Briquetting and Torrefaction of Agricultural Residues for Energy Production

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Abstract

Agricultural residues are a potential feedstock for renewable energy because they are abundant and CO_2 neutral. Due to their low energy density and heterogeneity, there are key challenges in handling, storage, transportation and utilization, therefore pre-treatment is required. The aim of this study was to evaluate a range of pre-treatment options of agricultural residues for energy applications. The effect of moisture content (7.14-16.94%), particle size (<2.36-<4.00mm), compression temperature (20-80^{o}C), pressure (100-250MPa), and type of agricultural residues (corn cob and bean straw) on briquette properties i.e. density, impact resistant and compressive strength was studied. Torrefaction of corn cob and bean straw were also investigated over a range of temperatures (200-300^{o}C) and holding times (0-90 min) to study the impact of operating conditions on yields and properties of torrefaction products (char, liquid and gas).

The results showed that density, impact resistance, and compressive strength significantly increased with increasing compacting temperature (20-80^{o}C) and compacting pressure (100-250MPa) but decreased with increasing moisture content and particle size. Briquettes that satisfied the German Standard DIN 51731(density >1000kg m^{-3}) and European Standard Committee CEN/TC 335 (durability >95%) standards for solid fuels were obtained with particle size <4 mm, compression temperature of 80^{o}C and (i) moisture content of 10-12% with pressure of 100-250MPa for bean straw and (ii) low moisture content (<10 %) and high pressure (200-250 MPa) for maize cob. Briquettes derived from a bean straw:maize cob blend had high density and strength at low pressure and temperature compared to those derived from maize cobs due to enhanced bonding via mechanical interlocking, thereby reducing the costs of production. Torrefied solid products obtained at 300^{o}C had properties comparable to coal with energy yields of 74.84-79.47% for maize cob and 90.08-92.93% for bean straw. The gaseous product (3.25-17.41% yield) was predominantly CO_2 due to decomposition of hemicellulose within the temperature range studied.

Briquettes that met the above certified standards were studied for pyrolysis and combustion in a fixed-bed reactor. The effects of pyrolysis temperature (410-650^{o}C), heating rate (10-20^{o}C min^{-1}), carrier gas flow rate (40-60 cm^{3} min^{-1}) and briquetting conditions (temperature (20-80^{o}C), pressure (150-200MPa) and blend ratio) on the yields and properties of pyrolysis products from maize cob and bean straw briquettes were investigated. It was found that bio-oil and gas yields increased while, char yields from both biomass feedstocks decreased with increasing pyrolysis temperature due to an increase in decomposition of lignocellulosic components and secondary decomposition of primary char. Briquetting conditions, heating rate and carrier gas flow rate had negligible effect on product yields and properties. Increasing maize cob content in briquettes resulted in an increase in the yield of bio-oil from 48 to 51% at the expense of char yield, due to the low ash and fixed carbon content of the maize cob.

Combustion and pyrolysis of raw/untreated and torrefied maize cob and bean straw in a thermogravimetric analyzer occurred through moisture release, devolatilization and char degradation. The kinetic study of raw maize cob and bean straw combustion/pyrolysis revealed that the average activation energies of maize cob and bean straw were 202.26 kJ mol^{-1} and 165.64 kJ mol^{-1} for combustion and 214.15 kJ mol^{-1} and 252.09 kJ mol^{-1} for pyrolysis. Modelled data of pyrolysis and combustion of bean straw and maize cob using the obtained kinetic parameters agreed well with the experimental data, which will be useful in reactor design for energy generation via pyrolysis and combustion from agricultural residues.

The findings of this study could help in promoting the use of agricultural residues for energy generation which will potentially lessen the impacts of global warming, diversify and decentralize the energy supply through the improved management/utilisation of agricultural wastes. Briquette production, torrefaction and pyrolysis could provide opportunities for the local population to increase employment and income in rural areas. This study will also provide a reference for future research on densification and utilisation of agricultural residues for energy generation.

Dedication

This work is dedicated to my family members.

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List of abbreviations/symbols

Al: Aluminium

ANOVA: Analysis of Variance

As: Arsenic

B: Boron

Ba: Barium

BET: Brunauer-Emmett-Teller

C: Carbon

Ca: Calcium

Ce: Cerium

Co: Cobalt

CO: Carbonmonoxide

CO_2: Carbon dioxide

Cpd: Specific heat capcity of dried feedstock

C_{pw}: Specific heat capacity of water

Cr: Chromium

CS: Compressive strength

Cu: Copper

DSC: Differential scanning calorimetry

DTG: Differential thermogravimetic

E: Energy required for torrefaction

E_c: Energy required to torrefy dried feedstock

E_d: Energy required to dry feedstock

ERA: Electricity Regulatory Authority

Fe: Iron

FTIR: Fourier transform infra-red radiation

Ga: Gallium

GC: Gas chromatography

GC-MS: Gas chromatography mass spectrometry

H: Hydrogen

HHV: Higher heating value

ICP: Inductively coupled plasma

IEA: Interntional Energy Agency

K: Potassium

L_v: Latent heat of vaporization of water

m_d: Mass of dried feedstock

MEMD: Ministry of Energy and Mineral Development

Mg: Magnesium

m_w: Mass of moisture in feedstock

Mn: Manganese

Mo: Molybdenum

N: Nitrogen

Na: Sodium

Ni: Nickel

NO_x: Oxides of nitrogen

O: Oxygen

P: Phosphorus

Pb: Lead

QMS: Quadrupole mass spectrometer

Rb: Rubidium

S: Sulphur

Sc: Scandium

SEM: Scanning electron microscopy

Sn: Tin

SO_2: Sulphur dioxide

SO_x: Oxides of Sulphur

Sr: Strontium

TGA: Thermogravimetric analysis

TG-DSC: Thermogravimetric-differential scanning calorimetry

Ti: Titanium

UBOS: Uganda Bureau of Statistics

V: Vanadium

Zn: Zinc

η: Effeciency of torrefaction sustem

Chapter 1: Introduction

1.1 Background

Energy is a pre-requisite for social and economic transformation. According to the (International Energy Agency (IEA), 2018a), the global energy demand and carbon dioxide (CO_2) emissions increased by 2.1% and 1.4% respectively in 2017. Therefore, energy shortages, climate change, and energy security still remain priority issues to be addressed in every nation (Long et al., 2013). Fossil fuel is still the predominant global energy source (Fig 1.1).

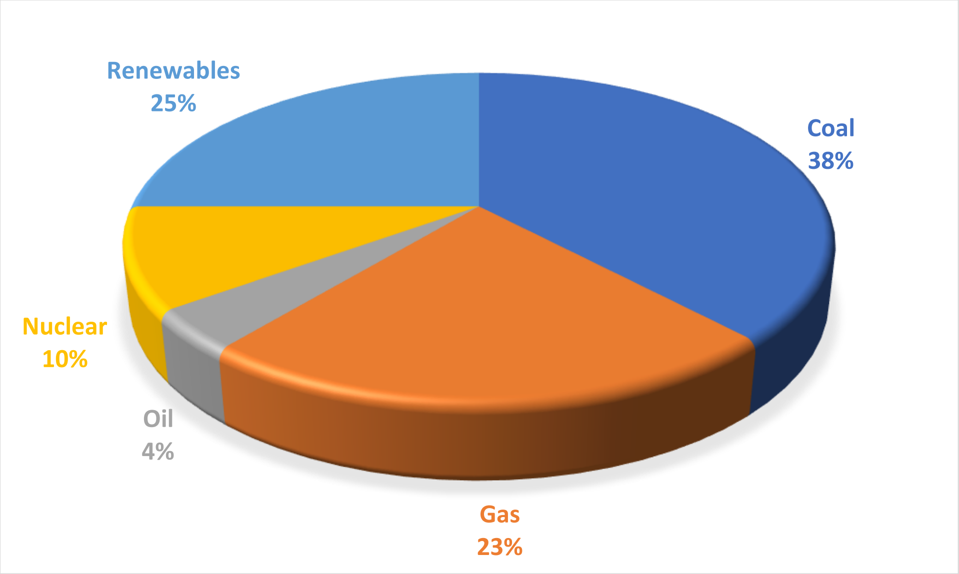


Fig 1.1: Global electricity generation in 2017 from different fuel sources (IEA, 2018)

The use of fossil fuel is very much associated with high greenhouse gas emissions, which is implicated for global warming. Renewable energy resources (hydro, geothermal, solar, wind and biomass) are being promoted to provide alternative energy sources and help solve the problems of global warming (Okello et al., 2013a). By 2017, the global electricity generation from renewables was second to coal (Fig 1.1). Although hydropower still remains the main source of electricity from renewables, i.e. with 65% of the overall electricity output from renewables (IEA, 2018), biomass is considered as a renewable energy source that can significantly help in diversifying fuels across a number of different countries where feedstocks are abundant (Suhartini et al., 2011). The use of biomass provides employment opportunities (Karkania et al., 2012) and results in reduced emissions of sulphur dioxide (SO_2) and oxides of nitrogen (NO_x) (Roy and Corscadden, 2012, Jahirul et al., 2012). However, biomass use requires high capital investment and is seasonal (Karkania et al., 2012).

Bioenergy derived from biomass materials such as agricultural, human, food, and animal residues and biodegradable industrial and municipal waste contributes to 10% of the total global energy consumption (World Energy Council, 2016) and it is estimated that its contribution will reach 12.4% by 2023 (International Energy Agency (IEA), 2018b). In developing countries, it is the major energy source for cooking and heating. For instance, the contribution of biomass to total energy consumption is about 80% in sub-Saharan Africa, (Okello et al., 2013a). Energy in biomass can be extracted by a number of routes: biochemical (anaerobic digestion, fermentation and transesterification) and thermochemical (pyrolysis, gasification and combustion) methods (Nhuchhen et al., 2014, Liu et al., 2017). Thermochemical processes are preferred over biological methods because of their potential to use a wide range of feedstock (Choudhury et al., 2014, Czajczyńska et al., 2017), short reaction times, potential to form multiple useful products and high conversion efficiency (Raheem et al., 2015, Azizi et al., 2018).

1.2 Energy situation in Uganda

Uganda has a population of 34.6 million people (with a population growth rate of 3.0% per annum) as of 2014, however, up to 52% of these still depend on paraffin (locally made candles) for lighting while only 20.4% of households use electricity from all forms i.e. from grid and others (UBOS, 2016). Therefore, a high percentage of Ugandans still have limited access to adequate, affordable, reliable, and safe energy services, which in turn has negative impacts on the socio-economic development of the nation and the standards of living. Currently, electricity is generated from hydro (77%), bagasse cogeneration (11%), thermal (11%) and solar 1% (ERA, 2018a). The government of Uganda is fully committed to expanding and strengthening the existing power distribution and transmission infrastructures, and supporting investments in renewable resources

(ERA, 2018a, MEMD, 2007). As the result, a number of companies such as Kakira Sugar Works Ltd (combined heat and power (cogeneration)), Kinyara Sugar Works Ltd, (ERA, 2018b), Green Heat (U) Ltd (biogas and briquetting technologies), and Kampala Jellitone Suppliers Ltd (biomass briquetting) (Okello et al., 2013a) are now promoting bioenergy projects. Despite the above efforts from the government, 71.2% and 22.9% of Ugandans still depend on firewood and charcoal respectively for cooking (UBOS, 2016) which has caused an in increased deforestation rate with associated effects such as climatic change and soil degradation (Josephat, 2018). It was reported that, Uganda is currently losing forest cover at a rate of 200,000 hectares annually and at this rate of deforestation, the country may not have any forest reserve in the next 40 years (Josephat, 2018). Approximately 1.2 million tons of agricultural residues (maize cobs, bean trash, banana peels, sweet potato peels, etc.) are wasted annually in the country. These residues are widely distributed throughout the country (Fig 1.2) which makes them suitable for decentralised energy production. It was also estimated that briquetting of these residues together with an estimated 1500 tons of municipal solid wastes produced daily in Kampala (the county's capital city) could replace about 6% and 50% of wood consumption and trade in charcoal respectively (Ferguson, 2012).

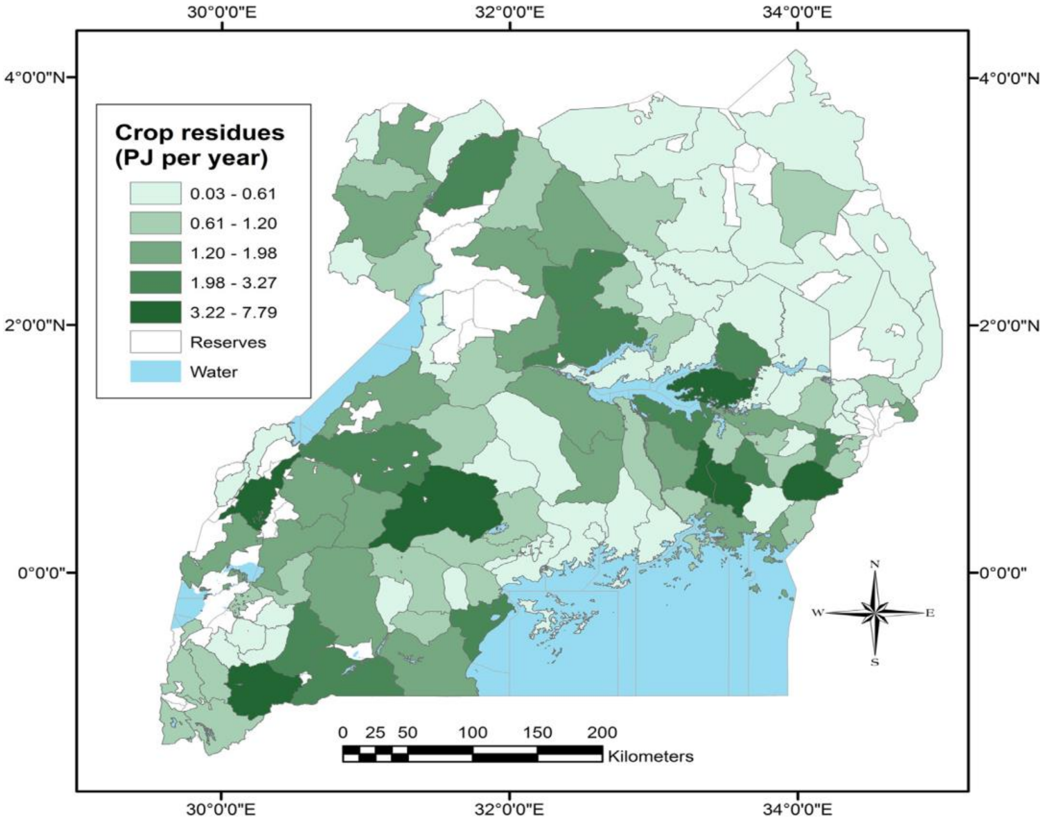


Fig 1.2: Map of Uganda showing the distribution of crops residue energy potential (Okello et al., 2013b)

1.3 Problem statement

Approximately 7020 kilotonnes of agricultural residues such as maize cobs, maize stalk, bean residues, and sweet potato vines and peels are generated annually in Uganda (Okello et al., 2013b). They are considered a waste and are either burnt in open air (without heat recovery) or dumped to decompose in uncontrollable ways, which contribute to increased greenhouse gas emissions (Mwampamba et al., 2013). With energy content of around 16-18 MJ kg^{-1}, these residues could provide alternative feedstocks for energy production via thermochemical processes. However, some undesirable properties such as heterogeneity (shape, size and properties), low bulk density, fibrous nature, hygroscopic nature, high moisture content and high oxygen content make the use of biomass for energy generation challenging (Nhuchhen et al., 2014). Low bulk density increases biomass costs of transportation, storage and handling of biomass, meanwhile, the fibrous nature increases cost of biomass grinding and causes inconsistency in particle size which reduces flowability. The highly hygroscopic nature leads to moisture absorption and high moisture reduces combustion/gasification temperature which increases tar yield and reduces calorific value. Furthermore, high moisture causes natural decomposition of biomass which changes the physical and chemical properties and lowers the quality of biomass (Nhuchhen et al., 2014). Pre-treatment methods which have been grouped as chemical (such as use of acid, bases and ionic liquid), biological, physical (e.g. milling and briquetting) and thermochemical (e.g. torrefaction, steam explosion, microwave radiation, liquid hot water) methods can be used to improve biomass quality. However, there is environmental concern arising from the use of chemicals (such as sulphuric acid and hydrochloric acids) during the chemical pre-treatment process due to their highly corrosive nature (Hosseini Koupaie et al., 2018). Biological pre-treatment requires a long time 10-14 days which makes this method unsuitable for industrial applications (Agbor et al., 2011). On the other hand, physical (briquetting) and thermochemical (torrefaction) methods are gaining interest because of their potential to enhance biomass energy density and homogeneity. The demand for densified products is on the rise e.g. an increase in demand of wood pellets from 19.5 - 28.0 million tones was registered from 2012-2015 (WPAC, 2017). Europe and North America are the main producers and consumers of wood pellets (Miranda et al., 2015). Briquettes and pellets offer the same benefits e.g. increasing energy density of the fuel, reducing costs of transport and storage together with minimizing issues associated with waste management (Roy and Corscadden, 2012). Meanwhile torrefaction is gaining interest because of its potential to improve biomass grindability, heating value and carbon content and reduce oxygen content (D. Chen et al., 2015). However, there is limited information available about conditions for briquetting and torrefaction for maize cob and bean straw residues. Furthermore, the potential applications of torrefied or briquetted maize cob and bean straw for pyrolysis and combustion have not been assessed.

1.4 Aim and objectives

To study the effect of pretreatment of agricultural residues on thermochemical behaviors. The objectives of the study were:

1. To investigate the effect of briquetting operating parameters on properties of briquettes derived from maize cob and bean straw.
2. To study the effect of torrefaction operating conditions on torrefaction product yields and properties of maize cob and bean straw.
3. To study the effect of pre-treatment conditions on the thermochemical conversion i.e. the case of briquettes.
4. To study the combustion behaviour of torrefied materials using thermogravimetric analysis.
5. To develop pyrolysis and combustion kinetic models for maize cob and bean straw.

1.5 Thesis structure

Chapter 1 provides an overview of bio-energy from biomass. **Chapter 2: Literature review:** In this chapter biomass pre-treatment methods (briquetting and torrefaction) and biomass conversion processes (combustion and pyrolysis) are reviewed. **Chapter 3: Biomass pre-treatment:** This chapter contains pre-treatment approaches: briquetting and torrefaction of maize cob and bean straw agricultural residues. Effects of torrefaction conditions: temperature and holding time on product yield and properties. **Chapter 4: Biomass conversion:** This chapter looked at the thermochemical conversions (pyrolysis and combustion) of maize cob and bean straw briquettes in a fixed bed reactor. The effect of pyrolysis conditions (temperature, heating rate and carrier gas flowrate) on yields and properties of pyrolysis products were discussed. The combustion characteristics of maize cob briquette were also assessed. Kinetic studies of combustion and pyrolysis of maize cobs and bean straw and combustion of terrified bean straw and maize cob were investigated using a thermogravimetric analyzer. **Chapter 5: General discussion:** Implementation and limitations to this study and the relevance of the findings to industry, society and the research community are discussed. **Chapter 6: Conclusions and recommendations for future work.**

Chapter 2: Literature Review

This chapter contains a review of biomass pretreatment approaches (briquetting and torrefaction) and biomass conversion pathways (pyrolysis and combustion). Effects of briquetting conditions on briquette quality, torrefaction technique and effects of torrefaction conditions are also presented. Furthermore, factors affecting combustion characteristic of fuels together with the effect of pyrolysis conditions on yields and properties of pyrolysis products (char, liquid and gas) are discussed.

2.1 Energy from biomass

Globally, bioenergy contributes 14% out of 18% of the global energy supply from renewables and contributes 10% of global energy consumption (World Energy Council, 2016). Biofuels i.e. solid, liquid and gas are obtained from biomass materials which are generally categorized based on their origins as 1st, 2nd or 3rd generation (Azizi et al., 2018). The 1st generation biofuels are derived from food crops: oilseeds, starch and sugar crops e.g. maize, oilseed rape, sugar cane, wheat, soybean, etc. First generation biofuels have been commercialized, however, they are considered unsustainable due to the 'food versus fuel' conflict arising from their utilization. Second generation biofuels are derived from wastes and lignocellulosic materials and are therefore generally not associated with the food versus fuel conflict. Third generation biofuels are derived from algae and genetically modified organisms (e.g. yeast, microalgae and fungi). However, large scale production of algae remains a challenge (Azizi et al., 2018). Biomass can be converted to solid, liquid, and gaseous fuels by bio-chemical (biological) or thermo-chemical (Okello et al., 2013a) (Fig 2.1) routes. The choice of the conversion route depends on biomass type, its availability and the form of energy desired (Goyal et al., 2008).

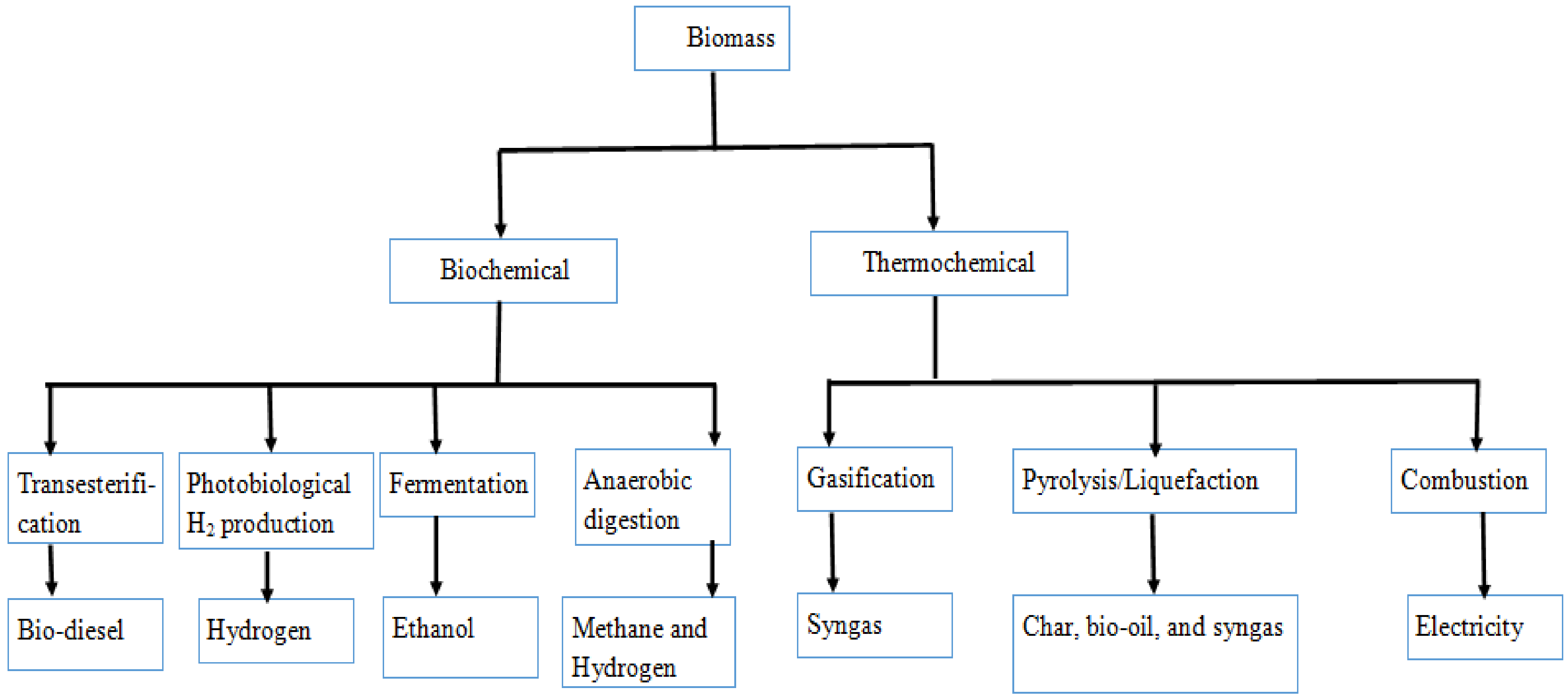


Fig 2.1: Pathways of biomass conversion (Azizi et al., 2018)

Biochemical processes convert biomass into high value biofuel by use of enzymes and micro-organisms (Sharma et al., 2015). Thermo-chemical processes involve thermal decomposition of biomass in the presence of air or a limited amount of air or inert atmosphere or steam. Compared to the bio-chemical processes, thermochemical processes require lower reaction time and produce multiple products (Bridgwater, 2012, Chew and Doshi, 2011). Furthermore, thermochemical processes have higher conversion efficiency and lower costs of production compared to biochemical processes (Azizi et al., 2018). Therefore, this study focuses on the thermochemical process.

2.2 Biomass pre-treatment methods

Biomass utilization for energy production is limited by several undesirable properties (Table 2.1) which requires pre-treatment. Pre-treatment causes some variations in the physical and chemical properties thereby causing variations in biomass behavior during the thermochemical and biological conversion processes (Bhutto et al., 2017). Biomass pre-treatment methods currently under study are categorized as mechanical, biological, chemical and thermal methods (Nhuchhen et al., 2014, Hosseini Koupaie et al., 2018).

(a) **Chemical/hydrolysis pre-treatment:** Chemical pre-treatment aims at removing hemicellulose and lignin to improve the biodegradability of cellulose (Zheng et al., 2009). Chemicals such as bases, ionic liquids and acids are used to change the physical and chemical properties of biomass (Nhuchhen et al., 2014, Hosseini Koupaie et al., 2018). However, the use of this method is associated with very high costs and there is also an environmental concern arising from the significant amount of residual chemicals which requires safe handling as well as disposal (Hosseini Koupaie et al., 2018).

(b) **Biological pre-treatment:** Structure and chemical composition of biomass are modified by use of microorganisms. This method uses small amount of chemical (compared to chemical pre-treatment method) and consumes less energy (compared to physical and thermochemical pre-treatment methods) (Hosseini Koupaie et al., 2018, Tabil et al., 2011). Biological methods require long reaction time (10-14 days) (Agbor et al., 2011), controlled environment and large space which makes them costly (Nhuchhen et al., 2014, Bhutto et al., 2017), and therefore unsuitable for industrial applications (Agbor et al., 2011).

Table 2.1: Disadvantages of the use of raw biomass materials for energy generation (Bach and Skreiberg, 2016, Barta-Rajnai et al., 2017, Werther et al., 2000, Nhuchhen et al., 2014)

Biomass properties	Effect
High moisture	• Lower HHV, • Lower durability in storage due to biological degradation • Increased transport and storage costs • Condensing water in flue gas increases corrosion potential. • Lower conversion efficiency
Low energy density	• Increased transport and storage costs • Requires in-feed system with high capacity
Low grindability/fibrous nature	• Increases production costs and reduces plant capacity. • Leads to inconsistency in particle size thereby affecting flow characteristics.
Highly hygroscopic in nature	• High moisture absorption capacity during transport and storage • Low durability in storage due to biological degradation
High oxygen content	• Lower HHV, energy density and thermal stability
High alkali metal content	• Increases ash related problems
Heterogeneity	• Causes variation in conversion

(c) **Mechanical/physical pre-treatment:** Includes grinding and briquetting which cause physical changes in the biomass (Nhuchhen et al., 2014). Mechanical pre-treatment uses physical forces to disrupt the structure of biomass to reduce the particle size (Hosseini Koupaie et al., 2018) and /or produce uniform size/shape particles in the form of briquettes/pellets. Physical pre-treatment does not enhance the hydrophobicity of biomass; however, milling increases the surface area of particles. Briquetting improves homogeneity (in terms of shape size and moisture), atomization of biomass fed into energy conversion systems and bulk density which reduces storage and transport costs (Nhuchhen et al., 2014, Porteiro et al., 2010). However, this pre-treatment method is energy intensive (Bhutto et al., 2017).

(d) Thermal pre-treatment: Includes techniques such as torrefaction, steam explosion, liquid hot water pre-treatment, ultrasound and microwave irrradiation (Liu et al., 2017). Heat energy is used to break hydrogen bonds in the crystalline structure of lignocellulosic biomass (Hosseini Koupaie et al., 2018). Thermal methods have the advantages of increasing biomass carbon content, heating value and resistance to moisture absorption (Liu et al., 2017). However, high energy requirement is the main drawback to thermal pretreatment methods (Hosseini Koupaie et al., 2018). In this study physical (briquetting) and thermal (torrefaction) techniques were analysed due to their potential to reduce the costs of biomass transport and storage (by increasing bulk/energy density), improving durability in terms of storage (by reducing moisture absorption capacity), and improving the efficiency of the biomass conversion system (by improving homogeneity, increasing carbon content and heating value). These factors may be key to improving sustainability in bioenergy supply since biomass especially agricultural residues are seasonal.

2.2.1 Briquettes

A briquette is a solid combustible material which is formed through densification of carbonaceous substances. Products from densification are classified as pellets and briquettes with bulk density in the range of 450 – 800 kg m^{-3} (Okello et al., 2013a; Kaliyan and Vance Morey, 2009). Briquettes differ from pellets according to their sizes, according to standards (Austrian: ONORM M 7135; German: DIN 51731), pellet diameter (D) is 4.0 - 10.0 mm its length is less than 5D respectively (Obernberger and Thek, 2004) while briquette length and diameter are in the range of 16 - 400 mm and 10 - 200 mm (Chaney, 2010, A Demirbaş, 1999, Amaya et al., 2007, Kaliyan and Morey, 2010a, Haykiri-Acma et al., 2013). However, according to other standards (Italian: CTI -R 04/05; European standard committee CEN/TC 335; Swedish SS 187120) the diameter of pellets can be up to ≤ 25 mm. Compared to pellets, briquettes are more eco-friendly and have lower production costs (Stolarski et al., 2013). Briquetting technologies have not been successful in Africa largely due to increased costs involved and limited awareness of the sustainability of the process (Emerhi, 2011). Briquetting improves energy density, handling characteristics, and reduces transport and storage costs (Oladeji, 2015) in addition provides employment opportunities, reduce deforestation, and minimizes health problems caused by pollutants emitted during handling and/or combustion of solid fuels (Danjuma et al., 2013).

2.2.1.1 Briquette production

Briquettes can be made from a wide range of biomass materials such as agricultural residues, wood waste, municipal solid wastes and from biomass derived materials e.g. charcoal and products of torrefaction. Generally, briquette making involves feedstock drying, feedstock preparation, binding (briquetting), and drying/cooling. These steps are discussed in the following sub-sections.

2.2.1.1.1 Feedstock drying

Drying is an important stage in briquette production to produce non-carbonized briquettes. It was reported (Ferguson, 2012) that the feedstock to be compacted has to be dried to a moisture content of about 13%. However, the maximum moisture content required for production of a stable briquette varies from one feedstock to another. e.g. wheat straw and waste paper have respectively 18.0 % and 22.0 % as their optimal moisture content (A Demirbaş, 1999), while olive refuse has 7.5 % (Yaman et al., 2000). Initial moisture content in the feedstock plays a key role in lignin plasticization (Križan et al., 2015) and also determines the energy requirement for briquetting (Antwi-Boasiako and Acheampong, 2016) with a potential significant impact on briquette quality and production costs. Moisture also acts as a lubricant for reducing friction between particles during the compaction process (Huang et al., 2017, Kaliyan and Vance Morey, 2009). However, if the moisture content is too high (>25 %), it can prevent particles from being completely flattened due to the incompressible nature of water. This limits the release of natural binders (Kaliyan and Vance Morey, 2009), leading to less stable and less dense briquettes. Sun drying is the predominant method used in Uganda for drying feedstocks and/or briquettes (Ferguson, 2012), however, solar or heated fans can also be used (Ngusale et al., 2014).

2.2.1.1.2 Feedstock preparation

The stability of a briquette is determined by particle size of the biomass (Chaney, 2010). Raw biomass wastes like sawdust and rice husks already in the form of small particles can just be sieved and briquetted directly. In contrast, heterogeneous raw materials such as banana peels, sweet potato peels, and maize cobs require powdering before briquetting either manually or by using a mechanized milling machine (Ferguson, 2012). Size reduction increases the surface area of contact of the particles thus improving binding as well as the mechanical properties of briquettes. Small particles have more contact points and their contact areas are more exposed (Ahmed et al., 2014, Tumuluru et al., 2011). However, compacting very fine particles to form pellets/briquettes is difficult since they can cause jamming of the briquetting machine (Tumuluru et al., 2011, Ahmed et al., 2014). Particle size above 6 mm together with 13-15% of small particles in powdered form is recommended for making briquettes because they result in better interlocking of particles thereby improving durability (Ahmed et al., 2014, Tumuluru et al., 2011). In this case the inter-particle bonding is formed with minimal space between particles (Kaliyan and Vance Morey, 2009). However, depending on the nature of feedstock, particle size for producing briquettes can vary from 0.1 to 6 mm (Yaman et al., 2000, Chin and Siddiqui, 2000, Kers et al., 2010, Mohammed and Olugbade, 2015), from 2 mm for pine (Križan, 2007), to between 0.85 and 5.6 mm for maize residues (Kaliyan and Morey, 2010b, Mani et al., 2006).

Different biomass materials have different composition (lignin, starch, protein contents, etc.) which result in varying densification characteristics. Materials with high lignin, starch or protein contents are easy to pelletize/briquette (Muazu and Stegemann, 2015). Different biomass materials can be blended to improve the combustibility characteristics and durability of briquettes (Chen et al., 2009, Oladeji, 2015). Addition of 15% of linen fiber (of length <0.2mm to 50mm) significantly increased impact resistance (measured by impact resistance index) of sawdust pellet from 83.33 to 200 (Kong et al., 2013). Increasing the ratio of palm oil mill sludge in a rice husk: palm oil mill sludge blend from 1:10 to 1:1 increased density and durability of briquettes from 333.46-498.55 kg m^{-3} and 76.19-99.61% respectively (Obi and Okongwu, 2016).

