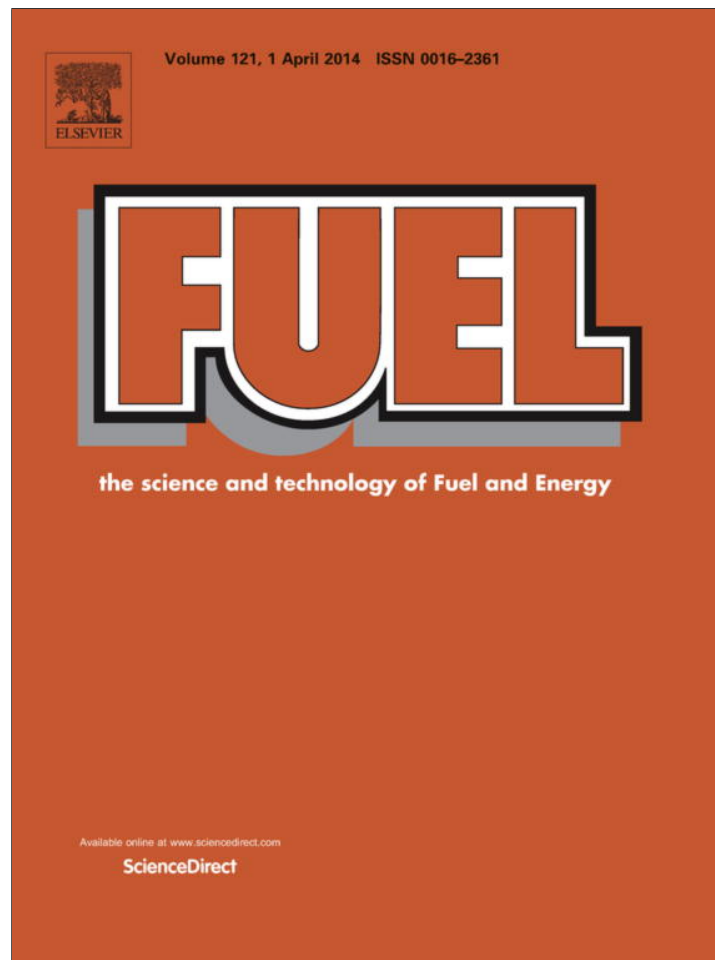


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Impact of torrefaction on properties of *Miscanthus* × *giganteus* relevant to gasification



Gang Xue^{a,c}, Marzena Kwapinska^{a,b}, Witold Kwapinski^{a,c}, Krzysztof M. Czajka^{a,d}, James Kennedy^{a,e}, James J. Leahy^{a,c,*}

^a Department of Chemical and Environmental Sciences, University of Limerick, Ireland

^b Competence Centre for Biorefining & Biofuels, University of Limerick, Ireland

^c Carbolea, University of Limerick, Ireland

^d Energy Engineering and Technology Division, Wrocław University of Technology, Poland

^e Athlone Institute of Technology, Athlone, Co. Westmeath, Ireland

HIGHLIGHTS

- The optimal torrefaction conditions for *Miscanthus* × *giganteus* are 250 °C and 30 min.
- The torrefied M × G has lower moisture and hemicellulose content as well as lower ratio of O/C.
- Torrefied biomass showed more porous structure with larger specific surface area and higher content of alkali metals.

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ABSTRACT

Miscanthus × *giganteus* (M × G) was torrefied to improve its thermal and physical properties prior to thermal conversion. Torrefaction was undertaken at a series of temperatures from 230 to 290 °C for residence times varying from 10 to 30 min and the product biomass was characterized in terms of its suitability as a feedstock for gasification. The properties of the torrefied M × G were improved following treatment. In particular the torrefied biomass showed reduced moisture and hemicellulose content a lower ratio of O/C, a more porous structure with larger specific surface area as well as higher content of alkali metals. All these features have positive effect on gasification reactivity suggesting that the torrefaction process is promising pretreatment method for biomass to combine with gasification or co-firing.

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1. Introduction

Sustainable biomass production for energy conversion is possible in large areas of the world. Currently only a small proportion of available agricultural land is cultivated for energy crops despite the fact that it offers considerable potential to augment rural economic development. A significant impediment to the economic production of biomass is the need to transport a low energy density feedstock long distances to conversion facilities. Pre-treatment of biomass is therefore necessary to increase its energy density for long distance transport [1].

Increasing demand for renewable energy has given rise to biomass energy crops such as *Miscanthus* becoming widely cultivated across Europe. The most common *Miscanthus* species currently

commercially grown is *Miscanthus* × *giganteus*, due to its rapid growth, low mineral content, high biomass yield and favorable carbon balance [2,3]. However raw *Miscanthus* shares the same weaknesses as other biomass, such as low bulk density, low energy density and non-uniform physical and chemical properties, which result in storage complications, lower thermal-conversion efficiency and utilization limitations. The process and efficiency of energy conversion depends on the properties of feedstock. The major challenge with biomass is how to efficiently remove the oxygen from biomass feedstock and convert the biomass into a product with the appropriate thermo-chemical properties. In order to overcome the problems mentioned above, the properties of raw *Miscanthus* need to be modified to improve its usability. Torrefaction is a thermal pre-treatment process that involves heating the biomass to moderate temperatures between 200 °C and 300 °C under an inert atmosphere. It has proven to be an effective method to convert low grade biomass into feedstock with better properties. During torrefaction, the moisture and some light volatiles are

* Corresponding author at: Department of Chemical and Environmental Sciences, University of Limerick, Ireland.

E-mail address: jj.leahy@ul.ie (J.J. Leahy).

released; the hygroscopic biomass is rendered hydrophobic, which makes it more convenient for long distance transport and long term storage [1] and reduces the cost. Torrefaction is also a means of homogenizing the physical and chemical properties of different biomass feedstock's [4].

There have been several recent reports in the scientific literature on the subject of biomass torrefaction. Deng et al. [5] torrefied rice straw and rape stalk at 200, 250 and 300 °C for 30 min and reported that the conversion rate of agricultural residue is higher than that of woody biomass due to the higher volatile matter content in raw biomass. Pimchuai et al. [6] studied the effect of torrefaction temperature and residence time on properties of agriculture residues (rice husk, sawdust, peanut husks, bagasse and water hyacinth). They found that the temperature has a greater impact on the increase in the energy density of the torrefied biomass than the residence time. Moreover, torrefaction improves those properties of biomass that are relevant to combustion; torrefied husk ignites faster and produces a higher bed temperature. Bridgeman et al. [7] came to a similar conclusion by studying the combustion behavior of raw and torrefied reed canary grass, willow and wheat straw. A recent study by Phanphanich et al. [1] reported that torrefaction at 300 °C resulted in a 10-fold reduction in energy consumption for pine chips and 6-fold reduction for logging residue compared to untreated biomass samples. Bridgeman et al. [8] compared the pulverization behavior of torrefied *Miscanthus* and torrefied willow and concluded that willow requires higher temperatures and longer residence times than *Miscanthus* in order to achieve grindability behavior similar to coal. To produce similar physical changes in *Miscanthus* thermal pre-treatment at temperatures around 290 °C were also required but considerably shorter residence time were necessary. Chen and Kuo [9] investigated the torrefaction characteristics of four different biomass feedstock's (bamboo, willow, coconut shell and wood – *Ficus Benjamin*) using thermogravimetry. Their experiments strongly suggest that to achieve a biomass fuel with higher energy density, torrefaction with a residence time less than 1 h is appropriate.

