Aromatics and phenols from catalytic pyrolysis of Douglas fir pellets in microwave with ZSM-5 as a catalyst

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ABSTRACT

Microwave assisted catalytic pyrolysis was investigated to convert Douglas fir pellets to bio-oils by a ZSM-5 zeolite catalyst. A central composite experimental design (CCD) was used to optimize the catalytic pyrolysis process. The effects of reaction time, temperature and catalyst to biomass ratio on the bio-oil, syngas, and biochar yields were determined. GC/MS analysis results showed that the bio-oil contained a series of important and useful chemical compounds. Phenols, guaiacols, and aromatic hydrocarbons were the most abundant compounds which were about 50–82% in bio-oil depending on the pyrolysis conditions. Comparison between the bio-oils from microwave pyrolysis with and without catalyst showed that the catalyst increased the content of aromatic hydrocarbons and phenols. A reaction pathway was proposed for microwave assisted catalyst pyrolysis of Douglas fir pellets.

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1. Introduction

Renewable energy which can be constantly replenished draws much attention in recent years due to limited fossil fuels and increasing energy consumptions. Biomass is the most attractive resource among renewable energies because it is the only renewable source that can be made into liquid carbon-based fuels and chemicals. Biomass can be converted to useful products by biological, thermochemical, and physical methods [1]. Biological process usually takes long time to producing single or special products while thermochemical process usually gives complex products in a short time. Pyrolysis is one of the best thermochemical conversion processes which runs at 350–650 °C in the absence of oxygen and can convert biomass directly into solid, liquid and syngas [2]. The liquid product from pyrolysis is called bio-oil. Bio-oil is a mixture of acid, phenols, guaiacols, furans, esters, aldehydes, ketones, alcohols, sugars, alkenes and aromatics. The oxygen content of bio-oils is about 35–40% which is one of the biggest differences [3,4] from petroleum fuels as bio-oils need to be upgraded before used as fuels.

Bio-oil can be upgraded in physical and chemical ways. Physical upgrading includes filtration which reduces ash contents [5]. Chemical upgrading of bio-oil includes hydrodeoxygenation [6,7], catalytic cracking [8,9], esterification [10,11], and steam reforming [12,13]. Catalytic cracking usually rejects oxygen in the form of carbon dioxide with catalysts such as zeolite. Catalytic cracking could be combined with or separated from pyrolysis processes. Integrated catalytic pyrolysis processes have been developed and drawn much attention in the recent years. Lappas and his coworkers [14–16] have found that the adding of zeolite and Al-MCM-41 could decrease the bio-oil yield from increasing amounts of water, gas and coke on the catalyst. Bridgwater and collaborators [17] have tested ZSM-5, Al-MCM-41, Al-MSU-F and alumina-stabilized ceria MI-575 and found that ZSM-5 was the most active catalyst. Huber et al. [9] tested several catalysts and found that ZSM-5 resulted in the highest aromatic yield. They also stated that the high heating rate and high catalyst to feed ratio could produce more aromatics.

Douglas fir is one of the widespread and abundant species in western North America. It is a soft wood and belongs to the coniferous family. Douglas fir contains 44% cellulose, 21% hemicelluloses and 32% lignin [18]. The decomposition reactions of cellulose has drawn many interests [9,19,20] since detailed understanding of reaction mechanisms could save research and development costs [21]. Huber and his coworkers [9,19] proposed that when using glucose as feedstock, the production of aromatics occurs in two
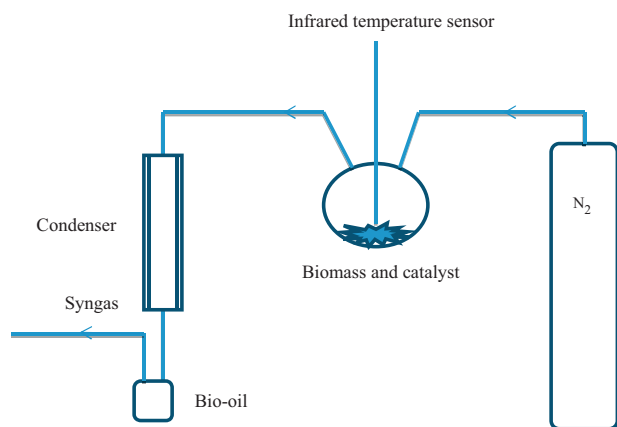
Fig. 1. Flow chart for the combined pyrolysis and zeolite cracking upgrading process.

