SOUTH AFRICAN JOURNAL OF CHEMICAL ENGINEERING 24 (2017) 168–175

Contents lists available at ScienceDirect

South African Journal of Chemical Engineering

journal homepage: http://www.journals.elsevier.com/south-african-journal-of-chemical-engineering

Energy densification of animal waste lignocellulose biomass and raw biomass

G. Pahla [a,*], T.A. Mamvura [b], F. Ntuli [a], E. Muzenda [c]

[a] University of Johannesburg, Department of Chemical Engineering, School of Mining, Metallurgy and Chemical Engineering, Faculty of Engineering and the Built Environment, P. O. Box 17011, Doornfontein, 2088, Johannesburg, South Africa

[b] Department of Civil and Chemical Engineering, College of Science, Engineering and Technology, University of South Africa, Christian de Wet and Pioneer Avenue, Private Bag X6, Florida, 1710, Johannesburg South Africa

[c] Materials and Metallurgical Engineering Department, College of Engineering and Technology, Botswana International University of Science and Technology, Private Mail Bag 16, Palapye, Botswana

ARTICLE INFO

Article history:
Received 4 July 2017
Accepted 10 October 2017

Keywords:
Torrefaction
Biomass
Temperature
Cow dung
Corn cobs
Pine wood

ABSTRACT

The need to reduce carbon emissions has encouraged more research into use of biomass energy in place of coal. Biomass is carbon neutral; its use can therefore lower net emissions. Biomass can be upgraded to a fuel similar to coal by torrefaction. Different biomass have been torrefied but there is limited research in possible use of lignocellulose biomass from animal waste. This study aims to compare extent of energy densification of torrefied cow dung, corn cob and pine wood. They were dried, ground and sieved. Proximate and ultimate analysis was conducted. The samples were then torrefied at 200, 250 and 300 °C at 10 °C/min for 40 min. The resulting biochar were characterized using mass yield, higher heating value, energy yield and density. Biochar obtained at 250 °C were analyzed for elemental composition. Results were compared to Anglo bituminous coal and other torrefied biomass in literature. Corn cob and pine wood reached a maximum of 25.98 MJ/kg and 20.90 MJ/kg in heating value respectively whilst cow dung only increased to a maximum of 18.60 MJ/kg. Increase in heating value for corn cob was attributed to reduction in oxygen due to release of volatiles as well as water. This lowered the O/C ratio thereby densifying the fuel. The O/C and H/C ratio for corncob and wood moved towards that of bituminous coal unlike that of cow dung. Cow dung had a high inorganic composition so its heating value could not be upgraded as much as the other 2 biomass. Its use as a torrefaction raw material was therefore discouraged.

© 2017 The Authors. Published by Elsevier B.V. on behalf of Institution of Chemical Engineers. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

The need for use of renewable energy in order to curb the effect of greenhouse gases such as CO_2 has paved way for more research into green technologies. Coal can be mixed or replaced with biomass to reduce net CO_2 emissions (Bergman et al., 2005). The benefit being that biomass uses CO_2 for photosynthesis during growth, so this can account for CO_2 produced when biomass is combusted. Biomass also has little or no sulfur content unlike fossil fuels which release sulfur oxides from oxidation of their organic sulfur. Sulfur oxides result in health and environmental problems such as acid rain.

Biomass has undesirable characteristics which make it uneconomic to blend with coal or to substitute coal. Biomass such as wood, organic waste and process byproducts usually

* Corresponding author.
E-mail address: gpahla44@gmail.com (G. Pahla).
https://doi.org/10.1016/j.sajce.2017.10.004
1026-9185/© 2017 The Authors. Published by Elsevier B.V. on behalf of Institution of Chemical Engineers. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

is bulky and has high moisture content (Chen et al., 2015a). This makes it expensive to transport and it also requires more energy for particle size reduction. Moisture also reduces the heating value of the biomass. Furthermore, it is hygroscopic and fibrous unlike coal (Ciolkosz and Wallace, 2011). There is therefore a need to improve these properties before incorporation into the coal energy mix. Torrefaction is a green technology process which can alter biomass structure to make it similar to that of coal. The idea being that of mixing a portion of processed biomass with bituminous coal, which is used in most coal fired boilers in electricity power plants.

Torrefaction is a mild pyrolysis process which thermochemically alters biomass structure by eliminating moisture and light volatiles. It also improves biomass structure through polymer alterations (Bridgeman et al., 2008; Pimchuai et al., 2010; Prins et al., 2006). It is a temperature sensitive process which is effective between 200 °C and 300 °C in an inert environment. Bergman et al. (2005), suggested that torrefaction reactions are complex, however it is believed that it follows the following 5 steps depending on the torrefaction temperature and type of biomass. These steps are as follows:

1 Drying
2 Glass transition/softening
3 Depolymerization and recondensation
4 Limited devolatilization and carbonization
5 Extensive devolatilization and carbonization (Bergman et al., 2005).

The first step in biomass torrefaction is drying in which biomass loses unbound moisture. This happens at temperatures below 120 °C. As temperature increases to 150 °C–200 °C biomass softens and begins to depolymerize. This happens by breakage of some H–C and O–C bonds, resulting in condensation of some short chain polymers in the solid structure (Antal and Grønli, 2003). However, biomass devolatilization starts at temperatures higher than 200 °C leading to a disruption of intermolecular and intramolecular hydrogen bonds, and C–C and C–O bonds in biomass resulting in the release of some oxygenated compounds such as alcohols, carboxylic acids, aldehydes, ethers, and some permanent gases as CO, CO_2 and CH_4. In the case where the torrefaction temperature is lower than 250 °C, hemicellulose is mostly decomposed while the decomposition of cellulose and lignin are limited. However, by increasing the torrefaction temperature up to 300 °C all the biomass compounds are involved in devolatilization (Antal and Grønli, 2003). Devolatilization increases energy density by reducing (O/C) and (H/C) ratios (Asadullah et al., 2014). The ultimate result is better grindability and higher calorific value compared to raw biomass (Wannapeera et al., 2011).