Torrefied biomass can be co-fired with coal [6,7]. However, compared with combustion, gasification technology has higher efficiency, more environmental friendly performance, and is considered to be a very important route for utilization of biomass. Gasification of low quality biomass however results in poor gas quality and high tar concentration. Tar is highly viscous and higher molecular weight volatile organic compound generated during biomass gasification process. In order to address these problems, the biomass needs to be pretreated to improve its quality for efficient energy conversion.

According to Bridgeman et al. [8] and Deng et al. [5] torrefied biomass can be successfully pulverized providing a suitable feedstock for entrained flow gasification or co-gasification with coal. Prins et al. [10] found that torrefied wood can be gasified in a more efficient way than wood in an oxygen-blown entrained flow gasifier. Couhert et al. [11] examined gas yields and reaction kinetics during steam gasification of torrefied beech wood in an entrained flow reactor and found that the torrefied wood produced more H₂ and CO than the virgin feedstock, but the chars from torrefied wood were found to be less reactive towards steam than the char from untreated wood. Fisher et al. [12] compared the reactivity of char samples produced from raw and torrefied willow. They concluded that the combustion and gasification (using H₂O/N₂) reactivity of chars produced from torrefied biomass is lower than that of raw biomass. Min et al. [13] gasified char from pyrolysis of agriculture waste with mixture of CO₂/N₂ and reported that the global char reactivity decreased with the pyrolysis temperature increase.

The objectives of this study were to investigate the impact of torrefaction temperature and residence time on the properties of *Miscanthus × giganteus* with an emphasis on the changes in

biomass characteristics which are relevant to gasification and the possible effects of torrefied fuel properties on gasification.

2. Experimental

2.1. Materials

The biomass feedstock used in this study, *Miscanthus × giganteus*, was supplied by JHM Crops, Ireland. The biomass particle size between 200 μm and 1.5 mm was obtained by sieving the feedstock using BS sieves. Proximate and ultimate properties of raw M × G are presented in Table 3.

2.2. Thermogravimetric analysis and torrefaction experiments

Torrefaction experiments were undertaken both in a horizontal furnace as well as using thermogravimetry.

In order to demonstrate the influence of torrefaction on the lignocellulose composition of biomass, the raw *Miscanthus* was torrefied and pyrolyzed by TGA. Torrefaction and pyrolysis tests were performed using a thermogravimetric analyzer SDT Q600 (TA Instruments). A crucible loaded with 10 mg of *Miscanthus* was placed into the TGA where the dynamics of biomass weight loss was measured and recorded with increasing temperature or time. The temperature was raised from room temperature to torrefaction temperature (230, 250, 270, 290 °C) at 20 °C/min and then held for different lengths of time (10 or 30 min). Subsequently, the temperature was ramped to 800 °C using the same heating rate. All the experiments were conducted in a purge of nitrogen (100 ml/min).

A horizontal furnace (Carbolite CTF 12/65/550) fitted with a thermal controller (Eurothermal 2416) and tubular quartz reactor (950 mm in length and 45 mm id) was also used to torrefy M × G samples. Biomass samples were charged into a cuboid metal mesh container, which was loaded in the reactor at room temperature, before heating at 20 °C/min to the desired temperature under a nitrogen flow.

Mass and energy yield of torrefied M × G were calculated, on a dry ash free basis, according to Eqs. (1) and (2) as proposed by Bergman et al. [14].

$$\text{Mass Yield (wt\%)} = \frac{M_{\text{torrefied}}}{M_{\text{raw}}} \times 100 \quad (1)$$

$$\text{Energy Yield} = \text{Mass Yield} \times \frac{\text{HHV}_{\text{torrefied}}}{\text{HHV}_{\text{raw}}} \times 100 \quad (2)$$

where $M_{\text{torrefied}}$ is the mass of biomass after torrefaction, M_{raw} is mass of untreated biomass, HHV is the high heating value.

2.3. Proximate and ultimate analysis of fuel

The proximate analysis was conducted according to BS EN 14774-1: 2009 (moisture content), BS EN 14775: 2009 (ash content) and BS EN 15148: 2009 (volatile matter content). Ash content and volatile matter content are expressed on a dry basis. Fixed carbon content was calculated according to Basu [15]. Fixed carbon (FC) represents the solid carbon in the biomass that remains after devolatilisation and it is not a fixed quantity; however its value, measured under standard conditions, gives a useful evaluation parameter for a fuel. For gasification, FC is an important parameter because in most gasifiers the conversion of fixed carbon into gases determines the rate of gasification and yield of gaseous products. The C, H, N and S analysis was performed using a Vario EL cube Elemental Analyzer. All measurements were repeated in triplicate and an average value on a dry basis is reported. The results of proximate and ultimate analysis are shown in Table 3. Higher heating

value (HHV) of raw and torrefied M × G was determined according to DD CEN TS 15400-2006 using an Iso-peribol Calorimeter 6200 (Parr Instrument Company).

2.4. Surface area and SEM-EDAX analysis

The surface area analysis was carried out using an ASAP 2010 Physisorption Analyzer (Micromeritics) with CO₂ used as the adsorption gas. Scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDAX) analysis was used to determine the mineral composition of the ash from raw and torrefied Miscanthus. The analysis was performed using an Ultra-High-Resolution Analytical FE-SEM SU-70 (Hitachi) and X-Max, Large Area EDS Silicon Drift Detector, (Oxford Instruments). The results obtained are an average value from 30 spots/points.

2.5. Chemical composition of biomass-cell wall

Raw and torrefied biomass were prepared for the analysis of chemical composition according to following standards: D 1150-96 (preparation of extractive free biomass), D 1107-96 (ethanol-toluene solubility of biomass), E1757-01 (preparation for compositional analysis).

Lignin, cellulose and hemicellulose were determined by hydrolyzing 300 mg of the biomass sample with 3.00 mL of 72% sulfuric acid and mixing thoroughly. The samples were incubated at 30 °C in a water bath for 60 min; they were stirred every five minutes without removing them from the bath. Upon completion of the first hydrolysis stage, 84 mL of deionized water was added to the samples. Subsequently for a second hydrolysis stage the samples were placed in an autoclave for one hour at 120 °C, following which the hydrolysate was filtered and the solid residue and hydrolysate collected. The hydrolysate was used for the determination of acid soluble lignin (ASL) and carbohydrates. The carbohydrate and ASL contents were analyzed by HPLC using an ICS-3000 ion chromatography system, (Dionex), fitted with a CarboPac PA1, 4 × 250 mm (Dionex) column and pulsed amperometric (PAD) and diode array detectors (Agilent HP 8452A). An aqueous 300 mM sodium hydroxide solution was used as the mobile phase. The remaining solid residue was rinsed with 50 mL of deionized water and placed in an oven at 100 °C overnight. Ash content was determined for the collected residue. The solid residue represents the Acid-Insoluble Residue, and its free-ash fraction corresponds to the Klason Lignin. All samples were analyzed in duplicate. Cellulose was quantified by content of glucan while other carbohydrates such as xylan and arabinan were counted as hemi-cellulose.