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

Level	X_1: reaction time (min)	X_2: reaction temperature (°C)	X_3: catalyst to biomass ratio
$-r = -1.68$	1.27	331.82	1.32
-1	4	400	2
0	8	500	3
1	12	600	4
$r = 1.68$	14.73	668.18	4.68
Δj	4	100	1

The weight of syngas was calculated using the following equation:

$$\text{weight of syngas} = \text{initial biomass mass} - \text{bio-oil mass} - \text{biochar mass} \qquad (1)$$

steps: the first step is the thermal decomposition of glucose into smaller oxygenates and followed by dehydration reactions to produce water and dehydrated species; the second step is that the dehydrated species are converted into aromatics, CO_2, CO, and water.

The key advantage of the microwave over conventional heating method is the nature of fast internal heating by microwave irradiation. The microwave pyrolysis could somehow overcome heat transfer rate limitation which is suitable for the pyrolysis of large fragment materials [22]. Lei and his co-workers investigated microwave pyrolysis of corn stover and found that bio-oil contained a series of important and useful compounds: phenols, aliphatic hydrocarbons, aromatic hydrocarbons, and furan derivatives [23]. There are upcoming interests in microwave assisted catalytic pyrolysis of biomass. A range of chlorides, nitrates, and metal oxides were used as catalysts to obtain high liquid yields [24]. Microwave pyrolysis over ZSM-5 and its optimization have not been reported in the literature. The objective of this study was to investigate catalytic pyrolysis of Douglas fir pellets by microwave heating with ZSM-5 as a catalyst and determine the effects of pyrolytic conditions on the yields of bio-oil, syngas, and biochar. The relationship between product yield and pyrolysis conditions was established and empirically developed models to predict product yields were presented.

2. Materials and methods

2.1. Materials

The feedstock used was Douglas fir pellets (Bear Mountain Forest Products Inc., USA, approximately 5 mm in diameter and 2 cm in length) with a moisture content of 8%. Catalyst ZSM-5 was used as received (Zeolyst International, SiO_2/Al_2O_3 mole ratio: 50).

2.2. Microwave pyrolysis apparatus

A Sineo MAS-II batch microwave oven (Shanghai, China) with a rated power of 1000 W was used at the 700 W power setting. This power setting gave a heating rate of 100 °C/min. It reached desired temperatures after about 4–5 min. The biomass and catalyst ZSM-5 with a fixed total loading of 100 g was placed in a 500 mL quartz flask inside of the microwave oven which is shown in Fig. 1. The volatile from the flask went through condensation system and the condensable liquid (bio-oil) was collected during pyrolysis. The biochar was left in the quartz flask after pyrolysis.

2.3. Experimental design and optimization

A central composite experimental design (CCD) was used to optimize the product yields (bio-oil, syngas and biochar). Three independent variables, reaction time (X_1, min), reaction temperature (X_2, °C), and catalyst to biomass ratio (X_3) were chosen and are shown at various levels in Table 1. Y_i was used as the dependent output variable. The reaction time was recorded after the desired temperature was reached. The reaction time was set from 1.27 to 14.73 min; the reaction temperature was from 331.82 to 668.18 °C; and the catalyst to biomass ratio was chosen from 1.32 to 4.68 with a fixed total loading of 100 g.

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

$$x_i = \frac{X_i - X_0}{\Delta X} \qquad (2)$$

where x_i is the dimensionless value of the independent variable while X_i is the real value. X_0 is the real value of the variable at the center point and ΔX is the step length.

A 2^3-factorial CCD, with 6 axial points ($a = 1.68$) and 6 replications at the center points ($n_0 = 6$) leading to a total number of 20 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, quadratic, and interactions. The predicted model for the response (Y_i) was:

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

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; and X_i is the independent variables; and ε is the random error. The statistical analysis of the model was performed by Design Expert 8 software. And 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. And F test was used to determine the model parameter's significance ($\alpha = 0.05$).

2.4. Analysis of bio-oil and syngas

The chemical composition of bio-oil 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 μL. The flow rate

of the carrier gas (helium) was 0.6 mL/min. The ion source temperature was 230 °C for the mass selective detector. The compounds were identified by comparing the spectral data with the NIST Mass Spectral library [25].

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. Response surface analysis

The experiment design and product yield is shown in Table 2. The volatile yields were from 67.49 to 96.63 wt%; the bio-oil yields were from 28.45 to 40.83 wt%; the syngas yields were from 39.04 to 65.95 wt%, and the biochar yields were from 3.27 to 32.51 wt%. In our previous report [26], the volatile yields were found ranging from 39.3 to 68.8 wt% while the bio-oil yields were from 33.8 to 57.8 wt% based on dry biomass; the syngas yields were ranged from 7.9 to 15 wt% and the biochar yields varied from 31.2 to 60.7 wt% without using catalysts. The volatile and syngas yields by ZSM-5 catalyst were much higher than those without using catalyst, while the bio-oil and biochar yields with catalyst were lower than those without catalysts.