The 5 stages in biomass torrefaction occur at different torrefaction residence times and torrefaction temperatures depending on the physical structure and type of the biomass. Generally, it is 15–60 min and 200–300 °C respectively (Van der et al., 2011). Torrefaction has been done on a wide range of biomass such as peaken nut shells, willow, corn cobs, wood and many agricultural by-products (Bridgeman et al., 2008; Prins et al., 2006; Haykiri-Acma et al., 2006; Zheng et al., 2013). The studies mainly focused on effect of temperature, residence time and heating rate on quality of torrefied biomass. Their findings reported energy densification of 15–30%. The calorific values increased from 17 to 19 MJ/kg (raw) up to 19–28 MJ/kg (torrefied) (Bridgeman et al., 2008; Prins et al., 2006; Haykiri-Acma et al., 2006; Zheng et al., 2013).

There are limited studies comparing the torrefaction of lignocellulose biomass which has passed through an animal's digestive system to raw lignocellulose biomass. It would be beneficial to biomass energy study to investigate whether waste such as cow dung, can also be upgraded by torrefaction. It can be compared to other lignocellulose biomass such as wood, grass and agricultural crops which have been successfully torrefied before. Generally, animal waste biomass like cow dung is expected to produce less energy when combusted than raw biomass such as wood (Dhungana et al., 2012). This might be because some of the original energy in animal food is lost during digestion. The cow dung might also contain some by-products of digestion which might lower its fixed carbon content and hence the heating value. Torrefaction aims to upgrade biomass by improving the heating value through energy densification. It can therefore help to investigate whether it will have the same effect on cow dung.

This study aims to compare energy densification during torrefaction of different types of lignocellulose biomass: animal waste biomass (cow dung) and raw biomass (wood and corn cob). The research can aid in determining suitable raw materials for torrefaction of biomass. The quality of torrefied cow dung will be compared to that of wood, corncob and bituminous coal to determine whether it can also be used in the coal energy mix. This study can be crucial in the design of biomass torrefaction reactors which can incorporate a wide range of biomass. Research has shown that torrefaction is more sensitive to temperature than any other parameter so effect of temperature is to be studied on different biomasses.

2. Materials and methods

2.1. *Materials*

Three different types of biomass were used in this study; Pine wood (Pinus radiate) collected at a wood farm located 3 km from Krugersdorp in Johannesburg, Cow-dung from Fochville at Kokosi Merafong City and Maize corn cobs from Limpopo. Pine wood was chosen because of their vast abundance in South Africa.

Corn cob is referred to as the central core of an ear of maize. It is the part of the ear in which the kernel grow. They are normally red or white in color depending on the type of maize. Dry corn cob is used as fuel in some of the developing countries. It is also used as industrial source of chemical furfural. The corn cob used was collected in the Limpopo province, Ga-kgole village due to its abundance in that province as Limpopo produces approximately 50,000 ton/month of maize.

Cow dung is also known as cow pats, cow pie or cow manure. It is a waste product of bovine animal species, which include domestic cattle. It is the undigested residue of plant matter which has passed through the animal gut. The resultant faecal matter is rich in minerals. It is usually dark magenta in color. It finds most of its uses in agriculture as fertilizer. In most developing countries, dried cow dung is used as fuel. It is also collected and used to produce biogas for generating electricity and heat. Moreover, the gas released when burning cow dung is rich in methane and is used in most countries to provide renewable and stable source of energy. In the villages, cow dung is used to manufacture mud bricks and when mixed with water and soil to line the walls as a form of cheap thermal insulator. The cow dung used in this experiment was collected in Kokosi Township, West Rand of Johannesburg. It was chosen due to its abundance and cost effectiveness because approximately 80% of South Africans are in cattle farming.

The samples were dried in a Labotec oven at 105 °C (Poudel et al., 2015). Pine wood logs were cut to smaller pieces using a saw prior drying to allow efficient heat transfer and moisture removal. The dry samples were then weighed and crushed for size reduction. A ball mill was used for cow-dung and corn cobs, and the rod mill for pine wood. The three samples were then sieved after the size reduction to collect particles with a particle size <750 μm.

Proximate and ultimate analysis was done and the results presented. Moisture content (MC), Volatile content (VC) and Ash content (AC) were determined using American standards ASTM E1358-97, E872-82 and E1534-93 respectively. Fixed carbon was then calculated by difference. Elemental composition was determined using a Thermo scientific flash 2000 CHNS-O analyzer fitted with auto sampler and quartz reactor.

The Higher Heating value of raw and torrefied biomass was measured using an e2k combustion calorimeter. The calorific value was determined according to BSI standard EN 14918 using e2k combustion calorimeter, in which 0.50 g of biochar was completely combusted under a pressurized O_2 atmosphere (3000 kPa). Calorific value of each raw biomass was obtained the same way.

2.2. Equipment and procedure

2.2.1. Torrefaction equipment

The torrefaction experiment was carried out in Elite Lenton (TSH12/38/500.2216E) tube furnace. It consists of a cylindrical cavity surrounded by heating coils that are embedded in a thermally insulating matrix. It uses molybdenum di-silicide heating elements located along two sides of the insulation. The furnace was connected to a nitrogen line to flash air and create an inert environment in the tube. Nitrogen flowrate was controlled using a Multi Gas Controller 647C. The experiment setup is shown in Fig. 1.

