Torrefaction and grinding performance of wheat and barley straw after microwave heating

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ABSTRACT Microwave irradiation was used in this study for the torrefaction of wheat and barley straw. The torrefaction effect was studied by varying the microwave power level (200-300 W), reaction time (10-20 min) and moisture content of biomass (5-15%). Mass yield and energy yield of the torrefied biomass was determined. Fuel properties like H/C and O/C ratio were assessed from elemental composition. Grinding characteristics and hydrophobicity of the torrefied sample were studied and compared with the raw biomass. Barley straw tended to carbonize more under microwave irradiation with 29.08% increase in the C content against 16.23% in the case of wheat straw when torrefied at 300 W for 20 min. Both H/C and O/C decreased with increase in power and reaction time. The energy density increased by 14-15% in wheat straw and 21-23% in barley straw under suitable reaction condition. Mass and energy yields were 64.04-97.83% and 73.78-98.4%, respectively for wheat straw. In barley straw, mass and energy yields were 42.66-90.34% and 52.49-97.27%, respectively. Moisture content of the biomass did not affect the reaction much and the mass yields were comparable between different moisture content. Grindability of the biomass material improved significantly after torrefaction. The particle size ratio between torrefied and untreated straw after grinding was 0.66 and 0.61 for wheat and barley, respectively. The torrefied biomass was more hydrophobic and the moisture uptake was reduced by 61-68% under suitable torrefaction condition. Microwave irradiation can be used effectively for torrefaction of the two biomass residues at moderate power and short process time.

Keywords: Torrefaction, microwave, wheat straw, barley straw, elemental composition

INTRODUCTION

In recent years biomass has been sought after as a major source of renewable energy. Biomass is a source of sustainable carbon neutral energy and has potential to play an important role in the future. Biomass is by far the most important source of renewable energy today, accounting for about 10% of total primary energy use and 78% of total renewable energy (IEA, 2010). Among all the types of biomass sources, agricultural residues are the most promising in terms of their abundance and non-association with the food versus fuel problem (Tabil et. al, 2011). Many agricultural residues are poorly utilized and often burnt in open fields causing massive air pollution. However, these valuable resources can be converted to green chemicals and biofuels with the use of suitable technologies. There are many thermo-chemical conversion technologies, including carbonization, torrefaction, pyrolysis, and gasification, that have been researched and developed to treat the agricultural waste (Mckendry, 2002). The products of these methods can be further upgraded into various useful biofuels to generate heat and electricity (Huang et.al, 2012).

Untreated biomass materials are known to possess certain disadvantages such as high water content, hydrophilic nature, low calorific value, low energy density, poor grindability, high transportation cost due to high bulk, low combustion efficiency, and thermal instability during combustion because of high oxygen content. Torrefaction is one of the pretreatment methods which can address most of these inherent issues and upgrade untreated biomass to a higher quality and more attractive biofuel (Sadaka and Negi, 2009). Torrefaction is a relatively mild thermo-chemical treatment of biomass carried out at low temperature range

of 200 to 300°C at atmospheric pressure under inert atmospheric conditions. The heating rates are usually kept below 50°C/min (Huang et. al., 2012). It helps remove water and low-molecular-weight organic volatiles and converts biomass materials into high quality fuels with low water content, low O/C ratio, and high energy density. In addition, it makes the biomass brittle and improves its grindability (Stelt et. al, 2011; Wang et. al, 2011; Medic et. al, 2012). Furthermore, torrefied biomass can be utilized as a solid fuel for home or industry use. It can also be co-fired with coal in a pulverized coal-fired boiler (Bergman et al., 2005). Torrefied products are hydrophobic, which makes them convenient for storage and transportation (Ibrahim et. al, 2012). Moreover, high energy torrefied pallets can also be made from torrefied biomass (Pirraglia et. al, 2013).

In recent years, there have been several studies on the torrefaction of biomass. Most of the studies used electric heating (conventional heating method) as the heating source. The effects of various processing temperature and processing time on torrefaction of biomass were discussed (Felfli et.al, 2005; Arias et.al, 2008; Bridgeman et. al, 2008; Couhert et. al, 2009; Deng et. al, 2009). In general, conventional heating-based torrefaction requires longer processing time. In conventional heating, energy is transferred to the material through three modes viz., conduction, convection, and radiation from outside to the inside of materials. However, microwave irradiation provides an alternative method of heat transfer in addition to these three heat transfer modes. Its frequency is usually in the range of 300 MHz and 300 GHz with corresponding wavelength between 1 m and 1 mm, respectively. Not all materials can absorb microwaves. According to the interaction with microwaves, materials can be classified into three types: insulators (transparent), conductors (reflective), and dielectrics (absorptive). Therefore, microwave heating can be regarded as dielectric heating. Heat is generated by the molecular rotation and friction induced by the microwave radiation. Because of the difference in how heat is being generated, microwave heating has many potential advantages in processing materials. Additionally, microwave heating provides shorter reaction time, accurate control, prevents undesirable secondary reactions that lead to formation of impurities, and provides volumetric heating with good penetration depth (Miura et al., 2004; Leonelli and Mason, 2010). Microwave heating is a selective, rapid, uniform, and energy-saving method without direct contact with the heated material (Jones et al., 2002). However, more polar components will absorb more energy, and thus, "hot spots" will be created in non-homogeneous materials like biomass. It is hypothesized that this unique heating feature results in an "explosion" effect in the particles and improves the disruption of the lignocellulosic structures (Tabil et. al, 2011).