2.6. Gasification reactivity

The gasification reactivity of raw and torrefied M × G experiments were carried out with a SETSYS Evolution TGA in the atmosphere of N₂ (55 ml/min) using CO₂ (11 ml/min) as gasification medium. The biomass samples were grinded and sieved between 105 and 250 μm. To achieve accurate and comparable data, samples of 5 ± 0.1 mg were loaded in the crucible. The biomass was heated from ambient temperature to 105 °C at the rate of 20 °C/min and kept for 20 min to remove the moisture. Then, the temperature was increased to gasification temperature 650, 750 or 850 °C at the rate of 100 °C/min. After the temperature reached the set point, the CO₂ was introduced (the start point of gasification) and maintained for 2 h.

The gasification reactivity, R , was calculated from the mass measurements using Eq. (3). R is the time derivative of the conversion, X , where m represents the mass at the start of gasification;

m_{ash} refers to the mass of residue after the gasification; and m_t stands for instantaneous mass [12].

$$R = \left(\frac{dx}{dt} \right); \quad X = \frac{m - m_t}{m - m_{\text{ash}}} \quad (3)$$

3. Results and discussion

3.1. Torrefaction behavior of M × G

To investigate the influence of torrefaction on lignocellulose characteristics of M × G, the TGA and DTG curves at four different torrefaction temperatures and two residence times are presented in Fig. 1. The heights of the peaks in the DTG curves show the intensity of mass loss rate. Mass loss is an effective indicator of the severity of torrefaction. It is primarily due to the thermal decomposition of hemi-celluloses and some short chain lignin compounds [4], which are released in the form of gaseous products such as H₂O, CO, CO₂ and CH₄ [7,16]. It can be seen that, at the lowest torrefaction temperature 230 °C, only a slight reduction in mass was observed in the TGA (Fig. 1a), which can be attributed to limited devolatilisation. Because of this the torrefaction peak observed in the DTG curve (Fig. 1c), representing the rate of mass loss, was not high; following torrefaction at 230 °C a broad pyrolysis peak was evident. The mass loss increases with the increase in torrefaction temperature. This effect is more pronounced for the longer residence time, Fig. 1b. Higher torrefaction peaks in the DTG suggests a greater influence of process conditions on biomass decomposition. At the same time the pyrolysis peak diminishes in intensity. It is noteworthy that the mass loss rate/intensity at 250 °C, for 10 min (Fig. 1c) is similar to that at 230 °C, 30 min (Fig. 1d). The torrefaction peaks in the DTG for 270 °C, 30 min and 290 °C, 30 min (Fig. 1d) have almost the same height, but the mass loss during torrefaction of the latter was greater. This suggests that a considerable portion of biomass had decomposed before the temperature reached 290 °C. Consequently the torrefaction experiments in the furnace were carried out for temperatures up to 270 °C. Following the torrefaction stage, the pyrolysis peak was smaller compared to samples torrefied under milder conditions.

Table 1 gives the results of mass yield for torrefied M × G on a dry and ash free basis. Mass yield represents the ratio of actual mass retained after the torrefaction to initial mass of biomass. It can be seen that the mass yield gradually decreases with torrefaction temperature. Smaller mass loss at short residence time can be attributed to limited devolatilisation. As expected the lowest mass yield (65.3%) was observed for the most severe torrefaction conditions 270 °C, 30 min while the highest mass yield (92.3%) was obtained for the mildest conditions.

Lignocellulosic biomass consists of three main constituents: cellulose, hemi-cellulose and lignin. Because of intrinsic differences in the structure of these constituents, they can be distinguished and identified using thermogravimetric analysis [9,17]. The decomposition temperature ranges for all these materials have been measured; however there are some differences between the reported temperature ranges. According to Yang et al. [16] hemi-cellulose decomposes mainly at 220–315 °C, cellulose at 315–400 °C, while lignin decomposes over a wide temperature range from 160 to 900 °C. However, according to Deng et al. [5] the hemi-cellulose breaks down at temperatures ranging from 200 to 250 °C, and then cellulose between 240 and 350 °C, with lignin decomposing between 280 and 500 °C. Fig. 2 shows the DTG distribution curves for pyrolysis of virgin and torrefied M × G. The first peak, in the DTG curve of raw biomass, is seen 312 °C suggesting the thermal decomposition of hemi-cellulose, with the second peak at 342 °C

