Effects of reaction temperature, time and particle size on switchgrass microwave pyrolysis and reaction kinetics

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Abstract: This study investigated microwave pyrolysis of switchgrass with particle sizes from 0.5 mm to 4 mm and determined the effects of reaction temperature and time on the yields of bio-oil, syngas, and bio-char. A prediction model was satisfactorily developed to describe the bio-oil conversion yield as a function of reaction temperature and time. Second-order reaction kinetics was also developed to model the switchgrass pyrolysis. Switchgrass with different particle sizes was found to be similarly pyrolyzed by microwave heating. The research results indicated that thermochemical conversion reactions can take place rapidly in large-sized switchgrass by using microwave pyrolysis. GC-MS analysis indicates that the bio-oil contained a series of important and useful chemical compounds: phenols, aliphatic hydrocarbons, aromatic hydrocarbons, and furan derivatives. These chemical compounds evolved were related to the pyrolysis conditions.

Keywords: switchgrass, microwave pyrolysis, kinetics, bio-oil, syngas, bio-char

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1 Introduction

Switchgrass shows potential as a sustainable herbaceous energy crop from which a renewable source of transportation fuel and/or biomass-generated electricity could be derived[1]. The US Department of Energy’s Bioenegy Feedstock Development Program (BFDP) has chosen to focus on several primary herbaceous crops including switchgrass. The choice of switchgrass as a model bioenergy species was based on its high yields, high nutrient use efficiency, and wide geographic distribution. Other important considerations include its positive environmental attributes, its positive effects on soil quality and stability, its cover value for wildlife, and relatively low inputs of energy, water and agrochemicals required per unit of energy produced[2]. The energy that can be generated from switchgrass depends on concentration of energy primarily derived from cell walls and particularly from lignin and cellulose[3].

Thermochemical conversions of lignocellulosic biomass (i.e., combustion, pyrolysis, and gasification) are receiving increasing interest and utility as methods for production of renewable energy and fuels because they offer numerous advantages over biochemical-based transformation methods[4]. Microwave pyrolysis is one of the many ways converting biomass into higher value products such as bio-oil, syngas, biochar and chemicals. The key advantage of the microwave heating process over conventional heating method is the nature of fast internal

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heating by microwave irradiation. Microwave energy deposition in the dielectric loss mode of heating can cause spatially uniform heating. Biomass fast pyrolysis can be achieved by microwave radiation[5]. Increased process yield, environmental compatibility, savings in process time, and low requirements for space and capital equipment are among the advantages reported about microwave processing of materials.

Bio-oil as a clean fuel has several environmental advantages over fossil fuels. Bio-oils are CO_2/greenhouse gas (GHG) neutral. Therefore, they can generate CO_2 credits. No SOx emissions are generated because plant biomass contains insignificant amount of sulfur. Bio-oil based fuels generated lower NOx emissions than diesel oil in a gas turbine[6]. Renewable and locally available bio-oil can be produced in countries with large volumes of organic wastes[7-8]. Bio-oils from microwave pyrolysis of sewage sludge were reported to contain no harmful compounds such as heavy polycyclic aromatic hydrocarbons (PAHs), which were the case for bio-oils from conventional pyrolysis of the same feedstock[9]. Thus, bio-oils from microwave assisted pyrolysis are cleaner and cause less pollution.

Understanding the chemical composition of produced bio-oils is a key feature in determining potential uses and values of biomass resources. Pyrolysis bio-oils of the biomass constitute a viable source of more than 230 organic chemicals[10]. The knowledge of pyrolysis products can also facilitate the research on the cheap chemicals and char for the preparation of carbon molecular sieves[11].

The objectives of this study were to investigate microwave pyrolysis of switchgrass with variable particle sizes and determine the effects of pyrolytic conditions on the yields of bio-oil, syngas, and biochar. The relationship between product yield and pyrolysis conditions was established and presented using empirically developed models to predict product yields. GC-MS methods were employed in this investigation.

2 Materials and methods

2.1 Materials

Switchgrass was obtained from the Department of Plant Science, South Dakota State University. These biomasses were grounded (Speedy King, Winona Attrition Mill Co, MN, USA) to produce pieces with particles of 0.5 mm, 1 mm, 2 mm, 3 mm, and 4 mm. Grounded sample were dried in oven at 80℃ for 24 hours and kept in sealed plastic bags at room temperature (25℃) prior to microwave pyrolysis.