Microwave technology has been applied for various purposes, such as chemical synthesis, digestion, extraction, drying, cooking, pyrolysis, etc. (Wang et. al, 2012; Huang et. al, 2012). Microwave induced torrefaction of some biomass like rice husk and sugar cane residue (Wang et. al, 2012), rice straw and pennisetum (Huang et. al, 2012), sugarcane bagasse (Chen et. al, 2012) and corn stover (Ren et al, 2011; Tumuluru et. al, 2012) have been reported in the last few years. In these studies, the effect of different experimental conditions viz., microwave power level, processing time, biomass particle size and water content of biomass on torrefied biomass characteristics and reaction kinetics have been

investigated. As per the literature review, there are no reports of any study on microwave induced torrefaction of wheat and barley straw.

The aim of the present research is to study the process of microwave induced torrefaction of wheat and barley straw at different experimental conditions viz., microwave power level, reaction time and raw biomass moisture content. In addition, the effect of microwave torrefaction on the characteristics of torrefied products, grinding performance, and hydrophobicity was tested.

MATERIAL AND METHODS

Crop residues

Wheat and barley straws in square bales were obtained from an experimental farm near Saskatoon, Saskatchewan, Canada. The bales were of standard dimension of 1:00 × 0.45 × 0.35 m with moisture content of 5.1% (wb) for wheat and 5.8% (wb) for barley. The straws were shredded by a hammer mill (Brookdale, St. Maywood, NJ) using a screen size of 3.2 mm. A dust collector (House of Tools, Model no. DC-202B, Saskatoon, SK) was connected to the outlet of the hammer mill to control dust during operation, provide flowability of chopped biomass through the hammer mill, and collect the ground biomass. The geometric mean particle diameter of wheat straw grinds was determined as per ASABE standard test method S319.3 (2008). A Ro-Tap sieve shaker (W. S. Tyler Inc., Mentor, OH) was used for particle size analysis. U.S. sieve numbers 16, 20, 30, 50, 70 and 100 (sieve opening sizes: 1.190, 0.841, 0.595, 0.297, 0.210 and 0.149 mm, respectively) were used for the analysis. The mean geometric particle size of wheat and barley straw grinds were 0.858 ± 0.001 mm and 0.873 ± 0.004 mm, respectively.

The raw biomass was conditioned to the desired moisture content of 10% (db) and 15% (db) by spraying water uniformly into the straw grinds. The wetted material was placed in a plastic bag and stored in a controlled environment chamber at 22°C for one week for moisture equilibration prior to experiments. The proximate analysis of the straw was carried out in accordance with ASTM standard procedures D3172 (2007). The ultimate analysis was done using an elemental analyser (Elementar-Vario EL III, Germany). The lignocellulosic composition was tested at the Department of Animal and Poultry Science Laboratory, University of Saskatchewan, Saskatoon, SK, Canada. In the analysis, moisture and dry matter content was determined by AOAC standard method 930.15 (2000). Lignin content, ADF and NDF were determined as per ANKOM method 08 (2005), ANKOM Method 5 (2006a) and ANKOM Method 6 (2006b) on a dry matter basis. Cellulose content was calculated as ADF minus lignin content and hemicellulose content was calculated as NDF minus ADF. The higher heating value (*HHV*) of the straw samples were calculated from their C, H and N contents in a dry basis, using the following expression, as derived by Friedl et. al (2005).

$$HHV = 3.55C^2 - 232C - 2230H + 51.2\, x\, Cx\, H + 131N + 20600 \qquad (1)$$

The general composition of wheat and barley straw is shown in Table 1. The compositions of both the biomass are similar. The hemicellulose content and volatiles are higher in barley straw than wheat straw. From Table 1, it can be observed that the combustible content (fixed carbon and volatiles) and *HHV* of both wheat and barley straw are very close.

Table 1: General composition of wheat and barley straw on a dry matter basis.

	Wheat straw	Barley straw
Moisture, wt.% (wb)	5.1	5.8
Dry matter, wt.%	94.9	94.2
Proximate analysis (wt. %)		
Volatiles	69.41	71.2
Fixed carbon	30.59	28.8
Ash	10.86	8.11
Fiber analysis (wt. %)		
Cellulose	41.53	37.77
Hemicellulose	22.92	26.34
Lignin	12.26	8.93
Ultimate analysis		
Carbon (C)	44.77	44.53
Hydrogen (H)	5.93	5.75
Nitrogen (N)	0.693	1.091
Sulphur (S)	0.149	0.165
Oxygen (O)[b]	37.60	40.35
Higher Heating Value (Mj/kg)	17.79	17.74

[b]calculated by difference as per ASTM D3176 (2009)

Torrefaction experimental set-up and procedure

The experimental setup used in the present study is shown in Fig. 1. The set up was developed using a bench top microwave convection oven with 2.45 GHz (LBM 1.2A/7296, Cober Electronics Inc, Stamford, Connecticut) for conducting experiments. The microwave power can be varied from 0 -1200 W through a power percent controller toggle switch located at the front panel. The power is indicated on an analog watt meter on the microwave control panel. Uniform heating is achieved through a mode stirrer which distributes the microwaves inside the cavity and minimizes reflected power. A custom-made cylindrical quartz container of 140 mm diameter and 108 mm height was used as the reactor (Fig. 1A). The container is made airtight by putting a lid on top of the container and a close fitting rubber 'O' ring in between. The joint was further sealed using paper tape. The container has one exhaust port on the side of the cover lid and three ports at the bottom of the side wall for thermocouple and nitrogen purging. A high temperature transition joint K-type thermocouple probe with a UTC-USB thermocouple connector

(Omega Engineering, Inc. Canada) with a measurement accuracy of ± 0.5°C was used for temperature measurement. The temperature data was recorded continuously on a laptop computer using the TRH Central data logging software (version 1.03.12.224, Omega Engineering, Inc., Stamford, Connecticut). The thermocouple was introduced in to the center of the sample through one port on the reactor bottom. The exhaust port at the top was connected with Teflon tubing to the condenser.

