



## Review article

## Biomass torrefaction as an emerging technology to aid in energy production

T.A. Mamvura<sup>\*</sup>, G. Danha*Department of Chemical, Materials and Metallurgical Engineering, College of Engineering and Technology, Botswana International University of Science and Technology, Plot 10071, Boseja Ward, Private Bag 16 Palapye, Botswana*

## ARTICLE INFO

## Keywords:

Energy  
 Biofuel  
 Bioconversion  
 Renewable energy resources  
 Energy sustainability  
 Energy conservation  
 Torrefaction review  
 Biomass  
 Renewable energy  
 Torrefaction phases  
 Torrefaction application  
 Biomass analysis

## ABSTRACT

Biomass torrefaction has gained widespread attention due to its benefits as a standalone process to improve biomass properties to be at par or similar to those for coal in electricity generation or as a pretreatment step before pyrolysis and gasification processes. It has also found application in other processes like steel production where it is aiming to replace coal or work alongside coal by co-firing the coal with biomass at certain proportions. There have been a lot of papers on biomass torrefaction review, but this paper tried to look at a different angle to show other aspects of torrefaction and how it links to other technologies as well as the chemistry behind it. Overall, the process has seen a big shift in the technology it utilizes, and the hope is that it will make the process more viable and applicable in future.

The focus starts from the raw biomass, how it is analysed and the different analysis that are performed to determine relevant information about biomass properties. There are different reactors that are used but to date there is not a preferred one as they have their pros and cons. However, the focus mostly is the process not which reactor to use as they have all not shown any significant differences. The main product of the process, torrefied biomass determines the efficiency and how it can be applied to other technologies. To date, biomass torrefaction is for co-firing with coal for energy generation and as a pretreatment step for pyrolysis and gasification. Due to varying types of biomass in different countries, the technology has not yet reached its full potential, but the hope is it will with calls for use of renewable sources of energy.

Other areas like modelling torrefaction of biomass have not been looked at in this review. However, the paper sets the foundations for such detailed reviews.

## 1. Introduction

Bioenergy derived from biomass is a renewable source of energy which can be utilized as an alternative to non-renewable sources of energy like coal for energy generation (and electricity production). However, biomass as provided by nature has less energy density, more moisture and volatiles when compared to coal (Wen et al., 2014). As a result of this, the biomass needs a pretreatment process so as to improve its properties before it can be used together with or as a replacement for coal. Torrefaction, a thermochemical process, is regarded as a simple and effective method to transform the biomass properties to become almost at par with those of coal (Ribeiro et al., 2018). Investigation of co-firing of coal and torrefied biomass for energy production was first started at the Energy Centre of the Netherlands (ECN) and resulted in a very exhaustive ECN report on the topic in 2005. This report has since been cited by many authors to date (Bergman et al., 2005a).

## 1.1. What is biomass?

Any organic materials, living or that have been dead for a short period of time, derived from plants or animals are classified as biomass. In plants, biomass is formed through conversion of carbon dioxide in the atmosphere into carbohydrates in the presence of the sun's energy. Biological species will then grow by consuming these botanical or other biological species adding to the biomass chain (Basu, 2018b). In the presence of light from the visible spectrum particularly blue range (425–450 nm) and red range (600–700 nm), green plants breakdown water to obtain electrons and protons and use them to turn carbon dioxide into glucose and release oxygen as a waste product through a process called photosynthesis (Krewald et al., 2015; Pessaraki, 2016).



<sup>\*</sup> Corresponding author.

E-mail addresses: [atmamvura@gmail.com](mailto:atmamvura@gmail.com), [mamvurat@biust.ac.bw](mailto:mamvurat@biust.ac.bw) (T.A. Mamvura).

Biomass can be determined from different sources such as wood, energy crops, forest and agricultural residue, industrial and municipal wastes (Basu et al., 2014). These sources are elaborated more in Basu (2018b). Virgin biomass includes vegetables and crops, leaves, plants, and wood whilst waste biomass includes municipal solid and liquid waste, sewage, animal, and human wastes and agricultural wastes (Begum et al., 2013). Municipal solid waste provides a large percentage of waste biomass, as much of it comes from renewables like leaves, papers, grass, clippings, organics and food residue (like fruits, rice etc.). Sewage sludge is considered an important biomass source because it contains fat, food waste and grease and another waste is produced in sawmills during the production of lumber from wood (Basu, 2018b). Typical composition of waste biomass is summarised in Basu (2018b).

Biomass has extractable and non-extractable portions. The extractable portions include fats, waxes, alkaloids, proteins, phenolics, simple sugars, pectins, gums, resins, terpenes, starches, glycosides, sapomins and essential oils (Tumuluru et al., 2012). Lignocellulose is the fibrous part of the plant material and it is known to contain no starch, that is, it is not consumed by human beings (Cherubini and Strømman, 2011). Due to that, it does not affect the food chain when it is collected and used for production of biochar, bio-oil or biogas. Plant biomass has a major part known as lignocellulose, consisting of three main polymeric components: hemicellulose, cellulose, and lignin and it is usually termed lignocellulose-based biomass. In general, lignocellulose-based biomass is widely used for renewable energy applications. The general chemical composition of plant biomass is shown in Figure 1.

Hemicellulose consists of complex, branched, and heterogeneous polymeric network with lower molecular weight polymers (short polymers of various sugars) and its role is to connect lignin and cellulose fibres together (Basu, 2018b). Cellulose is a long-chain polysaccharide and its structure has crystalline parts and amorphous parts. It consists of high molecular weight polymers of glucose that are held rigidly together as bundles of fibres to provide material strength (Basu, 2018b).

Lignin is an amorphous polymer made by different phenolic compounds and is the main component of cell walls (tri-dimensional polymer

of propyl-phenol that is imbedded in and bound to the hemicellulose). It provides rigidity to the structure and holds together cellulose and hemicellulose fibres and gives support, resistance, and impermeability to the plant (Galletti and Antonetti, 2012). The composition of some common lignocellulose materials and wastes are reported in Galletti and Antonetti (2012), whilst the structure and chemistry of lignin, hemicellulose and cellulose have been reported in Lange (2007) and Tumuluru et al. (2010). In addition, hardwoods have more cellulose, similar hemicellulose and less lignin (18–25 wt.% in hardwood versus 25–35 wt.% in softwood by dry weight) when compared to softwoods (Basu, 2018b).

## 1.2. Biofuel from biomass

Biomass can be converted into three different products (gaseous, liquid or solid) by using thermochemical treatment processes.

### 1.2.1. Gaseous products

Biomass can be converted into gaseous products by using gasification, a thermochemical process, where the whole biomass is subjected to high temperatures with low oxygen levels to produce syngas, a mixture of H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> gases (Barik, 2019). Initially combustion of biomass char (C) occurs to produce CO<sub>2</sub> and CO gases whilst H<sub>2</sub> combust to produce H<sub>2</sub>O (Molino et al., 2016). Afterwards, gasification reactions occur according to the reactions in Table 1.

### 1.2.2. Liquid products

Biomass can be converted into liquid products i.e. liquid fuels like bio-oil, biodiesel or bioethanol, by using pyrolysis, transesterification, fermentation, anaerobic digestion and/or saccharification processes (Chen et al., 2011a). Pyrolysis, a thermochemical process under inert conditions that results in the formation of charcoal (used to produce activated carbon), bio-oil (or pyrolysis oil), methanol and gases from wood or coke from coal (Molino et al., 2016) as in the following reaction:

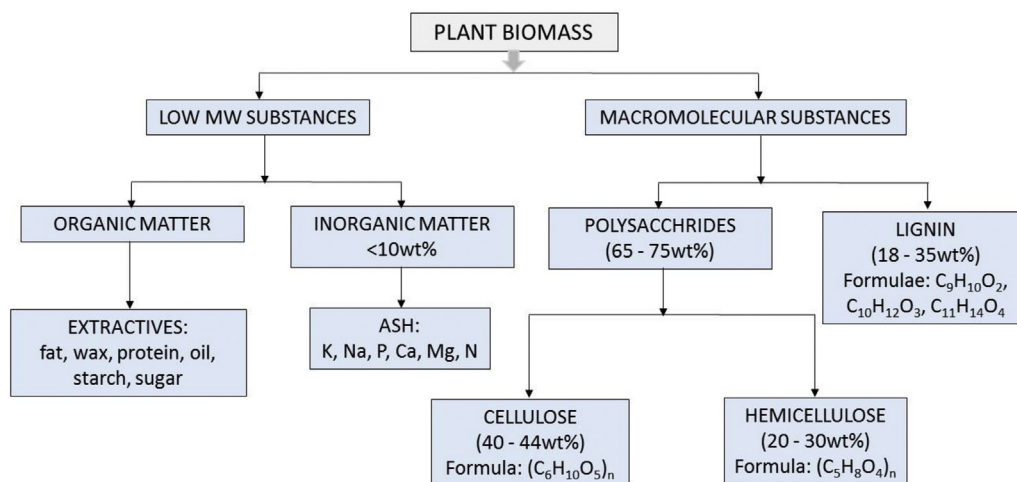


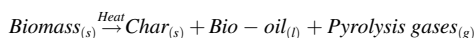
Figure 1. General chemical composition of plant biomass. (Adapted from Carpenter, 2014; Lange, 2007 and Basu, 2018b). MW means molecular weight.

Table 1. Gasification Chemical Reactions. Gasification occurs at temperatures from around 500 °C to around 1300 °C (Cherubini and Strømman, 2011).

Reaction name	Chemical equation	$\Delta H_{\text{reaction}}$ (kJ/mol)	Reference
Boudouard	$C_{(s)} + CO_{2(g)} \leftrightarrow 2CO_{(g)}$	+172	Molino et al. (2016)
Char reforming	$C_{(s)} + H_{2O(g)} \leftrightarrow CO_{(g)} + H_{2(g)}$	+131	Kumar et al. (2009)
Water-Gas Shift	$CO_{(g)} + H_{2O(g)} \leftrightarrow CO_{2(g)} + H_{2(g)}$	-41	Sikarwar et al. (2016)
Methanation	$C_{(s)} + H_{2(g)} \leftrightarrow CH_{4(g)}$	-75	Molino et al. (2016)

**Table 2.** Torrefaction conditions identified in some literature.

Torrefaction conditions	Values	Reference
Reaction temperature	200–300 °C	Basu et al. (2014)
Heating rate	≤50 °C/min	Tumuluru et al. (2012)
Residence time	≤60 min	Bergman et al. (2005a)
Some technologies use elevated pressures, but generally ambient pressures are used	P ≥ 1 atm	Basu et al. (2014)
Oxygen content	O <sub>2</sub> ≤ 20%	Chen et al. (2014); Rousset et al. (2012)
Different biomasses		Tumuluru et al. (2012)
Biomass moisture content		Basu (2018a)
Raw biomass particle size		Tumuluru et al. (2011)



(Barik, 2019)

Pyrolysis gases produced usually consists of H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>4</sub> (Barik, 2019; Sikarwar et al., 2016). Bio-oil is a mixture of moisture, pyrolytic water and tar (tar is a mixture of complex hydrocarbons) (Barik, 2019). Pyrolysis occurs typically from 300 to ~700 °C (Kumar et al., 2009), however, Neves et al. (2011) mentions that pyrolysis occurs over a wide temperature range between 200 and 1000 °C.

### 1.2.3. Solid products

Biomass can be converted to a solid fuel with properties similar to those for coal by using carbonization and torrefaction where it can be burned directly for the generation of heat and power (Chen et al., 2011a; Chew and Doshi, 2011). Gaseous products are also produced, and these can be subdivided into permanent gases and condensable gases: permanent gases are gases that remain in that state at room temperature like CO<sub>2</sub>, CO etc while condensable gases are converted to liquid products when the temperature reduces to room temperature like acetic acid, H<sub>2</sub>O etc (Agar and Wihersaari, 2012). Torrefaction occurs in the temperature range between 200 and 300 °C.

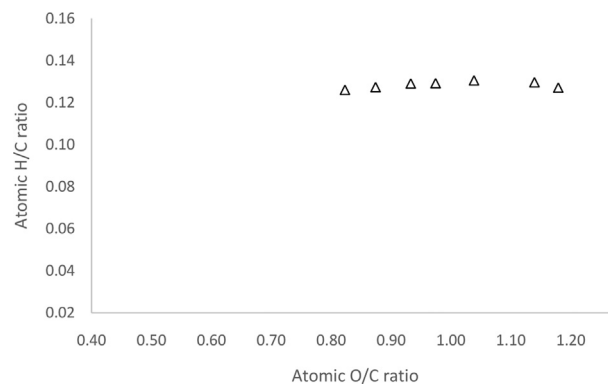
## 1.3. Some insights

During this review different literature has been considered and the major literature that has been used has been unpacked and the results and conclusions analyzed.

### 1.3.1. What we know from literature

Friedl et al. (2005) investigated prediction of heating values of 122 biomass samples from elemental composition. They developed an empirical model that uses elemental composition to predict heating value with a standard error of 2%.

Prins et al. (2006a) investigated the impact of torrefaction on wood for gasification purposes on different biomasses: deciduous wood (beech and willow) and coniferous wood (larch). They conducted mass and

**Figure 2.** An example of a van Krevelen diagram (Adapted from Basu, 2013).

energy balances and performed process modelling. They concluded that gasification of torrefied wood led to wood gasified at higher temperatures of 950 °C and above as compared to raw biomass gasification that leads to over-oxidation at around 700 °C.

