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Production of Hydrocarbons from Biomass-Derived Biochar Assisted Microwave Catalytic Pyrolysis

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Complete List of Authors:	Zhu, Lei; Washington State University, Biological Systems Engineer zhang, yayun; Washington State University, Lei, Hanwu; Washington State University, Dept. Biological Systems Engineering zhang, xuesong; washington state university wang, lu; washington state university Bu, Quan; Jiangsu University Wei, Yi; Washington State University,

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Lei Zhu[1], Yayun Zhang[1], Hanwu Lei*, Xuesong Zhang, Lu Wang, Quan Bu, Yi Wei

Abstract: In the present study, in situ catalytic pyrolysis of Douglas fir pellets was performed in a microwave reactor. A biochar catalyst derived from corn stover biochar was prepared for the experiment. Results showed that the highest amounts of hydrocarbons (52.77% of bio-oil) was achieved from microwave-assisted catalytic pyrolysis over biochar catalyst under the reaction temperature of 480 °C. A non-condensable gas enriched in H_2, CO, and CO_2 was observed and analyzed by micro-GC. The amounts of H_2 and CO increased during catalytic pyrolysis compare to the non-catalytic runs. GC/MS analysis results showed that the quantity of lignin-derived guaiacols decreased dramatically with the increase of the ratio of catalyst to biomass. The biochar catalyst exhibited good selectivity towards hydrocarbon and phenol compounds, simplifying the chemical composition, reducing undesirable compounds and producing pyrolysis oil at an acceptable yield. The reaction mechanism for hydrocarbon production from catalytic pyrolysis was also analyzed.

Introduction

Renewable energy is produced from an energy resource that is replaced or replenished rapidly by a natural process. Bioenergy has been identified as a green and renewable solution to decrease fossil fuel consumption and greenhouse gas (GHG) emission. A major objective of bioenergy research is the production of liquid biofuels as substitutes for crude oil products. Due to the negative implication of first-generation biofuels on food resources and energy safety, lignocellulosic biomass is being studied worldwide as a feedstock for second-generation biofuels production.[1,2]

Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin, and can be converted into liquid fuels and chemicals via biochemical or thermochemical methods.[3] Thermochemical methods, in general, can convert all fractions of biomass while biochemical conversions are limited to the carbohydrate fraction. A higher utilization of biomass resources could be achieved when using thermochemical methods. Pyrolysis, gasification and direct combustion are the major three thermochemical conversion processes.[4] Fast pyrolysis is one of the simplest and most promising methods of processing one fuel in order to produce a better fuel. In this process, biomass is heated to intermediate temperatures (400 – 600°C) at high heating rates in an oxygen-free atmosphere and thermally decomposes to biochar, syngas, and bio-oil.

Bio-oil is the major liquid product from fast pyrolysis, and usually has only half the energy content of crude oil. In addition, the product is highly oxygenated and contains acid contaminants that must be removed. Acids in bio-oil catalytic polymerization reactions and their presence further decreases the stability of the bio-oil. Furthermore, high acid content makes bio-oil corrosive and difficult to use in engines.[4] Researchers have been seeking an approach to refining and upgrading raw bio-oil for transportation fuels and other high-value chemicals.[2,5] One of the most promising processes to achieve this is the in-situ catalytic upgrading of biomass pyrolysis vapors.[6] The catalysts can be added directly to the pyrolysis reactor for in-situ vapor upgrading.

Zeolite catalysts have been studied for upgrading pyrolysis oil since the 1980s.[7] ZSM-5 has been found to change the composition of raw bio-oil dramatically by both reducing the amounts of oxygenated compounds via deoxygenation reactions and simultaneously increasing the aromatic species, producing a lighter fraction.[8] Catalytic upgrading of pyrolysis vapors using zeolites is a potential method for removing oxygen from organic compounds and converting them to hydrocarbons.[9, 10] The highest yield of hydrocarbons (approximately 16 wt.%, including 3.5 wt.% of toluene) was achieved using nickel, cobalt, iron, and gallium-substituted ZSM-5.[11] However, the deposition of coke and tar on the catalyst caused a gradual decrease in the activity of the catalyst up to complete poisoning. The catalysts used in the catalytic pyrolysis and bio-oil upgrading are expensive as they need to be doped with costly noble metals to promote oxygen removal and ring-opening reactions.[3]

Biochar can be produced by several thermal decomposition processes of biomass like pyrolysis and gasification.[12] It has a high porosity and surface area, high chemical stability, and is

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[a] Department of Biological Systems Engineering, Washington State University, Richland, WA 99354-1671, USA.
[b] *Corresponding author, Phone: 1-509-372-7628, Fax: 1-509-372-7690, E-mail: hlei@wsu.edu
[c] [1]Authors have equal contribution to the work

cost-effective. Besides the intrinsic nature of the biomass feedstock, pyrolysis process conditions could greatly affect the biochar quality and determine its resultant properties.[13] Biochar contains a high quantity of minerals and functional groups anchored on the surface, which make it for soil amendment, activated carbon production, and water treatment.[14] However, use of biochar as biochar catalyst for biofuel production is still in its infancy with only a few studies on biogas reforming and biodiesel production.[15,16] Therefore, developing an appropriate biochar based catalyst with the desired characteristics could be a new approach for the biomass pyrolysis and bio-oil upgrading.

The goal of the research presented here was to investigate the feasibility of a low-cost biochar catalyst for in-situ catalytic biomass pyrolysis and to obtain upgrading bio-oil with increased hydrocarbon yields and lower oxygen content. The effects of the biochar catalyst loadings on product yields were determined. The bio-oils obtained from the biomass in-situ catalytic pyrolysis using different catalyst loadings were characterized and a possible chemical reaction mechanism of this process was proposed.

