The Effect of Equivalence Ratio on the Gasification of Torrefied and Un-Torrefied Biomass – Miscanthus x giganteus

L.P.L.M. Rabou **(ECN)**
M. Kwapinska **(Competence Centre for Biorefining & Biofuels, University of Limerick)**
G. Xue **(Department of Chemical and Environmental Sciences, University of Limerick)**
W. Kwapinski **(Department of Chemical and Environmental Sciences, University of Limerick)**
S. Dooley **(Department of Chemical and Environmental Sciences, University of Limerick)**
J.J. Leahy **(Department of Chemical and Environmental Sciences, University of Limerick)**

January 2015
ECN-W--15-007

The Effect of Equivalence Ratio on the Gasification of Torrefied and Un-Torrefied Biomass – Miscanthus x giganteus

M. Kwapinska[1], G. Xue[2], W. Kwapinski[2], L.P.L.M. Rabou[3], S. Dooley[2], J.J. Leahy[2]

[1]Competence Centre for Biorefining & Biofuels, University of Limerick, Ireland
[2]Department of Chemical and Environmental Sciences, University of Limerick, Ireland
[3]Energy Research Centre of the Netherlands (ECN), Biomass & Energy Efficiency, Petten, The Netherlands

Abstract

Torrefaction is a thermal pre-treatment process to improve the properties of biomass prior to gasification. It involves heating the biomass between 200°C and 300°C under an inert atmosphere. Water and some light volatiles are released during this process; the hygroscopic biomass is rendered hydrophobic which makes it more convenient for long distance transport and long-term storage. The process also reduces the quantity of chemically bound oxygen in the biomass and so is suggested to improve the performance of the product material when gasified.

In order to investigate this proposition, torrefied and un-torrefied Miscanthus x giganteus (MxG) was gasified in a pilot scale electrically heated air-blown bubbling fluidized bed gasifier using olivine ($(Mg, Fe)_2SiO_4$) as the bed material. The influence of a series of initial conditions on the gas composition were parameterised by measurement of biomass (93−153.5 kg/m^2/hour) and air flow rates (110.3−234.9 kg/m^2/hour) corresponding to equivalence ratios of 0.18–0.32 (0.5 equates to 50% of stoichiometric oxygen) at a bed temperature of 800°C. At steady state operation, the flow rate of product gas obtained, and its fraction compositions of N_2, CO, CO_2, CH_4, H_2 ethylene, ethane and acetylene was determined by gas chromatographic. From this data, the corresponding higher heating value of the produced gas was calculated. In addition, from compositional information of the Miscanthus starting material, carbon and hydrogen conversion efficiencies were determined.

In order to understand any advantage arising from the torrefaction process, the experimental data set was further compared to the equivalent data we had previously reported in Xue et al. [1] for torrefied Miscanthus. This comparison shows that for fluidized bed gasification the yield of gas produced and hydrogen conversion are slightly higher for torrefied MxG, but the heating value and carbon conversion efficiency is higher for un-torrefied Miscanthus.

Introduction

Torrefaction is being widely investigated as a promising thermal pre-treatment method to upgrade the fuel properties of biomass prior to further thermochemical conversion, e.g. gasification [2, 3]. It involves heating the biomass between 200ºC and 300°C under an inert atmosphere. The moisture and some light volatiles are released during this process [4] and the hygroscopic biomass is rendered hydrophobic [5] which makes it more convenient for long distance transport and long term storage [6]. The majority of published reports on torrefaction investigate the influence of torrefaction conditions on the fuel properties of biomass; for instance the moisture content of biomass decreases after torrefaction which can increase the energy efficiency of the gasification processes, as extra energy is needed to evaporate the moisture and maintain the appropriate temperature in the gasifier [7]. The energy consumption required for biomass grinding is also significantly reduced after torrefaction [6, 8], which is important for those applications where a reduction of the fuel particle size is needed. The energy density of torrefied biomass is enhanced due to the reduced O/C and H/C in the biomass [4, 9, 10]. The reduced quantity of chemically bound oxygen in the biomass following torrefaction is suggested to improve the performance of the material when gasified.

