



# Aromatic hydrocarbons production from ex situ catalysis of pyrolysis vapor over Zinc modified ZSM-5 in a packed-bed catalysis coupled with microwave pyrolysis reactor

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## HIGHLIGHTS

- First time using ZnZSM5 for catalytic cracking of microwave pyrolysis vapor.
- Achieved high selectivity of aromatic hydrocarbon by catalytic pyrolysis.
- Zn/ZSM-5 catalyst resulted in less coking than ZSM-5 under most reaction conditions.

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## ABSTRACT

Ex situ catalytic pyrolysis of biomass through a packed-bed catalysis close coupled with microwave pyrolysis was investigated to convert Douglas fir sawdust pellets to aromatic hydrocarbons by Zn/ZSM-5 catalyst. A comparison test from five different Zn loadings (0, 0.5, 1, 2, 5 wt.%) was first conducted, and it was found that the highest amount of aromatic hydrocarbons was produced from 0.5% Zn loaded on ZSM-5. Then a central composite experimental design (CCD) was used to optimize the upgraded bio-oil and syngas yields with 0.5% Zn loaded in ZSM-5. In comparison to the non-catalytic experiment, all the catalysts decreased the bio-oil yield and increased the syngas production. The product yields from Zn/ZSM-5 were sensitive with reaction conditions as the bio-oil yields varied between 22.3% and 44.8% compared with 32.2% and 37.8% over ZSM-5 catalyst, and syngas yields from 33.3% to 55.5% vs. 38.8% to 43.7% on ZSM-5 catalyst. GC/MS analysis showed that aromatic hydrocarbons become the most abundant compounds in the bio-oil. The high amount of aromatic hydrocarbons in the upgraded bio-oils from GC/MS analysis was confirmed by the FTIR analysis. The aromatic hydrocarbon was increased when the packed-bed temperature and inverse weight hourly space velocity (WHSV)<sup>−1</sup> were increased. The comparison of coking on ZSM-5 and Zn/ZSM-5 catalysts at different reaction conditions showed that the coking increased with increasing (WHSV)<sup>−1</sup> and decreasing packed-bed temperatures. Zn/ZSM-5 had lower coking than ZSM-5 on all the reaction conditions except packed-bed temperature at 269 °C and (WHSV)<sup>−1</sup> at 0.048.

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## 1. Introduction

As the rapid growth of population and urbanization, the demand for energy is continuously increasing [1]. A main use of energy consumption is for transportation [2], which accounts for one fifth of the total energy consumption [3]. Biomass in the form of bio-fuels (solid, liquid and gaseous) directly replacing fossil fuels

has attracted interest over several years as a promising renewable energy [4]. There are numerous pathways to produce bio-fuel, while pyrolysis draws much attention because it could directly converts biomass into liquid fuels called bio-oils. Those fuels are possible to be drop-in the existing petroleum infrastructure for the production of fuels with little modification [5]. Bio-oil is a dark brown, multi-component organic mixture of highly oxygenated compounds derived from depolymerization of hemicellulose, cellulose and lignin. However, oxygen present in the bio-oil has a negative effect on its quality and stability [6]. In particular, the

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high oxygen makes bio-oil only 50% of the heating value of the petroleum fuels and immiscible with hydrocarbon fuels. Thus bio-oils must be catalytically upgraded if they are to be used as a conventional liquid transportation fuel [7].

Catalytic cracking is one method that could remove oxygen from bio-oil in the form of  $H_2O$ ,  $CO$  and  $CO_2$  through deoxygenation without hydrogen supply and at atmospheric pressure. Catalytic cracking could be operated with or right after (in situ and ex situ catalytic pyrolysis) pyrolysis and before the condensation of bio-oils which means that the bio-oil is in the vapor phase. In situ and ex situ catalytic pyrolysis of pine bark were compared [8] and found the ex situ catalytic pyrolysis decreased oxygen content and increased the carbon/oxygen ratio of bio-oil, which showed that it can improve the bio-oil quality. Park et al. [9] conducted direct conversion of the pyrolytic vapor of pine wood in a fixed catalyst bed reactor installed at the upper part of a bubbling fluidized bed reactor and found that the aromatic hydrocarbons were significantly formed after upgrading over HZSM-5 (proton-exchange of Zeolite Socony Mobil #5) which were not present in the pyrolysis bio-oil. And they also found HZSM-5 catalyst was more efficient in bio-oil upgrading than HY (proton-exchange of Y Zeolite) catalyst. Aho and his coworker [10] investigated the influence of zeolites and their iron modified counterparts during catalytic upgrading of pine wood pyrolysis vapor. They found that deoxygenation reaction over all the catalysts increased compared to the non-catalytic pyrolysis. Iliopoulou et al. [11] used different transition metal-modified ZSM-5 zeolite to catalytically upgrade biomass pyrolysis vapor and found that all metal-modified catalysts enhanced the production of aromatics and phenols. In our previously work [12], ex situ catalytic pyrolysis was conducted by a packed-bed reactor coupled with microwave pyrolysis of biomass. And we found that aromatic hydrocarbons were enriched and became the most abundant compounds accounting for about 15–92.6% in upgraded bio-oils. Ex situ catalytic upgrading of fast pyrolysis vapors could also produce bio-oil with improved quality thus has the potential to reduce subsequent hydrotreating costs [13].

A variety of efforts were attempted to test zeolites as catalysts in catalytic pyrolysis [4,7–9,11,12,14–18]. ZSM-5 displayed the highest selectivity of producing aromatic hydrocarbons [7,19,20] and reducing undesirable oxygen contained compounds [21]. The oxygen removal was found in the form of  $H_2O$  at lower temperature and  $CO$  and  $CO_2$  at higher temperature [22]. The  $CO$  and  $CO_2$  from oxygen removal is preferable, as more hydrogen would be saved for hydrocarbon formation, less carbon would deposit on the zeolite, and the water content of bio-oil would be reduced [23]. The oxygen removal, especially in the form of  $H_2O$  is due to the strong acidity of ZSM-5 [24], which is also leads to the decrease of the organic fraction of bio-oil via cracking. The acid sites are therefore the essential part of the mechanism for both deoxygenating reactions and deactivating mechanisms [2]. More acid sites give a higher yield of gasoline-like products, but also lead to more coke formation [25]. Many transition metals, such as nickel [17,24,26], cobalt [17,24], iron [17], cerium [27], and gallium [9,15,17], were tested to adjust the acidity of ZSM-5 catalyst to increase the yield of bio-oils and reduce the coke formation on catalyst. Zinc modified ZSM-5 have been shown to be an effective catalyst for aromatization of a wide range of feedstocks such as methanol [28], furfural [29], dimethyl ether [30], alkanes [31–33], and alkene [34] but few work has been down on using Zn/ZSM-5 for aromatic hydrocarbon production from catalytic pyrolysis of biomass. In this study, Zn/ZSM-5 was used as catalytic pyrolysis catalyst in a packed-bed catalysis reactor coupled with microwave pyrolysis reactor.