2.2.2. Procedure

Three crucibles were each filled with 3 g of Pine wood (PW), Cow dung (CD) and Corn Cobs (CC) respectively to an accuracy of ±0.01 g. The crucibles were put in the quartz glass tube before introducing the tube into the furnace. Nitrogen line was connected to the quartz tube and an exhaust line was connected at the other end. Nitrogen flowrate was adjusted to 150 ml/min, heating rate was adjusted to 10 °C/min and temperature was set to 200 °C for the first run. Torrefaction temperature was varied from 200 °C to 250 °C and 300 °C keeping heating rate at 10 °C/min and residence time at 40 min. The torrefied product was allowed to cool to room temperature in a nitrogen atmosphere after each run. The product was then weighed before calorific value determination.

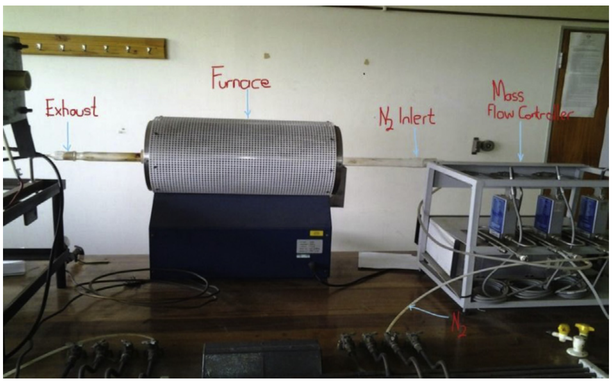

Fig. 1 – Torrefaction experiment setup.

Heating rate and Residence time were also investigated and reported elsewhere. Optimum temperature for each biomass was then obtained using mass yield, calorific value, energy yield and energy density. Mass yield, energy yield and energy density were computed using Equations (1)–(3) respectively.

$$Mass\ \ Yield = \frac{M_t}{M_r} \times 100 \tag{1}$$

where, M_t is mass of torrefied biomass and M_r is mass of raw biomass

$$Energy\ \ Yield = Mass\ \ yield \times \frac{CV_t}{CV_r} \tag{2}$$

where, CV_t and CV_r (MJ/kg) is the higher heating value of torrefied and raw biomass respectively

$$Energy\ \ Density = \frac{Energy\ \ Yield}{Mass\ \ Yield} \tag{3}$$

Samples obtained at the optimum temperature were analyzed for elemental composition using a Thermo scientific flash 2000 CHNS-O analyzer.

3. Results and discussions

3.1. Proximate and ultimate analysis

The fuel properties of the three samples were determined by proximate and ultimate analysis as explained in Section 3. The analysis can help predict if the biomass can be utilized as solid fuel. The results together with comparisons with raw biomass from previous studies are presented in Tables 1 and 2. Table 1 shows the composition of fixed carbon, volatile matter, ash content and moisture content, as well as the higher heating value. The quality of a solid fuel is determined mainly by its percentage of fixed carbon and moisture. Generally, more moisture content is associated with less fixed carbon which in turn reduces the heating value. High moisture content also entails that more energy would be required to evaporate water and hence the fuel will be less efficient.

Cow dung had the highest moisture content amongst the 3 biomass, having almost half of its mass composed of water. This was expected since it was wet waste biomass. Pine wood had a relatively high moisture content compared to corn cob which had the lowest at 10%. Cow dung also had the highest ash content and lowest volatile content. Ash content reduces quality of fuel as ash is associated with fouling. High volatile matter ensures easy ignition, so it would be easier to ignite corn cob than the other 2 biomass. All 3 biomass had comparable heating values with pine wood having a slightly higher value.

These results are close to those obtained by Chen and Kuo (2010) who studied bamboo, willow coconut shells and wood. The wood studied however had a lower fixed carbon percentage as compared to pine wood. Biomass in the current study as well as those investigated by Chen and Kuo (2010) had

Table 1 – Proximate analysis of raw biomass (dry basis).

Biomass	FC (%)	VM (%)	AC (%)	MC (%)	HHV (MJ/kg)	Researcher
Corn Cob	12.11	71.38	6.51	10.00	16.73	Current work
Cow Dung	15.46	15.13	21.41	48.00	16.78	
Pine Wood (Pinus radiate)	12.79	65.11	2.10	20.00	17.94	
Bamboo	12.85	63.54	6.75	16.86	17.32	Chen and Kuo (2010)
Willow	16.05	78.91	2.77	2.27	18.37	
Coconut shell	15.58	63.76	7.78	12.86	17.66	
Wood (*Ficus benjamina* L)	8.98	77.13	11.35	2.54	16.39	

Table 2 – Elemental analysis of raw biomass (dry basis).

Biomass	C	H	N	O	S	O/C	H/C	Researcher
Corn Cob	41.16	5.11	0.46	53.27	0	1.27	0.12	Current work
Cow dung	38.00	3.94	1.21	56.85	0	1.50	0.10	
Pine wood	43.28	5.10	0.35	51.27	0	1.18	0.12	
Corncob	44.78	6.02	0.22	48.77	0.21	1.09	0.13	García et al. (2012)
Saw dust	45.34	6.02	0.53	47.05	1.07	1.04	0.13	
Maize	40.96	6.92	1.17	50.71	0.23	1.24	0.17	
Potato plant waste	38.33	5.07	1.13	55.03	0.44	1.44	0.13	

heating values in the range 16–18.5 MJ/kg. For possible co-firing, the heating value has to be upgraded to values close to that of bituminous coal, which ranges between 24 and 30 MJ/kg (Li et al., 2012). This can be achieved by reducing the moisture and volatile content which in turn increases fixed carbon and HHV.