2.2 Microwave pyrolysis apparatus

A Sineo MAS-II batch microwave oven (Shanghai, China) with a rated power of 1 000 W was used to convert switchgrass to bio-oils at a 700 W power setting that gave a heating rate of about 70℃/min before desired temperature. After reaching desired reaction temperatures, the microwave reactor equipped with automatic temperature/power control used a minimum power (e.g. 0-100 W) to keep the desired reaction temperatures. 100 g biomass was fed into a 3-neck flask. One neck of the flask was connected to nitrogen that offered an oxygen-free environment during pyrolysis process. The second neck was connected with a set of condensers. During the process, volatiles were passed through a series of condensers filled with cold water where condensable volatiles were condensed as bio-oils while non-condensable volatiles escaped into the lab hood as syngas at the end of the condensers, where syngases were either burned or collected for analysis. The third neck of the flask was connected to a temperature sensor in order to investigate the effect of the pyrolysis temperatures. At the end of the experiments, the bio-oil fraction was collected from the condensers and weighed. The solid char was removed and weighed. Syngas yield was determined by overall material balance, as shown in Equation (1).

Weight of syngas = 100 g – weight of bio-oil – weight of bio-char (1)

2.3 Experimental design

This article was mainly focused on the yield of bio-oil and volatile (bio-oil+syngas). Three factors, pyrolysis temperature, residence time, and particle size were selected as independent variables. A central composite design (CCD) was performed according to the method of Liu et al[12]. The central values, step sizes, and ranges were as follows: central pyrolysis temperature of 600℃, step of 84℃, range of 516-684℃; central residence time of 13 min, step of 5 min, range of 4.6-21.4 min; and central particle size of 2 mm, step of 1 mm, range of 0.5-4 mm (Table 1). The experimental results were fitted using a polynomial quadratic equation in order to correlate the response variables to the independent variables.

Table 1 Experimental design and results for microwave pyrolysis of switchgrass

Std. ID	Pyrolysis temp/℃	Residence time/min	Particle size/mm	Bio-oil yield/%	Syngas yield/%	Volatile yield/%
1	550	8	1	24.1	33.4	57.5
2	650	8	1	27.3	31.9	59.2
3	550	18	1	27.7	43.2	70.9
4	650	18	1	33.7	39.3	73.0
5	550	8	3	16.9	20.3	37.2
6	650	8	3	31.8	35.5	67.3
7	550	18	3	19.5	26.2	45.7
8	650	18	3	36.3	39.8	76.1
9	516	13	2	15.4	21.1	36.5
10	684	13	2	33.4	43.0	76.4
11	600	4.6	2	13.4	16.0	29.4
12	600	21.4	2	30.1	45.0	75.1
13	600	13	0.5	28.0	49.0	77.0
14	600	13	4	21.2	30.0	51.2
15	600	13	2	27.3	31.0	58.3
16	600	13	2	27.3	30.1	69.9

2.4 GC-MS analysis

The bio-oil was analyzed by GC-MS using a Varian Star 3400 CX gas chromatograph coupled to a Varian Saturn 2000 detector. The gas chromatograph was equipped with a 10 m×0.25 mm ID, 0.5 μm film thickness RTX-5Sil MS capillary column (Restek, Bellefonte, PA, USA). Helium was used as a carrier gas at a constant flow rate of 1.2 mL/min. The initial temperature of oven was 45℃ held for 2 min and then programmed from 45℃ to 300℃ at 10℃/min with an isothermal hold for 10 min. The injector temperature was 300℃ and the injection size was 1 μL. The ion source temperature was 230℃ for the mass selective detector. The compounds were identified by comparing data with NIST98 Mass Spectral Library search.

2.5 Pyrolysis kinetics

A kinetic scheme to model thermal decomposition of biomass can be schematized as:

$$\text{Switch Grass} \rightarrow \text{Char} + \text{Volatiles} \tag{2}$$

where the reaction rate is a function of the remaining raw material and follows an Arrhenius law dependent on temperature[13-15].

The rate of decomposition can be expressed by Equation (3):

$$\frac{d_\alpha}{d_t} = A\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{3}$$

where, A is frequency or pre-exponential factor of the pyrolysis process (s-1); E is apparent activation energy (J/mol); T is temperature (K); R is universal gas constant, 8.3145 J/(mol·K); n is the order of reaction, and t is time (s).

The fractional reaction α is defined in terms of the change in mass of the switchgrass sample:

$$\alpha = \frac{X_0 - X}{X_0 - X_f} \tag{4}$$

where, X_0 is the initial weight; X is the actual weight, and X_f is the final weight.

