# High Quality Bio-oil Production from Catalytic Microwave-assisted Pyrolysis of Pine Sawdust

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The catalytic microwave-assisted pyrolysis of pine sawdust using SiC and Ni modified HZSM-5 as microwave absorbent and catalyst for high quality bio-oil production was investigated. The Ni modified HZSM-5 catalyst was successfully prepared through the co-precipitation method and further characterized by X-ray diffraction (XRD) and surface area and pore size analyses. The product yield results showed that Ni modified HZSM-5 catalyst decreased the bio-oil yield and increased the gas yield. Gas chromatography-mass spectrometry (GC-MS) analysis showed that the bio-oil mainly contained alcohols, aldehydes, ketones, carboxylic acids, furans, and phenolics. The Ni modified HZSM-5 catalyst dramatically decreased the carboxylic acids and ketones content, while it remarkably increased phenolics, especially the phenol content. The physical property analysis showed that the bio-oil with the Ni modified HZSM-5 catalyst had a higher calorific value. Therefore, under microwave-assisted pyrolysis conditions, Ni modified HZSM-5 catalyst had a remarkable effect for improving the quality of bio-oil.

*Keywords: Microwave-assisted pyrolysis; Pine sawdust; Bio-oil; Phenol; Ni modified HZSM-5*

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## INTRODUCTION

With growing concern about the depletion of fossil fuels and the environmental effects of greenhouse gas emissions resulting from the massive consumption of fossil fuels, some efforts are currently being made to develop renewable, environmentally friendly alternatives (Wang *et al.* 2016a). Biomass is an important and abundant source of renewable energy. Unlike fossil fuels, biomass sources, such as forestry and agricultural remnants, are planted and collected annually, and they can provide a continuous energy supply. Fast pyrolysis of biomass is considered to be one of the most promising ways of utilizing these resources (Bridgwater 2012). Conventional fast pyrolysis of biomass mainly focuses on the production of bio-oil, which can be readily stored and further used as biofuels or fine chemicals. However, the bio-oil obtained from conventional fast pyrolysis is a low-grade liquid fuel with undesirable properties such as low heating value, high viscosity, poor stability, and high corrosiveness (Lu *et al*. 2009). These properties significantly restrict its applications. Catalytic fast pyrolysis is one major way to improve the fuel properties of bio-oil, or produce valuable compound chemicals (Zhang *et al.* 2015a). Among various catalysts used, the hydrogen form of zeolite, HZSM-5, has been widely used for upgrading the pyrolysis of bio-oils due to its pronounced performance for shape selectivity of aromatics, and its deoxygenating capacity (Zhang *et al*. 2009; Bakar and Titiloye 2013; Zhang *et al*. 2014; Liu *et al*. 2016). The oxygenated compounds in contact with zeolite catalysts have been found to undergo a series of reactions including cracking, isomerization, aromatization, alkylation, polymerization, as well as deoxygenation, such as dehydration, decarboxylation, and decarbonylation (Liu *et al*. 2014). Moreover, some metal-modified HZSM-5 catalysts showed a more remarkable effect in improving the selectivity of aromatics in bio-oil, and produced less coke on the surface of catalysts (Li *et al.* 2016, 2017; Zheng *et al.* 2017).

Microwave pyrolysis is one novel way for utilizing biomass (Wang *et al.* 2009; Ren *et al.* 2012; Zhao *et al.* 2014; Wang *et al.* 2015). The key advantage of microwave pyrolysis over conventional fast pyrolysis is the nature of the fast internal heating by microwave irradiation (Miura *et al.* 2004). Research has shown that the bio-oil from microwave pyrolysis of sewage sludge contains fewer harmful compounds, such as polycyclic aromatic hydrocarbons (PAHs), than oil from conventional pyrolysis (Dominguez *et al.* 2005). However, biomass is a poor microwave absorber due to low-loss dielectric properties. To increase the heating rate as well as to induce much faster pyrolysis rates, biomass is usually mixed with carbonaceous materials such as coal char and activated carbon. In recent research, a novel concept of biomass fast microwave-assisted pyrolysis with microwave absorbents was presented (Wang *et al.* 2012; Bu *et al.* 2013; Borges *et al.* 2014; Mamaeva *et al.* 2016). Studies on catalytic microwave pyrolysis of biomass with different catalysts have also been previously reported (Chen *et al.* 2008; Wan *et al.* 2009; Shang *et al.* 2015; Wang *et al.* 2016b). Results have shown that a certain catalyst can improve the selectivity of target components in bio-oil. However, the catalytic microwave pyrolysis of biomass with supported metal catalysts is scarce (Zhang *et al.* 2015b). The study of catalytic microwave-assisted pyrolysis of biomass over HZSM-5-supported Ni catalyst has not yet been reported.