Fuel properties can also be predicted by elemental composition. Generally, fuels with more carbon content are expected to release more energy per unit mass during combustion. This can be explained by the high energy content in C–C bonds as compared to O–H, C–H or C–O bonds. A good quality fuel is therefore expected to have low O/C and H/C ratios. Table 2 shows that cow dung had the highest O/C ratio compared to corn cob and pine wood. Its O/C ratio is comparable to that of potato plant waste which also had a low carbon percentage. The corn cob studied in the current work had slightly less carbon and more oxygen as compared to that studied by García et al. (2012). This can be attributed to different climate conditions and different types of maize. Biomass in the current study had no sulfur content, unlike the one studied by García et al. (2012). This is desirable as it reduces air pollution through release of sulfur oxides.

It can also be observed that all the raw biomass had more oxygen than carbon. To improve the fuel properties, there is need to reduce the oxygen content which in turn would cause an increase in carbon content.

3.2. *Biomass torrefaction*

Torrefaction was conducted by varying temperature from 200 to 300 °C in 50 °C increments. The heating rate and residence time were kept constant at 10 °C/min and 40 min respectively. Mass yield, calorific value, energy yield and energy density were determined.

3.2.1. *Mass yield*

Mass after torrefaction was compared to mass of raw sample and presented in Fig. 1 together with mass yield from literature.

Fig. 2 shows that mass yield decreased with increasing torrefaction temperature for all biomass. Corn cob and cow dung, however recorded a slight difference in mass yield when temperature was increased from 200 to 250 °C. A noticeable difference was only observed between 250 and 300 °C. Torrefaction at 300 °C resulted in all biomass losing almost half of initial mass. The trend can be compared to that for corn stover which was studied by Medic et al. (2012); its mass loss was also close to 50% at 300 °C.

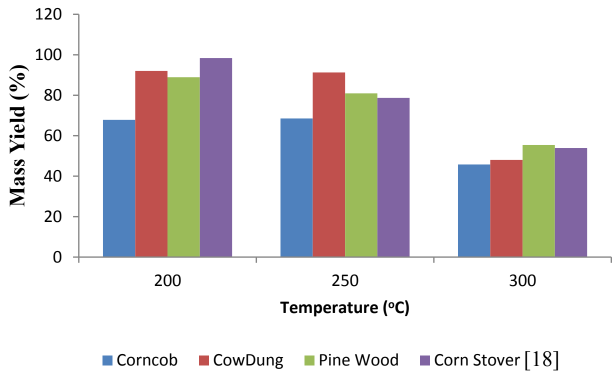

Fig. 2 – Variation of mass yield with torrefaction temperature.

At 200 °C, the slight weight loss can be attributed to loss of bound moisture which was still in the biomass after drying. Corn cob therefore had more inherent moisture since it had the lowest mass yield amongst the 3 at 200 °C. Pine wood was the most reactive of the 3 between 200 and 250 °C. This can be attributed to degradation of hemicellulose which produces mainly CO_2 and H_2O (Chen et al., 2012). Corn cob and cow dung required a higher temperature for the decomposition reactions. This is because a minimum activation energy is required to initiate a reaction. Corn cob and cow dung therefore had higher activation energies compared to pine wood.

Torrefaction at 300 °C resulted in drastic weight loss in all the biomass. This shows that all biomass were reactive between 250 and 300 °C. The main reactions being decomposition of hemicellulose as well as depolymerization of lignin (Zheng et al., 2013). Cellulose decomposition usually starts from 275 °C, whilst lignin gradually degrades from 250 °C (Chen and Kuo, 2010). The degradation of cellulose and lignin can be explained by a bimolecular nucleophilic substitution reaction. During this reaction, a hydroxyl group on one cellulose polymer chain is protonated. It is then attacked by another cellulose polymer acting as a nucleophile. The reaction results in production of ethers, water, formaldehyde, acetic acid as well as aromatic compounds. CO_2, H_2O and small amounts of CO and CH_4 are also released (Zheng et al., 2013). The condensable compounds such as aromatic compounds form tars whilst the non-condensables can be collected as gas. Downie et al. (2009) also observed that the amount of volatiles released increased with torrefaction temperature due to charring and devolatilization.

Practically, torrefaction at 300 °C results in a more severe mass loss for all the biomass. The severe mass loss was also witnessed by Chen and Kuo (2010) who recorded 45, 48, 61 and 61% as mass yields for bamboo, willow coconut shell and wood respectively. This entails loss of much of the raw material during the fuel upgrading process, making the process less efficient. On the other hand, torrefaction at 200 °C did not initiate the upgrade process in the case of pine wood and cow dung which had slight mass loss. A compromise temperature at which fuel upgrading is balanced off with mass loss has to be determined to ensure optimum torrefaction. Determination of this optimum temperature can be achieved by comparing mass yield to calorific value of torrefied biomass.