The objective of this study was to investigate the effect of Zn/ZSM-5 catalyst in ex situ catalytic pyrolysis which was conducted

by a packed-bed catalysis reactor coupled with microwave pyrolysis reactor.

## 2. Materials and methods

### 2.1. Materials

The feedstock used for this study was DF (Douglas fir pellets, Bear Mountain Forest Products Inc., USA) approximately 5 mm in diameter and 20 mm in length with moisture content of 8%. The catalyst Zn/ZSM-5 (with 0, 0.5, 1, 2, 5 wt.% Zn loading) in this study was prepared by an incipient wetness impregnation method using ZSM-5 (Zeolyst International, USA;  $SiO_2/Al_2O_3$  Mole Ratio: 50) and  $Zn(NO_3)_2$  (Fisher scientific). After impregnation, the catalyst was dried at 105 °C for 12 h and calcined at 500 °C for 6 h.

### 2.2. Catalyst activity evaluation in a packed-bed catalysis reactor

A Sineo MAS-II batch microwave oven (Shanghai, China) with a rated power of 1000 W was used for microwave pyrolysis. The detailed experiment setting was described in our previous study [12]. The reaction conditions of microwave pyrolysis were set as reaction temperature at 480 °C and reaction time of 9 min for all catalysis experiments. 20 g Douglas fir pellets were placed in a 500 mL quartz flask inside of the microwave oven. The pyrolysis volatile from the flask went through a packed-bed catalysis reactor (quartz tube reactor with inside diameter of 15 mm and length of 200 mm) which was filled with catalysts and then connected to a condensation system. The condensable liquid was collected as bio-oil. The non-condensable volatiles escaped as syngas at the end of the condensers and collected for analysis. The biochar was left in the quartz flask. In the catalytic process, carbonaceous materials were gradually accumulated on the surface of the catalyst; these deposits are defined as coke. The coke was calculated by difference of catalyst weights before and after catalysis. The weight of syngas was calculated using the following equation:

$$\text{Weight of syngas} = \text{initial biomass mass} - \text{bio-oil mass} - \text{biochar mass} - \text{coke mass} \quad (1)$$

The bio-oil yield (wt.%) was calculated by bio-oil mass divided by initial biomass mass. The syngas yield (wt.%) was calculated by syngas mass divided by initial biomass mass.

### 2.3. Experimental design and optimization

Inverse weight hourly space velocity (WHSV)<sup>−1</sup> ( $X_1$ , h), which was calculated by catalyst mass divided by mass flow, and cracking temperature ( $X_2$ , °C) were chosen as two independent variables to optimize the product yields (bio-oil and syngas). A central composite experimental design (CCD) was used at various levels shown in Table 1.  $Y_i$  was used as the dependent output variable. The weight of the Douglas fir sawdust feeding was 20 g. Catalyst mass varied from 2.2 to 7.8 g. The packed-bed temperature was from 268.9 to 481.1 °C, and the (WHSV)<sup>−1</sup> was from 0.021 to 0.075 h (WHSV was from 13.4 to 47.4 h<sup>−1</sup>).

**Table 1**  
Coded levels of independent variables in the experiment plan.

Level	$X_1$ : (WHSV) <sup>−1</sup> (h)	$X_2$ : cracking temperature (°C)
−1	0.029	300
1	0.067	450
− $r$ = −1.41	0.021	268.9
$r$ = 1.41	0.075	481.1

For statistical calculations, the variables  $X_i$  were coded as  $x_i$  according to Eq. (2):

$$x_i = (X_i - X_0) / \Delta X \quad (2)$$

where  $x_i$  is the dimensionless value of the independent variable while  $X_i$  is the raw value.  $X_0$  is the raw value of the variable at the center point and  $\Delta X$  is the step length. A  $2^2$ -factorial CCD, with 4 axial points ( $\alpha = 1.41$ ) and 5 replications at the center points ( $n_0 = 5$ ) leading to a total number of 13 experiments was employed to optimize the reaction conditions. A second order polynomial equation (Eq. (3)) was used to describe the effect of independent variables in terms of linear, squared, and interaction. The predicted model for the response ( $Y_i$ ) was:

$$Y_i = b_0 + \sum_{i=1}^2 b_i X_i + \sum_{i=1}^2 b_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^2 b_{ij} X_i X_j + \varepsilon \quad (3)$$

where  $Y_i$  is the predicted response;  $b_0$  is the interception coefficient,  $b_i$ ,  $b_{ii}$ , and  $b_{ij}$  are coefficients of the linear, quadratic, and interaction effects;  $X_i$  is the independent variables; and  $\varepsilon$  is the random error. The statistical analysis of the model was performed by Design Expert 8 software (Stat-Ease, MN). The coefficient of determination ( $R^2$ ) and  $F$  test were used to determine the quality of fit of the second order equation. The effect of each independent variable and their interactions were determined. An  $F$  test was used to determine the model parameter's significance ( $\alpha = 0.05$ ).

#### 2.4. Analysis of upgraded bio-oil and syngas

The chemical composition of upgraded bio-oils was determined by Agilent 7890A GC/MS (GC–MS; GC, Agilent 7890A; MS, Agilent 5975C) with a DB-5 capillary column. The GC was first maintained at 45 °C for 3 min and then increased at 10 °C/min to 300 °C. The injector temperature was 300 °C and the injection size was 1  $\mu$ L. 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. The compounds were identified by comparing the spectral data with the NIST Mass Spectral library [35]. An IRPrestige21 spectrometer in the attenuated total reflection (ATR) mode (Shimadzu, Ge crystal; software: IRRolution) was used to record the Transform Infrared Spectroscopy (FTIR) spectra of the upgraded bio-oils. Omnic 8.0 software (Thermo Nicolet) was used to analyze the data and fit the curves. The water content of the bio-oils was determined by Karl Fischer Titrator (Mettler Toledo V30).

The chemical compositions of syngas were determined by a Carle 400 gas chromatography (Chandler Engineering, Broken Arrow, OK, USA) system with a thermal conductivity detector (TCD).

