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Aromatic hydrocarbons production from packed-bed catalysis coupled with microwave pyrolysis of Douglas fir sawdust pellets

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The direct catalytic cracking of biomass pyrolysis vapour into aromatics derived from Douglas fir sawdust pellets was tested using an upfront microwave pyrolysis process coupled with a packed-bed catalysis process using a ZSM-5 Zeolite catalyst. A central composite experimental design (CCD) was used to optimize the bio-oil and syngas yields. The effects of temperature and inverse weight hourly space velocity $(WHSV)^{-1}$ on the bio-oil composition were determined. The gas chromatography–mass spectrometry (GC-MS) analysis results showed that the bio-oil contained aromatic hydrocarbons. The aromatic hydrocarbons were enriched and became the most abundant compounds accounting for about 15–92.6% in upgraded bio-oils, depending on the catalytic pyrolysis conditions. The aromatic hydrocarbons were mainly composed of benzene, toluene, xylene, naphthalene, and their derivatives. When the effect of the reaction temperature on the bio-oil chemical compositions was analysed with a fixed $(WHSV)^{-1}$ (0.048 h), we found that the aromatic hydrocarbons increased from 0.72% in raw bio-oil (no catalyst added) to around 92.6% when the catalysis temperature was 500 °C, clearly demonstrating that a high temperature with the ZSM-5 Zeolite catalyst favoured the production of aromatic hydrocarbons. At a lower temperature fixed at 375 °C, the aromatic hydrocarbon content was increased from 0.72% to 78.1% with a $(WHSV)^{-1}$ increase from 0 to 0.075.

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1 Introduction

As one of the major renewable resources to be converted to liquid fuels, biomass has been realized as one of the most significant sustainable replacements for petroleum fuels. Pyrolysis conversion is one of the most promising methods that can directly convert biomass into liquid fuels called bio-oils by treatment at 350–650 °C for a short time in the absence of oxygen.[1] Various efforts have been made on the pyrolysis process to improve bio-oil yield and quality.[2–6] Microwave-assisted pyrolysis is one of the promising attempts with a key advantage of fast internal heating by microwave irradiation. The microwave pyrolysis reactor could overcome the heat transfer rate limitation which is associated with the pyrolysis of large fragments of biomass materials.[7,8] Various kinds of biomass, such as agricultural residues,[8–13] woody biomass,[3,14] dried distillers grains with solubles (DDGS),[15] and coffee hulls[16] have been tested with microwave pyrolysis.

Bio-oil is a complex mixture of sugars, esters, furans, acids, ketones, alcohols, phenols, guaiacols *etc*.[17] Bio-oil has a high oxygen content and is acidic, viscous, reactive, and thermally unstable and is not suitable for direct use in engines or traditional refineries. It was found that the oxygen content of bio-oils is usually 35–40%, which is one of the most significant differences between bio-oils and petroleum fuels.[18,19] The high oxygen content could also lead to a low heating value, around 50% of that of petroleum fuel. The presence of oxygen creates the primary issue for using bio-oils as a fuel. Thus bio-oils must be catalytically upgraded before being used as a conventional liquid transportation fuel.[20]

Catalytic cracking is one approach which rejects oxygen in the form of H_2O, CO and CO_2 through deoxygenation with zeolite as a catalyst. This approach does not require the addition of hydrogen and could be operated at the atmospheric pressure. In earlier work, the catalytic cracking of bio-oil was studied over a number of catalysts which included HZSM-5, silicalite, H-mordenite, H-Y and silica-alumina.[21–24] Adjaye and Bakhshi[21] tested the performance of different catalysts in a fixed bed micro-reactor and concluded that the highest hydrocarbon yields were 27.9% from HZSM-5 and 14.1% from H-Y. However, bio-oils have to be re-vaporized before catalytic upgrading and bio-oils cannot be completely vaporized once they have been condensed from the vapour phase. If the bio-oil is heated to 100 °C or more, it will rapidly react and eventually produce a solid residue of around 50 wt%

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of the original liquid.[25] This will contribute to low yields of upgraded bio-oil.

Operating catalytic upgrading immediately after pyrolysis and before the condensation reaction of bio-oils has happened means that the bio-oil is in the vapour phase and could avoid these disadvantages. Park *et al.*[26] conducted a close coupled catalysis and pyrolysis process in a fixed bed reactor installed at the upper part of a bubbling fluidized bed reactor. Aho *et al.*[27] used a dual-fluidized bed reactor for pine wood pyrolysis, followed by an upgrading reactor where the pyrolysis vapours went over the zeolites. The production of synthesis gas (*i.e.* H_2 + CO) is one of the outcomes of the pyrolysis process.[28] The comparison of microwave pyrolysis and conventional pyrolysis showed that microwave pyrolysis gave rise to a syngas with a high content (up to 62%) of CO and H_2,[29] which could serve as the H_2 supply for the deoxygenation reaction in the bio-oil upgrading. There have been several reports about the microwave assisted catalytic pyrolysis of biomass,[14,30] but reports on packed-bed reactors close coupled with the microwave pyrolysis of biomass were not found in the literature.