Experimental section

Materials

Douglas fir sawdust pellets (7 mm in diameter and 15 mm in length) were purchased from Bear Mountain Forest Products Inc. (USA) and used in the experiments. The pellets were made from 100% natural Douglas fir wood sawdust, the element analysis data of which was presented in Table 1.

Table 1. The elemental analysis data of the feedstock

Feedstock	Douglas fir sawdust pellets
Main compositions, dry basis wt.%	
Carbon	47.8
Hydrogen	6.6
Oxygen	45.4
Nitrogen	0.08
Sulfur	0.01
Ash	0.2
Moisture, wt.% as received	4.8
Higher heating value (HHV), MJ/kg	19.4

Catalytic materials preparation and characterization

All biochar catalysts used in the study were produced from corn stover microwave pyrolysis. The corn stover was obtained from Brookings, South Dakota, USA and dried in air at room temperature. The proximate analysis of the corn stover was shown in Table 2. Prior to the experiments, it was then grounded to 1/8 inch (3.175 mm) and pyrolyzed at a temperature of 550 °C with a power input of 700 W. The cold biochar was collected after microwave pyrolysis and stored in a desiccator.

Table 3 lists the characteristics of the biochar catalyst. The surface areas were obtained from N_2 adsorption-desorption isotherms measured at -196 °C on a QuantachromeAutosorb-1analyzer with all samples outgassed at 200 °C prior to analysis for 16 h. BET surface areas are taken from a multipoint plot over a P/Po range of 0.05 – 0.35.

The total titrable surface functional groups were quantified based on Boehm's method.[17] It involved suspending 0.5 g of biochar catalyst in 25 mL of a 0.1 N solution of sodium ethoxide, sodium hydroxide or hydrochloride acid. The HCl/NaOH neutralized the unreacted base/acid and prevented further reaction between atmospheric carbon dioxide and the various bases from occurring. The acidified solutions where bubbled with N_2 for 1 h to expel dissolved CO_2 from solution. All samples were then back titrated with 0.1N NaOH/HCl, and the endpoints were potentiometrically determined using a pH meter (Oakton PC - 400). All titrations were carried out at room temperature (22 ±3 °C).

Table 2. The proximate analysis of corn stover

Characteristics		Corn stover
Proximate analysis (dry, wt.%)	Volatile matter	74.46
	Fixed carbon	20.06
	Ash	5.48
Moisture (wt.%)		6.29
HHV (MJ/kg)		16.82

Table 3. Characteristics of biochar catalysts used in this study

Properties	Biochar catalyst
BET surface area (m^2/g)	44.16
Average pore diameter (nm)	6.5
Single point total volume pores (cm^3/g)	0.02
Particle size (mesh)	6-30
Apparent density (g/ml)	0.12
Total number of carbon surface functional acidic groups (mmol/g)	1.85
Total number of carbon surface functional basic groups (mmol/g)	0.48

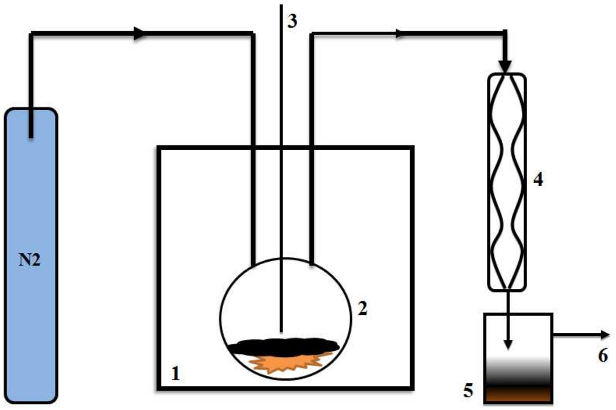

Figure 1. The schematic diagram of lab scale microwave-assisted pyrolysis: (1) Microwave cavity; (2) Quartz reactor; (3) Infrared temperature sensor; (4) Condensers; (5) Bio-oil; (6) Non-condensable gas

Microwave-assisted catalytic pyrolysis system

A Sineo MAS-II batch microwave oven (Shanghai, China) was used to conduct biomass catalytic pyrolysis at a reaction temperature of 480 °C and duration of 15 min. The pyrolytic temperature was selected based on our previous study, which indicated that the optimized bio-oil yield could be obtained at such temperature.[18] The reaction time was set to 15 min in order to obtain the maximum bio-oil yield. A constant power input of 700 W at the microwave frequency of 2450 MHz was used for each batch. Five different ratios of biochar catalyst to biomass (10%, 20%, 40%, 80%, and 100%) were tested with a fixed biomass loading of 20 g. The Douglas fir pellets were first introduced in a 500 mL quartz flask then the biochar catalyst was added to the flask to cover the feedstock. The system was purged with N_2 at a flow rate of 1000 mL/min for 30 min prior to microwave pyrolysis to create an oxygen-free environment. The temperature of biomass was measured by an infrared sensor through a dead-end quartz tube which penetrated to the center of the flask. After reaching the 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. Figure 1 shows the schematic diagram of the system. The volatiles from the flask passed through the condensation system and the condensable liquid was collected as bio-crude oil. The catalyst and pellet biochar were left in the quartz flask. The biochar catalyst and biochar pellets were separated due to their difference in particle size. All experiments were carried out in triplicate. The mass of syngas from the biomass catalytic pyrolysis was calculated based on a mass balance using the following equation:

Weight of syngas = initial pellet mass – bio-oil mass – pellet char mass (1)

GC/MS analysis of bio-oils

The chemical compositions of the bio-oil were determined using an Agilent gas chromatography-mass spectrometer (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 and finally held isothermal for 10 min. The injector temperature was 280 °C and the injection amount 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 NIST Mass Spectral libraries were used for the identification of the compounds found in the bio-oil.[19] In order to obtain the concentration of some typical hydrocarbons in bio-oils, different standard solutions with a various concentration of hydrocarbons were also injected to GC/MS and the obtained data (absolute peak area) was used to calculate the concentration of hydrocarbons in the obtained bio-oil.

