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Research article

Microwave torrefaction of *Prosopis juliflora*: Experimental and modeling study

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ABSTRACT

This study is focused on evaluating the effect of particle size and microwave power on torrefaction of the invasive biomass species, *Prosopis juliflora* (PJF), via experiments and theoretical model. Experiments were conducted using a central composite design (CCD) approach to construct response surfaces capturing the effects of these two factors on three key characteristics of the obtained char, viz. yield, calorific value and energy recovery. Highest char yield was obtained at an intermediate microwave power for a given particle size, while the calorific value increased with both the parameters. The response surface for energy recovery was convex with maxima at 481 W power for 1.9 mm particles. A microwave-based thermogravimetric study was conducted to obtain the mass loss profile during torrefaction. Assuming a global, single-step, power-law kinetic model with Arrhenius-type rate constant for torrefaction, the apparent activation energy and reaction order were estimated to be 173.93 kJ mol^{-1} and 1.3, respectively. To explain the trends of char yields, a new approach was proposed that integrates the temperature profile information with the inferred kinetic model. Two parameters, viz. torrefaction time and average temperature, are introduced to quantify the temperature profiles during torrefaction. The generic model can be extended to any biomass species and reactor configuration by conducting suitable experiments. Detailed composition analysis of the bio-oil revealed that, unlike conventional torrefaction, significant degradation of lignin also occurred along with hemicellulose degradation at low bulk temperatures during microwave torrefaction.

1. Introduction

Valorization of lignocellulosic biomass to produce second generation biofuels through a carbon-neutral cycle has gained momentum as a viable method to tackle our increasing energy needs. Raw biomass itself is not an ideal fuel. It suffers from several drawbacks such as high moisture content, low calorific value, poor grindability, hygroscopic nature, and high transportation and storage costs [1–3]. High oxygen content in biomass is the single most important factor that spawns all these drawbacks. With a focus on reducing the oxygen content, many thermochemical and biochemical routes have been explored to obtain high quality solid and liquid fuels from biomass.

Torrefaction is a thermochemical technique in which biomass is subjected to mild thermolysis in the temperature range of 200–300 °C in an inert atmosphere [2–4]. It produces solid char as the major product along with small amounts of condensable volatiles (bio-oil) and non-condensable gases. Torrefaction is found to effectively reduce the oxygen content of raw biomass by removal of bound moisture and by formation of low molecular weight (LMW) oxygenated volatiles. The resultant char has many desirable fuel properties such as low atomic O/C ratio, low moisture content, hydrophobic nature, high calorific value, high energy density and better grindability [2,5,6]. A number of studies have reported that the quality of char obtained from torrefaction is comparable to coals [5,7,8]. Apart from its inherent fuel value, this char can be co-fired with coal in thermal power plants [9], pelletized and used as feedstock for syngas production [10], and as a coal substitute in metallurgical industries [2]. Pre-treatment of biomass using torrefaction is also found to enhance the quality of biofuels produced by pyrolysis [11,12]. Owing to the high energy density of char, economic studies have shown that the overall cost, factoring in production and transportation costs, is lower for char pellets than raw biomass pellets [7,13]. Due to such an industrial importance of torrefaction, it is important to understand the various factors and underlying mechanisms that affect char yield and calorific value.

In the process of microwave torrefaction, heat energy required for torrefaction is provided by microwave irradiation. Microwave heating is superior to conventional heating methods as it involves fast, selective and uniform heating of the material [14]. In addition, many studies

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Table 1
Characterization of PJF feedstock of different particle sizes.

Size range (mm)	Proximate analysis (wt%)[a]				Elemental analysis (wt%)[b]					HHV (MJ kg^{-1})
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	S	O[c]	
2–4	12.0	62.7	24.8	0.5	45.0	7.1	1.9	0.1	45.9	17.4
1.4–2	10.8	65.4	22.8	1.0	44.5	6.9	1.9	0.1	46.6	17.0
0.25–0.5	12.0	66.6	16.8	4.6	43.9	6.6	1.4	0.2	47.9	16.8

[a] Wet basis.
[b] Dry basis.
[c] O = 100-C-H-N-S.

have also reported microplasma formation within the microwave susceptible material, resulting in local high temperature hotspots, which aids faster thermolysis [15,16]. Microwave torrefaction of various biomass feedstocks such as corn stover [11], rice husk [17], sugarcane residues [17], Douglas fir [8], rice straw [18], pennisetum [18] and sewage sludge has been reported [19]. For this study, *Prosopis juliflora* (PJF) has been used. PJF is an invasive shrub that can grow on arid lands and highly saline soil. It is an attractive biomass source as it fixes relatively large amounts of CO_2 from the atmosphere as biomass. It has been recognized to have a detrimental effect on local flora by wiping out native species. Recent policies of the state government of Tamil Nadu in India have encouraged removal of this species from fallow land. It is currently being co-fired with coal in small-scale thermal plants for electricity generation [20]. Instead of combustion, microwave torrefaction can aid in better energy and resource recovery from PJF. In our recent study, we reported the production of high quality bio-oil and char from PJF biomass through microwave pyrolysis, suggesting that microwave torrefaction could be a technology worth investigating [16].