The Coasts-Redfern method was used to solve Equation (3) to determine the values of the kinetic parameters.

2.6 Coats- Redfern method

For a constant heating rate β (β=dT/dt), Equation (3) can be expressed as

$$\frac{d_\alpha}{d_T} = \frac{A}{\beta} e^{-\frac{E}{RT}}(1-\alpha)^n \tag{5}$$

Equation (5) can be rearranged and integrated as

$$\int_0^\alpha \frac{d_\alpha}{(1-\alpha)^n} = \frac{A}{\beta}\int_0^T e^{-E/RT} dT \tag{6}$$

Integrating $\frac{1}{(1-\alpha)^n}$ and $e^{-E/RT}$ in Equation (6), following expression can be obtained:

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{\beta E} e^{-\frac{E}{RT}}\left(1-\frac{2RT}{E}\right) \tag{7}$$

Transforming Equation (7) into a logarithmic expression:

$$\ln\left(\frac{1}{T^2}\cdot\frac{1-(1-\alpha)^{1-n}}{1-n}\right) = \ln\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right) - \frac{E}{R}\cdot\frac{1}{T} \tag{8}$$

Assuming $1-\frac{2RT}{E} \approx 1$, Equation (8) becomes Equation (9) when $n \neq 1$ and Equation (10) when $n = 1$:

$$\ln\left(\frac{1}{T^2}\cdot\frac{1-(1-\alpha)^{1-n}}{1-n}\right)=\ln\frac{AR}{\beta E}-\frac{E}{R}\cdot\frac{1}{T}\qquad n\neq 1 \tag{9}$$

$$\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right)=\ln\frac{AR}{\beta E}-\frac{E}{R}\cdot\frac{1}{T}\qquad n=1 \tag{10}$$

Thus, a plot of $\ln\left(\frac{1}{T^2}\cdot\frac{1-(1-\alpha)^{1-n}}{1-n}\right)$ versus $\frac{1}{T}$ when $n\neq 1$ or $\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right)$ versus $\frac{1}{T}$ when $n = 1$ should result in a straight line with slope $= -\frac{E}{R}$ and intercept $= \ln\frac{AR}{\beta E}$.

3 Results and discussion

3.1 Effects of reaction temperature, residence time and particle size on yield of bio-oil and volatiles

The experimental volatile, syngas, and bio-oil yields are given in Table 1. The yield range of volatiles was found from 29.4% to 77.0% varied with different pyrolysis conditions. Bio-oil yield was from 13.4% to 36.3% and syngas yield was from 16% to 49.0%.

The most important physical factors which affected volatile production were the reaction time and temperature. The suitable levels for these parameters were also determined using statistical CCD. The experimental design matrix is given in Table 1. 16 experiments were performed using different combinations of the variables as per the CCD. Using the results of the experiments the following second order polynomial equation giving the volatile and bio-oil yields as a function of reaction temperature (X_1, ℃), reaction time (X_2, min), and particle size (X_3, mm) were obtained.

$$Y_{\text{Bio-oil}} = 2.40 + 0.07X_1 + 0.60X_2 + 0.06X_1X_3 \tag{11}$$

$$Y_{\text{Volatiles}} = 104.89 - 0.12X_1 + 3.56X_2 - 98.51X_3 + 7.09X_1X_3 \tag{12}$$

The corresponding analysis of variance (ANOVA) is presented in Tables 2 and 3. The full second-order multifactor regression equation model included interaction terms which were significant ($P < 0.05$). The Equations (11) and (12) were obtained by using backward statistical analysis with their significant terms ($P < 0.05$).

Table 2 Analysis of variance of regression equation for bio-oils

Item	Degrees of freedom	Sum of squares	Mean square	F statistic	Prob>F
Model	9	635.6	70.6	9.3	0.0009
Residual	10	76.2	7.6		
Cor total	19	711.8			
R^2=0.89					

Table 3 Analysis of variance of regression equation for volatiles

Item	Degrees of freedom	Sum of squares	Mean square	F statistic	Prob>F
Model	9	3350.6	372.3	11.1	0.0004
Residual	10	334.7	33.5		
Cor total	19	3685.2			
R^2=0.91					

The coefficients of determination (R^2) of Equations (11) and (12) were 0.89 and 0.91, respectively, which indicated that the reduced quadratic regression model can be used to explain the pyrolysis reaction, and the bio-oil and volatile variations were attributed to the independent variables of reaction time, reaction temperature, particle size, and their interaction. The small p-values (less than 0.05) confirmed that both reaction temperature and residence time significantly influenced the yields of both bio-oils and volatiles. Particle size was a significant factor ($P < 0.05$) on the yield of volatiles but not on the yield of bio-oils. The only significant interaction effect on the yields of bio-oil and volatiles was the one between reaction temperature and residence time.

