analysis of major components in the bio-oil

Table 1 shows mass contents of 8 major components of bio-oil analyzed by GC–MS quantitative method and physicochemical properties of the organic liquid phase. The identified compounds

**Table 1**

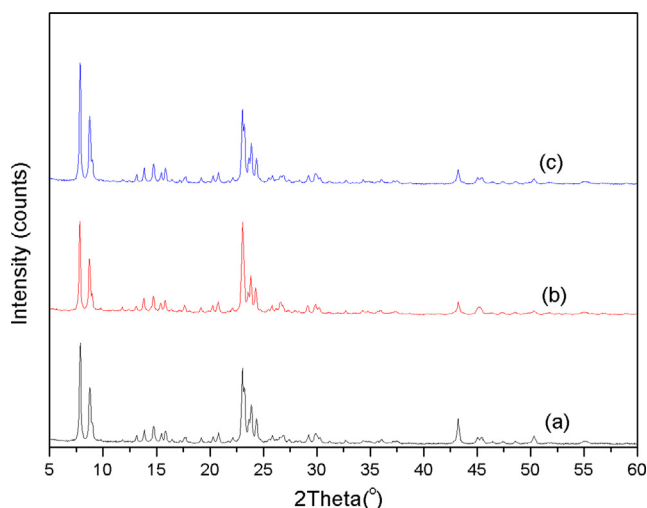
Mass contents of 8 major components of bio-oil analyzed by GC–MS quantitative method and physicochemical properties of the organic liquid phase.

Major component	Organic fraction <sup>a</sup>		No catalyst	
	Relative content (%)	Content in bio-oil (wt.%)	Relative content (%)	Content in bio-oil (wt.%)
Toluene	0.70	0.21	–	–
p-Xylene	2.68	1.33	–	–
Indene	1.87	0.86	–	–
Benzene, 1,2,3-trimethyl-	3.04	1.02	–	–
2,3-Benzofuran	1.01	1.52	–	–
Phenol	1.96	1.38	4.84	0.15
Phenol, 3-methyl-	4.55	2.37	2.32	0.08
Naphthalene	5.83	2.60	–	–
Elemental composition (wt.%)				
C	68.43		48.13	
H	6.51		8.16	
N	1.62		1.66	
O <sup>b</sup>	23.44		42.05	
HHV (MJ/kg) <sup>c</sup>	29.85		19.79	
Water content (wt.%)	9.11		29.82	

<sup>a</sup> Pyrolysis temperature: 550 °C, catalyst bed temperature: 425 °C, catalyst to biomass ratio: 1:5.

<sup>b</sup> Calculated by difference.

<sup>c</sup> Calculated using equation [24]  $HHV(MJ/kg) = (3.55 \times C^2 - 232 \times C - 2230 \times H + 51.2 \times C \times H + 131 \times N + 20,600) \times 10^{-3}$ .



**Fig. 6.** XRD patterns of catalyst: (a) the fresh HZSM-5; (b) spent (coked) HZSM-5 from two-step catalytic fMAP; (c) the regenerated HZSM-5 from two-step catalytic fMAP.

are as follows: toluene, p-xylene, indene, 1,2,3-Trimethylbenzene, 2,3-benzofuran, phenol, phenol, 3-methyl- and naphthalene. The aromatics are not detected in the non-catalytic pyrolysis, which indicates that HZSM-5 catalyst has a shape selectivity for aromatic hydrocarbons. Phenol, 3-methyl- and naphthalene were detected in large amounts in the organic liquid phase of catalytic pyrolysis at 2.37 wt.% and 2.60 wt.%, respectively. Most phenolic compounds were derived from thermal decomposition of lignin [33,34]. And the high weight percentage of naphthalene indicates that lignocellulosic biomass is mainly selectively converted to PAHs with the HZSM-5 catalyst. The water content and HHV of the organic liquid phase from catalytic pyrolysis were within 9–14 wt.% and 29.85 MJ/kg, respectively while those of bio-oil from non-catalytic pyrolysis were 29.82 wt.% and 19.79 MJ/kg, respectively. The results showed that high quality bio-oil was obtained through sequential two-step catalytic fMAP.

### 3.5. Catalyst characterization

The fresh, spent and regenerated HZSM-5 catalysts were characterized and analyzed using XRD technique to investigate the effect of coke on the catalyst structure. Fig. 6 shows XRD patterns of catalyst. The diffractogram comparison of the fresh, spent and regenerated HZSM-5 catalyst showed obvious similarities. The crystal structure and crystallinity of the HZSM-5 catalyst were intact before and after the pyrolysis and regeneration process. Therefore, HZSM-5 has good stability in the catalytic upgrading process.

## 4. Conclusion

This study investigated a sequential two-step catalytic fast microwave-assisted pyrolysis of biomass through a packed-bed catalyst for high quality bio-oil production. The pyrolysis and catalytic cracking and upgrading processes can be flexibly and independently controlled, and the catalyst recovery and regeneration process is simplified. The catalyst bed temperature and catalyst loading significantly affected the product distribution. The optimal pyrolysis and catalyst bed temperature were 550 °C and 425 °C, respectively. In addition, increasing the catalyst loading reduced the bio-oil yield but improved the bio-oil quality. Furthermore, the catalyst characterization indicated a good stability of HZSM-5 catalyst during the upgrading process.

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