The objective of this study was to investigate the effect of ZSM-5 assisted deoxygenation in a packed-bed catalysis reactor which was close coupled with the microwave pyrolysis of Douglas fir sawdust pellets. The relationship between the product yield and pyrolysis conditions was established and analysed. The characteristics of the bio-oil from ZSM-5 assisted deoxygenation in packed-bed catalysis were determined by GC-MS.

2 Materials and methods

2.1 Materials

The feedstock used was Douglas fir sawdust pellets (Bear Mountain Forest Products Inc., USA) which were approximately 5 mm in diameter and 20 mm in length with a moisture content of 8%. ZSM-5 (Zeolyst International, USA; SiO2/Al2O3 Mole Ratio: 50) was dried at 105 °C for 12 h and calcined at 550 °C for 5 h.

2.2 Microwave pyrolysis apparatus

The microwave pyrolysis of Dougals fir sawdust was conducted first in a Sineo MAS-II batch microwave oven (Shanghai, China) which is shown in Fig. 1. The reaction conditions of the microwave pyrolysis were set with a reaction temperature at 480 °C and reaction time of 9 min for all the experiments. 20 g Douglas fir pellets were placed in a 500 mL quartz flask inside of the microwave oven. The pyrolysis volatile vapour from the flask went through a packed bed catalysis reactor which was filled with catalyst. Then after the 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. The coke was formed on the catalyst. The weight of syngas was calculated using the following equation:

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

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

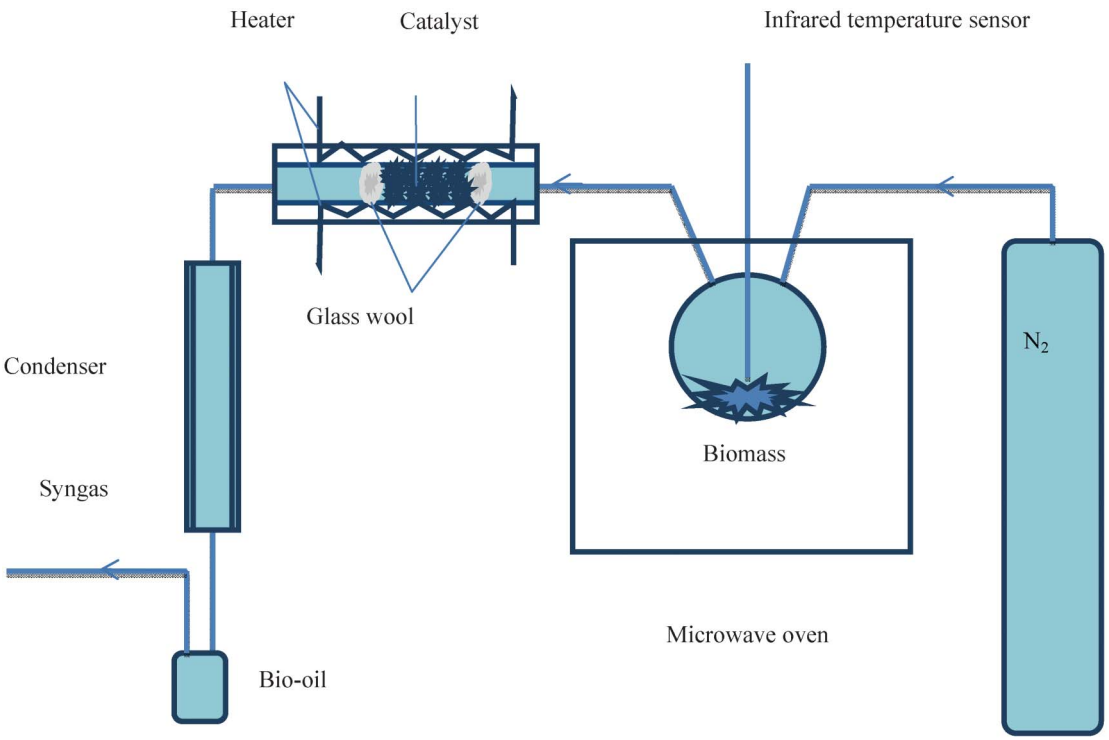

Fig. 1 Diagram showing the close coupled pyrolysis and zeolite cracking upgrading process.