Some research has been carried out to investigate the potential effects of torrefaction on the gasification process. For example Pins et al. [11] compared three gasification scenarios from the point of view of mass and energy balances, and reported that torrefaction prior to gasification is a promising method to achieve more efficient gasification of wood in an oxygen-blown entrained flow gasifier. This conclusion was based on process simulation for dry fuel by means of chemical equilibrium modelling. Publications reporting gasification of torrefied biomass in actual gasifiers are rare and most of them refer to entrained flow gasifiers. Couhert et al. [12] gasified raw and torrefied wood samples in a high temperature entrained flow reactor with 20 vol. % steam in N_2. They concluded that torrefied wood produced more H_2 and CO than raw wood at 1400 ºC. Chen and co-workers [13] numerically compared the performance of raw and torrefied bamboo and high volatile bituminous coal in an entrained flow gasifier using O_2 as the gasification medium. It was concluded that torrefaction enabledthe gasification behaviour of biomass to approach that of coal and that the torrefaction facilitated syngas formation from biomass gasification. Moreover, the cold gasification efficiency of torrefied bamboo was improved by 88% compared to raw bamboo under the optimum conditions. Van der Stelt et al. [7] reported that torrefaction is the most cost-effective and environmental friendly technology for a Biomass-to-Liquid (BTL) plant located in The Netherlands with a capacity of 1000 MWth synthesis gas. Berrueco et al. [14] reported

experimental results concerning O_2/steam gasification of torrefied biomass (spruce and forest residue-tops and branches) in a pressurized fluidized bed reactor. The main trend observed for both biomasses was an increase in gas yield with pressure and extent of torrefaction. Additionally it was noticed that tar yield increased with the experimental pressure together with a decrease of char yield.

Additionally, it is reported that the surface area and porosity of biomass changes with the conditions of torrefaction [15]. This suggests that biomass torrefied under appropriate conditions could give a higher gasification efficiency as higher surface area and porosity can increase the contact area between the fuel and gasification medium, and consequently accelerate the rate of chemical reaction and mass transfer.

Fisher et al. [16] reported that the combustion and gasification (using H_2O/N_2 as the gasifying medium) reactivities of chars produced from torrefied Willow are lower than those of raw Willow. It should be noted that the studies were carried out using a thermo-gravimetric analyser where the reactivity of the samples was evaluated by the rate of overall mass loss. In such studies, the mass loss rate is not always an unambiguous indicator of the rate of the gasification chemical reactions as for example the mass lost will also include the release of volatile materials, and the evaporation of water in addition to any chemical transformations.

There are relatively few reports in the scientific and engineering literature with a detailed investigation of process conditions for actual, or even laboratory scale, gasification studies of torrefied biomass. The objectives of this study are thus to investigate the influence of torrefaction on the product gas composition resulting from gasification in an air-blown bubbling fluidized bed gasifier. Here, we specifically report the influence of equivalence ratio (ER) on the performance of a torrefied grassy biomass, Miscanthus x giganteus (MxG), and compare its gasification characteristics to those of an otherwise identical un-torrefied material, at a fixed bed (reaction) temperature of 800 °C.

Experimental set-up, materials and methods

The biomass feedstock used in this study, Miscanthus x giganteus (MxG), was supplied by JHM Crops, Ireland as pellets, and subsequently crushed to particles of less than 5 mm. It was then torrefied using a batch reactor at 250 ºC at a temperature elevation of 20 °C/min. The average mass yield after torrefaction for all batches was 76 wt. % of initial. The torrefied MxG was milled in a ball mill prior to characterisation and testing.

The properties of the raw and torrefied MxG are presented in Table 1. Fixed carbon content was calculated according to Basu [17]. The bed material used in this study was non-calcined olivine ($(Mg, Fe)_2SiO_4$) (supplied by Eurogrit, ND) with a particle size of 250–500 µm bulk and absolute densities of 1574 and 3171 kg/m^3 respectively.