In this study, the high quality bio-oil production from catalytic microwave-assisted pyrolysis of pine sawdust using SiC and Ni modified HZSM-5 as a microwave absorbent and catalyst was investigated. The Ni modified HZSM-5 catalyst was successfully prepared through the co-precipitation method and further characterized by X-ray diffraction (XRD) and surface area and pore size analyses. The aim is to investigate the effects of Ni/HZSM-5 catalyst on products yield and the chemical composition of bio-oil from microwave-assisted pyrolysis of pine sawdust. The chemical reaction mechanism of this process was analyzed.

## EXPERIMENTAL

### Materials

*Biomass materials and reagents*

Pine sawdust biomass was obtained from Huainan Xiongdi timber processing factory, Huainan, China. The samples were air dried, then ground and sieved to less than 1 mm in size. The proximate analysis of the sample was conducted according to the GB/T 212 (2008) Chinese standard. The caloric value of pine sawdust was measured in an adiabatic bomb calorimeter (C6000, IKA (Guangzhou) works Co., Ltd., Guangzhou, China). Table 1 shows the proximate analysis of the sample.

**Table 1.** Proximate Analysis of Sample

| $M_{ad}$ (mass%) | $V_{ad}$ (mass%) | $A_{ad}$ (mass%) | $FC_{ad}$ (mass%) | $CV_{b,ad}$ (MJ kg$^{-1}$) |
|---|---|---|---|---|
| 12.69 | 73.42 | 0.28 | 13.61 | 18.05 |

Note: *M*, moisture; *V*, volatile; *A*, ash; FC, fixed carbon; $CV_b$, oxygen bomb caloric value; ad, air dry basis

The HZSM-5 zeolite (Si/Al = 38) used was purchased from the Catalyst Plant of Nankai University, Tianjin, China. Both $Ni(NO_3)_2·6H_2O$ and NaOH were purchased from the Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The purity grade of the $Ni(NO_3)_2·6H_2O$ and NaOH is analytical reagent (A.R.). The microwave absorbent, SiC, was purchased from the Shanghai Milling Material & Tool Co., Ltd., Shanghai, China. The particle size of SiC was 0.5 mm to 1 mm.

## Methods

### *Catalyst preparation and characterization*

The Ni modified HZSM-5 catalyst (the ratio of Ni loading to HZSM-5 mass is 5 wt%) was prepared using the co-precipitation method. The HZSM-5 was calcined in air at 500 °C for 2 h before use; 4.9 g $Ni(NO_3)_2·6H_2O$ was completely dissolved into a certain amount of deionized water, then 20 g of the parent HZSM-5 was added. The suspension was then stirred for 30 min. Subsequently, the 1 M NaOH was added dropwise until the solution pH reached 7 to 8, and maintained this pH for 1 h using the same stirring. Then, the suspension was rested for 6 h, filtered under a vacuum, then washed with deionized water until the pH reached approximately 7 to 8. The filtered cake obtained was dried at 120 °C for 5 h, and then it was calcined in a muffle furnace (BZ-12-10D, Shanghai Bozhen instrument factory, Shanghai, China) at 500 °C for 5 h. Finally, the calcined catalyst was crushed and sieved with 40-mesh, then stored in a sealed container. The Ni modified HZSM-5 catalyst was denoted as Ni/HZSM-5.