Lange (2007) looked at the chemistry, the process and the economics of the lignocellulosic biomass conversion using pyrolysis, gasification or hydrolysis (fermentation) processes. They concluded that lignocellulosic biomass is cheaper than crude oil as raw materials, but their conversion processes are still expensive as compared to crude oil processing. The costs associated with the processes need to be reduced but this reduction should not only focus on technology improvements only. They argued that it would be more economical to convert the biomass to energy without producing chemicals (pyrolysis or gasification). This argument is pointing towards torrefaction as a way to improve the biomass properties.

Bridgeman et al. (2008) investigated torrefaction of reed canary grass, wheat straw and willow coppice. They concluded that herbaceous biomass losses more mass during torrefaction as compared to woody biomass. Willow coppice had higher mass and energy yield as compared to the other two. This was attributed to the differences in the lignocellulosic composition with willow coppice having the least hemicellulose composition as compared to the herbaceous biomasses.

Bridgeman et al. (2010) investigated the effect of torrefaction on the grindability of two torrefied energy (willow and Miscanthus) crops. They varied torrefaction parameters during the investigations. They concluded that temperature is the most important parameter that affects the grindability of the energy crops. This meant that pulverization of the biomass was easier once the biomass was torrefied approaching properties similar to those of coal.

Tumuluru et al. (2010) looked biomass torrefaction and model development. They focused on (a) a detailed review of torrefaction of biomass torrefaction, and (b) a methodology for designing a moving bed torrefier. They produced a report for the US Department of Energy. They concluded that torrefaction improves biomass properties by devolatilization and carbonization of hemicellulose, followed by depolymerization

**Table 3.** Conditions used during proximate analysis of biomass and the standard methods (Basu, 2018a; Sadaka and Negi, 2009).

Parameter	Moisture content	Volatile matter <sup>+</sup>	Ash
Sample mass (g)	~50	~1	~2
Start T (°C)	25	105	25
End T (°C)	105	950	700
Time	16–24 h	~7 min	4–6 h
Covers	No	Yes	No
Atmosphere	Inert (N <sub>2</sub> )	Inert (N <sub>2</sub> )	Oxidative (O <sub>2</sub> )*

<sup>+</sup>Fixed carbon is calculated by difference from MC, Ash and VM.

\*Air can be used as a substitute for oxygen. However, the flowrate should be set to a higher level to account for lower O<sub>2</sub> levels in air as air contains approximately 79 vol% N<sub>2</sub> and 21 vol% O<sub>2</sub>.

and devolatilization of lignin and cellulose for lignocellulosic biomasses. This means that it can be applied in energy power generation along with coal especially if it densified. They managed to come up with the said model.

Chen et al. (2011) investigated torrefaction of pulverized biomasses (bamboo, banyan, willow) whilst optimizing the torrefaction parameters for use in boilers and blast furnaces. They concluded that the three biomass components degrade at different temperatures and different rates below 290 °C for their biomasses. They also concluded that torrefaction followed by pelletization resulted in biomass that can better cope in pulverized boilers or blast furnaces.

Chew and Doshi (2011) reviewed torrefaction of biomass. They first briefly looked at different treatment processes and then discussed in detail torrefaction of different biomasses at different conditions for woody and non-woody biomass. They looked at different kinetic models reported for different biomasses and recommended validation of the kinetic models using experimental results.

Tumuluru et al. (2011) had a review on torrefaction process and product properties for the purpose of application in energy generation. They first looked at the components that makeup biomass, looked at the torrefaction process and its technique, discussed the different reactions or processes that occur like devolatilization, depolymerization and carbonization of hemicellulose, cellulose and lignin leading to a products: solid product, condensable and non-condensable gases and their composition. Finally, they looked at the properties of the torrefied biomass and their advantages against those of coal leading to their use in coal-fired power stations.

Agar and Wihersaari (2012) undertook a literature study to perform a feasibility study on the potential use of torrefied biomass for co-firing with coal. They focused on mass and energy balances, grindability of

torrefied biomass and equilibrium moisture content. They found that mass yield of 70% and energy yield of 90% reported by Bergman et al. (2005a) could not be supported experimentally. They found that for woody biomass, the range of mass and energy yields was 61–82% and 73–92%, while for agro-biomass it was 25–76% and 29–81%, respectively. Grindability was improved by torrefaction technique but it differs from biomass to biomass. They also concluded that relative humidity is inversely proportional to torrefaction temperature i.e. torrefied biomass produced at higher temperatures would result in lower moisture content during storage and vice-versa.

Hill et al. (2013) investigated chemical and cellulose crystallite changes in *Pinus radiata* wood chips during torrefaction at different temperatures. They concluded that an increase in torrefaction temperature resulted in a crystallite structure that became hydrophilic in nature, energy density and grindability increased and there was a decrease in equivalent moisture content.

Asadullah et al. (2014) investigated torrefaction of palm kernel shell to produce densified bio-coal in a batch feeding reactor whilst varying torrefaction parameters with the hope to optimize them. They produced bio-coal with properties similar to those of coal with potential application as a replacement of coal or co-firing with coal.

Basu et al. (2014) investigated torrefaction of large wet wood particle to determine drying and kinetic models for the torrefaction process. They obtained optimum temperature, particle size and residence time as 290 °C, 24 mm and 10 h, respectively.

Nhuchhen and Basu (2014) investigated mildly pressurized (200–600 kPa) torrefaction on poplar wood in air and nitrogen in batch reactors with the view to replace nitrogen with air in full-scale industrial setups. They were assisted by the response surface methodology (RSM) method and they developed a correlation to predict mass loss. Torrefaction

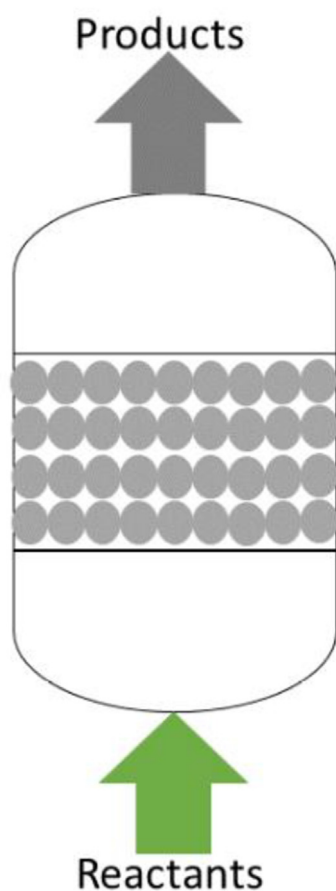


Figure 3. A fixed bed reactor.

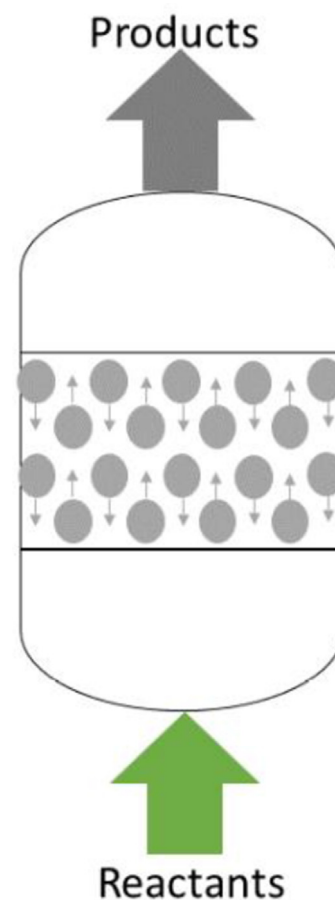


Figure 4. A moving bed reactor.

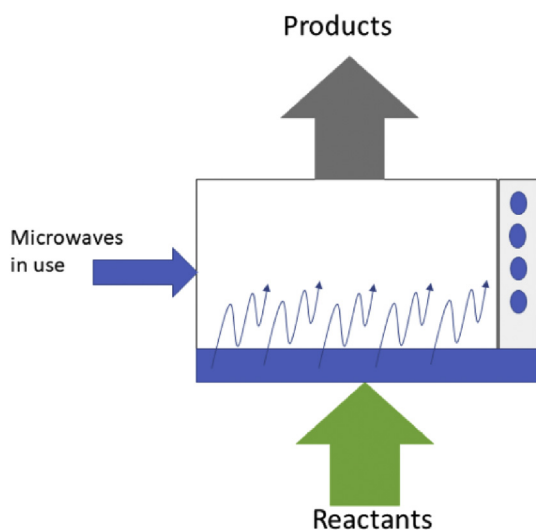


Figure 5. Microwave reactor.

parameters were varied during the study. They concluded that temperature had the biggest effect on torrefaction, but at higher temperatures, the effect of using air in place of nitrogen was significant. Yields obtained in air or nitrogen atmospheres were similar and this suggests that nitrogen can be replaced with air in large-scale industrial setups.

Pelaez-Samaniego et al. (2014) investigated the effect of temperature during torrefaction of ponderosa pine, a lignocellulosic biomass on the formation of liquid intermediates rich in lignin. They varied the temperature from 200 to 350 °C (which causes pyrolysis) and they concluded that liquid intermediates rich in lignin were formed with highest yield at 300 °C. They further concluded that the lignin reduced as the temperature increased. The lignin-rich liquid could be applied as a natural adhesive in the production of fuel pellets and wood composites.

Saadon et al. (2014) investigated torrefaction oil palm kernel shell in the presence of oxygen and carbon dioxide. They concluded that the presence of O<sub>2</sub> and CO<sub>2</sub> resulted in lower solid yield by 2–3% as compared to torrefaction in N<sub>2</sub> gas (under inert conditions). However, the difference not significant on a large scale.

Wen et al. (2014) investigated chemical and structural transformation of lignin macromolecule as a result of torrefaction for bamboo. They concluded that the optimum conditions were a temperature of 275 °C for a residence time of 1 h. They observed that during torrefaction, hemicelluloses degraded, for cellulose there was crystal transformation and degradation and for lignin macromolecule there was structural changes.

Chen et al. (2015) reviewed torrefaction technology and its applications. They first looked at the lignocellulosic components of biomass as Tumuluru et al. (2011) then torrefaction process. They looked at the

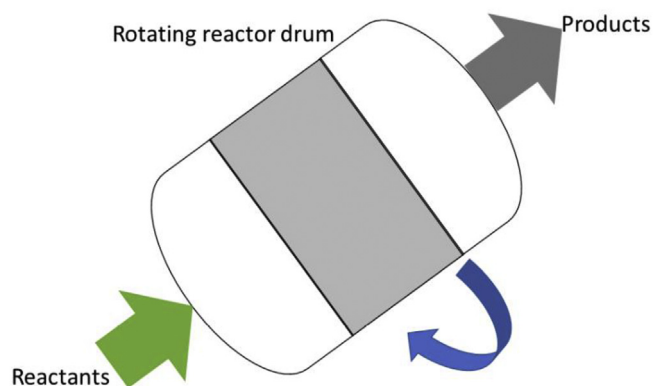


Figure 6. Rotary drum reactor.

products formed from different biomasses and different conditions. They looked at properties of torrefied biomass and potential applications in gasification and energy production. They also looked at torrefaction kinetics: one-step and multi-step kinetics at different conditions. The kinetics was associated to particle size effect, oxygen effect, and wet and steam torrefaction.

Poudel et al. (2015) investigated torrefaction of food waste from a university cafeteria by varying parameters to come up with kinetic data and analysis gaseous product composition. They determined activation energy between 78 – 83 kJ/mol for a reaction order of 2.1–2.6. They also concluded that temperature had a bigger effect than residence time which is in line with our previous studies (Mamvura et al., 2018). This study shows the potential re-use of waste that is being dumped at landfill sites to produce energy.

Nanou et al. (2016) investigated mass and energy balance for a torrefaction pilot plant of capacity 50kg·hr<sup>-1</sup> located at ECN for ash, spruce and willow biomasses. The mass and energy balances they got allowed them to calculate theoretical overall thermal efficiency of 88–89% when a flue gas dryer was used for pre-drying the wood from moisture content of ~45%. The pilot plant could be used to investigate new biomass or to scale up to full-scale plants.

Pahla et al. (2017) investigated torrefaction of different biomass sources: cow dung (animal waste), corn cobs and pine wood (*Pinus radiata*) to investigate the change in the properties against those of coal. They concluded that corn cobs and pine wood responded better to torrefaction and they could be co-fired with coal for energy production, but cow dung could be better utilized in biogas production through anaerobic digestion.

Álvarez-Álvarez et al. (2018) investigated three tree species namely chestnut coppice; maritime pine stands; and poplar and willow short-rotation woody crops (SRWC) to see their potential use for energy production. They concluded that pine plantations had the highest potential to generate energy, followed by SRWC and lastly chestnut coppice. Previous investigations have shown that applying to torrefaction to pine plantations gives better sources of energy and these results help in that respect.

Chen et al. (2018) investigated torrefaction based on three lignocellulosic components: beechwood xylan (representing hemicellulose), microcrystalline cellulose and alkali lignin at different temperatures. They linked the three components to the products they produced with hemicellulose degrading first. They concluded that hemicellulose had the lowest yield of solid product but had highest yield of volatile and nonvolatile gases. Cellulose and lignin had comparable solid and

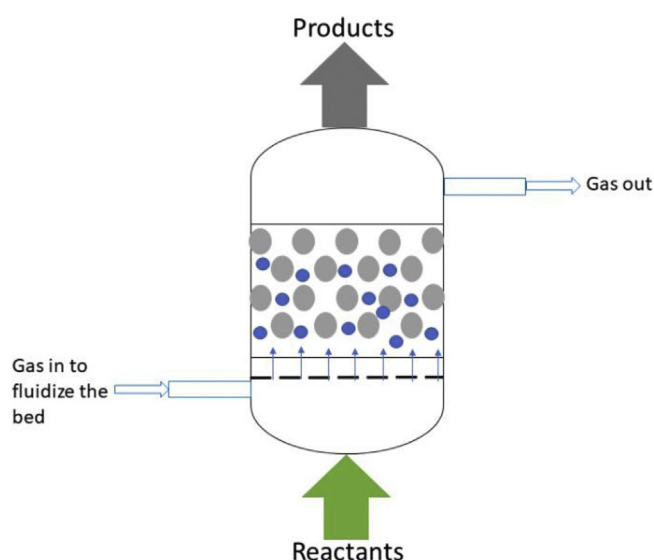


Figure 7. Fluidized bed reactor.