Table 1 Properties of torrefied and un-torrefied Miscanthus x giganteous [1].

	un-torrefied, wt. %	**Torrefied, wt. %**
Proximate analysis as received		
Moisture	8.76	2.41
Volatile Matter	77. 78	69.49
Ash	2.7 8	4.21
Fixed Carbon	10.68	23. 89
Ultimate analysis as received		
N	0.58	0.69
C	42.29	51.14
H	6.42	5.95
S	<0.01	<0.01
O (by difference)	39.16	35.60
Higher heating value (dry basis, MJ/kg)	17.13	20.90

The experiments reported here, were carried within the framework of the BRISK EU FP7 project using an air-blown bubbling fluidized bed gasifier at the Energy Research Centre of the Netherlands (ECN). The reactor consisted of a bed section (500 mm high and 74 mm internal diameter (ID)) and a freeboard section (600 mm high and an ID of 108 mm). Both sections were externally heated. The gasification medium (air and N_2) was introduced through a gas distributor at the base of the gasifier. The solid fuel was fed 50 mm above the gas distributor by means of a feeding screw.

Detailed information about the experimental set up, gasification procedure, and product gas analysis can be found in [1, 18].

Effect of Equivalence Ratio on Product Gas Composition and Gasification Performance

The effect of equivalence ratio (ER) was investigated at a fixed bed temperature of 800 °C. Different ERs in the range from 0.18 to 0.32 were achieved by changing the proportion of air and N_2 flows, retaining the total fluidizing medium at 12.3 dm^3/min (for most experiments) or 13.2 dm^3/min (for a set of experiments with torrefied MxG up to an ER = 0.28, which required a higher flow rate of air). A stream of pure N_2 was used in order to keep the fluidization conditions similar for all tests. It should be noted that only the N_2 from air was counted as being product gas. For torrefied MxG, ERs in the range of 0.18 - 0.28 were obtained, corresponding to biomass feeding rates of 0.55 - 0.60 kg/h, while for un-torrefied MxG, ERs were slightly higher, in the range of 0.22 - 0.31 and the feeding rate lower, in the range of 0.43 - 0.46 kg/h. Detailed information about the process operating conditions is presented in Table 2.

The effect of equivalence ratio on the volumetric yield of each gaseous species, on the basis of per unit mass of dry and ash free biomass ($m^3/kg_{biomass}$), is presented in Fig. 1 and

Table 2 Main process operating parameters for the gasification campaign.

Test #	1	2	3	18	20	21	22	9	12	14	15	16	17
Torrefied (T) or un-torrefied (UT)	T	T	T	T	T	T	T	UT	UT	UT	UT	UT	UT
Biomass flow rate,, kg/h	0.57	0.57	0.58	0.6	0.56	0.55	0.56	0.46	0.43	0.40	0.4	0.43	0.46
Equivalence ratio	0.18	0.21	0.23	0.22	0.26	0.27	0.28	0.32	0.22	0.25	0.27	0.30	0.305
Air flow rate, dm^3/min	8.3	9.7	11.2	11.1	12.05	12.15	13.2	9.7	6.2	6.4	7.3	8.5	9.2
N_2 flow rate, dm^3/min	4	2.6	1.1	2.1	1.15	1.05	0	2.6	6.1	5.9	5.0	3.8	3.1
Gasification medium, flow rate, dm^3/min	12.3	12.3	12.3	13.2	13.2	13.2	13.2	12.3	12.3	12.3	12.3	12.3	12.3

Fig 2. The yield of molecular hydrogen (H_2) was marginally lower for the torrefied miscanthus when compare to that of raw miscanthus. This could be a logical consequence of the pre-treatment; where less chemically bound hydrogen was available to the torrefied feedstock (see Table 1).

Fig. 1. The effect of equivalence ratio (ER) on the main gaseous compounds at 800 ºC: solid symbol and line – Un-torrefied MxG; dashed line and open symbol – Torrefied MxG.

In air gasification the influence of the fuel's moisture content is an important parameter, since it is converted into steam shortly after the fuel particle is fed into the bed, and can thus enhance the rate of the water-gas-shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$). Torrefied MxG contained less moisture than un-torrefied (2.4% vs. 8.8%), and therefore the limited presence of steam in gas phase may reduce the extent of the reaction of carbon monoxide toward production of hydrogen. In contrast, for un-torrefied MxG the concentration of steam during gasification was higher which could potentially promote the water-gas-shift reaction resulting in a higher yield of H_2 and lower yield of CO when compared to torrefied material.