A range of binders such as molasses, cassava flour, clay, wheat flour, press mud and distillers dry grain have been used in briquetting (Ferguson, 2012, Wakchaure and Mani, 2011). Binders act as lubricants thus minimizing mold wear during compaction. They form gel with water which helps to improve the cohesion characteristics and mechanical strength of briquettes (Tumuluru et al., 2011). Binders are generally applied to aid agglomeration when the particles have weak cohesive forces (Shankar et al., 2012) with a desire to use materials with low environmental impact and cost (Kaliyan and Vance Morey, 2009).

The effect of binders on the quality of briquettes such as density and strength depend on the type and nature of the feedstock. According to European Standard Committee CEN/TC 335 and ONORM M 7135, concentration of binder in a briquetted product should not exceed 2% (García-Maraver et al., 2011). Chin and Siddiqui, (2000) reported that increasing binder (molasses and starch) concentration from 5 to 40 % increased density of briquettes obtained from sawdust, peanut shells, coconut fibre, and palm fibre. Yank et al., (2016) reported that binders from cassava water waste, okra stem gam, and rice dust had no significant impact on HHV of briquettes from rice husk. The changing trend in compressive strength of rice husk char pellet with increasing binder concentration from 5-20 %, show that maximum compressive strength is attained by adding 10-15% NaOH, $Ca(OH)_2$ and lignin while, starch had no impact (Q. Hu et al., 2015).

2.2.1.1.3 Binding

Binding is the process of sticking together the biomass material (Ferguson, 2012). The physical forces responsible for holding the particles of a briquette together determine the strength and durability of the briquette. The forces that can bond the particles are solid bridges, forces of attraction between solid particles, mechanical interlocking bonds, adhesion and cohesion forces, and interfacial forces and capillary pressure (Matúš et al., 2015, Kaliyan and Vance Morey, 2009, Oladeji, 2015). The main bonding mechanism varies from one feedstock to another depending on the properties of the biomass material. According to Mitchual et al., (2013), sawdust briquettes mainly bond through mechanical interlocking. However, according to Kaliyan and Morey, (2010a), particles of corn stover and switchgrass briquettes/pellets bond mainly by soild brigdes resulting from natural binders (mainly lignin and protein). After size reduction, feedstocks may be pre-heated. Preheating activates natural binders (lignin, protein, and starch) in biomass and also causes plastic deformation of the feedstock (Kaliyan and Vance Morey, 2009). Natural binders such as lignin and hemicellulose can only undergo plastic deformation during compression at temperatures near the glass transition tempearture. Plastic deformation aids formation of permanent bonds between particles. Natural binders can also be squeezed out of particles at temperatures near the glass transistion temperature and improve particle bonding through formation of solid bridges on cooling (Kaliyan and Morey, 2010b). Feedstock heating minimizes wear and tear of the briquetting machine. However, compacting temperature should be below the minimum temperature (i.e. about 200 ^{o}C) required for the onset of biomass decomposition (Adapa et al., 2009). Application of high pressure and/or temperature during densification results in diffusion of molecules at the point of contact from one particle to another, thus forming solid bridges (Chou et al., 2009). Solid bridges also come into play as binders cool and harden, and as melted components solidify. During compression, bulky particles interlock which is responsible for formation of the interlocking bonds. The moisture between particles under compression is responsible for the formation of the cohesion force between particles. Short range forces such as molecular (van der Waals' forces), electrostatic, and valence forces result in particles which adhere to each other (Kaliyan and Vance Morey, 2009) increasing density, durability and impact resistance.

2.2.1.1.4 Cooling

Cooling is an important step in the briquetting process which determines the density, durability (Karkania et al., 2012) and consequently the combustion rate. Briquettes can come out of the mold when they are hot and cool down naturally, which is necessary for lignin to form solid bridges. Cooling is essential because briquettes can crack due to stress between layers at different temperatures. Cooling can increase briquette strength (Adzic and Savic, 2013). Unlike drying, cooling does not require additional energy (Karkania et al., 2012).

2.2.1.2 Properties of briquettes

Physical/mechanical and chemical properties as well as calorific/heat value are essential properties of briquettes for transport, storage and thermo-chemical applications. The chemical properties are proximate properties (moisture content, fixed carbon content, volatile matter content, and ash content), and ultimate properties (carbon, hydrogen, oxygen, sulphur, and nitrogen content) (Tusingwire, 2013). Both heating value and chemical properties are feedstock dependent and do not change with briquetting conditions. A study conducted by Suhartini et al., (2011), shows that compacting pressure has no significant impact on ash content of spent bleaching earth briquettes. This is in agreement with findings from Wakchaure and Mani, (2011), who analyzed briquettes from mustard stalk, mixed wastes of tree leaves and grass, and wood wastes. Faizal et al., (2010) and Lela et al., (2016) reported that variation in compacting pressure does not cause any significant variation in the HHV of briquettes from palm residues (empty branch fruit and mesocarp fibre) and a cardboard and sawdust blend respectively.

The mechanical properties are density, compressive strength, impact resistance and durability. There are no published national/international standards for briquettes, however literature shows some limiting values identified by different authors, whereas other authors have made references to pellets standards which are summarized in Table 2.2. The limiting values define the recommended range of values of briquette properties for use, transportation and storage.

Table 2.2: Limiting values of briquette properties (Miranda et al., 2015, Obernberger and Thek, 2004, Faizal et al., 2010, Križan, 2007, Deepak and Jnanesh, 2015, Haykiri-Acma et al., 2013, Alakangas et al., 2006, García-Maraver et al., 2011)

Properties	Limiting value
Moisture content (%)	<20
Ash content (%)	<10
Volatile mater content (%)	70-86
N (%) (For biomass which has been chemically treated)	< 3 .0
S (%) (For biomass which has been chemically treated or when additives containing sulphur have been used)	< 0.2
Density (kg m^{-3})	1000-1400
Durability (%)	>90.0
Fine content (% ≤ 3.15 mm)	< 2.0
Compressive strength (MPa)	>2.56
Impact resistance (%)	>80.0
Resistance to water penetration (min)	>20
Heating value (MJ kg^{-1})	>17.5

High density implies, high energy/volume ratio and therefore a briquette with high density (1-1.4 g cm^{-3} (Križan, 2007)) is desired during transportation and storage (A Demirbaş, 1999). Compressive strength is the maximum load that a briquette can withstand before it breaks and is a measure of durability (Hamidul Islam et al., 2014). It is used to estimate the compressive stress resulting from the weight of the top briquettes on lower briquettes during storage, transport and handling (Yank et al., 2016, Matúš et al., 2015, Garcia-Maraver et al., 2015). Durability defines the tendency of a briquette or pellet to produce dust or break when it is subjected to a destructive force (Zainuddin et al., 2014) and is a measure of the quality of briquettes. A durability test simulates the mechanical handling of briquettes and predicts the possible fine particles produced (Kaliyan and Vance Morey, 2009) as dusts have particular health related issues (Karunanithy et al., 2012). In addition, dust causes non uniformity in the combustion process (Temmerman et al., 2006). Fine content >5% is unacceptable as it limits storage space (Zainuddin et al., 2014). Impact resistance has been used in previous studies (Chin Yee Sing and M. Shiraz Aris, 2013, Ndindeng et al., 2015) to estimate durability of briquettes. Impact resistance is used to simulate the force briquettes encounter when they are emptied from trucks onto the ground and as such is also an indicator of a mechanical strength. It should be ≥80% for better handling and transportation (Haykiri-Acma et al., 2013). Briquettes with high density and mechanical strength (durability, impact resistance and compressive strength) are desirable during transportation, storage and handling. Density and strength of briquettes varies with biomass material with changes in briquetting parameters such as temperature, moisture content (Kaliyan and Morey, 2010b), particle size and pressure (Zhang and Guo, 2014, Demirbas and Sahin-Demirbas, 2004). For instance Panwar et al., (2010) reported an increase in density of mango and eucalyptus leaf briquettes from 600 to 1,100 kg m^{-3} when pressure was increased from 30 to 100MPa. A similar trend was reported for other materials such as waste paper, wheat straw (A Demirbaş, 1999), pine (Križan, 2007), palm oil mill residues i.e. empty fruit bunches mixed with mesocarp fibre in the ratio of 60:40 (Faizal et al., 2010). Rhén et al., (2005) observed a significant increase in density of spruce pellets with an increase in compacting temperature (26-144 ^{o}C). Similarly, Carone et al., (2011) reported a significant increase in density of pellets from olive tree pruning residue with an increase in temperature (60-150 ^{o}C) and a decrease in moisture content (20-5 %). Compressive strength of hazelnut shell charcoal briquettes increased with an increase in compacting pressure (300-800MPa) (Ayhan Demirbaş, 1999). Yaman et al., (2000) reported a reduction in the compressive strength (33-15 kg cm^{-2}) of olive refuse briquettes when pressure was increased from 150-250MPa. Plastic deformation of material during compaction causes mechanical strength to increase with an increase in pressure until an optimum pressure is reached. Above the optimal pressure dilation occurs and briquettes develop cracks which make them weaker (Yaman et al., 2000). Within a moisture content range of 7.4-22.0%, Matúš et al., (2015) maximized compressive strength in cleft (27.4Nmm^{-1}) at 12.6%. Andrejko and Grochowicz, (2007) reported an increasing trend in compressive strength of lupin seeds briquettes with increasing moisture content from 9.5-15.0%.

Although density and strength of briquettes from several biomass materials has been studied previously, there is little available information on the interactions between the briquetting variables used (temperature, pressure, moisture and particle size).

2.2.2 Torrefaction

Torrefaction is a biomass pre-treatment technique which enhances hydrophobicity, grindability, energy density and durability in terms of storage and increases calorific value of biomass (D. Chen et al., 2015, Joshi et al., 2015). There are two types of torrefaction i.e. dry and wet. Dry torrefaction is the thermal decomposition of biomass in an inert environment or in the presence of a limited supply of oxygen (which potentially reduces production costs) at a temperature between 200-300 ^{o}C (D. Chen et al., 2015, Colin et al., 2017, Martín-Lara et al., 2017, Leontiev et al., 2018) degrading mainly hemicellulose (Wannapeera et al., 2011). Dry torrefaction requires dried biomass materials <15% moisture (Nhuchhen et al., 2014) which increases operation costs due to energy requirement for the pre-drying step (Bach and Skreiberg, 2016). Wet torrefaction occurs at a temperature range of 180-250^{o}C (Nhuchhen et al., 2014). Sub-critical water acts as a solvent/catalyst/reagent facilitating dehydration and breakdown of biomass (P. Gao et al., 2016). Dehydration, decarboxylation, aromatization and condensation are the main reactions during hydrothermal pre-treatment (Nhuchhen et al., 2014). Advantages of wet torrefaction over dry torrefaction include:

- Wet torrefaction produces solid product with superior qualities in terms of hydrophobicity, HHV and energy yield than dry torrefaction (Bach et al., 2015).
- Wet torefaction can potentially be used in pre-treatment of high water content feedstock such as aquatic, agricultural, forest residues, food waste etc. since water in a sub-critical condition is used as a reaction mediato reduce the drying costs (Bach et al., 2015, Bach and Skreiberg, 2016).

Torrefaction has not yet been commercialized because the optimal operating conditions for different uses and biomass feedstocks are yet to be established (Leontiev et al., 2018). Handling/utilization of the gaseous (Leontiev et al., 2018) and liquid products is also still a challenge in torrefaction. Additionally, corrosion of the reactor and clogging resulting from precipitation of inorganic elements are problematic in wet torrefaction and all these are likely to increase the investment costs (Bach et al., 2015). Furthermore, at industrial scale, wet torrefaction would require very high-pressure in-feed system which increases the capital cost. Unlike dry torrefaction, it would also be challenging to integrate wet torrefaction with a thermochemical conversion system such as gasification, pyrolysis of combustion (Bach and Skreiberg, 2016).

2.2.2.1 Yields and properties of torrefaction products

Solid, liquid and gas are the products of torrefaction, with the gaseous product containing predominantly CO_2, CO and small amounts of H_2 and hydrocarbons (Chen et al., 2018). The liquid is acidic with very high water content of ~63-86% resulting in a low HHV of <9MJ kg^{-1} (Chen et al., 2018). However, the solid product is the main product of torrefaction (Bach et al., 2015). Literature shows that studies are conducted to determine the impact of torrefaction on the yields and properties and potential applications of torrefaction products. Yields and properties of torrefaction products depend on feedstock type and torrefaction conditions i.e. temperature, holding time, heating rate (Wannapeera et al., 2011, Uemura et al., 2011, Mamvura et al., 2018) and carrier gas type (Bach et al., 2014). Increasing torrefaction temperature of *loeucaena leucocephala* (holding time 30 min) from 200-275°C reduced solid yield from 91.1-54.5%. Furthermore, when the holding time (temperature of 250°C) was increased from 0-15h, solid yield decreased from 85.0-47.0% (Wannapeera et al., 2011). Increasing particle size (measured in terms of briquette thickness) from 3-6cm enhanced solid yield and lowered carbon content of torrefied birch briquettes (Leontiev et al., 2018). Varying heating rate from 5-15 °C min^{-1} during torrefaction of blue gum wood and marula seed had minor impact on solid yield from blue gum wood, however, solid yield from marula seed showed a decreasing trend as heating rate was increased from 10-15 °C min^{-1} (Mamvura et al., 2018).

The solid product has lower volatile, oxygen and hydrogen content but higher fixed carbon, carbon content and HHV than the parent biomass (Matali et al., 2017) (Table: 2.3). Torrefaction reduces hydrogen and oxygen content through removal of hydroxyl group and decarboxylation (Matali et al., 2017). Furthermore, torrefaction improves biomass grindability (reducing cost of grinding) and hygroscopic nature of the biomass which increase biomass durability in terms of storage (Chen et al., 2018). The resistance to moisture uptake of tomato peels improved with increasing torrefaction temperature and holding time from 214-316 ^{o}C and 30-60 min respectively (Toscano et al., 2015). Similar findings were reported for torrefied sawdust (torrefaction temperature: 270-300 ^{o}C) (Hui Li et al., 2012). Increasing trends in carbon content and a decreasing trend in hydrogen and oxygen contents of wet torrefied Norway spruce and birch wood were observed by increasing holding time from 10-60 min (at wet torrefaction of 200^{o}C) and temperature from 175-225 ^{o}C (at holding time of 30 min), however, nitrogen content did not change significantly (Bach et al., 2015). Donar et al., (2016) reported that increasing holding time (2-6h) had no significant impact on chemical composition of wet torrefied hazelnut shell and olive residues at a torrefaction temperature of 180-260^{o}C.

Table: 2.3: Proximate and ultimate properties and heating value of raw and torrefied biomass (Chen et al., 2018, D. Chen et al., 2015, Colin et al., 2017, Wannapeera et al., 2011)

Property	Non torrefied biomass	Torrefied biomass
Proximate properties: Moisture free		
Ash (%wt)	0.5-15.0	0.8-23.4
Volatile (%wt)	68.7-86.1	41.3-85.3
Fixed carbon (%wt)	13.1-18.1	15.8-36.7
HHV(MJ kg^{-1})	15.3-20.3	16.0-24.4
Ultimate analysis: Moisture free		
C (%wt)	40.8-50.1	41.6-65.4
H(%wt)	5.2-6.9	4.6-6.0
N(%wt)	0.2-1.1	0.5-1.0
O(%wt)	32.3-46.7	17.5-36.3

Torrefied biomass provides potential feedstocks for briquetting, combustion, gasification and pyrolysis (Chen et al., 2017, Gilbert et al., 2009). However, it was reported (Hui Li et al., 2012) that torrefaction of sawdust at 260-300°C increases energy requirement for pelletization. Density and strength of pellets from torrefied switchgrass was lower than those from raw biomass material (Gilbert et al., 2009). For instance, pellets from torrefied switchgrass were too brittle and not homogenous compared to pellets from raw switchgrass due to a loss in moisture during torrefication. Brittle densified products resulting from torrefaction could break and generate dust during transport, handling and storage and are therefore not desirable. However, such pellets/briquettes may be easy to pulverize and cofire with coal (Gilbert et al., 2009).

Torrefaction alters biomass degradation properties with the impact depending on the degree of torrefaction (Toscano et al., 2015) due to changes in chemical and structural properties. Lignin, cellulose and hemicellulose composition changed from 53.39-58.06 %, 28.76-28.88 % and 14.16-17.88 % with increasing sawdust torrefaction temperature from 270-280°C (Hui Li et al., 2012). The results from thermogravimetric analysis (TGA) of torrefied *Leucaena leucocephala* showed that the change in char yield (measured at 800°C) with increasing torrefaction temperature was minor, though a significant increase in char yield was observed with increasing holding time (Wannapeera et al., 2011). Increasing torrefaction temperature from 214-310 °C shifted the onset degradation temperature to a higher temperature and the char yield (measured at 550°C) increased from 23% for raw tomato peel to 32% for torrefied peel at 316°C (Toscano et al., 2015). Analysis in a TGA showed that increasing torrefaction temperature (200-300°C) and holding time increased char yield derived from olive tree pruning residues (from 19 to 30%wt) (Martín-Lara et al., 2017).

2.3. Thermochemical conversion process

2.3.1 Combustion

Combustion is the fully oxidation of organic matters into CO_2 and H_2O (Naik et al., 2010, Mandø, 2013) in excess air and is well-established technology (Zhang et al., 2010, Chhabra et al., 2016) for heat and/or power generation (Lim et al., 2012) . Equivalent ratio (λ), defined as a ratio of amount of air used in the process to a stoichiometric amount of air for complete combustion, is an important factor for combustion process. Theoretically, λ=1 is required for the combustion process, however, it is hard to attained because of mixing constraints therefore λ of 1.1-1.8 and 1.5-2.0 are commonly used in large and small scale combustion applications respectively (Obernberger et al., 2006). Material i.e. biomass should have moisture content below 50% for an efficient combustion (Goyal et al., 2008). Biomass undergoes the following stages of mass loss during combustion: drying, devolatilization and volatile combustion, and char combustion (Williams et al., 2012, Obernberger et al., 2006). Some of the systems used in biomass combustion include: simple stove, direct-fired gas turbine, grate firing, fluidized bed, and pulverized bed (Williams et al., 2012, Meng et al., 2017). Fluidized bed is complex and not widely used (Wolf and Dong, 2013), requiring a highly efficient system to separate solid from gas and has a high operational cost compared with grate combustor (Meng et al., 2017) and the capital cost is also higher than that of grate firing. However, it is an efficient technology where less NOx and CO are emitted due to combustion at low temperatures (650-900^{o}C) (Widell, 2013). Biomass at moisture content ≤60% and small size particles (≤100mm) is mixed with a medium e.g. sand and kept suspended in flowing air. Excess air ratio is required ranging between 1.1-1.3 (Widell, 2013). Fluidized bed uses relatively larger particle size with higher moisture compared to pulverized bed. Combustion in pulverized boilers occurs at relatively higher temperatures thus leading to corrosion and slagging problems and this requires cofiring with coal. However, the chemical components of coal such as sulphur, silicate and aluminum can only neutralize the corrosive compounds in biomass if the concentration of biomass in the coal-biomass mix is ≤10%. Pulverized boilers have high efficiency and are appropriate for large scale energy generation (600MWe). However, feedstock drying and grinding is energy consuming (Wolf and Dong, 2013) thus increasing production costs. Therefore, the choice of any of these technologies depend on its cost, plant size and biomass feed characteristics (Rosillo-Calle et al., 2007). Biomass contribution in the energy sector could be increased by co-firing with coal, conversion of the existing coal-fired plants and building dedicated biomass-fired plants. Co-firing is practiced in many countries especially in Europe and is seen as a transition step towards biomass only generation facilities.

In grate firing, biomass is placed on a grate containing holes through which air is passed. Biomass burns as the grate moves slowly through a boiler. Grate firing is widely practiced for biomass combustion. It is a simple and flexible technology which is suitable for large size particles even if they are not homogenous however; plant size is limited to ≤150MW$_{th}$/50MW$_e$ (Wolf and Dong, 2013, Nunes et al., 2014). Particle size and moisture content of up to 300mm and 55% respectively and access air ratio of 1.1-1.5 can be used (Widell, 2013). Nonetheless, the limited plant size may make it suitable for decentralized power generation. Furthermore, the potential of grate firing to use large size particles makes it suitable for briquette/pellet combustion, unlike fluidized or pulverized bed. Several researchers have used fixed bed reactor to simulate moving grate due to a known bed height (Meng et al., 2017). The used of fixed bed reactor makes data acquisition easy and reduces maintenance and operation costs (Meng et al., 2018). Combustion in fixed bed is quantified by ignition/flame front speed or reaction front speed and burning rate (Ryu et al., 2006). Ignition rate (kg m^{-2} h^{-1}) is the mass of fuel loss per unit area per unit time as the ignition front propagates (Ryu et al., 2006). Burning rate is defined as the rate at which mass is loss per unit cross-sectional area (Khor et al., 2007).

2.3.1.1 Factors affecting combustion

(a) Air flow rate/supply

Sufficient air and mixing of the fuel with air is required for complete combustion of fuel. In case of poor mixing, excess air is required to provide sufficient O_2 required for complete combustion of the fuel otherwise products of incomplete combustion such as CO will be produced with likely effects on human health and the environment. However, addition of excess air also increases the capital costs of the plant because of the requirements for ducts, fans, etc. with higher flow capacity (Malmgren and Riley, 2012). Air flow rate determines the convective heat transfer and the available O_2 (Ryu et al., 2006) thereby influencing ignition and combustion rate. Increasing primary air flow rate from 1.8-9.2 m^3 h^{-1} increased ignition rate and combustion rate of corn straw from 0.34-0.57mm s^{-1} and 0.025-0.042 kg m^{-2} s^{-1} respectively (Meng et al., 2017).

(b) Feedstock type and properties

Different materials such as wood pellets, brassica pellets, poplar pellets, refuse-derived fuel pellets, olive stone, almond shell, and pine shavings have different combustion characteristics

(Porteiro et al., 2010), due to variations in their chemical composition. Increasing moisture from 6.23-15%, delayed ignition, prolonged burning time and lowered combustion rate of corn straw (Meng et al., 2018). In addition, increasing the moisture content increased unburnt carbon content in residues/ash (Meng et al., 2018). Feedstock particle size also affects the burning rate and ignition front speed. Increasing particle size lowers ignition front speed, devolatilization rate and burning rate (Ryu et al., 2006). Increasing corn straw length from 2-10 cm increased ignition time from 100-300s, however, further increasing the corn straw length to 15cm reduced the ignition time to 164s (Meng et al., 2017). Furthermore, the content of unburnt carbon in the ash increased from 0.31-4.93% with increasing corn straw length due to incomplete combustion resulting from lower ignition rate for the larger size particles (Meng et al., 2017). Combustion of sewage sludge in TGA showed that increasing particle size from 0.250-1mm increased ignition temperature, maximum peak temperature and burnt out temperature by 5, 12 and 7°C respectively (Vamvuka and Sfakiotakis, 2011).

Combustion characteristics are affected by biomass chemical, physical and thermochemical pre-treatments. It was demonstrated (Liu et al., 2015) that, washing of char from pine wood and coconut fiber with de-ionized water, acetic acid and nitric strongly affected combustion behavior by reducing ash content, slagging and fouling and char reactivity. Meanwhile, the thermal stability and reactivity of beech wood char was reported (Guizani et al., 2017) to depend on pyrolysis temperature (500-1400°C). Much as pyrolysis and torrefaction change the chemical and structure properties of biomass (Guizani et al., 2017, Mei et al., 2016), briquetting changes biomass density which is briquetting condition dependent (pressure, temperature, feedstock particle size and moisture content). Compacting pressure, p (bar) is related to burning rate, $\dot{m}$ (g min^{-1}) by Equation (2.1) (Chin and Siddiqui, 2000).

$$\dot{m} = ap^{n} \tag{2.1}$$

Where a and n are constants which depend on the biomass feedstock used.

Mohammed and Olugbade, (2015) reported a decrease in combustion rate of briquettes from rice bran and palm kernel shells from 2.3 to 1.7 g min^{-1} when compacting pressure was increased from

3 to 9 MPa. According to Faizal et al., (2010), the burning rate of briquettes from palm oil mill residues i.e. mesocrap fibre blended with shell in the ratio of 60:40 showed a decreasing trend with increasing compacting pressure (3-11 MPa). Densification increases biomass density and reduces the porosity which reduces the ease of ignition of the material which is also limited by some of its properties such as high moisture content, low porosity, low volatile matter content, and high ash content (A Demirbaş, 1999). While briquetting, an increase in particle size reduces the quality of briquettes produced. The forces holding the particles of the briquette are reduced. This results in faster decay during thermal decomposition (Kers et al., 2010). The reduction in the forces holding the particles as particles size is increased can result in an increase in porosity index of a briquette. The rate of outflow of volatiles and moisture during combustion is high in feedstocks with large porosity (Mohammed and Olugbade, 2015).

2.3.1.2 Challenges with biomass combustion

Slagging and corrosion are the two main challenges associated with combustion of biomass particularly for high ash content biomass. During combustion, ash and particles of condensed gases are deposited inside a boiler which create a barrier to heat transfer. At high temperature, ash particles agglomerate causing problems with air and fuel flow in the combustion chamber (Mandø, 2013). Metal chlorides are formed during combustion and are deposited inside the boiler which are responsible for corrosion (Mandø, 2013). These problems can be minimized by co-firing with fossil fuel (coal). However, at more than 10% biomass in a mixture, the corrosive compounds in biomass are not neutralized by coal chemical constituents such as sulphur and silicate, so slagging cannot be stopped (Wolf and Dong, 2013). For non pre-treated biomass, properties such as moisture content, size and shape vary significantly within a batch and these make optimization of the combustion process and automation of feedstock conveying a challenge, however, these problems are minimized with the use of briquettes (Nikolaisen and Jensen, 2013).

2.3.1.3 Emissions during combustion

Pollutants emitted during combustion include: air born pollutants (CH_4 and volatile organic compounds), particulate matter, products of incomplete combustion (CO and hydrocarbons), nitrogen oxides, and sulphur oxides (Williams et al., 2012, Nunes et al., 2014). Some are sulfates and chlorides which are formed as a result of reactions of the inorganic components of biomass (Nunes et al., 2014). Unburnt pollutants such as char particles, tar, CO, and hydrocarbons are produced as a result of poor combustion resulting from poor mixing of the fuel with air, short residence time of volatiles in the combustion zone and low combustion temperature. Ash is also a pollutant whose quantity depends on the fuel ash content and the excess air ratio (Werther et al., 2000). The products of incomplete combustion (CO, tar, hydrocarbons, soot and polycyclic aromatic hydrocarbons) can be minimized through optimizing the combustion process by proving good fuel-air mixing, a sufficient retention time (e.g. >1.5s for temperature >850^{o}C) and low λ (Obernberger et al., 2006). Particulate matter especially the ultrafine particle emissions is of great concern due to their health implications to humans. Such particles originate mainly from incomplete combustion (char, soot and condensable organics) and particles from inorganic material in the ash (Johansson et al., 2003). Some technologies such as electrostatic precipitators and bag filters have been developed to minimize the amount of particulate matter in flue gases. Uses of wet and dry scrubbers have also shown a potential of removing SO_2 from flue gases. The emission of NO_x is one of the major threats to the use of biomass combustion systems. Unlike SO_x whose emissions depend on the fuel sulphur content, NO_x emissions depend on both fuel and firing conditions. Fuel NO_x can originate from fuel bound nitrogen, and thermal NO_x formation results from the reaction between gaseous nitrogen and oxygen at high temperatures i.e. ≥850 ^{o}C (Malmgren and Riley, 2012, Mandø, 2013). For combustion at small scale such as in the case of domestic stoves, only the fuel bound NO_x are emitted (Roy and Corscadden, 2012). So the primary concern is in the fuel bound nitrogen as nitrogen content varies from one biomass feedstock to another (Mandø, 2013). The same would apply to fuel bound sulphur, as SO_2 emissions from the combustion of briquettes depends on feedstock sulphur content (Roy and Corscadden, 2012). NOx can be minimized by selective catalytic or non-catalytic reduction where NOx is reduced to nitrogen (N_2) by adding ammonia (NH_3) with or without a catalyst. However, in the case of selective catalytic reduction, the possibility of deactivation of the catalyst by alkaline metal is of a concern and the investment costs are increased (Obernberger et al., 2006). In a combustion unit, oxides of sulphur, hydrochloric acid and heavy metals can be captured using sodium carbonate, limestone and active carbon. While, selective noncatalytic reduction is used to reduce NOx emissions (Malmgren and Riley, 2012).

2.3.2 Pyrolysis

Pyrolysis is the thermal decomposition of carbonaceous substance in the absence of oxygen/air to produce liquid, char, and gas (Mohan et al., 2006, Yaman, 2004, Açıkalın et al., 2012). Pyrolysis is classified (Table 2.4) based on the operating conditions as slow, fast and flash pyrolysis (Demirbas and Arin, 2002). Pyrolysis involves a number of reactions including dehydration, decarboxylation, depolymerization, charring, aromatization and isomerization which occur simultaneously or in series (Kan et al., 2016). Pyrolysis is the sub-step of combustion/gasification. Feedstock i.e. biomass will undergo drying process (up to 200^{o}C) to remove moisture. The decomposition occurs mainly in a temperature range of 250^{o}C-500^{o}C via decarboxylation, decarbonylation, condensation etc. Up to 82%wt mass loss was observed in this temperature range 350-650^{o}C (Aziz et al., 2015, Hao et al., 2013, Ji-lu, 2007).

Table 2.4: Operating parameters and yields of pyrolysis products by type of pyrolysis (Demirbas and Arin, 2002, Jahirul et al., 2012, IEA, 2007, Mohamed et al., 2013)

Pyrolysis type	Residence time (s)	Pyrolysis temperature (K)	Heating rate (K s^{-1})	Particle size (mm)	Pyrolysis product (%)		
					Oil	Char	Gas
Slow	450–550	550–950	0.1–1	5–50	30	35	35
Fast	0.5–10	850–1250	10–200	<1	50	20	30
Flash	<0.5	1050–1300	>1000	< 0.2	75	12	13

Due to the absence of oxygen, pyrolysis significantly emit less toxic gas than combustion and gasification (Klinghoffer and Castaldi, 2013). Pyrolysis of biomass is gaining interest because of its potential to produce solid (char), liquid (bio-oil), and gas (Jahirul et al., 2012, Yorgun and Yıldız, 2015). Char and bio-oil can easily be stored and transported compared to syngas from gasification.

Bio-oil, also known as pyrolysis oil, is highly oxygenated. Its color can be black, dark brown, dark red-brown or dark green depending on the feedstock and pyrolysis process (IEA, 2007). Bio-oil can either be a homogenous one-phase liquid or a heterogenous liquid which separates into two parts i.e. aqueous and oily phase (Yanik et al., 2007). Bio-oil contains more than 300 compounds (Ali et al., 2016) that can be grouped into aldehydes, carboxylic acids, carbohydrates, phenols, furfurals, alcohols, and ketones (Mohamed et al., 2013; Czajczyńska et al., 2017). Bio-oil can be used to produce electricity, heat, platform chemicals or synthetic gas (Czajczyńska et al., 2017, Asadullah et al., 2007). Though bio-oil has attracted much attention because it is easy to transport, store and handle (Naik et al., 2010, Ogunjobi and Lajide, 2013) which makes decoupling of fuel production from energy generation possible, its application on a commercial scale is not yet viable because of its undesirable properties such as low HHV, low pH, low stability and high oxygen and water content (Bridgwater et al., 1999, Wang et al., 2018). Table 2.5 illustrates properties of bio-oil compared to those of conventional fuels. A number of techniques such as solvent addition, emulsification, catalytic cracking, hydrotreating and steam reforming are under study to improve the properties of bio-oil (Saber et al., 2016**,** Ji-lu, 2007**,** Peng et al., 2000**,** IEA, 2007**,** Bridgwater, 2012).

Table 2.5: Properties of bio-oil and other liquid fuels (Park et al., 2012, Ji-lu, 2007, Imam and Capareda, 2012, Heo et al., 2010b, Jahirul et al., 2012, Demiral et al., 2012)

Property	Bio-oil	Gasoline	Diesel
High heating value (MJ kg^{-1})	5.01-36.3	47.3	45.5
Density (kg m^{-3})	920-1190	723	838
Viscosity at (mm^{2} s^{-1})	6.5-156	0.12	2.4
pH	<4.08	-	5.5-8.0
Water content (%wt)	13-60.00	<0.1	<0.1
Elemental composition			
C	14.42-66.76	84.5	86.0
H	7.43-9.3	13.1	11.1
N	≤1.5	-	1.0
S	≤0.6	0.0	0.8
O	24.96-76.30	0.0	0.0

Biochar contains up to 98%wt carbon with a small amount of hydrogen 1.1-7.2%wt (Hao et al., 2013, Ronsse et al., 2013) and oxygen of 1.03-34.3%wt (Fu et al., 2011, Sánchez et al., 2009, Özçimen and Karaosmanoğlu, 2004) with low volatile content of 9.5-39.4 (Sánchez et al., 2009, Özçimen and Ersoy-Meriçboyu, 2010, Angın, 2013). It can be used for preparation of activated carbon, as a soil amendment, and for carbon sequestration (Mythili and Venkatachalam, 2015).