**Table 4.** Degradation of lignocellulosic components.

Temperature range (°C)	Hemicellulose	Cellulose	Lignin	References
Overall degradation temperature range	180–300 °C	275–355 °C	250–500 °C	Chen et al. (2011b); Hill et al. (2013)
25–105	No effect	No effect	No effect	Yang et al. (2006)
105–150	No effect	No effect	Softening occurs at T > 130 °C but no degradation	Pelaez-Samaniego et al. (2014)
160–180	Degradation starts due to devolatilization and depolymerization reactions releasing mostly H <sub>2</sub> O and small amounts of CO <sub>2</sub>	No effect	No effect	Tumuluru et al. (2011)
180–200	Endothermic reactions	N/A	N/A	
200	Light torrefaction			
200–250	Degradation continues. Colour change for biomass is noticeable. Volatiles like acetic acid, methanol, CO, and CO <sub>2</sub> are formed	Colour change for biomass is noticeable	Colour change for biomass is noticeable	Chen et al. (2018); Pelaez-Samaniego et al. (2014)
250	Mild Torrefaction			
200–270	Partly endothermic reactions	Partly endothermic reactions	Partly endothermic reactions	Bergman et al. (2005b); Chen et al. (2011a); Pahla et al. (2017); Pelaez-Samaniego et al. (2014)
250–300	Total degradation forming char and release of CO, CO <sub>2</sub> and H <sub>2</sub> O	Degradation starts at ~275 °C releasing H <sub>2</sub> O and forming anhydrous cellulose and levoglucosan polymer	Degradation starts at ~250 °C. At 280 °C degradation gives phenols due to cleavage of ether bonds	
290	Severe torrefaction			
250–300	Depolymerization of remaining hemicellulose	Depolymerization of cellulose	Depolymerization of lignin	Bergman et al. (2005b); Chen et al. (2011a); Pahla et al. (2017); Pelaez-Samaniego et al. (2014)
270–300	Exothermic reactions	Exothermic reactions	Exothermic reactions	
330–370		Total degradation forming char	Total degradation forming char	Saadon et al. (2014); Tsamba et al. (2006)

**Table 5.** Reactions involved in Torrefaction and Heat of reaction (Adapted from Hill et al., 2013; Kuo and Wu, 2015; Pelaez-Samaniego et al., 2014).

Type of reaction	Reaction	$\Delta H_{298}$ (kJ/mol)	Reaction T, °C
Biomass Drying			
Unbound moisture	$H_2O_{(l)} \rightarrow H_2O_{(g)}$	+44.0	100–105
Biomass Torrefaction			
Torrefaction	$Biomass_{(s)} \rightarrow Biochar_{(s)} + Torrefaction\ gases_{(g)}$	Varies with biomass	200–300
H <sub>2</sub> O	$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$	-241.8	160–300
CO <sub>2</sub>	$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	-393.5	160–300
CO <sub>2</sub>	$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$	-283.0	160–300
CO	$2C_{(s)} + CO_{2(g)} + H_2O_{(g)} \rightarrow 3CO_{(g)} + H_{2(g)}$	+101.4*	200–300
Acetic acid	$2C_{(s)} + 2H_{2(g)} + O_{2(g)} \rightarrow CH_3COOH_{(g)}$	-432.8	200–300
Formic acid	$C_{(s)} + H_{2(g)} + O_{2(g)} \rightarrow HCOOH_{(g)}$	-378.6	200–300
Methanol	$C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(g)}$	-200.0	200–300
Lactic acid	$3C_{(s)} + 3H_{2(g)} + \frac{3}{2}O_{2(g)} \rightarrow CH_3CH(OH)COOH_{(g)}$	-599.6	200–300
Furfural	$5C_{(s)} + 2H_{2(g)} + O_{2(g)} \rightarrow C_4H_3OCHO_{(g)}$	-151.0	200–300
Acetol	$2C_{(s)} + 2H_{2(g)} + O_{2(g)} \rightarrow C_2H_3O_{5(g)}$	-366.0	200–300

\*Calculated from heat of formation data from Poling et al. (2008).

gaseous yields, higher solids yields but lower gaseous yields when compared to hemicellulose.

Mamvura et al. (2018) investigated torrefaction of waste biomass (marula trees and blue gum wood) abundant in South Africa at different conditions. They concluded that after torrefaction, marula tree samples had improved properties and it could be co-fired with bituminous coal while blue gum wood had a negative response to torrefaction.

### 1.3.2. What we have learnt

To use coal for power generation, its heating value is required. This is measured experimentally but there have been good attempts to predict the heating value; either higher heating value (HHV) or lower heating value (LHV), using theoretical models. The same principle has been applied for biomass as it is being touted as a replacement for coal or to be co-fired with coal. Its heating value can be estimated using theoretical models which have been proposed either for coal or modified or simply developed for biomass only.

Various investigations on torrefaction as a technique to improve the properties of biomass to be at par with those for coal have been conducted. There have been a lot of conclusions that have been reached from the different studies and there are some gaps that have been identified. Other literatures have reviewed the process and put forward different conclusions. This paper seeks to put a lot of these observations into perspective and also address the different gaps that have been identified.

It has been observed that torrefaction of biomass leads to better gasification, so it acts as a pretreatment step for gasification and pyrolysis which have been briefly discussed in Section 1.2. Lignocellulosic biomass is cheaper than crude oil or coal, but its conversion processes are expensive and there therefore need more research. The chemistry, the process and economics have been discussed but in this paper, the chemistry and the process will be looked at in detail. During torrefaction, different lignocellulosic components degrade at different rates and at different conditions and this will be discussed in detail. Temperature has been identified as the most important parameter and in this paper, the conditions have been identified but their discussions have been pointed to different literatures. The chemistry has been divided as the processes that occur; the phases of torrefaction with change in temperature (the important parameter); how they impact the reactants to produce the products and the crystalline changes that occur in the different lignocellulosic components. Torrefaction reactors in use are discussed as they impact on the chemistry and the products that are produced.

Model development has been discussed and in this paper, it has not been explored any further. Application of the torrefied product has been explored with densification and co-firing with coal being considered highly. There was no feasibility study conducted or discussed but it is important for implementation of the technology and the feasibility is specific to each country as it will determine which biomass to focus on. In other studies, waste biomass has found application, and this will lead to a reduction in waste on landfill sites. The paper has taken more or less the same approach as other review papers highlighted but it has sought to focus on the gaps identified mostly.

## 2. Torrefaction

### 2.1. What is torrefaction?

Torrefaction is referred to by different names in literature: roasting (similar to coffee roasting), slow pyrolysis, mild pyrolysis, wood cooking or high-temperature drying. Torrefaction is usually the first stage followed by pyrolysis and lastly gasification during biomass heat treatment or biomass decomposition (Lange, 2007). However, process conditions reported are not the same as some use inert conditions and others use other gases (CO<sub>2</sub>) and oxidative (O<sub>2</sub>) environments (Cherubini and Strömman, 2011).

**Table 6.** Subclassification of the mid-infrared region (Adapted from Griffiths and de Haseth, 2007; Nikolic, 2011; Acquah et al., 2016).

$\lambda$ (cm <sup>-1</sup> )	Region 1 4000–2500	Region 2 2500–2000	Region 3 2000–1500	Region 4 1500–400
Type of bonds	Single bonds	Triple bonds	Double bonds	Characteristic single bonds
Comments			C=O occurs btw 1800–1650 C=N; C=C; N=O occur btw 1650–1550	C–Cl; C–O; C–N; C–C and N=O occur btw 1500–650. The region is also called fingerprint region of the molecule.
Examples	N–H C–H O–H	C≡C C≡N X = C=Y	C=O C=N C=C	C–Cl C–O C–N C–C

**Table 7.** Summary of some of the torrefaction investigations conducted to date.

Biomass type	Conditions					References
	T (°C)	P (atm)	t (mins)	HR (°C/min)	O <sub>2</sub> (%)	
Beech; Willow; Larch, Straw	230–300	1	92	10–100	0	Prins (2005)
Beech; Willow	220–300	1	10–60	10–20	0	Prins et al. (2006b)
Larch wood	230–290	1	10–50	10–20	0	Prins et al. (2006b)
Straw	250	1	30	10–20	0	Prins et al. (2006b)
Rice straw; Rape stalk	200–300	0.019	30	30–45	0	Deng et al. (2009)
Rice straw; Cotton gin waste	260	1	15–60	-	0	Sadaka and Negi (2009)
Wheat straw	200–315	1	15–180	-	0	Sadaka and Negi (2009)
Sawdust	230–290	1	20–30	10	0	Chen et al. (2011)
Bagasse; Road side grass; Poplar; Straw	240–280	1	30	5	0	Verhoeff et al. (2011)
RDF/SRF; Grass seed hay; Spruce chips	240–300	1	30	5	0	Verhoeff et al. (2011)
Pine chips; Trockenstabilat	260–300	1	30	5	0	Verhoeff et al. (2011)
Beech	280	1	30	5	0	Verhoeff et al. (2011)
Leucaena leucocephala	200–275	1	20–120	10	0	Wannapeera et al. (2011)
Microalgae; Microalgal residue	200–350	1	30–90	30–50	0	Wu et al. (2011)
Corn stover	200–300	1	10–30	-	0	Medic et al. (2012)
Leucaena leucocephala	200–250	1–49	30	-	0	Wannapeera and Worasuwannarak (2012)
Pine chips; Spruce chips; Fir; SPF; Pine bark	280	1	52	-	0	Peng et al. (2013)
SPF shavings	240–340	1	60	-	0	Peng et al. (2013)
Fir Sawdust pellets	240–310	1	8–22	-	0	Ren et al. (2013)
Palm Kernel Shell	200–350	1	10–60	-	0	Asadullah et al. (2014)
Saw dust	200–300	1	166.8	-	0	Basu et al. (2014)
Oil palm fiber; Coconut fiber; Eucalyptus; Cryptomeria japonica	300	1	60	-	0–21	Chen et al. (2014)
Palm kernel shells	200–300	1	30	-	0	Li et al. (2014)
Poplar	220–300	1–5.9	15–35	-	0–21	Nhuchhen and Basu (2014)
Beech	220–300	1	25–175	10	0	Nocquet et al. (2014)
Palm kernel shell	250	1	30	10	0–15 CO <sub>2</sub> : 9–15%	Saadon et al. (2014)
Bamboo	200–300	1	60	5	0	Wen et al. (2014)
Food waste	150–600	1	60	10–30	0	Poudeh et al. (2015)
Pine wood; Cow dung; Maize corn cobs	200–300	1	40	10	0	Pahla et al. (2017)
Marula trees; Blue gum wood	200–300	1	20–60	5–15	0–20	Mamvura et al. (2018)

T = temperature; P = pressure; t = residence time; HR = heating rate and O<sub>2</sub> = oxygen content or level.

Torrefaction is a thermal pretreatment process conducted at temperatures between 200 and 300 °C in an inert atmosphere with the aim of modifying chemical properties of biomass (Lange, 2007). It is an endothermic process, meaning that it requires energy input to kick-start the process as well as to sustain it (Basu, 2018a). Torrefaction leads to: (i) improved energy density, (ii) better ignition, (iii) less moisture, (iv) higher C/O and C/H ratios, (v) improved grindability thereby reducing energy required for grinding, (vi) biomass that is hydrophobic i.e. that has less affinity for water, (vii) more homogenized biomass i.e. torrefaction devolatilize, depolymerize and carbonize the biomass and (viii) reduces microbial activity (Agar and Wihersaari, 2012; Bridgeman et al., 2010; Chew and Doshi, 2011; Prins et al., 2006a). This modification enhances the combustion performance particularly in boilers for energy production and for pyrolysis and gasification applications (Basu, 2018a) and also leads to better storage of the treated biomass.

Several authors have investigated and reported torrefaction process conditions in detail (Table 2).

Biomass particle size influences the reaction mechanism, kinetics and duration of the process for a specified heating rate. To be of use as a biofuel, biomass has to be depolymerized and deoxygenated.

### 2.1.1. Devolatilization process

Devolatilization results in a large percentage of weight loss from biomass during the initial stage of torrefaction. Devolatilization is

when the high molecular weight compounds in biomass fragment into smaller compounds with low molecular weight that will vaporise and escape from the biomass particles resulting in torrefaction gases (Basu et al., 2014; Sakhivadivel and Iniyar, 2017). On the other hand, the components with high molecular weight and low vapour pressures will remain in the biomass until they reattach themselves to the biochar, the solid product that is left after devolatilization is complete (Kim et al., 2009). This process is similar to that of pyrolysis of coal. Because of this, the energy yield is greater than the mass yield; giving a material with an increased heating value close to that of coal, that is, about 70% of mass is retained after torrefaction, as torrefied biomass with about 90% of the initial energy content (Agar and Wihersaari, 2012; Sakhivadivel and Iniyar, 2017).

The mass yield is less because the most volatile compounds, which are about 30% of mass are lost as torrefaction gases (volatile and permanent gases) mostly from hemicellulose degradation, normally the first to undergo thermal degradation (Sakhivadivel and Iniyar, 2017). These have around 10% of the energy content (Agar and Wihersaari, 2012). This means that energy densification for biomass increases from 1.0 to 1.3 on a mass basis. Pyrolysis only achieves energy yield between 55–65% but it drops down to as little as 20% using traditional technology (Chew and Doshi, 2011). This shows the significance of torrefaction to produce solid products to be used as a fuel in combination with coal.