Based on an extensive literature survey, the two factors that had the most effect on microwave torrefaction process were identified to be microwave power (MP) and biomass particle size (PS) [17–19]. MP determines the rate of delivery of heat energy to biomass, thereby affecting temperature profiles during the torrefaction process. Temperature profiles in turn dictate the atomic composition, mass and energy yield of the resultant char [17–19]. Biomass PS affects mass and heat transport within the reactor, thereby having a secondary effect on the thermochemistry [17].

To the best of our knowledge, there is no current literature studying the simultaneous effect of MP and PS on char yield, calorific value and energy recovery using microwave torrefaction. There have been very few thermogravimetric studies that have attempted to model the kinetics of microwave torrefaction [18]. Moreover, no real effort has been made to use the results of the kinetic study in conjunction with experimentally obtained temperature profiles to understand mass loss during torrefaction, and explain trends in char yields. We aim to address the above two issues through this paper.

To this end, a central composite design (CCD) was employed to understand the simultaneous effects of MP and PS on three important characteristics of char, viz. yield, higher heating value and energy recovery. Both proximate and elemental characterization of char and detailed organic composition analysis of bio-oil were performed to gain insights into the underlying chemistry of torrefaction. Microwave-based thermogravimetric analysis (TGA) was carried out to estimate the rate parameters of the global, single-step, power-law kinetic model for torrefaction with Arrhenius-type rate constant. A semi-empirical model using newly introduced parameters, viz. average temperature and average time, was developed by tying together the inferred kinetic model with experimentally obtained temperature profiles to understand the mass loss characteristics during torrefaction.

2. Materials and methods

2.1. Materials

PJF biomass was obtained from IIT Madras campus. Processing steps involved in PJF feedstock preparation are described in detail elsewhere [16]. In summary, PJF branches were cut, dried, ground and sieved to obtain three size ranges, viz. 0.25–0.5 mm, 1.4–2 mm and 2–4 mm, which were used for this study.

2.2. Material characterization

Moisture, volatile matter, fixed carbon and ash content of the samples were determined through proximate analysis done in a thermogravimetric analyser (SDT-Q600 TGA, TA Instruments) conforming to the ASTM E1131-08 method. Elemental analysis was done to characterize the elemental (C, H, N, S) composition of the samples using ElementarVario EL III analyser. The higher heating values were measured in an IKA 2000 bomb calorimeter by taking 200 mg samples for each analysis. Results of initial feedstock characterization are summarized in Table 1.

2.3. Torrefaction experiments

Design of the microwave reactor used for experiments is described in our earlier report [16], and the schematic is provided in Fig. S1 (in Supplementary data). The entire reactor setup was purged with N_2 at 1 L_{STP} min^{-1} for 10 min before the start, and throughout each experiment, to ensure an inert atmosphere for torrefaction. 20 g of PJF feedstock of the desired PS was charged into the reactor, and MP was set at the desired value. The feedstock was heated from room temperature to 250 °C after which the magnetron was switched off. Temperature was recorded every 30 s using a modified K-type thermocouple whose construction is described elsewhere [21]. Maximum temperature was set to 250 °C as PJF started to undergo pyrolysis beyond this temperature resulting in copious formation of volatiles. Unlike microwave pyrolysis, where susceptors are required to achieve heating comparable to fast pyrolysis, no susceptor was used for torrefaction. This demonstrates the simplicity of torrefaction over fast pyrolysis in a microwave reactor setting. The masses of char and bio-oil were measured using a weighing balance, and the mass of non-condensable gases was calculated using mass balance. The obtained bio-oil was an emulsion containing water and organics. Dichloromethane was used as a solvent to selectively extract the organics. It was later evaporated from the extract phase to obtain a residue rich in organics. This was used for composition analysis using gas chromatograph/mass spectrometer (GC/MS). The results of all nine torrefaction experiments are reported in Table 2.

2.4. Central composite design

The variations of yield, HHV and energy recovery of char with the two factors, viz. MP and PS, were studied by constructing a 2^2-factorial