### 3. Results and discussion

#### 3.1. Reactivity of Zn/ZSM-5

In order to find the best Zn loading, the experiments were conducted to test 5 different Zn loadings (0, 0.5, 1, 2, and 5 wt.%) on ZSM-5 in the packed-bed at a fixed reaction condition ((WHSV) $^{-1}$ : 0.048; packed-bed temperature: 375 °C).

##### 3.1.1. Catalyst effects on product yields

The upgraded bio-oil was prepared from the packed-bed catalysis coupled with microwave pyrolysis process in which the packed-bed reactor was kept at 375 °C and the (WHSV) $^{-1}$  was 0.048. The non-catalytic bio-oil was obtained from microwave pyrolysis of Douglas fir pellets with a pyrolysis temperature at 480 °C without using catalysts. The product yields of coupled catalytic upgrading of microwave pyrolysis vapor from different Zn loadings are summarized in Fig. 1. In comparison to the

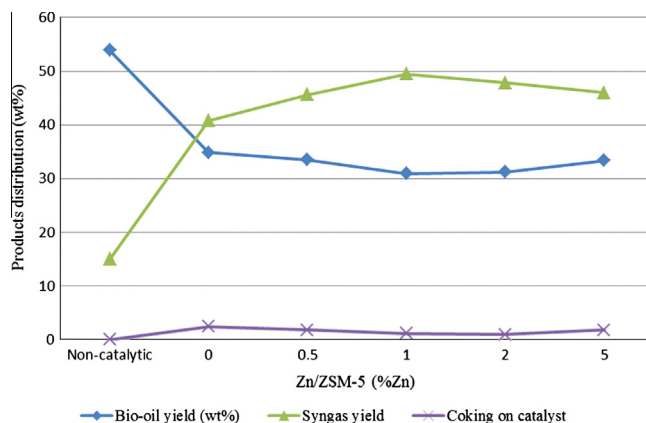


Fig. 1. Product yields of coupled catalytic upgrading and microwave pyrolysis of Douglas fir pellets with different Zn loadings ((WHSV) $^{-1}$ : 0.048 h, packed-bed temperature: 375 °C).

non-catalytic experiments, all the Zn/ZSM-5 catalysts at this reaction condition resulted in a decrease of the bio-oil yield and an increase of the syngas yield. The bio-oil first decreased from 34.85% to 30.96% then increased to 33.33% when the Zn loading increased from 0 to 5%.

##### 3.1.2. Catalyst effects on bio-oil composition

In order to further understand the Zn loading effect on bio-oil chemical compositions from coupled Zn/ZSM-5 catalysis and microwave pyrolysis, GC/MS was used to characterize the bio-oil chemical compounds (Fig. 2). The most representative organic compounds of the bio-oil were categorized into ten functional groups: acids, ketones/aldehydes, alcohols, aromatic hydrocarbons, phenols, guaiacols, furans, esters, sugars and others. Among them, aromatic hydrocarbons are considered as desirable products for biofuel product as they not only have good volumetric energy content, but also have a large positive influence on seal-swell, O-rings, self-sealing bladders, adhesives, etc. in jet engine systems. Phenols and furans are also regarded as high value chemicals. Other compounds such as acid, ketones/aldehydes, alcohols, and guaiacols are all undesirable because they are oxygen containing compounds, which are related to instability of bio-oils, low heating

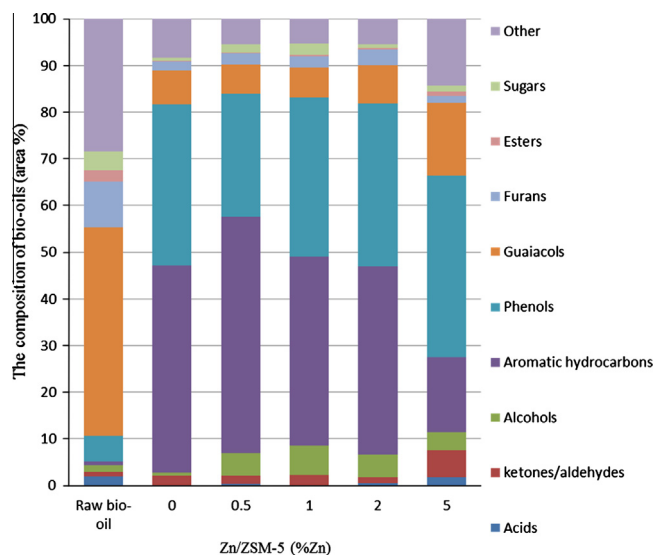


Fig. 2. The composition of bio-oils with different Zn loadings from GC/MS analysis ((WHSV) $^{-1}$ : 0.048 h, packed-bed temperature: 375 °C).

value, and other drawbacks. The non-catalytic bio-oil without catalyst from microwave pyrolysis of Douglas fir pellets was a mixture of acid, ketones, alcohols, phenols, guaiacols, furans, esters, sugars and so on. With Zn/ZSM-5 used in packed-bed catalysis close coupled with microwave pyrolysis, aromatic hydrocarbons which did not contain oxygen were enriched and become the most abundant compounds in upgraded bio-oils. The amount of aromatic hydrocarbons was increased from 44.4% to 50.7% when 0.5% Zn was loaded to ZSM-5 and then decreased to 16% when the Zn loading increased to 5%. The highest amount of aromatic hydrocarbons was produced from 0.5% Zn loading on ZSM-5. Phenols were decreased from 34.6% to 26.3% when 0.5% Zn was added to ZSM-5, but increased to 38.93% when the Zn loading increased to 5%. Guaiacols were following the similar trend to phenols.

### 3.2. Optimization of experiment parameters

Based on the effect of Zn loadings on chemical compositions of bio-oils, the 0.5% Zn/ZSM-5 was chosen to be the catalyst for the following reaction optimization research as it resulted in the highest yield of aromatic hydrocarbons.

#### 3.2.1. Response surface analysis of reaction condition effects on product yields

In our previously research [18], the inverse weight hourly space velocity (WHSV)<sup>-1</sup> ( $X_1$ , h) and cracking temperature ( $X_2$ , °C) were found have a significant influence on products yield distribution in ex situ catalytic pyrolysis of biomass. Therefore they were chosen as two independent variables to optimize the product yields (bio-oil and syngas) in this study. The experimental design and product yield are shown in Table 2. The bio-oil yields were from 22.3 to 44.8 wt.%, while the syngas yield was from 33.3 to 55.5 wt.%. The syngas was mainly composed of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>. The highest bio-oil yield of 44.80 wt.% was obtained with the shortest (WHSV)<sup>-1</sup> at 0.021 h and a moderate packed-bed temperature at 375 °C.