Micro-GC analysis of non-condensable gas (NCG)

The NCG released from the microwave catalytic pyrolysis apparatus was collected and analyzed using duel Channel Micro-GC (INFICON, 3000). The Micro-GC contains two channels and the operating condition are as follows: Channel A with molecular sieve 5A column (MS-5) was set at 95 °C for determination of H_2, CO, and CH_4; Channel B with Porapak Q (PPQ) was set at 60 °C for checking the release property of CO_2, C_2H_6, C_2H_4, C_3H_6, and C_3H_8. During the stable operation period, the NCG was sampled every 3 min and each gas sample was measured 3 times to get the average.

Results and discussion

Product fractional yield

The three fractions of products, i.e., bio-oil, syngas and biochar yields (wt.% based on biomass) obtained by the microwave-assisted in situ catalytic pyrolysis are shown in Figure 2. These values are compared to the yields obtained by the use of the non-catalytic Douglas fir pellets. The result shows that the catalysts used in our study affected the fractional yields to different degrees.

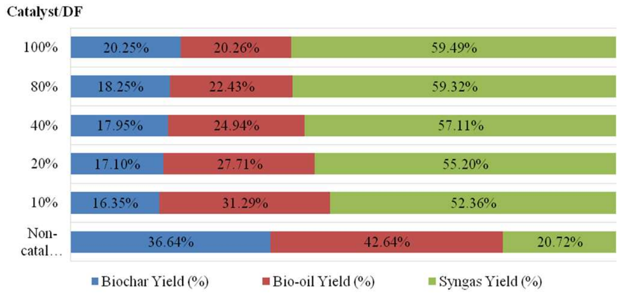

Figure 2. Yield distribution of catalytic pyrolysis of Douglas fir pellets with different loading of biochar catalysts.

In this study, the average heating rate observed was about 100 °C/min. The highest bio-oil (42.64 wt.%) and biochar (36.64 wt.%) yields were achieved in the non-catalytic run. The use of biochar catalysts led to a decrease in the bio-oil and biochar yields with a simultaneous increase in syngas yield. Depending on the loading of biochar catalysts, the bio-oil yield with catalysts addition was between 20.26 wt.% and 31.29 wt.% of biomass and the biochar yield with catalyst addition ranged from 16.35 wt.% to 20.25 wt.%. However, the syngas yields with catalyst addition were in the range of 52.36 wt.% to 59.49 wt.%, which were much higher than the results of non-catalytic runs (20.72 wt.%).

A similar phenomenon was found and reported by other studies as well.[20–22] It may be related to two factors. One is that some catalysts may increase the heating rate and temperature. The other is that some catalysts may actually promote biomass thermal decomposition. Graphite and char have been used and reported as microwave absorbers in pyrolysis of biomass.[22]In this study, the biochar catalyst used in biomass microwave pyrolysis has both functions. As a good microwave absorber, the temperature of biochar catalyst is much higher than the surrounding solids and gases during microwave heating, which creates heated areas called "hot spots". As a result, the target catalytic and pyrolysis temperatures can be obtained in the reactor, where biomass decomposition and bio-oil secondary cracking reactions can occur smoothly.[22,24]

According to Figure 2, the loading ratio of biochar catalysts to feedstock significantly influenced the product yields. The biochar catalysts favored syngas production. The bio-oil yield decreased significantly with the increase of the loading ratio of catalysts to feedstock, while the syngas yield and biochar yield slightly increased. This could be explained by the catalytic cracking of biomass and bio-oil secondary cracking reactions due to the higher temperature by using biochar catalyst in microwave-assisted pyrolysis.

GC/MS analysis of the bio-oils

In order to further understand the chemical reaction of catalytic biomass pyrolysis, the bio-oils were analyzed by GC/MS. In addition, the water content of attained bio-oils was in the range of 30~40 wt.%, which were calculated by the mass difference before and after organic compounds extraction from bio-oils by using an organic solvent. The obtained water in bio-oils mainly came from catalytic pyrolysis reactions and moisture in the original feedstock. The identified organic compounds were classified into 10 groups: acids, ketone/aldehydes, esters, alcohols, hydrocarbons, phenols, guaiacols, furans, sugars and others. The chemical composition of bio-oils by GC-MS analysis was categorized and depicted according to the differences of functional groups as shown in Figure3, which indicates that the chemical composition of bio-oils was greatly influenced by the addition of biochar catalyst and its loading ratio.

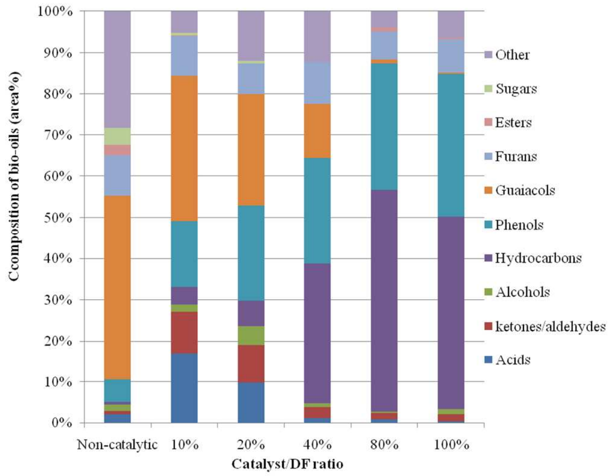

Figure 3. Chemical composition of bio-oils produced from different biochar catalysts loading by GC-MS analysis.