Table 1 Coded levels of independent variables in the experiment

level	X_1: $(WHSV)^{-1}$ (h)	X_2: Cracking T (°C)
−1	0.029	300
1	0.067	450
$-r = -1.41$	0.021	268.9
$r = 1.41$	0.075	481.1

was calculated by the syngas mass divided by the initial biomass mass.

2.3 Experimental design and optimization

It was noted that the degree of conversion increased with the inverse weight hourly space velocity $(WHSV)^{-1}$ and cracking rate constant k in a fixed bed plug flow reactor.[31] The cracking rate constant k is a function of cracking temperature, usually assumed to be given by the Arrhenius equation. So the $(WHSV)^{-1}$ (X_1, h) 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 and shown at various levels in Table 1. Y_i was used as the dependent output variable. The reaction time was set as 9 min. The weight of the Douglas fir sawdust feeding was 20 g. The catalyst mass varied from 2.2 to 7.8 g. The packed-bed temperature was from 268.9 to 481.1 °C, and thus the $(WHSV)^{-1}$ was from 0.021 to 0.075 h (WHSV was from 13.4 to 47.4 h^{-1}).

For statistical calculations, the variables X_i were coded as x_i, according to eqn (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 real value. X_0 is the real value of the variable at the center point and ΔX is the step length. A 2^2-factorial CCD, with 4 axial points ($a = 1.41$) and 5 replications at the center points ($n_0 = 5$) leads to the total number of 13 experiments that were employed to optimize the reaction conditions. A second order polynomial equation (eqn (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 ε is the random error. The statistical analysis of the model was performed by Design Expert 8 software. The coefficient of determination (R^2) and the 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. The F test was used to determine the model parameter's significance ($\alpha = 0.05$).

2.4 Analysis of the bio-oil and syngas

The chemical composition of the 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^{-1} 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^{-1}. 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.[15] The water content of the bio-oils was determined by a Karl Fischer Titrator (Mettler Toledo V30).

The chemical composition of the syngas was determined by a Carle 400 gas chromatographer (Chandler Engineering, Broken Arrow, OK, USA) system with a thermal conductivity detector (TCD).

2.5 Characteristics of the catalyst

The thermal behavior of the reacted ZSM-5 catalyst was analyzed by a thermogravimetric analyzer (Mettler Toledo 188 TGA/SDTA 851, Switzerland). For each measurement, about 8 mg of the sample was loaded into an alumina crucible and heated from 25 to 600 °C at a selected heating rate (20 °C min^{-1}) with a nitrogen flow rate of 20 ml min^{-1}.

An IRPrestige21 spectrometer in the attenuated total reflection (ATR) mode (Shimadzu, Ge crystal; software: IRSolution) was used to record the FTIR spectra of the reacted ZSM-5. Omnic 8.0 software (Thermo Nicolet) was used to analyze the data and fit the curves.

3 Results and discussion

3.1 Response surface analysis of product yields

The experiment design and product yield are shown in Table 2. The bio-oil yields were from 32.2 to 37.75 wt%, while the syngas yield was from 38.8 to 43.7 wt%. Comparing with the combined pyrolysis and zeolite cracking upgrading process,[32] from which a wide range of yields was resulted (28.45–40.83 wt% for bio-oil yields, and 39.04–65.95 wt% for syngas yields), the products yield variation in our coupled pyrolysis and zeolite cracking upgrading process was in a smaller range because mild pyrolysis conditions were applied in this close coupled process. The mild pyrolysis conditions showed a good performance of similar bio-oil yields (32.20 to 37.75 wt%).

The eqn (3) was reduced by using backwards statistical analysis, and the parameters were sequentially removed based on the coefficient's p-value until all remaining were significant ($p < 0.05$). Using the results of the experiments, the first order equations were obtained showing the yields of bio-oil (eqn (4)) and syngas (eqn (5) as a function of the $(WHSV)^{-1}$ (X_1, h) and cracking temperature (X_2, °C):

$$Y_{\text{bio-oil}} = 43.88 - 69.07X_1 - 0.02X_2 \quad (4)$$

$$Y_{\text{syngas}} = 32.53 + 38.68X_1 + 0.02X_2 \quad (5)$$

Table 2 Experiment design and product yield distribution

Run	$(WHSV)^{-1}$ (h)	Cracking T (°C)	Bio-oil yield (wt%)	Syngas yield (wt%)
1	0.029	300	35.6	40.5
2	0.067	300	35.4	40.65
3	0.029	450	35.1	43.65
4	0.067	450	32.65	42.45
5	0.021	375	37.75	38.8
6	0.075	375	32.2	43.7
7	0.048	268.9	37.15	39.05
8	0.048	481.1	32.9	43.6
9	0.048	375	35	40.85
10	0.048	375	34.35	41.35
11	0.048	375	34.75	42
12	0.048	375	35.25	40.4
13	0.048	375	34.05	42.5

The P value of eqn (4) was $0.0005 < \alpha = 0.05$, which meant the linear model was significant to describe the bio-oil yield. The coefficient of determination (R^2) for eqn (4) was 0.78, which suggested that the model was finely representing the relationships among the independent variables. The model term b_0, X_1, X_2, was significant because the P values for these model terms were 0.0005, 0.0011, 0.0027, which were smaller than α = 0.05. The model of the bio-oil yields with the $(WHSV)^{-1}$ (X_1, h) and cracking temperature (X_2, °C) is visualized in Fig. 2.