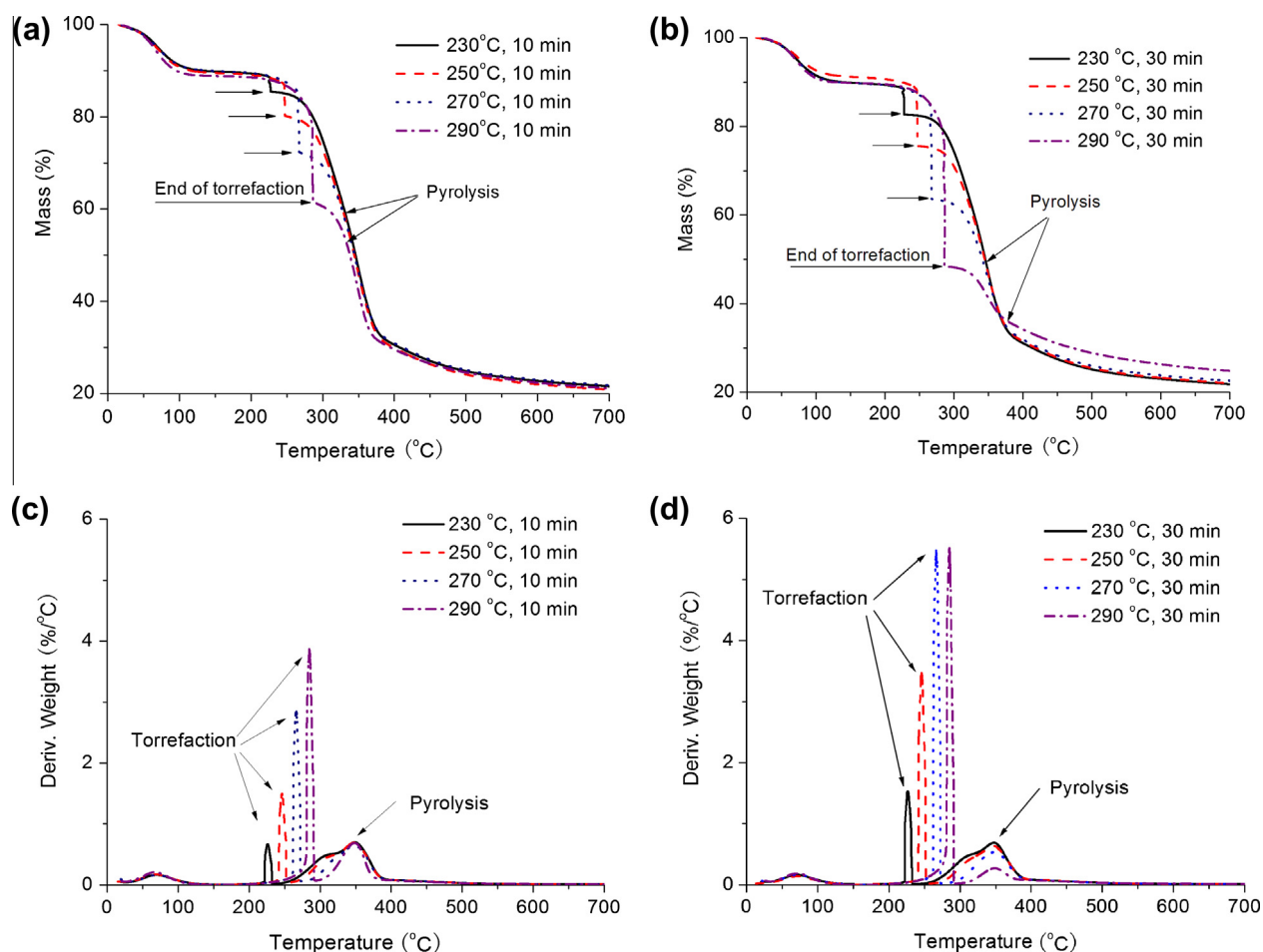


Fig. 1. TGA distribution for 10 and 30 min torrefaction – (a) and (b), respectively. DTG distribution for 10 and 30 min torrefaction – (c) and (d), respectively.

Table 1
Mass and energy yield of torrefied *Miscanthus × giganteus*.

Condition	Mass yield _{daf} (%)	Energy yield _{daf} (%)
230 °C, 10 min	92.3	96.0
250 °C, 10 min	87.0	91.8
270 °C, 10 min	76.9	85.6
230 °C, 30 min	88.8	94.1
250 °C, 30 min	81.1	96.3
270 °C, 30 min	65.3	76.7

representing cellulose decomposition. The peak for hemi-cellulose is partially merged with that of cellulose. The slow rate of mass loss at higher temperature is consistent with lignin decomposition. It was observed that the hemi-cellulose peak for the torrefied M × G gradually decays and finally disappears for the 270 °C, 30 min experiment. The height of cellulose peak decreases with an increase in torrefaction temperature suggesting that during torrefaction cellulose was partially decomposed.

The chemical composition of raw M × G and samples after torrefaction, obtained from HPLC and wet chemical analysis are presented in Table 2. Biomass torrefied for 30 min at 270 °C contains only 3.62% of hemicellulose and 36.71% of cellulose. The hemi-cellulose, which is the most unstable component, was almost completely decomposed during torrefaction while, the cellulose underwent only limited decomposition. The torrefaction did not have strong influence on lignin, but its relative content increased and comprises more than 50% of the torrefied miscanthus. The difference in the cell wall composition for raw and torrefied M × G corresponds closely with data from the TGA.

Table 2
Chemical composition of raw and torrefied *Miscanthus × giganteus* (dry and ash free basis).

Conditions	Lignin, %	Cellulose, %	Hemicellulose, %
Raw biomass	21.62	41.44	21.04
250 °C, 30 min	41.64	43.91	7.31
270 °C, 30 min	53.99	36.71	3.62

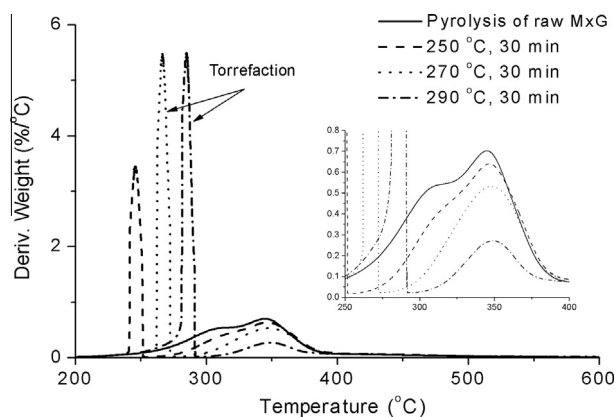


Fig. 2. DTG distribution (mass loss rate) of pyrolysis of torrefied and raw *Miscanthus × giganteus*.

3.2. Fuel characterization

Data from the proximate analysis of M × G at each experimental condition are given in Table 3. The observed trend was one of decreasing moisture and volatile content and increasing fixed carbon and ash content as the temperature and residence time increases. The moisture content of torrefied M × G decreased significantly (varying from 1.39% to 2.9%) compared to that of raw material (9.69%). These results are in agreement with Pimchua et al. [6] and Phanphanich and Mani [1]. The increase in moisture content of torrefied biomass at the highest temperature suggests that a small amount of moisture is re-absorbed during storage; however uptake of moisture is limited, other researchers observed similar phenomena [4,8].

The volatile matter content of biomass after torrefaction decreased by 1.73–19.34% and the fixed carbon content increased correspondingly and it was closely related to the intensity of torrefaction. It can be seen that, the change in volatile matter was not significant (2–3%) for the short torrefaction time-10 min experiments. When the duration of torrefaction was increased to 30 min the volatile matter reduction was about 4% at temperatures of 230 and 250 °C. A more significant change about 20% (from 82.33% to 62.99%) was observed after 30 min torrefaction at a temperature of 270 °C. At the lower temperatures (below 250 °C) the most reactive component of biomass, hemicellulose, undergoes limited devolatilisation and therefore any reduction in volatile matter was insignificant. Similar results were reported for other biomass species [6].

The ash content increased for all torrefied samples from 0.22% to 3.63% depending on experimental conditions. Similar observations were found in other reported studies [1,6,8]. The observed increase in ash and fixed carbon content was mainly due to mass loss (concentration effect) during the torrefaction process. The ratio between carbon and potentially catalytically active mineral substances is an important parameter for char reactivity during gasification [18,19]. The char reactivity increases with the increased concentration of metallic constituents (in particular potassium and sodium). In Table 4 the SEM-EDAX analyses of ash from torrefied and raw M × G are presented. As expected, there is a slight increase in the relative concentration of most elements/minerals. The chlorine content falls following torrefaction and this may have benefits for downstream conversion as high chlorine contents in some

biomass feedstocks imposes limitation on their use for some thermo-chemical conversion processes. It is reported that the chloride contained in biomass affects the potassium release mechanism during gasification. Potassium reacts with chloride when present to form KCl which could lead to deposit formation in the flue gas channel upon subsequent cooling of the flue gas [20]. The accumulation of deposit has the risk to block the downstream gas cleaning devices which cause unscheduled shut down and excessive maintenance work. Considering the higher mineral content of torrefied biomass, the concentration of individual elements was calculated relative to the mass of pretreated fuel (Table 5). The content of those constituents such as K, Na, Mg and Ca which exert a catalytic role on the reactivity of char increased from 13% to 87% when the miscanthus was subjected to torrefaction.