Eq. (2) was reduced by using backward statistical analysis, and parameters were sequentially removed based on the coefficient's  $P$ -value until all remaining were significant ( $P < 0.05$ ). Using the results of the experiment, the first order equations were obtained showing the yields of upgraded bio-oil (Eq. (4)) and syngas (Eq. (5)) as a function of the (WHSV)<sup>-1</sup> ( $X_1$ , h) and packed-bed temperature ( $X_2$ , °C):

$$Y_{\text{bio-oil}} = 64.43 - 272.19X_1 - 0.05X_2 \quad (4)$$

$$Y_{\text{syngas}} = 3.51 + 247.76X_1 + 0.08X_2 \quad (5)$$

**Table 2**  
Experiment design and product yield distribution.

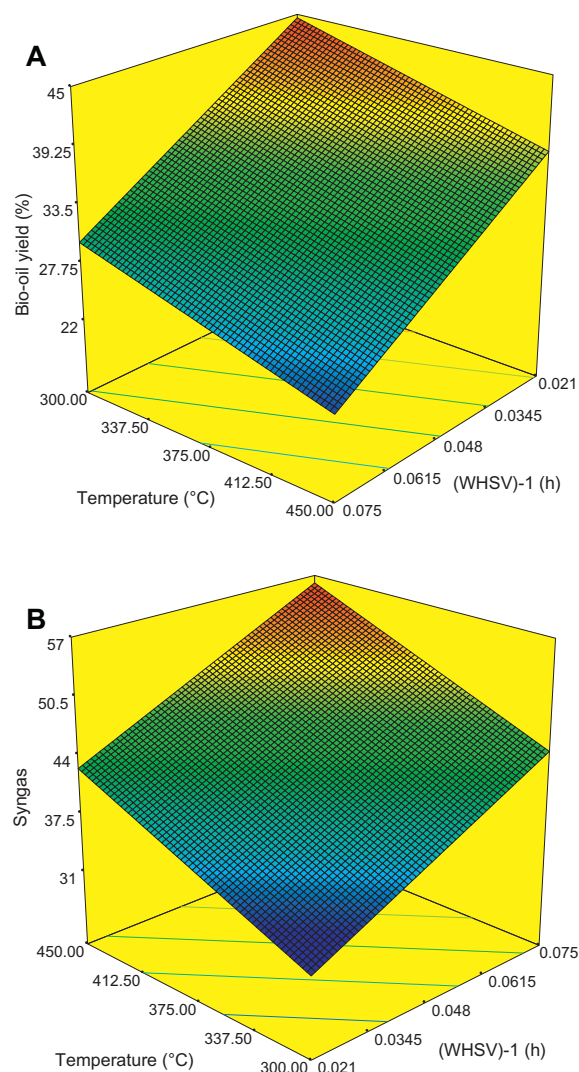
Run	(WHSV) <sup>-1</sup> (h)	Cracking temperature (°C)	Bio-oil yield (wt.%)	Syngas yield (wt.%)
1	0.029	300	41.36	36.82
2	0.067	300	37.68	38.43
3	0.029	450	38.08	40.76
4	0.067	450	28.69	50.86
5	0.021	375	44.80	33.28
6	0.075	375	24.75	51.67
7	0.048	269	33.48	39.95
8	0.048	481	22.27	55.45
9	0.048	375	34.60	44.44
10	0.048	375	32.42	46.77
11	0.048	375	33.48	45.61
12	0.048	375	33.28	45.51
13	0.048	375	34.24	44.29

The  $P$  value of Eq. (4) was  $0.0029 < \alpha = 0.05$ . Thus the linear model could adequately describe the bio-oil yield. The coefficient of determination ( $R^2$ ) for Eq. (4) was 0.70. This suggested that the model finely represents the relationships among the independent variables. The model term  $b_0$ ,  $X_1$ ,  $X_2$ , were significant because the  $P$  values for these model terms were 0.0029, 0.0030, 0.0247, which were smaller than  $\alpha = 0.05$ . The model of bio-oil yields with the (WHSV)<sup>-1</sup> and the packed-bed temperature can be visualized in Fig. 3A. Increasing the (WHSV)<sup>-1</sup> and packed-bed temperatures resulted in a decrease of the bio-oil yield.

The  $P$  value of Eq. (5) was  $0.0003 < \alpha = 0.05$ . Thus the linear model could adequately describe the syngas yield. The coefficient of determination ( $R^2$ ) for Eq. (5) was 0.81. This suggested that the model appropriately represents the relationships among the independent variables. And the model term  $b_0$ ,  $X_1$ ,  $X_2$  were significant because the  $P$  values for these model terms were 0.0003, 0.0020, and 0.0005 respectively, which were smaller than  $\alpha = 0.05$ . The linear model terms of the (WHSV)<sup>-1</sup> and the packed-bed temperature can be visualized in Fig. 3B. Increasing the (WHSV)<sup>-1</sup> and packed-bed temperatures caused an increase of the syngas yield.

#### 3.2.2. Catalyst effects on product yields distribution

The product yields in the ex situ catalytic pyrolysis of biomass with ZSM-5 and Zn/ZSM-5 as catalyst in different reaction



**Fig. 3.** Effect of independent variables interaction on bio-oil (A) and syngas (B) yields.



conditions are shown in Table 2 (the bio-oil yields were from 22.3% to 44.8% and the syngas yields were from 33.3% to 55.5%). The bio-oil and syngas yields from non-catalytic pyrolysis of Douglas fir pellets (pyrolysis temperature was 480 °C) were 53.3% and 15%, respectively. In comparison to the non-catalytic experiment, all the catalysts decreased the bio-oil yield and increased the syngas production. This is because of cracking, dehydration, aromatization, decarboxylation, decarbonylation, and oligomerization which are catalyzed by the zeolite Brønsted acid sites [2,4,36]. The water content of bio-oils from ex situ catalytic pyrolysis was ranged from 17.2 to 27.1 wt.% based on biomass, which was higher than 17.2–24.7 wt.% based on biomass for non-catalytic bio-oils. The increased water content was due to dehydration of oxygen contained compounds which reacted on the acid sites of ZSM-5 [37]. The product yields from Zn/ZSM-5 were sensitive with reaction conditions since the bio-oil yields varied between 22.3% and 44.8% compared with the yields from 32.2% to 37.8% over ZSM-5 catalysts. The syngas yields were from 33.3% to 55.5% vs. 38.8% to 43.7% on ZSM-5 catalyst.