The P value of eqn (5) was $0.0072 < \alpha = 0.05$, which meant the liner model was significant to describe the syngas yield. The coefficient of determination (R^2) for eqn (5) was 0.63, which suggested that the model was fairly representing the relationships among the independent variables. The model term b_0, X_1, X_2 was significant because the P values for these model terms were 0.0072, 0.0889, and 0.0045 which were smaller than α = 0.05. The linear model terms of the 1/WHSV (X_1, h) and cracking temperature (X_2, °C) is visualized in Fig. 3.

3.2 GC-MS characterization of bio-oil

In order to further understand the effect of the catalyst on the bio-oil chemical compositions from close coupled ZSM-5 cracking, GC-MS was used to characterize the bio-oil chemical compounds which were categorized into ten functional groups (Fig. 4). Without using catalysts, bio-oils from the microwave pyrolysis of Douglas fir pellets were a mixture of acid, ketones, alcohols, phenols, guaiacols, furans, esters, sugars and so on, which were similar to those compounds from the microwave pyrolysis of corn stover[8] and Douglas fir.[3] With ZSM-5 being used in packed-bed catalysis coupled with microwave pyrolysis, aromatic hydrocarbons which did not contain oxygen

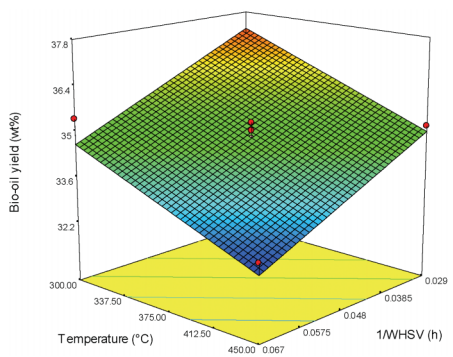

Fig. 2 Effect of the interaction of the independent variables on the bio-oil yield.

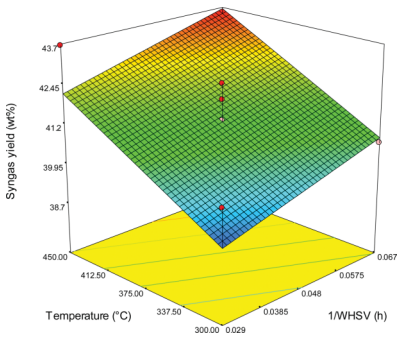

Fig. 3 Effect of the interaction of the independent variables on the syngas yield.

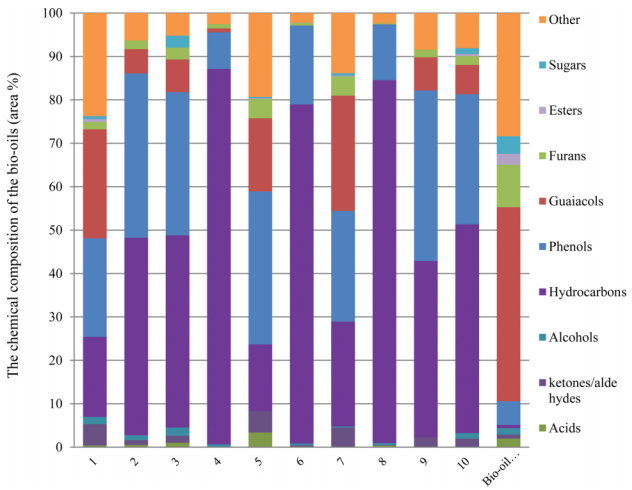

Fig. 4 The composition of the bio-oils from GC-MS analysis. The numbers on the X axis correspond to the run numbers in Table 2.

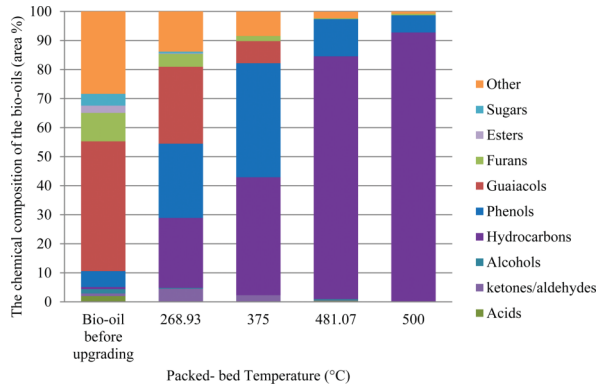

Fig. 5 The effect of the packed-bed temperature on the composition of the bio-oils.