About 70±0.05 g biomass was placed in the reactor for each experiment. Nitrogen gas was purged through one of the bottom ports of the reactor at a constant rate of 50 ml/min using a flow meter. Nitrogen gas was continuously purged for about 20 min before the start of each experiment and continued throughout the process. The carrier gas kept purging until the solid residues were cooled down to 80°C before removal and placement in the desiccators. In this study, three experimental parameters viz., microwave power level, reaction time, and moisture content of biomass were varied. The details of the operating conditions selected based on preliminary trials are given in Table 2. The mass of the torrefied biomass was recorded after cooling down to room temperature. Then the samples were placed in air tight plastic bags and stored in room temperature for further analysis. The weight of condensable volatiles yield was also recorded.
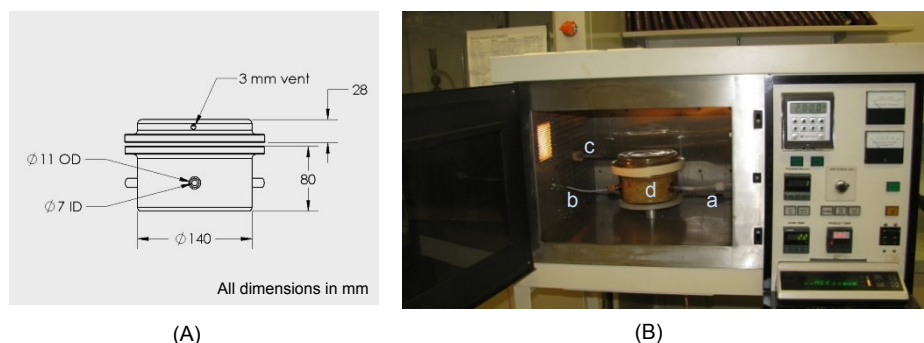

(A)   (B)

Fig. 1: The torrefaction reactor (A) and the experimental set-up (B) for the microwave torrefaction
(a: Nirogen gas supply; b: thermocouple; c: Exhaust tube; d: reactor with biomass)

Table 2: Operating conditions for microwave induced torrefaction of wheat and barley straw.

Experimental parameters	Levels
Microwave power (W)	200, 250, and 300
Reaction time (min)	10, 15 and 20
Moisture content (% db)	5, 10 and 15

Analytical methods

The moisture content of all the treated samples were determined by standard oven drying at 103±2°C for 24 h. The CHNS content of the torrefied samples were determined by ultimate analysis using the elemental analyser (Elementar-Vario EL III, Germany). The higher heating value (HHV) of the straw samples were calculated from their C, H and N

contents in a dry basis, using eq. (1), which was derived by Friedl et. al (2005). The ash content of the torrefied samples was determined in accordance with the American Society of Materials and Testing (ASTM) standard D3174 (2012)

Mass and energy yield

The energy yield of torrefied biomass is considered as a useful assessment of the process and can be calculated from mass yield, as described by Bridgeman et al. (2008) and Bridgeman et al. (2010). The mass yield (η_m), energy density ratio (ER) and energy yield (η_e) were calculated by using equation 2-4:

$$\eta_m = \left(\frac{m_{treated}}{m_{raw}}\right) \times 100 \tag{2}$$

$$ER = \left(\frac{HHV_{treated}}{HHV_{raw}}\right) \tag{3}$$

$$\eta_e = \eta_m \times ER \tag{4}$$

where, $m_{treated}$ and m_{raw} are the mass of the torrefied solid mass and the raw sample mass in dry basis respectively. The $HHV_{treated}$ and HHV_{raw} are the heating values calculated using eq. (1) on dry basis.

Grinding performance of the torrefied biomass

Torrefaction is believed to improve the grindability of the tenacious biomass. Mani et. al (2004) studied the grinding performance of barley straw, corn stover and switchgrass in terms of the specific energy consumption and particle size distribution. Chen et. al (2011) used particle size distribution of the torrefied biomass after grinding in a knife mill as a standard method to describe the grindability of the product. Arias et.al (2008) evaluated the grindability characteristics of the torrefied eucalyptus with respect to the original material by grinding in a cutting mill with a bottom sieve of 2 mm and then analysing the particle size distribution by sieving. Phanphanich et al. (2011) used a laboratory heavy-duty knife mill (Retsch SM 2000, Germany) in the grinding experiments of torrefied wood chips with a bottom sieve opening of 1.5 mm. Some researchers determined the Hardgrove Grindability Index (HGI) using a standard Hardgrove grinder and compared with samples of coal with known HGI (Shang et. al, 2012; Ibrahim et. al, 2012). However, the particle size distribution of the grind material was also assessed to give a greater insight into their grindability behavior, using the method described in Bridgeman et al. (2010). In the present study, about 30±0.05 g of the torrefied samples were ground using a knife mill (Dietz-motoren GmbH7&Co., Germany) using a screen size of 1.5 mm. The material was ground for 120 s and care was taken to uniformly feed the material through the feeding chute. The grinds were then analyzed for particle size distribution using standard Canadian sieve numbers 30, 40, 50, 60, 70 and 100 (595, 425, 297, 250, 210 and 150 μm, respectively) and a Ro-Tap sieve shaker (W. S. Tyler Inc., Mentor, OH). The particle size analysis was carried out and the geometric mean particle diameter was determined as per ASABE standard test method S319 (2008). The grinding performance of the torrefied samples was compared with that of the untreated biomass.