The non-condensable gases (CO, CO_2, H_2, CH_4, and light hydrocarbons up to C_5) are formed from primary biomass decomposition and secondary cracking of vapors. The HHV of the gaseous product is 5-17 MJ kg^{-1} (Raveendran and Ganesh, 1996). Gas yield and composition depend on feedstock properties and pyrolysis conditions. The gaseous product can be recycled for heating purposes.

2.3.2.1 Factors affecting yields of pyrolysis products

2.3.2.1.1 Feedstock type

Yields and properties of pyrolysis products (Table 2.6) varies for different feedstocks, which is likely due to variation in the chemical compositions. The decomposition of hemicellulose, cellulose, and lignin, three main components of biomass, contribute to pyrolysis product distribution. Cellulose and hemicellulose produce mainly volatiles (Basu, 2010) while lignin produces mainly char (Zhang et al., 2006, Shi-Xiang Zhao et al., 2017). Inorganic components mainly remain in the biochar as ash, however some are carried over to the bio-oil. Ash content in bio-oil of upto 0.3%wt has been reported (Özçimen and Karaosmanoğlu, 2004). Inorganic components could act as catalyst during the pyrolysis process and increases char yield via repolymerization or increases liquid/gas via cracking (Wei et al., 2006). Pre-treatment of biomass material by washing could significantly affect yields and properties of pyrolysis products. Water washing of rice husk increased bio-oil yield from 35.90-41.25% but decreased char yield (Zhang et al., 2015, S. Hu et al., 2015). Water washing of rice husk increased CH_4 and reduced H_2 yield, however CO_2 and CO composition were not affected significantly (Zhang et al., 2015).

Table 2.6: Yields of pyrolysis products from different materials (particle size: 0.5-2 mm, carrier gas flow rate: 50 cm^3 min^{-1}, heating rate: 20 ^oC min^{-1} and holding time of 1 h) (Biswas et al., 2017)

Temperature (^oC)	Bio-oil (%)			Char (%)			Gas (%)		
	Corn cob	Wheat straw	Rice straw	Corn cob	Wheat straw	Rice straw	Corn cob	Wheat straw	Rice straw
300	42.8	32.5	25.9	33.0	36.1	35.1	24.2	31.4	39.0
350	45.0	36.0	27.1	25.0	34.6	35.0	30.0	29.4	37.9
400	45.6	36.7	28.4	25.0	34.4	33.5	29.4	28.9	38.1
450	47.3	29.2	27.1	24.0	32.4	33.1	28.7	38.4	39.8

2.3.2.1.2 Particle size

Biomass particle size determines the rates of mass and heat transfer as well as the occurrence of secondary reactions (Yorgun and Yıldız, 2015). Fine particles are heated up quickly compared to large particles (Y. Gao et al., 2016) and less resistance to outflow of condensable gas, promoting bio-oil production. In contrast, high char yield was obtained from large particle sizes (Wei et al., 2006). Fast pyrolysis of bald cypress in a bubbling fluidized bed (Choi et al., 2012) showed that char (17.7-19.6 %) and gas (25.4-29.1 %) yields were increased while bio-oil yield (56.9-51.3 %) decreased when particle size was increased from 0.5mm to 2.5 mm.

Ateş et al., (2004) reported no significant impact of varying sesame stalk particle size (0.2-1.8 mm) on bio-oil yield in a fixed bed reactor operated at a pyrolysis temperature of 550 ^{o}C. Şensöz and Kaynar, (2006) reported a similar observation with a soybean particle size of 0.425-1.8 mm. However, Onay and Kockar, (2003) considered the same particle size range and maximized bio-oil yield at particles size of 0.6-1.8mm and 0.6-1.25 mm during slow (49.2%) and fast (65%) pyrolysis of rapeseed respectively. Large temperature gradient exists between the surface and center of large particles which reduces the average temperature and rate of volatile release, therefore minimizing boil-oil yield and maximizing char (Yip et al., 2007, Wei et al., 2006, Şensöz and Kaynar, 2006).

Feedstock particle size also affect pyrolysis product qualities. For instance, water content in bio-oil from eucalyptus loxophleba (pyrolysis temperature: 500 ^{o}C, particle size: 0.30-5.18 mm) showed increasing trend with increasing particle size (Shen et al., 2009). Gas composition also depends on particle size. Reducing particle size of pine sawdust and apricot stone within the range of 1.20-0.20mm increased H_2 yield as CO_2 yield showed a decreasing trend (Wei et al., 2006).

2.3.2.1.3 Pyrolysis temperature

Temperature is considered as the most important pyrolysis parameters (Shariff et al., 2016). An increase in temperature results in an increase in volatile release and consequently a reduction in char yield and this should increase the char heating value. Heating value increases due to loss in moisture and light oxygenated compounds (Recari et al., 2014). Asadullah et al., (2007) pyrolysed bagasse in a fixed bed reactor (50cm height and 10cm internal diameter) and reported that bio-oil yield increased from 19 to 66% when temperature increased from 300 to 500^{o}C and then slightly decreased to 60% with a further increase in temperature to 600^{o}C. However, gas yield increased (4-18%) at the expense of char yield (decreasing from 77 to 23%) as pyrolysis temperature was increased from 300-600^{o}C (Asadullah et al., 2007). Safflower char yield showed a decreasing trend with increasing pyrolysis temperature (400-600^{o}C) (Angın, 2013). The decrease in char yield could be attributed to an increase in primary decomposition and secondary char decomposition as temperature is increased (Şensöz and Can, 2002, Şensöz and Kaynar, 2006). Bio-oil yield from various feedstocks have been maximized within a pyrolysis temperature range of 450-600^{o}C (Phan et al., 2008, Ateş et al., 2004, Onay and Kockar, 2003, Park et al., 2012, Heo et al., 2010b). Above this optimal temperature range, thermal cracking reduces the bio-oil yield and increases gas yield (Onay and Kockar, 2003).

Pyrolysis temperature affects bio-oil, char and gas properties. For instance, an increase from 40-60 % in water content of bio-oil from waste furniture when temperature increased from 450-550^{o}C (Heo et al., 2010b). A similar trend was reported for rice husk as temperature was increased from 400-550 ^{o}C (Heo et al., 2010a). Increasing pyrolysis temperature from 350-600^{o}C increased carbon content in Douglas fir wood, popular wood and Douglas fir bark char from 70-5-87.5%, 69.9-83.1% and 66.1-78.1% respectively (Suliman et al., 2016). Table 2.7 shows the effect of temperature on elemental composition of char. Oxygen content reduced due to loss of oxygen containing functional groups (Sánchez et al., 2009). Carbon content increased due to an increase in level of carbonization. The contents of essential nutrients (P, K, Mg, Ca) increased when pyrolysis temperature is increased because they are not lost through volatilization. Nitrogen content may be increased due to incorporation of nitrogen into high resistance complex structures where nitrogen cannot be volatilized easily (Al-Wabel et al., 2013). The concentrations of manganese (Mn) and copper (Cu) in char apple tree branches were maximized at polysis temperature of 500^{o}C because they volatilize at high temperature (Shi-Xiang Zhao et al., 2017).

Table 2.7: Effect of temperature on properties of char from apple tree branches (particle size: 2mm pyrolysis temperature: 300-600 ^{o}C and heating rate: 10 ^{o}C min^{-1}) (Shi-Xiang Zhao et al., 2017)

	Temperature (^{o}C)			
Proximate analysis, dry basis	300	400	500	600
Ash (%)	6.72	7.85	10.06	9.40
Volatile (%)	60.77	29.85	23.19	14.86
Fixed carbon (%)	32.5	62.3	66.75	75.73
Elemental analysis, dry basis				
C (%)	62.20	71.13	74.88	80.01
H (%)	5.18	4.03	2.88	2.72
N (%)	1.69	1.94	1.77	1.28
O (%)	24.21	15.05	10.41	6.59
Nutrients analysis, dry basis				
K (%)	0.57	0.89	1.10	1.14
P (%)	0.21	0.28	0.34	0.34
Ca (µg/kg)	12900	16810	20190	20890
Mg (µg/kg)	3010	4040	4690	5640
Fe (µg/g)	268.35	361.62	480.52	583.50
Mn (µg/g)	56.96	79.26	102.89	89.41
Cu (µg/g)	20.29	50.53	85.07	58.90
Zn (µg/g)	33.06	53.30	60.50	61.68

An increase in pyrolysis temperature (Table 2.8) causes an increase in release of volatiles which in turn causes distortion of biomass particle surfaces thereby increasing surface area (Imam and Capareda, 2012, Açıkalın et al., 2012). The surface area of pistachio shell char was increased from 0.12-6.56 m^2 g^{-1} by increasing temperature from 350-650 ^oC (Açıkalın et al., 2012). Surface area and total pore volume of apple tree branch char increased from 2.39-108.59 m^2g^{-1} and 2.56×10^{-3} - 58.54 $\times10^{-3}$ cm^3g^{-1} with increasing temperature from 300-600 ^oC due to progressive degradation of hemicellulose, cellulose and lignin, while a positive correlation between pH and temperature was reported (Shi-Xiang Zhao et al., 2017). Increasing pyrolysis temperature from 450-600^oC increased surface area of char from pyrolysis of pellets (diameter 6mm) wood (pin), wheat straw, green waste, and spray-dried algae 23-127 m^2g^{-1}, 16-22 m^2g^{-1}, 17-46 m^2g^{-1} and 14-19 m^2g^{-1} respectively (Ronsse et al., 2013). Increasing temperature from 400-600^oC had no significant impact on the FTIR profile of safflower seed press cake char (Angın, 2013). Within a pyrolysis temperature range of 400-600 ^oC, empty fruit bunch biochar surface area was maximized at 500^oC (7.7 m^2g^{-1}), while the surface area reduced to 4.2×10^{-1} m^2g^{-1} when temperature was increased to 600 ^oC due to biochar shrinkage, cracking and rapture resulting from overheating (Aziz et al., 2015). An increase in temperature should increase surface area due to an increase in volatile release and consequently increasing the pore size (Aziz et al., 2015). Rehrah et al., (2016) reported a significant increase in pH of biochar due to an increase in char ash content when temperature was increased (300-700 ^oC).

Table 2.8: Surface area and volume of char from different biomass materials (Fu et al., 2011)

Temperature (°C)	Property								
	Surface area (m^2 g^{-1})			Micropore volume (cm^3 g^{-1})			Mesopore volume (cm^3 g^{-1})		
	Maize stalk	Rice straw	Cotton straw	Maize stalk	Rice straw	Cotton straw	Maize stalk	Rice straw	Cotton straw
600	12.99	4.76	-	0.0062	0.0023	-	0.0029	0.0059	-
700	9.32	11.53	17.29	0.0049	0.0054	0.0085	0.0018	0.0073	0.0026
800	48.63	16.12	39.87	0.0228	0.0076	0.0187	0.0088	0.0090	0.0074
900	81.63	30.94	66.52	0.0378	0.0144	0.0306	0.0293	0.0123	0.0226
1000	78.79	26.18	49.79	0.0367	0.0122	0.0230	0.0275	0.0135	0.0204

2.3.2.1.4 Residence time and carrier flow rate

The impact of residence time on the yield of pyrolysis products is well understood. However, its impact and the impact of its interaction with other pyrolysis parameters remains unclear. Within a pyrolysis temperature of 300-750 ^{o}C, (Rehrah et al., 2016) reported a significant reduction in biochar yield from pyrolysis of municipal solid waste at 300 ^{o}C when residence time was increased (2-6 h), due to an increased volatile release as residence time and temperature were increased. However, increasing holding time from 6-12 minutes did not have a significant effect on char yield from pyrolysis of empty fruit bunches (palm oil residue) (Mohamed et al., 2013).

Carrier gas flow rate determines vapor residence time both in the pyrolysis zone and the condenser (Choudhury et al., 2014, Açıkalın et al., 2012, Şensöz and Can, 2002) and vapor residence time determines the extent of secondary cracking and polymerization of pyrolysis vapor. Long residence time is favorable for secondary cracking and polymerization of vapor to form product gas and biochar respectively, but short residence time maximizes bio-oil yield (Sharma et al., 2015). During pyrolysis of jute dust (Choudhury et al., 2014), an increase in carrier gas (N_2) flow rate from 50-250 cm^3 min^{-1} decreased char yield from 34.3-28.7% and increased gas yield from 16.9-33.7% while the trend of bio-oil yield shows that it was maximized at 150 cm^3 min^{-1}. Similarly, bio-oil yield from pyrolysis of sesame stalk was maximized (37.20%) at carrier gas (N_2) flow rate of 200 cm^3 min^{-1} when carrier gas flow rate was increased from 50-800 cm^3 min^{-1} (Ateş et al., 2004). Choi et al., (2012) reported similar trend in bio-oil yield from pyrolysis of bald cypress for N_2 (fluidizing gas) flow rate of 25000-40000 cm^3 min^{-1}. However, Heo et al., (2010b) observed a decrease in bio-oil yield from 57.0-53.0 % though char yield remained unchanged when N_2 (fluidizing gas) flow rate decreased (5000-3000 cm^3 min^{-1}) during pyrolysis of waste furniture sawdust. Within a carrier gas (N_2) flow rate range of 50-450 cm^3 min^{-1}, bio-oil yield from pyrolysis of pistachio shell was maximized at a nitrogen flow rate of 150 cm^3 min^{-1}, while gas yield increased as char yield remained unchanged with increasing carrier gas flow rate (Açıkalın et al., 2012). Pütün et al., (2005) also reported no significant impact of carrier gas flow rate of 50-200 cm^3 min^{-1} on char yield.

2.3.2.1.5 Heating rate

Heating rate determines the rate of heat transfer from a reactor to feedstock and the extent of secondary reactions where high heating rate followed by low residence time reduces secondary reactions (Şensöz and Can, 2002). According to Mani et al., (2010), low heating rate enable heat to be transferred more effectively to the inner portions of the feedstock and among particles. This causes more release of volatiles and they observed an increase in char yield from 11.51-25.94 % when heating rate during pyrolysis of wheat straw was increased from 5-20 ^{o}C min^{-1}. However, it is reported elsewhere (Yaman, 2004, Debdoubi et al., 2006) that char yield decreases with an increase in temperature and heating rate. Increasing heating rate from 10-50^{o}C min^{-1} reduced char yield from pyrolysis of paulownia wood from 34.5-29.5% at 350^{o}C and from 25.4-24.0% at 600^{o}C (Yorgun and Yıldız, 2015). In the same study, increasing heating rate from 10-50^{o}C min^{-1} reduced gas yield from pyrolysis of paulownia wood from 25.3-22.4% at 350^{o}C and 29.2-27.1% at 600^{o}C (Yorgun and Yıldız, 2015). Similarly, Angın, (2013) reported a reduction in safflower seed press cake char yield of 4.48 % and 1.76% when heating rate was increased from 10-50 ^{o}C min^{-1} at pyrolysis temperatures of 400 ^{o}C, and 600 ^{o}C respectively. The trends of bio-oil, char yield and gas yields from pyrolysis of pine chip within pyrolysis temperature of 300-550^{o}C indicate that increasing heating rate from 7-40^{o}C min^{-1} increased bio-oil and gas yields but reduced char yield (Şensöz and Can, 2002). Y. Gao et al., (2016) reported an increasing trend in coconut shell bio-oil yield with increasing heating rate from 2.5-20 ^{o}C min^{-1}. Increasing heating rate from 10-50 ^{o}C min^{-1} had no significant impact on the HHV and FTIR profile of safflower seed press cake char, however, the HHV increased from 28.15-30.27MJkg^{-1} with increasing pyrolysis temperature from 400-600^{o}C (Angın, 2013).

2.3.3 Pyrolysis and combustion kinetics

Kinetic studies provide vital information during the design or modeling of combustion/pyrolysis systems (Agrawal and Chakraborty, 2013) providing a correlation between reaction temperature (T), conversion rate (α) and reaction rate (k) (Wang et al., 2016). Data for kinetic studies can be obtained from isothermal and non-isothermal processes. Experiments are performed under different temperatures under isothermal conditions to obtain isothermal kinetic data. However, this method is considered as time consuming and is gradually losing interest at the expense of non-isothermal conditions from which a range of temperatures can be investigated expeditiously (White et al., 2011). Thermogravimetric analysis (TGA) has been the most common technique used in analyzing the thermal behavior of biomass (Slopiecka et al., 2012, Damartzis et al., 2011, El-Sayed and Khairy, 2015) though it operates under different conditions (limited heat and mass transfer limitations) compared to that of a pyrolysis reactor (Jeguirim et al., 2014). TGA is categorized as isothermal or non-isothermal. The non-isothermal is more sensitive to experimental noise and is therefore preferred over isothermal TGA (Gai et al., 2013). Thermogravimetric analysis measures the rate of mass loss as a function of temperature or time and provides information about the thermal stability of a fuel. The data from TGA are used to determine the kinetic parameters: activation energy, frequency factor and order of reaction using different mathematical models (Table 2.9).

Table 2.9: Methodology for kinetic studies (Slopiecka et al., 2012, Agrawal and Chakraborty, 2013, Rukthong et al., 2015, Li et al., 2013, Liang et al., 2014)

Method	Equation	Plot
Friedman	$In(d \propto/dt) = In(\beta(d\alpha/dT))$ $= InA + In(f(\alpha) - E/RT$	$In(d\alpha/dt)$ versus $1/T$
Kissinger	$In(\beta/{T_m}^2) = In[AR/E] - E/RT_m$	$In(\beta/{T_m}^2)$ versus $1/T_m$
Flynn-Wall-Ozawa (FWO)	$log\,\beta = log[AE/Rg(\alpha)] - 2.315 - 0.4567E/RT$	$log\beta$ versus $1/T$
Kissinger-Akahira-Sunose (KAS)	$In(\beta/T^2) = In[AR/Eg(\alpha)] - E/RT$	$In(\beta/T2)$ versus$1/T$
Coats-Redfern	$In(g(\alpha)/T^2) = In(AR/\beta E) - E/RT$	$In(g(\alpha)/T^2)$ versus $1/T$
Distributed activation energy model	$In(\beta/T^2) = In[AR/E] + 0.6075 - E/RT$	$In(\beta/T^2)$ versus $1/T$

These data can vary depending on the feedstock, atmosphere and the mathematical models used to evaluate them (El-Sayed and Khairy, 2015). Biomass devolatilization is described in terms of the three main components: hemicellulose, cellulose and lignin (Slopiecka et al., 2012). The study of pyrolysis/combustion kinetics helps in understanding how the different pyrolysis/combustion parameters affects the biomass degradation process (Zhang et al., 2006). Literature shows significant variations in kinetics data for different feedstocks (Table 2.10).

Table 2.10: Kinetic studies for different fuels

Feedstock	Conversion method	Heating rate (^oC min^{-1})	Method of kinetic study	Activation energy (kJ mol^{-1})	Reference
Para grass (*Urocloa mutica)*	Pyrolysis	10-50	KAS	103-223	(Ahmad et al., 2017)
			FWO	117-233	
Melon (*Citrullus colocynthis* L.) seed husk	Pyrolysis	5-20	Distributed Action Energy Model	145.44-300.51	(Nyakuma, 2015)
Smooth cordgrass	Pyrolysis	5-40	FWO and KAS	183.5	(Liang et al., 2014)
Microalgae *Chlorella vulgaris*	Pyrolysis	10- 40	FWO and KAS	332.60	(Chen et al., 2012)
Palm kernel shell (PKS)	Combustion	10-60	Vyazovkin	139	(Idris et al., 2012)
Palm mesocarp fibre (PMF)				118	
Empty fruit bunches (EFB)				105	
Sub-butiminous coal (MB)				65	
MB:PKS ratio of 50:50				85	
MB:PMF ratio of 50:50				71	
MB:EFB ratio of 50:50				69	

Such variations are likely due to variations in the feedstock chemical composition or analytical approaches (Liang et al., 2014). The methods used in analyzing kinetic parameters are categorized as model fitting and model free. Model fitting involves fitting different models to the data and the model with the best statistical fit is chosen for determination of kinetic parameters. Model fitting methods requires only a single TGA measurement for a complete kinetic study, however their inability to uniquely determine the kinetic model is a challenge unlike model free methods. In model free methods, kinetic parameters are determined without pre-assumption of a model and the error associated with wrong presumption of the model can be eliminated (Slopiecka et al., 2012). Furthermore, the model free method is flexible (accommodating changes in reaction mechanism) and the uses multiple heating rates which minuses mass transfer limitation (My et al., 2017). Model free methods are the most common method which have been used to study kinetics of biomass materials such as microalgae (Gai et al., 2013) and cardoon (Damartzis et al., 2011). The isoconvensional (model free) methods are easy to use and give more accurate values of kinetic parameters compared to model fitting, they are based on assumption that the reaction rate at any conversion is only dependent on temperature (Idris et al., 2012).

2.4 Summary

Scattered information on the effect of pyrolysis conditions on yields and properties of biomass have been reported with variation in feedstock properties. Few research has been found on the effect of interactions between operating conditions on the pyrolysis products and their properties. In addition, limited studies were found on pyrolysis of briquettes/pellets or torrefied feedstock but on raw/loose biomass/agricultural residues. Information about combustion of pre-treated biomass/briquette is also scarce. Density, durability and compressive strength of briquettes strongly depends on briquetting conditions: pressure, temperature, moisture content and particle size, however more research work is required to determine how the interaction between the briquetting variable would affect properties of briquettes. Literature also show no optimal conditions identified for briquetting maize cobs and bean straw. Optimization of these briquetting parameters are essential in preparing quality briquettes for thermo-chemical applications, it is equally important to assess the impact of briquetting parameters on the chemical properties of briquettes. This work therefore focuses on analyzing the briquetting conditions of maize cob and bean straw on product quality. Several biomass materials responded differently to variation in torrefaction conditions and information about the impact of the interactions of the torrefaction parameters on the torrefaction process is scarce.

Chapter 3: Pre-treatment Methods

Bioenergy from biomass (waste, residues and woody materials) has attracted enormous attention and contributing 10% of total global energy consumption (World Energy Council, 2016). However, low energy density, hydrophobicity and grindability together with heterogeneity not only increase transport, storage and production costs but also reduces durability in terms of storage (prone to fungal decomposition) and conversion efficiency. Among other pretreatment approaches, torrefaction transforms biomass into charcoal-like material, enhancing calorific value and grindability whereas briquetting produces high energy density feedstock with uniform shape and size for storage and transportation with potential uses in combustion, pyrolysis and gasification (Adapa et al., 2009). Densification minimises particulate emissions per unit solid fuel transported and improves biomass combustion efficiency as well as conveyance efficiencies (less dust and wastage and lower labour cost) in commercial energy generation facilities (Muazu and Stegemann, 2015, Zainuddin et al., 2014). Several feedstocks have shown different responses to variation in torrefaction conditions (Mamvura et al., 2018, Uemura et al., 2011). Similarly different biomass materials have showed different responses to variations in briquetting variables (A Demirbaş, 1999, Yaman et al., 2000, Mitchual et al., 2013, Panwar et al., 2010, Carone et al., 2011, Rhén et al., 2005, Tumuluru et al., 2015) and different biomass materials can be blended to enhance the mechanical properties and the combustion characteristics of briquettes. However, there is little information available on the torrefaction and `densification characteristics of bean straw, maize cob or a combination of bean straw with maize cob. In this chapter, the impact of briquetting conditions and feedstock type on properties of briquettes were investigated. Yields and properties of torrefaction products were also examined over a tested range of temperature (200-300^{o}C) and holding time (0-90min). The contents of this chapter were published with Journal of Biomass and Bioenergy (Appendix A 1).

3.1 Experimental methododology

3.1.1 Materials

Bean straw obtained from Nafferton Farm a research/commercial farm owned and managed by Newcastle University, was part of an organic crop rotation left as residue in the field to dry before being collected and stored under cool/dry conditions. Maize cobs were kindly provided by Barfoots of Botley Ltd, UK. Maize (supersweet varieties) was harvested at Stage R3 (milk stage) of maturity in a range of countries (Senegal, Morocco, United State of America, South Africa, Greece, Germany, United Kingdom, France and Spain) and stored at 0-5^{o}C for 1-25 days. Waste cobs were stored in a cold room at 6^{o}C prior to briquetting. The waste maize cobs are representative of material that would be used in processing rather than the production of corn cobs grown to maturity as would be the case for many developing countries including Africa. Residue maize cobs were cut into pieces < 5mm and oven dried at 105^{o}C for 3.5-4.5 h to obtain a range of moisture contents of 16.94-7.14%. Bean straw was cut to <2 cm length sections. Both dried maize cobs and bean straw were crushed using a HGBTWTS3 laboratory blender 8010ES and separated using 2.36 and/or 4.00 mm sieves. The composition of the inorganic elements in both feedstocks were determined using Thermo XSeries 2 ICP-MS. About 50±0.1mg of biomass material (bean straw and maize cob) was boiled in Aqua Regia (3 parts hydrochloric acid of purity 34-37% to 1 part nitric acid of purity 67-69%) for 24 h and then later evaporated. The residue was then mixed with 2ml concentrated nitric acid (purity: 67-69%) and then diluted to 50ml with pure water (Milli-Q) and analyzed using Inductively Coupled Plasma Masss Sectrometry (ICP-MS).

3.1.2 Briquette preparation

A machine fabricated with a hollow cylindrical mould (Fig 3.1), internal diameter of 2 cm and length 12.5 cm was adapted from the work of Zafari and Kianmehr, (2014). The mould was fitted inside two 150W band heaters connected to a temperature controller (1-off Dual Control Box - Twin SSR) and was insulated with Fortaglas for operator safety and to reduce heat loss.

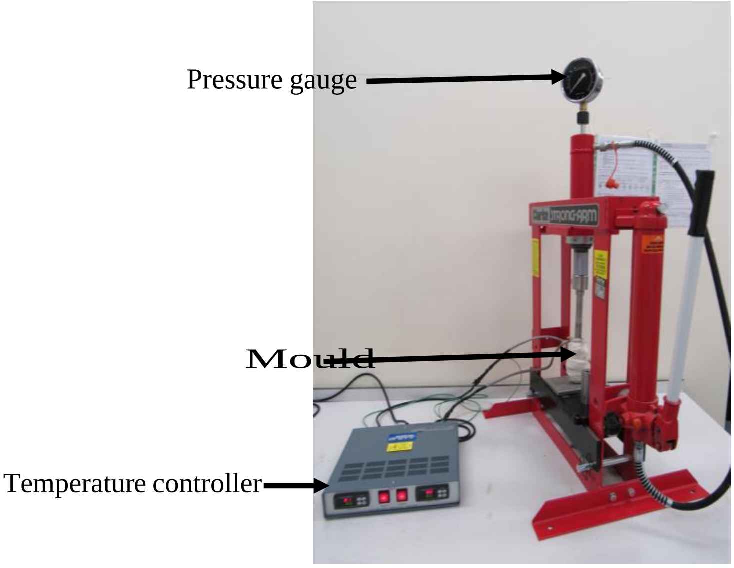


Fig 3.1: Briquetting machine

Prepared bean straw and maize cob were briquetted over moisture content (7.14-16.94%), temperature (20-80°C), particle size (<2.36 mm and <4.00 mm i.e. the sieve sizes which were available) and pressure (100, 150, 200, 250MPa. This range of pressure has previously been used for briquetting several biomass materials (Križan et al., 2015, Demirbas and Sahin-Demirbas, 2004). The maximum compacting temperature (80°C) used in this study was near the glass transition temperature of maize cob (80°C) and bean straw (70°C) because compacting around glass transition temperature aids plastic deformation which is essential in the formation of permanent bonds between particles (Kaliyan and Morey, 2010b).

Crushed bean straw and maize cob (both of particle size <4.00 mm) were mixed in the ratios of 100:0, 75:25, 50:50, 25:75 and 0:100 bean straw:maize cob on a weight basis. The effect of bean straw: maize cob blend on briquetting properties was assessed. Bean straw-maize cob mixtures were compressed at compacting pressure/temperature of 200MPa/80°C (i.e. the optimal pressure/temperature identified for both bean straw and maize cob) or 150MPa/50°C (i.e. to assess the possibility of minimising the energy requirement) and a particle size of <4.00mm which was optimal for both maize cob and bean straw.

About 7±0.05g of ground maize cob or bean straw or bean straw-maize cob mixture was fed inside the mould and manually compressed using a 10 ton Hydraulic Bench Press (Clarke CSA10BB). A dwell time (i.e. duration for which particles under compression remain under maximum/required compacting pressure during briquetting) of 20s was chosen for all experiments to minimise briquette relaxation (Panwar et al., 2010, Chin and Siddiqui, 2000) that may have negative impacts on briquette properties. Briquettes were stored in an air tight container at room temperature (approximately 20^oC) for 7 days to allow stabilisation (Wilaipon, 2009) prior to analysis of their properties (density, impact resistance and compressive strength).

3.1.3 Torrefaction

Torrefaction of bean straw and maize cob were studied within a range of temperature of 200-300^oC and holding time of 0-90 min to determine the effect of temperature and holding time on yields and properties of torrefaction products. These range of torrefaction parameters were reported in the literature for different biomass materials (Wannapeera et al., 2011, Zheng et al., 2013, Mamvura et al., 2018). Bean straw and maize cob were cut to <2cm and 0.5cm respectively. Maize cob was oven dried (as described in subection 3.1.1 materials) to moisture content of ~12% while the moisture content of bean straw was ~10.63%. Torrefaction was carried out in a 14cm internal diameter and 28cm height 316 stainless steel reactor (Fig 3.2). About 40g of dried maize cob or bean straw was fed in the reactor and heated to a desired temperature (200, 250^oC or 300^oC) at a heating rate of 2^oC min^{-1} and a fixed N_2 flow rate of 60cm^{3}min^{-1} (sufficient flow rate to carry the volatile component out of the hot reactor zone). As soon as the desired temperature reached, the sample was held for a period of time (i.e. 0, 30, 60 or 90 min). The evolved volatiles were cooled down in a condenser maintained at 0^oC in ice and the non-condensable gas samples were collected in gas bags for GC analysis at intervals of 30 min for the 90 mins of holding time. The solid and condensed (liquid) products were collected for analysis when the reactor temperature was below 50^oC. 3 replicates of each experiment were performed. Statsitical significance of the impact of torrefaction temperature and holding time and their interactions on yields of torrefaction products (char, liquid and gas) were analysed using Minitab 17 at a significance level of α=0.05, based on a 2-level factorial design of experiment (Appendix A 2).

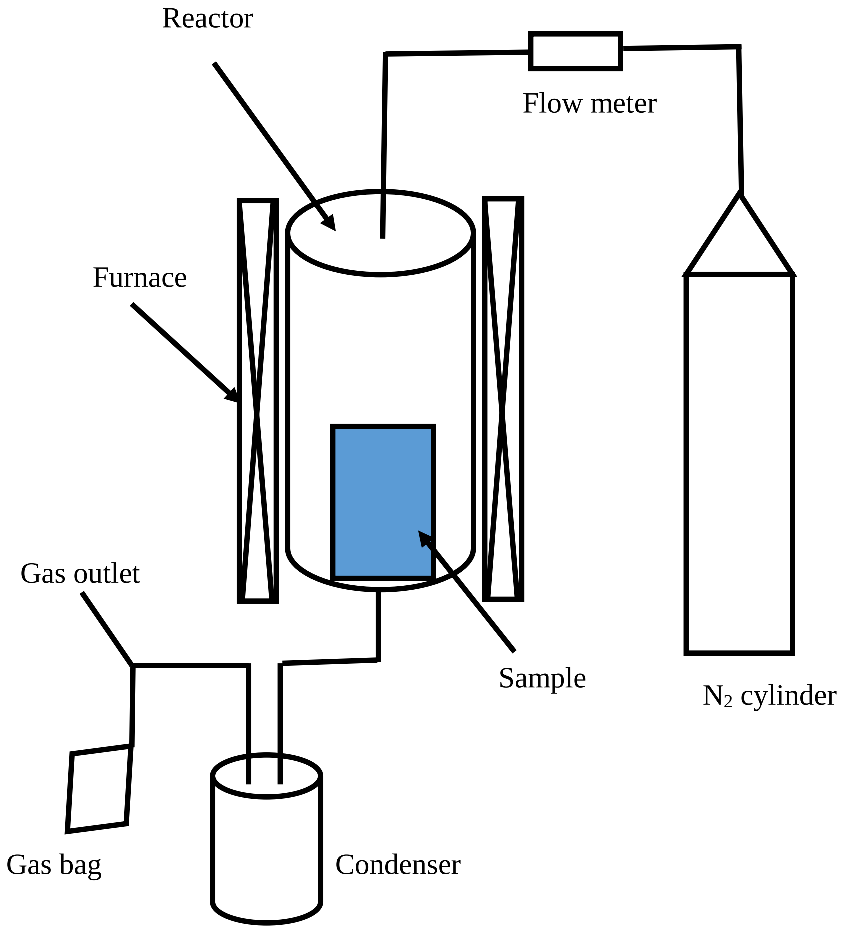


Fig 3.2: Experimental setup for dry torrefaction

3.1.4 Characterization of briquettes and torrefaction products

Proximate analysis such as moisture, ash, volatile matter and fixed carbon content of maize cobs and bean straw briquettes and char were determined according to BS1016-6 standards (Appendix A 3). Ultimate analysis (i.e. CHN) was carried out using a Carlo Erba 1108 Elemental Analyser. Each sample was burnt in an oxygen reach chamber. The product gas was passed through a copper contact (where NO and NO_2 were reduced to N_2) and through gas chromatography column (for separation of the gaseous product) and detected by thermal conductivity detector. High heating value (HHV) was determined using a CAL2K ECO bomb calorimeter (quick and accurate compared to the use of formula/model). About 0.5g of an oven dried sample in a crucible was loaded in a vessel of the calorimeter. The bomb was closed and charged up to 30 atm with oxygen. The bomb was then operating to ignite by itself to burn the sample after which the calorific value was read from the screen. Scanning electron microscopy (SEM) analysis was carried out using a TM3030 Hitachi Microscope to identify morphological/structural changes which occurred after pre-treatment or pyrolysis. The TM3030 Hitachi Microscope does not require gold coating of samples unlike other SEM machines such as Jeol JSM-6390LV. A sample attached to a platen using conductive carbon adhesive tape was placed inside a SEM holder and its image was viewed from a monitor. Differential Scanning Calorimetry (DSC) analysis was carried out using a DSC Q20 model to identify the range of compacting temperatures to be used in the briquetting experiments. About 6mg of sample was loaded into Tzero low mass pan and placed on one heating plate. An empty pan was put on the reference plate. The experiment was carried out at heating rate of 5 ^{o}C/min and nitrogen flow rate of 50 ml min^{-1}. DSC thermo-gram was generated using TA universal analyzer software. Analysis of neutral detergent fiber (NDF) was carried out by enzymatic gravimetry. Starch in feedstock was converted to soluble sugars by the action of α-amylase after de-fatting of the sample with petroleum spirit. The residue was boiled with a neutral solution and the soluble nutrients were separated from those which require microbial fermentation to make them available. The insoluble matter remaining was designated as NDF. While acid detergent lignin (ADL) and acid detergent fiber (ADF) were analysed using an Ankom 220 analyser. Each feedstock was de-fatted and digested with acid detergent. The residual organic matter was recorded as Acid Detergent Fibre. The residue from the Acid Detergent Fibre determination was dissolved using 72% sulphuric acid and the residue that remained was acid detergent lignin. The composition of cellulose, hemicellulose and lignin were subsequently determined (Mullen et al., 2010):

$$\text{Cellulose} = \text{Neutral detergent fiber (NDF)} - \text{Acid detergent lignin (ADL)} \tag{3.1}$$

$$\text{Hemicellulose} = \text{Neutral detergent fiber (NDF)} - \text{Acid detergent fiber (ADF)} \tag{3.2}$$

$$\text{Lignin} = \text{Acid detergent lignin (ADL)} \quad (3.3)$$

Density defined as the ratio of mass to volume was determined using the stereometric method which allows briquettes to be used for thermo-chemical applications to remain dry (Rabier et al., 2006). Briquette mass was measured by an analytical balance (Radwag AS220/C/2: error ±0.1mg). Height and diameter of a briquette was measured using a digital vernier calliper (error: ± 0.005 mm) to determine volume. For impact resistance, a briquette was released 4 times from a height of 1.85 m to fall freely under gravity onto a metallic plate to determine impact resistance (Ndindeng et al., 2015). Percentage residual weight of briquettes was determined after each drop. The remaining piece with the highest weight was taken as the residue and used for the next drop. Impact resistance was defined as the percentage residual weight after the 4th drop.