3.2.2. *Higher heating value*

Calorific value of raw and torrefied biomass was determined using e2k bomb calorimeter. The results are presented in Fig. 3. Generally, HHV had a direct relationship with torrefaction temperature. Corncob responded more positively to increase in torrefaction temperature, followed by pine wood although its HHV dropped when torrefied at 300 °C. Cow dung had a slight response to increase in torrefaction temperature. The trend is similar to that observed for invasive alien plants (Mundike et al., 2016). Corncob had the highest increase in HHV, it increased by 55.2% when torrefied at 300 °C. In comparison, torrefaction of lantana camara at 300 °C resulted in a 50.1% increase in HHV. Cow dung had the least change in HHV, only going to 18.64 MJ/kg from 16.78 MJ/kg which was just a 11% increase. Rousset et al. (2011) and Tsai and Liu (2013) reported HHV increments of 24% and 20% for torrefied coffee residue and bamboo respectively.

This was comparable to the 17% increment in the case of pine wood torrefied at 250 °C but less than the 55.2% increment in the case of corncob.

HHV is directly affected by carbon content as explained in Section 3.1. A higher percentage of fixed carbon means a

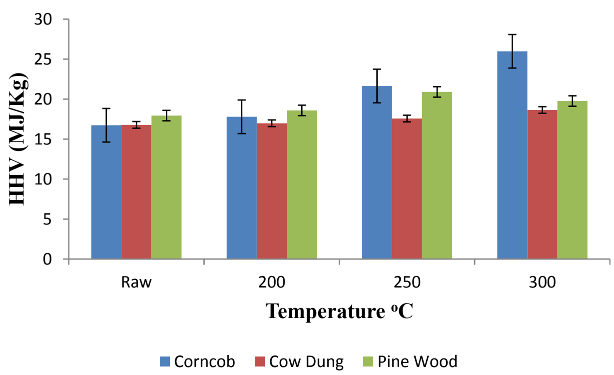

Fig. 3 – Variation of calorific value with torrefaction temperature.

higher calorific value. During torrefaction, fixed carbon is enhanced by thermal degradation of hemicellulose as well as part of cellulose and lignin (Rousset et al., 2011). The decomposition releases compounds which have low energy content, leaving organic compounds with more energy content. The low energy compounds released include H_2O, CO and CO_2, leaving rearranged polymers with more C–C bonds and hence more energy.

The results show that corncob released more low energy content compounds thereby enhancing its heating value. Cow dung however, did not experience much HHV enhancement because it had less volatile content and more ash content as shown in Table 1. It therefore has less energy content compounds which can be released as volatiles to enhance fixed carbon. The ash represents solid inorganic compounds which cannot be altered through torrefaction, hence the heating value did not have a significant change. This makes torrefied cow dung a low quality fuel as compared to other torrefied biomass. The HHV of pine wood dropped from 20.9 MJ/kg to 19.76 MJ/kg when torrefaction temperature changed from 250 to 300 °C. This can be explained by loss of carbon compounds with high energy content due to severe torrefaction.

HHV is the most important fuel property from an energy point of view (Tsai and Liu, 2013). It is therefore essential for torrefied biomass to have a calorific value similar or close to that of coal to ensure substitution without jeopardizing the energy balance of the combustion process. A bituminous coal sample from Anglo Mafube South Africa had a calorific value of 25.2 MJ/kg (Bar-Ziv et al., 2014). In comparison, corncob torrefied at 300 °C had 25.98 MJ/kg. This means the 2 can be mixed without reduction of energy output. Cow dung had a maximum HHV of 18.64 MJ/kg which is lower compared to bituminous coal, mixing these 2 would result in less process efficiency. Pine wood had an acceptable HHV (20.9 MJ/kg) at 250 °C. Bamboo torrefied at 250 °C also produced a biochar with 21 MJ/kg which is similar to that of pine wood (Chen et al., 2015b).

The Highest HHV for all the biomass in Fig. 3 was obtained after torrefaction at 300 °C except for pine wood. This shows that torrefaction favors HHV increment for most biomass. This HHV increment should however be compared to the extent of weight loss. Severe torrefaction is associated with more weight loss as explained in Section 3.2.1. As much as the HHV should increase to values closer to those of bituminous coal, it should not jeopardize the mass yield as this will negatively affect the energy balance of the process. Mass and HHV can however be used to determine energy yield which helps in choosing the optimum torrefaction temperature.

3.2.3. *Energy yield*

Energy yield refers to a percentage of the original energy content which still remains in the biochar after torrefaction. It is a measure of the balance between mass loss and HHV enhancement. The energy yield of each biomass was computed and presented in Fig. 4 (Bridgeman et al., 2008). It can be observed in Fig. 4 that the biomass experienced an increase in energy yield when temperature increased from 200 to 250 °C. The energy yield then had a pronounced decline with further increase in temperature to 300 °C. For pine wood there was only 1% difference in energy yield when torrefied at 200 °C as compared to 250 °C. Corncob had a significant increase in energy yield from 72% to 87% between 200 and 250 °C. The Energy yield for cow dung and pine wood dropped

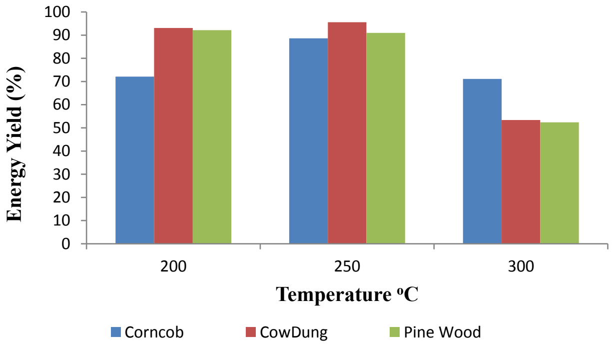

Fig. 4 – Variation of energy yield with torrefaction temperature.