The elements, which improve the reactivity of char during gasification, potassium and sodium, can also react with silica oxides and form low melting eutectic mixtures which can result in agglomeration. This is a particular problem for fluidized bed gasifiers as it may result in defluidization. Potassium is more damaging than sodium [15]. The biomass sintering tendency is severe when the constituents exceed boundary conditions proposed by Hulkkonen et al. [21]. To prevent undesired agglomeration phenomena it is necessary to consider not only ash composition, but also type of the in-bed material and the operating temperature within the bed [22,23].

The results of elemental analysis are also presented in Table 3. The raw miscanthus was characterized by high oxygen content and relatively low carbon and hydrogen content; from this perspective it can be classified as a low heating value biomass. The C content of torrefied M × G increased by 1.05% to 9.78% in comparison to the raw material with the O content decreasing by between 0.8% and

Table 3
Proximate and ultimate analysis and heating value of raw and torrefied M × G.

Conditions	Proximate analysis (wt%)				Ultimate analysis (wt%, dry basis)					
	Moisture	Volatile matter	Ash	Fixed carbon	N	C	H	O	HHV, MJ/kg	
Raw M × G	9.69	82.33	4.04	3.94	0.40	47.63	6.19	45.78	18.360	
230 °C, 10 min	2.07	80.60	4.26	13.07	0.37	48.68	6.13	44.82	19.101	
250 °C, 10 min	1.39	80.60	4.83	13.18	0.46	49.80	6.02	43.72	19.371	
270 °C, 10 min	2.70	79.23	5.72	12.35	0.48	50.48	5.74	43.30	20.431	
230 °C, 30 min	2.34	78.47	4.75	14.44	0.53	51.80	5.54	42.14	19.450	
250 °C, 30 min	2.30	78.00	5.62	14.08	0.63	52.88	5.54	40.94	21.805	
270 °C, 30 min	2.90	62.99	7.67	26.44	0.60	57.41	4.94	37.05	21.569	

Table 4
SEM-EDAX analyses of ash from Miscanthus × giganteus torrefied for 30 min.

Conditions	Elements, wt%												
	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Mn	Fe
Raw M × G	2.98	46.25	0.72	1.98	0.28	20.75	1.67	1.90	0.71	13.88	7.22	0.17	0.94
250 °C	3.32	47.58	0.59	1.82	0.90	21.31	1.89	1.46	0.38	11.71	6.68	0.10	0.84
270 °C	3.52	46.11	0.55	1.82	0.34	22.26	1.89	1.65	0.36	12.70	7.15	0.14	0.72
290 °C	1.75	46.58	0.98	2.83	0.44	18.08	1.88	2.10	0.16	16.39	5.18	0.28	1.10

Table 5
Absolute elements content in the raw M × G as well as torrefied for 30 min.

Conditions	Elements content, mg element/gram material							
	Na	Mg	Al	Si	Cl	K	Ca	Fe
Raw M × G	0.29	0.80	0.11	8.38	0.29	5.61	2.92	0.38
250 °C	0.33	1.02	0.50	11.98	0.21	6.58	3.75	0.47
270 °C	0.42	1.40	0.26	17.07	0.27	9.74	5.48	0.55
290 °C	0.92	2.65	0.41	16.94	0.15	15.36	4.85	1.03

8.58% depending on torrefaction conditions. Torrefaction resulted in a slight reduction in H content and small increase in the N content of the samples. This suggests that, gaseous compounds released during the thermal decomposition contain higher concentrations of oxygen and hydrogen than carbon.

The ratio of O/C and H/C has been plotted on a Van Krevelen diagram (Fig. 3), which illustrates the influence of elemental composition alterations on fuel characteristics. From this diagram it can be observed that thermal pretreatment improved the fuel properties of $M \times G$ providing a material which was similar to peat in terms of its fuel classification. The higher the torrefaction temperature or the longer the residence time the lower the O/C ratio. The samples of miscanthus torrefied at 270 °C for both 10 and 30 min, and 250 °C for 30 min (from left to right respectively) are comparable to peat. However, for short residence time (10 min) and temperatures below 270 °C mainly moisture is released from biomass; dehydration reaction between organic molecules may have occurred but changes in O/C, H/C ratio are insignificant. It can be concluded that the changes in fuel properties were not significant for short reaction time at low temperature, while short reaction time at high temperature gives similar results to long reaction time and low torrefaction temperature. The points in the diagram (Fig. 3) representing the most severe torrefaction conditions are close to coal; biomass has similar properties to peat and lignite. Experimental results are compared with results of Bridgeman et al. [8] (solid circles in Fig. 3), who torrefied Miscanthus at two residence times 10 and 60 min and two temperatures 240 and 290 °C.

Data from bomb calorimetry are presented in Table 3. The results show the influence of changes in chemical composition of torrefied biomass on its energy content. The HHV of torrefied samples increased by between 4.04% and 17.5% compared with the raw material and it was in the range of 19–21.8 MJ/kg. These values are similar to those of peat (21.23 MJ/kg) used for heat and power generation [15]. The increase in HHV can be attributed to the higher carbon content [20].

Energy yield is another indicator which evaluates intensity and practicability of torrefaction in terms of energy balance. Table 1 presents the influence of the temperature and residence time on energy yield and it can be seen that the percentage of energy yield decreases with the increase of the torrefaction temperature and residence time. The lowest energy yield 76.7% was at the most severe condition in this study (270 °C and 30 min).

Considering torrefaction as a method to improve fuel characteristics for further energy production and utilization, the energy input and output should be balanced carefully. Severe conditions,

literally mean high temperature and long residence time, consume considerable energy itself. On the other hand, it significantly reduces the mass yield. Although the HHV of torrefied material is much higher, the energy yield turns out to be too low. In other words, the high energy and effort input results in low energy output which is obviously counter to the purpose of torrefaction. Chen and Kuo [17] gave similar recommendation.

3.2.1. Contact angle

The contact angle is a measurement of the ability of a liquid to spread on a surface. Strongly hydrophilic solids will have a contact angle up to 90°. If the solid surface is hydrophobic, the contact angle will be larger than 90°. In Table 6 results from measurements of contact angle are presented. Contact angle increases with an increase in torrefaction temperature and is greater than 90°, suggesting that torrefied biomass is more hydrophobic. The biomass was dried during torrefaction and uptake of moisture is very limited. According to Bergman et al. [4] this is due to the destruction of many OH groups in the biomass through dehydration reactions, so torrefied biomass has lost the capability to form hydrogen bonds with water.