### 3.2.3. Chemical composition of upgraded bio-oils

The chemical composition of the bio-oil was investigated by FTIR (Fig. 4). FTIR identified chemical bonds and functional groups in bio-oils which are shown in Table 3. The broad peak between 3200 and 3500  $\text{cm}^{-1}$  (O–H stretch) indicated the presence of alcohols and phenols. The peak of alkyl C–H stretch vibrations between 2850 and 3000  $\text{cm}^{-1}$  indicated the presence of alkane which was only detected from upgraded bio-oils. The C=O stretch vibration at 1718  $\text{cm}^{-1}$  indicated the presence of carboxylic acids, aldehydes and ketones [9], which was only detected in non-catalytic bio-oil. The peaks around 1600  $\text{cm}^{-1}$  represented aromatic in-ring C=C stretch were only detected in upgraded bio-oils, which indicated that the aromatics were produced from catalytic pyrolysis of biomass. The carboxylic acids C–O stretch which vibrated at 1274  $\text{cm}^{-1}$  was only detected in non-catalytic bio-oil. The peaks at 1086  $\text{cm}^{-1}$  and  $\sim 1040 \text{ cm}^{-1}$  (aromatic in-plane C–H bending), and 878  $\text{cm}^{-1}$  (aromatic C–H oop) confirmed the high amount of aromatic hydrocarbons in the upgraded bio-oils.

In order to further understand the catalyst effect on bio-oil chemical compositions from close coupled Zn/ZSM-5 catalysis,

GC/MS was used to characterize the bio-oil chemical compounds (Fig. 5). The composition of the upgraded bio-oils from ex situ catalytic pyrolysis was obviously different from non-catalytic bio-oil. The aromatic hydrocarbons in the bio-oils from ex situ catalytic pyrolysis were from 7.47 to 89.92 area% depending on the reaction conditions, which were significantly increased, comparing to that from non-catalytic bio-oil which was composed of only 0.72 area% aromatic hydrocarbons. The optimum conditions to achieve the maximum amount of aromatic hydrocarbons was  $(\text{WHSV})^{-1}$  at 0.075 and packed-bed temperature at 375 °C with 0.5% Zn/ZSM-5. These aromatic hydrocarbons were mainly composed of benzene, toluene, xylene, naphthalene, and their derivatives. The phenols in the upgraded bio-oils from ex situ catalytic pyrolysis were ranged from 6.94 to 29.84 area%, which was more than that (5.46 area%) from non-catalytic bio-oils. The guaiacols, which were the most abundant compounds in the non-catalytic bio-oil, were significantly decreased from 44.7 area% in the non-catalytic bio-oil to 0–22.33 area% in the upgraded bio-oils from ex situ catalytic pyrolysis with Zn/ZSM-5 catalysts.

### 3.2.4. The effect of reaction conditions on chemical compositions of upgraded bio-oils

Using the results of the chemical composition of bio-oils, a first order equation was obtained showing the aromatic hydrocarbons content (Eq. (6)) as a function of the  $(\text{WHSV})^{-1}$  ( $X_1$ , h) and packed-bed temperature ( $X_2$ , °C):

$$A_{\text{aromatic Hydrocarbons}} = -107.51 + 1316.1X_1 + 0.24X_2 \quad (6)$$

The  $P$  value of Eq. (6) was  $0.0001 < \alpha = 0.05$ . Thus the linear model could adequately describe the produced aromatic hydrocarbons. The coefficient of determination ( $R^2$ ) for Eq. (6) was 0.92. This suggested that the model well represents the relationships among the variables. The model term  $b_0$ ,  $X_1$ ,  $X_2$ , were significant because their  $P$  values were 0.0001, 0.0001, 0.0011, respectively, which were smaller than  $\alpha = 0.05$ . Increasing the  $(\text{WHSV})^{-1}$  and packed-bed temperature resulted in the increase of aromatic hydrocarbons content.

The effect of packed-bed catalysis temperatures on chemical compositions of upgraded bio-oils was analyzed with a fixed  $(\text{WHSV})^{-1}$  (0.048) as shown in Fig. 6. Using Zn/ZSM-5 as a catalyst,

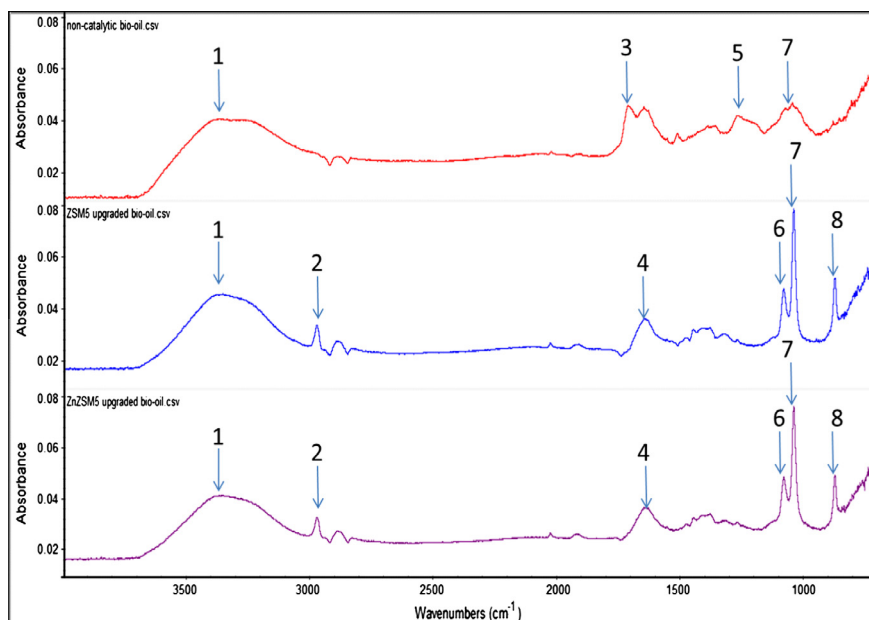
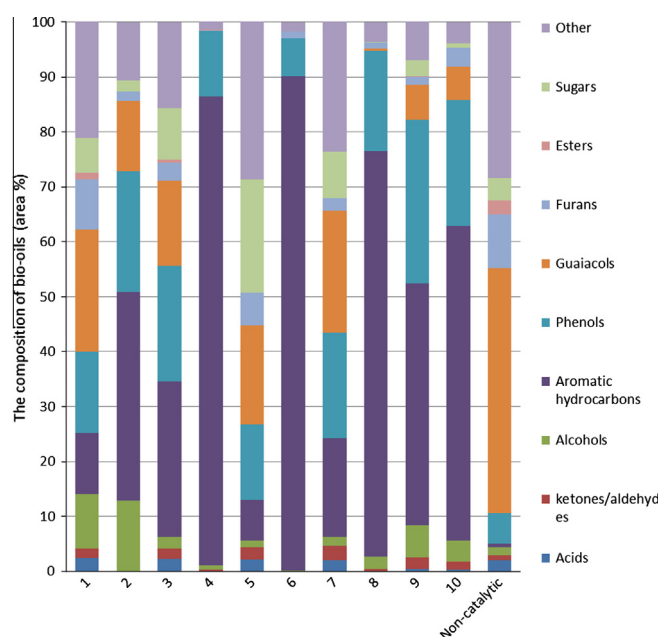
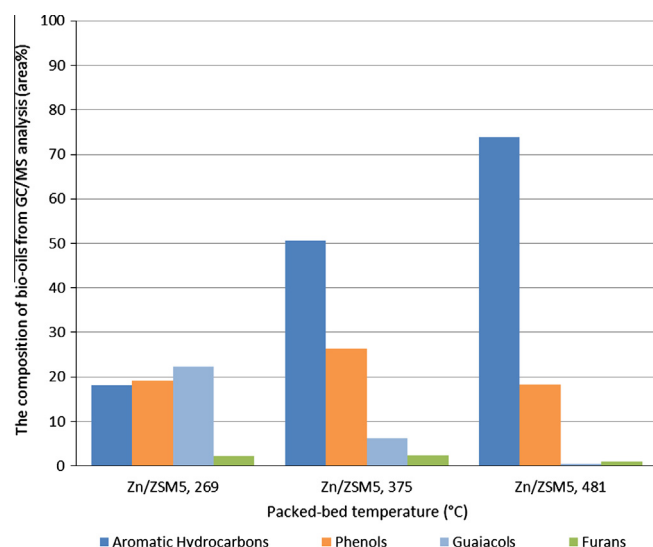