### 2.1.2. Deoxygenation process

Deoxygenation is the removal of oxygen resulting in an increase in C/O and C/H ratios in biomass and resulting in gaseous products such as CO<sub>2</sub>, CO, H<sub>2</sub>O and/or other compounds carrying carbon, oxygen and hydrogen (Cherubini and Strømman, 2011). Deoxygenation is an important step because it reduces the amount of oxygen that exists in the biomass structure which leads to lower heat content (due to formation of CO<sub>2</sub>, CO and H<sub>2</sub>O and evaporation of H<sub>2</sub>O). Oxygen also results in high polarity in the biomass and this leads to problems when blending biomass with coal for combustion purposes (Lange, 2007).

### 2.1.3. Depolymerization process

Depolymerization is the process of converting a polymer into monomers i.e., its building blocks (Bergman et al., 2005b). In this case, the lignocellulosic components will degrade to their building blocks during torrefaction depending on the temperature and this in case breaks down the biomass structure resulting in volatile and non-volatile fractions being formed.

### 2.1.4. Carbonization process

Torrefaction is similar to pyrolysis and also to carbonization. The most important difference between pyrolysis, carbonization, and torrefaction lies in their product purpose. The primary purpose of pyrolysis is to maximise its liquid production while minimising the char yield. The objective of carbonization is to maximise fixed carbon and minimise hydrocarbon content of the solid product, while that of torrefaction is to maximise solid biochar (thereby maximising energy and mass yields with reduction in) by reducing oxygen to carbon (O/C) and hydrogen to carbon (H/C) ratios (Chen et al., 2015).

## 2.2. Why torrefaction?

Torrefaction was borne because of the need to improve its properties to be at par for those of coal. This allows power stations to use torrefied biomass alone or in combination with coal for electricity production reducing the need to use a lot of coal.

During coal preparation for use in electricity production, the process uses a lot of water during washing of the coal and this put an enormous strain on this precious resource which is a scarce resource nowadays (Kumar and Kumar, 2018). Coal is a non-renewable resource and the focus currently has shifted to use of renewable resources so as to prolong our industrial gains. More and more countries are now pushing for renewable sources for energy, many are shifting towards electric cars meaning higher demand for electricity. For lighting some are moving towards solar power, wind power and biogas (Miller, 2017). There is need to replace coal in energy production and in metallurgical applications. Torrefied biomass can fit the bill in this instance.

On the other hand, during coal combustion, it gives off greenhouse gases (mainly CO<sub>2</sub> and also CO) that are responsible for global warming and climate change not to mention air and water pollution (Kumar and Kumar, 2018; Miller, 2017). Any reduction of coal use will help in mitigating some for these effects and torrefied biomass is being touted as the answer as it can be co-fired with coal or it can be used alone (Mamvura and Muzenda, 2015). However, using torrefied biomass alone is still not economical but it is the solution to eliminating greenhouse gases as the ones that the biomass gives off, it would have gained them during photosynthesis (Chen et al. (2018; Mamvura et al., 2018). Therefore, there is zero emission increase (Mamvura and Muzenda, 2015). These environmental concerns are pushing for a lot of research in torrefaction to better understand the process and also to make it as economical as possible.

## 2.3. Reactants of torrefaction process and their analysis

The reactants are usually the raw biomass after drying and nitrogen gas to provide the inert atmosphere for torrefaction. Some experiments

involving oxygen and carbon dioxide have been conducted, but it has been seen that biomass torrefaction under inert conditions gives the best products (Rousset et al., 2012). The biomass can be characterised to give different information that can then be compared to coal. The different analyses are now discussed.

### 2.3.1. Proximate analysis

The standard test is conducted to determine the moisture content (MC), ash content (Ash), volatile matter (VM) and fixed carbon (FC) of the biomass. These tests have been conducted on coal for years and they provide a basis for comparison on how the biomass, either raw or torrefied, can perform against coal for energy production. The standard testing methods for coal are found in literature and they can be adapted to biomass if there is no analysis equipment. Individual tests are performed to determine proximate analysis for biomass, and they are based on ASTM standards:

- (a) Moisture analysis is based on ASTM E871-82 (2019) for wood (ASTM, 2019b) and it is determined by drying a 50 g biomass sample at 105 °C to constant weight (usually in about 16 h) (Álvarez-Álvarez et al., 2018). Results for MC can be quoted as:

- (i) As received – in this case, mass loss is expressed in % of initial mass of sample:

$$\%MC = \left( \frac{\text{initial mass of sample} - \text{final mass of sample}}{\text{initial mass of sample}} \right) \times 100 \quad (1)$$

- (ii) On a dry-free basis – in this case, mass loss is expressed in % of final mass of sample:

$$\%MC = \left( \frac{\text{initial mass of sample} - \text{final mass of sample}}{\text{final mass of sample}} \right) \times 100 \quad (2)$$

Moisture content can be utilized when calculating the dry basis results of other analytical results. Prolonged drying of the biomass sample in the oven can lead to the loss of some volatile matter constituents due to decomposition.

- (b) Ash analysis is based on ASTM E1534-93 (2013) for wood (ASTM, 2019a) and it is the mass of the residue obtained after complete combustion of a 2 g sample at temperatures between 700 and 750 °C for 6 h (Álvarez-Álvarez et al., 2018):

$$\%Ash = \frac{\text{mass of residue}}{\text{initial mass of sample}} \times 100 \quad (3)$$

Ash content is required when calculating oxygen content by difference, and also when performing mass balances.

In coals, there is mineral matter (MM) which is not classified as ash. The mineral matter in coal is composed of CaCO<sub>3</sub> which can decompose to CaO and CO<sub>2</sub>; MgCO<sub>3</sub> which decomposes to MgO and CO<sub>2</sub>; Na<sub>2</sub>CO<sub>3</sub> which can decompose to Na<sub>2</sub>O and CO<sub>2</sub>; SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc (Matjie et al., 2016). So, ash is residue that remains after complete decomposition with compounds like CaO, MgO, Na<sub>2</sub>O, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc (Matjie et al., 2016). However, for biomass there is no such issues as mineral matter is negligible.

- (c) Volatile matter analysis is based on ASTM E872-82 (2013) for wood (ASTM, 2019c) and it is the weight loss obtained on heating a 1 g sample at 950 °C for 7 min in an inert atmosphere (Álvarez-Álvarez et al., 2018). This can be summarised by 2 equations:

- (i) Total weight loss of moist biomass = Weight loss due to Volatile matter + Moisture (4)

- (ii) Weight loss due to VM = Total weight loss – Moisture (5)

If the sample is dry, then weight loss is due to VM only, i.e.:

$$\%VM = \frac{\text{mass loss due to VM}}{\text{initial dry mass of sample}} \times 100 \quad (6)$$

Volatile matter consists of volatile substances formed during heating of biomass or coal in the absence of air (oxygen). Volatile matter are essentially gaseous products that are released like CO, H<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub> and other hydrocarbons (Tumuluru et al., 2011).

(d) Fixed carbon is calculated by difference from 100 and the sum of moisture, ash and volatile matter where all values are on the same moisture reference base (Álvarez-Álvarez et al., 2018), i.e.:

$$FC = 100 - (\%MC + \%VM + \%Ash) \quad (7)$$

Fixed carbon is the part of the carbon that remains behind when coal is heated in a closed vessel until all of the volatile matter (thermally unstable components) are driven off.

The conditions used to determine the proximate analyses are presented in Table 3.

The VM content of raw biomass before torrefaction is usually high, ranging between 70 and 88 wt.%, while its FC content is usually low, ranging between 10 and 21 wt.% (Chen et al., 2015). After torrefaction, the composition of VM (and MC) in biomass decreases, resulting in an increase in FC composition. The VM content of torrefied biomass is approximately in the range between 40 and 85 wt.% whilst the FC content is between 13 and 45 wt.% (Chen et al., 2015). For coals originating in Southern Africa, the average values for proximate analyses are: 2.5–6% for MC, 34–58% for Ash, 9–22% for VM and 19–39% for FC by mass and coals originating in South Africa have average values for proximate analyses by mass of 4% for MC; 32% for Ash and 44% for FC (Kalenga et al., 2011). Torrefaction is meant to change raw biomass properties to be similar to those for coal so as to be able to replace the coal. To analyse the extent of torrefaction, some authors use FC/VM ratio to analyse biomass and the ratio should increase with an increase in torrefaction temperature as FC content increases whilst VM content decrease after torrefaction (Nhuchhen and Basu, 2014). From the above the values, raw biomass has FC/VM ratio in the range 0.14–0.24; torrefied biomass has FC/VM ratio in the range 0.33–0.53 while coal from Southern Africa has FC/VM ratio in the range 1.78–2.11 and coal in South Africa has FC/VM ratio of 2.1.

### 2.3.2. Ultimate analysis

The main chemical elements in biomass and also coal (apart from associated mineral matter) are carbon (C), hydrogen (H), nitrogen (N), sulphur (S), and oxygen (O) content. This chemical analysis is very important to calculate material balance accurately and calorific value of the biomass sample or coal (Álvarez-Álvarez et al., 2018). The ultimate analysis is determined using the standard ASTM E870-82 (2013) for wood fuel (ASTM, 2019d). This standard describes the methods followed to determine CHNS. The standard test is conducted to determine the elemental state of biomass i.e. to determine C, H, N, S, and O of the biomass (ASTM, 2019d). These tests have been conducted on coal for years and they provide a basis for comparison on how the biomass, either raw or torrefied, can perform against coal for energy production as well. The standard testing methods for coal are found in literature and they can be adapted to biomass if there is no analysis equipment.

There are individual tests or a combined-test like CHNS test that can be performed to determine ultimate analysis. C, H, N, and S are determined by chemical analysis and expressed on a moisture free basis. Ash is also determined as in proximate analysis and reported on moisture free basis (Nhuchhen and Basu, 2014; Matjie et al., 2016). Then O is then determined by the difference as:

$$\%O = 100 - (\%C + \%H + \%N + \%S + \%Ash) \quad (8)$$

Alternatively, CHNS is reported separately without ash and O is determined by difference. Hydrogen is an important source of heat during combustion. However, more hydrogen contained in biomass or coal usually results in a lower carbon content (Basu, 2013). Oxygen contained in biomass improves fuel combustion properties as it supports combustion. However, more oxygen will result in a biomass with lower

calorific value due to a lower carbon content (Chen et al., 2015). Elemental analysis of biomass shows that usually O and C occur in higher proportion, followed by H, N and lastly S, if it exists (Nhuchhen and Basu, 2014). Coal analysis reports Cl<sub>2</sub> in addition to CHNSO but this is not found in biomass unless it is waste biomass. In some biomasses, C is more than O whilst other biomasses have more O than C (Matjie et al., 2016).

Some authors use the van Krevelen's diagram to represent ultimate analysis as it shows the change in H/C ratio on y-axis against O/C ratio on x-axis. This is a plot of atomic H/C ratio against atomic O/C ratio, with H/C on y-axis and O/C on x-axis (Brockman et al., 2018). This allows readers to follow how biomass higher elements from elemental analysis (C, H and O) change during and/or after a process like torrefaction. The change in the atomic ratios maybe due to a change with time, temperature or any parameter being investigated at the time. During torrefaction, however, the H/C and O/C ratios should all decrease with torrefaction progress and this should reflect on the van Krevelen's diagram plotted (see Figure 2).

### 2.3.3. Calorific value of raw biomass

Calorific value (CV) is the amount of heat released when there is complete combustion of fuel (coal or biomass) at the reference state of products of combustion (Sarkar, 2015). It is normally quoted at two temperatures:

- At 25 °C – it is Gross Calorific Value (GCV) and the products are CO<sub>2</sub>(g) and H<sub>2</sub>O(l). It is sometimes termed higher heating value (HHV) (Sarkar, 2015). GCV can be measured in a bomb calorimeter using ASTM standard ASTM E870-82 (2013d).
- At 100 °C – it is Net Calorific Value (NCV) and the products are CO<sub>2</sub>(g) and H<sub>2</sub>O(g). It is sometimes termed lower heating value (LHV) (Merckel and Heydenrych, 2017). The difference is the latent heat of vaporisation of water which is ~2260 kJ/kg. This means that HHV is greater than LHV as it includes the latent heat of vaporization of water (Sarkar, 2015). It also means that calorific value for biomass should be specified as either LHV or HHV.

### 2.3.4. Correlations for biomass calorific value

The standard testing methods for coal are found in literature and they can be adapted to biomass if there is no analysis equipment. Alternatively, correlations (theoretical analysis) developed over time can be used to determine heating values for biomasses. Dulong's formulae can be used to estimate calorific values of coal from elemental (ultimate) analysis with a few assumptions which can be determined in literature. The equations are as follows:

$$HHV = 339[\%C] + 1427 \left( [\%H] - \frac{[\%O]}{8} \right) + 92[\%S] \quad \text{kJ/kg} \quad (9)$$

(Friedl et al., 2005)

It follows that LHV is HHV minus the heat of vaporisation of water (available moisture and hydrogen), i.e.:

$$LHV = HHV - 24.44(9[\%H] + [\%MC]) \quad \text{kJ/kg} \quad (10)$$

(Friedl et al., 2005)

where 24.44 kJ/kg is assumed as the latent heat of water.