The raw bio-oil from the non-catalytic microwave pyrolysis has a very high content of guaiacols, plus a certain amount of furans, phenols, acids, sugars and other unclassified compounds. Guaiacols and acids are considered undesirable, especially for liquid transportation fuel production purposes. Highly oxygenated compounds like guaiacols, esters, and ethers reduce the heating value of the bio-oil and make it chemically unstable. The organic acids are corrosive and make the bio-oils difficult to use in engines.[4] Acids catalyze polymerization reactions and their presence further decrease the stability of bio-oils.[25] Hence, upgrading is necessary for a more stable and energy-intensive liquid product.

As seen in Figure 3, a much higher content of hydrocarbons and phenols were detected in the bio-oils from in-situ catalytic microwave pyrolysis of biomass with biochar catalyst. However, in our previous research, only a few hydrocarbons were reported in Douglas fir pellets microwave assisted pyrolysis without catalyst or with activated carbon (AC).[26,27] The presence of hydrocarbons (including aromatic hydrocarbons and aliphatic hydrocarbons) is highly desirable for liquid transportation fuel production. Phenols are high value-added chemicals which can be used for phenol formaldehyde resin production. These compounds can help the pyrolysis process become more economically attractive.

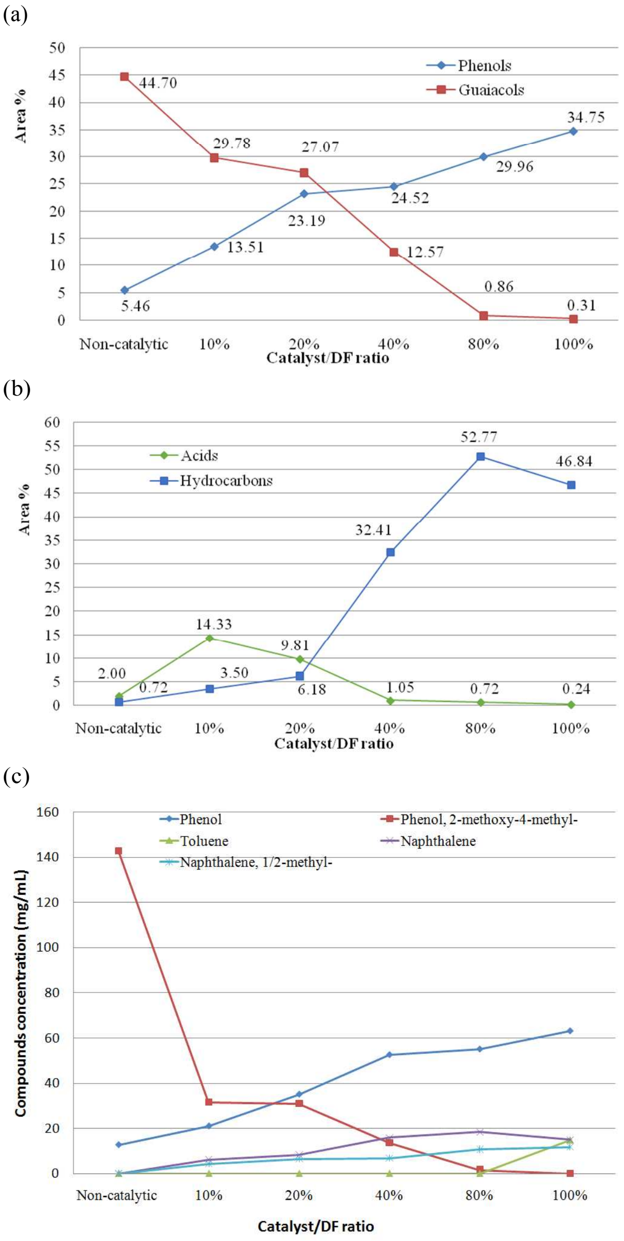

Figure 4. The effect of different biochar catalyst loadings on bio-oil composition: (a) Phenols and Guaiacols; (b) Acids and Hydrocarbons; (c) The concentrations of phenol, phenol,2-methoxy-4-methyl-, toluene, naphthalene, and naphthalene,1/2-methyl-.

More experiments were conducted on Douglas fir pellets using biochar catalyst at different loadings. The results of main chemical compounds of bio-oils from in situ catalytic microwave pyrolysis of biomass are shown in Table 4 and Figure 4. A gradual increase in phenols and a decrease in guaiacols was noticed. It was observed that the main components of the phenols were phenol, 2-methyl-phenol (o-cresol), 4-methyl-phenol (p-cresol), and the main components of guaiacols were 2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 4-ethyl-2-methoxy-phenol, 2-methoxy-4-vinylphenol and 2-methoxy-4-(1-propenyl)-phenol. Figure 4 (a) shows that the phenols were about 5.46 to 34.75% and gradually increased with the amount of the biochar catalyst loading in the catalytic microwave pyrolysis compared to the raw bio-oil from non-catalytic pyrolysis. The maximum phenol yield of 34.75% (including 11.89% phenol, 5.01% o-cresol and 10.16% p-cresol) was obtained with the catalyst-to-biomass ratio of 100%. However, the guaiacol content decreased dramatically with increases in catalyst loading ratios.