Fig. 4. FTIR spectra of non-catalytic, ZSM-5 upgraded and Zn/ZSM-5 upgraded bio-oils (the peak numbers correspond to those in Table 3).

**Table 3**

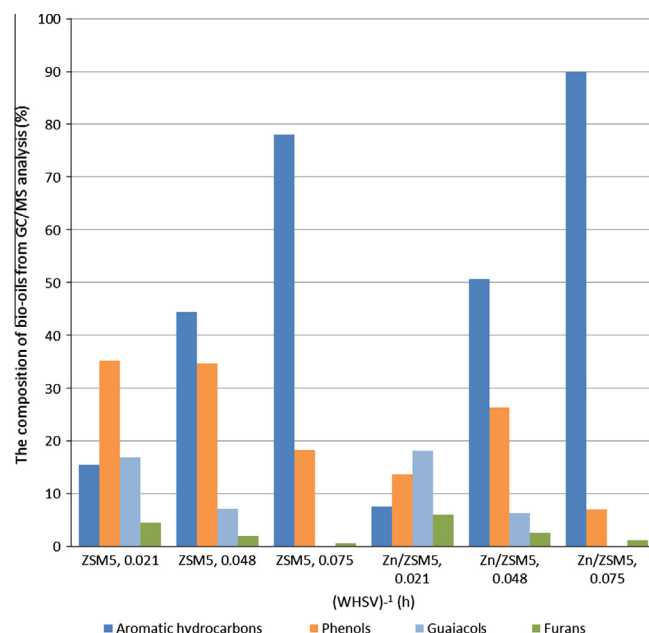
Comparison of FTIR functional groups in non-catalytic, ZSM-5 upgraded, Zn/ZSM-5 upgraded bio-oils.

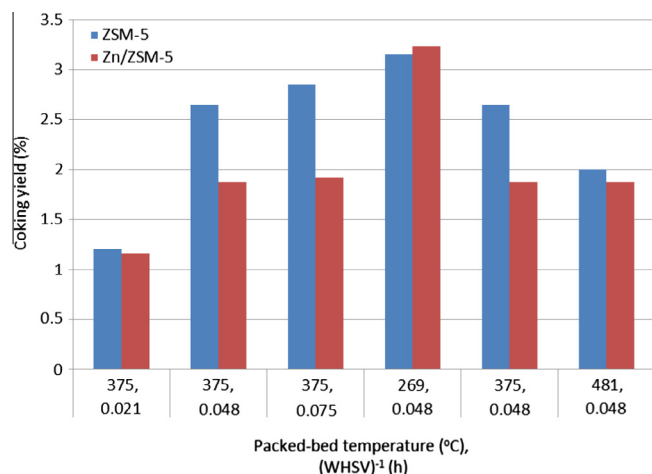
No.	Wave number range (cm <sup>-1</sup> )	Group	Compound	Non-catalytic bio-oil	ZSM-5 upgraded bio-oil	Zn/ZSM-5 upgraded bio-oil
1	3200–3500	O–H stretch	Alcohols, phenols	+	+	+
2	2850–3000	C–H stretch	Alkanes	–	+	+
3	~1718	C=O stretch	Carboxylic acids, aldehydes, ketones,	+	–	–
4	~1600	C=C stretch	Aromatic	–	+	+
5	~1274	C–O stretch	Acid	+	–	–
6	~1086	C–H bend	Aromatic	–	+	+
7	~1040	C–H bend	Aromatic	+	+	+
8	~878	C–H oop	Aromatic	–	+	+

**Fig. 5.** The composition of bio-oils from GC/MS analysis with Zn/ZSM-5 (the serial numbers correspond to those in Table 2).**Fig. 6.** The effect of packed-bed temperature on bio-oil composition ((WHSV)<sup>-1</sup> fixed at 0.048).

the aromatic hydrocarbons were increased from 18 to 74 area% when the packed-bed temperature was increased from 269 to 481 °C; the phenols were first increased from 19 area% at 269 °C to 26.33 area% at 375 °C then decreased to 18.31 area% when the temperature was 481 °C. As for guaiacols, the content was decreased from 22 to 0.4 area% when the temperature was increased to 481 °C. The same decreasing trend was also showed on furans (from 2 to 1 area%).