However, there are correlations that have been adapted and/or developed to be used to determine biomass' heating values. A few of them are discussed below:

- The Boie correlation (Merckel and Heydenrych, 2017), was originally developed for coals, but it is applied to biomass samples:

$$HHV = 351.69[\%C] + 1162.46[\%H] - 110.95[\%O] + 104.67[\%S] - 62.8[\%N] \quad \text{kJ/kg} \quad (11)$$

where [%C], [%H], etc. are on weight basis (wt.%) for biomass ultimate analysis on a dry basis i.e. it is the elemental analysis on a dry basis.

2. The HHV can be estimated by utilising the Milne equation (Hayes, 2013), which is:

$$HHV = 0.341[\%C] + 1.322[\%H] + 0.0686[\%S] - 0.12\{[\%O] + [\%N]\} - 0.0153[\%Ash] \quad \text{MJ/kg} \quad (12)$$

where [%C], [%H], etc. are on weight basis (wt.%) for biomass ultimate analysis on a dry basis i.e. it is the elemental analysis on a dry basis.

3. Friedl et al. (2005) formulated the correlation based on ultimate analysis:

$$HHV = 3.55[\%C^2] - 232[\%C] - 2230[\%H] + \{51.2[\%C] \times [\%H]\} + 131[\%N] + 20600 \quad \text{kJ/kg} \quad (13)$$

where [%C], [%H], [%N] are on a weight basis (wt.%) of dry material on dry basis i.e. it is the elemental analysis on a dry basis.

The model gives a standard error of calibration of 337 kJ/kg and an  $R^2$  of 0.943 based on analysing a number of biomass fuels. The high C content of the thermally pre-treated fuels may lead to inaccuracies in using this correlation so a Bomb Calorimeter may need to be used to validate the calculated values (Bridgeman et al., 2010; Friedl et al., 2005). Friedl et al. correlation was fitted/validated using ordinary least squares regression and partial least squares regression fitting for 122 biomass samples with higher heating values between 16 and 26 MJ/kg and carbon content between 42% and 50% (Bates and Ghoniem, 2013).

4. Channiwala and Parikh (2002) formulated a correlation with modified coefficients for biomass:

$$HHV = 349.1[\%C] + 1178.3[\%H] + 100.5[\%S] - 103.4[\%O] - 15.1[\%N] - 21.1[\%Ash] \quad \text{kJ/kg} \quad (14)$$

where [%C], [%H], etc. are on weight basis (wt.%) for biomass ultimate analysis on a dry basis i.e. it is the elemental analysis on a dry basis. The range for the components in proximate and ultimate analysis for the correlation are as follows:  $0\% \leq C \leq 92.25\%$ ;  $0.43\% \leq H \leq 25.15\%$ ;  $0\% \leq O \leq 50.00\%$ ;  $0\% \leq N \leq 5.60\%$ ;  $0\% \leq S \leq 94.08\%$ ;  $0\% \leq Ash \leq 71.40\%$

5. Cordero et al. (2001) developed the equation:

$$HHV = 354.3[\%FC] + 170.8[\%VM] \quad \text{kJ/kg} \quad (15)$$

where [%FC], [%VM] are on weight basis (wt.%) on a dry basis for biomass or coal.

6. The equation from Cordero et al. (2001) can also be expressed in terms of measured parameters (VM and Ash) as:

$$HHV = 35\,430 - 183.5[\%VM] - 354.3[\%Ash] \quad \text{kJ/kg} \quad (16)$$

Other correlations to estimate biomass calorific value (HHV) that can be found in Channiwala and Parikh (2002).

LHV of biomass, both woody and non-woody, are in the range from 12 to 26 MJ/kg (Chew and Doshi, 2011). However, the LHV of coal is usually between 25 and 30 MJ/kg on a dry basis whilst the HHV for coal is in the region 25–35 MJ/kg with the HHV for raw biomass is usually in the range 15–20 MJ/kg (Friedl et al., 2005).

## 2.4. Torrefaction reactors

There are several reactors that are used for biomass torrefaction. Some of the reactors falls under one of the following types: (i) fixed bed, (ii) microwave, (iii) rotary drum, and (iv) fluidized bed (Basu, 2018a; Chen et al., 2013; Nachenius et al., 2013). Batidzirai et al. (2013) showed various torrefaction reactors that were under development at that time

considered and some of them being patented. In addition, there are pros and cons which can assist when selecting a reactor type for torrefaction purposes. Nachenius et al. (2013) has also highlighted the torrefaction reactors available.

### 2.4.1. Fixed bed reactor

In a fixed bed reactor, the raw biomass is fed into the reactor and is then dried and torrefied in the furnace. Torrefied biomass is collected at the end after the torrefaction process and the reactor has cooled down (Ribeiro et al., 2018). This is the simplest reactor for torrefaction of any type of biomass (see Figure 3).

### 2.4.2. Moving bed reactor

In a moving bed reactor, raw solid biomass particles are fed from the top of a vertical reactor and the particles undergo drying and torrefaction and exit at the bottom of the reactor (Tumuluru et al., 2010). The biomass is directly heated by recirculating the gases and vapors that are produced during torrefaction (Nachenius et al., 2013). Tumuluru et al. (2010) demonstrated the design of a moving bed for drying and torrefaction of biomass (see Figure 4).

### 2.4.3. Microwave reactor

In a microwave reactor, water in the biomass absorbs microwave energy that is provided by microwaves, which are part of electromagnetic waves, and in the process produce heat energy that is used to achieve torrefaction (Batidzirai et al., 2013; Nachenius et al., 2013; Ren et al., 2013) (see Figure 5).

### 2.4.4. Rotary drum reactor

In this reactor, raw biomass is fed continuously through the reactor inlet into a rotating reactor and the product is discharged from the reactor outlet. Heat is applied either directly or indirectly to attain the required temperatures using superheated steam or exhaust gases that results from combustion of volatile gases formed during torrefaction (Tumuluru et al., 2010) (see Figure 6).

### 2.4.5. Fluidized bed reactor

In this reactor, hot inert gases are blown from the bottom of the reactor to fluidize (float) milled or pulverized raw biomass particles to form a fluid in the reactor that is at a certain height, called bed height to achieve a uniform temperature distribution throughout the bed (Nachenius et al., 2013). For this to be achieved, a suitable velocity for the inert gases should be reached and this velocity should be higher than the minimum fluidization velocity (see Figure 7).

Currently there is no preferred reactor type to use as they all perform differently when using different types of biomasses, but the choice is ultimately linked to the type of biomass chosen and the process conditions to be used.

## 2.5. Phases/Stages of torrefaction process

In general, biomass is composed of hemicellulose which is a branched polymer, cellulose which is the unbranched polymer, and lignin which is amorphous, highly-branched, cross-linked macromolecular polymeric resin (Hill et al., 2013; Wild et al., 2016). During torrefaction, the three biomass polymers degrade to different extents leading to the different stages of torrefaction (Hill et al., 2013; Pelaez-Samaniego et al., 2014). This is based on degradation temperature and also on the type of biomass involved. In essence, there are four important phases or stages of degradation that occur.

### 2.5.1. First phase

This occurs between 25 and 105 °C and it involves the removal of unbound water which occurs at the normal boiling point of water (100 °C) up to around 105 °C (Tsamba et al., 2006).

### 2.5.2. Second phase

This occurs between 105 and 250 °C and it involves the irreversible biomass degradation. Usually at temperatures below 200 °C, there is very little decomposition of the biomass that takes place because all physically bound moisture along with some light organic compounds do not escape from the biomass (Chen et al., 2018). Lignin, the binder component of biomass, starts softening above its glass-softening temperature of ~130 °C without degrading, this occurs within the temperature range 120 and 150 °C (Pelaez-Samaniego et al., 2014). This helps densification (pelletization) of torrefied biomass. At lower temperatures, between 160 and 180 °C, biomass dries releasing H<sub>2</sub>O and CO<sub>2</sub>, which do not contribute to the energy of the product gas and constitute a dominant portion of the weight loss during torrefaction (Chen et al., 2018). The H<sub>2</sub>O released is bound water and it is formed from the reaction of H<sub>2</sub> and O<sub>2</sub>, termed thermo-condensation which is a chemical change.

Within the temperature range of 100 and 260 °C, hemicellulose is the most chemically active component, but it usually starts to degrade at temperatures from 200 °C (200–250 °C) and the biomass can be observed to change its colour to brown in the temperature range 180–270 °C (Tumuluru et al., 2011). Alternatively, hemicellulose decomposes to give volatile products in the temperature range of 180 and 270 °C, according to Bergman et al., (2005a) or 150 and 280 °C, according to Basu (2018a). This is the devolatilization process/stage and at this stage, reactions are partly endothermic, releasing gases with small amount of heating value (Basu, 2018a). Hemicellulose component undergoes the greatest amount of degradation within the 200–300 °C temperature window (Yang et al., 2006). Hemicellulose depolymerization at temperature below 250 °C leads to an altered and rearranged polysugar structures (Bergman et al., 2005b). When biomass decomposes between 200 and 270 °C (mostly through hemicellulose degradation), volatiles like acetic acid, methanol, CO and CO<sub>2</sub> are released adding to the moisture (H<sub>2</sub>O) that will have been released earlier during drying and at the start of torrefaction (Pelaez-Samaniego et al., 2014).

Within the temperature range 105–250 °C, cellulose shows limited devolatilization and carbonization, it does not start to degrade until at temperatures of ~250 °C (Chen et al., 2018).

### 2.5.3. Third phase

This occurs between 250 and 330 °C and it usually involves the total destruction of the most reactive component of lignocellulosic biomass, hemicelluloses. In this stage, hemicellulose depolymerization leads to formation of chars, and release of CO, CO<sub>2</sub> and H<sub>2</sub>O (Pelaez-Samaniego et al., 2014). The hygroscopic property of biomass is partly lost in torrefaction because of the destruction of OH groups through dehydration, which prevents the formation of hydrogen bonds and also gives torrefied biomass its hydrophobic property (Pahla et al., 2017). At temperatures of ~290 °C, hemicellulose may be degraded completely but this depends on the type of biomass involved and the weight fraction of hemicellulose to some extent.

According to Chen et al. (2011a) and Tumuluru et al. (2011), cellulose will start to degrade at temperatures ~240 °C to give anhydrous cellulose and levoglucosan polymer. But according to Basu (2018a), cellulose starts to degrade at temperatures above 250 °C, or ~275 °C, within a narrow temperature band of 270–350 °C.

Lignin degrades gradually over the temperature range from 250 to 500 °C. At temperatures around 280 °C, lignin degrades to give phenols due to cleavage of ether bonds (Chen et al., 2018). At temperatures ≥280 °C, the reactions are mostly exothermic in nature; leading to an increase in the production of condensable and non-condensable vapours/gases like CO, hydrocarbons (like phenols and cresols), and other heavier products (Tsamba et al., 2006). When torrefaction temperature reaches 290 °C, all three biomass components start to lose weight at the same rate, i.e. all lignocellulosic components start to degrade at the same rate (Chen et al., 2011a).

### 2.5.4. Fourth phase

This occurs between 330 and 370 °C and it involves destruction of cellulose. Lignin, being the most resistant lignocellulosic component, is sometimes only degraded at high temperatures of above 350; but most agree that lignin starts to degrade from 275 °C (Saadon et al., 2014).

However, it is known that torrefaction occurs within the temperature range of between 200 and 300 °C, so part of third phase and the whole of fourth phase fall outside torrefaction and into pyrolysis leading to extensive devolatilization of the biomass (Basu, 2013).

### 2.5.5. Light, mild and severe torrefaction

Torrefaction can also be classified as either light, mild or severe torrefaction:

- o Light torrefaction occurs ~210 °C where only hemicellulose is degraded leaving lignin and cellulose unaffected. Light torrefaction retains maximum amount of mass and energy of the dry biomass but attains the lowest energy density (Wen et al., 2014)
- o Mild torrefaction occurs ~250 °C where cellulose is mildly affected. The mass and energy loss of dry biomass are on average (Hill et al., 2013)
- o Severe torrefaction occurs ~290 °C and is characterised by depolymerization of lignin, cellulose, and any remaining hemicellulose. Severe torrefaction results in the greatest mass and energy loss, but it gives highest energy density in the torrefied biomass (Chen et al., 2011b)

### 2.5.6. Summary of torrefaction phases

During torrefaction, hemicellulose is the component that degrades to a higher degree, but lignin and cellulose are degraded to a smaller extent and this usually occurs at higher temperatures from 250 °C and above (Hill et al., 2013). With an increase of torrefaction temperature, there is a decrease of solid biochar yield with an increase of the yield in volatile fraction, including liquid and non-condensable/permanent gases (Galletti and Antonetti, 2012). Therefore, we can conclude that hemicellulose decomposition is the primary mechanism of torrefaction (Chen et al., 2015). It also means that, volatile matter (VM) and moisture (MC) reduce in weight whilst fixed carbon (FC) and ash increase in content, all from proximate analysis (Chew and Doshi, 2011). This means proximate analysis does play an important role in assessing how torrefaction will affect biomass, that is, more volatile matter will result in more mass loss and therefore, more torrefaction gases to be produced, and vice versa (Basu, 2013). Biomass ash is usually reactive and will reduce in weight in some instances, however, the weight reduction is small and sometimes negligible (Chew and Doshi, 2011).

Lignocellulosic components degradation during torrefaction can be summarized based on each component and the temperature range. This is shown in Table 4.

## 2.6. Products of torrefaction process and their analysis

The yield of torrefaction product usually depends on torrefaction conditions, mainly temperature and time as well as the properties of the biomass (Bergman et al., 2005a).

