CATALYTIC MICROWAVE PYROLYSIS OF DOUGLAS FIR PELLETS WITH CARBON CATALYSTS DERIVED FROM CORN STOVER

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Abstract

This study investigated catalytic microwave pyrolysis of Douglas fir sawdust pellets using carbon catalysts produced from corn stover. The effects of catalyst to biomass ratio on the bio-oil, syngas, and biochar yields were determined. Functional groups (carbonyls, phenolics, lactones, carboxylics) of carbon catalysts and GC/MS analysis were used to study the catalytic pyrolysis of Douglas fir sawdust pellets. Surface functional groups of carbon catalysts were quantified by titration with bases of different ionization potential before and after catalytic pyrolysis. GC/MS analysis results showed that the phenols and hydrocarbons in bio-oil increased with the increase of the carbon catalyst loading while the guaiacol decreased. Comparison between the carbon catalyst from before and after microwave catalytic pyrolysis showed that the variation in the amount of carbonyl group has a close relationship with the upgrading bio-oils. The carbon catalyst might be served as a cost-competitive catalyst in biomass conversion and bio-oil upgrading.

Keywords. Microwave, Catalytic Pyrolysis, Carbon Catalyst, Surface Functional Group, Corn Stover

1. Introduction

Energy has always played an important role in life, survival, and the development of mankind. Biomass fuels can provide more environmental advantage in comparison with fossil fuels or other types of alternative energy. It is considered to be a clean and abundant future energy. Biomass can be converted to useful products by biological, thermal, chemical, and physical technologies (Bridgwater, 2006). Pyrolysis is one of the thermo-chemical conversion processes which conducted at 350-650 °C in the absence of air or oxygen (Scott and Piskorz, 1984). During pyrolysis, large complex hydrocarbon molecules of biomass break down into relatively smaller and simpler molecules of gas, liquid, and char (Scott and Piskorz, 1984).

Microwave pyrolysis is one of the many ways of converting biomass into higher value products. Compare to conventional heating mechanisms, where energy is first converted to heat then transferred along temperature gradients from the surface to the core of the material, microwaves induce heat at the molecular level by direct conversion of the electromagnetic energy into heat. The microwave pyrolysis could somehow overcome heat transfer rate limitation which is suitable for the pyrolysis of large fragment materials (Huang and Kuan, 2008). Lei and his co-workers successfully pyrolyzed and produced comparable liquid yield from the woody pellets biomass by microwave heating (Ren et al., 2012), also 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. There are upcoming interests in microwave assisted catalytic pyrolysis of biomass. (Wan et al., 2009).

The primary product of biomass fast pyrolysis is bio-oils which are carbon based liquids with some similar properties to the petroleum fuel such as low solid content and low viscosity (Mohan et al., 2006). Bio-oils also have low nitrogen and sulfuric contents. Therefore, bio-oils are considered as promising alternative transportation fuels for displacing the gasoline and other petroleum fuels.

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However, the crude bio-oils are acidic and reactive due to the existence of organic acids. The bio-oils are unstable and immiscible with gasoline due to their high oxygen and organic acidic contents. Furthermore, the bio-oils contain few hydrocarbons which are dominant chemicals in petroleum and the heating value of bio-oil is about 17MJ/kg which is lower than half of crude oil. Therefore, the bio-oils need to be upgraded to obtain transportation fuels by removing organic acids, reducing oxygen content, and improving hydrocarbon content.

Some reports the microwave absorption materials or catalysts were added to increase the heating rate and bio-oil production during microwave pyrolysis. Biochar is one of the main co-products in biomass pyrolysis and gasification. With the development of biomass thermochemical conversion, abundant of biochar will be produced. The properties analysis for biochar indicated that the biochar is porosity and has relatively high surface area (Chun et al., 2004; Mullen et al., 2010). The application of biochar has been widely investigated in area of water treatment (Mohan et al., 2012), soil amendment (Chan et al., 2007; Van Zwieten et al., 2010), activated carbon production (Azargohar and Dalai, 2006), and catalyst support (Dehkhoda et al., 2010). Recently, the biochar based catalysts were developed and studied for biodiesel production (Dehkhoda et al., 2010; Chen and Fang, 2011), catalytic esterification (Kastner et al., 2012), biogas reforming (Muradov et al., 2012), and biomass hydrolysis (Ormsby et al., 2012). However, few reports were published for biochar as a carbon catalyst in biomass pyrolysis and bio-oil upgrading.