3.2.2. Surface area and total pore volume

The data in Table 7 show the specific surface area as well as pore diameter and pore volume of $M \times G$. For short residence time and relatively low temperature (230 °C), the average pore diameter, total pore volume and specific surface area were not improved compared to the raw biomass. This indicates that the release of H₂O, CO₂ as main products at low temperature [16,24] has little effect on the pore structure. During torrefaction at higher temperature the biomass develops a porous structure, and the surface area increased from 12.18 to 32.68 m²/g. Torrefied biomass with the largest specific surface area were produced at 250 °C and 30 min. This can be attributed to intensified volatilization of gaseous products which results in generation of enlarged pores. The volume of pores was enlarged almost 20 times relative to the raw $M \times G$. These results show that torrefaction can improve the surface area of the feedstock. Whilst, further increases in torrefaction temperature to 270 °C led to decrease in pore diameter and volume as well as surface area. At this condition some pores were closed due to softening, and the plastic deformation of the pores and carbonization of the particles. The results about surface area changes during torrefaction are in agreement with Chen et al. [24] however observed trend in average pore diameter is in contrary to his results.

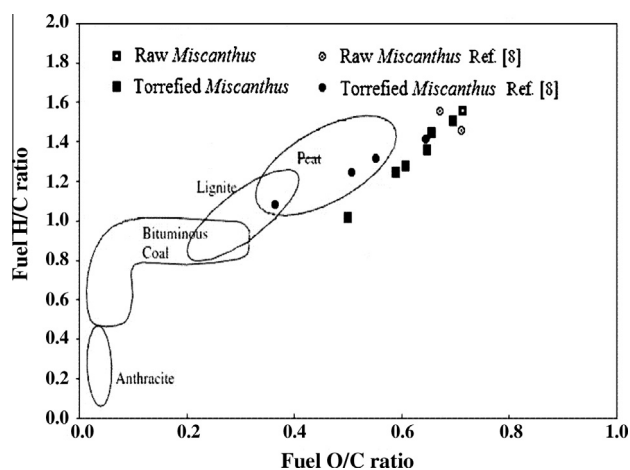


Fig. 3. Van Krevelen diagram for coals, raw and torrefied Miscanthus \times giganteus. Comparison with Miscanthus biomass in Ref. [8].

Table 6
Contact angle of torrefied Miscanthus \times giganteus.

Condition	Contact angle ^o
Raw $M \times G$	87
230 °C, 10 min	107
250 °C, 10 min	113
270 °C, 10 min	123

Table 7
Surface area, total pore volume and diameter of raw and torrefied $M \times G$.

Samples	Langmuir surface area, m ² /g	Single point, total pore volume, cm ³ /g	Average pore diameter, nm
Raw material	12	0.000634	0.317
230 °C 10 min	9	0.001251	0.656
270 °C 10 min	24	–	–
250 °C 30 min	33	0.011645	1.853
270 °C 30 min	26	0.007460	1.212

3.3. Gasification reactivity

In order to investigate the effect of torrefaction conditions on the reactivity of $M \times G$, both raw and torrefied samples were gasified in an isothermal mode at 850 °C in the atmosphere of N_2 using CO_2 as gasification medium. As shown in Fig. 4(a), the shapes of conversion curves of torrefied and untreated $M \times G$ versus time are quite similar to each other. Among the samples, the raw $M \times G$ showed the fastest conversion, followed by two samples from the condition of 250 and 230 °C-30 min which showed very similar tendency. The slowest conversion was observed for the most intensive torrefaction condition 270 °C and 30 min. Kinetics of conversion is influenced by surface area, surface accessibility and intrinsic kinetic parameters. $M \times G$ torrefied at 250 °C for 30 min has the highest pore volume and pore size in contrary to biomass pretreated at 270 °C for 30 min (see Table 7). Small pores in the chars lead to CO_2 with difficulty react with char's surface and slower the conversion rate. Fig. 4(b) presents the variation of instantaneous reactivity (%/s) versus conversion (%). It can be seen that the instantaneous reactivity of torrefied $M \times G$ decreased slightly at the beginning of gasification. After that it started to increase, peaked at the conversion around 54% and began to decrease. The decreasing rate was very high at the end of gasification. The reactivity of raw $M \times G$ was higher than that of torrefied one at low levels of conversion (<60%) and after that it started to decrease quickly. The shape of gasification rate curve is different from findings of other researchers' [12,13] who studied gasification reactivities of willow, wheat and corn straw which after torrefaction were pyrolyzed in a separated process prior to the gasification experiment. In this study in, in order to simulate the process of gasification, the torrefied and raw $M \times G$ samples were heated in N_2 atmosphere to 850 °C with the rate of 100 °C/min followed by turning on the gasifying agent CO_2 . It was anticipated that thermal decomposition might have not been completed by the time when the CO_2 flow was started, particularly for the raw $M \times G$ which has higher initial volatile matter content comparing to torrefied ones. Therefore, its global conversion based on mass loss was higher. It is assumed that instantaneous reactivity of raw $M \times G$ at low conversion rate (Fig. 4b) was higher than torrefied one because of simultaneously occurring gasification of the char at the surface and decomposition of biomass at the bottom layer of fuel. At higher conversion rates reactivity of torrefied biomass was higher than raw $M \times G$ and it can be attributed to catalytic effects of inorganic elements/ash [12].

It can be seen that the $M \times G$ torrefied at 230 °C and 250 °C for 30 min showed similar conversion and instantaneous reactivity tendency, but combining the results of HHV and mass/energy yield,

250 °C-30 min is considered as the optimal condition of torrefaction in this study.

Since temperature has remarkable influence on the gasification efficiency, torrefied $M \times G$ from the optimal condition (250 °C-30 min) was gasified at 650 and 750 °C to illustrate the change of gasification reactivity at different temperature (Fig. 5). Fig. 5(a) demonstrates that the full conversion of torrefied $M \times G$ was accomplished in shortest period of time at 850 °C, however at the beginning of gasification its conversion was lower than that of 650 and 750 °C. On the other hand, Fig. 5(b) reveals that the instantaneous reactivity at the gasification temperature of 650 and 750 °C had an overall decreasing tendency, which is opposite to that of at 850 °C. The reason is that the biomass was devolatilized at a significantly lower rate [25] at lower temperatures and the shape of conversion curve is probably related to the thermal degradation process. Since the rate of gasification with CO_2 is order of magnitude lower than that of pyrolysis (thermal degradation) the conversion of char formed was limited during the release of volatiles within fuel [26]. At higher temperature of 850 °C the thermal decomposition occurred at much higher rate (initial decrease in the instantaneous reactivity at low conversion); and as soon as it was completed the char itself was gasified by CO_2 . As the performance of gasification at 850 °C was better than that of 650 and 750 °C, it can be concluded that higher temperature is more suitable for the gasification of torrefied $M \times G$. But it should be noted that the risk of agglomeration should be carefully considered when high temperature is planned to be used for the gasification of torrefied biomass in the real gasification setups.