Using the results of the experiment, three second order regression equations were obtained showing the bio-oil (Eq. (4)), syngas (Eq. (5)) and biochar yields (Eq. (6)) as a function of the reaction time (X_1, min), temperature (X_2, °C), and ratio of catalyst to biomass (X_3):

$$Y_{\text{bio-oil}} = 92.57 - 0.21X_2 - 12.23X_3 + 0.02X_2X_3 + 1.64X_2{}^2 \quad (4)$$

$$Y_{\text{syngas}} = -124.98 + 0.47X_2 - 5.72X_1X_2 \\ - 0.03X_2X_3 - 0.22X_1{}^2 - 3.1X_2{}^2 \quad (5)$$

$$Y_{\text{biochar}} = 132.88 - 0.26X_2 - 6.96X_3 + 3.94X_1X_2 \\ + 0.19X_1{}^2 + 1.47X_2{}^2 \quad (6)$$

The *P* value of Eq. (4) was $0.032 < \alpha = 0.05$, which meant the quadratic equation was significant to describe the bio-oil yield. The coefficient of determination (R^2) for Eq. (4) was 0.91, which suggested that the model was suitable to adequately represent the relationships among independent variables. The model terms b_0, X_2, X_3, X_2X_3 and $X_2{}^2$ were also significant as the *P* values for these model terms were 0.0071, 0.0008, 0.0038, 0.0081, 0.013 which were smaller than $\alpha = 0.05$, while the other model terms were not significant as the *P* values for them were all larger than $\alpha = 0.05$. The quadratic terms of reaction time, temperature, and ratio of catalyst to biomass for the yield of bio-oils can be visualized in Fig. 2.

The *P* value of Eq. (5) was $0.0001 < \alpha = 0.05$, which meant the quadratic equation was significant and can be used to describe the syngas yield. The coefficient of determination (R^2) for Eq. (5) was 0.98, which suggested that the model adequately represented the relationships among the independent variables. The model terms b_0, X_2, X_1X_2, X_2X_3, $X_1{}^2$, $X_2{}^2$ were significant as the *P* values for these model terms were <0.0001, 0.001, 0.0037, 0.0011, 0.0001, and 0.0003 respectively, which were much smaller than $\alpha = 0.05$, while the other model terms were not significant as their *P* values were all larger than $\alpha = 0.05$. The quadratic terms of reaction time, temperature, and ratio of catalyst to biomass on the yield of syngas can be visualized in Fig. 3. A similar result was obtained for Eq. (6) of biochar (*P*-value = 0.0009). The quadratic terms of reaction time,
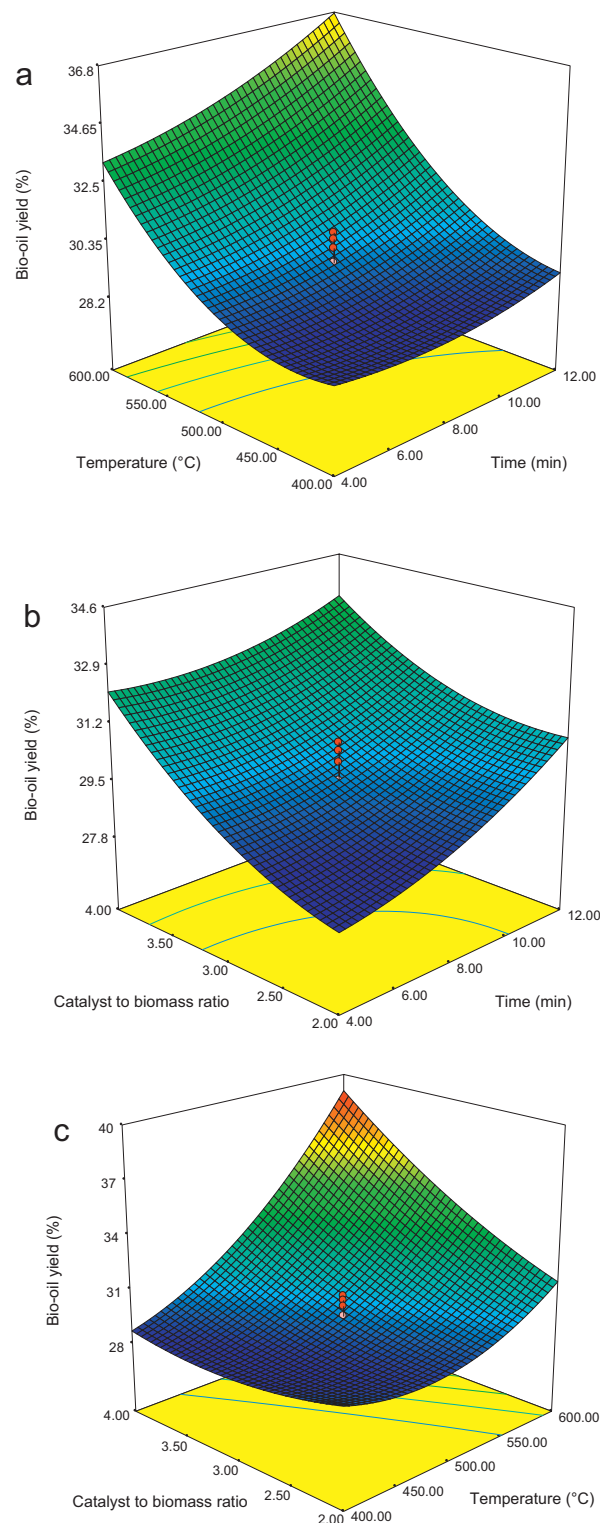
Fig. 2. Effect of independent variables interaction on bio-oil yield.