Hydrophobicity test

Many studies on torrefaction reported that torrefaction enhances the hydrophobic characteristics of biomass; however, no standardized method exists yet for hydrophobic testing of biomass. Pimchuai et al. (2010) reported a hydrophobic test by immersing raw and torrefied biomass in water for 120 min, allowed to dry and determined the weight change as a measure of moisture absorption. Ibrahim et al. (2012) compared the hydrophobicity of the torrefied mass by immersing approximately 0.5 g of biomass (particle size < 1 mm) in deionised water at room temperature in a sintered glass filter for two hours, followed by air drying for an hour, prior to the determination of its moisture content. Acharjee et al. (2011) studied the water uptake in torrefied biomass by determining the equilibrium moisture content at relative humidity ranging from 11% to 97% at a constant temperature of 30°C. In the present study, the raw and torrefied samples were oven dried at 105°C for 24 h. About 2 g of the dried samples were taken in aluminum containers and kept in a controlled environment system (Angelantoni Climatic Systems, Italy) at constant temperature of 30°C and 95% RH for 72 h. The final weights of the samples were measured to assess the moisture uptake.

RESULTS AND DISCUSSION

Microwave heating depends on the dielectric properties of the material. High microwave frequencies and large values of the dielectric properties result in surface heating, while low frequencies and small values of dielectric properties result in more volumetric heating (Clark et al., 2000). In the present study, volumetric heating of the biomass materials was observed. The biomass colour changed to dark brown to black with increasing power level and reaction time.

Temperature profiles

Due to selective nature of the microwave heating mechanism, the primary task was to test whether wheat straw and barley straw are proper dielectric materials or not and to assess the heating characteristics. Initially torrefaction was tried at 150 W but the temperature barely reached 220ºC even after 30 min. Therefore, the reaction was tried at 200, 250, 300 and 400 W for wheat straw. The temperature profiles and heating rates are shown in Fig. 2 and Fig. 3. The temperature at 400 W increased rapidly to more than 450ºC in about 5 min with initial heating rates varying from 74-134ºC/min, which was high as per the torrefaction requirement. The maximum temperatures of 242, 381 and 401ºC were achieved as microwave power level was increased from 200 to 300 W. The heating rates were below 50ºC/min for most of the time at all of these power levels. The heating rates increased with increase in power level. In view of the above, barley straw samples were also tried at 200 to 300 W power levels. The temperature profiles and heating rates are shown in Fig. 4 and Fig. 5. The heating rates in the initial five minutes varied from 58-16ºC/min, 73-22C/min and 109-25ºC/min in barley straw at 200, 250, and 300 W respectively, which were higher as compared to that of the wheat straw. Consequently, the maximum temperatures were also higher in barley straw than wheat straw. The temperatures were as high as 406, 420, and 396ºC at 200, 250, and 300 W respectively in about 20, 13, and 10 min time respectively. This shows that barley straw has better microwave absorbance than wheat

straw. Further experiments were conducted at three power levels: 200, 250, and 300 W and three reaction times: 10, 15, and 20 min.
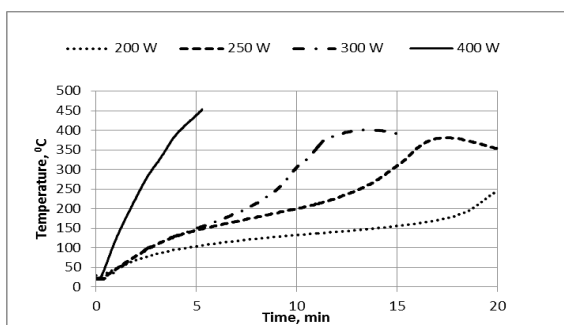

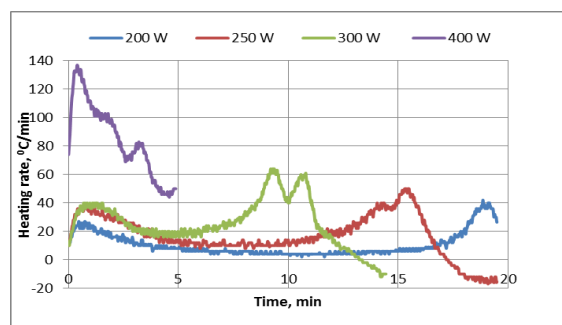Fig. 2: Temperature profiles of wheat straw at various microwave power levels.

Fig. 3: Heating rate profiles of wheat straw at various microwave power levels.
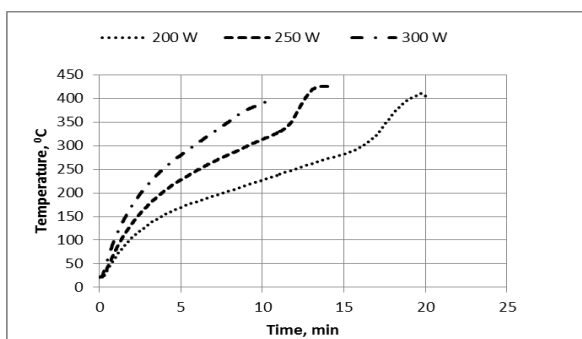

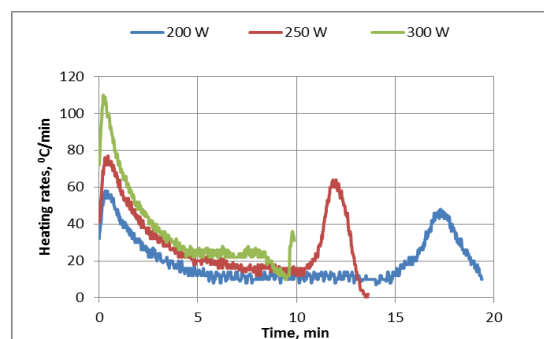Fig. 3: Temperature profiles of barley straw at various microwave power levels.