The crystalline structure and metal doping on the catalyst were analyzed by X-ray diffraction (XRD) (XRD-7000; Shimadzu, Kyoto, Japan) employing Cu-Kα radiation and operating at 36 kV and 20 mA. The catalysts were scanned at $2\theta$ from 5° to 80° with a step size of 0.025º. Moreover, the specific surface area of the catalysts was measured using a surface area and pore size analyzer (ASAP2020; Micromeritics, GA, USA). The specific surface area and the pore volume were calculated using the Brunauer-Emmett-Teller method and the Barrett-Joiner-Halenda method, respectively.

### *Experimental apparatus and procedure*

A schematic diagram of the microwave pyrolysis device is shown in Fig. 1. The experimental apparatus was mainly composed of a nitrogen cylinder, a microwave oven with a maximum power of 2000 W at a frequency of 2.45 GHz (NJL4-2, Nanjing Jiequan Microwave Oven Equipment Co., Ltd., Nanjing, China), condensation system, and bio-oil collecting system.

The sample of the uniform mix of 20 g of pine sawdust with 20 g of SiC was placed in the lower zone of a quartz reactor (13 cm in length, 12 cm outer diameter), and silica wool was placed in the middle zone of the quartz reactor. Then, 2 g of the prepared Ni/HZSM-5 was evenly spread onto the silica wool. Next, the quartz reactor was placed in the microwave cavity. To keep an anoxic atmosphere, the carrier gas ($N_2$), with a flow rate of 0.5 L min$^{-1}$, was introduced for 10 min, then set to 0.3 L min$^{-1}$. Then, the microwave oven was turned on and set to 800 W. The pyrolysis time was set for 12 min. After the designated reaction time passed, the microwave was turned off. The bio-oil was collected using three U-shaped tubes immersed in an ice water condenser. The solid char was collected using the quartz reactor. The gaseous product was discharged into the atmosphere. The bio-oil, as well as solid char yields, were calculated by the ratio of the each fraction mass to biomass mass. The gas yield was calculated by difference based on the mass balance. In this study, each experiment was repeated at least three times to ensure accuracy of the result. The data are the average values of three time trials with less than a 5% difference.

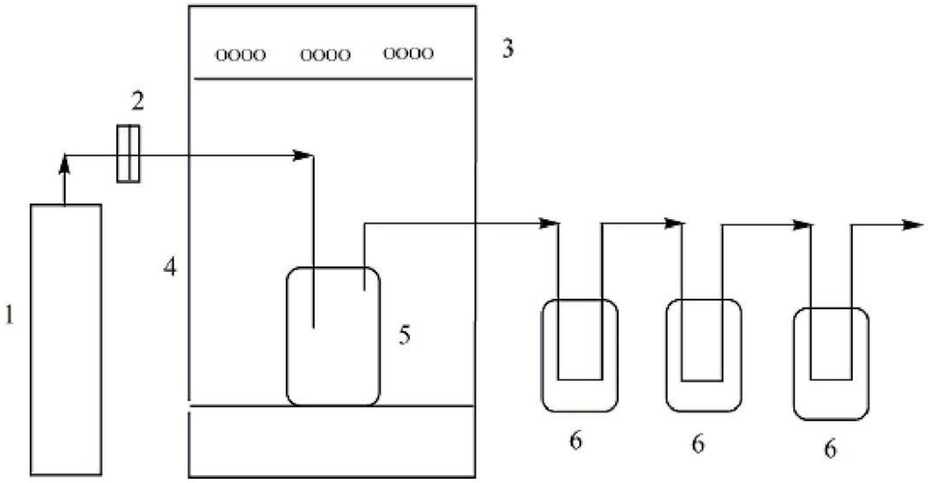

**Fig. 1.** Schematic diagram of experimental apparatus: (1) $N_2$ cylinder; (2) flow meter; (3) control system of microwave oven; (4) microwave oven; (5) quartz reactor; (6) condensation system