The objectives of this study were to investigate the feasibility of a cost competitive corn stover derived carbon catalyst in biomass microwave pyrolysis. The effects of loading amounts of carbon catalyst on products yields were determined. The characterizations of products from the biomass catalytic pyrolysis over carbon catalyst were investigated to determine the effects of carbon catalyst. The surface functional groups of different carbon catalyst samples were investigated. The comparison of products from original and used carbon catalyst conducted to explain the possible reaction mechanism.

### 2. Materials and Methods

#### 2.1 Materials

Douglas fir sawdust pellets were purchased from Bear Mountain Forest Products Inc. (USA). The pellets were made from 100% natural Douglas fir wood sawdust with heating value of 19.4 MJ/Kg and a water content of 7 wt%. The pellets had an average diameter of 6mm and an average length of 10mm. Proximate and elemental analysis of Douglas fir pellet were showed in Table 2.1.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Douglas fir pellet</th>
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<tbody>
<tr>
<td>Moisture</td>
<td>4.82</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>76.08</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>18.89</td>
</tr>
<tr>
<td>Ash</td>
<td>0.21</td>
</tr>
<tr>
<td>Carbon</td>
<td>47.9</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.55</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.08</td>
</tr>
<tr>
<td>Oxygen</td>
<td>45.57</td>
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</table>
2.2 Preparation of Carbon Catalyst
Corn stover derived carbon catalysts produced from microwave pyrolysis. The corn stover (collected from Brookings, South Dakota, USA and dried in air at the room temperature) were ground to 2 mm and pyrolyzed at the temperature of 650°C with the power input of 700W. The cold carbon catalyst was collected after microwave pyrolysis and used for the following catalysis experiments. Mineral analysis for the biochar catalyst was previously reported (Lei et al., 2009).

2.3 Biomass catalytic pyrolysis
A Sineo MAS-II batch microwave oven (Shanghai, China) was used to conduct the biomass catalytic pyrolysis at the reaction temperature of 450°C and time of 15min with 700W power setting. The ratios of carbon catalyst to biomass were 1:4, 1:2, and 1:1 with a fixed biomass loading of 25g. The Douglas fir pellets were first introduced in a 500mL quartz flask then the carbon catalyst in a certain ratio to pellets was added in the flask to cover the feedstock. The system was purged with nitrogen on a flow rate of 1000 mL/min for 30 min prior to microwave pyrolysis to create an oxygen free background. The temperature of biomass was measured by an infrared sensor through a dead end quartz tube which was penetrated to the central of the flask. After reaching desired reaction temperatures, the microwave reactor equipped with automatic temperature/power control used a minimum power (e.g. 0-100 W) to maintain the desired reaction temperatures. At the end of process, the corn stover derived carbon catalyst and pellets biochar were left in the quartz flask. The carbon catalyst and pellets biochar were separated due to their difference in particle size. All experiments were carried out in triplicate. The weight of syngas for biomass catalytic pyrolysis was calculated by difference using the following equation:

2.4 GC/MC analysis for bio-oil
Chemical compositions of the bio-oil were determined using an Agilent 7890A GC/MS with a DB-5 capillary column. The GC was programmed at 45 °C for 3 min and then increased at 10 °C /min to 300 °C and finally held isothermal for 10 min. The injector temperature was 300 °C and the injection size was 1 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.