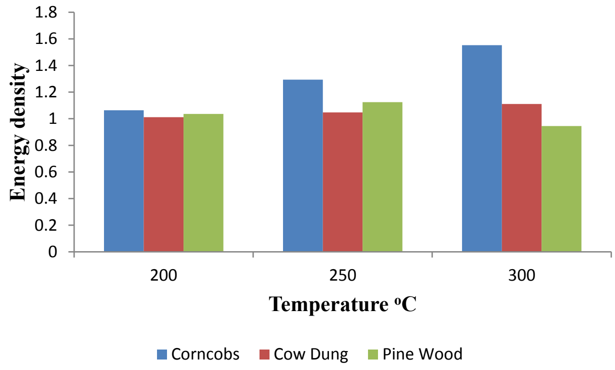

Fig. 5 – Variation of energy density with torrefaction temperature.

below 60% during severe torrefaction at 300 °C whilst that of corn cob remained above 70%.

The initial increase in energy yield can be attributed to insignificant increase in heating value when comparing raw biomass to biochar produced at 200 °C. At 250 °C decomposition reactions ensured a pronounced increase in HHV as explained in Section 3.2.2. The drop in energy yield at 300 °C was because drastic mass loss overshadowed HHV enhancement. At this temperature there was severe torrefaction which resulted in loss of more carbon compounds with high energy content. This reduced the energy yield, making the process less efficient (Li et al., 2015).

Torrefaction of biomass produces a biochar which is supposed to retain most of the original energy, a thick liquid from condensable gases and non-condensable gases (Basu, 2010). When torrefaction temperature increases, there is an increase in volatile yield due to increased devolatilization reactions (Downie et al., 2009; Lehmann and Joseph, 2015). Increase in volatile yield reduces char yield thereby reducing energy retained.

Initially hemicellulose and cellulose degrade together with a small portion of lignin, producing CO_2, CO, CH_4, acetic acid and furfural compounds. With increase in temperature to severe torrefaction range (290–300 °C) aromatic compounds such as phenol, 3-methylphenol, 2-methoxyphenol, 4-ethylphenol and 4-ethyl-2-methoxyphenol are released (Zheng et al., 2012). The aromatic compounds have a significant amount of energy due to their vast C–C bonds. Severe torrefaction is therefore not encouraged especially in the case of cow dung and pine wood as well as biomass studied by Bridgeman et al. (2008). Corncob however had energy yield above 70% at 300 °C which is acceptable for practical application. This was because corn cob had more lignin content than the other biomass which had higher compositions of hemicellulose and cellulose. The decomposition of the later, is more than that of lignin at 300 °C (Phanphanich and Mani, 2011).

3.2.4. *Energy density*

Decomposition of hemicellulose and cellulose leaves a biochar with more carbon density. Energy density therefore increased with increasing torrefaction temperature for corncorb as shown in Fig. 5. Cow dung had a slight densification whilst that of pine wood decreased at 300 °C.

Severe torrefaction is not ideal for pine wood as it reduces its energy density. This can be explained by less lignin in pine wood as compared to corncob. Cow dung did not experience much densification because of its composition. It is waste from the digestive system so it has high inorganic content. Its carbon cannot be enhanced as much as the raw biomass.

In general, high torrefaction temperatures are associated with release of more aromatic compounds and increase in carbon content (Tsai and Liu, 2013). This in turn increases the degree of coalification and change of biomass structure into a hydrophobic and brittle biochar (Li et al., 2015). Hydrophobicity prevents loss of fuel quality during storage and transportation whilst brittleness reduces size reduction energy costs.

The results show that it is essential to have a lignocellulose biomass with more lignin content as a raw material for torrefaction. It is also not advisable to use cow dung because some of the energy is lost in the digestive system. Digestive processes also increase inorganic composition of the biomass, making it less suitable for torrefaction. This can be proved by the slight energy densification of cow dung as compared to other biomass.

The previous sections have shown that although HHV is enhanced at 300 °C, more energy is lost due to severe torrefaction. On the other hand, torrefaction at 200 °C did not result in much HHV enhancement. This leaves 250 °C as the compromise optimum torrefaction temperature for pine wood, cow dung and corn cob.

3.3. *Elemental analysis*

Elemental composition of torrefied biomass was determined in order to compare with that of raw biomass as well as that of bituminous coal. Ideally torrefaction should increase the percentage of carbon by reducing that of oxygen. Samples torrefied at 250 °C were used for elemental analysis, the results are shown in Table 3.

In Table 3, R and T represent raw and torrefied whilst W, CD and CC stand for wood, cow dung and corncob

Table 3 – Elemental analysis of raw and torrefied biomass.

	C (%)	H (%)	N (%)	O (%)	S (%)	O/C	H/C
RW	43.275	5.100	0.350	51.275	0.000	1.185	0.118
TW	49.520	5.345	0.220	44.915	0.000	0.907	0.108
RCD	38.005	3.940	1.210	56.845	0.000	1.496	0.104
TCD	38.195	3.995	1.190	56.620	0.000	1.482	0.105
RCC	42.155	5.110	0.455	52.280	0.000	1.240	0.121
TCC	53.565	5.125	1.490	39.820	0.000	0.743	0.096
Anglo coal	67.290	3.480	1.580	6.720	0.350	0.100	0.050

Table 4 – Elemental analysis of torrefied biomass from literature.