The effect of (WHSV)<sup>-1</sup> on upgraded bio-oil chemical composition was analyzed when the packed-bed temperature was fixed at 375 °C (Fig. 7). Using Zn/ZSM-5 as a catalyst, the aromatic hydrocarbon increased from 15 to 89.92 area% with the increase of (WHSV)<sup>-1</sup> from 0.021 to 0.075; the content of phenols was first increased from 13 area% ((WHSV)<sup>-1</sup> at 0.021) to 26 area% ((WHSV)<sup>-1</sup> at 0.048) then decreased to 7 area% with the (WHSV)<sup>-1</sup> increased to 0.075. Guaiacols and furans were decreased to almost 0% when the (WHSV)<sup>-1</sup> increased to 0.075. At the packed-bed temperature fixed at 375 °C, the aromatic hydrocarbon content from Zn/ZSM-5 catalyst was more than those from ZSM-5 catalyst when the (WHSV)<sup>-1</sup> was more than 0.048. Zinc centers probably promote the initial dehydrogenation and then influence the subsequent H-transfer reactions [38], which resulted in significantly increased aromatic hydrocarbon content.

**Fig. 7.** The effect of (WHSV)<sup>-1</sup> on bio-oil composition (packed-bed temperature fixed at 375 °C).



**Fig. 8.** The comparison of coking of ZSM-5 and Zn/ZSM-5 catalyst on different reaction conditions.

### 3.3. The comparison of coking on ZSM-5 and Zn/ZSM-5 catalyst at different reaction conditions

Fig. 8 shows the comparison of coking on ZSM-5 and Zn/ZSM-5 catalyst at different reaction conditions. It showed that the coking was increased by long (WHSV)<sup>-1</sup> and low packed-bed temperature. And Zn/ZSM-5 had lower coking than ZSM-5 on all the reaction conditions except packed-bed temperature at 269 °C and (WHSV)<sup>-1</sup> at 0.048. This results may be due to the formation of coking was inhibited by the reduction of the strong acidic sites in ZSM-5 via the incorporation of Zinc.

### 3.4. Mechanism analysis for catalytic pyrolysis of Douglas fir pellets

Based on previous description, a mechanism was proposed for catalysis close coupled with microwave pyrolysis of Douglas fir pellets. It is known that furfural was obtained through the cleavage of the bond between O—C5 and ring forming between C2—C5 positions of the main chain of xylan, which is the most abundant compound in hemicelluloses [39]. Furan was then formed from decarbonylation of furfural. At the same time, cellulose was decomposed and dehydrated to form anhydrosugars such as levoglucosan and furans [40]. Then those furans from cellulose and hemicellulose were converted to intermediates (e.g., cyclohexene and 3,4-dimethylbenzaldehyde) in the ZSM-5 pores. These intermediates could then undergo a series of decarboxylation, decarbonylation, oligomerization, dehydration, and deoxygenation inside the ZSM-5 pores to form aromatics, coke, light olefins, and carbon oxides [29].

Lignin was primarily depolymerized and dehydrated to produce propenyl-guaiacols. Phenols could be generated from demethoxylation reaction of guaiacols. The cleavage of O—CH<sub>3</sub> bond in guaiacols was verified by the increase of CH<sub>4</sub> in syngas, which was observed by the GC analyzer. Then aromatic hydrocarbons such as toluene could be obtained from catalyzed deoxygenation of phenols.

The Zinc modified catalyst was prepared using a wet incipient impregnation method in this study, which resulted in the replacement of a portion of the protons in the ZSM-5 with Zinc ions. The Zinc ions and Lewis acid newly formed by Zinc implementation which could stimulate H-atom migration [29] through C—H activation which are used to catalyze the oligomerization of the DF pyrolysis vapor (intermediates) to aromatic hydrocarbons. In addition to serving as an oligomerization catalyst, the Zinc ions are designed

to maintain the functionality of the catalyst by preventing coke formation over protons which was verified by coking comparison.

## 4. Conclusions

Zn/ZSM-5 catalyst is an effective catalyst to catalytic cracking of biomass pyrolysis vapor to aromatic hydrocarbons. The bio-oil yield decreased while gas yield increased after Zn/ZSM-5 catalysis, and the water content of bio-oils was higher than that of non-catalytic bio-oils. The syngas was mainly composed of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>. GC/MS and FTIR analysis showed that aromatic hydrocarbons become the most abundant compounds in the bio-oil. The packed-bed temperature and (WHSV)<sup>-1</sup> significantly affected product yield and bio-oil composition.

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## Reference

- [1] Conti PDH John J, Beamon Joseph A, Napolitano Sam A, Michael Schaal A, Turnure James T. Annual energy outlook 2012. In: Administration USE, editor. Washington, DC 20585: U.S. Energy Information Administration; 2012.
- [2] Mortensen PM, Grunwaldt JD, Jensen PA, Knudsen KG, Jensen AD. A review of catalytic upgrading of bio-oil to engine fuels. *Appl Catal*, A 2011;407:1–19.
- [3] van Ruijven B, van Vuuren DP. Oil and natural gas prices and greenhouse gas emission mitigation. *Energy Policy* 2009;37:4797–808.
- [4] Park H, Jeon J-K, Suh D, Suh Y-W, Heo H, Park Y-K. Catalytic vapor cracking for improvement of bio-oil quality. *Catal Surv Asia* 2011;15:161–80.
- [5] Goyal HB, Seal D, Saxena RC. Bio-fuels from thermochemical conversion of renewable resources: a review. *Renew Sust Energy Rev* 2008;12:504–17.
- [6] Zhang Q, Chang J, Wang TJ, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. *Energy Convers Manage* 2007;48:87–92.
- [7] Carlson TR, Tompsett GA, Conner WC, Huber GW. Aromatic Production from catalytic fast pyrolysis of biomass-derived feedstocks. *Top Catal* 2009;52:241–52.
- [8] Güngör A, Önenç S, Uçar S, Yanik J. Comparison between the “one-step” and “two-step” catalytic pyrolysis of pine bark. *J Anal Appl Pyrolysis* 2012;97:39–48.
- [9] Park HJ, Dong JI, Jeon JK, Yoo KS, Yim JH, Sohn JM, et al. Conversion of the pyrolytic vapor of radiata pine over zeolites. *J Ind Eng Chem* 2007;13:182–9.
- [10] Aho A, Kumar N, Lashkul AV, Eränen K, Ziolek M, Decyk P, et al. Catalytic upgrading of woody biomass derived pyrolysis vapours over iron modified zeolites in a dual-fluidized bed reactor. *Fuel* 2010;89:1992–2000.
- [11] Iliopoulou EF, Stefanidis SD, Kalogiannis KG, Delimitis A, Lappas AA, Triantafyllidis KS. Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite. *Appl Catal B* 2012;127:281–90.
- [12] Wang L, Lei H, Lee J, Chen S, Tang J, Ahring B. Aromatic hydrocarbons production from packed-bed catalysis coupled with microwave pyrolysis of Douglas fir sawdust pellets. *RSC Adv* 2013;3:14609–15.
- [13] Biddy MJ, Dutta A, Jones SB, Meyer PA. Ex situ catalytic fast pyrolysis technology pathway. 2013. p. Medium: ED; Size: PDFN.
- [14] Aho A, Kumar N, Eränen K, Salmi T, Hupa M, Murzin DY. Catalytic pyrolysis of woody biomass in a fluidized bed reactor: influence of the zeolite structure. *Fuel* 2008;87:2493–501.
- [15] Cheng YT, Jae J, Shi J, Fan W, Huber GW. Production of renewable aromatic compounds by catalytic fast pyrolysis of lignocellulosic biomass with bifunctional Ga/ZSM-5 catalysts. *Angew Chem – Int Ed* 2012;51:1387–90.
- [16] Foster AJ, Jae J, Cheng Y-T, Huber GW, Lobo RF. Optimizing the aromatic yield and distribution from catalytic fast pyrolysis of biomass over ZSM-5. *Appl Catal A* 2012;423–424:154–61.
- [17] French R, Czernik S. Catalytic pyrolysis of biomass for biofuels production. *Fuel Process Technol* 2010;91:25–32.
- [18] Wang L, Lei H, Ren S, Bu Q, Liang J, Wei Y, et al. Aromatics and phenols from catalytic pyrolysis of Douglas fir pellets in microwave with ZSM-5 as a catalyst. *J Anal Appl Pyrolysis* 2012;98:194–200.
- [19] Pütün E, Uzun BB, Pütün AE. Rapid pyrolysis of olive residue. 2. Effect of catalytic upgrading of pyrolysis vapors in a two-stage fixed-bed reactor. *Energy Fuels* 2009;23:2248–58.
- [20] Samolada MC, Papafotica A, Vasalos IA. Catalyst evaluation for catalytic biomass pyrolysis. *Energy Fuels* 2000;14:1161–7.