Compressive strength was determined via both the cleft and simple pressure tests using a Tinius Olsen H50KS compressing machine. Briquettes were placed between two flat parallel surfaces with surface area greater than the briquette. Briquettes were placed horizontally for the cleft test and vertically for the simple pressure test. An increasing load was then applied to compress briquettes at a rate of 1 mm min^{-1} until the briquette failed/cracked. The ultimate load at the point where the briquette cracks, F was used to calculate the compressive strength using Equations (3.4) and (3.5).

$$Compressive\ strengt, \sigma = F/A \quad (3.4)$$

$$Compressive\ strength, \sigma = F/l \quad (3.5)$$

Where A and l are the cross-sectional area (m^2) and length (m) of briquettes.

The impact of pressure, moisture content, particle size and temperature and their interactions on density, impact resistance and compressive strength of briquettes were analysed using Minitab 17 at a significance level of $\alpha=0.05$ baesed on a 2 level factoral design of experiment (Appendix A 4 and Appendix A 5).

Density, pH and water content of the liquid product from torrefaction were measured using density meter (Mettler Toledo Densito 30 Px), pH meter (Mettler Toledo LE409) and 915 Karl-Fisher Ti-

Touch titrator with Hydranal-methanol dry (titration solvent) and Hydranal composite -5 (titration reagent). Fourier transform infrared radiation (FTIR) analysis of the liquid and solid products (grounded to <0.25mm size) was carried out using Cary 630 FTIR. Grindability of raw and torrefied maize cob and bean straw were determined in terms of particle size distributions. The raw and torrefied maize cob and bean straw (measured in a 200 cm^3 container) was crushed using a HGBTWTS3 laboratory blender 8010ES (for fixed grinding time of 20s) and separated using 1.00-4.00 mm sieves with a Retsch sieve shaker AS 200 (for fixed sieve time of 10 min).

Gas composition was analyzed by a Varian 450 GC with thermal conductivity detector (TCD) and flame ionization detectors (FID). The GC consists of 2 ovens with the first oven housing 3 columns (Hayesep T0.5mx1/8" ultimetal, Hayesep Q0.5mx1/8" ultimetal and Molsieve 13X1.5mx1/8" ultimetal) to detect permanent gases. The second oven housed two columns: a CP-SIL 5CB FS 25X.25 (0.4mm ID) for detecting hydrocarbons and a CP-WAX 52CB FS 25X.32 (1.2mm ID) for detecting oxygenated compounds. The first oven was maintained at a temperature of 100 ^{o}C, while the second oven temperature was changed from 40-120^{o}C i.e. initial temperature of 40^{o}C, held for 2 min; 40-50^{o}C at heating rate of 0.5 ^{o}C min^{-1}; 50-100^{o}C at heating rate of 8 ^{o}C min^{-1}, 100-120 ^{o}C at heating rate of 10 ^{o}C min^{-1}.

GC-MS analysis of liquid product was performed on an Agilent 7890A GC split/split less injector (280°C) linked to a Agilent 5975C MSD (electron voltage 70eV, source temperature 230°C, quad temperature 150°C, multiplier voltage 1000V, interface temperature 310°C). Separation was performed on a Restek fused silica capillary column (50m x 0.32mm i.d) coated with 0.17µm dimethyl polysiloxane (RTx-1) phase. The GC was temperature programmed from 30-310°C at 5°C min and held at final temperature for 20 minutes with Helium as the carrier gas (flow rate of 1ml min $^{-1}$, initial pressure of 12kPa, split at 30 mls min^{-1}). Peaks were identified and labelled after comparison of their mass spectra with those of the NIST05 library if > 90% fit and from their elution order or chemistry literature. At least 3 replicates were performed for the characterization of briquettes and torrefaction products.

3.2 Results and discussion

3.2.1. Briquetting

3.2.1.1 Fuel characteristics of maize cobs and bean straw

Bean straw had moisture content of 10.63±0.88% whereas fresh maize cobs had high moisture content (76.0±3.3%), which is much higher than in other work e.g. 30.3% (Umogbai and Iorter, 2013). The high moisture content is likely due to the use of fresh maize cobs which were harvested at an early stage of maturity (R3 i.e. milk stage) and also stored at 0-5°C prior to analysis. They cannot be used directly for briquetting according to European Standard Committee CEN/TC 335 for solid fuels as the moisture content in briquettes is required to be 5-15%. In addition, high moisture feedstock/products are prone to fungal decomposition during transportation and storage (Matúš et al., 2015) and poor combustion properties such as low heat output, low combustion temperature, and long fuel residence time in the combustion chamber (Miranda et al., 2015). Therefore, the fresh maize cobs were therefore dried/partly dried prior to being briquetted. Maize cob (Table 3.1) had high volatiles (~80.7%) and low ash content (3.0%), which agreed well with other work (Shah et al., 2012, Du et al., 2015). Fresh maize cobs had a similar HHV to that of woody materials, around 18 MJ/kg.

Table 3.1: Characteristics of maize cobs and bean straw

Property	Maize cob	Bean straw
Proximate properties (dry basis)		
Ash (%wt)	3.0 (±0.5)	6.2 (±0.7)
Volatile (%wt)	80.7 (±0.7)	72.7 (±4.9)
Fixed carbon* (%wt)	16.3(±0.9)	21.1 (±4.9)
Ultimate properties (dry and ash free)		
C (%)	46.6 (±1.9)	45.0 (±2.6)
H (%)	7.7 (±1.2)	5.8 (±0.0)
N (%)	2.1 (±0.6)	2.0 (±1.0)

Property	Maize cob	Bean straw
Ultimate properties (dry and ash free)		
O* (%)	43.6 (±2.3)	47.2(±2.8)
High heating value (HHV) (MJ/kg)	18.9 (±0.1)	17.3 (±1.0)
Cellulose (%)	17.7	21.4
Hemicellulose (%)	29.4	19.6
Lignin (%)	1.5	10.2
Extractives (%)	51.4	48.8
Inorganic composition		
B (µg/g)	7.2	102.2
Na (µg/g)	12.9	2523.8
Mg (µg/g)	778.8	1939.8
Al (µg/g)	-	9.3
P (µg/g)	351.8	68.1
K (µg/g)	3854.5	4014.6
Ca (µg/g)	375.4	18047.9
Sc (µg/g)	0.2	0.1
Ti (µg/g)	0.6	0.9
V (µg/g)	0.3	0.3
Cr (µg/g)	2.1	1.1
Mn (µg/g)	13.3	26.6
Fe (µg/g)	-	53.6
Co (µg/g)	-	0.1
Ni (µg/g)	0.6	0.6
Cu (µg/g)	19.0	46.6
Zn (µg/g)	33.7	36.3
Ga (µg/g)	0.2	4.7

Property	Maize cob	Bean straw
Inorganic composition		
As (µg/g)	0.2	-
Rb (µg/g)	1.4	3.6
Sr (µg/g)	1.2	49.5
Mo (µg/g)	0.2	-
Sn (µg/g)	0.4	0.5
Ba (µg/g)	2.8	91.6
Ce (µg/g)	-	0.1
Pb (µg/g)	2.2	2.1

* by difference

Nonetheless, maize cob ash content was lower than that of bean straw and some other feedstocks such as sawdust (6.12%) (Prasityousil and Muenjina, 2013), wheat straw (13.6%) (A Demirbaş, 1999), and rice husks (19.6%) (Muazu and Stegemann, 2015). Nitrogen content in maize cob and bean straw were higher than that in wheat straw (0.61%), mango leaves (1.06 %), eucalyptus leaves (0.77 %) (Panwar et al., 2010) and switchgrass (0.48%) (Gilbert et al., 2009). The nitrogen could end in the char after pyrolysis and could be a sort of nutrient if char is used as fertilizer. A slightly higher HHV for maize cob than for bean straw is due to the high carbon content (46.6 %) and low ash content.

Bean straw ash content was about double that of maize cob (Table 3.1). Inorganic elements determine formation of deposits, fly ash emissions and ash melting point during combustion (Moreno et al., 2016). Potassium (K), sodium (Na), silicon (Si) and aluminium (Al) decrease the ash melting point while calcium (Ca) and magnesium (Mg) increase the ash melting point. Furthermore, increasing K content increases aerosol formation during combustion and hence fouling inside boilers and increased particulate emissions (Obernberger and Thek, 2004, Moreno et al., 2016). Variations in the effect of the inorganic elements on ash melting point are likely due to variation in their melting temperatures. Generally, the composition of the inorganic elements was higher in bean straw than in maize cob (Table 3.1). This demonstrates the variability in biomass properties which may indicate requirement for varying optimal conditions for processing different biomass materials for energy. Ca, K, Na, and Mg were the dominant inorganic elements in bean straw while K, Mg, Ca and phosphorous (P) were the dominant inorganic elements in maize cob. Mullen et al., (2010) also reported that the inorganic fraction of maize cob was predominantly K which in this study is over 3 times the concentrations of Ca and Mg combined which is likely to lower the ash melting point of maize cob. While the high Ca concentration in bean straw is likely to increase the ash melting point of bean straw. The K concentration is high in both bean straw and maize cob which may increase aerosol formation during combustion and hence fouling inside the boiler and increased particulate emissions (Obernberger and Thek, 2004). However, the content of the alkali metal (K and Na) may be reduced by leaching these biomass materials with water (Moreno et al., 2016). The content of heavy metals such as As, Cr, Cu, Pb and Zn were determined as a requirement by the German standard DIN 51731. The concentrations of heavy metals in both maize cob and bean straw were within the acceptable limits by the German standard DIN 51731 i.e. As <0.8mg/kg, Cr < 8mg/kg, Pb < 10mg/kg and Zn < 100mg/kg, except Cu >5mg/kg,. Heavy metal content is required to be as low as possible as it affects ash quality and particle emissions (Obernberger and Thek, 2004). Therefore, fuel ash content has to be minimised for process efficiency (Obernberger and Thek, 2004).

3.2.1.2 Differential scanning calorimetry (DSC) Analysis

Differential scanning calorimetry analysis was carried out to identify the glass transition temperature of maize cob and bean straw. The glass transition temperature of bean straw was ~70^{o}C. However, no transition steps were observed for maize cob (Fig 3.3a) mostlikely due to interference from moisture endothermic at ~100^{o}C (Ruiz et al., 2013). Based on the findings of Karunanithy et al., (2012), glass transition temperature of corn stover was 79 ^{o}C, and therefore a maximum compacting temperature of 80 ^{o}C was chosen for this study. Compacting around the glass transition temperature aids plastic deformation which is essential in the formation of permanent bonds between particles (Kaliyan and Morey, 2010b).

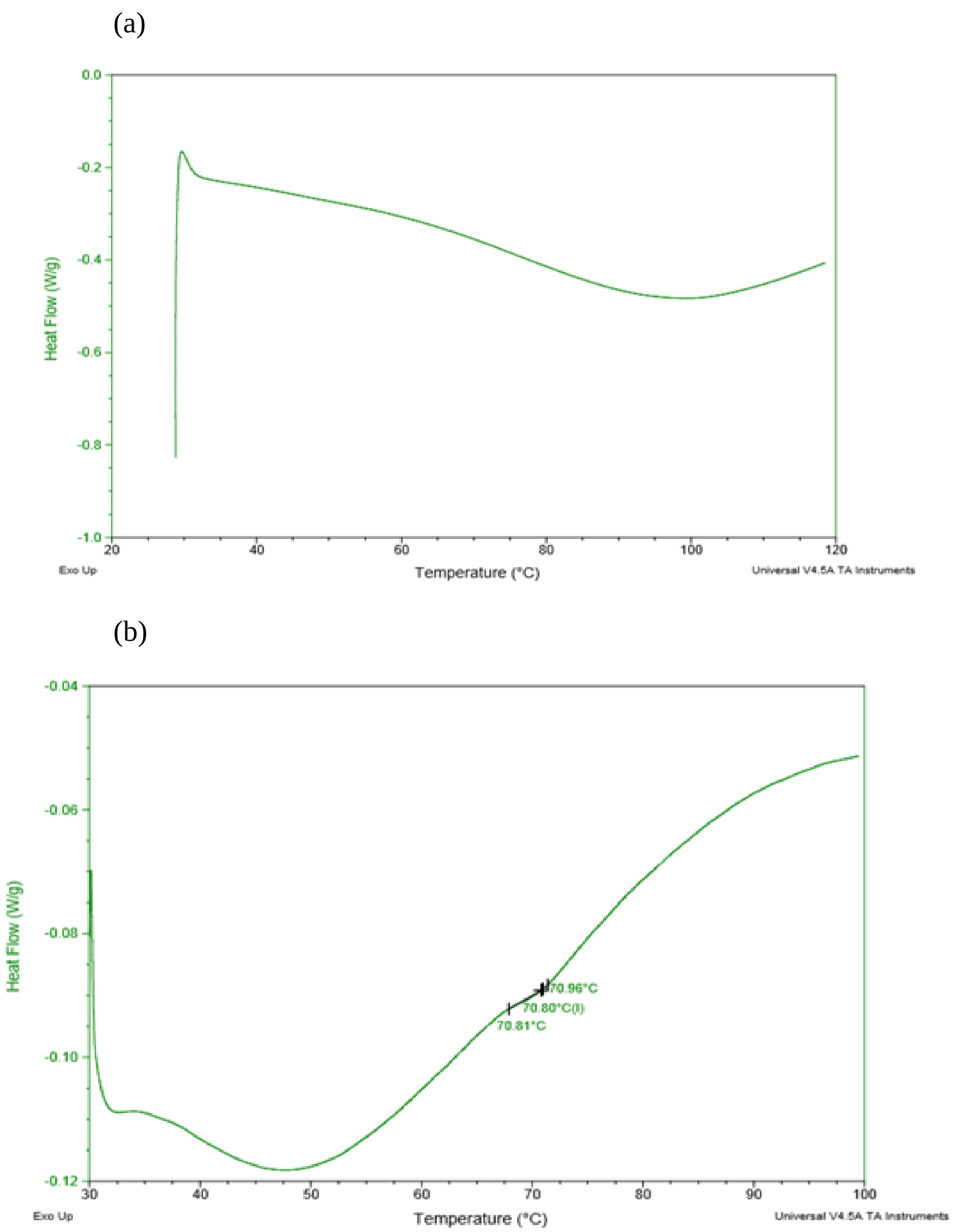


Fig 3.3: Differential scanning calorimetry thermo-grams for (a) maize cob and (b) bean straw

3.2.1.3 Effect of briquetting conditions on properties of briquettes

3.2.1.3.1 Density

Density is an important property that directly relates to the energy to volume ratio of briquettes (A Demirbaş, 1999) and is key in determining the handling, transportation (reducing logistic costs), ignition and combustion characteristics (Sotannde et al., 2010). However, increasing density reduces porosity thereby reducing air penetration, hence reducing combustion rate and heat release (Faizal et al., 2010). The extent of this impact is feedstock and briquetting condition (i.e. pressure, temperature and particle size) dependent. Density of maize cob briquette ranged between 516 kgm^{-3} and 1058.2kgm^{-3} with variations in briquetting parameters used in this study. The lowest density of 516 kgm^{-3} was obtained at a pressure of 150MPa, temperature of 20 ^{o}C, high moisture content of 16.94 % and a particle size <4.0 mm. Apart from operating conditions of 250 MPa, particle size <2.36 mm and 80^{o}C, all maize cob briquettes produced from feedstock containing moisture content of 16.94% had density below 1000 kg m^{-3} (Fig 3.4a), which falls below the range of 1-1.4 gcm^{-3} required to meet the German Standard DIN 51731. Density of maize cob briquettes remained in a range of 1054.4-1058.2 kgm^{-3} from particle size of <2.36 mm, moisture content of 7.14% and pressure of 200-250 MPa. This could be due to a reduction in void spaces between particles and an increase in inter-particle bonding at high pressures i.e. > 200 MPa. This trend is consistent with results reported for briquettes from palm oil mill residues (Faizal et al., 2010) and pine (Križan, 2007).

At low moisture content (7.14%), compacting pressure and temperature had little effect on maize cob briquette density, i.e. less than 4 % increase for particle sizes <2.36 mm but significantly influenced (20% increase in density) for a particle sizes <4 mm when increasing pressure from 150MPa to 200MPa. In contrast, at high moisture content (16.94%), increasing pressure and temperature significantly increased density for all particle sizes which was due to the combined effect of high pressure and heat softening the particles and evaporating moisture. Therefore, with maize cob feedstock at moisture content 7-8%, high density briquettes (≥ 1000 kgm^{-3}) could be produced at either 150 MPa/80 ^{o}C or 200 MPa/20 ^{o}C for particle size <2.36 mm whereas a pressure >200 MPa for particle size <4 mm was required. At high moisture content (16.94 %), briquettes with a density ≥ 1000 kgm^{-3} could only be produced at particle sizes <2.36 mm and high pressure and temperature i.e. 250 MPa and 80 ^{o}C.

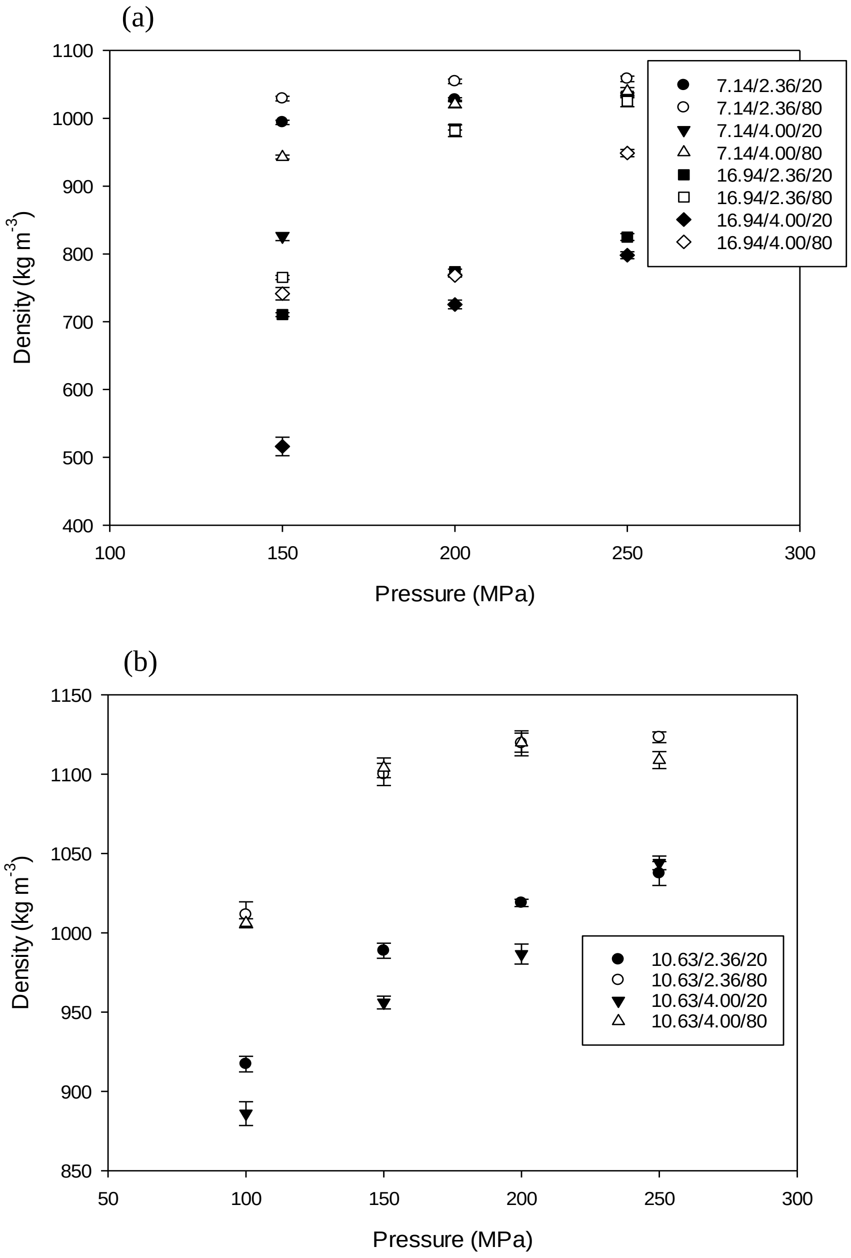


Fig 3.4: Effect of pressure on (a) maize cob and (b) bean straw briquette density (legend: moisture content (%)/particle size (mm)/ compacting temperature (^{o}C)).

Density of bean straw briquettes was higher than that of maize cob, ranged between 886.0-1123.3 kg m^{-3} over tested briquetting parameters (compacting pressure: 100-250MPa, temperature: 20-80^{o}C, particle size: <2.36-<4mm) (Fig 3.4b). The lowest density of 886 kgm^{-3} was produced at a low compacting temperature of 20 ^{o}C with a large particle size <4mm and a low pressure of 100MPa whereas the highest density (1063.0-1123.3kg m^{-3}) was produced at both tested particle sizes (<2.36 mm and <4.00mm), pressure $\geq$ 150MPa and high temperatures (50-80^{o}C). All briquettes produced at a temperature of 20 ^{o}C and a pressure range of 100-200 MPa and large particle size (<4.00 mm) did not meet the German Standard DIN 51731. Irrespective of the compacting pressure and particle size, all bean straw briquettes produced at a high compacting temperature (80^{o}C) had density >1000 kg m^{-3}.

Both maize cob and bean straw briquette densities increased with increasing temperature and pressure (Fig 3.5a Fig 3.6a). Increasing particle size and moisture content caused a reduction in briquette densities (Fig 3.4, Fig 3.5a). Increasing temperature above 50^{o}C had little effect on bean straw briquette density (Fig 3.6a), indicating that briquetting temperature of 50-80 ^{o}C could be used to produce high-density bean straw briquettes. Temperature and pressure were the predominant factors (Fig 3.6a) affecting bean straw briquette density (agreed well with findings on tropical hardwood sawdust briquettes (Mitchual et al., 2013) whereas moisture content and pressure were the predominant factors affecting maize cob briquette density. However, Zhang and Guo, (2014) found that particle size (0.16-5mm) and moisture content of 5-17% were the predominant factors affecting density of *Caragana Korshinskii Kom* briquettes within a range of compacting temperatures of 70-150 ^{o}C and compacting pressure of 10-170 MPa. Rhén et al., (2005) reported that density of spruce pellet was predominantly affected by moisture content (6.3-14.7 %) and compacting tempearture (26-144 ^{o}C) for particle size <3.15 mm and compacting pressure of 46-114 MPa. A similar observation was reported (Carone et al., 2011) on density of olive tree pruning residue pellets produced from various particle size ranges <1 mm to <4 mm, moisture content of 5-20%, compacting temperature of 60-150^{o}C and pressure of 71-176 MPa. Variable results for factors affecting briquette density are likely due to variation in feedstock properties in addition to which many of the comparative studies have mainly focused on the effects of single factors rather than looking at the interaction between them.

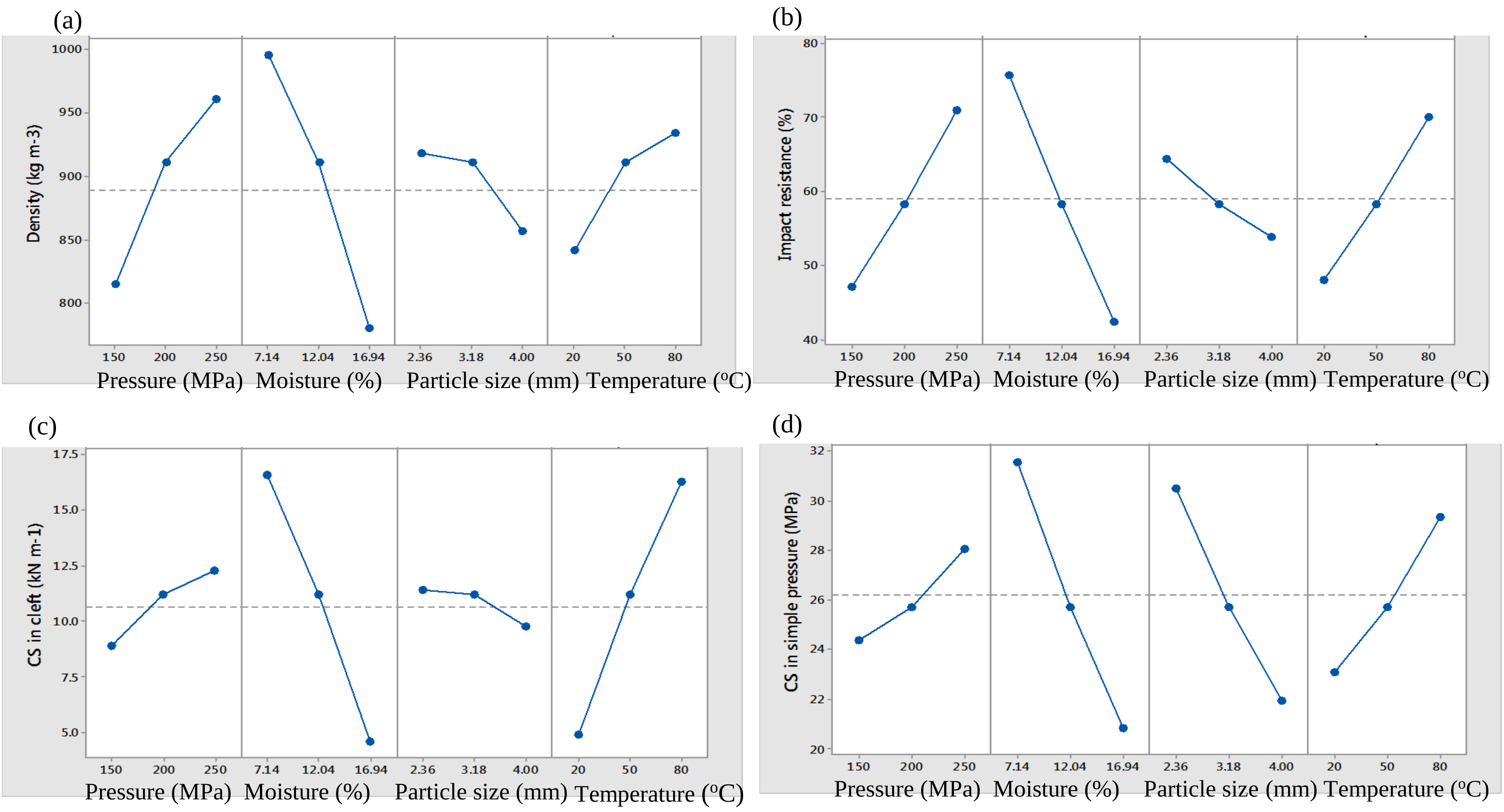


Fig 3.5: Effects of briquetting parameters: pressure, moisture content, particle size and temperature on (a) density, (b) impact resistance, (c) compressive strength (CS) in cleft and (d) compressive strength in simple pressure of maize cob briquettes.

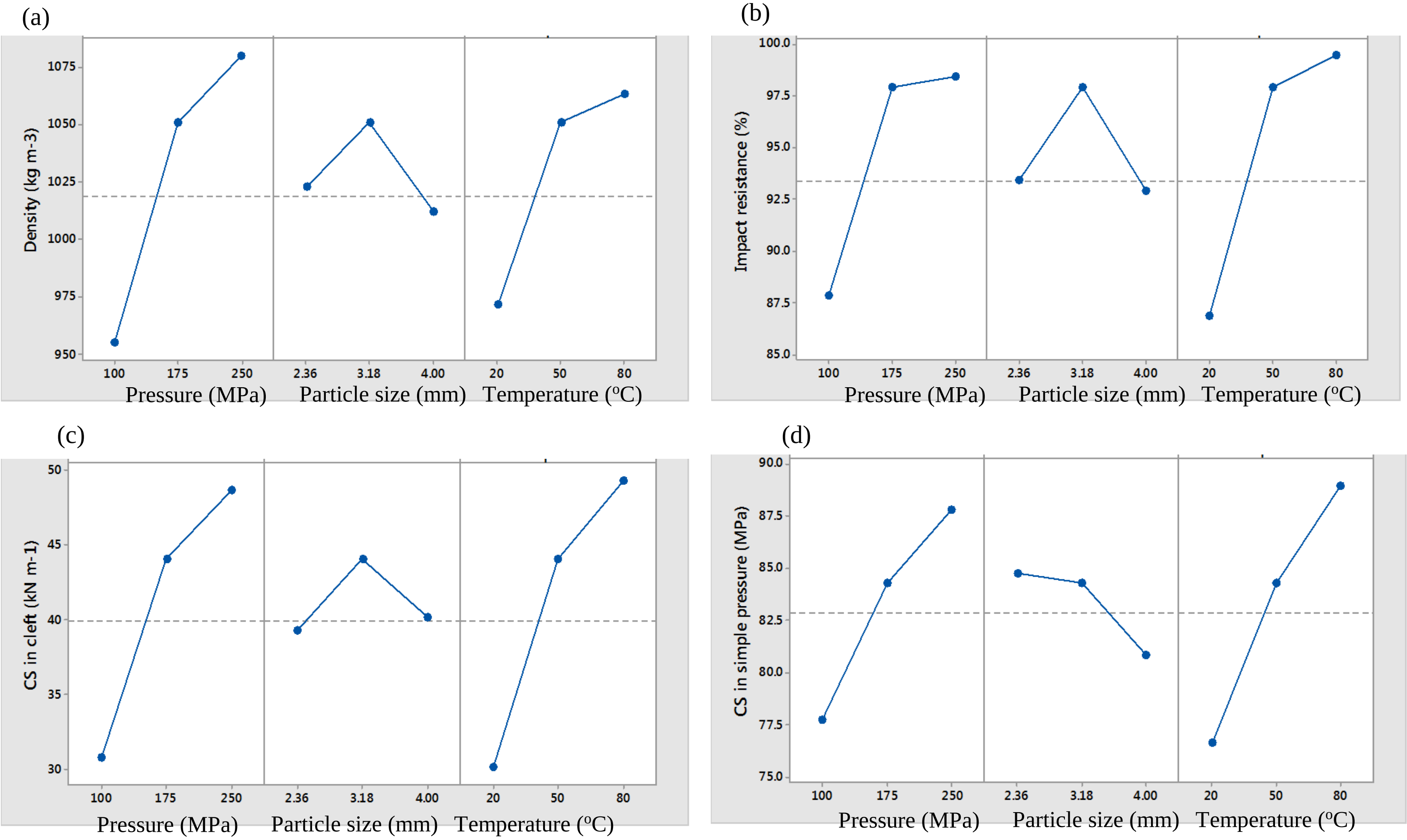


Fig 3.6: Effects of briquetting parameters: pressure, particle size and temperature on (a) density, (b) impact resistance, (c) compressive strength (CS) in cleft and (d) compressive strength (CS) in simple pressure of bean straw briquettes.