Biomass	Temperature	C	H	N	O	S	Researcher
Bamboo	Raw	47.99	2.88	0.31	46.30	0	Chen et al. (2015b)
	250 °C	55.81	1.51	0.40	38.45	0	
Empty fruit bunches	Raw	45.53	5.46	0.45	43.40	0.04	Wang et al. (2011)
	250 °C	47.07	4.95	1.35	42.24	0.11	
Mesocarp fiber	Raw	46.92	5.89	1.85	43.30	0.10	
	250 °C	47.70	5.20	1.74	40.18	0.10	
Kernel shell	Raw	46.68	5.86	1.01	42.01	0.06	
	250 °C	51.89	5.71	0.47	38.50	0.01	

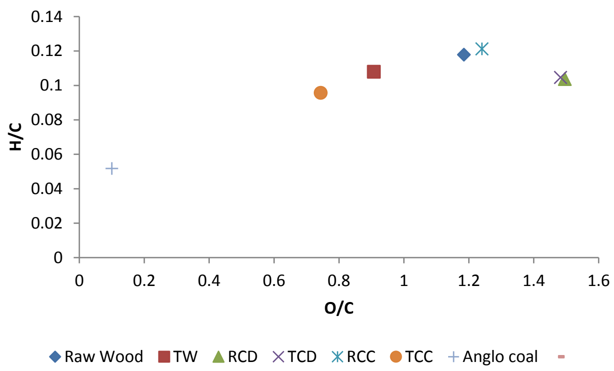

Fig. 6 – Van Krevelen plot of biomass and coal.

respectively. Torrefied biomass had more carbon content and less oxygen content compared to raw biomass. This is desirable as it reduces the O/C ratio thereby improving the higher heating value of the biochar. Corncob had the highest increase (27%) in carbon content due to a pronounced decline in oxygen content from 52.28 to 39.82%. This ensured reduction of O/C from 1.24 to 0.74. Wood also showed a positive response as its O/C was reduced to below 1 coupled with a slight reduction in H/C. However, cow dung did not respond well to torrefaction. Its carbon content remained at 38% with only a small difference of 0.19% between raw and torrefied product.

The O/C ratio of cow dung remained at 1.4 showing that the biomass was not successfully upgraded like the other 2 whose ratios dropped to below 1 after torrefaction. For comparison, elemental compositions of torrefied biomass from literature are presented in Table 4.

Table 4 shows that torrefaction of bamboo and oil palm waste resulted in a similar increase in carbon content when compared to torrefaction of pine wood and corn cob. Amongst the biomass in Table 4, kernel shells were the most sensitive to torrefaction as the carbon content increased by 11%. This was lower than that for corncob, showing that corncob is a better raw material for biomass torrefaction.

Reduction in oxygen content during torrefaction shows that deoxygenation is the primary reaction. This reaction decomposes biomass, causing restructuring and release of CO_2, CO and H_2O as well as oxygen-containing organic compounds such as acetic acid, methanol, and phenols (Wang et al., 2011). This leads to an apparent increase in carbon content, thereby improving fuel quality.

The results show that, the O/C and H/C ratios for pine wood and corn cob were reduced by torrefaction towards bituminous coal values. The O/C and H/C ratios for cow dung did not change much, showing that it was relatively insensitive to torrefaction. Fig. 6 compares the elemental ratios using the Van krevelen plot.

Fig. 6 shows that corncob and pine wood responded well to torrefaction as their position in the plot moved towards that of bituminous coal after torrefaction. Corncob had a more positive response than pine wood. Cow dung did not respond well to torrefaction as the position of the biochar remained close to that of its raw counterpart. This agrees with results obtained by Dhungana et al. (2012), who investigated the torrefaction of biomass which had gone through animal digestive system (Poultry litter), the HHV could only be upgraded to 19.18 MJ/kg.

4. Conclusions

Cow dung, corncob and pine wood samples were torrefied with the aim of comparing quality of the different biochar. The main focus was on comparing the extent of energy densification between lignocellulose biomass from animal waste and raw lignocellulose biomass. The biomass was torrefied at different torrefaction temperatures, the resulting biochar was analyzed by measuring calorific value and computing mass and energy yield as well as energy density. Elemental composition of raw and torrefied biomass were also determined and analyzed. Corncob and pine wood had more positive responses to torrefaction. Their heating values were upgraded to 25.98 MJ/kg and 20.90 MJ/kg respectively. These values are comparable to that of Anglo Mafube bituminous coal (25.20 MJ/kg) which was used for comparison. Torrefied Corncob and pine wood can therefore be considered for co-firing. Cow dung however did not respond well to torrefaction as its HHV only increased to a maximum of 18.60 MJ/kg which is quite low compared to bituminous coal. Mixing torrefied cow dung with coal will therefore reduce energy output and lower combustion process efficiency. Increase in heating value for corn cob was attributed to reduction in oxygen content due to release of low energy volatiles together with water. Reduction in oxygen caused an apparent increase in carbon content thereby reducing the O/C ratio and densifying the fuel. The O/C and H/C ratio for corncob and wood moved towards that of bituminous coal unlike that of cow dung. Cow dung had a high inorganic composition so its heating value could not be upgraded as much as the other 2 biomass. Its use as a torrefaction raw material was therefore discouraged. It can still be used in other applications such as organic fertilizer and biogas production.

Acknowledgements

The authors would like to acknowledge Makhubela G.L, Dlova S and Sehoane M.P who conducted the experiments under the guidance of senior researchers. Also, acknowledgement goes to department of Chemical Engineering and PEETS for all their assistance. Lastly, acknowledgement goes to Chemistry department at The University of Johannesburg for assistance in elemental analysis and Metallurgy department for assistance with size reduction and calorific value determination.