3.4. Discussion

During gasification when biomass is exposed to high temperatures (above 700 °C), a complex mixture of steam, vapors of organic compounds and gaseous products are evolved, leaving a carbon skeleton – char [27]. The conversion of char in the gasification step determines the overall efficiency of the gasifier [28]. Char conversion is a heterogeneous process where the char surface is the location of chemical reactions [29]. Furthermore, the char conversion directly depends on its reactivity with gasifying agent, whilst reactivity depends on three main characteristics: chemical structure, inorganic constituents and porosity.

During torrefaction of $M \times G$ all these characteristics underwent changes. The alteration in chemical composition of torrefied biomass results in a decrease in the O/C ratio (Section 3.2). The lower ratio of O/C can improve the gasification properties of the torrefied biomass compared to the raw material [10]. According to Blasi [24] char reactivity is affected by the morphology and

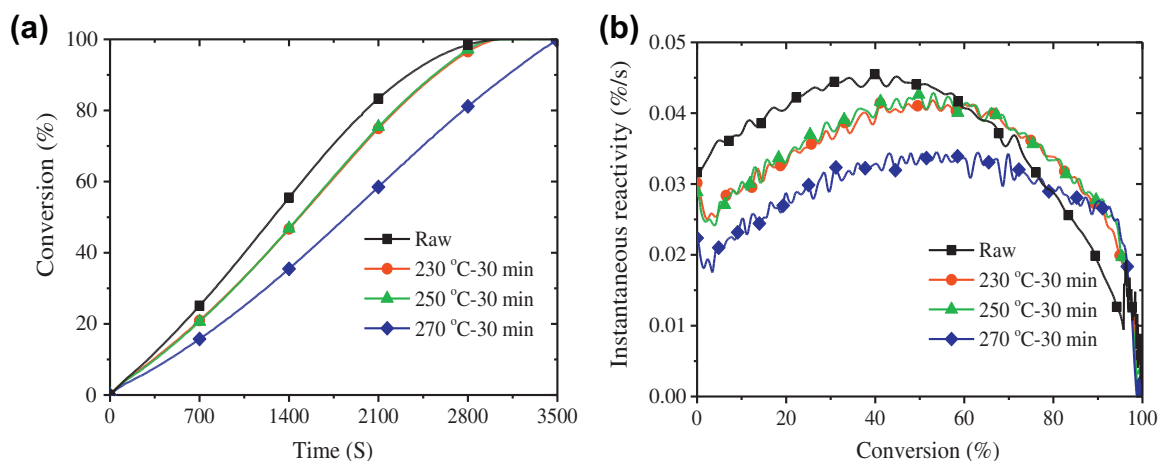


Fig. 4. Effect of torrefaction conditions on the gasification reactivity of $M \times G$ at 850 °C (a) conversion versus time (b) instantaneous reactivity versus conversion.

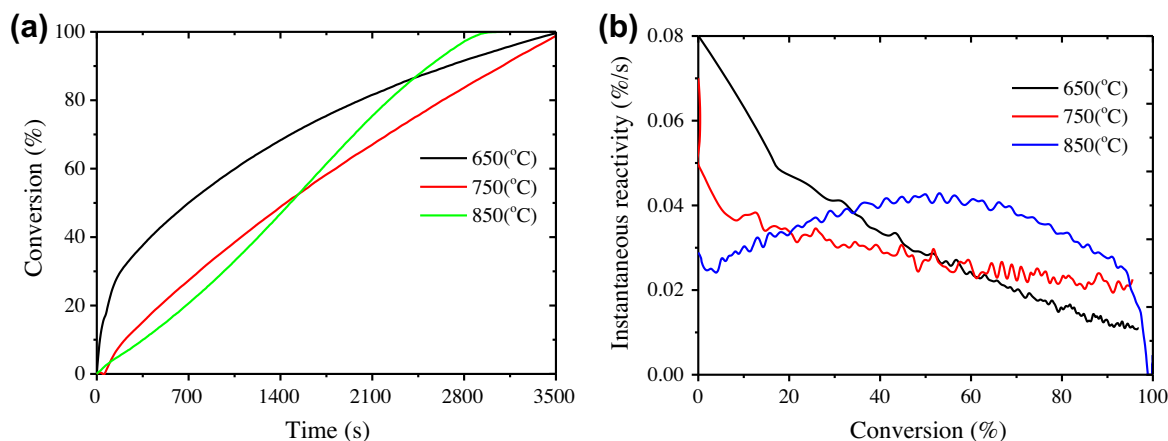


Fig. 5. Gasification reactivity of torrefied $M \times G$ (250 °C-30 min) at different temperatures: (a) conversion versus time (b) instantaneous reactivity versus conversion.

the amount and composition of inorganic matter. As shown in Section 3.2.2, torrefaction can increase the surface area and pore volume of feedstock. When pore volume/size is small the penetration of gaseous reagents into the particle is limited and conversion is confined to the exterior surface of the particle. An increase in pore volume and average size facilitates diffusion of CO_2 inside the particles and improves gasification reactivity. The relatively low temperature of the devolatilisation that occurs during torrefaction allows the alkali metals to be retained in the solid product [30,31]. According to Lv et al. [32] alkali and alkaline metal species present in biomass increase char reactivity. Higher content of inorganic matter (particularly potassium and sodium) due to increase of ash content in torrefied $M \times G$ (Section 3.2) may improve efficiency of gasification.

The composition of the product gas obtained from gasification depends on the nature of the feedstock used, because different feedstocks are distinguished by their unique chemical compositions. A recent study reported that feedstock composition has an effect on tar formation during gasification [33]. The presence of moisture and high concentration of hemi-cellulose and lignin in the feedstock produce more tar in the syngas than that of high cellulose concentrations. Moreover higher cellulose content in biomass elevates the temperature of gasification and prolongs the gasification time [32]. Considering that *Miscanthus × giganteus* torrefied at 250 °C for 30 min contains much less hemi-cellulose but more cellulose than raw biomass (Section 3.1), from this perspective it might be more suitable for gasification.

4. Conclusions

Torrefaction of *Miscanthus × giganteus* has been performed to investigate the effects of temperature and residence time on the properties of the fuel.

Experimental results show that torrefaction at 230 or 250 °C and short residence time 10 min only released some moisture and light volatiles from the samples; it had a relatively minor impact in improving the properties of biomass. The torrefaction at 250 °C for 30 min resulted in a certain amount of hemi-cellulose decomposition, whereas cellulose and lignin were only slightly affected. When miscanthus was subjected to torrefaction at 270 °C for 30 min large amounts of hemi-cellulose and some cellulose were destroyed. These pretreatment conditions disadvantaged the torrefied biomass, as a consequence of a large portion of mass being consumed (for 270 °C, mass yield was 57.56% and energy yield 67.62%).