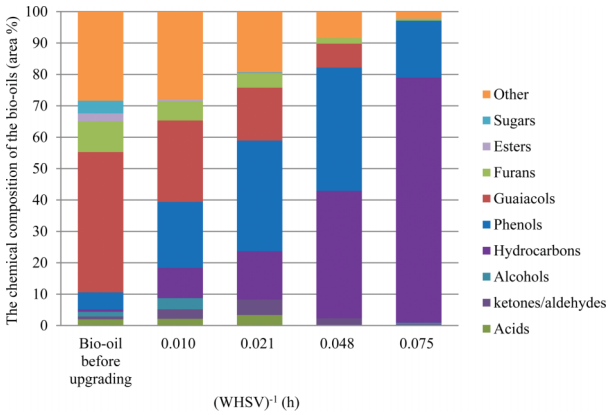

Fig. 6 The effect of $(WHSV)^{-1}$ on the composition of the bio-oils.

were enriched and became the most abundant compounds in upgraded bio-oils. Aromatic hydrocarbons were about 15.4–86.5% of the upgraded bio-oils, depending on the catalytic pyrolysis conditions. These aromatic hydrocarbons were mainly composed of benzene, toluene, xylene, naphthalene, and their derivatives. Phenols became the second highest amount of compounds, which were from 8 to 39%, and there were five main phenols: phenol, 2-methyl-phenol, 3-methyl-phenol, 2,4-dimethyl-phenol, and 3,4-dimethyl-phenol in the bio-oils depending on the reaction conditions. The guaiacols were significantly decreased by our coupled catalysis from 45% in raw bio-oils to 0–26% in upgraded bio-oils depending on the reaction conditions. The guaiacols were mainly composed of 2-methoxy-phenol, 2-methoxy-4-methyl-phenol and 4-ethyl-2-methoxy-phenol.

3.2.1 The effect of reaction temperature on the chemical compositions of bio-oils. The effect of the packed-bed catalysis temperatures on the chemical compositions of the upgraded bio-oils was analysed with a fixed $(WHSV)^{-1}$ (0.048 h), as shown in Fig. 5. The aromatic hydrocarbons were increased from 0.72% in raw bio-oil to around 92.6% when the catalysis temperature was increased to 500 °C, which showed that high temperatures favoured the production of aromatic hydrocarbons. The content of phenols was first increased from 5.5% in raw bio-oil to 39% at 375 °C, and then decreased to 5.9% when the temperature was increased to 500 °C. The guaiacols content was decreased from 44.7% in raw bio-oil to 0% when the temperature was higher than 481 °C. The content of furans was decreased from 9.8% in raw bio-oil to around 1% when the catalysis temperature was higher than 375 °C. The content of sugars decreased from 4 to 0% as the temperature was increased to more than 375 °C.

3.2.2 The effect of $(WHSV)^{-1}$ on the chemical composition of the bio-oils. It was observed that when the packed-bed catalysis temperature was fixed at 375 °C, the aromatic hydrocarbon content was increased from 0.72% in raw bio-oil to 78.1% with the increase of $(WHSV)^{-1}$ from 0 to 0.075, (Fig. 6) which is consistent with the same trend claimed by Carlson and his co-workers.[20] The content of phenols was first increased from 5.5% (bio-oil before upgrading) to 39.3% ($(WHSV)^{-1}$ of 0.048 h), then decreased to 18.2% with the increase of $(WHSV)^{-1}$ to 0.075 h. The content of guaiacols was decreased from 44.7% in bio-oil before upgrading to 0% when the $(WHSV)^{-1}$ was increased to 0.075 h, which indicated that a higher $(WHSV)^{-1}$ favoured the production of aromatic hydrocarbons as guaiacols, which were cracked by ZSM-5 to produce aromatic hydrocarbons.

3.3 Characteristics of the ZSM-5 catalyst

3.3.1 Selectivity. The chemical compounds of the bio-oil (cracking temperature: 500 °C; catalyst: 5 g) with ZSM-5 catalyst reused for different (0–5) cycles is shown in Fig. 7. The acid content didn't change much as the run cycle number increased. The content of hydrocarbons was high with fresh ZSM-5 catalyst (more than 90%), then decreased to around 8% after the 2nd cycle and stayed at this level for the next 3 cycles. The phenol content increased from 6% with fresh ZSM-5 catalyst to around 40% after the 1st cycle and stayed at this level for the next 5 runs, more than that from the non-catalytic reaction (only 5%). The content of guaiacols with catalyst at different cycles were all much lower than that from the non-catalytic reaction. The furan content increased from less than