During torrefaction, the products of the process consists of solid biochar and volatile gases that can be separated into liquid (condensable gases) and permanent gases, considering room temperature as the reference temperature (Tumuluru et al., 2012). When dry biomass is torrefied, it results in a water content of about 50 wt.% and 10 wt.% CO<sub>2</sub> in the torrefaction gas due to chemical reactions (Tumuluru et al., 2010). Torrefied gas can be used to generate process heat which can be used to dry wet biomass (Jansen and Carbo, 2013).

### 2.6.1. Solid product

Torrefied biomass (biochar or char), which is a dry, partially carbonised solid is left after volatile gases have been driven off together

with bio-ash from proximate analysis and unreacted carbon are the main products that are left behind (Bridgeman et al., 2010). The torrefied biomass mostly contains unreacted lignin and cellulose polymeric structures whilst hemicellulose mostly contributes to volatile gases products (Bergman et al., 2005a). About 70% of the mass is retained as the torrefied biomass while 30% escapes as volatile gases and vapors (Agar and Wihersaari, 2012). The solid fraction retains about 90% of the initial energy content meaning the heating value of torrefied biomass is 15–20% higher than the original untreated biomass (Chew and Doshi, 2011).

Torrefied biomass can be processed and densified into either pellets or briquettes obtaining a solid bioenergy carrier with high energy density with properties approaching those of coal, and better suited to logistics and end-use requirements (Jansen and Carbo, 2013).

### 2.6.2. Liquid product (Condensable gases)

The volatile gases that are released can be passed through a condenser where different liquid products are formed at room temperature. The products will consist mainly of moisture, organics and lipids (Tumuluru et al., 2011). Moisture consist of freely bound moisture and moisture from the reaction of H<sub>2</sub> and O<sub>2</sub> gases during torrefaction (Tumuluru et al., 2012).

The organics consists mainly of sugars, polysugars, acids, alcohols, furans, aldehydes and ketones; examples include acetic acid, formic acid, methanol, lactic acid, furfural and hydroxyl acetate (acetol) (Tumuluru et al., 2012). Lipids consist of terpenes, benzene, phenols (like toluene), fatty acids, waxes and tanins. Water is the main condensable product of torrefaction as it is released during drying when moisture evaporates and during dehydration reactions between organic molecules (Prins et al., 2006a).

Acetic acid is the dominant product of the trace gases before condensation has been done to remove volatile gaseous products, consisting between 8 and 15% (Bergman et al., 2005a). Acetic acid is formed mainly from acetoxy- and methoxy-groups that are found as side chains in xylose units and acetyl pendant groups. Xylose units are part of hemicellulose while acetyl pendant groups in cellulose (Tumuluru et al., 2011). Lipids such as terpenes, phenols, fatty acids, waxes and tanins are not reaction products but inert compounds that are evaporated during torrefaction and they condense when the temperature drops down to room temperature (Bergman et al., 2005a).

### 2.6.3. Gas product (permanent gases)

Permanent gases mainly consist of CO, CO<sub>2</sub>, small amounts of CH<sub>4</sub>, low molecular weight hydrocarbons (C<sub>x</sub>H<sub>y</sub>) together with unreacted H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>; with CO<sub>2</sub> produced usually in the range ~75–80% of all gaseous products followed by CO which is around 10–12% (Bergman et al., 2005a). Most other gases are detected in trace amounts (Chen et al., 2015). The formation of CO<sub>2</sub> is due to decarboxylation, while CO comes mainly from the reaction between CO<sub>2</sub> and steam with porous char surface of the biomass (Chen et al., 2018). This means that CO only starts being produced after CO<sub>2</sub> has been produced. CO is the main source of the heating value for permanent gases during torrefaction (Tumuluru et al., 2011).

### 2.6.4. Major chemical reactions during torrefaction

The purpose of torrefaction is the removal of O, H, S, N elements whilst leaving most of C intact, so it therefore means that, gaseous products with C are not desirable as they result in reduction of carbon efficiency (Tumuluru et al., 2011). During formation of CO and CO<sub>2</sub>, a mole of oxygen removes a mole of carbon and half a mole of carbon, respectively, thus reducing carbon efficiency, while in the formation of H<sub>2</sub>O, one mole of oxygen removes 2 mol of hydrogen that usually need to be added particularly for gasification (Redissi and Bouallou, 2013). Ideally, it would be preferable to reject oxygen as O<sub>2</sub>, but this is not a typical output of any biomass conversion process (Cherubini and Strømman, 2011). When S and N are removed, their oxides (SO<sub>2</sub> and NO<sub>2</sub>) are formed and this contributes to the removal of excess oxygen. However, in biomass there is usually little or no sulphur and nitrogen is

not removed as an oxide, i.e. it tends to stay in that form during torrefaction (Cherubini and Strømman, 2011).

Based on the major products that have been observed, the chemical reactions that occur during torrefaction are summarized in Table 5.

Most of the oxidation reactions are heterogeneous reactions (reactions 4 and 6), so they can be slowed down by mass transport resistances that the hydrogen and oxygen must overcome to come into contact with the solid carbon. The importance of the oxidation reactions grows with non-bounded molecular oxygen within the biomass feedstock itself, i.e. biomass with more oxygen will result in more torrefaction gas products from oxidation reactions (Chen et al., 2014).

### 2.6.5. Pollutant gaseous products

The possible formation of pollutants is also considered during torrefaction. The possible pollutants considered to be formed are nitrogen monoxide (NO), nitrogen dioxide (NO<sub>2</sub>), ammonia (NH<sub>3</sub>), sulphur dioxide (SO<sub>2</sub>), sulphur trioxide (SO<sub>3</sub>) and hydrogen sulphide (H<sub>2</sub>S) (Wu and Williams, 2011). However, appreciable quantities have been found only for NH<sub>3</sub>, whilst there is very few biomass (except waste biomass) that has S in its ultimate analysis, that can result in the formation of H<sub>2</sub>S and SO<sub>2</sub> (Wu and Williams, 2011). As a result, most of these pollutants are produced in negligible quantities.

### 2.6.6. Torrefaction efficiency

Efficiency of the torrefaction process is assessed using different techniques.

**2.6.6.1. Solid yield and energy yield.** The solid and energy yields determine the transition of mass and chemical energy from biomass to biochar. Solid Yield (Mass Yield) is defined as the fraction of the original organic component of biomass that is converted into solid char (Nanou et al., 2016). It is defined on dry basis for biomass with high inorganic content or on dry ash free (daf) basis for biomass with low inorganic content:

$$y_{solid} = \frac{m_{torr}}{m_{raw}} \quad (17)$$

(Nanou et al., 2016)

where  $m_{raw}$  is the mass of raw biomass input after drying,

$m_{torr}$  is the mass of product output (biocoal or torrefied biomass).

On the other hand, energy yield gives the fraction of the original energy in the biomass retained after torrefaction:

$$E_{yield} = \frac{m_{torr}}{m_{raw}} \frac{HHV_{torr}}{HHV_{raw}} \quad (18)$$

$$E_{yield} = y_{solid} \frac{HHV_{torr}}{HHV_{raw}} \quad (19)$$

(Bridgeman et al., 2008)

where  $HHV_{torr}$ ,  $HHV_{raw}$  are higher heating values of torrefied biomass and raw biomass respectively.

Torrefaction yield (solid or mass) can vary between 24% and 95% of the original weight. However, biomass with higher hemicellulose content will lean towards lower yield while biomass with lower hemicellulose content leans toward higher yield (Chew and Doshi, 2011). This is because hemicellulose decomposition is mostly achieved in torrefaction where all the hemicellulose degrades before 300 °C, leading to volatiles and lower mass yield.

Another term to consider is energy density, which is the amount of energy released when unit mass of the torrefied product is fully combusted and its products are cooled to room temperature (Nanou et al., 2016).

**2.6.6.2. Heating value (HV).** During torrefaction, there is a decrease in O/C ratio in biomass. This is attributed to an increase in lignin content which has low O/C ratio when compared to O/C ratio that is in

hemicellulose and cellulose (Chen et al., 2018). This can be seen in Figure 1 when comparing the structures of lignin, hemicellulose and cellulose. Reduction of O, results in an increase or enrichment of elemental carbon in torrefied biomass leading to an increase in the calorific value of the torrefied materials.

In addition, there is a decrease in H/C ratio in biomass during torrefaction. This is attributed mainly to the release of volatile compounds, many of which carry bonded hydrogen in them. However, as there is an increase in lignin content with an increase in torrefaction temperature, this has a small significant difference on H/C ratio, as there is higher hydrogen content in lignin compared to oxygen content. Using the same principle, reduction of H, results in enrichment of elemental carbon in torrefied biomass leading to an increase in the calorific value of the torrefied materials to certain extent (Basu, 2013). However, the increase in calorific value due to a decrease in O/C and H/C ratios cannot keep up with the loss in weight during torrefaction and as such; it leads to a decrease in total energy of biomass as the torrefaction temperature rises (Chen et al., 2011a).

Carbon plays an exothermic role as the fuel is burned, while hydrogen and oxygen play endothermic roles, so controlling the O/C and H/C ratios result in high or low value of calorific value for the biomass (Senneca, 2017).

In general, though there is an increase in heating value of torrefied biomass against raw biomass. LHV of torrefied biomass is usually within the range 18–23 MJ/kg on a dry basis as compared to LHV of coal that is usually between 25 and 30 MJ/kg on a dry basis. The HHV of torrefied biomass is in the range between 20 and 29 MJ/kg whilst the HHV of coal generally is in the range between 25 and 35 MJ/kg (Bergman et al., 2005a).

**2.6.6.3. Thermogravimetric analysis (TGA) with gas chromatography (GC).** The technique involves a small sample of biomass or coal (usually 10 mg) being heated in a specified atmosphere (usually inert atmosphere) at the desired rate in an electronic microbalance from ambient temperature to 1400 °C at a specified heating rate like say 10 °C/minute (Chen and Wu, 2009). This allows continuous recording of the weight change of the fuel sample in a TGA apparatus with change in time (Hill et al., 2013). The result is the rate of change in the weight of the fuel sample continuously, that is, measured weight loss versus time graph where MC, VM and Ash content of the sample can be determined, i.e. it can be used to determine the proximate analysis of the biomass sample (Sakthivadivel and Iniyar, 2018). The FC is determined by difference.

There are three stages of thermal degradation that can be seen on TGA curves. The first stage occurs from ambient temperature to 105 °C, showing biomass drying or moisture loss/analysis (Sakthivadivel and Iniyar, 2018). The second stage occurs between 200 and say 500 °C, where the highest mass loss is usually recorded as shown in Section 2.4 and attributed to the degradation of volatile materials, hemicellulose, cellulose and part of the lignin (Chen and Wu, 2009). The third stage occurs at temperatures above 500 °C and it is attributed to the lignin part which has still not been degraded, and ash that will be left behind (Chen and Wu, 2009; Sakthivadivel and Iniyar, 2018).

In addition to this, TGA does provides additional information as to determine the reaction mechanisms, kinetic parameters, thermal stability, and heat of reaction for torrefaction (Basu, 2013). This assists in determining reaction rate of a biomass sample or when comparing the reaction mechanisms between different biomass samples.

**2.6.6.4. Fourier Transform Infrared spectroscopy (FTIR).** Fourier Transform Infrared (FTIR) Spectroscopy uses infrared light to detect and identify the structure of molecules by identifying functional groups present in the molecules (Chen et al., 2012). In biomass it can be used to identify hemicellulose, cellulose and lignin components during torrefaction. Infrared light used is in the region between 12800 and  $\sim 10$   $\text{cm}^{-1}$  for the wavelength ( $\lambda$ ). However, this infrared light region can be sub-divided into three regions (Griffiths and de Haset, 2007):

1. Near-infrared region = 12800~4000  $\text{cm}^{-1}$
2. Mid-infrared region = 4000~200  $\text{cm}^{-1}$
3. Far-infrared region = 50~1000  $\text{cm}^{-1}$

Most organic and inorganic ions are detected in the region 4000–400  $\text{cm}^{-1}$  (mid-infrared region) with an error of  $\pm 0.01$   $\text{cm}^{-1}$ . This region can then be further subdivided into four parts which are useful when using FTIR to identify components (Nikolic, 2011). The subclassification is shown in Table 6.

When FTIR is used to analyse a molecule/compound and an FTIR spectrum is available, the following steps can be used to interpret results so as to identify the molecule/compound:

1. Check conformity on axes of the spectrum: The x-axis, labelled as “Wavenumber” indicates the wavelength, starting from right to left-hand side and ranging from 400 to 4000  $\text{cm}^{-1}$ . The y-axis, labelled as “% Transmittance” indicates transmittance, i.e. how much light energy passes through a molecule without being absorbed by the vibrating bonds (Chen et al., 2012).
2. Identify characteristic peaks in the IR spectrum since all IR spectra contains many different peaks. Pay attention to large peaks on the spectrum as these provide important information that will assist you in being able to identify the molecule/compound (Griffiths and de Haset, 2007).
3. Identify the areas of the spectrum in which the characteristic peaks are found. IR spectrum can be divided into four regions as shown in Table 6 (Griffiths and de Haset, 2007). Peaks that fall into region 4 are unique to that compound/molecule and they are often called fingerprint peaks as they lead to the identification of that molecule/compound.
4. Finally make a conclusion: If you can identify all peaks on the spectrum, then you can identify your compound/molecule and how it changes during torrefaction. If all the peaks in an IR spectrum are the same as the peaks of another spectrum for another compound/molecule, then you can rest assured that the two molecules/compounds are exactly the same (Chen et al., 2012).

When FTIR is used to analyse biomass before and after torrefaction, the presence of cellulose, hemicellulose and lignin can be detected through detection of their functional groups. FTIR absorption bands at 1463, 1412, 1248, 1164, 1043 and 987  $\text{cm}^{-1}$  usually show presence of hemicellulose; FTIR absorption bands at 1429, 1378, 1168, 1106, 1064, 1030 and 897  $\text{cm}^{-1}$  show presence of cellulose, while FTIR absorption bands at 1599, 1511, 1462 and 1420  $\text{cm}^{-1}$  show presence of lignin (Chen et al., 2012; Acquah et al., 2016).