All interactions between briquetting variables such as pressure×moisture and pressure×particles (Fig 3.7a, Appendix A 6) had significant impact on density of maize cob briquettes ($P<0.05$) except for the interaction between moisture and particle size. Briquettes produced at around 16.94% moisture content and pressure <250 MPa (Fig 3.4a) had a density below the German Standard (DIN 51731) for pellets (1-1.4 gcm^{-3}) regardless of particle size and compacting temperature. This is likely due to the incompressibility of water that prevents particles from being completely flattened at high moisture content. Low briquette density could have been attributed to a reduction in briquette weight or an increase in briquette volume upon drying and stabilizing. It was also observed that a high proportion of large cracks (Fig 3.9) were formed in briquettes produced at high moisture content i.e. 16.94%. Matúš et al., (2015) also reported appearance of cracks on spruce briquettes produced at a moisture content >16.5 % with a particles size of <0.5mm and >4mm.

Similarly, bean straw briquettes are affected by all variables and their interactions (Fig 3.8a, Appendix A 7) except for the particle size × temperature. Density of bean straw briquettes decreased when increasing particle size only at low compacting temperature (20^{o}C) and compacting pressure of 100-200 MPa (Fig 3.4b). This could be due to high resistance to plastic deformation of particles at these conditions. Therefore, high pressure (250MPa) is required to crush and bind large particles (<4.00mm) together, producing equally high density briquettes as those formed from a particle size <2.36mm. At low compacting temperature (20^{o}C), density increased with increasing compacting pressure (100-250MPa) (Fig 3.4b), which is consistent with briquettes from waste paper and wheat straw (A Demirbaş, 1999), palm kernel cake pellet (Razuan et al., 2011), beech sawdust (Križan et al., 2015) and neem powder and sawdust (Rajaseenivasan et al., 2016). The increasing trend in density with increasing compacting temperature (Fig 3.5 and Fig 3.6) from 20-80^{o}C agreed well with other biomass feedstocks e.g. spruce, birch, reed canary grass (Huang et al., 2017), wheat straw and wheat straw extract pellets with an increase from 30-100^{o}C (Stelte et al., 2012).

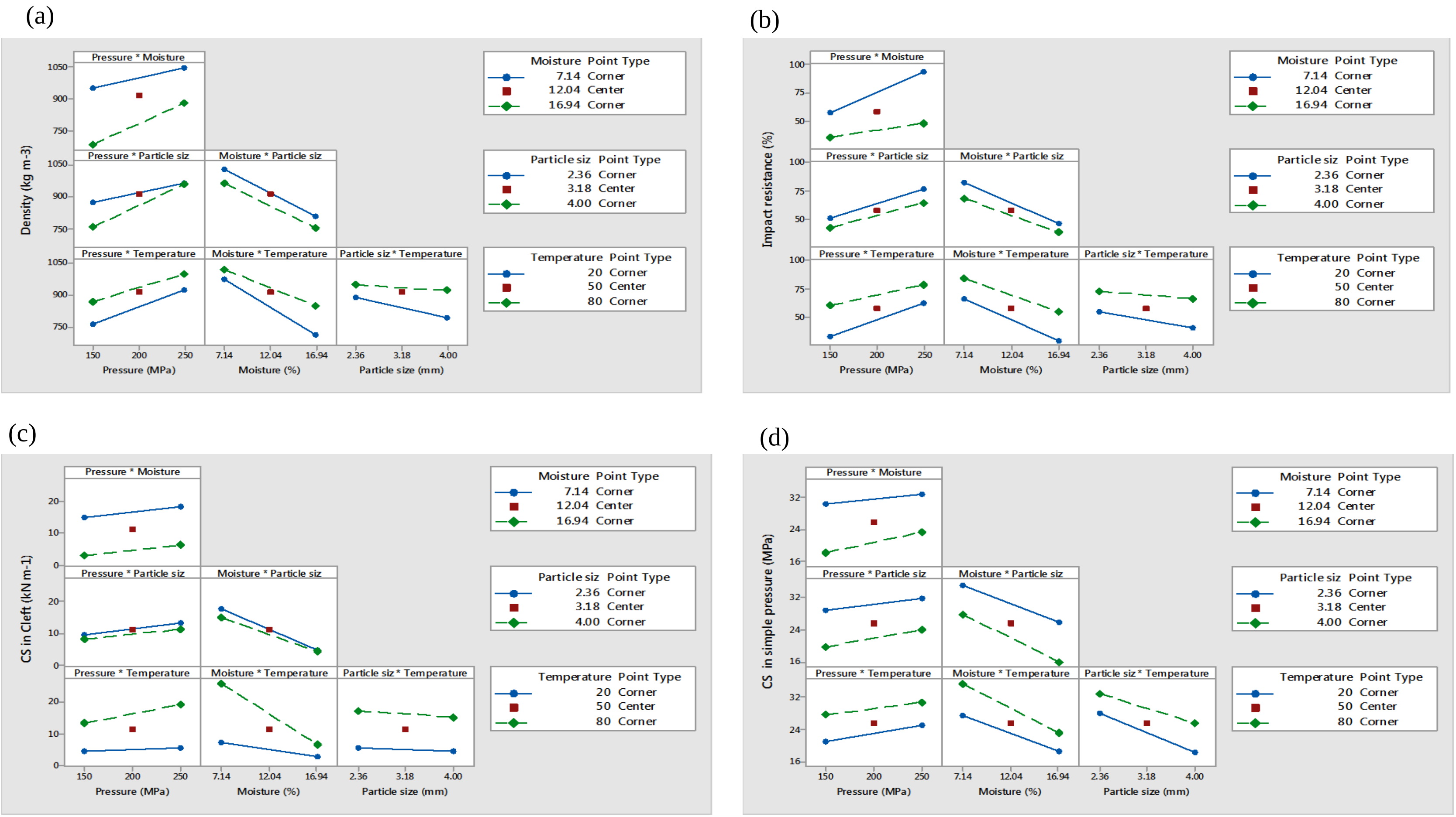


Fig 3.7: Interaction effects of briquetting parameters: pressure, moisture content, particle size and temperature on (a) density, (b) impact resistance, (c) compressive strength (CS) in cleft and (d) compressive strength in simple pressure of maize cob briquettes. Red squares represent the mid-point.

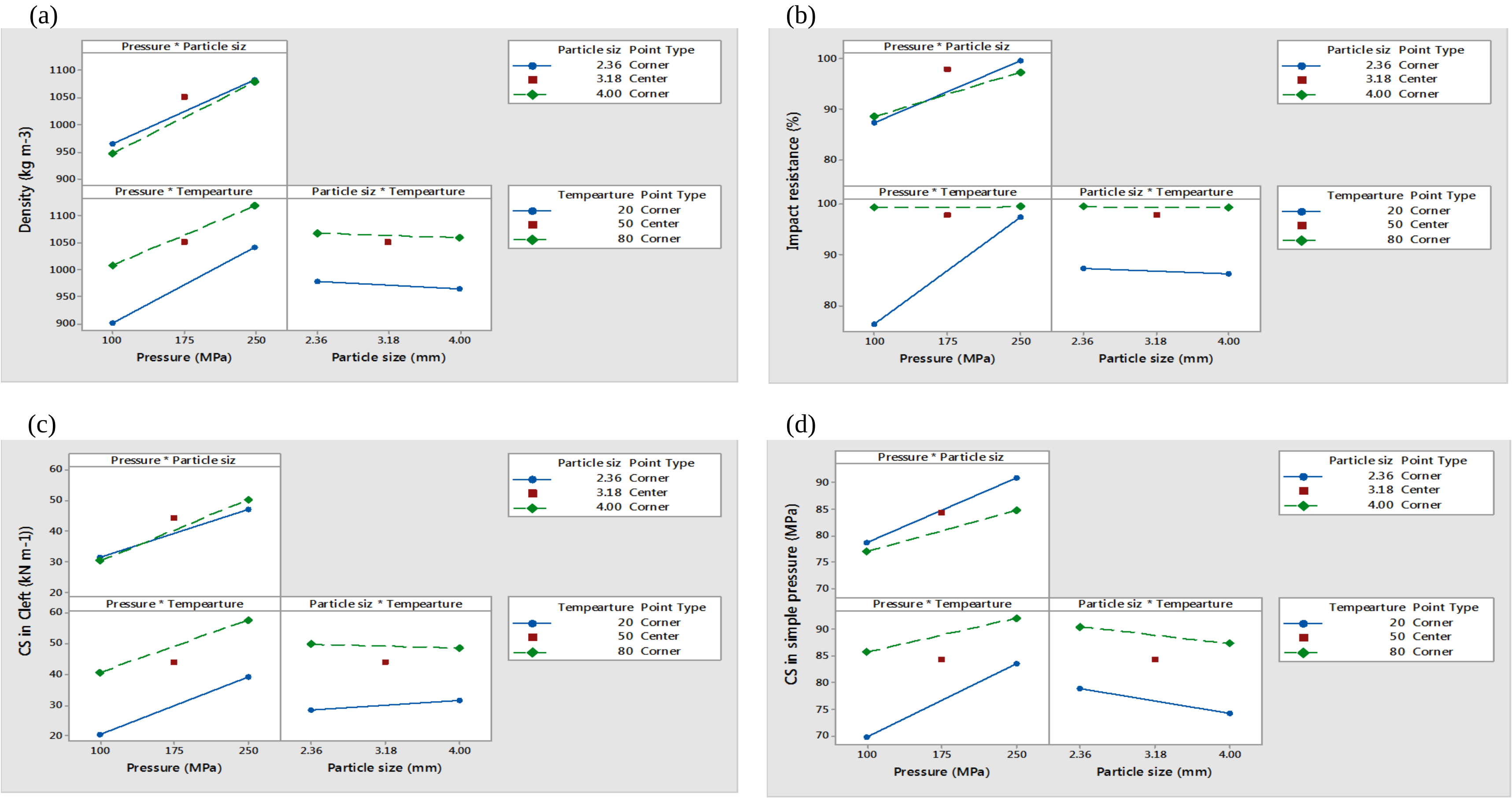


Fig 3.8: Interaction effects of briquetting parameters: pressure, particle size and temperature on (a) density, (b) impact resistance, (c) compressive strength (CS) in cleft and (d) compressive strength (CS) in simple pressure of bean straw briquettes. Red squares represent the mid-point.

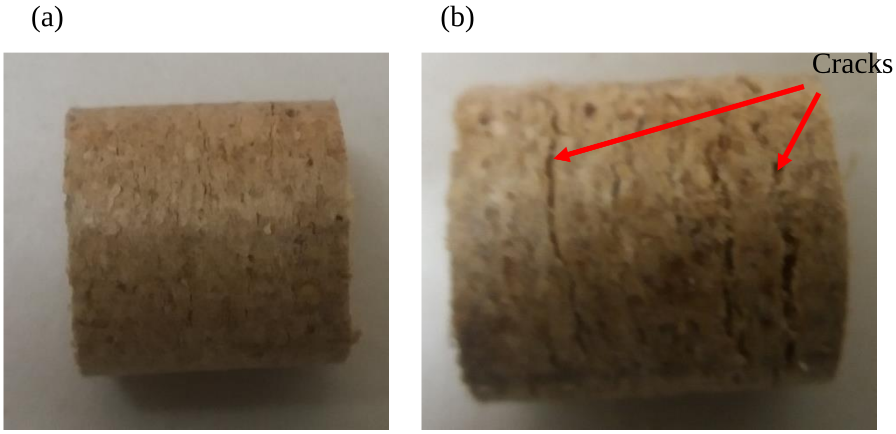


Fig 3.9: Briquettes produced at pressure of 200 MPa, compacting temperature of 80 ^{o}C and particle size of 2.36 mm with moisture content of (a) 7.14% and (b) 16.94 %.

3.2.1.3.2 Impact resistance

Impact resistance is a measure of durability of briquettes which defines the tendency of a briquette to produce dust or break when it is subjected to a destructive force. It is an indicator of mechanical strength (Haykiri-Acma et al., 2013) where briquettes with high impact resistance/durability are desirable to minimise breakage and dust formation during transport and conveying. Impact resistance of >80% is required for high handling and transportation efficiency (Haykiri-Acma et al., 2013, Antwi-Boasiako and Acheampong, 2016).

Impact resistance varied from 17.7 % to 99.8 % for maize cob briquettes (Fig 3.10) and 75.7-99.8% for bean straw briquettes over a range of pressure (100-250^{o}C), particle size (<2.36-<4mm), temperature (20-80^{o}C) and moisture content (7.14-16.94%). Impact resistance of both bean straw and maize cob briquettes increased with increasing pressure and temperature (Fig 3.5b and Fig 3.6b, section 3.2.1.3.1). Particle size had negligible effect on impact resistance on bean straw briquettes (Fig 3.6b section 3.2.1.3.1) but significant on maize cob briquettes (Fig 3.5b section 3.2.1.3.1). The optimal moisture content (7.14%) and pressure (200MPa) for maize cob briquetting were comparable with other studies based on olive waste briquettes (Yaman et al., 2000) and sawdust briquette (Panwar et al., 2010).

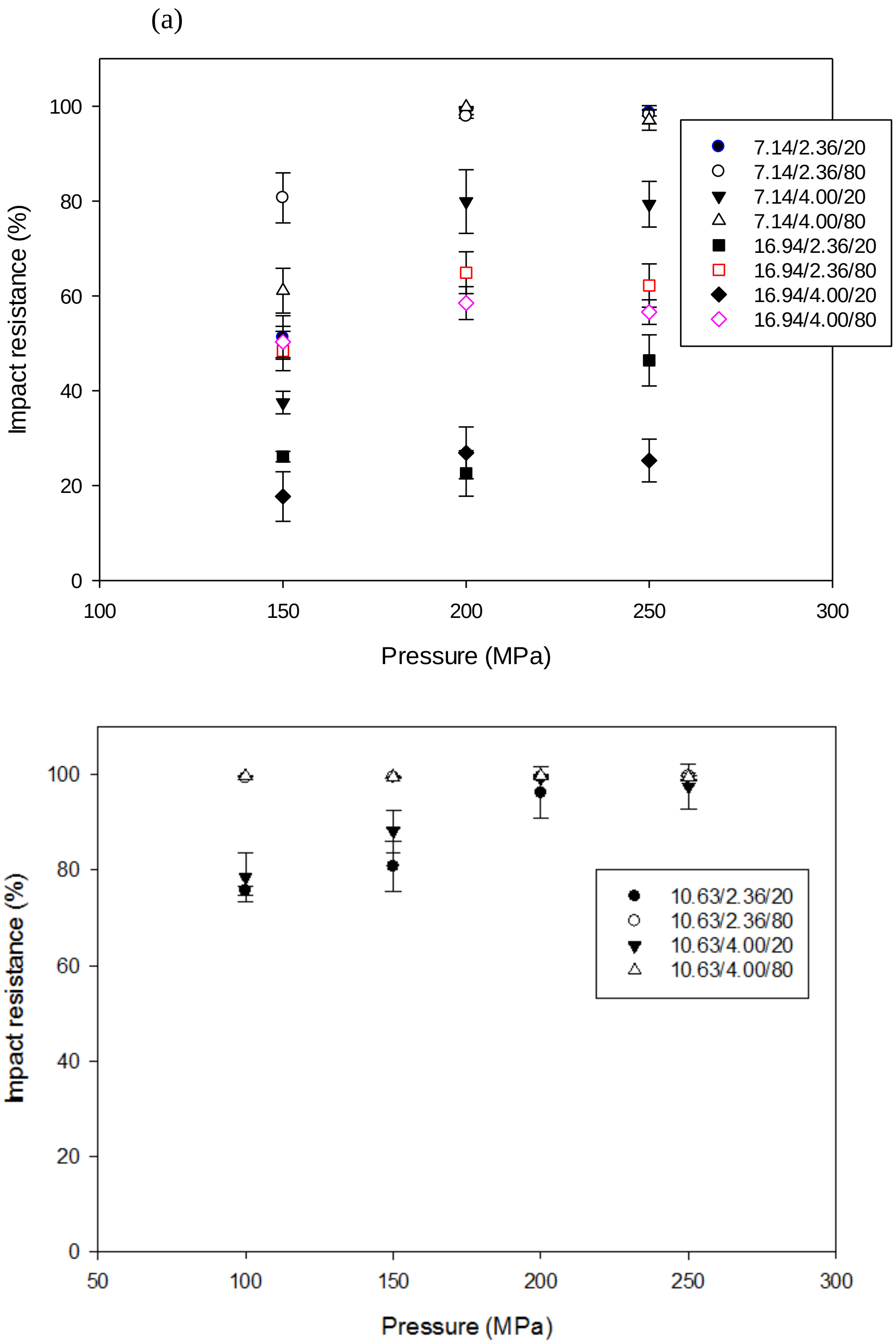


Fig 3.10: Effect of compacting conditions (temperature, pressure) and feedstock properties (moisture content, particle size) on impact resistance of (a) maize cob and (b) bean straw briquettes (legend: moisture content (%)/particle size (mm)/ compacting temperature (^{o}C))

At high temperature and pressure, moisture evaporates and partially hydrolyses hemicellulose, lignin and cellulose to lower molecular mass products which act as binders and improve the mechanical strength of briquettes (Adzic and Savic, 2013). However, very high moisture prohibits complete flattening of particles which lowers inter-particle bonding (Kaliyan and Vance Morey, 2009), causing less stable and weak briquettes. Application of temperature and pressure enhances the diffusion of molecules thus reducing void space and forming solid bridges which increases bonding between particles and hence the strength of briquettes. Lee et al., (2013) also reported that increasing particle size from <1.41mm to 1.41-3.17mm significantly decreased the durability of larch pellets but had no impact on the durability of tulipwood pellets. The authors further found that increasing compacting temperature (120-180^{o}C) significantly increased the durability of pellets from both feedstocks. However, it was also reported (Demirbas and Sahin-Demirbas, 2004) that impact resistance of pulping residue and spruce sawdust briquettes increased with increasing moisture content from 7 to 15 %. From all of the aforementioned studies, it can be concluded that the effect of particle size is feedstock dependent.

At a fixed compacting temperature of 20 ^{o}C, impact resistance of maize cob briquettes derived from high moisture content (16.94%) and particle size <4mm were not influenced by compacting pressure and remained around 20 %. This was due to the incompressibility of water. Decreasing particle size to <2.36mm had little affect on impact resistance at low compacting pressures but led to a significant increase at 250 MPa. This could be due to the heat generated at high compacting pressure enhancing the release of water within small particles, enhancing the binding process. Impact resistance of maize cob briquettes was almost 3 fold higher at 150 MPa when temperature was increased from 20-80^{o}C. There were significant interactions ($P<0.05$) between briquetting parameters on impact resistance of maize cob briquettes (Appendix A 8, Fig 3.7b section 3.2.1.3.1) except for the pressure × particle size, moisture content × particle size × temperature and pressure × moisture content × particle size × temperature interactions.

The impact resistance of bean straw briquettes was above 80%, except for briquettes derived at a low compacting pressure of 100MPa, with particle size <2.36mm and 20°C (Fig 3.10b). All briquettes from maize cob and bean straw with impact resistance <80% lost more than 20% of their weight and therefore are less resistant to the destructive forces experienced during transport and handling. The large amount of fine particles and dust (>20%) generated could cause disturbance to boiler feed systems, lead to reduced efficiency of combustion and increase the risks of fire and explosion during transport, handling and storage (Temmerman et al., 2006). All bean straw briquettes produced at (i) high temperature (80°C) and (ii) high compacting pressure (200-250MPa) had high impact resistance with <2.5 % weight loss. High-quality maize cob briquettes (with impact resistance above 95%) were obtained at (i) small particle size (<2.36 mm), low moisture content (7.14%) and high pressure (>200 MPa) and (ii) high particle size (<4.00 mm), low moisture content (7.14%), high temperature (80°C) and high pressure >200 MPa. These briquettes lost only <3.5 % of their weight after shattering and are therefore durable thus satisfying the European Standard Committee CEN/TC 335 (durability >95 %) and are also suitable for transportation, storage and handling with minimal breakage and dust generation. These highly durable briquettes (impact resistance >95%) would also help minimise health related problems resulting from fine particles/dust (Zainuddin et al., 2014).

Moisture and pressure were the predominant factors affecting impact resistance of maize cob briquettes (Fig 3.5b section 3.2.1.3.1) whereas temperature and pressure were dominant factors affecting impact resistance of bean straw briquettes (Fig 3.6b section 3.2.1.3.1). The interaction between pressure and temperature had a significant effect on impact resistance of bean straw briquettes (Fig 3.8b, Appendix A 9). At compacting temperature 20°C, bean straw briquette impact resistance increased with increasing pressure 100-200 MPa and remained constant with further increase to 250 MPa (Fig 3.10b, Fig 3.6b). This indicates that maximum inter-particle bonding was achieved at a compacting pressure ranging between 200-250MPa at 20°C. Rajaseenivasan et al (2016) also observed an increasing trend in impact resistance of neem powder and sawdust briquettes when pressure was increased from 7 to 33 MPa. At high temperature of 80°C, bean straw briquette impact resistance was independent of compacting pressure and particle size.

3.2.1.3.3 Compressive strength (CS)

Compressive strength is the maximum load that a briquette can withstand before it breaks (Rubio et al., 1999). It is used to estimate the compressive stress resulting from the weight of the top briquettes on the lower briquettes during storage, transport and handling. Compressive strength (CS) tests were performed via both cleft and simple pressure tests. These two tests have been used independently (Muazu and Stegemann, 2015, Ayhan Demirbaş, 1999, Rhén et al., 2005, Lela et al., 2016) to determine compressive strength of briquettes and it was found from this study (Appendix A 10) that there was a strong positive correlation between the two tests. It is recommended (Faizal et al., 2010) that the minimum compressive strength in simple pressure for briquettes is 2.56 MPa to enable storage, transportation and handling with minimum breakage. Compressive strength in simple pressure of all briquettes in this study was above the recommended value (Fig 3.11). The smallest value of 10 MPa was obtained from maize cob briquettes at large particle size (<4 mm), with low compacting pressure and temperature (150 MPa and 20 ^{o}C) and high moisture content (16.94 %).

Moisture content and compacting temperature were the predominant factors affecting compressive strength in cleft of maize cob briquettes whilst simple pressure was mainly affected by moisture content and particle size (Fig 3.5c and d section 3.2.1.3.1). Meanwhile temperature and pressure were the predominant factors affecting both CS in cleft and simple pressure of bean straw briquettes (Fig 3.6c and d section 3.2.1.3.1). CS (both in cleft and simple pressure) increased with increasing pressure and temperature but decreased significantly with increasing moisture content (in the case of maize cob briquettes) and particle size (Fig 3.5c and d, Fig 3.6 c and d, section 3.2.1.3.1; Appendix A 11-Appendix A 14. The CS in cleft of bean straw however did not vary with particle size (Fig 3.6 section 3.2.1.3.1; Appendix A 13).

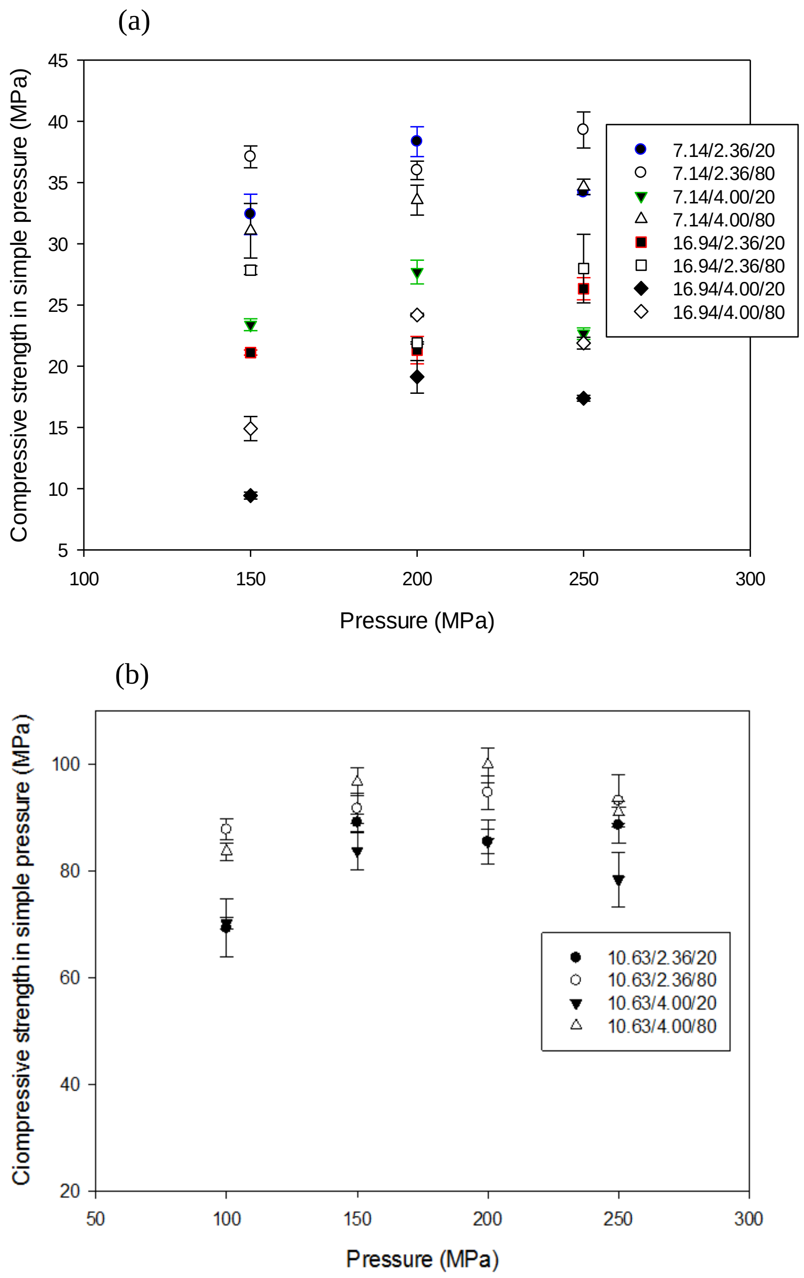


Fig 3.11: Effect of briquetting conditions (temperature, pressure) and feedstock properties (particles size, moisture content) on compressive strength in simple pressure of (a) maize cob and (b) bean straw briquettes (legend: moisture content (%)/ particle size (mm)/compacting temperature (^{o}C)

Mechanical strength and density depend on the strength of inter-particle bonds governed by particle size, moisture content, compacting pressure and temperature. At a fixed pressure, small particles are more densely packed than large particles (Ndindeng et al., 2015) and have large surface area which enhance heat transfer for strong bond formation between particles (Carone et al., 2011). Furthermore, the large surface area helps to create strong inter-particle bonding (with and without solid bridges) whereas large particles cause cracks in briquettes (Zafari and Kianmehr, 2014, Rahaman and Salam, 2017). In bonding without solid bridges, solid particles are attracted to each other via molecular (van der Waal's forces and valence forces i.e. free chemical bond) and electrostatic forces. Valence and Van der Waals' forces can contribute to bonding at a distance between particles of about 10 Å and 0.1µm respecticely (Kaliyan and Morey, 2010a). Bonding via electrostatic forces occurs due to the presence of excess charge which may by created from grinding and inter-particle friction (Kaliyan and Morey, 2010a), therefore less effective for large pore sizes. Bonding by solid bridges occure due to application of high pressure and temperature which cause diffusion of molucules from one particle to another. Solid brigdes can also be formed as a result of solidification of melted components (Kaliyan and Morey, 2010a, Kaliyan and Vance Morey, 2009).

CS in simple pressure of bean straw briquettes only increased with increasing pressure in a range of 100-150MPa and remained relatively constant with further increments in pressure to 250 MPa (Fig 3.11b). It could be because increasing compacting pressure increases interparticle bonds resulting from an increase in cohesion forces (Mitchual et al., 2013). However, above the optimal compacting pressure, the phenomenon of dilation occurs, producing cracks in briquettes and consequently weakening them (Wakchaure and Mani, 2011).

All interactions between briquetting variables significantly affected CS in cleft for maize cob briquettes (Fig 3.7c and d section 3.2.1.3.1; Appendix A 11) except for the interactions: pressure x moisture, pressure x particle size, pressure x particle size x temperature, moisture x particle size x temperature and, pressure x moisture x particle size x temperature. For compressive strength in simple pressure all variables showed significant interactions with the exception of particle size x temperature and, pressure x moisture x particle size x temperature (Appendix A 12). While pressure x temperature and pressure x particle size x temperature interactions significantly affected compressive strength in simple pressure ($P<0.05$, Fig 3.8d, section 3.2.1.3.1; Appendix A 14), the pressure x particle size and particle size x temperature interactions significantly affected CS in cleft of bean straw briquettes ($P<0.05$, Fig 3.8c, section 3.2.1.3.1; Appendix A 13).

At a compacting temperature of 20°C, CS in cleft of maize cob briquettes was below 10 kNm^{-1} for all tested moisture content and particles sizes (Fig 3.12a). Increasing compacting pressure from 150 to 200 MPa resulted in more than 100% increase in CS in cleft of maize cob briquettes for particle size <4 mm and high moisture content but had little impact where small particle size <2.36 mm and low moisture content were applied. Though the CS in cleft of bean straw at 20°C increased with increasing pressure, its dependence on particle size was not obvious. Increasing pressure squeezes natural binder components out of biomass particles and increases inter-particle bonding by solid bridge formation (Zhang and Guo, 2014). Increasing pressure also causes plastic and elastic deformation of particles thereby reducing void spaces between particles and increasing contact areas (Mitchual et al., 2013, Carone et al., 2011) (which increase short range forces such as molecular and electrostatic forces) and through mechanical interlocking (Tumuluru et al., 2011, Zhang and Guo, 2014), consequently increasing both density and strength. High compacting pressure could also crush large size particles, leading to increased densification (Yumak et al., 2010).

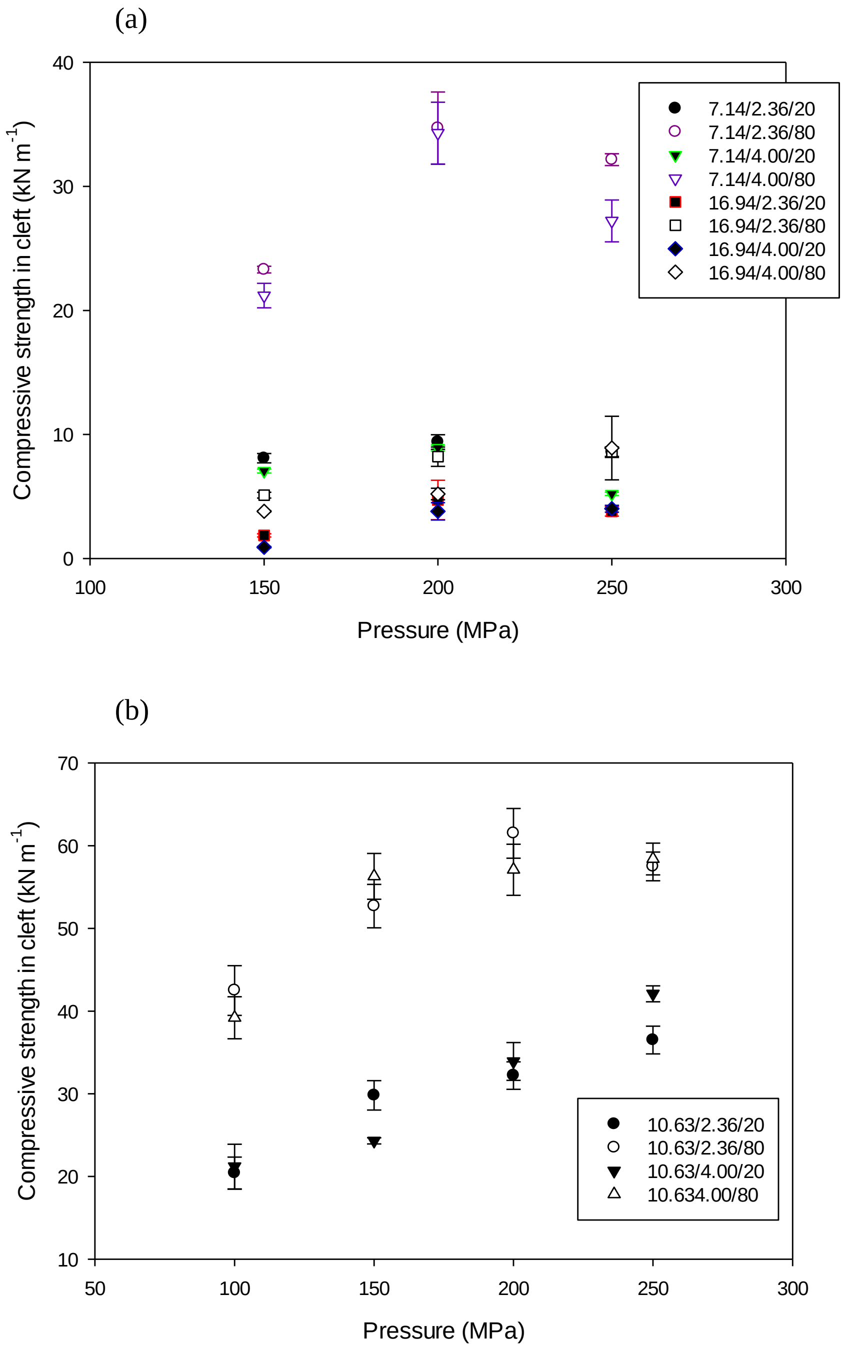


Fig 3.12: Effect of briquetting conditions (temperature, pressure) and feedstock properties (particles size, moisture content) on compressive strength in cleft of (a) maize cob and (b) bean straw briquettes (legend: moisture content (%)/ particle size (mm)/compacting temperature (^{o}C)

According to Kers et al., (2010) and Antwi-Boasiako and Acheampong, (2016), too much moisture in the feedstock leaves cracks/void space in briquettes due to the escape of moisture within the briquettes. The formation of cracks/void spaces makes briquettes more porous thereby reducing their strength and density. Therefore, a minimum amount of moisture in a feedstock is required to act as a binding/catalyst to release low molecular mass products which binds particles together thereby improving briquette strength. However, low moisture content is associated with low rate of heat transfer between particles and therefore the requirement for high compacting pressure (Adzic and Savic, 2013). In addition, moisture is responsible for bringing interfacial forces and capillary pressure into play to increase forces of attraction between particles (Matúš et al., 2015)

The effect of increasing temperature from 20-80°C on briquette properties was highly significant both with high and low moisture content feedstocks. Temperature minimises relaxation and improves the degree of densification by: (i) softening biomass particles, consequently aiding plastic deformation upon compression and increasing the inter-particle bonding through mechanical interlocking (Tumuluru et al., 2011, Kaliyan and Vance Morey, 2009) and (ii) facilitating the release of natural binders such as lignin, cellulose and hemicellulose which form solid bridges upon cooling thereby increasing the mechanical strength and density (Gilbert et al., 2009, Yumak et al., 2010, Lee et al., 2013). Natural binders such as lignin and hemicellulose in agricultural residues can undergo plastic deformation or be squeezed out of particles during compression at temperatures near the glass transition tempearture ~80°C for maize cob and ~70 °C for bean straw (Kaliyan and Morey, 2010b). Increasing temperature (from 20-80°C) not only improved briquette density and mechanical strength but also reduced the briquetting pressure required, which can potentially reduce production costs by reducing the energy required for compression. The use of high pressure is associated with high electrical energy consumption and high wear and tear of briquetting equipment (Grover and Mishra, 1996). Heat softens biomass particles, reduces friction between particles and the mould, thereby reducing depreciation, repair and maintenance costs resulting from wear and tear (Grover and Mishra, 1996).