As expected on the basis of results reported in the literature [21, 22] an increase of ER results in a reduction of hydrogen yield for un-torrefied MxG as a consequence of the increased amount of oxygen available for reaction with volatiles in the pyrolysis zone and is associated with a simultaneous increase in CO_2, whereas, for torrefied MxG, an increase in ER appears not to have any effect on the H_2 yield, which remains relatively constant over the range of ER studied. The yield of CO_2 was higher for the gasification of torrefied miscanthus which could be the results of lower reactivity of torrefied MxG char towards CO_2. In a more fundamental study, Xue and co-workers [23] investigated gasification reactivity of torrefied and non-torrefied MxG and reported that the torrefied biomass showed lower overall conversion rate and instantaneous reactivity than raw. Following torrefaction, the chemical composition of the biomass is changed; the relative content of lignin and cellulose increases, whereas the

content of hemicellulose, the most reactive component, was significantly reduced. Xue et al. reported that torrefied MxG showed a higher conversion rate at 850 °C, and it was concluded that torrefied biomass, as a result of physical and chemical changes, requires higher gasification temperatures for comparable conversion. With regard to the present study, the yield of methane was similar for torrefied and un-torrefied miscanthus. Moreover, modification of ER did not have any influence on CH_4 yield in the final product gas, (Fig1).

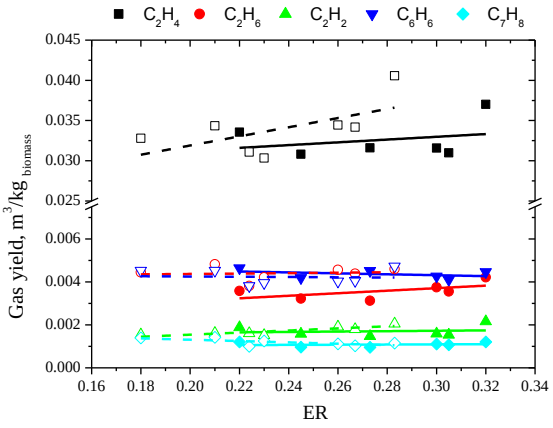

Fig. 2. The effect of equivalence ratio on the minor gas compounds at 800 ºC: solid symbol and line – un-torrefied MxG; dashed line and open symbol – Torrefied MxG.

Regarding light hydrocarbons (Fig. 2), the yields of ethylene and ethane were marginally higher for torrefied than for un-torrefied MxG, though overall, this data set is comparable in quality and extent. Generally, an increase in ER didn't have a significant influence on the yield of acetylene, ethane, benzene and toluene for both torrefied and un-torrefied MxG. Only for ethylene, a slight increase in the yield with increasing ER was observed in case of torrefied biomass.

Figures 3 to 6 present the variation of the main process performance parameters [24] as a function of ER: the specific yield of product gas, its LHV (calculated based on gas composition but excluding the contribution of tar compounds), its specific energy (the chemical energy of the producer gas per kg of biomass), carbon and hydrogen conversions as well as cold gas efficiency (the fraction of the chemical energy of biomass transferred to the product gas). An increase of ER caused an increase in specific yield of product gas from 1.9 to 2.3 $m^3/kg_{biomass}$ for un-torrefied and 1.8 to 2.5 for torrefied MxG (see Fig. 3). The specific gas yield was slightly higher for torrefied MxG,whereas an increase of ER induces a reduction of syngas heating value for both un-torrefied (from 6.45 to 4.87 MJ/m^3) and torrefied MxG (from 6.63 to 5.03 MJ/m^3) (see Fig. 4). The LHV was slightly higher for the un-torrefied biomass. These opposite effects balance each other for un-torrefied biomass, and a product gas specific energy of about 11 $MJ/kg_{biomass}$, was observed. While for torrefied biomass, the specific energy yield fluctuated around $12MJ/kg_{biomass}$ with increasing ER (see Fig. 5).