temperature, and ratio of catalyst to biomass for biochar yields can be visualized in Fig. 4. The coefficient of determination (R^2) for Eq. (6) was 0.99, which suggested that the model was suitable to adequately represent the relationships among the independent variables. The model term b_0, X_2, X_3, X_1X_2, $X_1{}^2$, and $X_2{}^2$ were significant as the *P* values for these model terms were all smaller than 0.05, while the other model terms (*P*-values > 0.05) were not significant.

Table 2
Experiment design and product yield distribution.

Run	Reaction time (min)	Reaction temperature (°C)	Catalyst to biomass ratio	Volatile yield (wt%)	Bio-oil yield (wt%)	Syngas yield (wt%)	Char yield (wt%)
1	4	400	2	67.49	28.45	39.04	32.51
2	12	400	2	73.79	29.69	44.10	26.21
3	4	600	2	84.34	28.72	55.61	15.66
4	12	600	2	84.70	34.33	50.37	15.30
5	4	400	4	75.64	28.43	47.21	24.36
6	12	400	4	78.59	29.33	49.26	21.41
7	4	600	4	89.84	38.58	51.26	10.16
8	12	600	4	94.09	40.83	53.26	5.91
9	1.27	500	3	76.83	30.60	46.23	23.17
10	14.73	500	3	92.31	32.80	59.51	7.69
11	8	331.82	3	72.23	30.36	41.87	27.77
12	8	668.18	3	96.63	30.68	65.95	3.37
13	8	500	1.32	81.95	30.32	51.63	18.05
14	8	500	4.68	90.35	34.55	55.80	9.65
15	8	500	3	85.59	28.92	56.67	14.41
16	8	500	3	84.11	30.68	53.43	15.89
17	8	500	3	85.05	29.02	55.79	14.95
18	8	500	3	84.93	29.54	54.38	15.07
19	8	500	3	84.87	30.43	54.63	15.13
20	8	500	3	84.72	30.09	55.45	15.28

3.2. Effect of reaction conditions on product distribution

3.2.1. Effect of reaction time
The effect of reaction time on product yield distribution is shown in Fig. 5(A). It was found that reaction time has less significant effects than other variables on product distribution, which was similar to the trend when using active carbon as catalyst in our previous work [27].

3.2.2. Effect of reaction temperature on product distribution
As shown in Fig. 5(B), the bio-oil yield was first increased from around 30 wt% (331.82 °C) to 42 wt% (584.09 °C) then decreased to around 30 wt% (668.18 °C), while the biochar yield was decreased from 27.8 wt% (331.82 °C) to 3.4 wt% (668.18 °C). This observation indicated that when the temperature was lower than 584 °C, increasing the temperature increased the yield of bio-oil which was caused by depolymerization; while when temperature was higher than 584 °C, higher reaction temperatures increased the yield of syngas and decreased the yield of bio-oil and biochar as high temperatures contributed to gasification. These results are similar to those reported in the literature [20,28,29]. 584.09 °C was selected as the optimum reaction temperature.

3.2.3. Effect of ratio of catalyst to biomass on product distribution
The effect of catalyst to biomass ratio on the product yield is shown in Fig. 5(C), which was not as significant as reaction temperatures. Bio-oil yields were slightly increased from 30.3 to 35.3 wt% when the ratio was increased from 1.32 to 3.84. The ratios between 3.84 and 4.68 were considered to be the optimum catalyst to biomass ratio to obtain the high bio-oil yield.