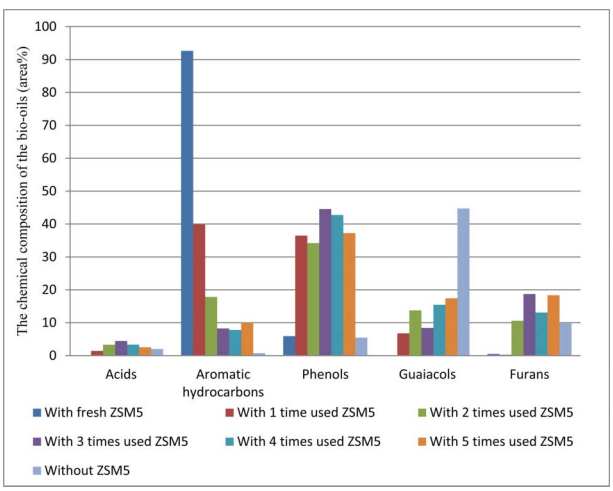

Fig. 7 The chemical composition of the bio-oils with reused ZSM-5 catalyst.

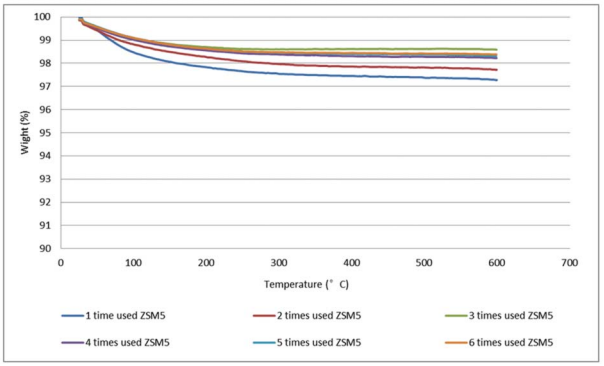

Fig. 8 TG profiles for the ZSM-5 catalyst after being used for various numbers of cycles.

1% in the first two runs to more than 10% in the next 3 runs. This shows that the fresh ZSM-5 catalyst has a high selectivity for hydrocarbon, and the reacted ZSM-5 catalyst has a high selectivity for phenols.

3.3.2 The stability of the ZSM-5 catalyst. Fig. 8 shows the thermogravimetric curves of the ZSM-5 catalyst after 1 to 6 cycles. The overall weight loss was less than 3 wt% in all curves and there was no significant weight loss change between different cycles. The measurements indicate that the ZSM5 catalyst was stable during the catalytic reaction cycles.

The FTIR measurements showed similar results (Fig. 9) for the stable ZSM-5 catalysts. All the fresh and used ZSM-5 catalysts showed a characteristic three-peak shape with peaks at 800 cm^{-1}, 1088 cm^{-1} and 1220 cm^{-1}, which are mainly related to the symmetric stretch, the symmetric stretch and the symmetric bend stretch respectively.[33]

3.4 GC analysis for syngas

Syngas was one of the main products of the Douglas fir sawdust pellet from packed-bed catalysis coupled microwave pyrolysis. The syngas yield varied from 38.8 to 43.7 wt%. The knowledge of the composition of the syngas would be helpful to investigate the reactions in the reactor. The uncondensed syngas was mainly composed of H_2, CO, CO_2, CH_4, and C_2H_4. The richest content of H_2 was around 23% (v/v) of the total volume of the syngas at a condition of 500 °C and 5 g ZSM-5 catalyst. The CO, CO_2, CH_4 components were around 51%, 10%, and 10% (v/v) respectively.

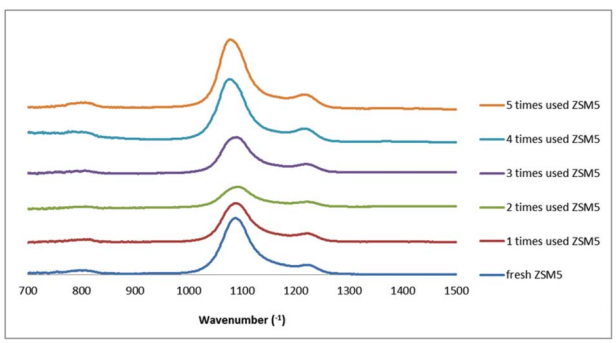

Fig. 9 FTIR spectra for the used ZSM-5 catalyst.