- [21] Stefanidis SD, Kalogiannis KG, Iliopoulou EF, Lappas AA, Pilavachi PA. In situ upgrading of biomass pyrolysis vapors: catalyst screening on a fixed bed reactor. *Bioresour Technol* 2011;102:8261–7.
- [22] Horne PA, Williams PT. Premium quality fuels and chemicals from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading. *Renew Energy* 1994;5:810–2.
- [23] Taarning E, Osmundsen CM, Yang X, Voss B, Andersen SI, Christensen CH. Zeolite-catalyzed biomass conversion to fuels and chemicals. *Energy Environ Sci* 2011;4:793–804.
- [24] Iliopoulou EF, Stefanidis SD, Kalogiannis KG, Delimitis A, Lappas AA, Triantafyllidis KS. Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite. *Applied Catalysis B: Environmental*. 2012;127:281–90.
- [25] Huang J, Long W, Agrawal PK, Jones CW. Effects of acidity on the conversion of the model bio-oil ketone cyclopentanone on H–Y zeolites. *J Phys Chem C* 2009;113:16702–10.
- [26] Valle B, Gayubo AG, Aguayo AT, Olazar M, Bilbao J. Selective production of aromatics by crude bio-oil valorization with a nickel-modified HZSM-5 zeolite catalyst. *Energy Fuels* 2010;24:2060–70.
- [27] Neumann G, Hicks J. Effects of cerium and aluminum in cerium-containing hierarchical HZSM-5 catalysts for biomass upgrading. *Top Catal* 2012;55:196–208.
- [28] Ni Y, Sun A, Wu X, Hai G, Hu J, Li T, et al. The preparation of nano-sized H[Zn, Al]ZSM-5 zeolite and its application in the aromatization of methanol. *Microporous Mesoporous Mater* 2011;143:435–42.
- [29] Fanchiang W-L, Lin Y-C. Catalytic fast pyrolysis of furfural over H-ZSM-5 and Zn/H-ZSM-5 catalysts. *Appl Catal A* 2012;419–420:102–10.
- [30] Fang Y, Tang J, Huang X, Shen W, Song Y, Sun C. Aromatization of dimethyl ether over Zn/H-ZSM-5 catalyst. *Chin J Catal* 2010;31:264–6.
- [31] Smiešková A, Rojasová E, Hudec P, Šabo L. Aromatization of light alkanes over ZSM-5 catalysts: influence of the particle properties of the zeolite. *Appl Catal A* 2004;268:235–40.
- [32] Luzgin MV, Rogov VA, Arzumano V, Toktarev AV, Stepanov AG, Parmon VN. Methane aromatization on Zn-modified zeolite in the presence of a co-reactant higher alkane: how does it occur? *Catal Today* 2009;144:265–72.
- [33] Viswanadham N, Pradhan AR, Ray N, Vishnoi SC, Shanker U, Prasada Rao TSR. Reaction pathways for the aromatization of paraffins in the presence of H-ZSM-5 and Zn/H-ZSM-5. *Appl Catal A* 1996;137:225–33.
- [34] Li Y, Liu S, Xie S, Xu L. Promoted metal utilization capacity of alkali-treated zeolite: preparation of Zn/ZSM-5 and its application in 1-hexene aromatization. *Appl Catal A* 2009;360:8–16.
- [35] Lei HW, Ren SJ, Wang L, Bu Q, Julson J, Holladay J, et al. Microwave pyrolysis of distillers dried grain with solubles (DDGS) for biofuel production. *Bioresour Technol* 2011;102:6208–13.
- [36] Corma A, Huber GW, Sauvanaud L, O'Connor P. Processing biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) reaction pathways and role of catalyst. *J Catal* 2007;247:307–27.
- [37] Lappas AA, Bezerianni S, Vasalos IA. Production of biofuels via co-processing in conventional refining processes. *Catal Today* 2009;145:55–62.
- [38] Biscardi JA, Iglesia E. Reaction pathways and rate-determining steps in reactions of alkanes on H-ZSM5 and Zn/H-ZSM5 catalysts. *J Catal* 1999;182:117–28.
- [39] Shen DK, Gu S, Bridgwater AV. Study on the pyrolytic behaviour of xylan-based hemicellulose using TG–FTIR and Py–GC–FTIR. *J Anal Appl Pyrolysis* 2010;87:199–206.
- [40] Carlson TR, Jae J, Lin YC, Tompsett GA, Huber GW. Catalytic fast pyrolysis of glucose with HZSM-5: the combined homogeneous and heterogeneous reactions. *J Catal* 2010;270:110–24.