3.3. GC/MS characterization of bio-oil

To further understand the catalyst effect on chemical reactions during microwave pyrolysis, GC/MS analysis was carried out to determine the chemical composition of bio-oils and the results are shown in Fig. 6. Without using catalysts, bio-oils from microwave pyrolysis of Douglas fir were a mixture of acid, ketones, alcohols, phenols, guaiacols, furans, esters, sugars and so on, which were similar to those compounds from microwave pyrolysis of corn stover [23]. With ZSM-5 as a catalyst, phenols and guaiacols and aromatic hydrocarbons were enriched and become the most abundant compounds which were about 50–82% in bio-oils depending on

the catalytic pyrolysis conditions. There were five main phenols: phenol, 2-methyl-phenol, 3-methyl-phenol, 2,4-dimethyl-phenol, and 3,4-dimethyl-phenol which were from 5 to 58% in bio-oils depending on the reaction conditions. The guaiacols were mainly composed of 2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 4-ethyl-2-methoxy-phenolwhich were from 15 to 45% depending on the reaction conditions. The aromatic hydrocarbons which did not contain oxygen were observed in catalytic biomass pyrolysis, and the main aromatic hydrocarbons were toluene, azulene, xylene and naphthalene.

3.3.1. The effect of catalyst on chemical compositions of bio-oils
Comparing the chemical compositions of bio-oils from direct pyrolysis without using catalysts, it was found that ZSM-5 catalysts increased the aromatic hydrocarbon content from 0.72% (500 °C, without catalyst) to 6.89% (332 °C, catalyst to biomass ratio is 3:1) (Fig. 7). This indicated that ZSM-5 catalysts can deoxygenate oxygenated compounds derived from microwave pyrolysis of Douglas fir pellets. Carlson and his co-workers have also reported that introduction of zeolite catalysts into pyrolysis can convert oxygenated compounds into aromatics [9]. It was observed that the phenols content was increased from 5.46% (500 °C, without catalyst) to 58.03% (500 °C, catalyst to biomass ratio of 3:1). The guaiacols were decreased from 44.7% (500 °C, without catalyst) to 23.68% (500 °C, catalyst to biomass ratio of 3:1). The furans content was decreased from 9.8% (500 °C, without catalyst) to 1.57% (500 °C, catalyst to biomass ratio of 3:1). And the sugar content was decreased from 4.1% (500 °C, without catalyst) to 0% (more than 500 °C, catalyst to biomass ratio of 3:1).

3.3.2. The effect of reaction temperature on chemical compositions of bio-oils
The effect of reaction temperatures on bio-oil chemical compositions was analyzed with a fixed ratio of catalyst to biomass (3:1) as shown in Fig. 7. The aromatic hydrocarbons were decreased from 6.89% at 332 °C to around 2% when the temperature was more than 500 °C, which showed that high temperatures did not favor the production of aromatic hydrocarbons. The phenols content was increased from 33.25% at 332 °C to more than 55% when the temperature was higher than 500 °C. These phenols could be used as a raw material to produce phenolic resin or used as pesticide or through deoxygenating and upgrading by a well-established and commonly operated process in a typical oil refinery to produce
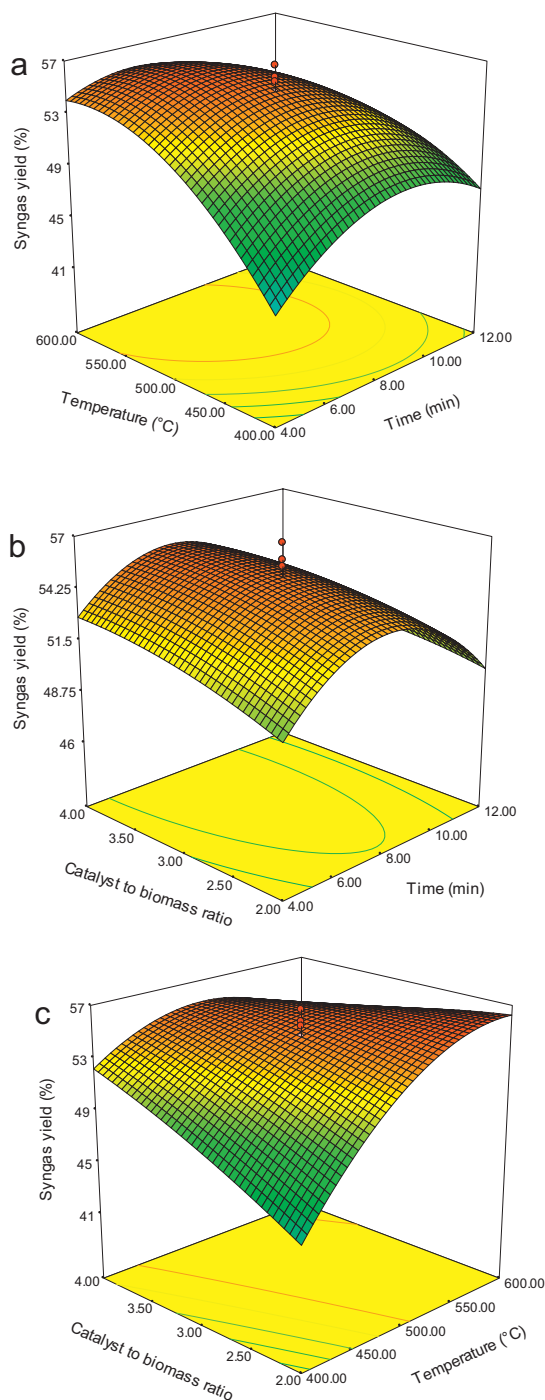
Fig. 3. Effect of independent variables interaction on syngas yield.