For catalyst-to-biomass ratios of 80% and 100%, the guaiacol contents are only 0.86 and 0.31%, respectively, indicating that most guaiacols were converted to phenols and hydrocarbons via cracking and hydrogenolysis reactions. However, the content of phenols and guaiacols for the raw bio-oil from non-catalytic pyrolysis was 5.46 and 44.70%, respectively. Therefore, the results revealed that the biochar catalyst used in the Douglas fir pellets microwave catalytic pyrolysis act selectively towards the hydrogenolysis of the oxygen-aromatic bonds of methoxyl or hydroxyl functions. Table 4 shows that the primary hydrocarbons from the in-situ microwave catalytic pyrolysis with biochar catalyst addition are aromatics, which mainly include indene, naphthalene, biphenyl and fluorine compounds. The typical results of hydrocarbon selectivity versus biochar catalyst loadings are shown in Figure 4 (b). The yield of hydrocarbons increased significantly from 0.72 to 52.77%. Increases in the catalyst-to-biomass ratio resulted in an increase of hydrocarbon yield for microwave catalytic pyrolysis of Douglas fir pellets. However, when the catalyst-to-biomass ratio increased to 100%, the hydrocarbon content decreased slightly. The maximum hydrocarbon yield of 52.77% (including 12.84% naphthalene, 7.92% indene, and 7.40% methylnaphthalene) was obtained with the catalyst-to-biomass ratio of 80%. At a higher catalyst-to-biomass ratio, xylene and toluene are gradually produced, whereas the yield of indene, naphthalene and biphenyl are decreased. This result can be explained in terms of the biochar catalyst hydrogenation of biphenyl and naphthalene, respectively, using hydrogen generated in situ.

At low levels of biochar catalyst loading, the results showed either a sudden increase in the appearance of acids, ketones, and aldehydes, which were higher than in the original bio-oil from non-catalytic pyrolysis. A possible explanation for these atypical results is that for low catalyst loading, the bio-oil cracking process and secondary reactions are not fully complete, leading to a high yield of acid compounds. And, when the catalyst-to-biomass ratio is higher than 40%, the acid amount is decreased dramatically.

The concentrations of the typical compounds (phenol, phenol,2-methoxy-4-methyl-, toluene, naphthalene, and naphthalene,1/2-n) were also quantified by GC/MS, which were depicted in Figure 4 (c) with the respect of different catalyst loading ratios. It can be seen that the concentration of phenol,2-methoxy-4-methyl- decreased gradually with the increasing catalyst/DF ratio from 142.97 mg/mL without a catalyst to 0.0 mg/mL with the catalyst/DF being 100%. The decreased phenol,2-methoxy-4-methyl- was proposed to undergo deoxygenation and demethylation reactions induced by biochar catalysts during catalytic processes, which was evidenced by the increase of concentration in phenol production. For the concentration of phenol, the maximum was 63.14 mg/mL with the catalyst/DF ratio of 100%. The concentration of aromatic hydrocarbons, such as naphthalene and naphthalene,1/2-n also increased gradually with more catalyst applied. Both of them were not detected in the bio-oil obtained in the absence of a catalyst, whereas these compounds were generated by using the biochar catalyst and the highest concentration of naphthalene and naphthalene,1/2-n were 18.48 and 11.76 mg/mL with catalyst loading ratio of 80% and 100%, respectively. It was worthy to notice that a slight drop in concentration of naphthalene was observed by increasing catalyst/DF ratio from 80 to 100%, which can be ascribed to the further decomposition caused by additional catalyst loading. On the other hand, with enough catalyst loading ratio, toluene was detected and the concentration of that was 14.92 mg/mL at the catalyst/DF ratio of 100%.

These results indicated that the loading amount of biochar catalyst is a significant factor affecting the bio-oil composition and hydrocarbon production, which also indicate that the bio-oil chemical profiles can be altered by adjusting the loading of catalysts, suggesting that it is possible to target specific desired products by controlling the loading. The obtained valuable phenols in upgraded bio-oil by using bio-char catalyst could be applied in various industrial processes such as the production of plastics, phenol resins, caprolactam, and even pharmaceutical drugs.[28] Additionally, aromatics e.g. toluene, indene, and naphthalene are jet-fuel range hydrocarbons, which can be used directly or undergo further hydrogenation to cycloalkanes for aviation fuels.[29, 30] Currently, zeolite-based catalysts are regarded as promising catalysts for hydrocarbons production from raw biomass and up to 24.68% carbon yield of aromatics could be obtained, which dominated by mono-ring and double-ring[30, 31] The bio-char catalyst used here also showed comparable catalytic performance in hydrocarbons generation. In addition, the bio-char catalysts are produced economically and environment-friendly. Besides, various modifications are accessible with facile methods to fully release its potential as promising alternative catalysts in the bio-oil upgrading. Therefore, in this study, biochar catalyst exhibited a high selectivity towards hydrocarbons and phenols, which offered a promising route to generate better-quality bio-oils for fuel production.

Table 4. Main chemical compounds of bio-oils from microwave pyrolysis of biomass using different biochar catalysts loadings.