3.2 Response surface analysis

Figure 1 illustrates a typical response surface for bio-oil production from switchgrass with a particle size of 2 mm. The bio-oil yield increased with the increase of reaction temperatures and residence time. Reaction temperatures showed a similar positive impact on the bio-oil yield as residence time. The maximum bio-oil yield of 36.3% was obtained at the reaction temperature of 650℃ and residence time of 18 min while the maximum volatiles yield of 77% was obtained at 600℃ and 13 min.

Equation (11) shows that the particle size of switchgrass is not a significant factor affecting the yield of bio-oils ($P > 0.05$). Thus the switchgrass with different particle sizes (from 0.5 mm to 4 mm) was found to be similarly pyrolyzed by microwave heating. At the same level of reaction temperature, the volatile yields were similar for all particle sizes. It was also noticed by the insignificant model terms ($P > 0.20$) of particle size and its interactions with other two process variables from Equation (11). It can be concluded that thermochemical reactions can take place rapidly in large-sized biomass materials by using microwave pyrolysis. This is a great advantage of microwave pyrolysis from a practical point of view as it does not require the expensive particle size reduction steps. Therefore, very fine feedstock grinding required by conventional pyrolysis is not necessary for microwave pyrolysis process, resulting in substantial energy savings.

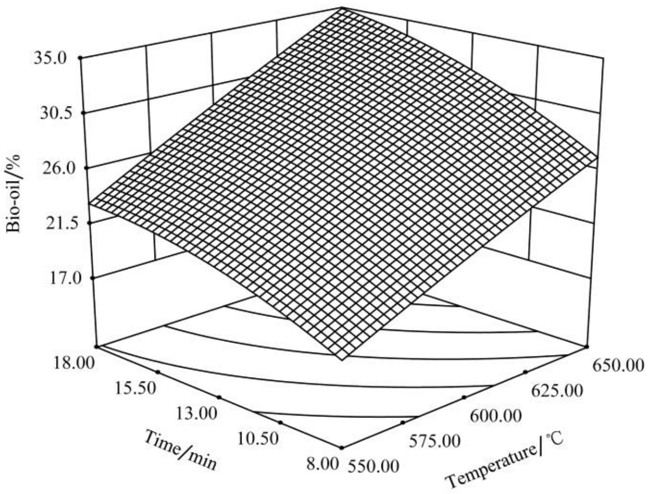
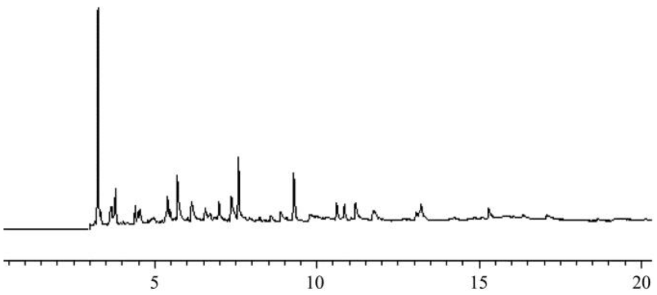


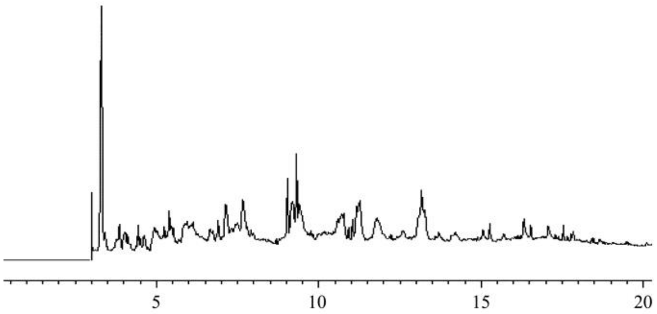
Figure 1 Response surface plot of bio-oil yield versus time and temperature with particle size of 2 mm