At ER=0.22 and 0.23 lower values of 10.4 and 10.8 $MJ/kg_{biomass}$ were observed. A corresponding variation for both materials was observed in terms of cold gas efficiency reported in Fig. 6. An increase in ER didn't have a significant influence on the CGE of untreated biomass, it oscillated around 66 to 70%; while CGE of torrefied MxG fluctuated between 50 and 61 % for the range of ERs studied. For gasification at 800 °C, the amount of chemical energy of torrefied MxG transferred into the product gas was on average 18% (from 13 to 24 %) lower when compared to non-torrefied MxG.

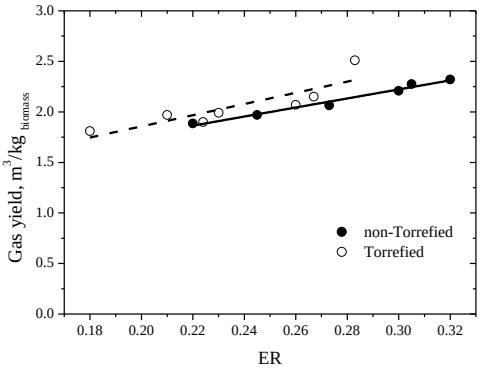

Fig. 3. The effect of equivalence ratio on the specific yield of product gas at 800 ºC.

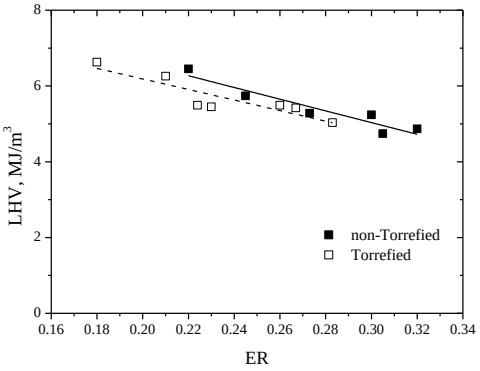

Fig. 4. The effect of equivalence ratio on the heating value of the product gas, for gasification at 800ºC.

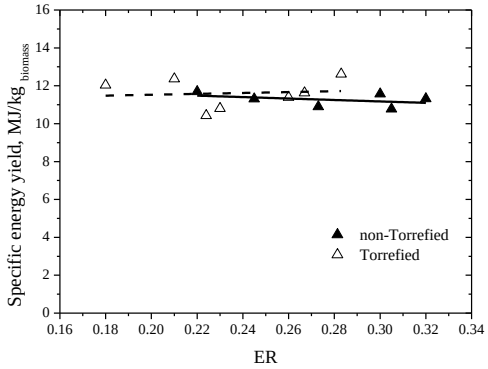

Fig. 5. The effect of equivalence ratio on the specific energy yield for gasification at 800 ºC.

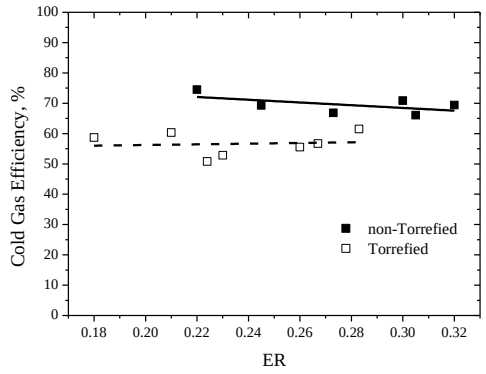

Fig. 6. The effect of equivalence ratio on cold gas efficiency (gasification at 800 ºC).

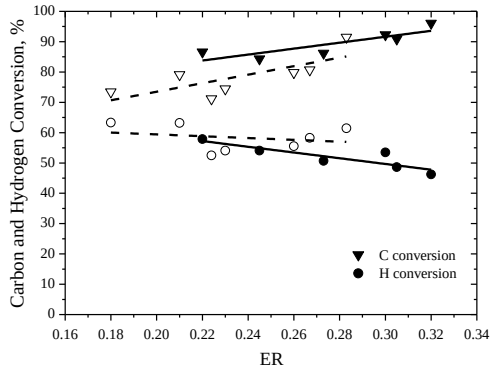

Fig. 7. The effect of equivalence ratio on C and H conversion (gasification at 800 ºC): solid symbol and line – un-torrefied MxG; dashed line and open symbol – Torrefied MxG.