particular bio-fuel products, such as naphthenic or aromatic components of jet or rocket fuels and aromatic gasoline. The guaiacols content was decreased from 30.8% at 332 °C to around 15% at 668 °C. The furans content was decreased from 4.3% at 332 °C to 1% at 668 °C. The sugars content was decreased from 0.5% to 0% as the temperature increased from 332 °C to 668 °C.

3.3.3. The effect of catalyst to biomass ratio on bio-oil chemical compositions

It was observed that when the temperature was fixed at 500 °C, the aromatic hydrocarbon content was increased with the increase of catalyst to biomass ratios (Fig. 8), which is consistent with the same trend claimed by Carlson and his co-workers [9]; while the
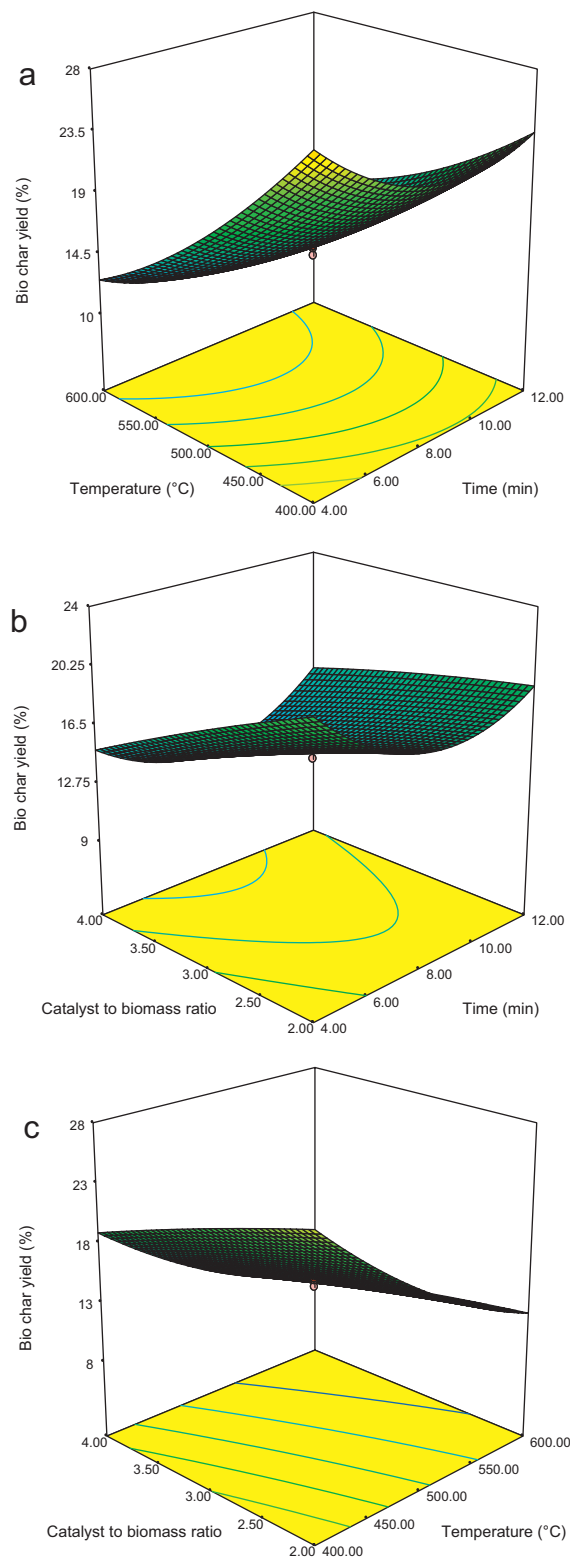

Fig. 4. Effect of independent variables interaction on bio char yield.