3.3 Determination of chemical compositions of bio-oil by GC-MS

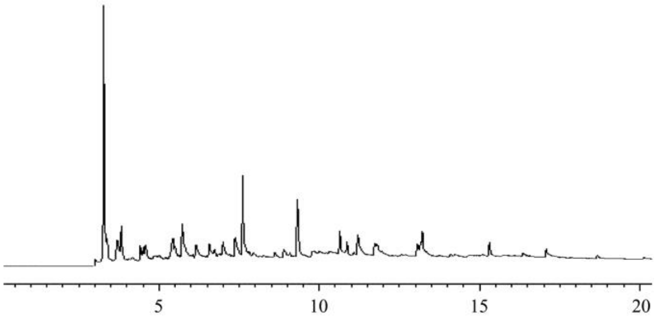
To further understand the chemical reactions from microwave pyrolysis, GC-MS analysis was carried out to determine the chemical composition of bio-oils. The bio-oil samples were prepared from the pyrolysis of switchgrass by microwave heating at 550℃ and 650℃ with different reaction time. Figure 2 shows the total chromatograms spectra of bio-oils with different pyrolysis conditions. The results of the chemical compositions of different bio-oils are shown in Table 4. The product peaks were assigned by automatic library search NIST98.



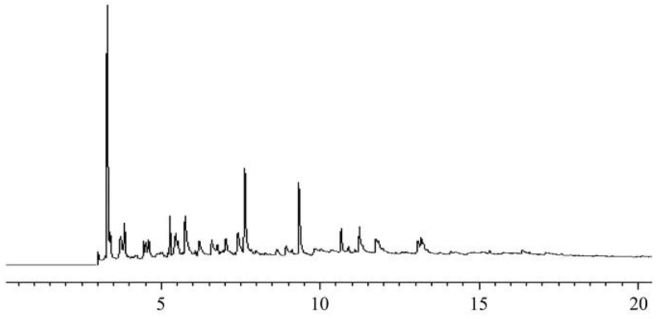
a. 550℃ and 8 min



b. 650℃ and 8 min



c. 550℃ and 18 min



d. 650℃ and 18 min

Figure 2 GC-MS profile for bio-oils from pyrolysis conditions (particle size = 2 mm)

According to Ateş and Iskdag[16], the most important point at investigating the similarity of bio-oils is the aliphatic compounds, i.e., alkanes and alkenes. Alkanes and alkenes presented in the bio-oils from switchgrass were about 5.7%-17.1%, depending on the pyrolysis conditions. Bio-oil was mainly composed of phenols, aliphatic hydrocarbons, aromatic hydrocarbons, furan derivatives, and some acids. Phenols presented in the bio-oil were about 22%-29% depending on the pyrolysis conditions, which were made up of phenol, diphenols, methyl phenols, ethyl phenols, and methoxy phenols. Carboxylic acids were determined in the oils as 3.5%-6.3%, thus the bio-oils showed an acidic structure.

Table 4 Chemical composition of bio-oils from microwave pyrolysis of switchgrass at different conditions