The increasing CS with increasing pressure or temperature agreed well others for palm oil mill residue briquettes (pressure 3-11MPa) (Faizal et al., 2010), torrefied switchgrass (Gilbert et al., 2009) and hazelnut shell charcoal (particle size of >2.0 mm, pressure of 800 MPa, using 6.5-18.0

%wt pyrolysis liquid as a binder) (Ayhan Demirbaş, 1999). However, the effect of moisture content found in this study contradicts with others. For example, for lupin seed with an average particle size of 0.5 mm, compressive strength of briquettes increased with an increase in moisture content from 9.5 % to 15.0 % (Andrejko and Grochowicz, 2007). A 30% increase in CS of olive refuse briquettes was observed when moisture content was increased from 5 % to 15 % (Yaman et al., 2000) at a compacting pressure of 200 MPa and particle size of <0.250mm. An increase in CS of pulping reject briquettes from 13.0-37.2 MPa was reported with increasing moisture content (7-18%) and compacting pressure (300 - 800 MPa) (Demirbas and Sahin-Demirbas, 2004). Pressure (10-50 MPa) was the predominant factor affecting CS of tropical hardwood sawdust briquettes at particle size <3.35 mm and moisture content of 11.46% (Mitchual et al., 2013) whereas both moisture (6.3-14.7%) and temperature (26-144 ^{o}C) predominantly affected CS of spruce pellets (Rhén et al., 2005). For birch, spruce and reed canary grass pellets, CS was predominantly affected by moisture (between 2 and 14%) from compacting pressures of 200-400MPa and a particle size of <1.00mm (Huang et al., 2017). However, Zhang and Guo, (2014) reported that for varying *Caragana Korshinskii Kom* particle size (0.16-5.0 mm), minimum briquette compressive strength (62.16 MPa) was obtained at a particle size <0.16 mm under a compacting pressure and temperature of 10-170 MPa and 70-150 ^{o}C. Such variations can be attributed to variations in feedstock properties and briquetting parameters used in the different studies and confirms the need to analyse variations in briquettes properties on an individual feedstock basis.

3.2.1.4 Bean straw-maize cob blended briquettes

Different biomass materials can be blended to enhance the mechanical properties and the combustion characteristics of briquettes due to changes in the chemical composition. It is expected that blending maize cob with bean straw could improve maize cob briquetting characteristics at low compacting pressure. Therefore, the effects of blending maize cob with bean straw at different ratios on the properties of briquettes were investigated.

Increasing percentage of bean straw enhanced density, impact resistance and compressive strength of mixed feedstock briquettes (Table 3.2) at all conditions studies i.e. pressure/temperature of

200MPa/200^{o}C and 150MPa/50^{o}C. Blend ratio had no effect on impact resistance at high pressure and temperature of 200MPa/80^{o}C (Table 3.2). However, at a low compacting pressure/temperature of 150MPa/50^{o}C, impact resistance was reduced by ~36% as maize cob content increased from 75-100%. Although increasing maize cob content from 0-75% reduced density by <5%, CS decreased by 47-49% (Table 3.2). This is most likely due to higher resistance of maize cobs to plastic deformation. From scanning electron microscopy (SEM) imaging (Fig 3.13), maize cob is highly porous compared to bean straw which could have increased resistance to plastic deformation thereby increasing the energy requirement (high pressure) to minimise separation between and within (pores) particles. During briquetting, pressure causes particles to first rearrange to form closely packed mass and secondly to elastically and plastically deform when pressure increases. During plastic and elastic deformation, particles move and fill void spaces which increases contact area, consequently increasing both density and strength (Tumuluru et al., 2011, Carone et al., 2011). Lastly, volume is significantly reduced, resulting in the density of the material approaching the true density of the component ingredients. By the end of this stage, the deformed/broken particles cannot change position because of a decreased number of cavities (Tumuluru et al., 2011). Sole bean straw and a bean straw:maize cob blend ratio of 75:25 by weight were the best substrates for producing briquettes with high density and mechanical strength (Table 3.2). Blending improved both the density and mechanical strength of maize cob briquettes but these properties were lower when compared with bean straw only briquettes. The optimal bean straw:maize cob blend ratio was 75:25 producing equally high density briquettes as sole bean straw.

Table 3.2: Effect of blending ratio (bean straw:maize cob) on proximate properties, density, impact resistance and compressive strength of briquettes

Bean straw:maize cob ratio (wt:wt)	Pressure: 200 MPa and temperature: 80 °C						Pressure: 150 MPa and temperature: 50 °C		
	Ash (%)	Volatile (%)	Fixed carbon (%)	Density (kg m^{-3})	Impact resistance (%)	CS (MPa)	Density (kg m^{-3})	Impact resistance (%)	CS (MPa)
100:0	6.2	72.7	21.1	1153	99.8	99.6	1063	99.8	92.6
75:25	5.4	76.9	17.7	1154	99.4	83.6	1053	99.5	69.0
50:50	4.5	77.5	18.0	1127	99.6	65.4	1038	97.7	56.5
25:75	3.0	79.9	17.1	1114	99.4	52.4	1019	98.6	47.5
0:100	3.0	80.7	16.3	1018	99.8	40.4	949	63.2	30.5

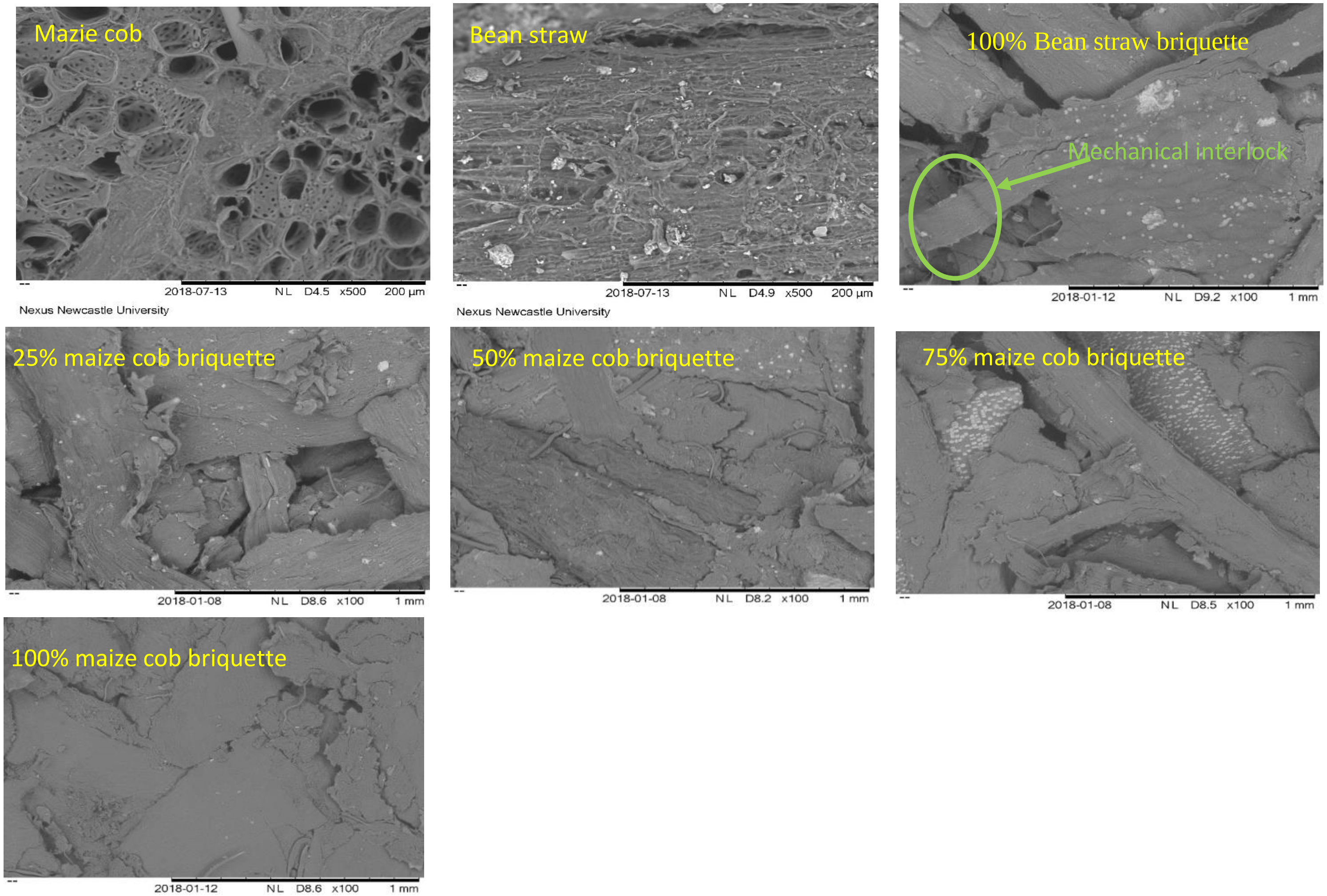


Fig 3.13: Bonding in bean straw:maize cob briquettes produced at compacting pressure of 200MPa with a moisture content of 10.63% for bean straw and 8.62% for maize cobs

Scanning electron microscopy (SEM) images (Fig 3.13) of briquettes which were broken from the middle in a direction perpendicular to the axis of the cylindrical briquettes shows that bonding in bean straw is strongly enhanced by mechanical interlocking (intertwine of particles) while for maize cobs bonding was mainly by solid bridge formation. Application of high pressure and/or temperature during densification results in diffusion of molecules at the point of contact from one particle to another, thus forming solid bridges while fibrous or bulky particles interlock to form mechanical interlocking bonds (Kaliyan and Vance Morey, 2009). Particles of corn stover and switchgrass briquettes/pellets are bonded mainly by solid brigdes resulting from natural binders i.e. mainly lignin and protein (Kaliyan and Morey, 2010a). Variations in the bonding mechanism are likely to be due to differences in the nature of biomass materials and in particular the more fibrous nature of the bean straw. During compression, interlocking bonds are formed (Kaliyan and Vance Morey, 2009) with increasing strength and density. As the proportion of maize cob content was increased, the extent of bond formation by mechanical interlocking was reduced (Fig 3.13), most likely due to maize cob particles only filling the void spaces between the fibrous bean straw particles. The reduction in the extent of bonding by mechanical interlocking could explain the reduced strength and density of bean straw briquettes with increasing content of maize cob in the blend. In addition, variations in lignin content (maize cob 1.5% and bean straw 10.2% (Table 3.1)) coud have also caused a difference in densification characteristics of these materials since high lignin content provides better densification properties (Muazu and Stegemann, 2015). Maize cob has lower lignin content than bean straw therefore, increasing maize cob composition would lower the lignin content of the blend thereby reducing density and strength of resulting briquettes. A decreasing trend in density of briquettes was observed by increasing corn stover content from 0-100% in corn stover:peanut shell blends (Gong et al., 2015). Increasing palm kernel shell content from 0-10% reduced sawdust briquette density from 420 to 380 kg m^{-3} and durability from 64.74 to 32.28%. However, further increasing palm kernel content to 50% increased density and durability to 480kg m^{-3} and 73.40% respectively (Obi, 2015). Blending bamboo with rice straw in the ratio of 5:0-0:5 by weight (i.e. bamboo : rice straw) reduced density of sole bamboo (1250 kgm^{-3}) and sole rice straw (1350 kgm^{-3}) pellets (to around 1000-1100kg m^{-3}), however, durability was maximised (99.03%) with a blend ratio of 2:3 (Liu et al., 2013).

In this study, increasing maize cob content in the blend: (i) increased briquette volatile composition due to higher volatile content in maize cobs compared to bean straw and (ii) reduced ash and fixed carbon content (Table 3.2). Blending had a higher impact on ash content than on volatile and fixed carbon contents. Increasing maize cob content from 25-50% did not result in a significant change in HHV (17-17.9 MJ kg^{-1}), fixed carbon and volatile contents. The high heating values (HHV) of the bean straw-maize cob blend in the current study are comparable with that of switchgrass (17.3 MJ kg^{-1}) (Gilbert et al., 2009), peanut shells (17.55 MJ kg^{-1}) and coconut fiber (17.74 MJ kg^{-1}), but higher than those of sawdust (14.99 MJ kg^{-1}), rice husk (14.77 MJ kg^{-1}) and palm fibre (16.84 MJ kg^{-1}) (Chin and Siddiqui, 2000) which means from the same amount of fuel, more energy can be generated from the blend.

Briquetting only altered the physcial and mechanical properties without changing chemical properties. Proximate properties results from briquettes (Table 3.3) were similar to those obtained from raw feedstock (Table 3.1 Section 3.2.1.1). The impact of briquetting on HHV was not significant, which was similar to the findings reported elsewhere (Faizal et al., 2010, Wakchaure and Mani, 2011).

Table 3.3: Proximate properties and HHV of maize cob and bean straw briquettes

Pressure (MPa)	Maize cob: Moisture/particle size/temperature of 7.14%/ <2.36mm/20^{o}C				Bean straw: Moisture/particle size/temperature of 10.6%/ <2.36mm/80^{o}C			
	Ash (%wt)	Volatile (%wt)	Fixed carbon (%wt)	HHV (MJ kg^{-1})	Ash (%wt)	Volatile (%wt)	Fixed carbon (%wt)	HHV (%MJ kg^{-1})
150	3.8	78.3	17.9	18.3	5.7	76.5	17.8	17.1
200	3.8	78.1	18.1	18.4	5.4	75.7	18.9	17.6
250	3.6	78.1	18.3	18.4	4.7	76.1	19.2	17.4

3.2.2 Torrefaction

3.2.2.1 Product yields

Increasing temperature and/or holding time increased liquid and gas yields at the expense of char (Table 3.4, Table 3.5, Fig 3.14, Fig 3.15). The decrease in char products with increasing temperature was feedstock dependent. Hemicellulose and cellulose decomposed or partially decomposed at the tested range temperature of 200-300°C to produce H_2O, CO_2, CO and some organic compounds such as acetic acid, phenol and furfural (Uemura et al., 2011; Poudel et al., 2015a).

Temperature was the predominant factor affecting yields of torrefaction products irrespective of feedstock type (Fig 3.14, Fig 3.15). This results agreed well with food waste feedstock (Poudel et al., 2015b) and beech wood chip (Colin et al., 2017). Furthermore, statistical analysis revealed that changes in char and gas yields occurs predominantly between a temperature range of 250-300°C and holding time ranging between 45-90 min (Fig 3.14 and Fig 3.15). This was likely due to increased devolatilization of hemicellulose, cellulose and lignin above 250°C. The colour of the torrefied biomass materials became darker with increasing torrefaction temperature (Fig 3.16, Appendix A 15) likely due to an increase in carbonisation. Similar colour changes were reported for empty fruit brunches, mesocarp fiber and kernel shell (Uemura et al., 2011).

Table 3.4: Yields from torrefaction of maize cob. Maximum error in yields ±2.35%wt

Holding time (min)	Liquid (%wt)			Char (wt)			Gas* (%wt)		
	200 °C	250 °C	300 °C	200 °C	250 °C	300 °C	200 °C	250 °C	300 °C
0	6.51	9.57	20.07	89.51	85.50	66.46	3.98	4.93	13.47
30	6.09	10.59	22.58	90.66	82.81	62.32	3.25	6.60	15.10
60	6.12	12.95	22.12	90.57	79.34	60.48	3.31	7.71	17.40
90	5.65	12.98	24.95	90.13	78.08	57.64	4.22	8.94	17.41

* by difference

Table 3.5: Yields from torrefaction of bean straw. Maximum error in yields ±2.33%wt

Holding time (min)	Liquid (%wt)			Char (%wt)			Gas* (wt)		
	200 °C	250 °C	300 °C	200 °C	250 °C	300 °C	200 °C	250 °C	300 °C
0	4.64	8.43	11.16	90.78	87.59	79.49	4.58	3.98	9.35
30	6.17	9.44	15.15	90.47	86.74	74.71	3.36	3.82	10.14
60	6.95	9.79	15.75	89.34	84.92	72.00	3.71	5.29	12.25
90	5.21	8.88	16.32	89.61	83.71	71.32	5.18	7.41	12.36

* by difference

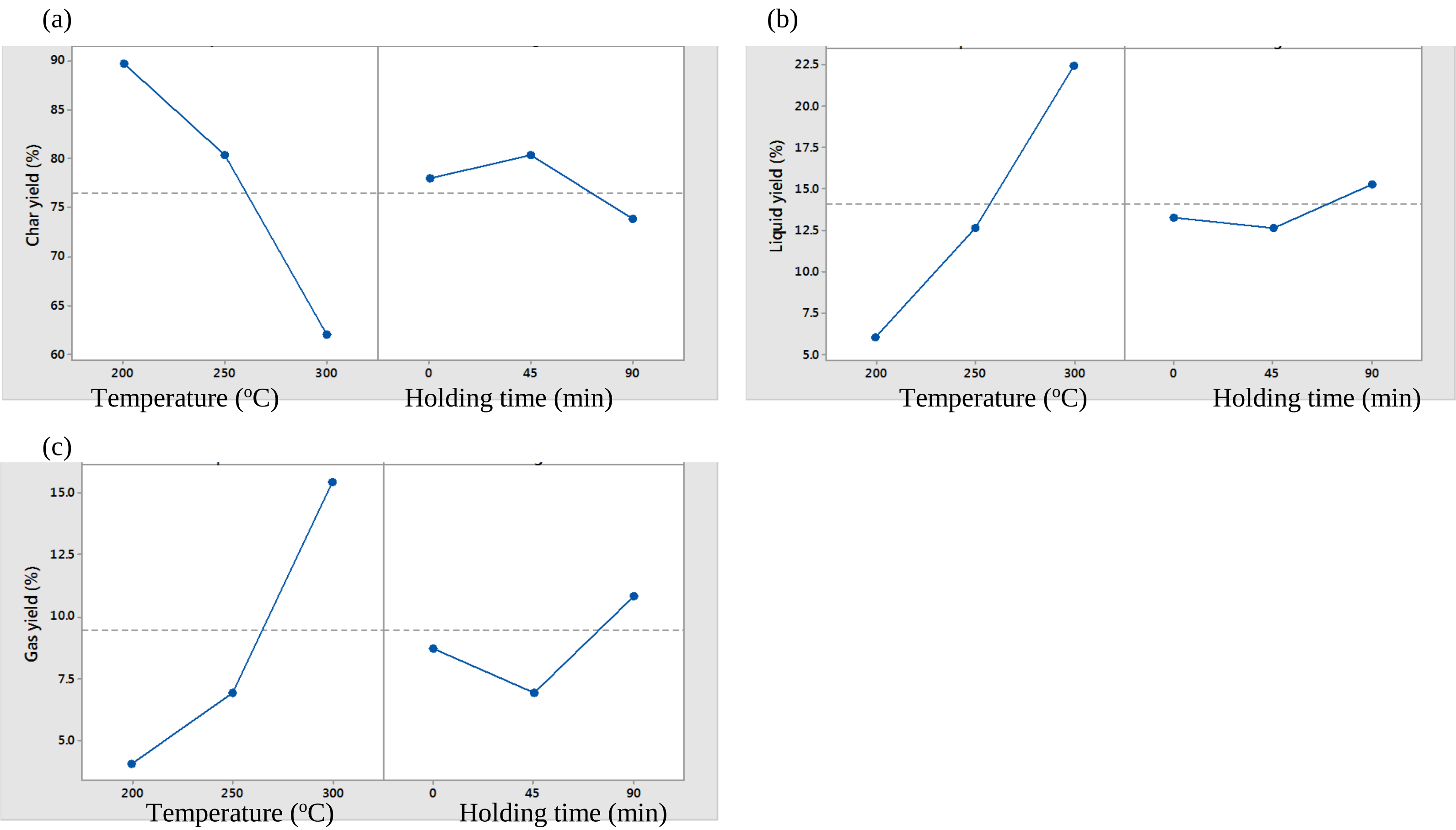


Fig 3.14: Effects of torrefaction conditions: temperature and holding time on (a) char, (b) liquid and (c) gas yields from maize cob.

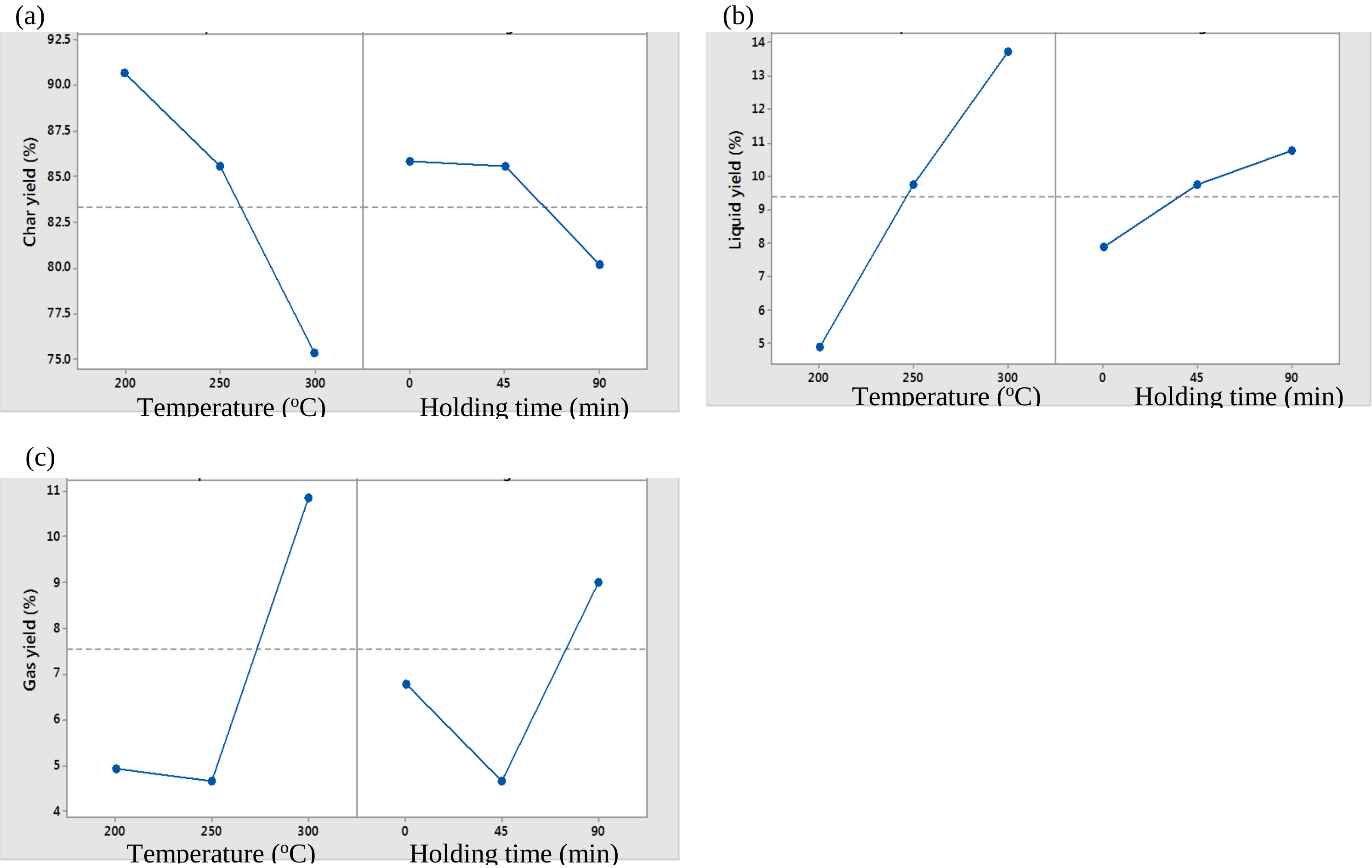


Fig 3.15: Effects of torrefaction conditions: temperature and holding time on (a) char, (b) liquid and (c) gas yields from bean straw.

(a) Maize cob (b) 200 ^{o}C

(c) 250 ^{o}C (d) 300 ^{o}C

Fig 3.16: Torrefied maize cob at different temperatures. Holding time: 30 min

The temperature × heating rate interaction (Fig 3.17 and Fig: 3.18, Appendix A 16-Appendix A 21) significantly affected yields of all products irrespective of the feedstock type except gas yield from bean straw. This study agrees well with the literature where Zheng et al., (2013) reported a reduction in char yield from 93.42-63.78% when maize cob torrefaction temperature was increased from 250-300 ^{o}C. Furthermore, increasing holding time from 10-60 min (at temperature of 275 ^{o}C) reduced char yield from 88.14-80.13% (Zheng et al., 2013). Char yield from torrefaction of food waste showed a decreasing rend with increasing torrefaction temperature (200-300^{o}C) (Pahla et al., 2018). Increasing holding time from 2-10h had no significant impact on the solid yield of eucalyptus bark char yield (P. Gao et al., 2016).

Energy yield, defined as a ratio of char yield x its energy to energy in feedstock, was decreasing with increasing temperature for maize cob (Table 3.6) due to a decrease in char yield. At 200^{o}C, increasing holding time slightly increased energy yield due to an increase in HHV (Table 4.6). At temperatures of 250-300^{o}C, although there was an increase in HHV (Table 3.6), increasing holding time caused a small decrease in energy yield due to char yield decrease (Table 3.4). It was similar to other studies (Uemura et al., 2011; Mei et al., 2016).

As shown in Table 3.6, increasing torrefaction increased the HHV. The HHV of torrefied maize cob in this study was similar to that of coal (25-35 MJ kg^{-1}) (W.-H. Chen et al., 2015) at torrefaction temperature of 300^{o}C and holding time of 30 min. This suggests that maize cob could be a better substrate for torrefaction and also for co-firing with coal. A similar trend in HHV was reported for empty fruit brunches, mesocarp fiber and kernel shell with increasing temperature from 220-300^{o}C (heating rate: 10 ^{o}C min^{-1} and holding time: 30 min) (Uemura et al., 2011).

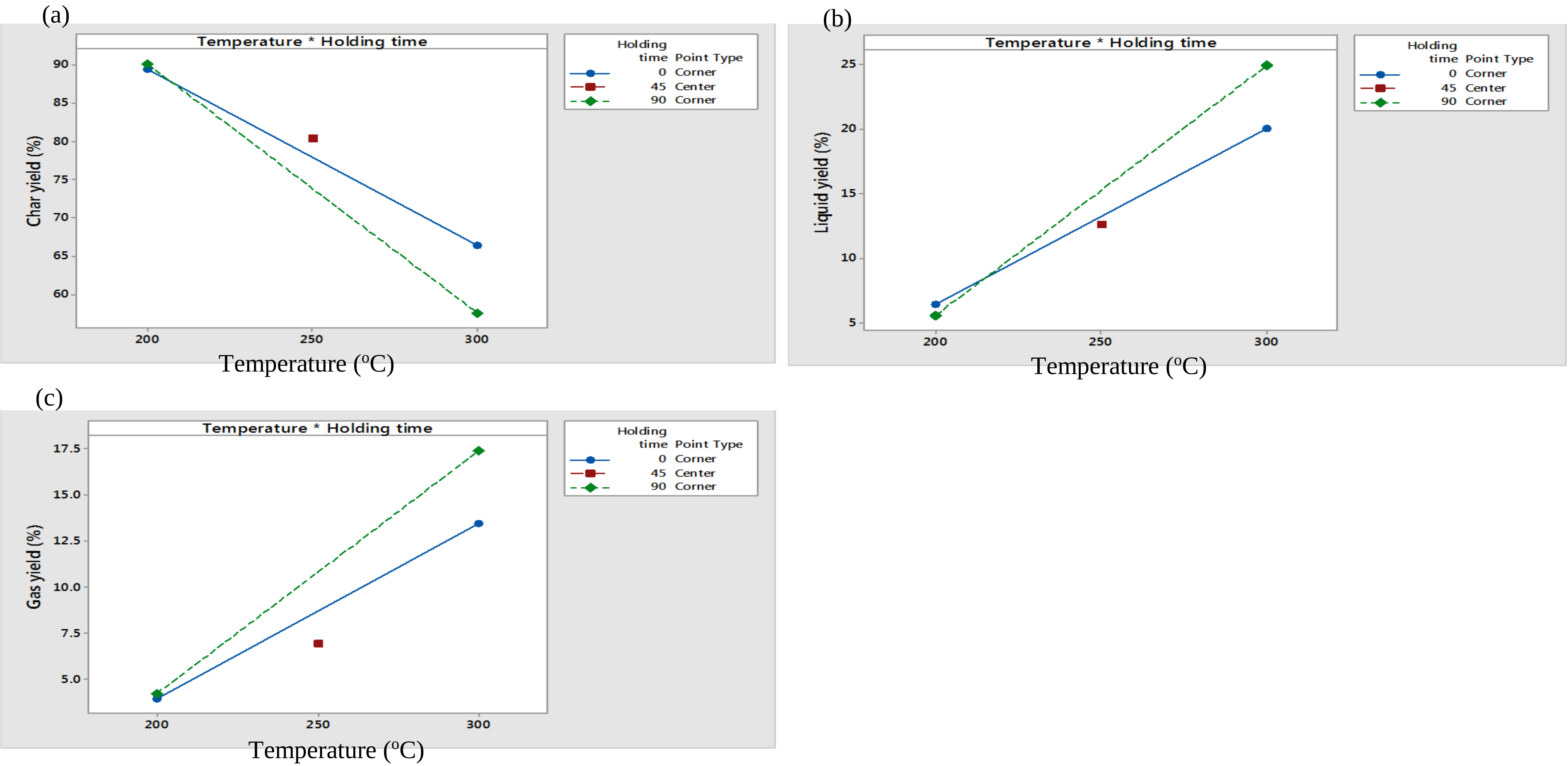


Fig 3.17: Interaction effects of torrefaction conditions: temperature and holding time on (a) char (b) liquid and (c) gas yield from maize cob. Red squares represent the mid-point.