guaiacols content was decreased from 44.7% (500 °C, without catalyst) to 25% (catalyst to biomass ratio of 1.32), and then decreased to 18.9% (catalyst to biomass ratio of 4.68). The content of phenols was first increased then decreased with the increase of catalyst to biomass ratios, which indicated that higher ratios of catalyst to biomass favored aromatic hydrocarbons production as phenols were cracked by ZSM-5 to produce aromatic hydrocarbons.
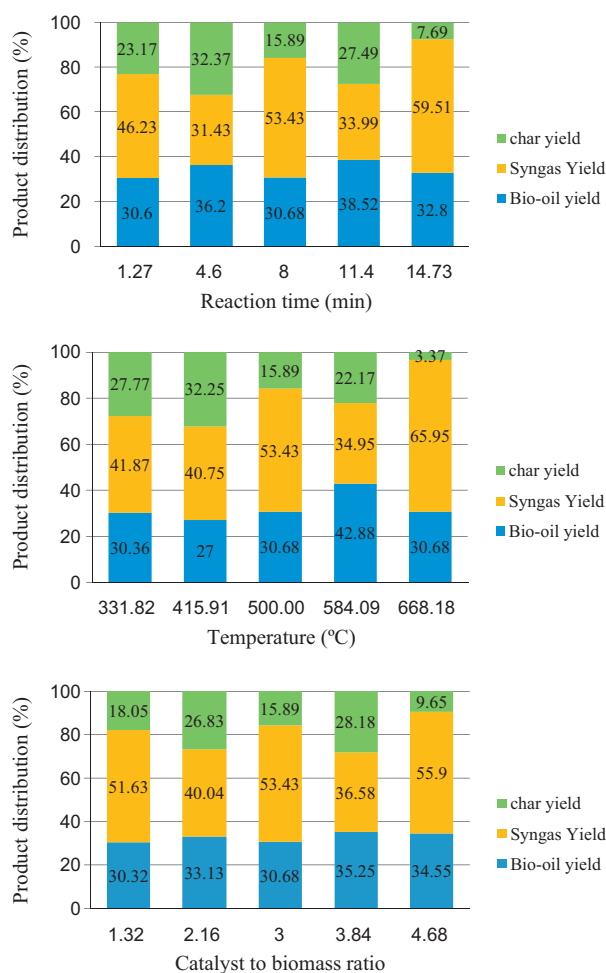
Fig. 5. (A–C) The effect of reaction conditions on the performance of product yield distribution. (A) The effect of reaction time, temperature is 500 °C and catalyst to biomass ratio is 3. (B) The effect of temperature, reaction time is 8 min and catalyst to biomass ratio is 3. (C) The effect of catalyst to biomass ratio, reaction time is 8 min and temperature is 500 °C.
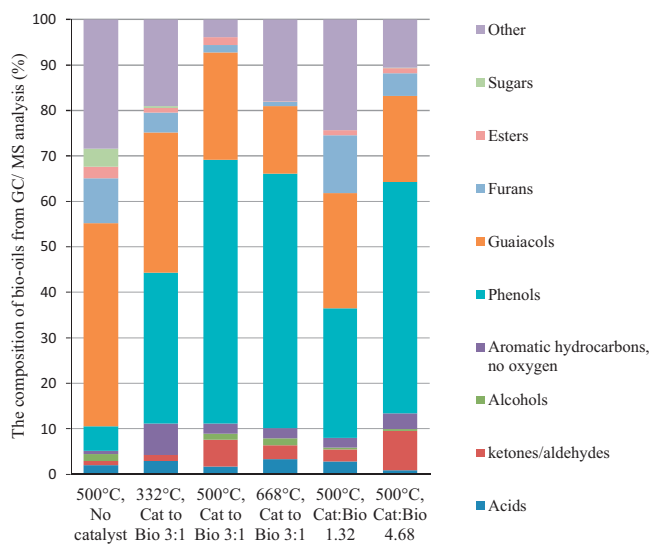

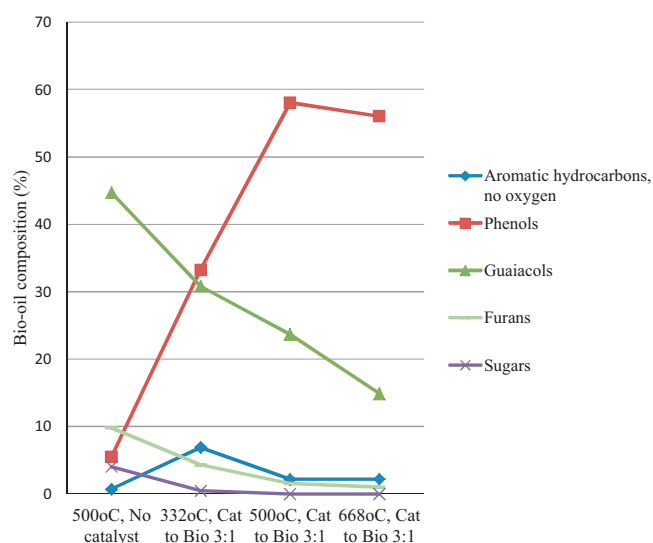**Fig. 6.** The composition of bio-oils from GC/MS analysis.