Categories	*Compounds Name*	*Retention Time(min)*	*Non-catalytic (%)*	*Cat/DF 10% (%)*	*Cat/DF 20% (%)*	*Cat/DF 40% (%)*	*Cat/DF 80% (%)*	*Cat/DF 100% (%)*
Furans	Furfural	6.43	4.98	4.06	4.97	5.31	2.51	1.38
	Furan, tetrahydro-2,5-dimethoxy-	7.69	3.47	0.48	0.27	~	~	~
	Benzofuran	11.31	~	0.31	1.07	2.29	2.98	3.46
	Benzofuran, 2-methyl-	14.85	~	~	~	0.27	1.14	1.20
	Dibenzofuran	26.23	~	0.31	0.31	0.58	1.13	1.04
	Dibenzofuran, 4-methyl-	29.10	~	~	~	0.40	0.38	0.40
	Other furan compounds		1.44	2.98	0.79	1.10	1.32	0.87
	Total		9.80	8.14	7.41	9.55	9.08	7.95
Phenols	Phenol	10.82	1.68	4.25	6.23	8.03	12.97	11.89
	Phenol, 2-methyl-	13.12	0.97	1.58	2.88	3.24	4.85	5.01
	Phenol, 4-methyl-	13.81	~	2.25	5.80	6.04	8.63	10.16
	Phenol, 2/3/4-ethyl-	14.81/16.58	~	0.65	1.04	1.72	2.23	0.20
	Phenol, 2,3/4/6-dimethyl-	14.82/16.89	0.89	2.28	3.02	3.07	0.20	4.19
	Phenol, 3,4/5-dimethyl-	16.70/17.41	~	0.67	0.52	0.32	0.15	2.11
	Phenol, 2/3-ethyl-4/5-methyl-	18.66/16.67	~	~	~	0.59	0.30	0.52
	Other phenol compounds		1.92	1.83	3.70	1.51	0.11	0.67
	Total		5.46	13.51	23.19	24.52	29.96	34.75
Guaiacols	Phenol, 2-methoxy-	14.15	5.32	4.19	3.98	2.64	~	~
	Phenol, 2-methoxy-4-methyl-	17.29	14.03	10.03	7.43	~	~	~
	1,2-Benzenediol	17.50	3.67	0.97	1.68	0.55	~	~
	1,2-Benzenediol, 4-methyl-	19.37	0.93	1.23	1.98	~	~	~
	Phenol, 4-ethyl-2-methoxy-	19.72	4.98	2.30	2.25	1.50	0.45	0.31
	2-Methoxy-4-vinylphenol	20.76	5.93	3.69	4.13	3.94	~	~
	Phenol, 2-methoxy-4-(1-propenyl)-	23.27	9.10	5.85	4.87	2.55	~	~
	Other guaiacols compounds		0.74	1.52	0.75	1.39	0.41	~
	Total		44.70	29.78	27.07	12.57	0.86	0.31
Hydrocarbons	Toluene	4.30	~	~	~	~	0.69	2.94
	p-Xylene	7.42	~	~	~	~	0.28	0.67
	Styrene	8.06	~	~	~	~	1.46	3.63
	Indene	12.83	0.11	0.37	1.40	5.40	7.92	5.95
	Undecane	14.56	~	1.41	1.28	1.43	1.00	1.13
	Naphthalene	17.20	~	~	~	10.69	12.84	7.66
	Naphthalene, 1,2-dihydro-3-methy-	19.54	~	~	~	~	0.20	0.23
	Naphthalene, 1-methyl-	20.40	~	~	~	2.33	3.83	3.52
	Naphthalene, 2-methyl-	20.82	0.21	0.43	0.62	1.04	3.57	3.06
	Naphthalene, 1-ethyl-	23.07	~	~	~	0.22	0.42	0.46
	Naphthalene, 1,3/6/7-dimethyl-	23.37/24.24	~	~	~	0.17	0.98	0.66
	Naphthalene, 2,3/6-dimethyl-	23.82/24.24	0.12	0.18	0.24	0.40	0.65	1.06
	Naphthalene, 2-ethenyl-	24.03	~	~	~	0.74	0.84	0.67
	Naphthalene, 1,4,5/6-trimethyl-	25.93/26.57	~	~	~	~	0.10	0.22
	Biphenyl	22.68	~	~	0.36	0.56	0.78	0.69
	Acenaphthylene	24.50	~	~	~	1.05	3.69	0.25
	Biphenylene	24.51	~	~	~	~	0.02	2.88
	Acenaphthene	25.36	~	~	~	0.68	0.79	0.76
	1,1'-Biphenyl, 3-methyl-	25.67	~	~	~	0.13	0.79	0.74
	Fluorene	27.85	0.16	0.44	0.44	2.41	3.18	2.58
	9H-Fluorene, 4/2/1-methyl-	30.59	0.02	0.12	0.19	0.88	1.22	1.24

Anthracene	32.46	~	~	~	1.51	2.25	2.26
Phenanthrene	32.72	~	~	0.34	1.27	1.10	0.56
Anthracene, 1-methyl-	35.13	~	~	~	0.10	0.16	0.21
Fluoranthene	38.63	~	~	0.07	0.10	0.72	0.52
Pyrene, 1-methyl-	41.97	~	~	0.04	0.40	0.51	0.62
Other hydrocarbon compounds		0.10	0.55	1.20	0.90	2.78	1.67
Total		0.72	3.50	6.18	32.41	52.77	46.84

Micro-GC analysis of non-condensable gas (NCG)

A Micro-GC was used for determining the quantitative NCG compound yields from the microwave catalytic pyrolysis of biomass. The Douglas fir pellet microwave pyrolysis and catalytic pyrolysis gas product distributions are shown in Figure 5. The NCG products from the microwave pyrolysis of biomass mainly contain CO_2, CO, H_2, CH_4, and some other hydrocarbons (<C4), such as C_2H_6, C_2H_4, C_3H_6, and C_3H_8. These results indicate that the NCG generated from the Douglas fir pellet catalytic pyrolysis has higher amounts of CO, H_2, CH_4 and short chain hydrocarbons except CO_2 when compared to non-catalytic runs. In previous research, smaller hydrogen yields (<1%) were observed in the biomass pyrolysis. This is because hydrogen is evolved out at a higher pyrolysis temperature and longer residence time.[9,24] However, in raw Douglas fir pellet microwave pyrolysis, about 22.64 vol% hydrogen was observed and a higher hydrogen yield (30.15 vol%) was obtained in the catalytic runs with biochar catalysts.