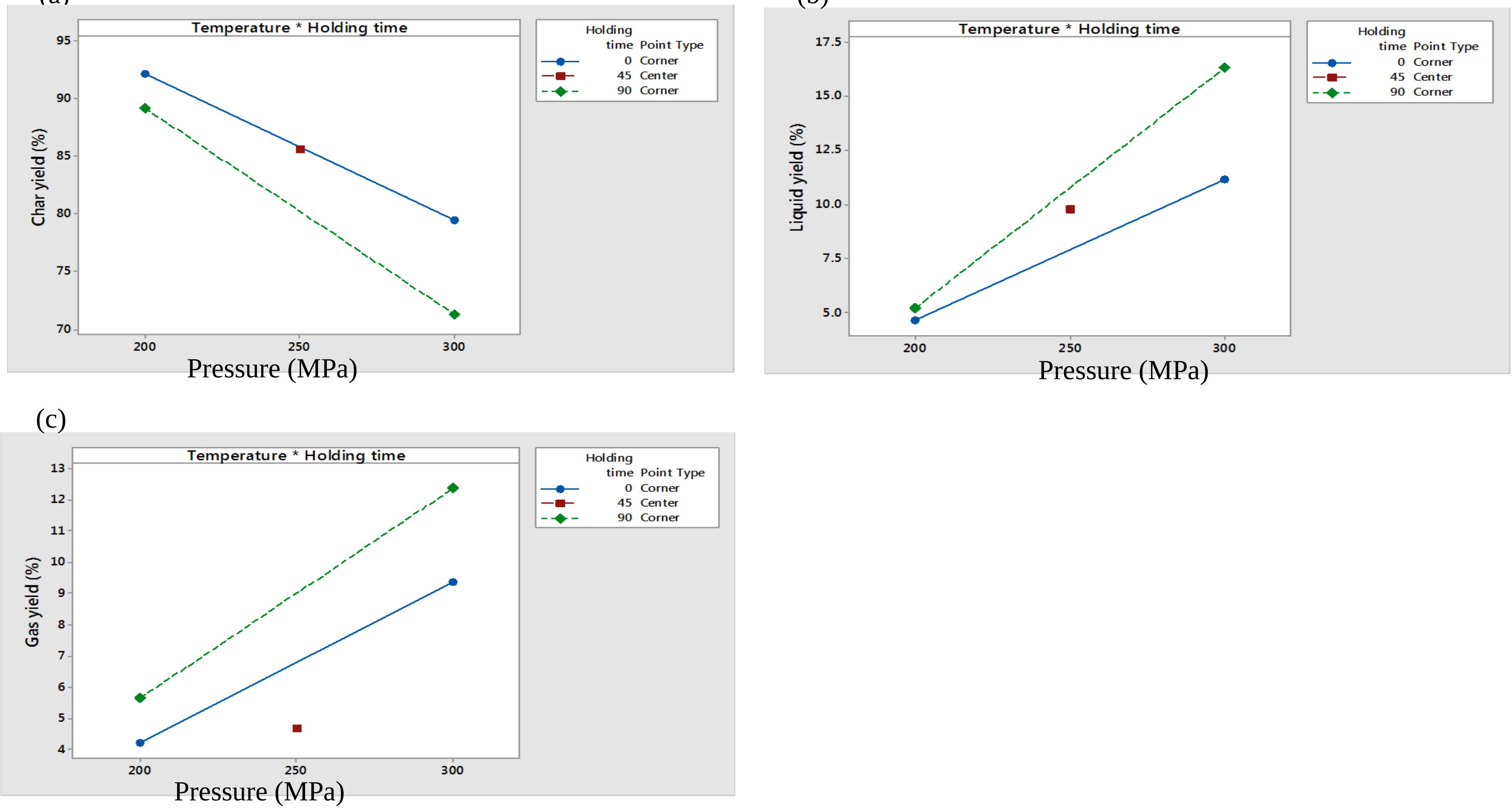

(a) (b) (c)

Fig: 3.18:Interaction effects of torrefaction conditions: temperature and holding time on (a) char(b) liquid and (c) gas yield from bean straw. Red squares represent the mid-point.

Table 3.6: Energy yield for torrefaction of maize cob and bean straw

Holding time (min)	Heating value (MJ kg^{-1})						Energy yield (%)					
	Maize cob			Bean straw			Maize cob			Bean straw		
	200^{o}C	250^{o}C	300^{o}C	200^{o}C	250^{o}C	300^{o}C	200^{o}C	250^{o}C	300^{o}C	200^{o}C	250^{o}C	300^{o}C
0	18.51	19.52	22.20	17.51	17.93	19.99	87.66	88.30	78.06	91.88	90.78	91.85
30	19.18	19.70	24.10	17.57	18.79	21.52	92.00	86.32	79.47	91.88	94.21	92.93
60	19.73	20.47	24.67	17.61	18.42	21.98	94.55	85.93	78.94	90.94	90.42	91.48
90	19.91	20.35	24.58	17.41	19.15	21.85	94.95	84.07	74.84	90.18	92.66	90.08

3.2.2.2 Char properties

Increasing torrefaction temperature increased ash content in char (Table 3.7and Table 3.8). This is because ash (inorganic compounds) in feedstock remain in char fraction at the tested temperatures (200-300^{o}C) (D. Chen et al., 2015). Devolatilisation via decarboxylation and decarbonylation occurs at temperatures above 200^{o}C (Mei et al., 2016, W.-H. Chen et al., 2015), increasing fixed carbon content at the expense of volatile when increasing torrefaction temperature. This also results in an increase in carbon content but decrease oxygen and hydrogen (Table 3.9). Torrefaction holding time had no impact on proximate properties of char derived from bean straw but affected the proximate properties of maize cob derived chars (decreasing volatile content and increasing fixed carbon content, at temperature of 250-300^{o}C).

Table 3.7: Proximate analysis of torrefied maize cob

Holding time (min)	Ash (%wt)			Volatile (%wt)			Fixed carbon (%wt)		
	200^{o}C	250^{o}C	300^{o}C	200^{o}C	250^{o}C	300^{o}C	200^{o}C	250^{o}C	300^{o}C
0	3.15	3.67	3.6	79.19	77.99	68.15	17.66	18.34	28.25
30	2.88	3.81	4.89	79.76	75.48	64.79	17.36	20.71	30.32
60	2.90	3.83	3.91	80.07	74.41	62.57	17.03	21.76	33.52
90	3.08	3.81	4.09	79.09	74.77	60.08	17.83	21.42	35.83

Table 3.8: Proximate analysis of torrefied bean straw

Holding time (min)	Ash (%wt)			Volatile (%wt)			Fixed carbon (%wt)		
	200^{o}C	250^{o}C	300^{o}C	200^{o}C	250^{o}C	300^{o}C	200^{o}C	250^{o}C	300^{o}C
0	6.16	5.50	8.07	76.28	77.13	63.72	17.56	17.37	28.21
30	6.27	6.71	9.31	78.92	69.73	65.36	14.81	23.56	25.33
60	5.17	8.06	7.26	75.83	75.72	64.11	19.00	16.22	28.63
90	5.57	7.33	8.47	78.32	73.16	62.45	16.11	19.51	29.08

Table 3.9 : Elemental composition of terrified char at holding time of 30 min

Element: dry and ash free. (%)	Maize cob			Beans straw		
	200°C	250°C	300°C	200°C	250°C	300°C
N	1.87	2.33	2.69	0.95	0.86	1.03
C	47.87	57.59	63.43	52.28	57.40	65.29
H	6.66	6.31	6.16	5.87	6.02	5.87
O*	43.60	33.77	27.72	40.90	35.72	27.81

* by difference

As illustrated in Table 3.9 the temperature applied for torrefaction is only sufficient for decarboxylation (CO_2) and decarbonylation (CO) and dehydration (H_2O). This is confirmed via FTIR analysis identical functional groups but varying intensities from various torrefaction conditions. The intensity of O-H at 3050-3600cm^{-1} (Fig 3.19) decreased with increasing temperature due to decomposition of lignocellulosic components especially hemicellulose (D. Chen et al., 2015; Mei et al., 2016) and dehydration. SME analysis (Fig 3.20 and Fig 3.21) confirmed the alteration in the morphology of terrified biomass (char products).

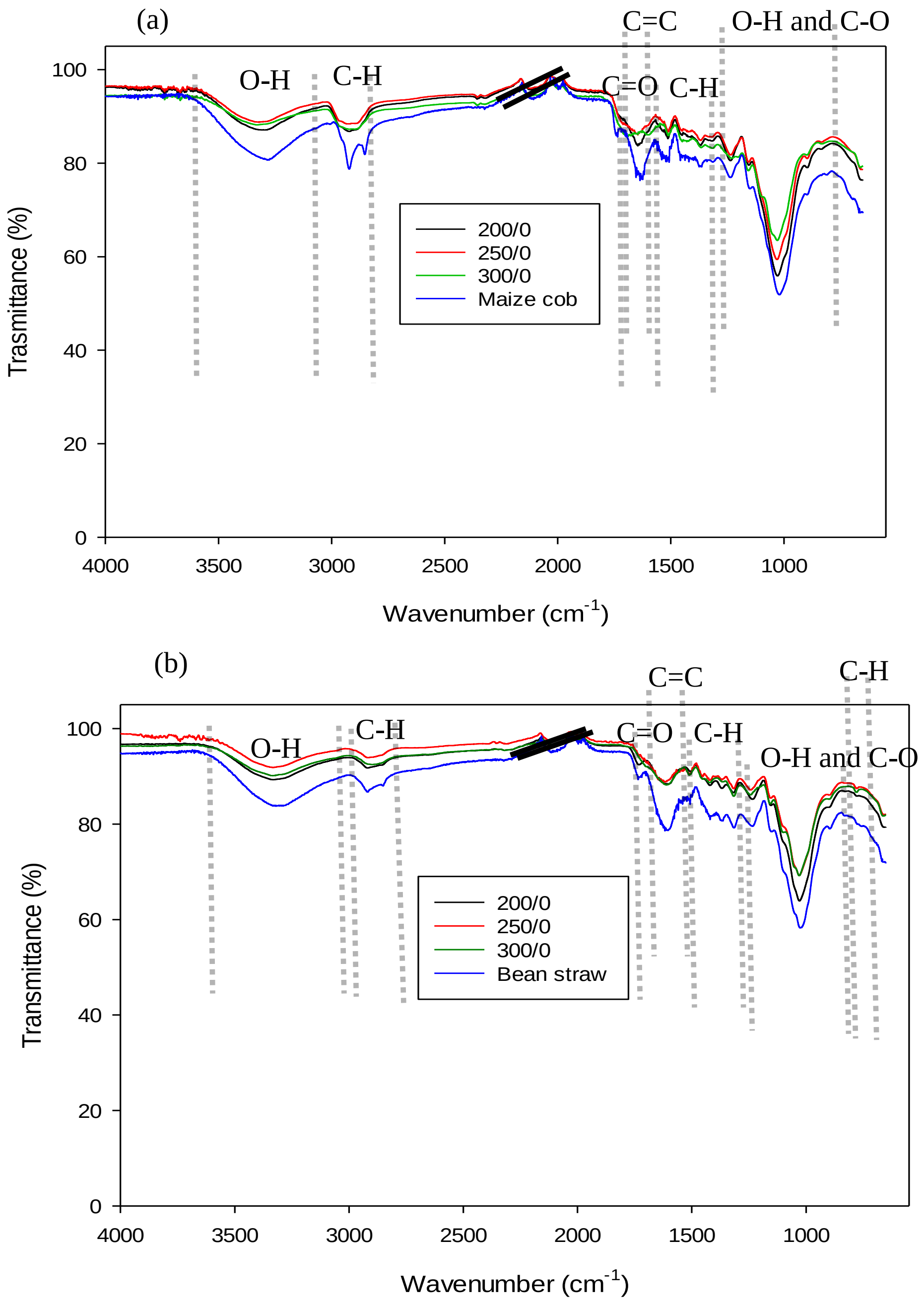
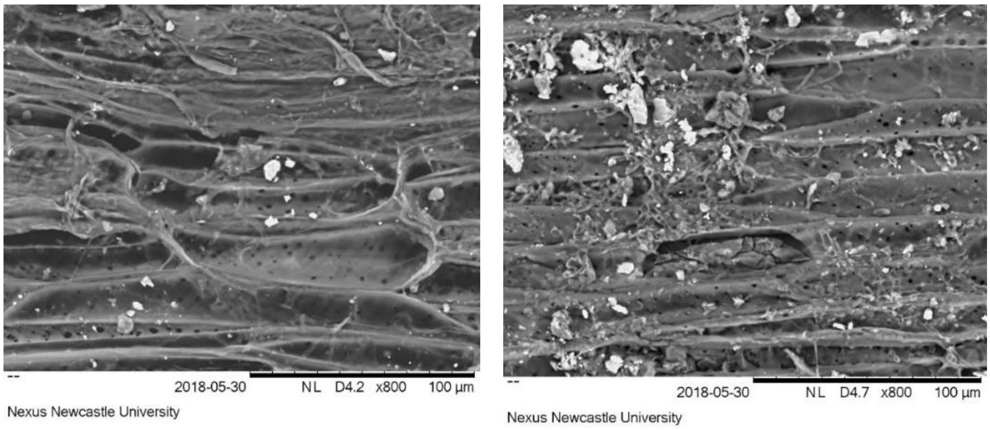
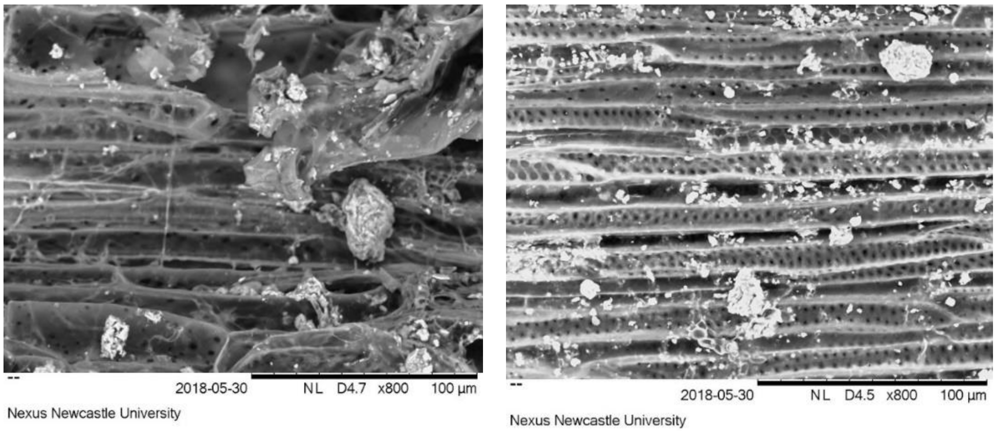


Fig 3.19: FTIR spectra of char products from torrefaction of (a) maize cob and (b) bean straw. Legend: torrefaction temperature (°C)/holding time (min)


(a) Bean straw

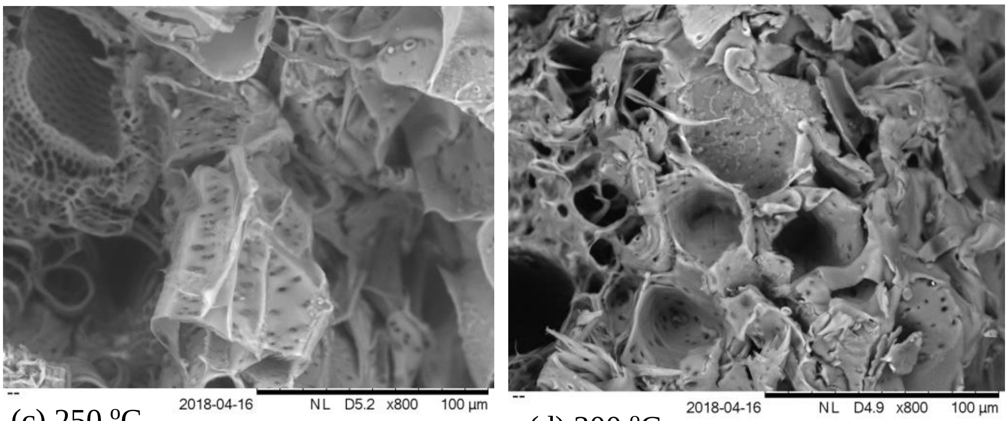
(b) 200 °C


(c) 250 °C

(d) 300 °C

Fig 3.20: SEM images of torrefied bean straw

(a) Maize cob (b) 200 ^{o}C



(c) 250 ^{o}C (d) 300 ^{o}C

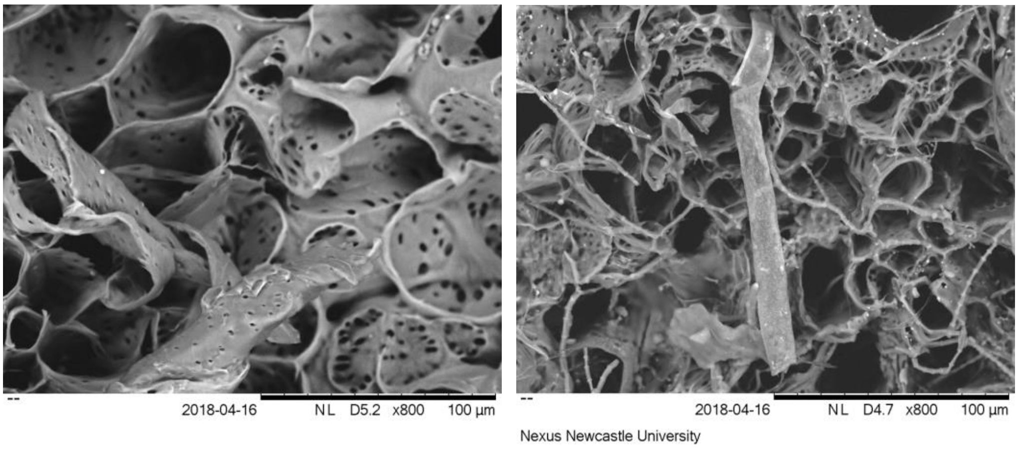


Fig 3.21: SEM of torrefied maize cob

Char samples derived from torrefaction were examined for their grindability. As shown in Table 3.10, the grindability increased with torrefaction temperature as evidenced by an increase in fine particle size (<1mm), leading to less energy required. Torrefaction weekens fibre structure as hemicellulose, cellulose and lignin have different thermal stabilities which makes biomass materials more brittle and fragile (D. Chen et al., 2015). However, holding time had little effect in energy requirement.

Table 3.10: Grindability of biomass torrefied at temperature of 200-300^{o}C and holding time of 0-30min. Maximum error in grindability was ±3.95%wt

Holding time (min)	Temperature (^{o}C)	Maize cob (%wt)				Bean straw (%wt)			
		<1mm	1.00-<2.36	2.36-<4.00	>4.00	<1mm	1.00-<2.36	2.36-<4.00	>4.00
Raw	-	17.98	31.51	7.19	43.32	52.73	35.97	3.71	7.59
0	200	32.14	31.07	8.45	28.33	64.83	32.52	1.58	1.07
	250	40.96	36.27	10.25	12.51	73.91	23.60	1.49	1.01
	300	50.94	40.66	7.01	1.40	85.05	13.92	1.03	0.00
30	200	38.10	32.97	9.89	19.05	65.35	31.68	1.98	0.99
	250	42.91	36.84	9.31	10.93	75.93	21.3	2.78	0.00
	300	61.20	28.56	5.12	5.13	84.54	13.40	2.06	0.00
60	200	36.64	31.90	9.49	21.98	64.58	32.29	2.08	1.04
	250	43.58	39.54	9.83	7.05	74.39	23.17	1.22	1.22
	300	56.04	38.65	4.35	0.97	85.08	14.92	0.00	0.00
90	200	34.94	32.13	7.23	25.70	69.86	26.92	2.15	1.08
	250	45.46	40.67	8.13	5.74	75.90	22.89	1.20	0.00
	300	57.21	37.11	5.15	0.52	85.75	13.69	0.56	0.00

3.2.2.3 Liquid product

Liquid obtained from torrefaction contained mainly high water content (93-97%wt) and was very acidic (Table 3.11 and Table 3.12). GC-MS analysis shows the liquid products contained acid, furfural, phenols and sugar (Table 3.13). Liquid from torrefaction of bamboo contained acids, alcohols, ketones, phenols, aldehydes and esters (W.-H. Chen et al., 2015). Acid, furan and sugar are produced from decomposition of hemicellulose and cellulose (Mullen and Boateng, 2008, Ogunjobi and Lajide, 2013, Mei et al., 2016) while phenolic compounds are produced mainly from lignin. The high-water content and acidity make these liquids undesirable fuels for energy production. However, they could be valuable feedstocks in the petrochemical industries.

Table 3.11: Liquid analysis following torrefaction of maize cob at different temperature and holding time

Holding time (min)	pH			Water (%wt)		
	200°C	250°C	300°C	200°C	250°C	300°C
0	3.19	2.78	2.76	93.37	86.15	77.55
30	3.2	4.00	2.90	92.88	85.81	77.73
60	3.54	2.77	2.76	92.70	83.55	77.59
90	3.44	4.01	2.91	92.01	84.92	78.21

Table 3.12: Liquid analysis following torrefaction of bean straw at different temperature and holding time

Holding time (min)	pH			Water (%wt)		
	200°C	250°C	300°C	200°C	250°C	300°C
0	3.48	2.50	2.57	95.80	92.90	80.67
30	3.11	2.47	2.56	95.94	92.24	78.02
60	4.05	3.28	2.59	96.89	90.59	80.07
90	3.01	2.56	2.58	96.97	92.17	81.15

Table 3.13: GCMS analysis of liquids produced at torrefaction temperature of 200-300°C and holding time of 30 min.

Compound	Maize cob: Area (%)			Bean straw: Area (%)		
	200°C	250°C	300°C	200°C	250°C	300°C
Acetic acid	30.51	7.00	13.01	-	-	-
Butanediol	15.43	9.60	5.25	-	-	-
Phenol	3.42	3.64	8.89	-	-	-
Methoxyphenol	6.47	7.52	8.89	-	-	-
4-Ethylphenol	4.45	5.25	4.68	-	-	-
Benzenediol	1.19	2.97	4.98	-	-	-
Dianhydro mannitol (Sugar)	1.97	5.51	4.46	-	-	-
Benzofuran 2,3 dihydro	2.61	5.18	3.98	-	-	-
Phenol-4-ethyl-2-methoxy	2.10	3.83	2.62	-	-	-
Methoxy Vinylphenol	1.80	1.76	2.36	-	-	-
Phenol 2,6-dimethoxy	2.45	4.74	6.19	4.96	5.27	4.25
Vanillin	1.82	1.97	3.22	12.74	5.93	5.39
Furfural	-	-	-	14.2	32.12	26.75
Furancarboxyaldehyde	-	-	-	16.36	6.98	9.66
Acetylmethy 2-furalcdehyde	-	-	-	2.54	1.55	1.42
2-Propanone hydroxyphenyl	-	-	-	3.69	1.76	2.01
Phthalate	-	-	-	0.41	1.05	0.46

3.2.2.4 Gas product

CO_2 is the dominant product over 78%wt for maize cob and 89%wt for bean straw (Table 3.14 and Table 3.15) which compares well with literature (Chang et al., 2012). CO_2 could be used as carrier gas in torrefaction (Li et al., 2018). CO appeared at a temperature range 250-300^oC and it ranged between 6.33-21.40%wt for maize cob and 0.23-10.09%wt for bean straw. The yields of H_2, CH_4 and C_2-C_5 were <1%wt. Holding time had no impact on CO_2 and CO yields from torrefaction of maize cob except at 250^oC. At bean straw torrefaction temperature of 250-300^oC, CO_2 yield decreased while CO yield showed a decreasing trend with increasing holding time from 0-90 min.

Table 3.14: Gas composition from torrfeactionof maize cob. Maximum error for gas compositions: ±3.36%wt

Holding time (min)	CO_2 (%wt)			H_2 (%wt)			CH_4 (%wt)			CO (%wt)			C_2-C_5 (%wt)		
	200^{o}C	250 ^{o}C	300 ^{o}C	200 ^{o}C	250 ^{o}C	300 ^{o}C	200 ^{o}C	250 ^{o}C	300 ^{o}C	200 ^{o}C	250 ^{o}C	300 ^{o}C	200 ^{o}C	250 ^{o}C	300 ^{o}C
0	100.00	93.63	80.01	-	-	0.01	-	-	0.02	-	6.33	20.11	-	0.00	0.12
30	100.00	86.30	79.10	-	-	0.01	-	-	0.03	-	13.51	20.70	-	0.13	0.16
60	100.00	80.99	79.38	-	-	0.01	-	-	0.05	-	18.91	20.26	-	0.09	0.31
90	100.00	79.28	78.22	-	-	0.01	-	-	0.07	-	20.62	21.40	-	0.11	0.31

Table 3.15: Gas composition from torrefaction of bean straw. Maximum error for gas compositions: ±1.48%wt

Holding time (min)	CO_2 (%wt)			H_2 (%wt)			CO (%wt)			C_2-C_4 (%wt)		
	200^{o}C	250 ^{o}C	300 ^{o}C	200 ^{o}C	250 ^{o}C	300 ^{o}C	200 ^{o}C	250 ^{o}C	300 ^{o}C	200 ^{o}C	250 ^{o}C	300 ^{o}C
0	100	99.90	95.94	-	-	0.01	-	0.23	4.60	-	-	0.00
30	100	99.15	92.01	-	-	0.01	-	0.87	7.81	-	-	0.13
60	100	98.95	90.78	-	-	0.02	-	1.04	9.08	-	-	0.11
90	100	98.40	89.76	-	-	0.02	-	1.07	10.09	-	-	0.14

3.2.2.5 Briquetting of torrefied maize cob

To analyse the impact of torrefaction and addition of binder (maize cob briquette bio-oil from pyrolysis temperature of 650^{o}C) on briquette properties, torrefied maize cob (temperature: 300^{o}C and holding time: 30 min) was compressed at a compacting pressure of 200MPa and temperature of 80^{o}C and 140^{o}C. This torrefaction condition was sufficient to produce a coal like fuel in terms of HHV and carbon content. Briquettes from torrefied maize cob had density, impact resistance and CS ranging bewteen 831-974 kg m^{-3}, 14.8-49.5% and 11.1-17.3MPa. It was found that increasing compacting temperature from 80 to 140^{o}C increased density, impact resistance and compressive strength by ~17%, over 100% and ~56% (Table: 3.16). Addition of 5%wt bio-oil at compacting temperature of 80^{o}C and pressure of 200MPa lowered density, impact resistance and compressive strength to 780kg m^{-3}, <10%, and 7.9MPa. The reduction in density and strength with bio-oil added could have been attributed to high water content in the bio-oil due to its incompressibility which also caused cracking. Compared to briquettes from raw/untorrefied maize cob (Fig 3.4a section 3.2.1.3.1, Fig 3.10, section 3.2.1.3.2), briquettes from torrefied maize cob (with and with bio-oil) had lower density and strength. These briquettes (with and without) binder did not meet the minimum standard in terms of density (1000-1400 kg m^{-3}) and impact resistance (at least 80%) required to minise breakage during transportation, storage and handling. It was reported (Hui Li et al., 2012) that torrefaction (temperature: 260-300^{o}C, holding time: 10-90 min) lowered the density and strength of sawdust pellets which was attributed to loss of low melting point compounds (during torrefaction) which when softened could act as binders.

Table: 3.16: Properties of briquettes from torrefied maize cob. Compacting pressure of 200MPa. Maximum error on density, impact resistance and compressive strength were (±7kg m^{-3}), (±7.2%) and (±1.8MPa) respectively

Compacting temperature (^{o}C)	Density	Impact resistance	Compressive strength
80	831	14.8	11.1
140	974	49.5	17.3
80 (with 5%wt bio-oil)	780	2.0	7.9

3.3 Conclusions

Briquettes properties are an important characteristic to meet the increasing demand for biomass feedstocks, enabling long-term handling, storage and transport. This study revealed that increasing pressure and temperature improved maize cob and bean straw briquette density and mechanical strength. Decrease in moisture content and particle size increased density, impact resistance and compressive strength of maize cob briquettes. Compressive strength in simple pressure was in the recommended range (≥ 2.56MPa) for all tested conditions and feedstocks. Pressure ≥ 200MPa and temperature had no effect on properties of maize cob briquettes made from low moisture content (<10 %), or small particle size (<2.36mm). However, by increasing compacting temperature to 80^{o}C, large particle size can be used without trading off any durability properties. This is because heat soften biomass materials and aid in plastic deformation. There was a strong moisture and temperature interaction on all the maize cob briquette properties because moisture accelerates heat transfer between maize cob particles which eases elastic and plastic deformation during compression.

Bean straw particle size in the tested range (<2.36-<4mm) had little impact at compacting pressure/temperature of 250MPa/20^{o}C and at compacting temperature of 80^{o}C irrespective of compacting pressure tested. All bean straw briquettes at pressure 100-200MPa and temperature of 80^{o}C satisfied the German Standard DIN 51731 (density 1000-1400 kg m^{-3}). A strong pressure × temperature interaction was observed significantly affecting density, impact resistance and compressive strength. Blending of bean straw:maize cob enhanced briquette characteristics with an optimum 75:25 (wt:wt) ratio producing equally high density briquettes similar to sole bean straw. However, sole bean straw produced briquettes with highest density and mechanical strength with a lower energy expenditure (pressure and /temperature) and therefore is a preferred substrate over maize cob for briquette production. Briquettes from the torrefied maize cob were of lower quality than those from the raw feedstock. While pyrolysis oil showed limited benefit when used as a binder due to it high water content.

Maize cob and bean straw had different torrefaction properties (measured in terms of product yields and properties) due to variation in their chemical composition. Torrefaction holding time had little influence on yields and properties of torrefaction products than temperature. Char yield consequently energy yield decreased whereas gas and liquid yields increased with increasing torrefaction temperature. Increasing temperature from 200 to 300^{o}C removed oxygen in the form of CO_2, CO and H_2O and enhanced the grindability. The liquid product was mainly water and highly acidic.

Chapter 4: Biomass Conversion

Various approaches i.e. bio-chemical and thermochemical processes have been applied to convert biomass to solid, liquid, and gaseous fuels (Okello et al., 2013a). Combustion is the common process to produce heat and electricity with high energy efficiency (~93%) (Samuli et al., 2014). In contrast, pyrolysis decomposes biomass into multiple products such as gas, liquid and solid which can be used for energy production or fuel for transportation (Onay and Kockar, 2003). Pyrolysis is flexible and uses a wide range of feedstocks (Czajczyńska et al., 2017). Previous studies indicate contrasting findings on the impact of pyrolysis conditions on yields and properties of pyrolysis product and pyrolysis of briquettes had not been researched. Furthermore, information about combustion of pretreated biomass is scarce. In this study, the effect of pyrolysis temperature (410-650^{o}C), heating rate (10-20^{o}C) and carrier gas flow rate (40-60cm^{3} min^{-1}) on yields and properties of pyrolysis products were investigated. Combustion of briquette in a fixed bed was discussed. Kinetic studies were carried out for pyrolysis and combustion using TGA experimental data.

4.1 Materials and experimental methodologies

4.1.1 Thermogravimetric- differential scanning calorimetry (TG-DSC) analysis

Thermogravimetric analysis (TG) is the most common technique used in analyzing thermal behavior of feedstock for kinetic studies (Yi et al., 2013). Prior to the TG experiments, raw/dried maize cob and bean straw samples (properties shown in Table 3.1 section 3.2.1.1) were ground to a particle size <250μm to minimize mass and heat transfer limitations (Damartzis et al., 2011). A known amount of sample (~10mg) was placed in a Netzsch Jupiter STA 449C TG-DSC system connected to a Netzsch Aeolos 403C quadrupole mass spectrometer (QMS). The system was heated from 25°C to 1000°C at a heating rate of 10, 20, 30 and 40°C min^{-1} in either helium or a mixture of 20%vol oxygen + 80%vol helium (referred to as air in the subsequent discussions) at a flow rate of 30 ml min^{-1}. The QMS was operated in full scan mode over the range m/z 10-300 and mass spectrometric data were acquired and processed using Quadstar version 7.x.

4.1.2 Kinetic modelling

In the pyrolysis and combustion kinetic study of maize cob and bean straw, iso-conventional methods such as Kissinger-Akahira-Sunose (KAS) and Flynn -Wall-Ozawa (FWO) were used to determine activation energies without knowledge of the reaction mechanism (Agrawal and Chakraborty, 2013, Slopiecka et al., 2012). The methods assume that the reaction kinetic is independent of heating rate and the conversion of biomass into products is a one step process (Damartzis et al., 2011). The conversions outside the range 0.1-0.8 were not considered in the KAS and FWO plots while determining the activation energy due to low correlation values (Nyakuma, 2015). The pre-exponential factor and the reaction order were determined following the Universal Integral method (Gai et al., 2013). Data obtained from TGA experiments was used to determine conversion, α (a fraction of the fuel decomposed in time t) (El-Sayed and Khairy, 2015).

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \tag{4.1}$$

Where m_o : initial mass of the feedstock, m_t :mass of the feedstock at time t and m_f: final mass

The rate of thermal degradation/conversion of biomass is defined by Equation (4.2) (Nocera et al., 2016, Gai et al., 2013).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{4.2}$$

Where: $f(\alpha)$ is a reaction model and k(T) is a rate constant as a function of temperature (Arrhenius equation) as described by Equation (4.3).

$$k(T) = Aexp\left(-\frac{E}{RT}\right) \tag{4.3}$$

Where A: pre-exponential factor (min^{-1}), R is the universal gas constant (8.314 $JK^{-1}mole^{-1}$), E($kJ\ mol^{-1}$) is the activation energy and T is the temperature (K).

For non-isothermal process, temperature of experiment at time, t is determined by Equation (4.4) (Chen et al., 2012).

$T = \beta t + T_0$ (4.4)

Where T_0 is the initial temperature of experiment and

$$\beta = \frac{dT}{dt} \quad (4.5)$$

Combining Equations (4.2), (4.3) and (4.5) and integrating;

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_{T_0}^{T} \frac{A}{\beta} e^{\left(-\frac{E}{RT}\right)} dT = \frac{AE}{\beta R} \int_x^{\infty} x^{-2} e^{-x} dx = \frac{AE}{\beta R} P(x) \quad (4.6)$$

Where $g(\alpha)$: the integral reaction model, $x{:}\frac{E}{RT}$ and P(x) is a temperature integral with no exact analytical solution. Equation 4.6 is solved by either numerical integral or by use of approximation. The difference between the iso-conventional methods is therefore based on the type of approximation used in solving Equation 4.6 (Damartzis et al., 2011).

(a) Kissinger-Alkahira-Sunose (KAS)

Kissinger-Alkahira-Sunose (KAS), uses the approximation (Damartzis et al., 2011),

$$P(x) = x^{-2} e^{-x} \quad (4.7)$$

which is substituted in Equation (4.6) giving.

$$In\left(\frac{\beta}{T^2}\right) = In\left(\frac{AR}{Eg(\alpha)}\right) - \frac{E}{RT} \quad (4.8)$$

A plot of $In\left(\frac{\beta}{T^2}\right)$ against $\frac{1}{T}$ for each conversion ratio produces a straight-line graph whose slope is used to obtain the activation energy.

(b) Flynn-Wall-Ozawa (FWO)

Flynn-Wall-Ozawa (FWO), uses Doyle’s approximation:

$$log(p(x)) \approx -2.315 - 0.457x \quad (4.9)$$

Combining Equations (4.6) and (4.9) gives Equation (4.10), the FWO model.

$$log\,\beta = log\left(\frac{AE}{Rg(\alpha)}\right) - 2.315 - 0.457\frac{E}{RT} \tag{4.10}$$

The activation energy is obtained from the slope of the plot of $log\,\beta$ against $\frac{1}{T}$.