The comparison of carbon and hydrogen conversion for both biomasses as a function of ER is shown in Fig. 7. In the same ER range the carbon conversion of un-torrefied was higher than torrefied MxG. This is in agreement with observations of other researchers [11, 14]. Throughout torrefaction, permanent gases like CO_2, CO, CH_4 [19, 20] were released but not utilized in the gasification process contributing to the lower carbon conversion of torrefied biomass. Carbon conversion was in the range from about 70 to 90% for torrefied, and from about 85 to 95% for un-torrefied MxG, increasing with increasing ER for both feedstocks. Another reason for the lower carbon conversion of torrefied biomass is carbon loss due to char elutriation. The elutriation rate of particulates (char + ash) from the gasifier for torrefied MxG was at about 60-70 $g/kg_{biomass}$ as opposed to about 30 $g/kg_{biomass}$ for un-torrefied biomass. In contrast, hydrogen conversion was slightly higher for torrefied than un-torrefied MxG. Relatively low hydrogen conversion when compared to carbon conversion, is mainly due to the hydrogen losses with unreacted water/moisture in the product gas, which is condensed out with the tar compounds. The hydrogen conversion of un-torrefied MxG decreased with ER, since more oxygen was available for reactions with hydrogen containing volatiles, and more water was produced as a result of oxidation. The hydrogen conversion for un-torrefied was decreasing with ER in the range from 58 to 46%, whereas for torrefied MxG an average hydrogen conversion value of about 60% was obtained for the studied range of ER.

Conclusions

This work reports experimental results concerning the influence of torrefaction on products yields during air-blown fluidized bed gasification.

Gasification experiments varying equivalence ratio (ER) and using torrefied and un-torrefied grassy biomass, Miscanthus, were carried out. On the basis of the data obtained for allothermal gasification in the studied range of operating process parameters (temperature 800ºC, ER 0.18-0.32, biomass feeding rates of 0.55 - 0.6 kg/h for torrefied and 0.43 - 0.46 kg/h for un-torrefied) the following conclusions can be drawn:

- A marginally higher specific gas yield was observed for torrefied MxG;
- The higher heating value of the product gas was slightly higher for un-torrefied biomass;
- The cold gas efficiency of un-torrefied MxG oscillated between 66 and 70% (vs Equivalence Ratio), while for torrefied MxG it fluctuated from 50 to 61 % with an increase in ER;
- The carbon conversion of un-torrefied MxG was higher (from 85 to 95%) than that of torrefied MxG (from 70 to 90%). Lower carbon conversion for pre-treated biomass was a result of volatile losses during torrefaction, and carbon losses through char elutriation from the bed during gasification;
- The elutriation rate of char from the gasifier for torrefied MxG was about two fold that of un-torrefied.
- The hydrogen conversion was higher for torrefied MxG since gasification of this feedstock results in higher yields of C_2H_4, C_2H_6 and lower yields of unreacted process water. Hydrogen conversion for un-torrefied decresedwith ER in the range from 58 to 46%. Whereas for torrefied MxG an average hydrogen conversion value of about 60% was observed.

Acknowledgements

The financial support provided by the EU project Biomass Research Infrastructure for Sharing Knowledge (BRISK, funded by the European Commission Seventh Framework Program (Capacities)) and Enterprise Ireland Competence Centre for Biorefining & Biofuels as research Grants (CC/2009/1305A) are gratefully acknowledged. The authors wish to thank the Energy Research Centre of Netherlands (ECN) for the technical support and

cooperation. Gang Xue acknowledges the postgraduate research scholarship received from Chinese Scholarship Council. Stephen Dooley is supported by Science Foundation Ireland under Grant No: 799 06/CP/E007.