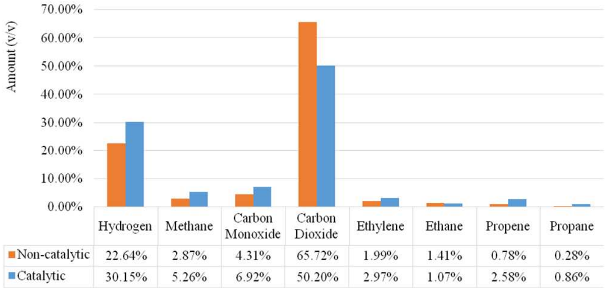

Figure5. Non-condensable gas products distribution from Douglas fir pellet pyrolysis and catalytic pyrolysis (catalyst-to-biomass ratio: 80%)

CO_2 and CH_4 mainly evolved at 400-600 °C. CH_4 can be formed from methoxyl function decomposition and ring hydrogenation. The higher yield of the H_2 and CH_4 can be attributed to the higher content of aromatic rings and O-CH_3 functional groups in the lignin-derived compounds. The H_2 from organics pyrolysis mainly comes from the cracking and deformation of aromatics (C=C and C-H) while the CH_4 mainly comes from the cracking of methoxyl.[32] Furthermore, at higher temperatures, the endothermic steam reforming reaction also contributes to a higher hydrogen production. The pyrolysis temperature in this study might not be high enough to promote the reforming reaction. However, the biochar catalyst derived from biochar is a good microwave absorber, and much higher temperatures in the solid matter could be reached due to the formation of hot spots caused by by microwave heating.[22,33] These results also suggested that the biochar catalyst derived from biochar favors hydrogen production, and furthermore, that endothermic reforming reaction might play a significant role during microwave in situ catalytic pyrolysis.

The Figure 5 results also indicated that Douglas fir pellet pyrolysis with biochar catalyst leads to a lower yield of CO_2 (50.20 vol%) compared to the 65.72 vol% obtained by raw Douglas fir pellet pyrolysis. These results are caused primarily by the secondary cracking of volatiles, followed by the increase of CO and hydrocarbons. A similar phenomenon was reported and analyzed in the catalytic pyrolysis over H-ZSM5.[34] The strong acid sites in H-ZSM5 catalyst have proven to be more active for decarbonylation to produce CO than decarboxylation to CO_2 from oxygenates during catalytic pyrolysis.[8]

As literature indicates that the surface functional groups anchored on/with carbon were found to be responsible for the variety of catalytic and physicochemical properties of the matter considered.[35] Hence, it is reasonable to speculate that the oxygen acidic sites on the surface of biochar catalyst promote the formation of CO by catalyzed decarbonylation and formation of aromatics.[36] The metal elements contained in the biochar catalyst might also enhance the secondary reaction. This indicates that oxygenates primarily went through decarbonylation other than decarboxylation to form reaction intermediates which subsequently were converted into aromatic hydrocarbons over the biochar catalyst.

Reaction mechanism analysis

The in-situ upgrading of biomass pyrolysis vapors over biochar catalyst was studied in the microwave assisted catalytic pyrolysis system. In general, the catalytic pyrolysis process goes through a series of pyrolysis reactions followed by catalytic conversion of biomass-derived oxygenates.[2]

Since the biochar catalysts were placed on the top of the Douglas fir pellets, the volatiles from biomass decomposition first passed through the biochar catalyst zone before condensing. The cracking and reforming of the volatiles might occur within this catalysis zone, which involves a series of the heterogeneous solid-gas reactions and gas-gas reactions. A reaction pathway was proposed by integrating the findings from the different catalyst to biomass loadings and the analysis of chemical profiles of bio-oils for in-situ microwave assisted catalytic pyrolysis of Douglas fir pellets. The reaction network of microwave assisted in-situ catalytic pyrolysis of lignocellulosic biomass is summarized in Figure 6.

Cellulose, hemicellulose, and lignin are the major components of biomass, which decompose at different temperatures. At low temperatures (200-400 °C), cellulose and hemicellulose decompose into small molecule compounds such as acids, ketones, aldehydes, sugars, and furans.[28, 37-38] With the effects of catalyst, anhydrosugars will undergo dehydration, decarbonylation or decarboxylation reactions to form smaller furanic compounds. Then the acid sites presented on biochar catalyst surface promote a series of decarbonylation and oligomerization reactions inside the pores of biochar catalyst, which further convert these furans to aromatic hydrocarbons and olefins.

However, lignin decomposes more slowly over a broader temperature range (200-500 °C) than cellulose and the hemicellulose components of biomass. It primarily generates guaiacols and phenolics compounds, which could also contribute to the production of aromatic hydrocarbons.[39, 40] One reaction pathway is the lignin and furans derived guaiacols cracking by the cleavage of methyl from O−CH_3 to phenols over biochar catalysts. This demethoxylation reaction of guaiacols can be verified by the increased presence of CH_4 in NCG. A further microwave specific mechanism must also be considered. Dominguez and Russell have observed, particular types of carbon "microplasmas" could be generated in the interaction of the electromagnetic microwave field, which creates charge imbalances.[41, 42] The pyrolysis vapors passing through this area will be cracked to a greater extent due to the considerably higher temperature of these microplasmas, compared to the surroundings.