3.5 Mechanism analysis for the close coupled catalysis process

In this study, the highest aromatic hydrocarbon content (92.6%) was achieved when the catalysis temperature was 500 °C and the $(WHSV)^{-1}$ was 0.048 h. The content of acids, ketones, alcohols, phenols, guaiacols, furans, esters, and sugars were 0.1%, 0%, 0.05%, 5.95%, 0%, 0.5%, 0%, and 0%, respectively, in the upgraded aromatic bio-oil. Comparing with the raw bio-oil (500 °C) which contained 0.71% aromatic hydrocarbons, 2% acid, 0.89% ketones, 1.5% alcohols, 5.46% phenols, 44.7% guaiacols, 9.8% furans, 2.51% ester, and 4.05% sugars, the content of aromatic hydrocarbons was significantly increased in upgraded bio-oils, while the other compounds, except phenols, all decreased to about 0%. The disappearance of these oxygenated compounds after catalysis in the packed-bed was associated with dehydration, decarboxylation and decarbonylation reactions.

Douglas fir is a soft wood which contains 21% hemicelluloses, 44% cellulose, and 32% lignin.[34] In our coupled catalysis with the microwave pyrolysis of Douglas fir sawdust pellets, furfural was first obtained through the cleavage of the bond between O–C5 and the ring forming between the C2–C5 positions of the main chain of xylan, which is the most abundant compound in hemicelluloses.[35] Furans were then formed from the decarbonylation of furfurals. Cellulose was decomposed and dehydrated to form anhydrosugars, such as levoglucosan and furans.[36] Those furans were converted to intermediates (*e.g.*, cyclohexene and 3,4-dimethylbenzaldehyde) in the ZSM-5 pores. Then these intermediates were transformed into aromatics, light olefins, and carbon oxides.[37] Lignin was primarily depolymerized and dehydrated to produce propenyl-guaiacols. Then phenols were generated from the demethoxylation reaction of propenyl-guaiacols. The cleavage of the O–CH_3 bond in guaiacols was verified by the increased CH_4 in syngas, which was observed by the GC analyser and mainly contained H_2, CO_2, CO, CH_4, and C_2H_4. Then aromatic hydrocarbons, such as toluene, were obtained from the catalysed deoxygenation of phenols during zeolite catalysis.

5 Conclusions

The direct catalytic cracking of biomass pyrolysis vapour through packed-bed catalysis close coupled with microwave pyrolysis was investigated to convert Douglas fir sawdust pellets to aromatics by a ZSM-5 Zeolite catalyst. The effects of cracking temperature and $(WHSV)^{-1}$ on the bio-oil composition were determined by using a central composite experimental design (CCD). GC-MS analysis showed that the upgraded bio-oil contained aromatic hydrocarbons which did not contain oxygen. Aromatics were enriched and become the most abundant compounds which were about 15–92.6% in upgraded bio-oils, depending on the catalytic pyrolysis conditions. The aromatic hydrocarbons were mainly composed of benzene, toluene, xylene, naphthalene, and their

derivatives. The effect of the reaction temperature on the bio-oil chemical compositions was analysed with a fixed $(WHSV)^{-1}$ at 0.048 h and found that the amount of aromatic hydrocarbon was increased from 9.4% at 0 °C to around 92.6% when the temperature was 500 °C, which showed that high temperatures favoured the production of aromatic hydrocarbons. At a low temperature fixed at 375 °C, the aromatic hydrocarbon content was increased from 9.4 to 78.1% with the increase of $(WHSV)^{-1}$ from 0 to 0.075 h.