Fig. 4: Heating rate profiles of barley straw at various microwave power levels.

Composition of torrefied biomass

The composition of torrefied biomass is presented in Table 3. The results indicate that with the increase of power and reaction time, the torrefied product became increasingly dry but with some residual moisture. The C content increased, whereas, the H and O content decreased with increase in power and reaction time, which is due to removal of volatiles. The C content increased by 16.23% and 29.08% in wheat and barley straw, respectively when torrefied at 300 W for 20 min. This shows that barley straw tended to carbonize more under microwave irradiation, which is also supported by the temperature profiles discussed earlier. Hence, both H/C and O/C ratios decreased with increasing microwave power levels. The atomic H/C and O/C ratios of untreated wheat straw were 0.13 and 0.84 and those of untreated barley straw were 0.13 and 0.91, respectively. After torrefaction at 300 W microwave power levels for 20 min processing time, the atomic H/C and O/C ratios of torrefied wheat straw were 0.10 and 0.49, and those of torrefied barley straw were 0.07 and 0.41, respectively. Low H/C and O/C ratios may contribute to less smoke and water–

vapor formation and reduced energy loss during combustion and gasification processes (Tumuluru et al., 2011). These characteristics are quite similar to rice husk, while wheat and barley straw seems to be less torrefied as compared to sugarcane bagasse in similar power levels as reported by Wang et al. (2011).

Table 3: Composition of torrefied wheat and barley straw

Reaction condition	Moisture (wt. %)	ash (wt.%)[a]	Ultimate composition[a]					H/C	O/C
			C	H	N	S	O[b]		
Wheat straw									
Untreated	5.1	10.86	44.77	5.93	0.693	0.149	37.60	0.13	0.84
300 W,10 min	3.58	12.74	49.03	6.12	0.807	0.260	31.04	0.12	0.63
300 W,15 min	2.44	13.61	50.71	5.96	0.851	0.220	28.65	0.12	0.56
300 W,20 min	1.55	16.25	52.04	5.16	0.861	0.174	25.51	0.10	0.49
250 W,10 min	3.75	13.32	46.89	5.73	0.763	0.174	33.13	0.12	0.71
250 W,15 min	3.56	14.58	50.41	5.33	0.870	0.156	28.65	0.11	0.57
250 W,20 min	2.00	14.71	51.03	5.33	0.872	0.167	27.89	0.10	0.55
200 W,10 min	4.02	11.86	45.08	5.77	0.667	0.287	36.34	0.13	0.81
200 W,15 min	2.59	9.74	46.59	5.76	0.748	0.167	37.00	0.12	0.79
200 W,20 min	3.04	11.02	48.55	5.59	0.790	0.157	33.89	0.12	0.70
Barley straw									
untreated	5.81	8.11	44.53	5.75	1.091	0.165	40.35	0.13	0.91
300 W,10 min	4.10	10.52	46.49	5.69	1.262	0.174	35.87	0.12	0.77
300 W,15 min	5.43	17.15	57.48	3.80	1.436	0.323	19.81	0.07	0.34
300 W,20 min	3.60	15.22	56.02	4.01	1.374	0.248	23.14	0.07	0.41
250 W,10 min	5.03	7.11	45.82	5.67	1.271	0.221	39.92	0.12	0.87
250 W,15 min	4.97	12.76	49.37	5.22	1.286	0.153	31.21	0.11	0.63
250 W,20 min	4.42	12.13	48.83	5.40	1.362	0.164	32.12	0.11	0.66
200 W, 10 min	4.65	9.49	44.57	5.82	1.201	0.307	38.61	0.13	0.87
200 W, 15 min	4.20	10.29	48.30	5.63	1.340	0.199	34.24	0.12	0.71
200 W, 20 min	3.40	11.80	47.69	5.66	1.332	0.171	33.35	0.12	0.70

a: dry basis; b: calculated by difference

Torrefaction products, mass and energy yield

The details of solid mass yield, condensable liquids, and non-condensable gases along with the energy yield, all in dry matter basis, of the solid mass are presented in Table 4. From Table 4, it can be observed that both mass and energy yield of torrefied biomass decreased with increase in microwave power and reaction time. This low mass yield at higher microwave power may be explained due to high weight loss resulting from drying, volatilization, and decomposition of biomass feedstock (Huang et. al. 2012). The energy density increased by 14-15% in wheat straw torrefied at 300 W and 15-20 min process time with corresponding decrease in mass yield of 66.29-64.04% and energy yield of 75.49-

73.78%. For barley straw, energy density was found to increase by 21-23%, which was higher than wheat straw but with reduced mass yield of 21.48-21.89% and energy yield of 52.49-53.23% at 300 W and 15-20 min processing time. The energy yield in barley at 250 W is comparable to that of wheat straw at 300 W. A similar type of negative effect of microwave power and processing time on mass and energy yield has been reported by Wang et al. (2012) for microwave torrefied rice husk and sugarcane residues. From Table 1, the highest liquid yield of 20.92% in wheat and 21.91% in barley was observed at operating conditions of 300 W/20 min and 300 W/15 min, respectively. It can also be observed from Table 4 that at operating conditions of 250 W/ 20min., more than 70% of mass and 75% of energy has been retained in the solid torrefied biomass and about 30% of mass and 25% of energy was shifted to liquid and gaseous products for both biomass. At this operating condition, the energy density increased by 13% and 9% for torrefied wheat and barley straw, respectively.