References

Antal, M.J., Grønli, M., 2003. The art, science, and technology of charcoal production. Ind. Eng. Chem. Res. 42 (8), 1619–1640.
Asadullah, M., Adi, A.M., Suhada, N., Malek, N.H., Saringat, M.I., Azdarpour, A., 2014. Optimization of palm kernel shell torrefaction to produce energy densified bio-coal. Energy Convers. Manag. 88, 1086–1093.
Bar-Ziv, E., Saveliev, R., Korytnyi, E., Perelman, M., Chudnovsky, B., Talanker, A., 2014. Evaluation of performance of Anglo-Mafube bituminous South African coal in 550MW opposite-wall and 575MW tangential-fired utility boilers. Fuel Process. Technol. 123, 92–106.
Basu, P., 2010. Biomass Gasification and Pyrolysis: Practical Design and Theory. Academic Press.
Bergman, P.C.A., Boersma, A.R., Zwart, R.W.R., Kiel, J.H.A., 2005. Torrefaction for Biomass Co-firing in Existing Coal-fired Power Stations. Energy Centre of Netherlands. Report No. ECN-C-05–013.
Bridgeman, T.G., Jones, J.M., Shield, I., Williams, P.T., 2008. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel 87 (6), 844–856.
Chen, W., Kuo, P., 2010. A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. Energy 35 (6), 2580–2586.
Chen, W., Lu, K., Tsai, C., 2012. An experimental analysis on property and structure variations of agricultural wastes undergoing torrefaction. Appl. Energy 100, 318–325.
Chen, W., Peng, J., Bi, X.T., 2015. A state-of-the-art review of biomass torrefaction, densification and applications. Renew. Sustain. Energy Rev. 44, 847–866.
Chen, W., Liu, S., Juang, T., Tsai, C., Zhuang, Y., 2015. Characterization of solid and liquid products from bamboo torrefaction. Appl. Energy 160, 829–835.
Ciolkosz, D., Wallace, R., 2011. A review of torrefaction for bioenergy feedstock production. Biofuels Bioprod. Biorefin. 5 (3), 317–329.
Dhungana, A., Dutta, A., Basu, P., 2012. Torrefaction of non-lignocellulose biomass waste. Can. J. Chem. Eng. 90 (1), 186–195.
Downie, A., Crosky, A., Munroe, P., 2009. Physical properties of biochar. Biochar Environ. Manag. Sci. Technol. 13–32.
García, R., et al., 2012. Characterization of Spanish biomass wastes for energy use. Bioresour. Technol. 103 (1), 249–258.
Haykiri-Acma, H., Yaman, S., Kucukbayrak, S., 2006. Effect of heating rate on the pyrolysis yields of rapeseed. Renew. Energy 31 (6), 803–810.
Lehmann, J., Joseph, S., 2015. Biochar for Environmental Management: Science, Technology and Implementation. Routledge.
Li, J., et al., 2012. Co-firing based on biomass torrefaction in a pulverized coal boiler with aim of 100% fuel switching. Appl. Energy 99, 344–354.
Li, M.-F., Li, X., Bian, J., Xu, J.-K., Yang, S., Sun, R.-C., 2015. Influence of temperature on bamboo torrefaction under carbon dioxide atmosphere. Ind. Crops Prod. 76, 149–157.
Medic, D., Darr, M., Shah, A., Potter, B., Zimmerman, J., 2012. Effects of torrefaction process parameters on biomass feedstock upgrading. Fuel 91 (1), 147–154.
Mundike, J., Collard, F.-X., Görgens, J.F., 2016. Torrefaction of invasive alien plants: influence of heating rate and other conversion parameters on mass yield and higher heating value. Bioresour. Technol. 209, 90–99.
Phanphanich, M., Mani, S., 2011. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. Bioresour. Technol. 102 (2), 1246–1253.
Pimchuai, A., Dutta, A., Basu, P., 2010. Torrefaction of agriculture residue to enhance combustible properties. Energy Fuels 24 (9), 4638–4645.
Poudel, J., Ohm, T., Oh, S.C., 2015. A study on torrefaction of food waste. Fuel 140, 275–281.
Prins, M.J., Ptasinski, K.J., Janssen, F.J.J.G., 2006. Torrefaction of wood: part 2. Anal. Prod. J. Anal. Appl. Pyrolysis 77 (1), 35–40.
Rousset, P., Aguiar, C., Labbé, N., Commandré, J., 2011. Enhancing the combustible properties of bamboo by torrefaction. Bioresour. Technol. 102 (17), 8225–8231.
Tsai, W., Liu, S., 2013. Effect of temperature on thermochemical property and true density of torrefied coffee residue. J. Anal. Appl. Pyrolysis 102, 47–52.
Van der, S.M.J.C., Gerhauser, H., Kiel, J.H.A., Ptasinski, K.J., 2011. Biomass upgrading by torrefaction for the production of biofuels: a review. Biomass Bioenergy 35 (9), 3748–3762.
Wang, G., Luo, Y., Deng, J., Kuang, J., Zhang, Y., 2011. Pretreatment of biomass by torrefaction. Chin. Sci. Bull. 56 (14), 1442–1448.
Wannapeera, J., Fungtammasan, B., Worasuwannarak, N., 2011. Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass. J. Anal. Appl. Pyrolysis 92 (1), 99–105.
Zheng, A., Zhao, Z., Chang, S., Huang, Z., He, F., Li, H., 2012. Effect of torrefaction temperature on product distribution from two-staged pyrolysis of biomass. Energy Fuels 26 (5), 2968–2974.
Zheng, A., Zhao, Z., Chang, S., Huang, Z., He, F., Li, H., 2013. Effect of torrefaction on structure and fast pyrolysis behavior of corncobs. Bioresour. Technol. 128, 370–377.