Acknowledgements

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Notes and references

1 B. Digman, H. S. Joo and D. S. Kim, *Environ. Prog. Sustainable Energy*, 2009, **28**, 47–51.
2 A. Pattiya, *Bioresour. Technol.*, 2011, **102**, 1959–1967.
3 S. Ren, H. Lei, L. Wang, Q. Bu, S. Chen, J. Wu, J. Julson and R. Ruan, *J. Anal. Appl. Pyrolysis*, 2012, **94**, 163–169.
4 J. N. Brown and R. C. Brown, *Bioresour. Technol.*, 2012, **103**, 405–414.
5 J. Meng, J. Park, D. Tilotta and S. Park, *Bioresour. Technol.*, 2012, **111**, 439–446.
6 Z. Hu, X. Ma and C. Chen, *Bioresour. Technol.*, 2012, **107**, 487–493.
7 B. Kriegerbrockett, *Res. Chem. Intermed.*, 1994, **20**, 39–49.
8 H. W. Lei, S. J. Ren and J. Julson, *Energy Fuels*, 2009, **23**, 3254–3261.
9 Y. F. Huang, W. H. Kuan, S. L. Lo and C. F. Lin, *Bioresour. Technol.*, 2010, **101**, 1968–1973.
10 V. L. Budarin, J. H. Clark, B. A. Lanigan, P. Shuttleworth, S. W. Breeden, A. J. Wilson, D. J. Macquarrie, K. Milkowski, J. Jones, T. Bridgeman and A. Ross, *Bioresour. Technol.*, 2009, **100**, 6064–6068.
11 Y. Wan, P. Chen, B. Zhang, C. Yang, Y. Liu, X. Lin and R. Ruan, *J. Anal. Appl. Pyrolysis*, 2009, **86**, 161–167.
12 X. Zhao, M. Wang, H. Liu, L. Li, C. Ma and Z. Song, *Bioresour. Technol.*, 2012, **104**, 673–678.
13 Y. F. Huang, W. H. Kuan, S. L. Lo and C. F. Lin, *Bioresour. Technol.*, 2008, **99**, 8252–8258.
14 Q. Bu, H. Lei, S. Ren, L. Wang, Q. Zhang, J. Tang and R. Ruan, *Bioresour. Technol.*, 2012, **108**, 274–279.
15 H. W. Lei, S. J. Ren, L. Wang, Q. Bu, J. Julson, J. Holladay and R. Ruan, *Bioresour. Technol.*, 2011, **102**, 6208–6213.
16 A. Domínguez, J. A. Menéndez, Y. Fernández, J. J. Pis, J. M. V. Nabais, P. J. M. Carrott and M. M. L. R. Carrott, *J. Anal. Appl. Pyrolysis*, 2007, **79**, 128–135.
17 Z. Luo, S. Wang, Y. Liao, J. Zhou, Y. Gu and K. Cen, *Biomass Bioenergy*, 2004, **26**, 455–462.
18 A. Oasmaa and S. Czernik, *Energy Fuels*, 1999, **13**, 914–921.
19 Q. Zhang, J. Chang, T. J. Wang and Y. Xu, *Energy Convers. Manage.*, 2007, **48**, 87–92.
20 T. R. Carlson, G. A. Tompsett, W. C. Conner and G. W. Huber, *Top. Catal.*, 2009, **52**, 241–252.
21 J. D. Adjaye and N. N. Bakhshi, *Fuel Process. Technol.*, 1995, **45**, 161–183.
22 J. D. Adjaye and N. N. Bakhshi, *Fuel Process. Technol.*, 1995, **45**, 185–202.
23 S. Vitolo, M. Seggiani, P. Frediani, G. Ambrosini and L. Politi, *Fuel*, 1999, **78**, 1147–1159.
24 R. K. Sharma and N. N. Bakhshi, *Bioresour. Technol.*, 1991, **35**, 57–66.
25 A. V. Bridgwater, in *Thermochemical Processing of Biomass*, John Wiley & Sons, Ltd, 2011, pp. 157–199.
26 H. J. Park, J. I. Dong, J. K. Jeon, K. S. Yoo, J. H. Yim, J. M. Sohn and Y. K. Park, *J. Ind Eng Chem.*, 2007, **13**, 182–189.
27 A. Aho, N. Kumar, A. V. Lashkul, K. Eränen, M. Ziolek, P. Decyk, T. Salmi, B. Holmbom, M. Hupa and D. Y. Murzin, *Fuel*, 2010, **89**, 1992–2000.
28 Y. Fernández and J. A. Menéndez, *J. Anal. Appl. Pyrolysis*, 2011, **91**, 316–322.
29 J. A. Menéndez, A. Domínguez, M. Inguanzo and J. J. Pis, *J. Anal. Appl. Pyrolysis*, 2004, **71**, 657–667.
30 Y. Q. Wan, P. Chen, B. Zhang, C. Y. Yang, Y. H. Liu, X. Y. Lin and R. Ruan, *J. Anal. Appl. Pyrolysis*, 2009, **86**, 161–167.
31 D. Decroocq and É. n. s. d. p. e. d. moteurs, *Catalytic cracking of heavy petroleum fractions*, Éditions Technip, 1984.
32 L. Wang, H. Lei, S. Ren, Q. Bu, J. Liang, Y. Wei, Y. Liu, G.-S. J. Lee, S. Chen, J. Tang, Q. Zhang and R. Ruan, *J. Anal. Appl. Pyrolysis*, 2012, **98**, 194–200.
33 H. Sutrisno, E. D. Siswani, S. Kristianingrum and Suharto, *Indo. J. Chem.*, 2005, **5**, 283–289.
34 R. C. Pettersen, in *The Chemistry of Solid Wood*, ed. R. M. Rowell, American Chemical Society, Washington, DC, 1984, pp. 57–126.
35 D. K. Shen, S. Gu and A. V. Bridgwater, *J. Anal. Appl. Pyrolysis*, 2010, **87**, 199–206.
36 T. R. Carlson, J. Jae, Y.-C. Lin, G. A. Tompsett and G. W. Huber, *J. Catal.*, 2010, **270**, 110–124.
37 W.-L. Fanchiang and Y.-C. Lin, *Appl. Catal., A*, 2012, **419–420**, 102–110.