Table 4: Torrefaction products, mass yield (η_m), energy ratio (ER), and energy yield (η_e) for wheat and barley straw.

Operating condition	η_m	HHV[a] (Mj/kg)	ER	η_e	Liquid yield[a] (wt %)	Gas yield [a,b] (wt %)
Wheat straw						
Untreated	100	17.79	1.00	100	-	-
300 W,10 min	81.28	19.58	1.10	89.46	7.64	11.08
300 W,15 min	66.29	20.26	1.14	75.49	11.94	21.77
300 W,20 min	64.04	20.50	1.15	73.78	20.92	15.04
250 W,10 min	89.34	18.61	1.05	93.43	3.98	6.68
250 W,15 min	75.53	19.91	1.12	84.54	11.87	12.60
250 W,20 min	74.17	20.16	1.13	84.05	15.26	10.57
200 W,10 min	97.83	17.89	1.01	98.40	0.12	2.05
200 W,15 min	92.72	18.49	1.04	96.37	3.71	3.57
200 W,20 min	80.33	19.24	1.08	86.88	12.20	7.47
Barley straw						
Untreated	100	17.74	1.00	100	-	-
300 W,10 min	83.93	18.51	1.04	87.55	5.61	10.47
300 W,15 min	42.66	21.89	1.23	52.49	21.91	35.43
300 W,20 min	44.08	21.48	1.21	53.23	19.74	36.17
250 W,10 min	90.34	18.25	1.03	92.66	3.62	6.04
250 W,15 min	64.18	19.52	1.10	70.43	16.45	19.37
250 W,20 min	70.11	19.37	1.09	76.33	17.25	12.65

200 W, 10 min	97.37	17.77	1.00	97.27	2.25	0.38
200 W, 15 min	80.86	19.22	1.08	87.37	10.72	8.42
200 W, 20 min	79.56	18.98	1.07	84.89	9.98	10.47

a: dry basis; b: calculated by difference (100 - η_m-liquid yield)

Regression analysis between mass yield (100% for untreated biomass) and energy ratio (ER) produced linear relationship given in eq. (5) and eq. (6) for wheat and barley straw, respectively. Strong negative correlation was found between the two parameters with correlation coefficient of 0.98 for both the biomass residues.

$$ER_W = 1.44 - 0.004\eta_m \qquad\qquad (R^2 = 0.97) \qquad\qquad (5)$$

$$ER_B = 1.38 - 0.004\eta_m \qquad\qquad (R^2 = 0.96) \qquad\qquad (6)$$

where, ER_w and ER_B are energy ratios for wheat and barley straw, respectively and η_m is mass yield in weight percentage in dry basis.

Effect of moisture content of biomass on torrefaction temperature and mass yield

Water molecule is polar in nature and considered as a good microwave radiation absorber. Hence, water content in the biomass may help in the heating and reactions. Wheat straw and barley straw at 10% and 15% moisture content on dry basis were torrefied at 200-300 W for 15-20 min of process time. The temperature profile of wheat straw at 15% moisture is shown in Fig. 5. The temperatures were higher as compared to wheat straw (untreated, 5.1% moisture content) shown earlier in Fig. 1. The initial heating rates in the first minute varied from 108-139°C/min, 119-144°C/min and 133-173°C/min for microwave power levels of 200, 250 and 300 W respectively. The heating rates were considerably higher than that of wheat straw at 5.1% moisture content. Mass yield is an indicator of the severity of the torrefaction reaction. Mass yield at various reaction conditions for wheat and barley straw at 10% and 15% moisture content is presented in Table 5. The torrefaction of wheat straw at higher moisture is less severe in all the tested reaction conditions except at 300 W for 20 min. However, considerable reduction in mass yield was noted in the case of barley straw when torrefied at 300 and 250 W for 20 min. The mass yield at 10% moisture content is less than the mass yield at 15% at higher power and higher reaction time. The energy is absorbed by the water for vaporization.
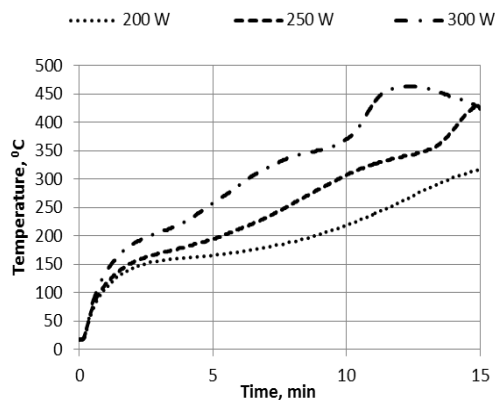

Fig. 5: Temperature profiles during microwave   heating
of wheat straw (15% moisture content)

Table 5. Mass yield of wheat and barley straw at different moisture contents (dry basis) after torrefaction.

Reaction condition	Mass yield (% dry basis)					
	Wheat			Barley		
Moisture content ➡	5.3%	10%	15%	6.2%	10%	15%
300 W, 15min	66.29	66.72	68.70	42.66	49.44	50.36
300 W, 20 min	64.04	64.41	67.62	44.08	34.39	35.88
250 W, 15min	75.53	80.77	74.97	64.18	60.80	71.03
250 W, 20min	74.17	72.99	70.73	70.11	39.85	49.34
200 W, 15min	92.72	98.52	98.46	80.86	92.77	95.17
200 W, 20 min	80.33	85.42	83.45	79.56	71.18	77.40

Grinding performance

The raw and torrefied biomass were ground as per the procedure detailed earlier in the methodology section of this article. The geometric mean diameter (GMD) of the wheat and barley straw torrefied under different reaction conditions after grinding test is presented in Table 6. The size reduction ratio is defined as the ratio between GMD of treated samples to the GMD of untreated sample. The size reduction ratio signifies the grindability of the biomass. The data clearly indicates that the GMD decreases with increase in power and reaction time in both wheat and barley straw indicating improvement in the grindability of the material after torrefaction.