### *Bio-oil characterization*

The chemical component analysis of the microwave pyrolysis bio-oil product was performed using a GC-MS (QP5050A; Shimadzu, Kyoto, Japan) with a capillary column (DB-17, 30 m × 0.25 mm i.d. × 0.25 μm) after dehydration using anhydrous sodium sulfate. Acetone was used as a solvent to dilute the dehydrated bio-oil. The solvent cut time was 2 min. High pure helium (99.999%) with a flow rate of 1 mL min$^{-1}$ was employed as a carrier gas. The detector temperature and injector temperature were both 240 °C. The initial temperature was set to 50 °C and kept for 5 min and then increased to 240 °C with a heating rate of 10 °C min$^{-1}$ and held for 5 min. The injection size was 1 μL with a split ratio of 20:1. The *m*/*z* used was within the range of 50 to 500. The compounds of bio-oil were identified by comparing their respective mass spectra with those from the National Institute of Standards and Technology mass spectral database.

The physical properties of the bio-oils were analyzed in terms of water content and calorific value. The water content of the bio-oil was determined using a Karl Fischer Moisture Titrator (KF-1, Shanghai Chemical Research Institute, Shanghai, China). The calorific value was determined using an adiabatic bomb calorimeter (C6000, IKA (Guangzhou) Works Co., Ltd., Guangzhou, China).

## RESULTS AND DISCUSSION

### Characteristics of Catalysts

Phase analysis of the HZSM-5 and Fe/HZSM-5 catalysts was determined by XRD, as illustrated in Fig. 2. The XRD profiles showed that the two catalysts presented the typical specific peaks of the HZSM-5 catalyst at 7.96°, 8.83°, 23.18°, 23.99°, and 24.45°, evidencing the typical high crystallinity of the HZSM-5 structure (Zheng *et al.* 2017). Therefore, the crystal structure of HZSM-5 was not changed after Ni modification. The specific peaks at $2\theta$ value of 37.2° and 43.3° as a sign of NiO was observed from the XRD pattern of the Ni/HZSM-5 catalyst. The result showed that nickel oxide crystals were loaded on the support of the HZSM-5.

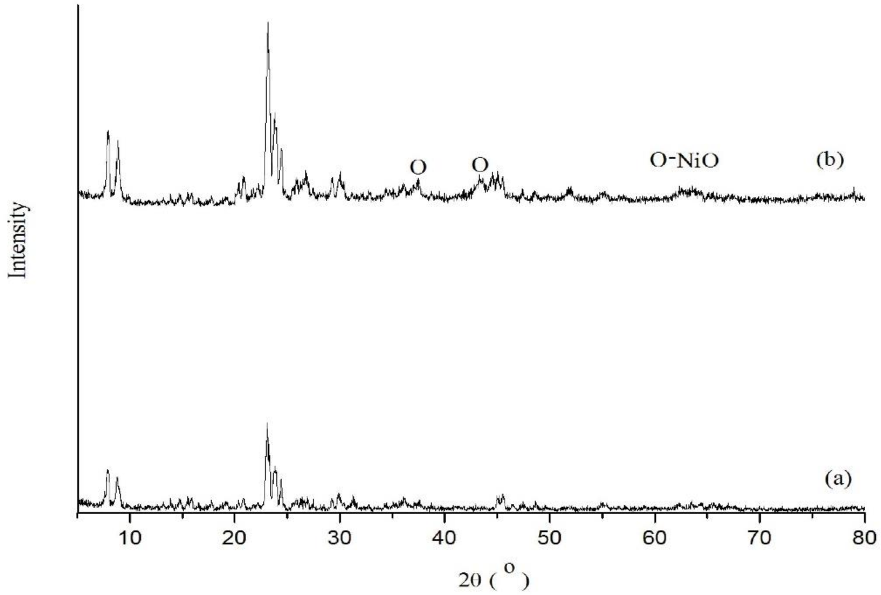

**Fig. 2.** XRD patterns of catalyst: (a) HZSM-5 and (b) 5 wt% Ni/HZSM-5

The physical properties of the catalysts are listed in Table 2. The surface area and pore volume of the Ni/HZSM-5 was reduced. This was because the nickel oxide crystals were dispersed on the surface of HZSM-5 catalyst, and at the same time nickel oxide crystals entered into the pore channel of HZSM-5 and thus occupied a part of the pore volume.