2.5. Total titrable surface functional groups analysis
Various types of oxygen containing group on the carbon surface could be quantified by Boethm’s method. (Boehm, 1994; Voll and Boehm, 1970) It involved suspending 0.5 g of carbon catalyst in 25 mL of a 0.1 N solution of sodium ethoxide, sodium hydroxide or sodium bicarbonate. The samples were agitated by shaking in closed vessels for 24 h. After this time, the slurry was filtered and a 10 mL aliquot was added to 15 mL of 0.1 N HCl (Sigma-Aldrich, 99.999%). The HCl neutralized the unreacted base and kept further reaction between atmospheric carbon dioxide and the various bases from occurring. The acidified solutions where bubbled with N2 for 1 h to expel dissolved CO2 from solution. (Goertzen and Theriault, 2010; Christopher and Wayne, 1999) All samples were then back-titrated with 0.1N NaOH (Sigma-Aldrich, 99.999%), and the endpoints were potentiometrically determined using a pH meter (Oakton PC - 400). In all cases, results are expressed as mmol H+ equivalent /g carbon. (Pohorecki and Moniuk, 1988) All solutions were prepared with 18.2 MΩ water, sodium ethoxide were made up with 100% ethanol. All titrations were carried out at room temperature ( ).

3. Results and Discussions
3.1 Products yields

The corn stover derived carbon catalyst in biomass microwave pyrolysis has both functions of microwave receptor and catalyst to promote the pyrolysis by increasing the heating rate and inducing self-gasification by forming “micro plasma” (Menendez et al., 2007; Menendez et al., 2010; Salema and Ani, 2011).

In this study the average heating rate observed was reached about 100 °C/min. The yields of products had high relationship with biochar catalyst loading as showed in Figure. 3.1. The syngas yields were within the range of 44.18–46.06 wt% in catalytic pyrolysis of raw Douglas fir pellets, which were much higher than those in the previous findings at the same pyrolysis condition without catalyst addition. This result implied that the biochar catalyst favored the syngas production which is consistent with the previous report (Menendez et al., 2007). The bio-oil yields were within the range of 25.84–37.11 wt% in catalytic pyrolysis of raw Douglas fir pellets. The biochar yields were within the range of 18.71–28.1 wt% in catalytic pyrolysis of raw Douglas fir pellets. In this study, both bio-oil and biochar yields were reduced compared to those from pyrolysis without catalyst.

Figure 3.1. The effects of biochar catalyst loading on product yields of raw Douglas fir pellets (DF) catalytic pyrolysis

The ratio of carbon catalyst to biomass significantly influenced the products yields especially the bio-oil and biochar yields. Figure 3.1 shows the bio-oil yields significantly decreased with the increase of the ratio of biochar catalyst to biomass in raw Douglas fir pellets catalytic pyrolysis but the DF biochar yields were increased. Syngas yield was about 41 to 46 wt % which was relatively stable under different ratios of biochar catalyst to biomass.

3.2 Bio-oil analysis by GC/MS

Figure 3.2 shows the chemical distribution in bio-oils based on the functional groups. The compositions of bio-oils were greatly influenced by the carbon catalyst and its loading amounts. Few organic acids were detected in the bio-oils from the raw Douglas fir pellets catalytic pyrolysis over biochar catalyst. Large amount chemicals, such as phenols and guaiacols, were significantly changed.
compared to those from the biomass pyrolysis without catalyst in our previous research (Ren et al., 2012) The Phenols were about 30 to 38 area% and slightly increased with the increase of the carbon catalyst loading in Douglas fir pellets catalytic microwave pyrolysis while the guaiacols slightly decreased. But at the high amount of carbon catalyst loading (the ratio of carbon catalyst to biomass=1:1), the phenols and guaiacols were 46 and 14 area% respectively, indicating that most guaiacols were converted to phenols. Few hydrocarbons were reported in Douglas fir pellets pyrolysis without catalyst or with activated carbon (AC) catalyst in our previous studies (Bu et al., 2012). In this study, the hydrocarbons were about 4.25 to 8.31 area% and increased with the increase of carbon catalyst loading in microwave catalytic pyrolysis of raw Douglas fir pellets. These results indicated that the loading amount of carbon catalyst is an important factor to affect the bio-oil composition and hydrocarbons production.