Fig. 7. The effect of catalyst on bio-oil composition.

From the analysis of GC/MS characterization of bio-oils, it was found that the production of sugars, furans, and guaiacols were all significantly decreased by ZSM-5 catalysis; while the production of aromatic hydrocarbons and phenols were significantly increased. The decrease of furans and guaiacols and the increase of aromatic hydrocarbons and phenols content corresponded to the increase of ratios of catalyst to biomass.

A reaction pathway was proposed by integrating the findings from different reaction conditions and the analysis of chemical profiles of bio-oils for microwave assisted catalytic pyrolysis of Douglas fir pellets. We proposed that hemicellulose and cellulose decomposition mainly includes two steps. The first step is that hemicelluloses was depolymerized and dehydrated to furfural and cellulose was dehydrated to anhydrosugars such as levoglucosan which was formed through the cellulose initial partial depolymerization. This step was confirmed by up to 28% of levoglucosan isolated from pyrolysis oil [30]. The second step was that C=O linkage was broken and recombined to β-methoxy-(S)-2-furanethanol and tetrahydro-2,5-dimethoxyfuran. The dehydrated products such as furans were produced from catalyst assisted dehydration reaction. Then aromatic compounds which include phenols, guaiacols, and aromatic hydrocarbons were
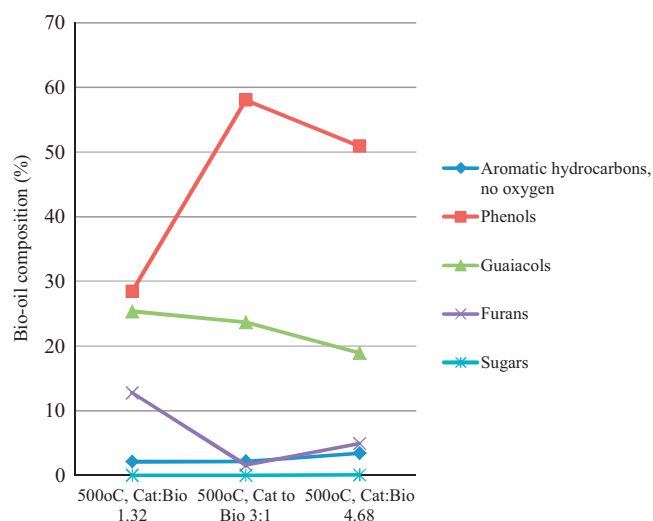

Fig. 8. The effect of catalyst to biomass ratio on bio-oil composition.

produced from decarbonylation, deoxygenation, and dehydrogenation reactions. Carlson and his coworkers [9,19] also claimed that the aromatic hydrocarbons were produced from a series of reactions of dehydration, decarboxylation, decarboxylation, and oligomerization. The distribution of these aromatic compounds was depending on the reaction conditions, such as temperature, retention time, and catalyst to biomass ratio. Compared to hemicelluloses and cellulose, lignin decomposition involving depolymerization, dehydration, cracking and hydrogenation was much complex. Lignin was primarily depolymerized and dehydrated to produce propenyl-guaiacols. The propenyl-guaiacols can be further hydrogenated to propyl-guaiacols through microwave assisted pyrolysis. The positions of C—C bond broken were highly related to the temperature [26]. Lignin and furans derived guaiacols were stabilized as phenols by demethoxylation reaction of guaiacols. The cleavage of O—CH_3 bond in guaiacols could be verified by the increased presence of CH_4 in syngas, which was observed by the GC analyzer which mainly contained H_2, CO_2, CO, CH_4, C_2H_4, and C_2H_6. Van Ngoc Bui [31] and Maria [32] used molybdenum and cobalt catalyst to investigate the deoxygenation reaction of guaiacols, and raise the similar pathway from guaiacols to phenols. Then aromatic hydrocarbons such as toluene could be obtained from catalyzed deoxygenation of phenols.

4. Conclusions

Microwave assisted catalytic pyrolysis was investigated to convert Douglas fir pellets to bio-oils over ZSM-5 zeolite catalysts. Three second order regression equations were obtained to optimize the products yield as a function of the reaction time, temperature, and ratio of catalyst to biomass. GC/MS analysis indicated that the bio-oil contained a series of important and useful chemical compounds: phenols, guaiacols, and aromatic hydrocarbons. The ZSM-5 catalyst deoxygenated the bio-oil and increased the content of aromatic hydrocarbons and phenols. A reaction pathway was proposed for microwave assisted catalytic pyrolysis of Douglas fir pellets.

Acknowledgement

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