**Table 2.** Physical Property of the Catalysts

| Catalyst | Surface Area ($m^2$ $g^{-1}$) | Pore Volume ($cm^3$ $g^{-1}$) |
|---|---|---|
| HZSM-5 | 430.22 | 0.2853 |
| Ni/HZSM-5 | 390.62 | 0.2682 |

### Product Yields

The product yields of microwave-assisted pyrolysis without catalyst and with catalysts are given Fig. 3. The highest bio-oil yield (approximately 43 wt%) was obtained from the microwave-assisted pyrolysis without catalyst. The presence of the catalysts decreased the yields of bio-oil and solid, and increased the yield of gas. With the addition of the Ni/HZSM-5 catalyst, the change in the yields of bio-oil and gas was especially obvious. The result was similar to previous studies (Iliopoulou *et al.* 2012; Saracoglu *et al.* 2017). This may be because the Ni/HZSM-5 catalyst with the high surface area remarkably promoted the degradation of high oxygenated compounds. Consequently, more light gases products were produced.

Microwave-assisted pyrolysis of biomass produced lower yields of bio-oil in previous reports. Bu *et al.* (2013) found that different activated carbon catalysts decreased the bio-oil yield of microwave-assisted pyrolysis of fir sawdust pellets: the bio-oil yield decreased from about 45 wt% to about 30 wt%. Zhang *et al.* (2015b) noted that approximately 24 wt% bio-oil yield was obtained from microwave pyrolysis of rice husk. However, rice husk char and rice husk char-supported metallic (Ni, Fe, and Cu) catalysts all contributed in reducing the bio-oil yield.

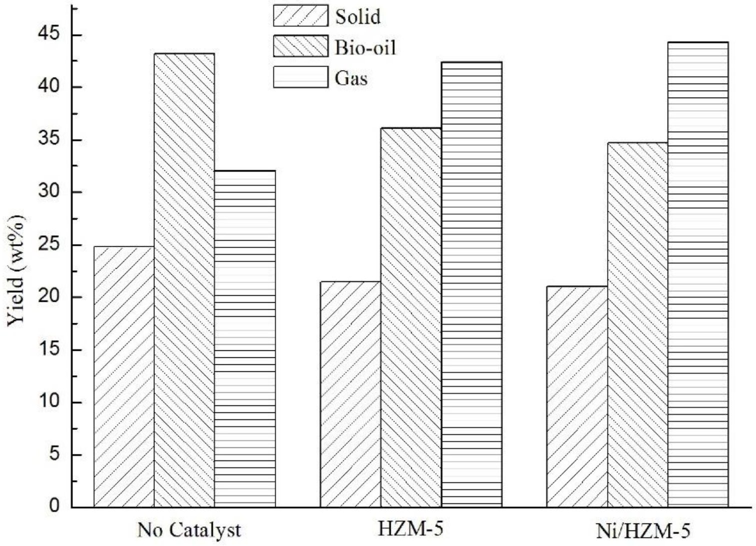

**Fig. 3.** Product yields without catalyst and with catalysts

## Bio-oil Analysis

An analysis of chemical compositions of the bio-oils was performed using GC-MS. A semi-quantitative analysis was made to compare the distribution of the compounds in the bio-oils. The area percent (%) from the total ion chromatogram peak areas was used in calculating the relative content of compounds in the bio-oils. The bio-oils from the microwave-assisted pyrolysis of pine sawdust without catalyst and with catalysts were a very complex mixture of organic compounds. The peak area percent of the main chemical compounds in the bio-oils is shown in Table 3.

The peak area percent of the main chemical compositions of bio-oils without catalyst and with catalysts is shown in Fig. 4. The main chemical compositions without catalyst identified in the bio-oil mainly included alcohols, aldehydes, ketones, carboxylic acids, furans, and phenolics. The bio-oil contained a large number of carboxylic acids (26.7%) and ketones (24.1%). The largest component was acetic acid (22.7%). At the same time, the bio-oil contained high phenolics (18.6%).