## 2.7. Research in torrefaction

To date different methods and various biomass types have been investigated at different conditions. Table 7 gives a summary of some of the investigations conducted to date. Wood is by far the most investigated biomass, but other unutilized types of biomasses have been investigated as well including waste biomass.

The information also show how far torrefaction has come from and the different investigations being conducted from different researchers across the globe. However, most of the research has focused on optimizing torrefaction parameters (temperature, residence time, heating rate and sometimes  $\text{O}_2$  levels) and application of biomass for energy production.

## 3. Application of torrefaction process

### 3.1. Densification of torrefied biomass

Simply put, densification (or pelletization) is when a mechanical force is applied to biomass to compact it and obtain uniform particle size

distribution of solid particles as pellets or briquettes (Bridgeman et al., 2008; Nanou et al., 2016). This implies that during densification, the mass or volumetric energy density of the biomass is increased to improve its storage and handling, thereby reducing the associated costs such as transport or storage costs (Agar and Wihersaari, 2012; Chen et al., 2015; Nachenius et al., 2013).

After biomass has been torrefied, its properties improve, and this also allows any further treatment to be done. The first one is usually size reduction either grinding or pulverizing, then there is densification (Nanou et al., 2016; Poudel et al., 2015). In other circumstance, densification is carried out straight after torrefaction (Bridgeman et al., 2008).

From section 2.4, it was mentioned that lignin is the binder component of biomass and it starts to soft at  $\sim 130$  °C without degrading and this helps in biomass densification (pelletization) of torrefied biomass (Pelaez-Samaniego et al., 2014). After the biomass has been torrefied, its mass and energy density increase, and its hydrophobic properties are improved (Asadullah et al., 2014). This makes it easier and less costly to densify it usually into briquettes or pellets by using conventional densification equipment to obtain a solid bioenergy carrier (Asadullah et al., 2014; Jansen and Carbo, 2013; Nachenius et al., 2013). Torrefaction makes biomass friable, i.e. 80–90% less energy is consumed when grinding torrefied biomass (Tumuluru et al., 2011). This can be attributed to the following: after torrefaction, biomass has lost weight as volatiles and so it shrinks, becomes fragile, losing its mechanical strength, and this makes it easier to grind and pulverize it (Tumuluru et al., 2011).

### 3.2. Blending different biomass types for single purpose

The torrefaction process improves the properties of different biomass types and their properties become close to those for coal allowing blending of different biomass types for energy production without losing process efficiency (Gil et al., 2015; Mamvura and Muzenda, 2015). The advantage is that even waste biomass can be pretreated and then blended with other local biomass types to get a bigger pool of torrefied biomass which can be applied for either gasification or co-firing with coal for energy production (Gil et al., 2015; Sikarwar et al., 2016).

### 3.3. As a pretreatment step for gasification process

Torrefaction is used as a pre-treatment stage for combustion, pyrolysis and gasification processes by blending coal with torrefied biomass (Basu et al., 2014; Chen et al., 2011a). This results in reduced greenhouse gases during these processes as CO<sub>2</sub> released is part of the carbon cycle (Chen and Wu, 2009). Some researchers have shown that torrefied biomass improves gasification efficiency as compared to use of raw biomass (Prins et al., 2006a). This is because when biomass is raw, there is high oxygen content (O/C ratio) that results in over-oxidation during gasification processes, increasing the thermodynamic losses of the process (Bergman et al., 2005b; Deng et al., 2009; Poudel et al., 2015). Torrefaction process can reduce this loss by reducing the oxygen content in the biomass i.e. O/C ratio is reduced and in the process the carbon content of the biomass is increased (Chen et al., 2011a; Prins et al., 2006a).

### 3.4. Energy production by co-firing torrefied biomass with coal

The world is moving towards co-firing torrefied biomass with coal to reduce pollution effects of coal (Asadullah et al., 2014; Basu et al., 2014). Most countries are leading in this regard with UK having the majority of its coal fired power stations being co-fired with biomass. Statistics in 2008 showed that  $\sim 1.6$  TW h of UK's electricity was produced from co-firing domestic and imported biomass with coal (Department of Energy and Climate Change, 2009) and this figure increased to  $\sim 54$  TW h in 2018 (Department of Energy and Climate Change, 2018). During co-firing of torrefied biomass with coal, there will be a reduction in mill capacity during addition of biomass to the boilers because of the fibrous

nature of some biomass feedstocks. However, to prevent this challenge, different co-firing procedures can be developed to achieve required throughputs (Bridgeman et al., 2010). An alternative to this is to co-mill torrefied biomass together with coal first and then charging in boilers. The advantage is that it does not require a separate biomass feed system to act in parallel with the coal feed system, and it also avoids additional maintenance and installation costs (Bridgeman et al., 2010).

### 3.5. Steel production

In steel production, pulverized coal is used in blast furnaces during iron making. Blending some of the coal with torrefied biomass of similar properties and amounts, thereby reducing the amount of coal being used help to reduce emissions from coal whilst still achieving the desired product (Chen et al., 2015). Steel production requires torrefied biomass with LHV in the range of  $\sim 25$  MJ/kg alternatively, the torrefied biomass can be co-fired with coal to improve the calorific value.

## 4. Conclusion

The review has discussed in detail torrefaction as a technology that is gaining acceptance to pretreat raw biomass to have properties similar to those for coal. The main product of torrefaction, torrefied biomass can either be used for electricity generation alone but mostly by co-firing with coal or as a first step in biomass gasification or for steel production. The advantage of co-firing with coal is that it reduces the coal used in electricity generation and it therefore reduces the carbon dioxide that is emitted into the atmosphere during electricity generation mitigating the effects of global warming and climate change. Several techniques are used to analyse raw and torrefied biomass so as to determine the efficiency of the process and these techniques are used mostly for coal as well and in other studies. However, their importance to this technology have been highlighted so that novice researchers in the field can easily see how to apply them during their investigations.

The chemical reactions that occur during torrefaction have mostly been modelled from the products that have been detected to date. Researchers are still not yet sure of how the chemical reactions occur but with further research the research gap being closed up and the process will be fully understood. This works well in the drive for use of renewable resources to produce electricity and it add to the bigger mix of renewable energy resources that also includes solar, wind, hydrogen fuel cells amongst other technologies.

## Declarations

### Author contribution statement

TA Mamvura: Conceived and designed the analysis; Analyzed and interpreted the data; Contributed analysis tools or data; Wrote the paper.

G Danha: Analyzed and interpreted the data; Contributed analysis tools or data; Wrote the paper.

### Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

## References

- Acquah, G.E., Via, B.K., Fasina, O.O., Eckhardt, L.G., 2016. Rapid quantitative analysis of forest biomass using fourier transform infrared spectroscopy and partial least squares regression. *J. Anal. Methods Chem.* 2016, 1839598.
- Agar, D., Wihersaari, M., 2012. Bio-coal, torrefied lignocellulosic resources - key properties for its use in co-firing with fossil coal - their status. *Biomass Bioenergy* 44, 107–111.
- Álvarez-Álvarez, P., Pizarro, C., Barrio-Anta, M., Cámara-Obrigón, A., Bueno, J.L.M., Álvarez, A., Gutiérrez, I., Burslem, D.F.R.P., 2018. Evaluation of tree species for biomass energy production in Northwest Spain. *Forests* 9 (4), 160.
- 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.
- ASTM E1534-93, 2019a. Standard Test Method for Determination of Ash Content of Particulate Wood Fuels. ASTM International, West Conshohocken, PA. [www.astm.org](http://www.astm.org).
- ASTM E871-82, 2019b. Standard Test Method for Moisture Analysis of Particulate Wood Fuels. ASTM International, West Conshohocken, PA. [www.astm.org](http://www.astm.org).
- ASTM E872-82, 2019c. Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels. ASTM International, West Conshohocken, PA. [www.astm.org](http://www.astm.org).
- ASTM E870-82, 2019d. Standard Test Methods for Analysis of Wood Fuels. ASTM International, West Conshohocken, PA. [www.astm.org](http://www.astm.org).
- Barik, D., 2019. Energy extraction from toxic waste originating from food processing industries. In: Barik, D. (Ed.), *Energy from Toxic Organic Waste for Heat and Power Generation*. Woodhead Publishing, Massachusetts, USA, pp. 17–42.
- Basu, P., 2013. Biomass Characteristics in: Biomass Gasification, Pyrolysis and Torrefaction – Practical Design and Theory, second ed. Academic Press, San Diego, pp. 47–86.
- Basu, P., 2018a. Torrefaction. Biomass Gasification, Pyrolysis and Torrefaction – Practical Design and Theory, third ed. Academic Press, San Diego, USA, pp. 93–154.
- Basu, P., 2018b. Biomass characteristics. Biomass Gasification, Pyrolysis and Torrefaction – Practical Design and Theory, third ed. Academic Press, San Diego, USA, pp. 49–91.
- Basu, P., Sadhukhan, A.K., Gupta, P., Rao, S., Dhungana, A., Acharya, B., 2014. An experimental and theoretical investigation on torrefaction of a large wet wood particle. *Bioresour. Technol.* 159, 215–222.
- Bates, R.B., Ghoniem, A.F., 2013. Biomass torrefaction: modeling of reaction thermochemistry. *Bioresour. Technol.* 134, 331–340.
- Batidzirai, B., Mignot, A.P.R., Schakel, W.B., Junginger, H.M., Faaij, A.P.C., 2013. Biomass torrefaction technology: techno-economic status and future prospects. *Energy* 62, 196–214.
- Begum, S., Rasul, M.G., Akbar, D., Ramzan, N., 2013. Performance analysis of an integrated fixed bed gasifier model for different biomass feedstocks. *Energies* 6, 6508–6524.
- Bergman, P.C.A., Boersma, A.R., Zwart, R.W.R., Kiel, J.H.A., 2005a. Torrefaction for Biomass Co-firing in Existing Coal-Fired Power Stations. Energy Research Centre of The Netherlands. ECN Biomass Report ECN-C-05-013.
- Bergman, P.C.A., Boersma, A.R., Kiel, J.H.A., Prins, M.J., Ptasiński, K.J., Janssen, F.J.J.G., 2005b. Torrefaction for Entrained-Flow Gasification of Biomass. Energy Research Centre of The Netherlands. ECN Report ECN-C-05-067.
- 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.
- Bridgeman, T.G., Jones, J.M., Williams, A., Waldron, D.J., 2010. An investigation of the grindability of two torrefied energy crops. *Fuel* 89 (12), 3911–3918.
- Brockman, S.A., Roden, E.V., Hegeman, A.D., 2018. Van Krevelen diagram visualization of high resolution-mass spectrometry metabolomics data with OpenVanKrevelen. *Metabolomics* 14, 48.
- Carpenter, N.E., 2014. Biomass. In: *Chemistry of Sustainable Energy*, first ed. CRC Press, New York, USA, pp. 287–354.
- Channiwala, S.A., Parikh, P.P., 2002. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 81 (8), 1051–1063.
- Chen, W.-H., Wu, J.-S., 2009. An evaluation on rice husks and pulverized coal blends using a drop tube furnace and a thermogravimetric analyzer for application to a blast furnace. *Energy* 34 (10), 1458–1466.
- Chen, W.H., Cheng, W.Y., Lu, K.M., Huang, Y.P., 2011a. An evaluation on improvement of pulverized biomass property for solid fuel through torrefaction. *Appl. Energy* 88 (11), 3636–3644.
- Chen, W.H., Tu, Y.J., Sheen, H.K., 2011b. Disruption of sugarcane bagasse lignocellulosic structure by means of dilute sulphuric acid pre-treatment with microwave-assisted heating. *Appl. Energy* 88 (8), 2726–2734.
- Chen, Q., Zhou, J.S., Liu, B.J., Mei, Q.F., Luo, Z.Y., 2011. Influence of torrefaction pretreatment on biomass gasification technology. *Chin. Sci. Bull.* 56 (14), 1449–1456.
- Chen, W.-H., Lu, K.M., Tsai, C.M., 2012. An experimental analysis on property and structure variations of agricultural wastes undergoing torrefaction. *Appl. Energy* 100, 318–325.
- Chen, W.-H., Lu, K.M., Liu, S.H., Tsai, C.M., Lee, W.J., Lin, T.C., 2013. Biomass torrefaction characteristics in inert and oxidative atmospheres at various superficial velocities. *Bioresour. Technol.* 146, 152–160.
- Chen, W.H., Lu, K.M., Lee, W.J., Liu, S.H., Lin, T.C., 2014. Non-oxidative and oxidative torrefaction characterization and SEM observations of fibrous and ligneous biomass. *Appl. Energy* 114, 104–113.
- Chen, W.H., 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, D., Gao, A., Cen, K., Zhang, J., Cao, X., Ma, Z., 2018. Investigation of biomass torrefaction based on three major components: hemicellulose, cellulose, and lignin. *Energy Convers. Manag.* 169, 228–237.
- Cherubini, F., Strömman, A.H., 2011. Principles of biorefining. In: Pandley, A., Larroche, C., Ricke, S.C., Dussap, C.G., Gnansounou, E. (Eds.), *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels*, first ed. Elsevier Inc, Massachusetts, USA, pp. 3–24.
- Chew, J.J., Doshi, V., 2011. Recent advances in biomass pretreatment – torrefaction fundamentals and technology. *Renew. Sustain. Energy Rev.* 15 (8), 4212–4222.
- Cordero, T., Marquez, F., Rodríguez-Mirasol, J., Rodríguez, J.J., 2001. Predicting heating values of lignocellulosics and carbonaceous materials from proximate analysis. *Fuel* 80 (11), 1567–1571.
- Department of Energy and Climate Change, 2009. Digest of United Kingdom Energy Statistics. A National Statistics Publication. Department of Energy and Climate Change, 2009. [https://webarchive.nationalarchives.gov.uk/20130106092455/http://www.decc.gov.uk/assets/decc/statistics/publications/dukes/1\\_20100208131106\\_e\\_@dukes09.pdf](https://webarchive.nationalarchives.gov.uk/20130106092455/http://www.decc.gov.uk/assets/decc/statistics/publications/dukes/1_20100208131106_e_@dukes09.pdf). (Accessed 15 November 2018).
- Department of Energy and Climate Change, 2018. Digest of United Kingdom Energy Statistics. A National Statistics Publication. Department of Energy and Climate Change, 2018. [https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment\\_data/file/736148/DUKES\\_2018.pdf](https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/736148/DUKES_2018.pdf). (Accessed 15 November 2018).
- Deng, J., Wang, G.J., Kuang, J.H., Zhang, Y.L., Luo, Y.H., 2009. Pretreatment of agricultural residues for co-gasification via torrefaction. *J. Anal. Appl. Pyrol.* 86 (2), 331–337.
- Friedl, A., Padouvas, E., Rotter, H., Varma, K., 2005. Prediction of heating values of biomass fuel from elemental composition. *Anal. Chim. Acta* 554 (1–2), 191–198.
- Galletti, A.M.R., Antonetti, C., 2012. Biomass pretreatment: separation of cellulose, hemicellulose, and lignin – existing technologies and perspectives. In: Aresta, M., Dibenedetto, A., Dumeignil, F. (Eds.), *Biorefinery - from Biomass to Chemicals and Fuels*. de Gruyter, Göttingen, Berlin, pp. 101–121.
- Gil, M.V., García, R., Pevida, C., Rubiera, F., 2015. Grindability and combustion behavior of coal and torrefied biomass blends. *Bioresour. Technol.* 191, 205–212.
- Griffiths, P.R., de Haseth, J.A., 2007. *Fourier Transform Infrared Spectrometry*, second ed. John Wiley & Sons, New Jersey, USA.
- Hayes, D.J.M., 2013. Biomass composition and its relevance to biorefining. In: Triantafyllidis, K.S., Lappas, A.A., Stöcker, M. (Eds.), *The Role of Catalysis for the Sustainable Production of Bio-Fuels and Bio-Chemicals*, first ed. Elsevier Science, Oxford, UK, pp. 27–65.
- Hill, S.J., Grigsby, W.J., Hall, P.W., 2013. Chemical and cellulose crystallite changes in *Pinus radiata* during torrefaction. *Biomass Bioenergy* 56, 92–98.
- Jansen, A.H.H., Carbo, M.C., 2013. Report on Requirements of End Users on Densified and Torrefied Materials. FP7 EU Project Sector, 2013 December, 18 pgs, Deliverable No. D 4.1.
- Kalenga, P.M., Cukrowska, E., Tutu, H., Chimuka, L., 2011. Characterization of South African coal for metals, inorganic and organic sulfur compounds. *S. Afr. J. Chem.* 64, 254–262.
- Kim, Y.H., Jun, K.W., Joo, H., Han, C., 2009. A simulation study on gas-to-liquid (natural gas to Fischer–Tropsch synthetic fuel) process optimization. *Chem. Eng. J.* 155 (1–2), 427–432.
- Krewald, V., Retegan, M., Pantazis, D.A., 2015. Principles of natural photosynthesis. In: Tüysüz, H., Chan, C. (Eds.), *Solar Energy for Fuels*, Topics in Current Chemistry, 371. Springer, Cham, pp. 23–48.
- Kumar, A., Jones, D.D., Hanna, M.A., 2009. Thermochemical biomass gasification: a review of the current status of the technology. *Energies* 2, 556–581.
- Kumar, D., Kumar, D., 2018. *Sustainable Management of Coal Preparation*. Woodhead Publishing, New York, USA.
- Kuo, P.C., Wu, W., 2015. Design of co-gasification from coal and biomass combined heat and power generation system. *Energy Procedia* 75, 1120–1125.
- Lange, J.P., 2007. Lignocellulose conversion: an introduction to chemistry, process and economics. *Biofuels Bioprod. Biorefining* 1 (1), 39–48.
- Li, J., Zhang, X., Pawlak-Kruczek, H., Yang, W., Kruczek, P., Blasiak, W., 2014. Process simulation of co-firing torrefied biomass in a 220 MWe coal-fired power plant. *Energy Convers. Manag.* 84, 503–511.
- Mamvura, T.A., Muzenda, E., 2015. Effect of blending coal with torrefied biomass for possible application in energy production. *S. Afr. J. Chem. Eng.* 20 (2), 18–30.
- Mamvura, T.A., Pahla, G., Muzenda, E., 2018. Torrefaction of waste biomass for application in energy production in South Africa. *S. Afr. J. Chem. Eng.* 25, 1–12.
- Matjie, R.H., Li, Z., Ward, C.R., Bunt, J.R., Strydom, C.A., 2016. Determination of mineral matter and elemental composition of individual macerals in coals from Highveld mines. *J. S. Afr. Inst. Min. Metall.* 116, 169–180.
- 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.
- Merckel, R.D., Heydenrych, M.D., 2017. Mass-fraction of oxygen as a predictor of HHV of gaseous, liquid and solid fuels. *Energy Procedia* 142, 4124–4130.
- Miller, B.G., 2017. *Clean Coal Engineering Technology*, second ed. Butterworth-Heinemann, New York, USA.
- Molino, A., Chianese, S., Musmarra, D., 2016. Biomass gasification technology: the state of the art overview. *J. Energy Chem.* 25 (1), 10–25.
- Nachenius, R.W., Ronsse, F., Venderbosch, R.H., Prins, W., 2013. Biomass pyrolysis. In: Murzin, D.Y. (Ed.), *Chemical Engineering for Renewables Conversion*. Academic Press, Massachusetts, USA, pp. 75–139.
- Nanou, P., Carbo, M.C., Kiel, J.H.A., 2016. Detailed mapping of the mass and energy balance of a continuous biomass torrefaction plant. *Biomass Bioenergy* 89, 67–77.
- Neves, D., Thunman, H., Matos, A., Tarelho, L., Gomez-Barea, A., 2011. Characterization and prediction of biomass pyrolysis products. *Prog. Energy Combust. Sci.* 37 (5), 611–630.