References

[1] Xue, G., Kwapinska, M., Horvat, A., Kwapinski, W., Rabou, L. P. L. M., Dooley, S. Czajka, K. M., Leahy, J. J., Bioresource Technology 159 (0) (2014) 397-403.
[2] Chew, J. J., Doshi, V. Renewable and Sustainable Energy Reviews 15 (8) (2011) 4212-4222;
[3] Bergman, P. C. A., Boersma, A. R.; Kiel, J. H. A.; Prins M.J.; Ptasinski, K. J.; Janssen, F.J.J.G. Energy Research Centre of the Netherlands, Report ECN-C--05-067 (2005).
[4] Bridgeman, T. G.; Jones, J. M.; Shield, I.; Williams, P. T., Fuel 87 (6) (2008) 844-856.
[5] Ibrahim, R. H. H.; Darvell, L. I.; Jones, J. M.; Williams, A., Journal of Analytical and Applied Pyrolysis 103 (0) (2013) 21-30.
[6] Phanphanich, M.; Mani, S., Bioresource Technology 102 (2) (2011) 1246-1253.
[7] van der Stelt, M. J. C.; Gerhauser, H.; Kiel, J. H. A.; Ptasinski, K. J., Biomass and Bioenergy 35 (9) (2011) 3748-3762.
[8] Bridgeman, T. G.; Jones, J. M.; Williams, A.; Waldron, D. J., An investigation of the grindability of two torrefied energy crops. Fuel 89 (12) (2010) 3911-3918.
[9] Bergman, P. C. A.; Boersma, A. R.; Zwart, R. W. R.; Kiel, J. H. A. Energy Research Centre of the Netherlands (ECN), Report ECN-C--05-013 (2005).
[10] Arnsfeld, S.; Senk, D.; Gudenau, H. W. Journal of Analytical and Applied Pyrolysis 107 (0) (2014) 133-141.
[11] Prins, M. J.; Ptasinski, K. J.; Janssen, F. Energy 31 (15) (2006) 3458-3470.
[12] Couhert, C.; Salvador, S.; Commandré, J. M., Fuel 88 (11) (2009) 2286-2290.
[13] Chen, W.-H.; Chen, C.-J.; Hung, C.-I.; Shen, C.-H.; Hsu, H.-W. Applied Energy 112 (2013) 421-430.
[14] Berrueco, C.; Recari, J.; Güell, B. M.; Alamo, G. D. Energy 70 (0) (2014) 68-78.
[15] Chen, Q., Zhou, J. S., Liu, B. J., Mei, Q. F. and Luo, Z. Y. Chinese Science Bulletin, 56 (14) (2011) 1449-1456.
[16] Fisher, E.M., Dupont, C., Darvell, L.I., Commandre, J.M., Saddawi, A., Jones, J.M., Grateau, M., Nocquet, T., Salvador, S. Bioresource Technology 119 (2012) 157-165.
[17] Basu, P., Biomass gasification and pyrolysis: practical design and theory. Elsevier Inc.: 2010.
[18] Xue, G. Fluidized bed gasification of raw and torrefied Miscanthus x giganteous. PhD Thesis, University of Limerick, 2014
[19] Deng, J.; Wang, G. J.; Kuang, J. H.; Zhang, Y. L.; Luo, Y. H. Journal of Analytical and Applied Pyrolysis 86 (2) (2009) 331-337.
[20] Medic, D.; Darr, M.; Shah, A.; Potter, B.; Zimmerman, J., Fuel 91 (1) (2012) 147-154.
[21] Gil, J.; Corella, J.; Aznar, M. a. P.; Caballero, M. A., Biomass and Bioenergy 1999, 17 (5) (1999) 389-403.
[22] Arena, U.; Di Gregorio, F. Fuel 117 Part A (0) (2014) 528-536.
[23] Xue, G., Kwapinska, M., Kwapinski, W., Czajka K.M., Kennedy J., Leahy, J.J. Fuel 121 (2014) 189–197.
[24] Arena, U., Waste Management 2012, 32 (4) (2012) 625-639.

ECN
Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

T +31 88 515 4949
F +31 88 515 8338
info@ ecn.nl
www.ecn.nl