**Table 3.** Peak Areas of the Main Chemical Compound in Bio-oils

| Compound Name | Peak Areas (%) | | |
|---|---|---|---|
| | No Catalyst | HZSM-5 | Ni/HZSM-5 |
| Acetone | 2.56 | - | 1.04 |
| Propenol | - | 0.78 | 0.44 |
| Vinyl methylketone | 1.12 | - | 0.97 |
| 3-Methoxy propylaldehyde | 2.31 | - | 0.8 |
| Acetic acid | 22.7 | 8.73 | 10.8 |
| Propionic acid | 4.03 | 1.81 | 1.2 |
| Propaldehyde | 2.56 | 1.03 | 1.24 |
| Cyclopentone | 2.03 | 1.56 | 1.13 |
| 1-Hydroxyl-2-butanone | 8.59 | 4.81 | 3.2 |
| Furfural | 3.45 | 1.29 | 7.39 |
| 2-Cyclopentenone | 7.02 | 4.83 | 6.83 |
| Furfuralcohol | 1.35 | 7.64 | 4.78 |
| 3-Methyl-1,2-cyclopentane glycol | 0.39 | 2.97 | 0.59 |
| Phenol | 2.49 | 5.23 | 13.97 |
| 3-Methyl-1,2-Cyclopentanedione | 2.76 | 2.87 | 2.12 |
| *o*-Cresol | - | 4.5 | 0.78 |
| Guaiacol | 3.56 | 4.85 | 4.53 |
| *p*-Cresol | - | 1.22 | - |
| 2,6-Dimethylphenol | 0.47 | - | - |
| Naphthalene | 0.82 | - | - |
| 2-Methoxy-4-methylphenol | 3.55 | 4.01 | 4.55 |
| 4-Ethyl-2-methoxyphenol | 1.19 | 2.02 | 2.6 |
| Catechol | - | 4.53 | 12.2 |
| 2-Methoxy-4-vinylphenol | 5.01 | 1.28 | 1.22 |
| 2,5-dihydroxytoluene | - | 1.04 | 4.55 |
| Eugenol | 0.65 | 0.32 | - |
| Vanillin | 1.23 | - | - |
| 4-Propenyl-2-methoxyphenol | 0.48 | - | - |

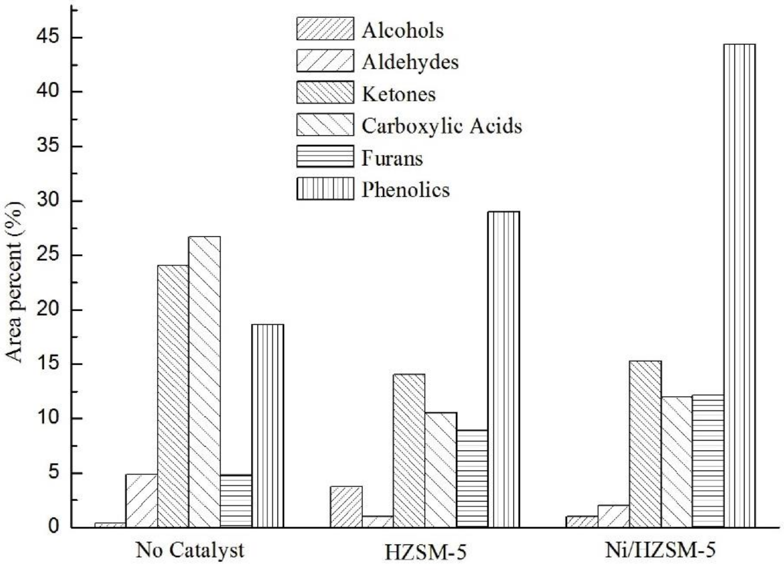

**Fig. 4.** Peak area % of main chemical composition of bio-oils without catalyst and with catalysts

As mentioned in previous literature, carboxylic acids (high corrosivity), aldehydes/ketones (thermally instability), esters (low heating value), and PAHs (carcinogenic) are the main undesired products from the biomass pyrolysis of bio-oil, whereas phenols, furans, and hydrocarbons are much more desirable as valuable chemicals and fuel production (Iliopoulou *et al.* 2012; Saracoglu *et al.* 2017). In the presence of the Ni modified HZSM-5 catalyst, phenolics in the bio-oil prominently increased to 44.4%, especially, phenol remarkably increased from 2.5% to 14.0%. While carboxylic acids and ketones in the bio-oil significantly decreased to 12.0% and 15.3%, respectively.