Table 6. Geometric Mean Diameter (GMD) of torrefied wheat and barley straw after grinding test.

Reaction condition	GMD (µm)		Size reduction ratio	
	Wheat straw	Barley straw	Wheat straw	Barley straw
Untreated	386	355	-	-
300 W,10 min	316	294	0.82	0.83
300 W,15 min	268	218	0.70	0.61
300 W,20 min	253	218	0.66	0.61
250 W,10 min	315	316	0.82	0.89
250 W,15 min	281	273	0.73	0.77
250 W,20 min	274	267	0.71	0.75
200 W,10 min	334	348	0.86	0.98
200 W,15 min	305	280	0.79	0.79
200 W,20 min	293	293	0.76	0.83

Hydrophobicity

The data of moisture uptake by the untreated and torrefied samples of untreated wheat and barley straw is presented in Table 7. The moisture uptake ratio was calculated by dividing the moisture content of untreated sample by moisture content of treated samples. Lower

moisture uptake ratio indicates higher hydrophobic nature of the product. The moisture uptake decreased with the increase in microwave power level and reaction time. The moisture uptake ratio decreased considerably after torrefaction at 300W and 15-20 min reaction time both for wheat and barley. The torrefied products became more hydrophobic in nature after torrefaction. Xingjun Li et.al (2011) reported equilibrium moisture content of untreated wheat straw 4.2-34.2% over a wide range of relative humidity (11.3-96.0%) and temperature (10-35 ^{0}C). Acharjee et. al (2011) reported equilibrium moisture content of untreated and torrefied Loblolly pine biomass. The EMC attained after 9-15 days for torrefied biomass was 5.3-12.8% as against 15.6% for untreated biomass at 83.6% RH and 30 ^{0}C temperature.

Table 7. Moisture content (MC) and moisture uptake ratio of wheat and barley straw after hydrophobicity test

Reaction condition	Wheat straw		Barley straw	
	MC (% dry basis)	Moisture uptake ratio	MC (% dry basis)	Moisture uptake ratio
Untreated	18.36	1.00	20.4	1.00
300 W,10 min	13.83	0.75	14.21	0.70
300 W,15 min	8.29	0.45	7.14	0.35
300 W,20 min	7.25	0.39	6.54	0.32
250 W,10 min	15.32	0.83	15.60	0.76
250 W,15 min	10.13	0.55	12.71	0.62
250 W,20 min	9.21	0.50	10.21	0.50
200 W,10 min	15.22	0.83	19.13	0.94
200 W,15 min	13.80	0.75	16.06	0.79
200 W,20 min	12.67	0.69	13.58	0.67

CONCLUSIONS

Microwave irradiation can effectively be used for torrefaction of wheat and barley straw. Microwave power and reaction time should be the primary parameters to be considered. Moisture of the biomass does not affect the process as much as other parameters at moderate power levels. Barley straw is more easily torrefied than wheat straw under similar reaction conditions. Power levels are suggested to be set between 250-300 W for wheat straw and 200-250 W for barley straw and torrefaction should be carried out for 15-20 min. Microwave torrefaction significantly improved the fuel characteristics like H/C, O/C, HHV, energy density of the samples. There is a mass and energy loss in the process, which may be recovered by the suitable utilization of liquid and gaseous products. The grindability and hydrophobicity of the biomass improved greatly by torrefaction. However, hot spots and localized initiation of the reaction was observed in the samples, which is due to the selective heating mechanism in microwave irradiation and the non-homogenous nature of biomass.

REFERENCES

Acharjee, T.C., C.J. Coronella and V.R. Vasquez. 2011. Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass. Bioresource Technology 102: 4849–4854

ANKOM Method 5. 2006a. Acid Detergent Fiber in feeds-filter bag technique. ANKOM technology. Macedon, New York

ANKOM Method 6. 2006b. Neutral Detergent Fiber in feeds-filter bag technique. ANKOM technology. Macedon, New York

ANKOM Method 8. 2005. Determining Acid Detergent Lignin in beakers. ANKOM technology. Macedon, New York

ANSI/ASAE S319.3 (2003) Method of Determining and Expressing Fineness of Feed Materials by Sieving.

AOAC method 930.15. 2000. Loss on drying (moisture) for feeds (at 135°C for 2 hours)/dry matter on oven drying for feed (at 135°C for 2 hours) official methods. Official methods of analysis. 17th Ed., AOAC International, Gaithersburg, MD

Arias B., C. Pevida, J. Fermoso, M.G. Plaza, F. Rubiera and J.J. Pis. 2008. Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Process Technology 89: 169-75.

ASTM D3172. 2007. Standard practice for proximate analysis of coal and coke

ASTM D3174. 2012. Standard test method for ash in the analysis sample of coal and coke from coal.

Bridgeman T.G., J.M.Jones, I. Shield., and P.T. Williams. 2008. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel 87: 844-56.

Bridgeman, T.G., J.M. Jones, A. Williams, and D.J. Waldron. 2010. An investigation of the grindability of two torrefied energy crops, Fuel 89(12): 3911–3918.