Time	Name	Formula	Run1[a]	Run2	Run3	Run4
3.002	Acetic acid, anhydride with formic acid	$C_3H_4O_3$	0.211	2.232	ND	ND
3.015	meso-5,6-Decanediol	$C_{10}H_{22}O_2$	ND	ND	ND	0.879
3.284	1,3-Methanopentalene, octahydro-	C_9H_{14}	ND	ND	17.936	ND
3.300	Cyclohexanol, 4-rthenyl-4-methyl-3-(1-methylethenyl)-, (1.alpha.,2.alpha.,4.beta.)-	$C_{12}H_{20}O$	ND	ND	ND	18.78
3.356	Oxacyclopentadec-6-en-2-one, (Z)-	$C_{14}H_{24}O_2$	21.584	20.375	ND	ND
3.371	2-Hydroxy-2-methyl-but-3-enthyl-2(Z)-butenoate	$C_{10}H_{16}O_3$	ND	ND	0.285	1.961
3.655	1-Cyclohexen-1-ol, acetate	$C_8H_{12}O_8$	2.682	ND	2.382	2.905
3.783	1,2,4,5-Tetroxane,3,3,6,6-tetramethyl	$C_6H_{12}O_4$	3.276	1.198	ND	ND
3.826	1,6;2,3-Dianhydro-4-O-acetyl-, beta,-d-talopyranose	$C_8H_{10}O_5$	ND	ND	2.492	3.031
4.169	Pentadienal, 2-methyl-	C_6H_8O	1.387	ND	ND	ND
4.419	Cyclopentene	C_5H_8	ND	ND	0.953	0.951
4.426	Acetic acid, anhydride with formic acid	$C_2H_8N_2$	ND	0.979	ND	ND
4.479	Cyclopropane, 2-(1,1-dimethyl-2-pentenyl)-	$C_{12}H_{22}$	0.891	ND	ND	1.446
4.494	Ethanone, 1-(2-furanyl)-	$C_6H_6O_2$	ND	0.642	0.892	ND
4.542	3-Hexene	C_6H_{12}	2.129	ND	ND	ND
4.574	3-Dodecen-1-ol, 12-[(tetragydro-2H-pyran-2-yl)oxy]-, (Z)-	$C_{17}H_{32}O_3$	ND	ND	2.041	ND
4.597	Lyratol	$C_{10}H_{16}O$	ND	ND	ND	2.194
4.965	cis-Bicyclo[5,1,0]octane	C_8H_{14}	ND	ND	0.286	0.967
5.241	Lyratol	$C_{10}H_{16}O$	ND	ND	0.129	ND
5.275	trans,trans-and trans,cis-1,10-Dimethylspiro[5,5]undecane	$C_{13}H_{24}$	ND	ND	ND	1.898
5.387	Pentane, 1-propoxy	$C_8H_{18}O$	3.146	ND	ND	ND
5.432	2-Furancarboxaldehyde, 5-methyl-	$C_6H_6O_2$	ND	ND	3.121	ND
5.449	2-Cyclopenten-1-one, 2-hydroxy	$C_5H_6O_2$	ND	ND	ND	3.452
5.468	3-Heptyne, 5-methyl-	C_8H_{14}	1.202	ND	1.719	ND
5.516	Lyratol	$C_{10}H_{16}O$	ND	0.545	ND	1.607
5.698	3-Penten-1-yne, (Z)-	C_5H_6	6.51	ND	ND	ND
5.834	Phenol	C_6H_6O	1.17	ND	5.22	5.464
6.132	Hexane, 2,2,3,4,5,5-hexamethyl-, (meso)-	$C_{12}H_{26}$	3.813	1.104	ND	ND
6.153	4-Octene, 2,2,3,7-tetramethyl-, [s-(E)]-	$C_{12}H_{24}$	ND	ND	2.509	ND
6.184	1,2,3-Cyclohexanetriol, (1.alpha.,2.alpha.,3.beta.)-(..)-	$C_6H_{12}O_3$	ND	ND	ND	2.367
6.545	2,3,3-Trimethyl-1-hexene	C_9H_{18}	1.974	ND	ND	ND
6.563	1-Cyclohexyl-1-(4-ethylcyclohexy)ethane	$C_{16}H_{30}$	ND	ND	1.899	ND
6.594	2-Ethyl-5-propylcyclopentanone	$C_{10}H_{18}O$	ND	ND	ND	1.958
6.708	1,6-Decadiene, 2,6,9-trimethyl, (E)-	$C_{13}H_{24}$	0.984	ND	ND	ND
6.737	Lyratol	$C_{10}H_{16}O$	ND	ND	1.147	1.033
6.889	Indene	C_9H_8	0.404	0.927	ND	ND
6.910	4-Methyl-2-hydroxycyclopent-2-en-1-one	$C_6H_8O_2$	ND	ND	1.079	0.148
6.974	3-Penten-1-yne, 3-methyl- 80	C_6H_8	1.761	ND	ND	ND
7.154	Phenol, 2-methyl-	C_7H_8O	ND	4.24	2.254	1.31
7.516	Phenol, 4-methyl-	C_7H_8O	4.9	0.979	3.219	3.66
7.772	Mequinol	$C_7H_8O_2$	6.741	7.056	6.895	9.141
7.911	Benzofuran, 7-methyl-	C_9H_8O	ND	0.994	0.4	ND
8.582	1,4-Cyclohexadiene, 1-methyl-	C_7H_{10}	0.923	ND	ND	ND
8.825	Phenol, 2-ethyl-	$C_8H_{10}O$	2.251	ND	ND	ND
8.895	Phenol, 4-ethyl-	$C_8H_{10}O$	0.570	ND	1.11	1.525
9.035	1H-Indene, 1-methylene-	$C_{10}H_8$	ND	6.148	ND	ND
9.286	(-)-Methyl norcaryl ketone	$C_9H_{14}O$	4.977	8.329	5.796	6.936