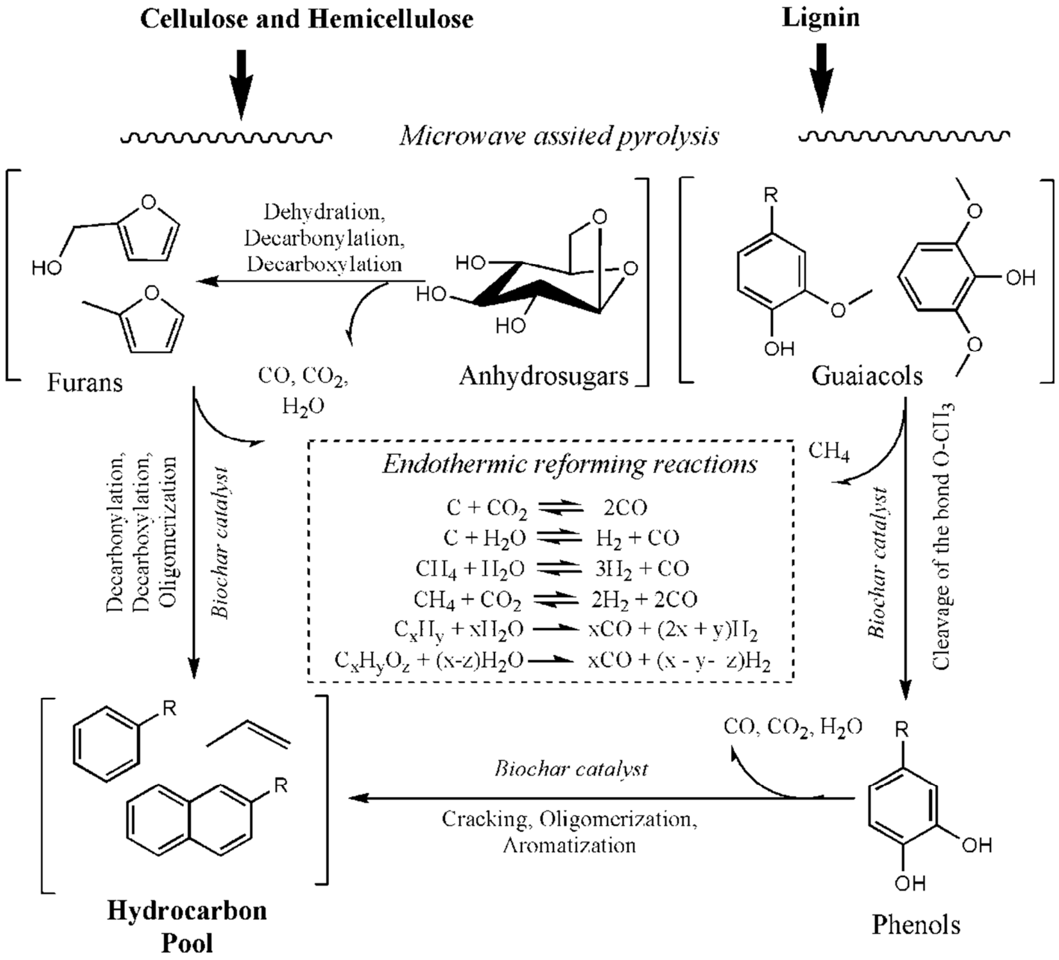

Figure6. Proposed reaction pathway for guaiacol and phenolic aromatics to hydrocarbons over biochar catalyst under microwave pyrolysis.

The high H_2 favored gas generated by endothermic reforming reactions promotes the deoxygenation reactions of the lignin-derived oxygenate during the in situ catalytic pyrolysis. The phenols could be further cracked to aromatic hydrocarbons by the cleavage of –OH. Olefins produced from alkyl-phenol cracking might be another intermediate for aromatic hydrocarbons production.[32] The biochar catalyst with high-energy surface functional groups (e.g. acidic sites) also contributes to the extra cracking and upgrading of pyrolysis oils.

The proposed pathway illustrated in Figure. 6 may also be confirmed by the GC/MS analysis of the chemical composition of bio-oils, This GC/MS analysis showed that the concentration of the small molecular compounds, such as acid, sugars, ketones, and aldehydes were all significantly decreased compared to the raw pyrolysis oils by conventional pyrolysis; while the production of aromatic hydrocarbons and phenols were significantly increased with the significant decrease of guaiacols content. The bio-oil chemical profile from microwave-assisted catalytic pyrolysis over biochar catalysts was simplified to phenols and hydrocarbons, and their concentrations were strengthened by the increase of ratios of biochar catalyst to biomass.

Conclusions

This study investigated the production of hydrocarbons from biomass through in-situ microwave-assisted catalytic pyrolysis with a biochar catalyst. High hydrocarbon concentrations (52.77%) of the bio-oil were obtained from catalytic pyrolysis over a biochar catalyst, as compared to 0.72% of the bio-oil from non-catalytic runs. The biochar catalyst deoxygenated the raw bio-oil and in situ upgrading occurred, resulting in a narrowly targeted hydrocarbon and phenol product, with a higher potential commercial value. The increased amounts of H_2 and CO observed in NCG from biomass catalytic pyrolysis also demonstrated the biochar catalyst selectivity towards hydrocarbons. A possible reaction pathway was proposed for this *in-situ* microwave assisted catalytic pyrolysis. The results indicated that the corn stover derived biochar catalyst might be a cost-competitive catalyst in fuels and chemicals production from biomass-derived feedstocks. Further studies are needed to investigate the effect of functional group sites on the carbon surface and catalyst regeneration, which could also help better understand the catalytic mechanism and optimize this biochar catalyst. The commercial application of lignocellulose biomass to hydrocarbons through in-situ microwave-assisted catalytic pyrolysis processes will depend on the development of technologies for hydrodeoxygenation and on the market price of the crude oil.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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For Table of Content Use Only:

Synopsis: A new route of phenols and hydrocarbons production through biomass microwave-induced pyrolysis over home-made biochar catalysts has been developed.

Content graphic: