

Investigation of microwave-assisted pyrolysis of biomass with char in a rectangular waveguide applicator with built-in phase-shifting

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ABSTRACT

Fast biomass pyrolysis is a promising technique for thermochemical conversion of biomass into chemicals and biofuels (bio-oil and syngas). Microwave heating can increase process efficiency. The effect of microwave absorber and microwave power level are studied for their effect on pyrolysis process temperature, product yields, and product composition. A novel microwave system was designed with a continuous sliding short enabling phase shifting to mitigate standing wave effects in the low loss load. Pyrolysis experiments on pine sawdust were carried out at varying microwave input powers (600, 900, 1200, and 1500 W) and with varying amounts of biochar added to the feedstock (0, 10, and 20% by weight) in a 4×3 full factorial experimental design. Pine sawdust without the aid of microwave absorber failed to reach pyrolysis temperatures by dielectric heating, only reaching 200 °C even at 1500 W power. Pyrolysis yields were correlated to absorbed power rather than input power as temperature is more strongly correlated to absorbed power. Addition of biochar was found to have a significant effect on the absorbed powers and resulting pyrolysis temperatures, increasing temperatures 4 fold from 0% to 10% char, however, no significant difference was found when char mixture was increased from 10 to 20%. Yields of char decreased with increasing absorbed microwave power, while non-condensable gas increased, indicating increased thermal cracking to non-condensable gases with increasing process temperature. Water-free bio-oil yields were found to increase with absorbed power. The liquid product from microwave pyrolysis of pine sawdust is composed primarily of phenols, with little changes in yield at all absorbed powers. Carbonyl functional groups and furans decreased while polyaromatics increased with increasing absorbed power due to the increased decomposition of lignin. The greatest net energy yields were observed for pyrolysis run at 900 W applied microwave power and 20% char.

1. Introduction

Substitution of liquid biofuels for fossil fuels can help mitigate atmospheric CO₂, reduce dependence on foreign energy, and slow the depletion of petroleum reserves. Lignocellulosic biomass, composed of hemicellulose, cellulose, and lignin, can be converted into hydrocarbon products by thermochemical conversion processes, including combustion, pyrolysis, gasification, and liquefaction [1]. Of these, pyrolysis produces a liquid product that can be upgraded to biofuels and other valuable chemicals and does not require high processing pressures, as in liquefaction. In typical applications of pyrolysis, lignocellulosic biomass is heated in the absence of oxygen to 400–700 °C, at which biomass macromolecules (hemicellulose, cellulose, and lignin) depolymerize by thermochemical decomposition to produce biochar, bio-oil, and non-condensable gas. The specific conversion of biomass to pyrolysis products is dependent on a number of variables including feed-

stock composition, pyrolysis temperature, heating rate, and vapor residence time, among others [2,3]. Research efforts have focused on fast pyrolysis for maximizing liquid yields, characterized by rapid heating rates, carefully controlled pyrolysis temperature, short residence times, rapid char removal, and rapid pyrolysis vapor quenching [2,4].

Typically, pyrolysis temperatures are reached by conventional heating in which heat is transferred to the material by conduction and convection. Drawbacks of conventional heating include the need for small particle size to attain rapid heat and mass transfer, poor temperature control, as well as incurred heat losses to the reactor walls, fluidizing beds (sand), and the surroundings. These characteristics of conventional heating result in potentially high processing costs in large-scale systems due to the need for biomass pretreatment (i.e. milling) and reduced process efficiency, limiting industrial applications of conventional pyrolysis technology [5]. Microwave heating can help mitigate these costs as heat is generated directly within the material by both selective and volumetric heating, which reduces losses to the system. Mi-

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microwave pyrolysis may also obviate the need for biomass grinding as microwaves can penetrate large particle sizes, provided good coupling of microwave energy with the material exists, as well as an appropriate applicator configuration [6]. A review of scaled up microwave pyrolysis configurations can be found elsewhere [5].

Effective microwave heating is dependent on material dielectric properties, i.e. dielectric constant (ϵ') and dielectric loss factor (ϵ''), which describe the ability of materials to couple with an applied electric field. For microwave heating of low loss materials, addition of a microwave absorber is necessary to catalyze dielectric heating in the bulk material. A number of microwave absorbers have been reported in the literature for pyrolysis applications including carbonaceous materials [7,8], metal oxides [9,10], other inorganic additives [10,11] and ionic liquids [12]. Mixtures of char with biomass feedstocks were found to significantly increase the dielectric properties of the bulk mixture [13]. Char is conveniently produced as a byproduct of biomass pyrolysis, thus, it is a readily available as a feedstock additive. By the use of a microwave absorber mixed with the biomass feedstock, the absorber particles are selectively heated and the heat is transferred to neighboring particles resulting in bulk heating of the material. Once the process starts within the biomass particles, they partially convert to char and become good absorbers themselves. Homogeneous mixing of absorber with the feedstock is important to ensure uniform heating within the material.

The power absorbed (P_{abs}) by a unit volume of a dielectric load as heat is described theoretically by Eq. (1) [14]:

$$P_{abs} = 2\pi f \epsilon_0 \epsilon'' |E|^2 [W] \quad (1)$$

where f is microwave frequency (Hz), ϵ_0 is the permittivity of free space (8.854F/m), ϵ'' is the dielectric loss of the load, and E is the electric field intensity. Frequency and free space permittivity remain constant for a given system, however, as dielectric loss may change with temperature, the electric field (which is also dependent on dielectric properties) is extremely difficult to estimate due to the complex interaction of load parameters and applicator configuration. In some application, absorbed power can be grossly estimated calorifically based on measured temperature change of the load according to Eq. (2):

$$P_{abs} = \frac{V \times C_p \times \rho \times \Delta T}{t} [W] \quad (2)$$

where V , C_p , and ρ are the volume (m^3), specific heat ($J/kg \cdot K$), and density (kg/m^3) of the load, respectively, and ΔT is the average change in temperature of the load (in Kelvin) over time t of microwave irradiation (s). However, for many practical applications, the power absorption is more easily estimated as the difference between measured forward and reflected power, and is used as a parameter throughout this study.

Microwave-assisted pyrolysis is an emerging research area with applications in conversion of coal [15,16], plastics [17], biomass [18,19], as well as co-utilization of different feedstocks [20,21]. Many microwave-assisted pyrolysis studies have utilized multimode microwave cavities, which form randomly distributed standing wave patterns. For the purpose of laboratory-scale studies, a single mode microwave configuration is better suited as the electric field distribution is predictable, leading to greater experimental repeatability. In a scaled-up microwave process, single mode or multimode configuration may be used. A single mode applicator has the advantage of delivering greater power densities while a multimode applicator is capable of irradiating a larger volume than is possible with a single mode waveguide. Regardless of the configuration, standing waves occur resulting in non-uniform heating especially in low loss loads such as biomass. Improved heating uniformity can be achieved by various means, including mode stirrers, phase shifting, varying frequency, and constant sample movement (e.g. turntables and conveyor belts) [22]. For these reasons,

the present study utilizes a single mode (TE_{10}) waveguide applicator with continuous phase shifting by means of a sliding short to mitigate standing wave effects. A moving sliding short is applicable to both single mode and multimode microwave configurations and could be implemented in a scaled-up microwave system to continuously shift the phase of the electromagnetic field in the applicator and improve heating uniformity.

Phase shifting has been previously demonstrated to improve heating uniformity in waveguide applicators [23]; however to our knowledge this configuration has never been applied to the pyrolysis process. Ma et al simulated the electric field distributions during pyrolysis of raw sludge and attributed the standing wave effect to variability in pyrolysis efficiencies [24]. Further, in a review article on microwave biomass pyrolysis, the authors discuss the occurrence of standing waves leading to non-uniform heating [25]. In the present study, utilizing a continuously moving (1/2 wavelength oscillations) sliding short provides an innovative solution to microwave field non-uniformity in the waveguide applicator and improves overall heating uniformity.

To gain a better understanding of microwave pyrolysis parameters, the effect of residual pyrolysis char microwave absorber and microwave power level on the pyrolysis product yields and composition was studied here for the first time in this unique microwave reactor configuration. The knowledge of the combined effects of microwave absorber and microwave power could lead to processing insights for biomass microwave pyrolysis for enhanced production of biofuels and chemicals.

2. Materials and methods

2.1. Feedstock preparation

Biomass samples were prepared by shaving pine wood boards, grinding the shavings in a lab blender, and sieving the sawdust to a particle size distribution in the range of 0.5 to 2.5 mm. The particle size distribution mostly consists of particles between 1 and 2.5 mm (85%) with the remaining 15% of biomass less than 1 mm. If the biomass bed particles are too fine, gases could build up pressure in the bed and carry the biomass out of the tube. This size distribution consisting of larger particles was selected to ensure adequate mass flow through the reactor tube. Moisture content of the pine samples were determined gravimetrically by drying overnight at 110 °C. Proximate and ultimate analysis of pine sawdust are presented in Table 1. Biochar collected from the residue of prior induction pyrolysis experiments [26] was used as a microwave absorber. Char was ground and sieved to

Table 1
Characteristics of pine sawdust.

Properties	Pine
Proximate analysis ^a (wt%)	
Moisture	8.33
Volatile	74.99
Fixed carbon	16.2
Ash	0.48
Ultimate analysis ^b (wt%)	
C	46.05
H	6.09
N	0.17
O ^c	47.21
Lignin (Klason) (%)	29.3
Hollocellulose (%)	70.7
High heating value (MJ/kg)	18.6

^a Wet basis.

^b Dry basis.

^c Calculated by difference, O(%) = 100-C-H-N-Ash.

less than 500 μm particle size. For each pyrolysis run, 15 g pine sawdust was mixed with a specified amount of char (0, 10, or 20 wt% char). Critical to microwave processing are the material dielectric properties, i.e. dielectric constant and dielectric loss factor. Dielectric properties of each pine and char feedstock mixture were determined based on mixture correlations determined by Ellison et al. (2017) and presented in Table 2 [13].

2.2. Experimental setup

The experimental setup, depicted in Fig. 1, consists of a quartz U-tube reactor filled with the feedstock and placed at the center of a microwave waveguide applicator. The tube inlet was fed by nitrogen and its outlet was connected to the condensing system, comprising a flask placed in an ice bath and an electrostatic precipitator supplied with 12 kV. A FLIR infrared camera (A40M, FLIR systems, Wilsonville, OR) was used to continuously measure the temperature during each pyrolysis experiment. The material was visible through 1 cm diameter holes placed in the top plate of the waveguide, carefully dimensioned and spaced to minimize radiation leakage and to minimize diffraction of infrared radiation. The microwave leakage was continuously monitored during microwave operation by an electrosmog meter with readings well under the 5 mW/cm² recommendation as measured from a 10 cm distance. The emissivity of the tube (0.90) was calibrated based on known temperatures of the tube measured by a thermocouple, to ensure accurate infrared temperature readings.

Two different microwave generators were used to perform the experimental pyrolysis runs: a 1.2 kW generator (Richardson Electronics, LaFox, Illinois, USA) for experiments run at 600, 900 and 1200 W, and a 6 kW generator (Sairem, Neyron, France) for experiments run at 1500 W. The microwave system consisted of a 2.45 GHz magnetron supplied by a 1.2 kW or 6 kW microwave generator, an isolator to pro-

tect the magnetron from reflected microwaves, a 4-stub automatic tuner (Sairem, Neyron, France) to enable impedance matching and reduce the reflected power, a waveguide applicator in which the pyrolysis reaction took place, and a sliding short termination with continuous $\frac{1}{2}$ wavelength periodic movement at a rate of 1.5 mm/s to provide the phase shifting of the electric field and reduce standing wave patterns in the applicator. The generator and sliding short were operated via a LabVIEW program (LabVIEW 9.1, National Instruments, Austin, TX) to control the microwave power and the sliding short position. The isolator/coupler was equipped with a pair of USB power meters (PWR-SEN-6G+, Mini-circuits, Brooklyn, NY), which continuously measured and recorded forward and reflected microwave power during each experiment via the Mini-circuits software.

2.3. Experimental design

A full factorial experimental design was carried out to investigate the effects of microwave power and char mixture on pyrolysis temperature, product yields, and composition. Four microwave power levels including 600, 900, 1200, and 1500 W, and three char mixture levels (0%, 10%, and 20% on the basis of char weight in the pine feedstock) were tested to create a 4×3 full factorial experimental design. Experiments were carried out for each combination of power and char mixture in duplicate and experiments were performed in random order as suggested by the experimental test conditions outlined in Table 3.

2.4. Experimental procedure

For each run, 15 g of biomass and a specified amount of char (0, 10, or 20% on basis of char weight) were weighed, mixed, and loaded into the center of a quartz U-tube. The tube was placed into the microwave reactor and supported such that the material was centered in the waveguide. A nitrogen gas line was connected to the inlet of the U-tube and the system purged of oxygen under a nitrogen flow of 1 L min⁻¹ for 15 min before each experiment. The condensation system, consisting of a condensing flask placed into a 0–5 °C ice bath and an electrostatic precipitator (ESP) supplied by 12 kV, described elsewhere [26], was connected at the outlet of the U-tube via a short connecting tube. For each experimental run, the waveguide was initially excited by 600 W and the power was increased at a rate of 100 W per minute until the target power was reached to prevent overloading of the ESP with pyrol-

Table 2
Dielectric properties of pine/char mixtures used in this study.

Char mixture (wt%)	ϵ'	ϵ''	ϵ''/ϵ'
0	1.506	0.0402	0.0267
10	1.549	0.0507	0.0327
20	1.677	0.0823	0.0491

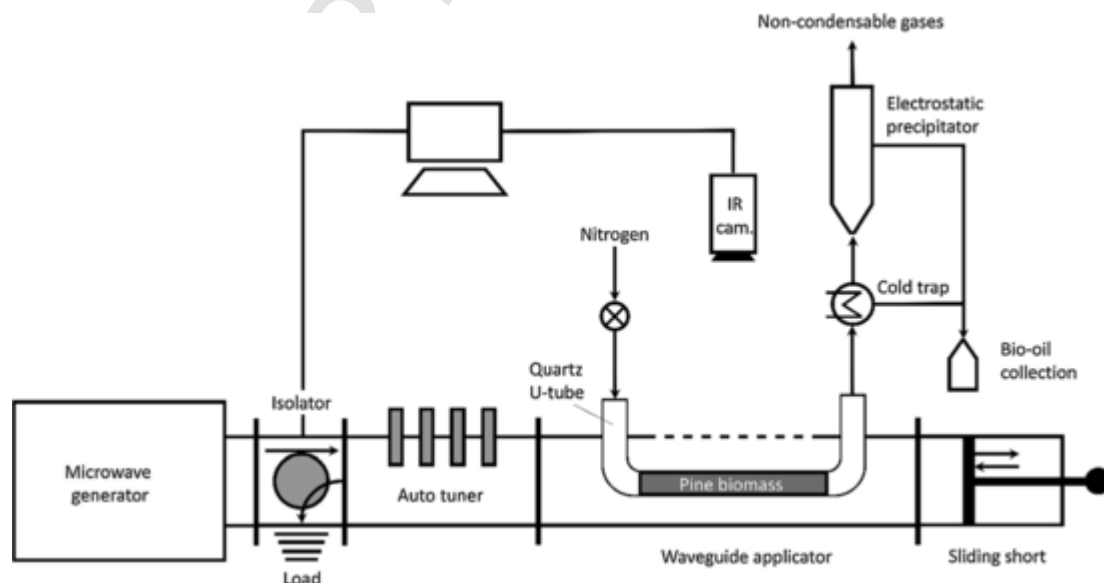


Fig. 1. Schematic of experimental setup.

Table 3
Full factorial experimental design conditions.

Exp. No.	Pattern	Power (W)	Char (%)
1	13	600	20
2	42	1500	10
3	21	900	0
4	31	1200	0
5	12	600	10
6	43	1500	20
7	42	1500	10
8	32	1200	10
9	11	600	0
10	12	600	10
11	41	1500	0
12	32	1200	10
13	11	600	0
14	23	900	20
15	33	1200	20
16	13	600	20
17	41	1500	0
18	33	1200	20
19	31	1200	0
20	22	900	10
21	43	1500	20
22	23	900	20
23	21	900	0
24	22	900	10

ysis vapors. This also resulted in similar heating rates for each run, regardless of power. The pyrolysis reaction was carried out for 22 min, then allowed to cool to room temperature before disassembling the pyrolysis system. Forward/reflected power and temperature data were recorded continuously for the duration of each experiment.

Residual char, liquid, and gas yields were determined by weight. The char product was quantified by weighing the quartz U-tube after each experiment and subtracting the known weight of the empty U-tube. Each of the other pieces used in the experimental setup (connecting tube, condensing flask, and ESP) were weighed before and after each experiment and the sum of their weight changes were assumed to be the yield of liquid product. Product yields of char and liquid were initially determined as a mass percent of the initial feedstock mixture (biomass and added char) according to the following:

$$Y_{i,mixture} = \frac{m_i}{m_{mixture}} * 100\%$$

where $Y_{i,mixture}$ is the yield of product i (char or liquid) from pyrolysis of the feedstock mixture, m_i is the mass of product i , and $m_{mixture}$ is the mass of the initial feedstock mixture. Gas yields were determined by closure of the mass balance (mass feedstock = mass biochar + mass liquid + mass gas).

Separately, a sample of the char used as absorber was pyrolyzed to determine product yields from its decomposition. The pyrolysis test of the char absorber was repeated twice and yields of char and liquid were calculated by the following:

$$Y_{i,charabsorber} = \frac{m_i}{m_{charabsorber}} * 100\%$$

where $Y_{i,charabsorber}$ is the percent yield of product i (char or liquid) from pyrolysis of the char absorber, m_i is the mass of product i , and $m_{charabsorber}$ is the mass of the initial char. Gas yields were calculated by difference. Average product yields from pyrolysis of the char ab-

sorber were found to be $73 \pm 2\%$ char, $7 \pm 3\%$ liquid, and $19 \pm 5\%$ gas.

Final product yields from microwave pyrolysis of biomass, neglecting the added char absorber, were calculated by taking the contribution of products from pyrolysis the char absorber itself (weighted for the amount that was added to the biomass) and subtracting from the product yields of the mixture of biomass and char absorber according to the following:

$$Y_i = Y_{i,mixture} - Y_{i,charabsorber} * \frac{\text{mass of char absorber added}}{\text{mass of raw biomass}}$$

where Y_i is the yield product i (char, liquid or gas) excluding those generated by decomposition of the char absorber. The final calculated product yields enable direct comparison between pyrolysis experiments with different additions of char absorber.

2.5. Temperature determination

Temperature measurement was obtained by a FLIR infrared camera through view ports on the top of the waveguide. Temperature was recorded throughout the duration of each experiment and final pyrolysis temperatures were determined by analysis of radiometric thermal images at steady state temperature using ThermoCAM Researcher Professional 2.9 (FLIR Systems, Wilsonville, OR) software (Fig. 2). Spatial temperature data were analyzed by obtaining temperature values along a specified line on the thermal image and graphs were produced to observe the temperature profile. The seven center most waveguide view ports were used for analysis to avoid apparent temperature deviations due to diffraction effects that occur on the outermost view ports. Final pyrolysis temperatures were obtained by taking the averages of each peak in the temperature profile graph at steady state temperature (the dips correspond to colder waveguide surface between the viewports).

2.6. Product characterization and analysis

Char, liquid, and gas products were collected for each experiment and analyzed by several characterization methods. Water content was determined for each liquid sample by standard coulometric Karl Fisher titration (Metrohm Model 831 KF Coulometer, Revview, FL). A PerkinElmer 2400 Series II CHN Elemental Analyzer (PerkinElmer, Waltham, MA) was used to determine carbon, hydrogen, and nitrogen (oxygen calculated by difference) composition of all bio-oil and char samples according to standard procedures [27]. Char samples were folded into tin capsules while liquid samples were transferred to aluminum capsules designed for volatile liquid samples and then crimped closed to prevent sample volatilization before combustion analysis.

Liquid product was extracted with dichloromethane (1:4 ratio of bio-oil to DCM by volume) and analyzed by gas chromatography mass spectrometry (Varian Saturn 2200 GCMS). The GC was equipped with a DB-5 ultra-inert column (30 m \times 0.2 mm \times 0.2 μ m film thickness) and a helium flow rate of 1 mL min⁻¹. For each sample, a 1 μ L aliquot was injected into the GC (splitless injector) with an injection temperature of 40 °C. The oven was held at 40 °C for 6 min, then heated to 240 °C at a rate of 4 °C min⁻¹ and held for 10 min, then heated at a rate of 20 °C min⁻¹ to 280 °C. Compounds were semi-quantitatively analyzed based on relative integrated peak areas and tentatively identified by their mass spectra. Peak areas were assumed to sum to 100% of the liquid composition. Water soluble compounds were not analyzed by this method and may include acids, sugars, alcohols, ketones, and aldehydes.

Gas samples were collected in 0.5 L Tedlar bags and analyzed by gas chromatography (GC-2040, Shimadzu) and peaks were identified tentatively based on standards and verified by mass spec-

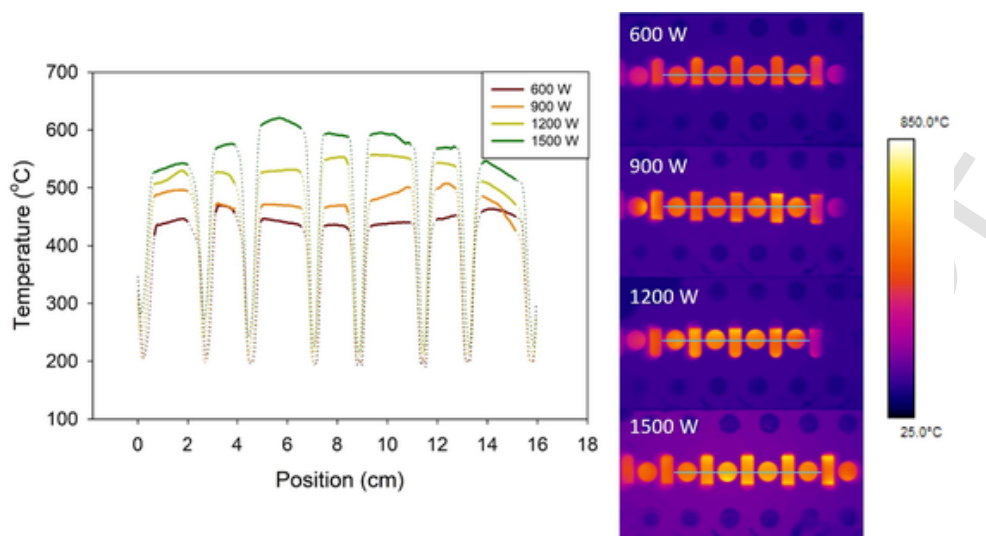


Fig. 2. Temperature profile and radiometric thermal images at each power level for 20% char mixtures.

troscopy (GCMS-QP2010). Gas components were detected by FID (CH_4 and light hydrocarbons), 100 mA TCD (CO_2 , CO), and 40 mA TCD (H_2). A Restek 30 m column was used with 0.53 mm inner diameter and 20 μm film thickness. The injector temperature was maintained at 250 $^{\circ}\text{C}$ with helium carrier gas flow rate of 14.6 mL min^{-1} . The oven was held at 40 $^{\circ}\text{C}$ for 5 min, ramped at 20 $^{\circ}\text{C min}^{-1}$ to 150 $^{\circ}\text{C}$ and held for 10 min, ramped at 10 $^{\circ}\text{C min}^{-1}$ to 175 $^{\circ}\text{C}$, then ramped at 40 $^{\circ}\text{C min}^{-1}$ to 250 $^{\circ}\text{C}$ and held for 5 min. Gas composition was analyzed quantitatively based on known concentrations of analytical gas standards.

Higher heating value (HHV) of liquid and char were determined by bomb calorimetry (Parr Model 6100, Parr Instruments, Moline, IL) according to ASTM D240-17. Non-condensable gas from pyrolysis consists of H_2 , CO, CO_2 , CH_4 , and light hydrocarbons. An estimate of the energy content of the gas was calculated as the sum of the chemical energy of the product gas constituents as follows [28]:

$$E = \sum_i n_i \text{HHV}_i \quad (3)$$

where n_i and HHV_i are the molar concentration (mol/kg) and higher heating value (kJ/kmol) of the i^{th} gas component, respectively. Properties of gases at dead state conditions (obtained from [29]) were used for the calculations.

An energy balance was calculated to evaluate the conversion of biomass energy to products. Energy inputs were determined from the sum of microwave input energy and the biomass energy. Biomass input en-

ergy, determined by bomb calorimetry measurements, was found to be 18.6 MJ/kg, which remained constant for all tests. Input microwave energy values are calculated from the total forward power and 22 min reaction time for all tests according to $E = P \cdot t$, where E is the microwave energy, P is the microwave input power, and t is the pyrolysis reaction time. Energy outputs were evaluated based on the chemical energy of each pyrolysis product, determined by calorimetric analysis of the obtained pyrolysis liquid, gas, and char. Energy density of liquid and char were measured by bomb calorimetry while energy from gas was calculated based on higher heating values of its constituents according to Eq. (3). Energy density of char, liquid, and gas were multiplied by the yields of each product, respectively, to obtain energy breakdown of products of the initial biomass feedstock in MJ/kg biomass.

3. Results

3.1. Pyrolysis temperature and absorbed microwave power

Final pyrolysis temperatures increased linearly with power for all char mixtures at the power levels studied (Fig. 3a). Samples without char only increased from 150 to 191 $^{\circ}\text{C}$ for microwave output powers of 600 to 1500 W, respectively, while samples with 10 and 20% char increased from 443 to 618 $^{\circ}\text{C}$ on average for 600 to 1500 W power, respectively. For samples without char, biomass moisture acts as the initial microwave absorber increasing the feedstock temperatures to

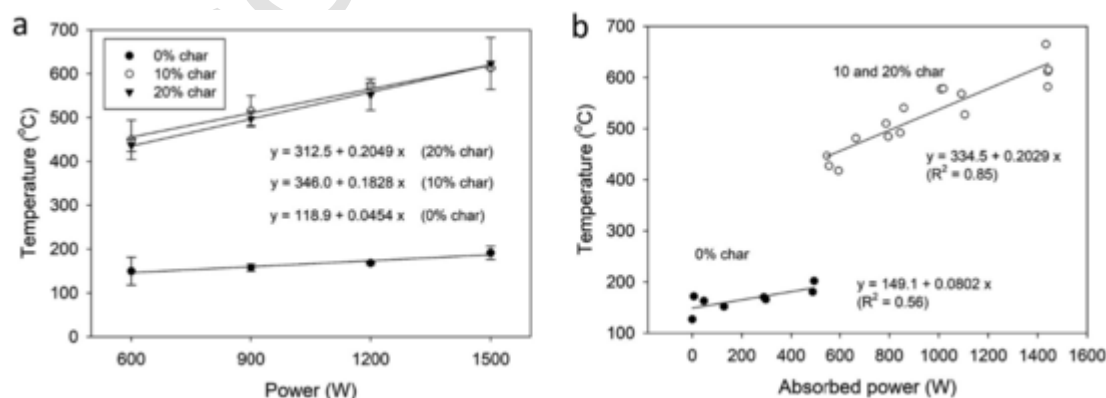


Fig. 3. Final pyrolysis temperatures (a) as a function of power level for each char mixture with $R^2 = 0.93$, 0.99, and 0.97 for 0%, 10%, and 20% char mixtures, respectively, and (b) as a function of absorbed power.

the boiling point of water. After water evaporates from the biomass, the temperature increase is not sustained. Without addition of a microwave absorber, temperatures reached a maximum of 200 °C at the highest input power level of 1500 W. Addition of char to the feedstock resulted in a three-fold temperature increase compared to feedstocks without char.

For each experimental run, input power and reflected power were measured for the duration of the experiment and the difference between input and reflected power was used to estimate the total power absorbed by the load. Microwave output power and percent char were also found to directly correlate to the total power absorbed by the feedstock. Addition of char as a microwave absorber was found to be effective at increasing absorbed power compared to power absorption in pine sawdust without any absorber. As the absorbed power is directly correlated to temperature increase according to Eq. (2), pyrolysis temperature is plotted as a function of absorbed power in Fig. 3 (b). Basically, two independent linear trends are observed for samples with and without char microwave absorber.

The temperatures obtained by 10% and 20% char mixtures for each power level were statistically similar (p -value = 0.989 according to Nemenyi post-hoc test), indicating that 10% char is sufficient to yield maximum microwave power absorption. From a processing perspective, as the amount of char yielded by complete microwave pyrolysis of pine is 13% on average, the total amount of residual pyrolysis char can be sustainably added to the feedstock as a part of a closed loop pyrolysis system to produce maximum microwave absorption benefits.

3.2. Product yields

During pyrolysis, lignocellulosic biomass was converted into biochar and volatiles (condensable and non-condensable gases). An overall mass balance is presented in Fig. 4 for all experimental runs. Without microwave absorber, char yields are around 55 to 65% of the products while bio-oil and gas yields make up the remaining 35 to 45%, depending on input power. Far greater conversion to bio-oil and pyrolysis gas are obtained from pyrolysis with 10% and 20% char absorber. Microwave pyrolysis utilizing 600 W generates greater yield of char (36%) and less gas (32%), compared to higher power levels in which conversion to gas is 54–61%, depending on power level.

Typically, pyrolysis product yield distributions are dependent on pyrolysis reaction temperature and heating rate. In this study, product conversion was also found to have a good correlation with total absorbed power, which is ultimately responsible for the specific reaction temperatures and heating rates attained during microwave pyrolysis. Thus, total absorbed power is used to draw correlations to yields

of biochar, liquid, and gas. To our knowledge, this is the first time this correlation is described in literature (rather than incident power or temperature) for study of microwave pyrolysis. Pyrolysis of feedstock char was carried out separately to quantify any products produced from its decomposition. All total product yields were corrected for any products which would be produced from pyrolysis of the added feedstock char. In any case, product yields from feedstock char only contributed a maximum of 0.2% to product formation.

Pyrolysis product yields were found to show a better correlation with absorbed power than with temperature or incident power. Hot spots are a well-known characteristic of microwave material processing and may have influenced biomass temperature, especially at the local level [30]. Micro plasma formation is a common phenomenon in microwave heating of carbonaceous materials, in which kinetic energy of some π -electrons increase due to microwave excitation and ionize the surrounding local environment [31]. At the microscopic level plasmas form in a finite region of space and for only short durations. The temperatures measured by the infrared camera are representative of the bulk material temperature, however, it is not sensitive to local hot spots that occur within the material. Due to these hot spots, local temperatures are likely much greater than the measured bulk temperature, which may have implications for the pyrolysis reactions occurring. For these reasons, absorbed microwave power was used to correlate product yields and composition as it is more representative of the energy input into the material compared to bulk temperature. Absorbed microwave power was calculated as the difference in the measured forward and reflected power. In general, as the absorbed power increases, biochar yields decrease, liquid yields increase to a plateau, and gas yields increase (Fig. 5). Yields of each product are hereby discussed individually.

Some deviation between the empirical model with the experimental data is observed by relatively lower correlation coefficients for some data. Deviations in the data could be due to inhomogeneity of the biomass/char mixture as it is difficult to obtain a homogeneous mixture of these two components. One solution for homogeneous mixing would be to grind the materials to a fine particle size, which would defeat the purpose of utilizing microwaves that can penetrate into large particle sizes and provide internal heating once the biomass particles start pyrolyzing. Also, the way the biomass/char mixtures are packed into the reactor can significantly influence the temperature distributions and thus the yields. A slight difference between different experiments can result in relatively large differences in yields, contributing to the deviations observed between the empirical models and the experimental data.

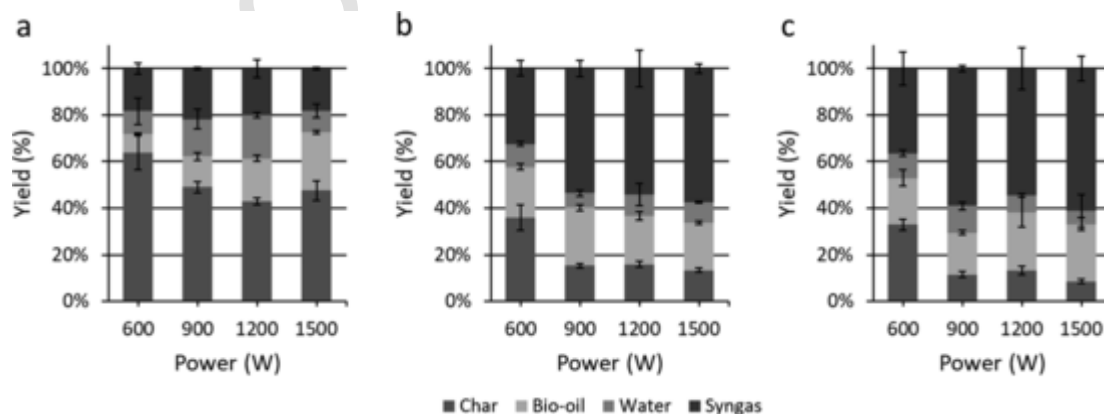


Fig. 4. Mass balance of products from microwave pyrolysis with addition of (a) 0% char, (b) 10% char, and (c) 20% char absorber. Error bars represent standard deviations between duplicate tests.

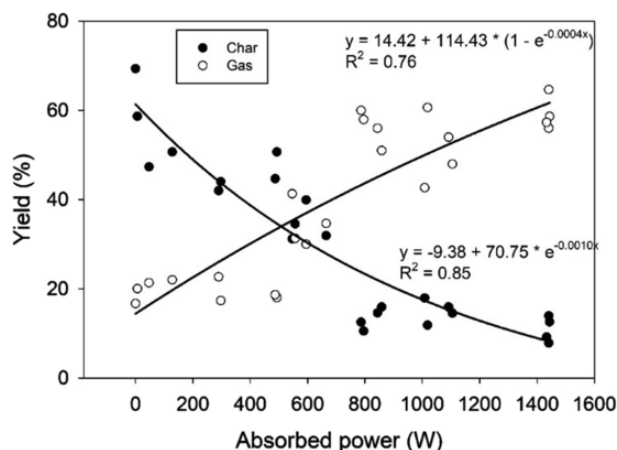


Fig. 5. Char and non-condensable gas yields as a function of absorbed power fitted to exponential decay and exponential rise to a maximum, respectively.

3.2.1. Char yields

Char is the remaining feedstock residue after decomposition of biomass, and in general, char was found to decrease exponentially with increasing power ($R^2 = 0.85$). At low absorbed microwave powers, biomass is not fully decomposed to biochar, which is reflected by the greater char residue yields. Char yields decreased from 69 to 32% as absorbed power increased from 0 to 750 W. Above 795 W absorbed power, corresponding to temperatures greater than 484 °C, char yields reached a minimum and remained constant at $13.1\% \pm 3.0\%$. As char yields were based on the weight of the feedstock residue after pyrolysis, this is an indication that the feedstock was not fully converted to char at temperatures less than 484 °C. Incomplete pyrolysis was also observed by visual inspection of the feedstock residue. Residues collected from incomplete pyrolysis runs were only partially blackened, while complete pyrolysis char residues were completely blackened. Interestingly, char yields produced from microwave pyrolysis in this study (13.1%) are less than char yields from pyrolysis by conventional heating of the same material (about 18% for pyrolysis at 700 °C) [32]. This indicates that microwaves were capable of decomposing more of the fixed carbon than conventional heating, implying that local temperatures within the material were likely much greater than the measured bulk temperatures during microwave-assisted pyrolysis.

3.2.2. Liquid yields

Liquid yields (bio-oil and water) remain mostly constant with increasing absorbed microwave power, except for markedly lower yields at very low absorbed powers from 0 to 200 W. At low power lev-

els, corresponding to pyrolysis temperatures in the range of 150 to 200 °C, liquid yields increase rapidly from 14 to 38%. At greater absorbed powers, corresponding to temperatures from 400 to 650 °C, liquid yields remain approximately constant with an average value of $31.2 \pm 3.6\%$.

The liquid product, produced from condensation of pyrolytic vapors, consists of water and bio-oil. The origin of water present in the liquid product are due to moisture present in the pine feedstock and water produced by dehydration reactions during pyrolysis [33,34]. The water compositions of the liquid products were determined by Karl Fisher titrations and the mass fractions of water and bio-oil that make up the liquid product were calculated (Fig. 6a). At low absorbed powers, corresponding to temperatures in the range of 150 to 200 °C, pyrolysis liquid is composed of roughly 50% water and 50% bio-oil. These low temperatures are only enough to evaporate the water and only break weak bonds such as those in hemicellulose and cellulose. With increasing absorbed powers, the proportion of bio-oil in the liquid increases while the proportion of water decreases. Yields of water-free bio-oil, obtained by subtracting the water content from the liquid yields, increase exponentially with absorbed power to a maximum of $22.1 \pm 3.3\%$ for powers greater than 500 W (Fig. 6b).

3.2.3. Pyrolysis gas yields

Biomass conversion to non-condensable gas increases exponentially to a maximum with increasing absorbed microwave power with a coefficient of determination of 0.76 (Fig. 5). From 0 to 500 W, corresponding to 125 to 200 °C, non-condensable gas yields remain constant at $19.6 \pm 2.3\%$, followed by an increase to $59.1 \pm 3.8\%$, on average, for absorbed power levels greater than 1400 W (corresponding to temperatures greater than 580 °C). At high pyrolysis temperatures, thermal cracking of pyrolysis vapors results in greater production of low molecular weight, non-condensable gases.

3.3. Bio-oil composition

Bio-oils produced from pyrolysis of pine are composed of a complex mixture of oxygenated organic molecules produced by thermal degradation of cellulose, hemicellulose, and lignin. Bio-oil component species were identified by GCMS and categorized based on the major functional groups to which they belong, including furans, ketones, aldehydes, carboxylic acids, phenols, polyaromatics, and others. Relative abundance of each functional group are correlated to absorbed microwave power (Fig. 7). Overall, furans and carbonyls (ketones, aldehydes, and carboxylic acids) decreased with absorbed power as polyaromatics increased, while phenol composition remained generally constant.

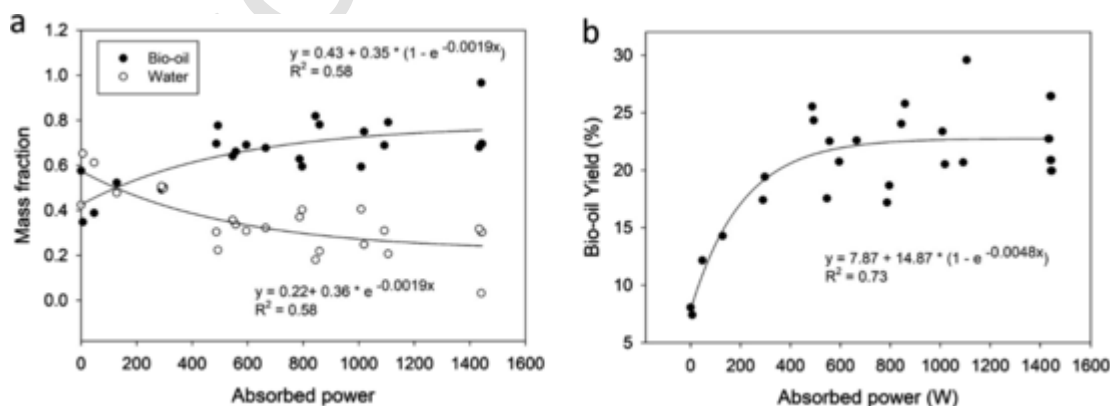


Fig. 6. Mass fraction of water and bio-oil in the liquid product (a) and water-free bio-oil yield as a function of absorbed microwave power (b).

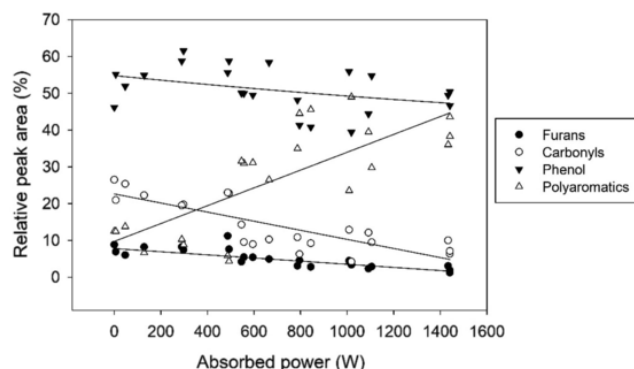


Fig. 7. Effect of absorbed microwave power on bio-oil composition.

Furan composition in the bio-oil ranges from 1.2 to 8.8% decreasing linearly with absorbed power ($R^2 = 0.81$). Furans are produced primarily from volatilization of cellulose, which occur at moderate pyrolysis temperatures. Carbonyl functional groups (ketones, aldehydes, and carboxylic acids) decrease quadratically with absorbed power ($R^2 = 0.84$) from 26.5% and reaching a minimum of $9.0 \pm 2.5\%$ on average for absorbed powers greater than 450 W. Ketones and acids are primarily generated by decomposition of hemicellulose which is the dominant volatilization pathway at low absorbed powers and low pyrolysis temperatures [35]. Phenols, typically produced by volatilization of lignin, represent the greatest fraction of the bio-oils produced from pyrolysis of pine. The relative percent of phenols remained relatively constant for all power levels tested with an average value of $60.0 \pm 6.2\%$. This is an indication that even at low bulk temperatures, there may be local hot spots in the feedstock at lignin decomposition temperatures. Additionally, phenols are produced as a result of secondary reactions of light organic fractions derived from cellulose and hemicellulose, which contribute to the high phenol yield at low absorbed powers [35]. Finally, the abundance of polyaromatic species in the bio-oil were found to increase linearly with absorbed microwave power ($R^2 = 0.76$), ranging from a minimum of 4.3% to a maximum of 49.0%. Polyaromatics are a product of lignin decomposition indicating the increased decomposition of lignin with increasing absorbed power. As previously noted, this analysis is not inclusive of water soluble species due to limitations of the GCMS analysis technique.

3.4. Gas composition

Results from GC analysis of pyrolysis gases show some wide variation, however some general trends were observed and are hereby discussed. For pyrolysis experiments without microwave absorber, H_2 was not detected in the gas product. However, for experiments run with ad-

dition of char, H_2 was found to increase from 10% to 30% by volume with increasing absorbed power. Production of CH_4 was in the range of 5 to 10% for samples without absorber and increased to a range of 11 to 15% with addition of char. CO production was 6 to 30% without char and increased to 50 to 65% for pyrolysis with char. CO_2 decreased from a range of 24 to 73% without char absorber to a range of 5 to 15% for pyrolysis with char. Other light hydrocarbons accounted for around 3 to 10% for all char mixtures and power levels. In general, with addition of char and resulting increased absorbed microwave powers, the produced gas shows an increase in H_2 , a slight increase in CH_4 , a major increase in CO, and a decrease in CO_2 . These gas concentrations are in agreement with microwave pyrolysis of wheat straw reported by other researchers [25]. Microwave pyrolysis has been shown to favor syngas (H_2 and CO) production compared to conventional heating and therefore, non-condensable gas from microwave pyrolysis have a greater energy content than non-condensable gas from conventional pyrolysis [25].

3.5. Elemental analysis

Combustion analysis was performed on char and liquid pyrolysis products to determine elemental composition of carbon, hydrogen, nitrogen, and oxygen for each sample (Fig. 8). Biochar carbon content increased and oxygen content decreased with absorbed microwave power. This result is due to the pine biomass releasing oxygenated volatiles as temperature increases and its conversion into carbon-dense char. Non-pyrolyzed pine biomass has a carbon content of 46% while fully pyrolyzed biomass char has a carbon content of 87%, almost doubling in carbon content after its conversion to char. The carbon content of bio-oil produced from pyrolysis decreased with increasing microwave power, while oxygen content increased. The increase in oxygen is indicative of greater formation of oxygenated species in the bio-oil. Char and bio-oil compositions show inverse trends with respect to carbon and oxygen content indicating the mass transfer of these species from the feedstock to the liquid product.

3.6. Energy balance

An energy balance was performed for all pyrolysis conditions considered in this study (Table 4). For reference, the amount of power absorbed during experiments is reported as an average from duplicate runs. During pyrolysis of biomass without char, power absorption was low ranging from 0.5 to 32.6% depending on input power level. With addition of 10 and 20% char to the biomass, absorbed power increases to greater than 87% resulting in the improved heating as previously discussed.

For pyrolysis without microwave absorber the biomass only reached a maximum of 200 °C, which only partially converted the biomass

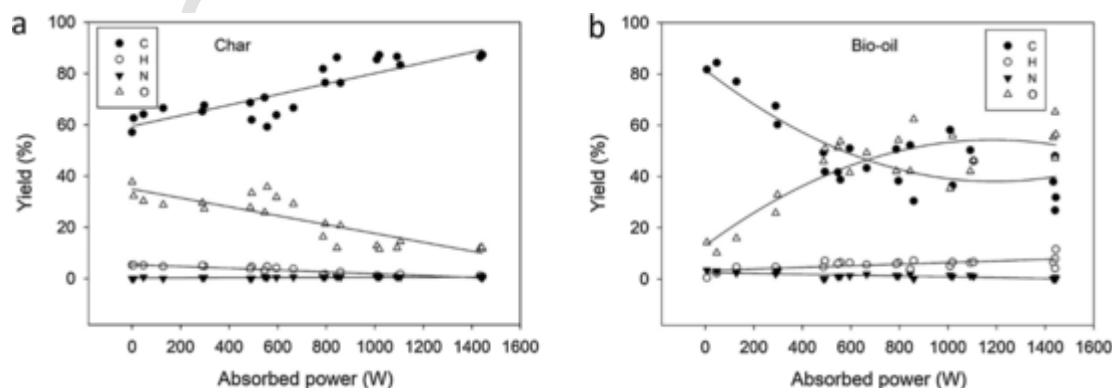


Fig. 8. CHNO analysis of char (a) and water-free bio-oil (b) fit to exponential curves.

Table 4
Energy balance of overall microwave pyrolysis system.

Input Power (W)	Absorbed power (%)	Energy inputs (MJ/kg biomass)		Energy outputs (MJ/kg biomass)				Conversion to liquid and gas (%)
		Microwave energy	Biomass energy	Liquid	Gas	Char	Total	
0% char								
600	0.5	52.8	18.6	1.6	0.5	14.1	16.2	11.3
900	9.7	79.2	18.6	3.6	0.6	12.4	16.7	22.6
1200	24.4	105.6	18.6	4.3	0.4	11.5	16.2	25.3
1500	32.6	132.0	18.6	4.4	1.0	13.0	18.4	29.0
10% char								
600	99.1	52.8	18.6	3.4	4.0	7.8	15.2	39.8
900	94.6	79.2	18.6	3.1	4.4	4.1	11.5	40.3
1200	87.5	105.6	18.6	4.0	3.2	4.6	11.8	38.7
1500	96.2	132.0	18.6	1.9	5.3	3.8	11.0	38.7
20% char								
600	91.9	52.8	18.6	3.0	6.2	7.1	16.2	49.5
900	87.9	79.2	18.6	2.9	9.3	3.8	15.0	65.6
1200	88.5	105.6	18.6	3.3	9.5	3.2	16.0	68.8
1500	95.8	132.0	18.6	3.3	11.0	2.1	16.3	76.9

to pyrolysis products. Because of the low conversion of biomass to gas and liquid, 62 to 76% of the original biomass energy remained in the partially converted char fraction. For pyrolysis assisted by 10% char microwave absorber, 39 to 40% of the original biomass energy was converted to liquid and gas, and for pyrolysis with 20% microwave absorber, 50 to 77% of the total biomass energy was converted to liquid and gas. Samples with 20% char microwave absorber showed the greatest energy conversion to biofuel precursors (liquid and gas products), whereas most of the energy remained in the char for pyrolysis runs without microwave absorber.

Input microwave energy is reported in Table 4 although it is of little value for a non-optimized system at lab scale. During these experiments, microwave power was constantly on for the duration of the experiment (22 min), leading to very high input energy values. Less energy could be used if power is controlled to maintain a setpoint temperature and experiments are to be stopped after completion of pyrolysis. For experimental consistency, the duration of the experiments was 22 min for each run, however the authors observed that for many of the runs vapor generation ceased after much less time signaling the end of pyrolysis. Additional energy reductions could be realized, for example, by optimizing the applicator design, scaling the system, determining an optimal char mixture for microwave absorption, or insulating the quartz reactor tube, thereby reducing the amount of microwave power required for the process and increasing the overall net energy production.

Based on the volumetric nature of dielectric heating, the required microwave input energy is largely dependent on the volume of the material being processed. In our lab scale experiments using 15 g biomass and filling only a small volume of the waveguide, the microwave system was not used to its maximum loading capacity for the powers tested in this study and thus much of the power was wasted. Based on previously published data, at 2.45 GHz the penetration depth of 20 wt% char mixed with pine biomass is about 50 cm [13]. Since the sample volume used was much smaller than the penetration depth of the microwaves into the material, this system could potentially process a much larger quantity of biomass with the same input energy if scaled. It is difficult to estimate the energy requirements for a scaled microwave pyrolysis system due to lack of data on scaled up microwave pyrolysis processes and no known commercial plants, but data reported in literature on pilot scale processes suggests improved conversion of electrical energy into heat with potential increase from 40 to 48%

at lab scale to 80–90% at pilot scale [36]. Others have also reported increased process efficiencies for microwave-assisted processes with increase in scale [37–39]. According to Bermudez et al., specific energy consumption decreases by about 90–95% with an increase in scale from 5 g to 100 g, regardless of the process and microwave equipment used [37]. These estimates were based on normalized data from six different microwave processes that were scaled incrementally. By applying the correlations found in Bermudez's work for the scale up of microwave heating of similar materials, the potential energy input for scale up of our microwave pyrolysis of biomass tests from 15 g (lab scale) to 100 g (pilot scale) were estimated in the range of 8.3 to 38 MJ/kg. Further reductions to input microwave energy could be realized by process optimization.

In the current experimental configuration, heat losses were estimated to be 50 MJ/kg for samples heated to 600°C (10% and 20% char mixtures irradiated with 1500 W microwave power). The calculation is based on the sum of both convective and radiative heat losses, but they are mostly coming from radiative losses. These losses could be potentially avoided by simply insulating the quartz tube, effectively subtracting the 50 MJ/kg heat losses (or a significant fraction of it) from the 132 MJ/kg input energy for the 1500 W condition if insulated, a 37% reduction in input energy. For these experiments the reactor was not insulated in order to obtain surface temperature data using the IR camera, but preliminary tests (not reported here) indicate a 2–3 fold reduction in energy requirements for thermally insulated reactors in other electromagnetic heating systems.

Assuming that only liquid yields are desired from the process, with the char being considered of additional value, a microwave power of about 600 W and either 10 or 20% char as absorber seems to be best suited for this process (Figs. 4, 5, and 6) as it results in both phenols and a significant amount of polyaromatics. However, if the purpose is to maximize the values of both bio-oil and syngas, then power as high as 1200/1500 W are desired, as at these parameters the syngas has much higher energy values due to production of H₂ and CO at the expense of CO₂ at lower powers. At the same time, liquid yields do not change much from the lower power, but its energy value is much improved due to a major increase in polyaromatics content of the bio-oil. For the most practical purpose, the amount of char to be added would be exactly the amount of char produced in previous runs, so a power level of 900–1200 W seems to be the most suitable (Fig. 4).

4. Conclusion

This study successfully demonstrates the microwave-assisted pyrolysis of pine with char as a microwave absorber in a varied-phase single-mode microwave system. Phase shifting by means of a continuously moving sliding short enabled uniform heating across the biomass bed. Microwave power and percent residual char absorber were studied for their effect on process temperature, pyrolysis product yields and composition. Addition of char greatly improved dissipation of microwave energy compared to biomass alone resulting in ability to reach pyrolysis temperatures, which could not be reached with biomass alone. There was no significant difference between 10% and 20% char on temperature, and thus, utilizing the char yielded by biomass pyrolysis is sufficient to catalyze the microwave heating of the mixture. The product yields and compositions were ultimately found to be a function of microwave power absorption. For all power levels tested, bio-oil composition was dominated by phenolic functional groups. With increasing microwave power, lignin was more fully volatilized as seen by increase in polyaromatics in the bio-oil. According to the energy balance performed, samples with 10 and 20% char proved to yield the greatest energy conversion to biofuel precursors (liquid and gas), demonstrating the need for microwave absorber in the conversion of biomass feedstocks to fuels.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apenergy.2019.114217>.

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