- Nhuchhen, D.R., Basu, P., 2014. Experimental investigation of mildly pressurized torrefaction in air and nitrogen. *Energy Fuel* 28 (5), 3110–3121.
- Nikolic, G.S., 2011. In: Nikolic, G.S. (Ed.), *Fourier Transforms - New Analytical Approaches and FTIR Strategies*. InTech, Rijeka, Croatia.
- Nocquet, T., Dupont, C., Commandre, J.M., Grateau, M., Thiery, S., Salvador, S., 2014. Volatile species release during torrefaction of wood and its macromolecular constituents: Part 1 – experimental study. *Energy* 72, 180–187.
- Pahla, G., Mamvura, T.A., Ntuli, F., Muzenda, E., 2017. Energy densification of animal waste lignocellulose biomass and raw biomass. *S. Afr. J. Chem. Eng.* 24, 168–175.
- Pelaez-Samaniego, M.R., Yadama, V., Garcia-Perez, M., Lowell, E., McDonald, A.G., 2014. Effect of temperature during wood torrefaction on the formation of lignin liquid intermediates. *J. Anal. Appl. Pyrol.* 109, 222–233.
- Peng, J.H., Bi, X.T., Sokhansanj, S., Lim, C.J., 2013. Torrefaction and densification of different species of softwood residues. *Fuel* 111, 411–421.
- Pessaraki, M., 2016. *Handbook of Photosynthesis*, third ed. CRC Press, Florida, USA.
- Poling, B.E., Thomson, G.H., Friend, D.G., Rowley, R.L., Wilding, W.V., 2008. Physical and chemical data. In: Green, D.W., Perry, R.H. (Eds.), *Perry's Chemical Engineers' Handbook*, eighth ed. McGraw-Hill, New York, USA, pp. 2-1–2-157.
- Poudel, J., Ohm, T.I., Oh, S.C., 2015. A study on torrefaction of food waste. *Fuel* 140, 275–281.
- Prins, M.J., 2005. *Thermodynamic Analysis of Biomass Gasification and Torrefaction*. Technische Universiteit Eindhoven, Eindhoven.
- Prins, M.J., Ptasiński, K.J., Janssen, F.J.J.G., 2006a. More efficient biomass gasification via torrefaction. *Energy* 31 (15), 3458–3470.
- Prins, M.J., Ptasiński, K.J., Janssen, F.J.J.G., 2006b. Torrefaction of wood Part 2. Analysis of products. *J. Anal. Appl. Pyrol.* 77 (1), 35–40.
- Redissi, Y., Bouallou, C., 2013. Valorization of carbon dioxide by co-electrolysis of CO<sub>2</sub>/H<sub>2</sub>O at high temperature for syngas production. *Energy Procedia* 37, 6667–6678.
- Ren, S., Lei, H., Wang, L., Bu, Q., Chen, S., Wu, J., Julson, J., Ruan, R., 2013. The effects of torrefaction on compositions of bio-oil and syngas from biomass pyrolysis by microwave heating. *Bioresour. Technol.* 135, 659–664.
- Ribeiro, J.M.C., Godina, R., de Oliveira Matias, J.C., Nunes, L.J.R., 2018. Future perspectives of biomass torrefaction: review of the current state-of-the-art and research development. *Sustainability* 10, 2323, 17 pages.
- Rousset, P., Macebo, L., Commandré, J.M., Moreira, A., 2012. Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product. *J. Anal. Appl. Pyrol.* 96, 86–91.
- Saadon, S., Uemura, Y., Mansor, N., 2014. Torrefaction in the presence of oxygen and carbon dioxide: the effect on yield of oil palm kernel Shell. *Procedia Chem.* 9, 194–201.
- Sadaka, S., Negi, S., 2009. Improvements of biomass physical and thermochemical characteristics via torrefaction process. *Environ. Prog. Sustain. Energy* 28 (3), 427–434.
- Sakthivadivel, D., Iniyar, S., 2017. Combustion characteristics of biomass fuels in a fixed bed micro-gasifier cook oven. *J. Mech. Sci. Technol.* 31 (2), 995–1002.
- Sakthivadivel, D., Iniyar, S., 2018. Characterization, density and size effects of fuels in an advanced micro-gasifier stove. *Biofuels*.
- Sarkar, D.K., 2015. *Fuels and combustion. Thermal Power Plant – Design and Operation*. Elsevier, Oxford, UK, pp. 91–137.
- Senneca, O., 2017. Oxidation of carbon: what we know and what we still need to know. *Energy Procedia* 120, 62–74.
- Sikarwar, V.S., Zhao, M., Clough, P., Yao, J., Zhong, X., Memon, M.Z., Shah, N., Anthony, E.J., Fennell, P.S., 2016. An overview of advances in biomass gasification. *Energy Environ. Sci.* 9 (10), 2939–2977.
- Tsamba, A.J., Yang, W., Blasiak, W., 2006. Pyrolysis characteristics and global kinetics of coconut and cashew nut shells. *Fuel Process. Technol.* 87 (6), 523–530.
- Tumuluru, J.S., Sokhansanj, S., Hess, J.R., Wright, C.T., Boardman, R.D., 2010. *Biomass Torrefaction Process Review and Moving Bed Torrefaction System Model Development*. Idaho National Laboratory, Idaho Falls, USA. Report INL/EXT-10-19569.
- Tumuluru, J.S., Sokhansanj, S., Hess, J.R., Wright, C.T., Boardman, R.D., 2011. A review on biomass torrefaction process and product properties for energy applications. *Ind. Biotechnol.* 7 (5), 384–401.
- Tumuluru, J.S., Sokhansanj, S., Wright, C.T., Kremer, T., 2012. GC analysis of volatiles and other products from biomass torrefaction process. In: Mohd, M.A. (Ed.), *Advanced Gas Chromatography – Progress in Agricultural, Biomedical and Industrial Applications*. InTech, Rijeka, Croatia, pp. 211–234.
- Verhoeff, F., Adell i Arnuelos, A., Boersma, A.R., Pels, J.R., Lensselink, J., Kiel, J.H.A., Schukken, H., 2011. *Torrefaction Technology for the Production of Solid Bioenergy Carriers from Biomass and Waste*. Energy Research Centre of the Netherlands. ECN-E-11-039.
- 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. Pyrol.* 92 (1), 99–105.
- Wannapeera, J., Worasuwannarak, N., 2012. Upgrading of woody biomass by torrefaction under pressure. *J. Anal. Appl. Pyrol.* 96, 173–180.
- Wen, J.-L., Sun, S.-L., Yuan, T.-Q., Xu, F., Sun, R.-C., 2014. Understanding the chemical and structural transformations of lignin macromolecule during torrefaction. *Appl. Energy* 121, 1–9.
- Wu, K.T., Tsai, C.J., Chen, C.S., Chen, H.W., 2011. The characteristics of torrefied microalgae. *Appl. Energy* 100, 52–57.
- Wu, C., Williams, P.T., 2011. Nickel-based catalysts for tar reduction in biomass gasification. *Biofuels* 2 (4), 451–464.
- Yang, H., Yan, R., Chen, H., Zheng, C., Lee, D.H., Liang, D.T., 2006. In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. *Energy Fuel* 20 (1), 388–393.