Chen, W., H. Hsu, K. Lu, W. Lee and T. Lin. 2011. Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass. Energy 36: 3012-3021

Chen, W.H., S.C. Ye, and H. K. Sheen. 2012. Hydrothermal carbonization of sugarcane bagasse via wet torrefaction in association with microwave heating. Bioresource Technology 118: 195–203

Clark, D.E., C.F. Diane, and K.W. Jon. 2000. Processing materials with microwave energy. Materials Science and Engineering A287: 153–158

Couhert C., S. Salvador, and J.M. Commandr. 2009. Impact of torrefaction on syngas production from wood. Fuel 88: 2286-90.

Deng J., G.J. Wang, J.H. Kuang, Y.L. Zhang, and Y.H. Luo. 2009. Pretreatment of agricultural residues for co-gasification via torrefaction. J Anal Appl Pyrolysis 86: 331-7.

Felfli F. F., C.A. Luengo, J.A. Suarez, and P.A. Beaton. 2005. Wood briquette torrefaction. Energy Sustain Dev 9: 19-22.

Huang Y.F., W.R. Chen, P.T. Chiueh, W.H. Kuan and S.L. Lo. 2012. Microwave torrefaction of rice straw and pennisetum. Bioresource Technology 123: 1–7

Ibrahima R.H.H., I. D. Leilani, J.M. Jonesa, and A.Williams. 2012. Physicochemical characterisation of torrefied biomass Journal of Analytical and Applied Pyrolysis (article in press)

International Energy Agency (IEA). 2010. Energy Technology Perspectives. OECD/IEA, Paris.

Jones, D.A., T.P. Lelyveld, S.D. Mavrofidis, S.W. Kingman, and N.J. Miles. 2002. Microwave heating applications in environmental engineering–a review. Resour. Conserv. Recycl 34: 75–90.

Leonelli, C. and T.J. Mason. 2010. Microwave and ultrasonic processing: Now a realistic option for Industry. Chemical Engineering and Processing Journal 49(9): 885 – 900.

Li, X., Z. Cao, Z. Wei, Q. Feng, and J. Wang. 2011. Equilibrium moisture content and sorption isosteric heats of five wheat varieties in China. Journal of Stored Products Research 47: 39-47

Mani, S., L.G. Tabil, and S. Sokhansanj. 2004. Grinding performance and physical properties of wheat and barley straws,corn stover and switchgrass. Biomass and Bioenergy 27: 339 – 352

Mckendry, P. 2002. Energy production from biomass (part 2): conversion technologies. Bioresource Technology 83: 47-54.

Medic D., M. Darr, A. Shah, B. Potter and J. Zimmerman. 2012. Effects of torrefaction process parameters on biomass feedstock upgrading. Fuel 91: 147–154

Miura M., H. Kaga, A. Sakurai, T. Kakuchi, and K. Takahashi. 2004. Rapid pyrolysis of wood block by microwave heating. Journal of Analytical and Applied Pyrolysis 71: 187–199.

Phanphanich, M. and S. Mani. 2011. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. Bioresource Technology 102: 1246–1253

Pimchuai A., A. Dutta, and P. Basu. 2010. Torrefaction of agricultural residue to enhance combustible properties. Energy Fuel Journal 24(9): 4638–4645.

Pirraglia A., R. Gonzalez, D. Saloni, and J. Denig. 2013. Technical and economic assessment for the production of torrefied ligno-cellulosic biomass pellets in the US. Energy Conversion and Management 66: 153–164

Ren, S., H. Lei, J. Julson, L. Wang, Q. Bu, and R. Ruan. 2011. Microwave Torrefaction of Corn Stover. Paper Number: 1110765. ASABE Annual International Meeting. Kentucky, August 7 – 10, 2011

Sadaka, S., and S, Negi. 2009. Improvements of biomass physical and thermochemical characteristics via torrefaction process. Environmental Progress & Sustainable Energy, 28(3): 427–434.

Shang, L., J. Ahrenfeldt, J.K. Holm, A.R. Sanadi, S. Barsberg, T. Thomsen, W. Stelte, and U.B. Henriksen. 2012. Changes of chemical and mechanical behavior of torrefied wheat straw. Biomass and Bioenergy. 40: 63-70

Stelt M.J.C. van der, H. Gerhauser, J.H.A. Kiel and Ptasinski K.J. 2011. Biomass upgrading by torrefaction for the production of biofuels: A review. Biomass and Bioenergy 35: 3748-3762

Tabil L., P. Adapa and M. Kashaninejad. 2011. Biomass Feedstock Pre-Processing – Part 1: Pre-Treatment, Biofuel's Engineering Process Technology, Dr. Marco Aurelio Dos Santos Bernardes (Ed.), ISBN: 978-953-307-480-1, InTech, Available from: http://www.intechopen.com/books/biofuel-s-engineering-processtechnology/ biomass-feedstock-pre-processing-part-1-pre-treatment

Tumuluru, J.S., T. Kremer, C.T. Wright, and R.D. Boardman. 2012. Paper Number: 121337398. Proximate and Ultimate Compositional Changes in Corn Stover during Torrrefaction using Thermogravimetric Analyzer and Microwaves. ASABE Annual International Meeting. Texas. July 29 – August 1, 2012

G.J. Wang, Y.H. Luo, J. Deng, J.H. Kuang, and Y.L. Zhang. 2011. Pretreatment of biomass by torrefaction. Chin. Sci. Bull 56: 1442–1448

Wang, M.J., Y.F. Huang, P.T. Chiueh, W.H. Kuan, and S.L. Lo. 2012. Microwave-induced torrefaction of rice husk and sugarcane residues. Energy 37: 177-184