From the analysis of fuel properties it can be concluded that the optimal process conditions for torrefaction of *Miscanthus × gigan-*

teus are: 250 °C and 30 min. The mass and energy yield for these conditions were 71.6% and 85.1% respectively (during torrefaction at this condition 71.6% of mass and 85.1% of energy was retained). The HHV of torrefied samples was 21.81 MJ/kg. The reactivity of torrefied sample from this condition was higher than other torrefied samples and then that of raw *Miscanthus*. In addition, it is revealed that torrefied $M \times G$ showed better conversion rate and instantaneous reactivity characteristics at 850 °C, which means torrefied material favors high gasification temperature.

The torrefied $M \times G$ has favorable properties compared to the original material, such as very low moisture and hemi-cellulose content, lower ratio of O/C, porous structures and larger specific surface area as well as higher content of alkali metals. All these features have positive effect on *Miscanthus* gasification efficiency.

References

- [1] Phanphanich M, Mani S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresour Technol* 2011;102:1246–53.
- [2] Angelini LG, Ceccarini L, Nasso Di Nasso N, Bonari E. Comparison of *Arundo donax L.* and *Miscanthus × giganteus* in a long-term field experiment in Central Italy: analysis of productive characteristics and energy balance. *Biomass Bioenergy* 2009;33:635–43.
- [3] Heaton EA, Dohleman FG, Miguez AF, Juvik JA, Lozovaya V, Widholm J, et al. *Miscanthus*: a promising biomass crop. In: Jean-Claude K, Michel D, editors. *Advances in botanical research*. Academic Press; 2010. p. 75–137.
- [4] Bergman PCA, Boersman AR, Zwart RWR, Kiel JHA. Torrefaction for biomass co-firing in existing coal-fired power stations. In: ENC-C-05-013, editor. The Netherlands, Energy Research Center of the Netherlands (ECN); 2005.
- [5] Deng J, Wang GJ, Kuang JH, Zhang YL, Luo YH. Pretreatment of agricultural residues for co-gasification via torrefaction. *J Anal Appl Pyrol* 2009;86:331–7.
- [6] Pimchua A, Dutta A, Basu P. Torrefaction of agriculture residue to enhance combustible properties. *Energy Fuels* 2010;24:4638–45.
- [7] Bridgeman TG, Jones JM, Shield I, Williams PT. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. *Fuel* 2008;87:844–56.
- [8] Bridgeman TG, Jones JM, Williams A, Waldron DJ. An investigation of the grindability of two torrefied energy crops. *Fuel* 2010;89:3911–8.
- [9] Chen WH, Kuo PC. A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. *Energy* 2010;35:2580–6.
- [10] Prins MJ, Ptasiński KJ, Janssen F. More efficient biomass gasification via torrefaction. *Energy* 2006;31:3458–70.
- [11] Couhert C, Salvador S, Commandré JM. Impact of torrefaction on syngas production from wood. *Fuel* 2009;88:2286–90.
- [12] Fisher EM, Dupont C, Darvell LI, Commandré JM, Saddawi A, Jones JM, et al. Combustion and gasification characteristics of chars from raw and torrefied biomass. *Bioresour Technol* 2012;119:157–65.
- [13] Min F, Zhang M, Zhang Y, Cao Y, Pan W-P. An experimental investigation into the gasification reactivity and structure of agricultural waste chars. *J Anal Appl Pyrol* 2011;92:250–7.
- [14] Bergman PCA, Boersman AR, Kiel JHA, Prins MJ, Ptasiński KJ, Janssen FGGJ. Torrefaction for entrained-flow gasification of biomass, in: 2005.
- [15] Basu P. In: *Biomass Gasification and Pyrolysis: Practical Design and Theory*. Elsevier Inc.; 2010. p. 365.

- [16] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007;86:1781–8.
- [17] Chen WH, Kuo PC. Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass. *Energy* 2011;36:803–11.
- [18] Marquez-Montesinos F, Cordero T, Rodríguez-Mirasol J, Rodríguez JJ. CO₂ and steam gasification of a grapefruit skin char. *Fuel* 2002;81:423–9.
- [19] Tancredi Ns, Cordero Ts, Rodríguez-Mirasol J, Rodríguez JJ. CO₂ gasification of eucalyptus wood chars. *Fuel* 1996;75:1505–8.
- [20] Zevenhoven-Onderwater M, Backman R, Skrifvars B-J, Hupa M. The ash chemistry in fluidised bed gasification of biomass fuels. Part I: predicting the chemistry of melting ashes and ash-bed material interaction. *Fuel* 2001;80:1489–502.
- [21] Hulkkonen S, Fabritius M, Enestam S. Application of BFB technology for biomass fuels: technical discussion and experiences from recent projects. *ASME Conf Proc* 2003;2003:663–71.
- [22] Olofsson Gr, Ye Z, Bjerle I, Andersson A. Bed agglomeration problems in fluidized-bed biomass combustion. *Ind Eng Chem Res* 2002;41:2888–94.
- [23] Kuo J-H, Lin C-L, Wey M-Y. Effect of alkali concentrations and operating conditions on agglomeration/defluidization behavior during fluidized bed air gasification. *Powder Technology* 2011;214:443–6.
- [24] Chen Q, Zhou JS, Liu BJ, Mei QF, Luo ZY. Influence of torrefaction pretreatment on biomass gasification technology. *Chin Sci Bull* 2011;56:1449–56.
- [25] Gómez-Barea A, Leckner B. Modeling of biomass gasification in fluidized bed. *Prog Energy Combust Sci* 2010;36:444–509.
- [26] Neves D, Thunman H, Matos A, Tarelho L, Gómez-Barea A. Characterization and prediction of biomass pyrolysis products. *Prog Energy Combust Sci* 2011;37:611–30.
- [27] Asadullah M, Zhang S, Min ZH, Yimsiri P, Li CZ. Effects of biomass char structure on its gasification reactivity. *Bioresour Technol* 2010;101:7935–43.
- [28] Baratieri M, Baggio P, Fiori L, Grigiante M. Biomass as an energy source: thermodynamic constraints on the performance of the conversion process. *Bioresour Technol* 2008;99:7063–73.
- [29] Di Blasi C. Combustion and gasification rates of lignocellulosic chars. *Prog Energy Combust Sci* 2009;35:121–40.
- [30] Blasi CD, Branca C, D'Errico G. Degradation characteristics of straw and washed straw. *Thermochim Acta* 2000;364:133–42.
- [31] Olsson JG, Jäglid U, Pettersson JBC. Alkali metal emission during pyrolysis of biomass. *Energy Fuels* 1997;11:779–84.
- [32] Xu M, Lv D, Liu Xiaowei, Zhan Zhonghua, Li Zhiyuan, Yao Hong. Effect of cellulose, lignin, alkali and alkaline earth metallic species on biomass pyrolysis and gasification. *Fuel Process Technol* 2010;91:903–9.
- [33] S.V.B.v.P. Kiel JHA, Neeft JPA, Devi L, Ptasinski KJ, Janssen FJJG, Meijer R, Berends RH, Temmink HMG, Brem G, Padban N, Bramer EA. Primary measures to reduce tar formation in fluidized-bed biomass gasifiers. ECN-C-04-014, The Netherlands, Energy Research Center of the Netherlands (ECN); 2004.