Time	Name	Formula	Run1[a]	Run2	Run3	Run4
9.315	1H-Indene, 1-methylene-	$C_{10}H_8$	ND	5.648	ND	ND
9.869	Benzaldehyde, 4-methyl-	C_8H_8O	1.569	ND	0.831	1.283
9.974	trans-Chrysanthenol	$C_{10}H_{16}O$	1.066	ND	ND	ND
10.020	2-Propenoic acid, 3-(1-cyclopenten-1-yl)-, methyl ester,(E)-	$C_9H_{12}O_2$	ND	ND	ND	1.712
10.290	2,6-Dimehtyl-3,7,9-trioxabicyclo[4,2,1]nonane	$C_8H_{14}O_3$	0.095	ND	ND	1.035
10.82	Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	1.727	ND	1.643	2.293
10.867	Fluoren-9-ol, 3,6-dimethoxy-9-(2-phenylethynyl)-	$C_{23}H_{18}O_3$	ND	ND	0.832	0.681
11.037	4H-1-Benzopyan-4-one, 3-(3,4-dimethoxnyl)-6,7-dimethoxy	$C_{19}H_{18}O_6$	1.661	ND	ND	ND
11.042	1H-Indene, 1-ethylidene	$C_{11}H_{10}$	ND	0.993	ND	0.249
11.383	2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	3.069	1.098	1.934	2.788
11.731	Phenol, 3,4-dimethoxy-	$C_8H_{10}O_3$	2.088	ND	0.966	1.294
11.918	Phenol, 2,6-dimethoxy-	C8H10O3	ND	ND	0.938	1.153
12.477	Naphthalene, 2-ethenyl-	$C_{12}H_{10}$	ND	8.912	ND	ND
12.814	1-Phenyl-1-(2-oxocyclopentyl)-propan-2-o	$C_{14}H_{16}O_2$	ND	1.863	ND	ND
13.053	3-Hydroxy-4-methoxybenzoic acid	$C_8H_8O_4$	1.261	ND	ND	1.448
13.164	Phenol, 2-methoxy-4-(1-propenyl)-	$C_{10}H_{12}O_2$	0.903	ND	ND	1.095
13.209	Coumaran-3-one, 6-methoxy-2-[4-methoxybenzylidene]-	$C_{17}H_{14}O_4$	2.421	ND	ND	ND
13.225	3-Hydroxy-4-methoxybenzoic acid	$C_8H_8O_4$	ND	ND	1.296	ND
13.243	1,4-Benzenedicarboxylic acid, bis(4-butylphenyl) ester	$C_{28}H_{30}O_4$	ND	ND	ND	0.825
13.306	Phenol, 2-methoxy-4-(1-propenyl)-	$C_{10}H_{12}O_2$	ND	ND	0.817	ND
13.700	Undecane, 3,4-dimethyl-	$C_{13}H_{28}$	ND	0.893	ND	0.094
13.735	Acenaphthene	$C_{12}H_{10}$	ND	0.49	ND	ND
14.097	Benzene, 1,1'-ethylidenebis-	$C_{14}H_{14}$	0.147	ND	0.204	0.424
14.259	Homovanillyl alcohol	$C_9H_{12}O_3$	ND	ND	ND	0.809
15.067	1H-Phenalene	$C_{13}H_{10}$	ND	0.861	ND	ND
15.473	Benzoic acid, 2,4-bis[(trimethylsilyl)oxy]-, trimethylsilyi ester	$C_{16}H_{30}O_4Si_3$	1.545	1.531	1.136	0.308
16.126	3-Hexene, 2,2,3,4,5,5,-hexamethyl, (E)-	$C_{12}H_{24}$	ND	0.97	ND	ND
16.502	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	$C_{11}H_{14}O_3$	0.541	2.442	0.318	ND
17.064	Benzoic acid, 2,4-bis[(trimethylsilyl)oxy]-,trimethylsilyi ester	$C_{16}H_{30}O_4Si_3$	ND	1.061	0.672	ND
17.272	2,4(1H,3H)-Quinolinedione, 3-benzoyl-3-(	$C_{23}H_{17}NO_3$	1.107	1.006	ND	ND

Note: [a]Run1: 550℃ and 8 min; run2: 550℃ and 18 min; run3: 650℃ and 8 min; run4: 650℃ and 18 min; ND: Not detectable.