Physical properties of the bio-oils with HZSM-5 and Ni/HZSM-5 catalysts are listed in Table 4. With the addition of the catalysts the water content increased, and at the same time the caloric value increased. The Ni/HZSM-5 catalyst obviously increased the caloric value.

**Table 4.** Physical Property of Bio-oils

| Catalyst | Water Content (wt%) | Caloric Value (MJ kg$^{-1}$) |
|---|---|---|
| No Catalyst | 22.68 | 20.85 |
| HZSM-5 | 23.82 | 22.42 |
| Fe/HZSM-5 | 24.58 | 25.96 |

The above analysis showed that under microwave-assisted pyrolysis conditions, Ni modified HZSM-5 catalyst had a remarkable effect for improving the quality of bio-oil.

## Reaction Mechanism Analysis

Microwave-assisted pyrolysis is a very complex thermal chemical conversion process, and a series of chemical changes and physical changes of the sample occur. The chemical changes comprise a series of complex chemical reactions, and the physical changes comprise energy conversion, heat transfer, and mass transfer. Through study of conventional pyrolysis mechanisms, integrated microwave heating characteristics, reaction mechanisms of microwave-assisted pyrolysis were analyzed.

Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin components. The three components decompose at different temperature ranges. In general, the decomposition of cellulose and hemicellulose occurs at a low temperature range of 200-400 °C (Yang *et al.* 2007) and results in the acid, ketones, aldehydes, sugars,, and furans (Shen and Gu 2009; Shen *et al.* 2010a). Compared to pyrolysis of cellulose, the pyrolysis of hemicellulose produces more gaseous products and less liquid product. Lignin is the most heat-resistant component among the three components, and it is typically decomposed in the temperature range of 280 to 500 °C (Yang *et al.* 2007), which generates the phenolics (Shen *et al.* 2010b). Compared with cellulose and hemicellulose, lignin pyrolysis produces more char.

Because SiC is a good microwave absorber, the formation of hot spots due to microwave heating will result in much higher temperature (Borges *et al.* 2014). According to the related literature (Vichaphund *et al.* 2014), the intermediate oxygenated compounds diffused into ZSM-5 pores and reacted with the protons at active sites *via* various reaction pathways including dehydration, decarboxylation, decarbonylation, and oligimerization. Ni/HZSM-5 catalyst with well-developed porosity and effective active sites could promote the formation of phenol through deoxygenation and aromatization of both acids and ketones, or Ni/HZSM-5 catalyst would result in the catalytic decomposition of the large molecular intermediates formed from lignin to produce more small molecular phenolic compounds, thus increasing the relative content of phenolics. This was confirmed by the GC-MS analysis of the chemical compositions of bio-oils, which showed that the main compositions of the upgraded bio-oil were phenolics such as phenol. The small molecular mass compounds, such as acids and ketones were decreased significantly in comparison to the raw bio-oil.

## CONCLUSIONS

In this study, the high quality bio-oil production from catalytic microwave-assisted pyrolysis of pine sawdust over Ni modified HZSM-5 catalyst was investigated.

1. The results showed that the presence of Ni/HZSM-5 catalyst decreased the bio-oil yield while increasing the gas yield.
2. A GC-MS analysis of the bio-oils showed that in the presence of the Ni/HZSM-5 catalyst, carboxylic acids and ketones decreased prominently, while phenolics increased remarkably, especially, phenol significantly increased. Moreover, the bio-oil with the addition of Ni/HZSM-5 catalyst had a higher caloric value. So, the high quality bio-oil was obtained from catalytic microwave-assisted pyrolysis of pine sawdust using SiC and Ni modified HZSM-5 as a microwave absorbent and catalyst.

## ACKNOWLEDGMENTS

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