Figure 3.2. Chemicals distribution of bio-oil from raw Douglas fir pellets pyrolysis under different carbon catalyst loading

In this study, the corn stover derived carbon catalysts were placed on the top of the biomass. Therefore, the volatiles from biomass decomposition first passed through the carbon catalyst zone before condensed. At this catalysis zone, the cracking and reforming for the volatiles might occur involving the heterogeneous solid-gas reactions and gas-gas reactions. One reaction mechanism is the guaiacols cracking by the cleavage of methyl from O-CH3 to phenols over carbon catalysts. It can be explained by the findings that the guaiacols decreased while the phenols increased with the increase of catalyst loading. However, the concentration of hydrocarbons increased with the amount of carbon catalyst loading and more than 15 area% was obtained at the high catalyst loading. The hydrocarbons
might be produced from both phenolics and aliphatic compounds as they all noticeably reduced.

### 3.3 Surface oxygen functional groups analysis

Figure 3.3 is a major functional groups comparison plot of the used carbon catalysts and the original carbon catalysts from this study. In this case the data shown in the figure have been subtracted from each other in the following manner in Table 3.1. (Christopher et al., 1999) The products of the three equations, namely carbonyls, phenolics, lactones and carboxyls were plotted on the Figure 3.3.

<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>Calculation Manner</th>
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<tbody>
<tr>
<td>Carbonyls</td>
<td>Total surface functional groups (NaOEt titn.) Surface charge (NaOH titn.)</td>
</tr>
<tr>
<td>Phenolics and Lactones</td>
<td>Total surface charge (NaOH titn.) Surface charge(NaHCO3 titn.)</td>
</tr>
<tr>
<td>Carboxyls</td>
<td>Total surface charge (NaHCO3 titn.)</td>
</tr>
</tbody>
</table>

We can find that the carbon catalyst after pyrolysis with Douglas fir pellets, appear to have a much higher level of carbonyl groups than the original carbon catalysts. However, the carboxyls, phenolics and lactones do not have a big alteration. Thus we interfere, in the microwave catalytic pyrolysis process; we can regard the carbon catalyst as the reductant, which means it help to the oxygen removal of the pyrolysis oil.

![Figure 3.3](image.png)

**Figure 3.3.** Major surface functional groups in original carbon catalyst and used carbon catalyst under different loading

The bio-oil chemical profile from catalytic pyrolysis and bio-oil upgrading over corn stover
derived carbon catalyst was simplified to phenols and hydrocarbons, and their concentrations were strengthened by the increase of carbon catalyst loadings. Figure 3.3 shows that the amount of carbonyl groups increases in proportion to the ratio of carbon catalyst and Douglas fir pellet. One reaction mechanism is the carbon catalyst help guaiacols cracking to phenols, the cleavage of methyl from O–CH3 via the proton donation from the catalyst surface, thus CH4 and carbonyl groups are generated in this cracking process. In this mechanism, the generation of carbonyl sites is responsible for the upgrading bio-oils chemical distributions that guaiacols decreased while the phenols increased. It can be explained by the findings that the guaiacols decreased while the phenols increased with the increase of catalyst loading.

4. Conclusions

A new corn stover derived carbon catalyst prepared successfully, and investigated the effects of different carbon catalyst loading amount in biomass catalytic pyrolysis and bio-oil upgrading. The corn stover derived biochar as a carbon catalyst had positive influence on the bio-oil quality. The bio-oil chemical profile from catalytic pyrolysis and bio-oil upgrading over carbon catalyst was simplified to phenols and hydrocarbons, and their concentrations were strengthened by the increase of biochar catalyst loadings. The surface functional groups of the different carbon catalyst samples were investigated in this study, and the amount of carbonyls increases steadily with the decrease of biochar catalyst loadings. A possible reaction mechanism was discussed in the study. These results indicated that the corn stover derived carbon catalyst might be a cost-competitive catalyst in biomass conversion and bio-oil upgrading for fuels and chemicals production.

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References