3.4 Carbon number distribution

Figure 3 shows the carbon number distributions for bio-oil samples prepared from the pyrolysis of switchgrass by microwave heating at 550℃ and 650℃ with different reaction time. The analysis of chromatograms and carbon number distribution confirmed that the chemical composition of bio-oils was temperature and time dependent. It was noted that the range of carbon sizes run from C3 to C20, with the most prevalent sizes, C5, C6, C7, C8, C9, C12 and C14. At the pyrolysis condition of 550℃ and 18 min, the phenol and its derivatives represented only 22.3% of the bio-oil, whereas the phenol and its derivatives increased to 26.6% at 550℃ for 18 min, 23.4% at 650℃ for 8 min, and 28.8% at 650℃ for 18 min. Phenols derived from bio-oil have been looked at as a potential substitute for petroleum-based phenols[17], which are quite expensive.

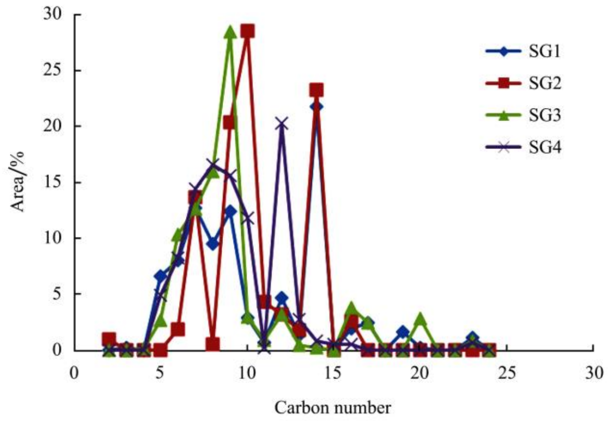


Figure 3 Carbon number distribution for bio-oils (particle size = 2 mm). SG1: 550℃ and 8 min, SG2: 650℃ and 8 min, SG3: 550℃ and 18 min, and SG4: 650℃ and 18 min.

3.5 Kinetic evaluation

Switchgrass is mainly comprised of cellulose, hemicellulose, and lignin. Switchgrass is a complex solid which released volatiles during pyrolysis. Products of microwave pyrolysis were obtained in three fractions, bio-char, bio-oil, and syngas from which proportions depended on the process conditions. Parameters like temperature and residence time influenced the products through the kinetics of the reaction; therefore knowledge of the kinetics is a key factor to predict product yields. Using data from the study, the kinetic parameters including activation energy (E) and frequency factor (A) were estimated and listed in Table 5. As can be seen in Table 5, a second-order reaction mechanism fitted well the microwave pyrolysis of switchgrass with R^2 = 0.96. A constant heating rate was used with activation energy around 14.25 kJ/mol for switchgrass and a frequency factor of 2.55 per second. The model gives a good approximation of the temperature range where the reaction takes place at the constant heating rate of pyrolysis process. The good fit of the pyrolysis path was carried out depending on the temperature and time. Regarding to the evolution of the total volatiles with temperature and heating rate, the model is able to describe properly the experimental data.

Table 5 Details of experiment design and results of microwave pyrolysis process

Raw materials	Reaction order	Activation energy E/(kJ mol^{-1})	Frequency factor A/s^{-1}	R^2
switchgrass	n=1	4.02	3.64	0.86
	n=2	14.25	2.55	0.96
	n=3	32.90	56396	0.87

4 Conclusions

In this research, microwave-assisted pyrolysis of switchgrass was performed under various conditions. The pyrolysis process variables included reaction temperature (515-685℃), residence time (4-22 min), and particle size (0.5-4 mm). The maximum yield was 36.3% for bio-oils, 76.1% for volatiles, and 23.9% for bio-char. These maximum occurred at a reaction temperature of 650℃, residence time of 18 min, and particle size of 3 mm. Reaction temperature and residence time were observed to be significant factors affecting the production of bio-oils. The effect of particle size was found to be insignificant on the pyrolysis of switchgrass for bio-oil production. The research results indicate that thermochemical conversion reactions can take place rapidly in large-sized biomass materials. Very fine feedstock grinding required by conventional pyrolysis is not necessary for microwave pyrolysis process, resulting in substantial energy savings. The pyrolysis oils were found from GC-MS to be composed of phenols, aliphatic hydrocarbons, aromatic hydrocarbons, and furan derivatives. The range of carbon sizes run from C3 to C20, with the most prevalent sizes are C5, C6, C7, C8, C9, C12 and C14. The composition of bio-oils was related to pyrolysis conditions.

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