(c) Universal integral

Combining Equations 4.2 and 4.3 and integrating both size

$$g(\alpha) = A\,exp\left(\frac{-E}{RT}\right)t \tag{4.11}$$

Substituting for t from Equation 4.4,

$$g(\alpha) = \frac{A}{\beta}(T - T_0)\,exp\left(-\frac{E}{RT}\right) \tag{4.12}$$

Rearranging Equation (4.12) and introducing natural log (ln) on both sides,

$$In\left[\frac{g(\alpha)}{T-T_0}\right] = In\left[\frac{A}{\beta}\right] - \frac{E}{RT} \tag{4.13}$$

A plot of $In\left[\frac{g(\alpha)}{T-T_0}\right]$ against $\frac{1}{T}$ gives a straight line whose gradient is $-\frac{E}{R}$, from which the activation energy is calculated and compared with the value obtained from FWO and KAS, and intercept is $In\left[\frac{A}{\beta}\right]$ from which pre-exponential factor A is calculated (Gai et al., 2013).

4.1.3 Pyrolysis experiments

Pyrolysis was conducted in a 316 stainless fixed bed reactor of internal diameter 3.6 cm and length 60 cm as shown in (Fig 4.1). Non-torrefied bean straw, maize cob and bean straw-maize cob blended briquettes that met minimum standard (i.e. density, impact resistance and compressive strength of ≥1000 kg m^{-3}, ≥80% and ≥2.36MPa respectively) to minimise transport and storage costs and breakage during transportation, handling and storage were used as feedstock for pyrolysis. These briquettes were made from compacting pressure (150 and 200MPa), temperature (20°C, 50°C and 80°C), particle size (<2.36mm and <4.00mm) and blend ratio (75:25, 50:50 and 25:75 by weight i.e. bean straw:maize cob) as described in chapter 3. The effects of pyrolysis temperature (410, 530 and 650 °C), heating rate (10, 15 and 20 °C min^{-1}), and N_2 flow rate (40, 50 and 60 cm^3 min^{-1}) on the yield and properties of pyrolysis products were investigated. These temperatures and heating rates are within the range of values reported in literature (Li et al., 2016, Yang et al., 2016, Bartocci et al., 2018). Meanwhile the N_2 flow rate used was just sufficient to carry the pyrolysis vapor out of the hot pyrolysis zone. About 40g of briquettes were placed in the centre of the reactor and heated up to a desired temperature at a heating rate of 10-20°C min^{-1}. As soon as the desired temperature was reached, the system was held for a further 30 mins to ensure volatiles within the briquettes were released. The condensable volatiles were collected in the condenser maintained at 0°C in ice whereas the non-condensable gas was collected in a gas bag for analysis. The gas samples were collected in an interval of 50°C starting at 250°C to the desired pyrolysis temperature (650°C) and then collected at 5 min interval during the 30 min holding time. The solid (char inside the reactor) and the liquid (known as bio-oil hereafter) were collected for analysis when the reactor temperature was below 50°C. The yields of char and bio-oil were determined based on the initial mass of briquettes (%wt) whereas gas yield was calculated by the difference. Gas analysis, char proximate analysis, ultimate and high heating value (HHV) analysis together with bio-oil water content, pH and GC-MS analysis were conducted as described in sections 3.1.4 (chapter 3). Surface area of char was determined by Thermo Scienctific Surfer analyser through nitrogen gas adsorption at 77K. The effect of pyrolysis conditions on yields of bio-oil, char and gas was analysed by Minitab 17 at significant level, $\alpha=0.05$ based on surface response (Box-Behnken) design of experiment (Appendix B 1). At least 3 replicates of each experiment were performed.

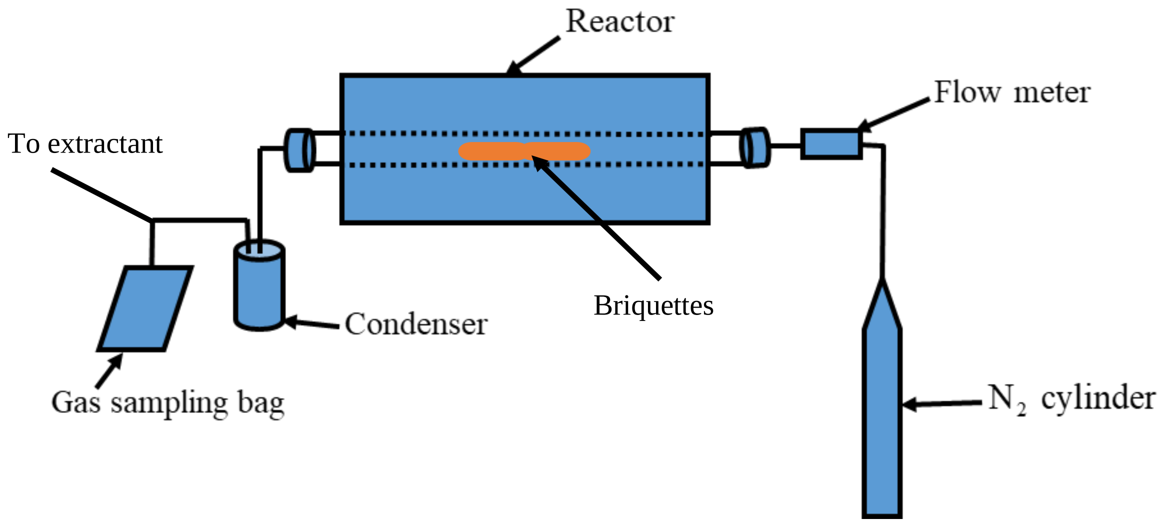


Fig 4.1 Pyrolysis experimental setup

4.1.4 Combustion in a packed bed reactor

Maize cob briquette was produced following the procedure discussed in subsection 3.1.2 from pressure (MPa)/particle size (mm)/temperature (°C) of 200/2.36/80 because this condition met the quality standards in terms of both density and durability. The fixed bed reactor which was made from stainless steel of length 60 cm and internal diameter 4.85cm and insulated with calcium magnesium silicate thermal insulation for safety and to minimize heat loss, was used for combustion tests as shown in Fig 4.2. The ignition point was 30cm above the grate. The reactor had a perforated plate (grate at the bottom) and was suspended on a load cell to determine the weight of the fuel. Each sample was fed inside the reactor to a bed height of 25 cm from the grate and was ignited at 30cm above the grate. Air flow rate used was 10 L min^{-1} beacuse it was sufficient to sustain the combustion process. Temperature inside the reactor was measured using 6 K-type thermocouples as shown in Fig 4.2. Thermocouples at 0, 10 and 20 cm were aligned at the center of the reactor while those at 5, 15 and 25 cm were aligned at the inner surface of the wall of the reactor. Weight loss and temperature profile were recorded by a PICO TC-08 logger because it fast, accuracy and has a potential to measure both weight loss and temperature simultaneously.

Gas samples were collected in gas bags after igniting the bed at 5 min intervals until no CO_2 was detected (determined by GC analysis). The residue and time for complete combustion (i.e. when the weight became constant) were obtained from the bed weight profile and used to computed burning rate following Equation 4.14 (Mohammed and Olugbade, 2015). 3 replicants of the experiment were performed.

$$Burning\ rate = \frac{Mass\ of\ briquette\ burnt}{Time\ for\ complete\ combustion} \tag{4.14}$$

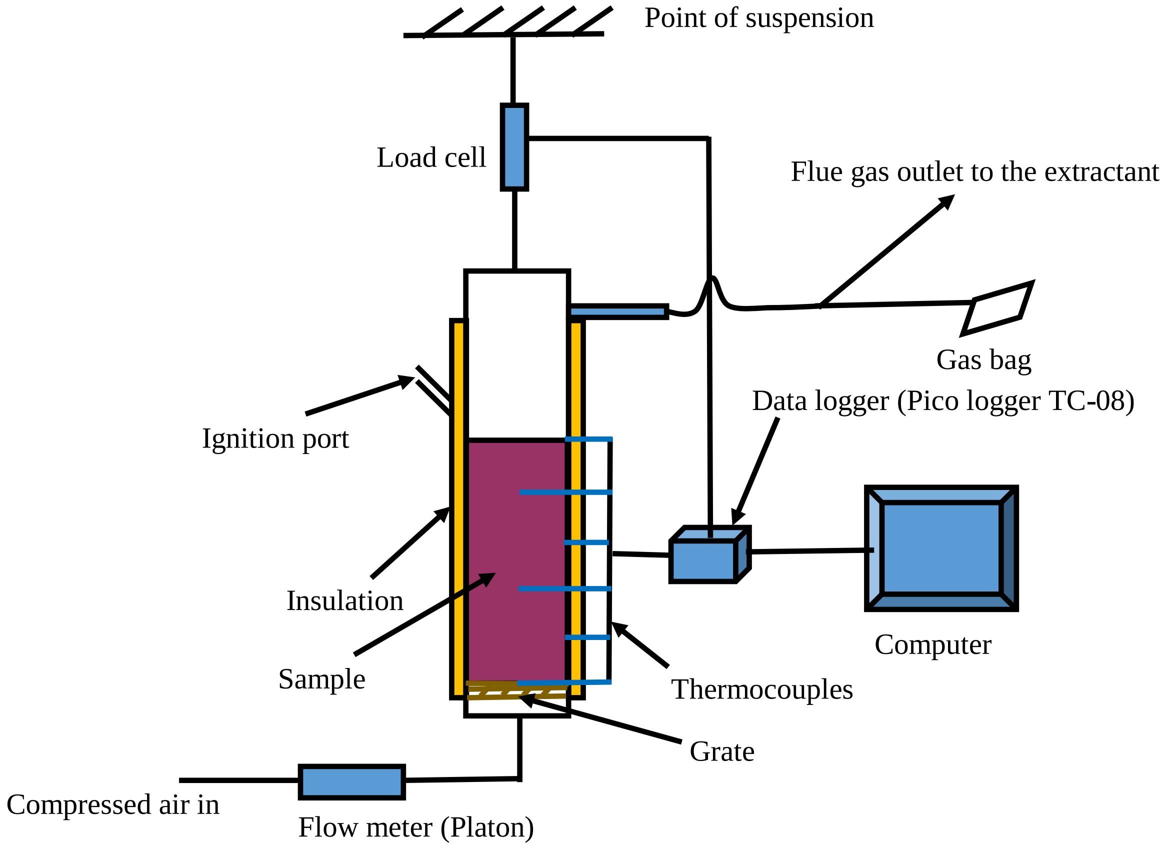


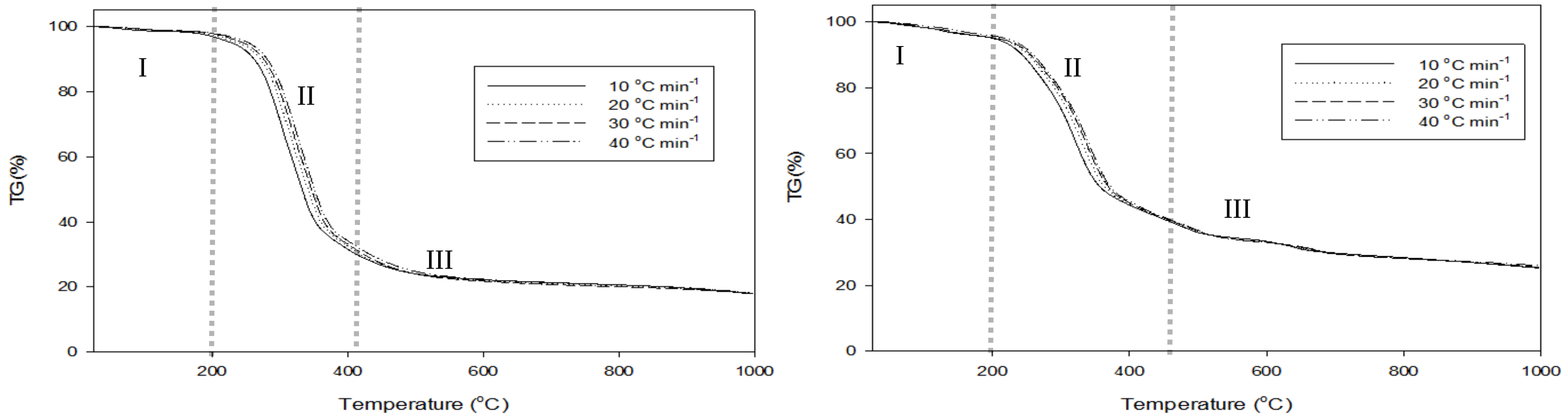
Fig 4.2: Schematic of fixed bed reactor

4.2 Results and Discussion

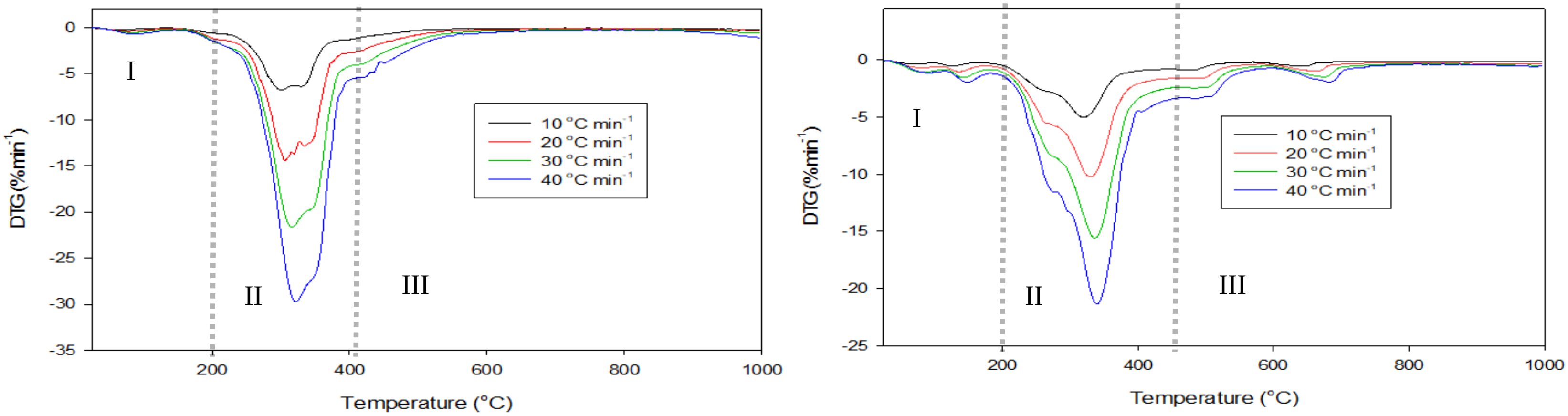
4.2.1 Pyrolysis

4.2.1.1 TGA analysis

Maize cob and bean straw showed three decomposition stages in Helium (He) (Fig 4.3): moisture release at temperatures below 200^{o}C (stage I); decomposition of hemicellulose and cellulose and partial decomposition of lignin >200-409^{o}C for maize cob and >200-465^{o}C for bean straw (stage II) and lignin and primary char decomposition between >409-1000^{o}C for maize cob and >465-1000^{o}C for bean straw (stage III).


(a) TG: Maize cob

(b) TG: Bean straw


(c) DTG: Maize cob

(d) DTG: Bean straw

Fig 4.3: TG and DTG of maize cob and bean straw under He at heating rates of 10, 20, 30 and 40°C min $^{-1}$.

The highest rate of weight loss was attained at stage II due to the release of the volatiles. The remaining was 18% and 25-26% for maize cob and bean straw respectively. The rate of weight loss increased with increasing heating rate from 10^{o}C min^{-1} to 40^{o}C min^{-1} (Fig 4.3 c and d). The peak weigh loss rate became higher and broader with increasing heating rate is because the components in biomass degrade simultaneously at high heating rate thereby causing overlap in peaks (Liang et al., 2014). CO_2, CO and H_2O increased with increasing heating rate (Fig 4.4 and Fig 4.5). The trends of the TG and DTG curves agree well with other biomass materials such as cardoon leaves and stem (Damartzis et al., 2011), para grass (Ahmad et al., 2017) and smooth cordgrass (Liang et al., 2014).

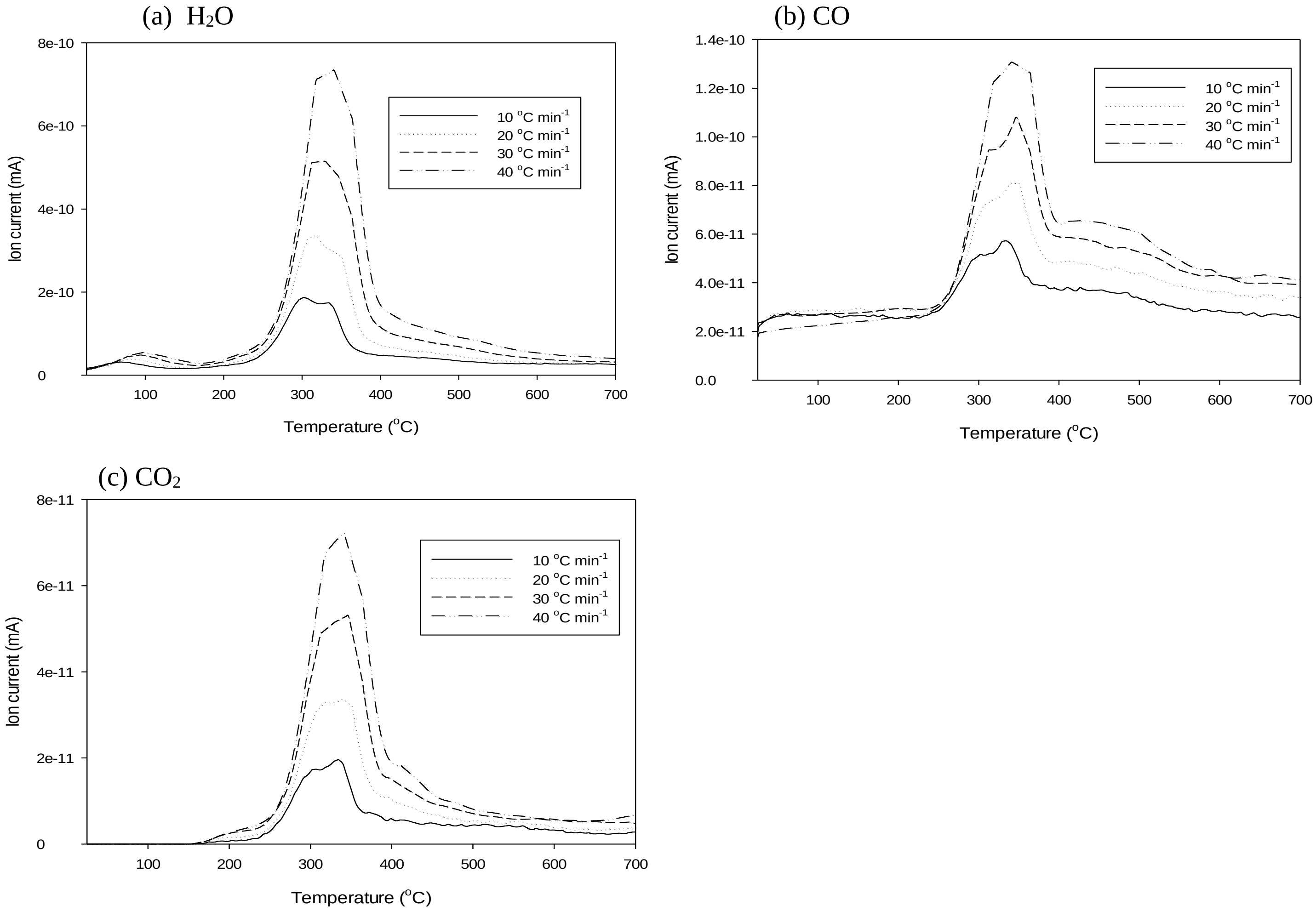
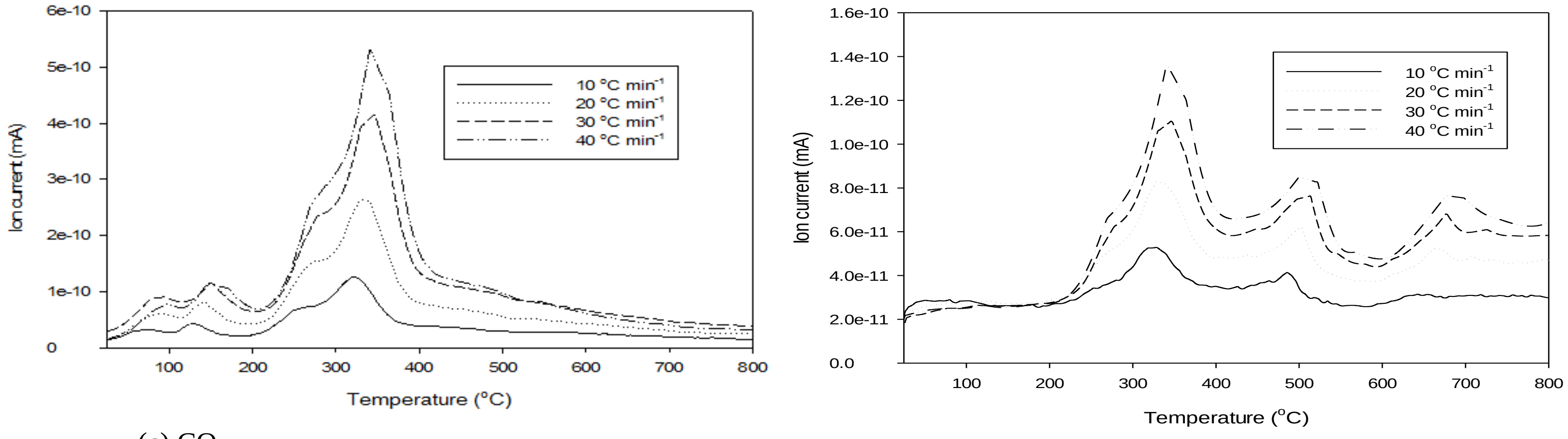


Fig 4.4: Effect of heating rate on (a) H_2O, (b) CO and (c) CO_2 released from maize cob in He.



(a) H_2O

(b) CO

(c) CO_2

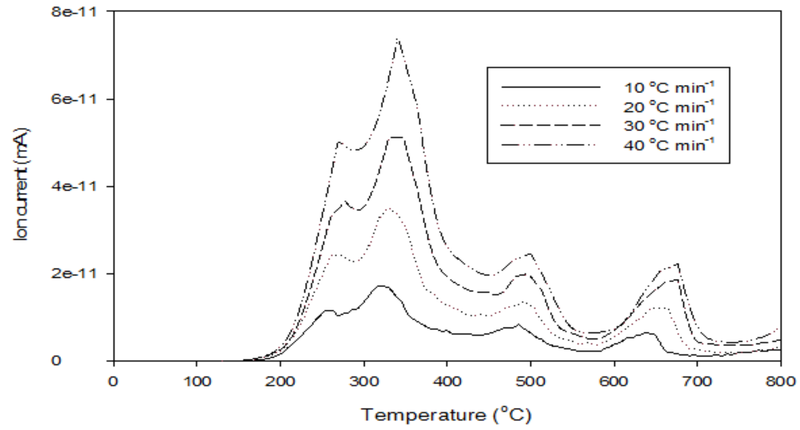


Fig 4.5: Effect of heating rate (a) H_2O, (b) CO and (c) CO_2 released from bean straw in He.

4.2.1.2 Pyrolysis of briquettes in a fixed bed reactor

4.2.1.2.1 Product yield

Table 4.1 shows the bi-oil, char and gas yields from pyrolysis of maize cob and bean straw. Bio-oil, char and gas yields from maize cob briquettes ranged between 48.0-53.0%, 23.8-32.6% and 18.2-26.1%, while from bean straw ranged between 42.6-46.8%, 25.9-35.9% and 16.3-27.5% respectively with variations in the pyrolysis conditions i.e. temperature (410, 530 and 650 °C), heating rate (10, 15 and 20 °C min^{-1}) and carrier gas (N_2) flow rate (40,50 and 60 cm^3 min^{-1}). The impact of heating rate, carrier gas flow rate (Table 4.1, Appendix B 2-Appendix B 7) and briquetting conditions (Table 4.2) on yields of all pyrolysis products were negligible. The char yield decreased from 32.57-24.36% for maize cob briquette and 35.85-27.92% for bean straw briquette with increasing temperature from 410 to 530°C and remained almost constant with further increasing temperature (Table 4.1). This is because the decomposition of cellulose, hemicellulose and lignin ceases at temperature above 500°C (confirmed by TG analysis Fig 4.3 a and b section 4.2.1.1). A similar observation of variation in char yield with temperature was reported for apple tree branches within a temperature range of 300-500°C (Shi-Xiang Zhao et al., 2017).

Bean straw briquettes had higher char yield than maize cob briquettes due to the higher lignin content (10.2% for bean straw and 1.5% for maize cob) and ash content (6.2% for bean straw and 3.0% for maize cob). Hemicellulose and cellulose produce mainly volatiles whereas lignin produces mainly char (Wei et al., 2006, Ogunjobi and Lajide, 2013). Alkali metals in ash such as sodium and potassium was reported (Shariff et al., 2016) to catalyze repolymerization thereby increasing char yield. The char yield from pyrolysis of maize cob briquette in the fixed bed at 410°C was similar to those from TGA (Fig 4.3a section 4.2.1.1) at varying heating rate (10-40°C min^{-1}). However, the char yields for maize cob briquettes were different to those obtained in TGA temperature of 530 and 650°C. Meanwhile, char yield from pyrolysis of bean straw briquettes at both tested temperature (410, 530 and 650°C) were lower than those obtained in TGA. Char yield from TGA at a temperature of about 410°C, 530°C and 650°C were 30%, 24% and 22% for maize cob and 44%, 35% and 31% for bean straw respectively.

Table 4.1: Yields of pyrolysis products from maize cob (briquetting conditions: pressure: 200MPa, temperature: 80 °C and particle size: <2.36mm) and bean straw briquettes (briquetting condition: 150MPa, temperature: 80 °C, particle size: <4mm). Mximum error on yields of products ±3.61%.

Pyrolysis temperature (°C)	Heating rate (°C min^{-1})	Flow rate (cm^3 min^{-1})	Maize cob			Bean straw		
			Bio-oil (%)	Char (%)	Gas* (%)	Bio-oil (%)	Char (%)	Gas* (%)
410	10	40	49.47	30.86	19.67	45.20	32.43	22.37
	10	50	48.00	32.57	19.43	44.63	34.88	20.49
	10	60	50.83	30.96	18.21	47.82	35.92	16.26
	15	40	49.31	32.51	18.18	44.01	33.96	22.03
	15	50	49.43	30.20	20.37	46.62	33.09	20.29
	15	60	50.82	30.74	18.44	44.38	34.07	21.55
	20	50	49.43	32.40	18.17	42.64	34.48	22.88
530	10	40	52.12	25.97	21.91	44.07	29.01	26.92
	10	50	51.15	26.14	22.71	44.89	30.16	24.95
	10	60	52.18	27.79	20.03	45.93	29.03	25.04
	15	40	49.39	25.90	24.71	46.73	27.85	25.42
	15	50	51.43	26.31	22.26	44.65	29.87	25.48
	15	60	53.03	26.49	20.48	45.26	29.93	24.81
	20	40	51.27	25.55	23.18	46.60	29.35	24.05
	20	60	51.09	24.36	24.55	44.86	29.99	25.15

Pyrolysis temperature (°C)	Heating rate (°C min^{-1})	Flow rate (cm^{3} min^{-1})	Maize cob			Bean straw		
			Bio-oil (%)	Char (%)	Gas* (%)	Bio-oil (%)	Char (%)	Gas* (%)
650	10	40	53.02	24.04	22.94	47.06	27.48	25.46
	10	50	52.75	24.93	22.32	46.78	26.59	26.63
	10	60	51.86	25.10	23.04	45.15	28.57	26.28
	15	40	50.85	23.87	25.28	45.85	27.12	27.03
	15	50	49.98	23.97	26.05	46.42	27.41	26.17
	15	60	52.42	24.09	23.49	46.58	25.89	27.53
	20	50	52.84	23.81	23.35	48.21	26.05	25.74

* By difference

Table 4.2: Effect of briquetting conditions: Pressure (MPa)/particle size (mm)/temperature (^{o}C) on yields of pyrolysis products from for maize cob and bean straw briquettes. Pyrolysis temperature (^{o}C)/carrier gas flow rate (cm^{3} min^{-1})/heating rate (^{o}C min^{-1}) of 650/40/10. Maximum error on yields of pyrolysis products: ±2.11%.

Briquetting conditions	Maize cob			Bean straw		
	Bio-oil (wt)	Char (%wt)	Gas* (%wt)	Bio-oil (%wt)	Char (%wt)	Gas* (%wt)
200/2.36/20	50.49	24.63	24.88	45.45	27.13	27.42
150/2.36/80	50.80	24.43	24.77	-	-	-

* By difference

The effect of a bean straw-maize blend on yields and properties of pyrolysis products was investigated with pyrolysis temperature of 650^{o}C, heating rate of 10 ^{o}C min^{-1}and carrier gas flow rate, of 40 cm^{3} min $^{-1}$. Increasing maize cob content from 25-75wt% had a 8% increase bio-oil yield at the expense of char and gas (Table 4.3). The increase in bio-oil yield from blend briquettes with increasing maize cob was due to the increase in volatiles and a decrease in ash composition as discussed previously in section 3.2.1.4. The decrease in char yield with increasing maize cob blend is likely due to lower ash and fixed carbon content in the maize cob as a result of the lower lignin content.

Table 4.3: Yields of pyrolysis products from bean straw-maize cob blended briquettes (briquetting conditions: pressure: 150 MPa, particle size: <4mm and temperature: 80^{o}C). Pyrolysis temperature (^{o}C)/carrier gas flow rate (cm^{3} min^{-1})/heating rate (^{o}C min^{-1}) of 650/40/10. Maximum error on product yields: ±3.21%

Bean straw:maize cob blend ratio (wt%:wt%)	Bio-oil (%wt)	Char (%wt)	Gas* (%wt)
25:75	51.35	25.35	23.30
50:50	48.74	26.42	24.84
75:25	47.70	26.35	25.95

* By difference

4.2.1.2.2 Properties of pyrolysis products

(a) Char

All chars produced at pyrolysis temperature of 410^{o}C, 530^{o}C and 650^{o}C for maize cob and bean straw briquettes (Table 4.4) had volatile <30% for bean straw briquettes and <24% for maize cob briquette and fixed carbon >57% for bean straw briquette and >67% for maize cob briquette. However, the char ash contents were up to 11% for maize cob briquette and 17% for bean straw briquette. Ash content in raw material is accumulated in char as volatiles are released during pyrolysis (Al-Wabel et al., 2013, Suliman et al., 2016). A higher ash content may cause more clinker thereby reducing the efficiency of the combustion system (Mythili and Venkatachalam, 2015). Converting heterogeneous agricultural residues to carbon-like char for energy may therefore require pre-treatment steps to reduce the ash content. Liu et al., (2015) demonstrated that ash content of pinewood and coconut fiber chars can be reduced by washing with deionized water, acetic acid and citric acid. Furthermore, combustion of char may require cleaning of flue gas by an ash removing device to minimize particle emissions. In this study, volatile content decreased as fixed carbon content increased with increasing pyrolysis temperature (Table 4.4).

Table 4.4: Proximate analysis, high heating value (HHV) and energy yield of char from maize cob briquettes (briquetting conditions: pressure: 200MPa, temperature: 80 ^{o}C, particle size: <2.36mm) and bean straw briquettes (briquetting conditions: pressure: 150MPa, temperature: 80 ^{o}C, particle size: <4mm). Maximum error on proximate analysis and HHV were ±1.94% and ±0.81MJ kg^{-1}

Pyrolysis temperature (^{o}C)	Heating rate (^{o}C min^{-1})	Flow rate (cm^{3} min^{-1})	Maize cob					Bean straw				
			Ash (%)	Volatile (%)	Fixed carbon (%)	HHV (MJ kg^{-1})	Energy yield (%)	Ash (%)	Volatile (%)	Fixed carbon (%)	HHV (MJ kg^{-1})	Energy yield (%)
410	10	40	8.50	21.13	70.37	28.20	46.05	13.66	27.34	59.00	23.32	43.71
	10	50	8.04	22.25	69.71	28.67	49.41	14.38	25.00	60.62	23.87	48.13
	10	60	9.06	23.86	67.08	28.25	46.28	13.53	28.79	57.68	23.98	49.79
	15	40	8.20	21.10	70.70	28.85	49.63	15.01	23.80	61.19	22.89	44.93
	15	50	8.78	22.66	68.56	28.68	45.83	14.87	24.65	60.48	23.79	45.50
	15	60	8.64	19.98	71.38	28.35	46.11	15.41	23.99	60.60	22.86	45.02
	20	50	8.20	22.01	69.79	28.74	49.27	16.14	24.78	59.08	23.74	47.32
530	10	40	10.39	9.11	80.50	29.26	40.21	15.00	15.47	69.53	24.88	41.72
	10	50	11.12	10.07	78.81	30.03	41.53	14.46	16.55	68.99	24.99	44.72
	10	60	10.09	11.95	77.96	29.57	43.48	13.14	15.68	71.18	24.47	41.06
	15	40	10.84	10.16	79.00	29.07	39.84	15.66	17.75	66.59	24.50	39.44

Pyrolysis temperature (^{o}C)	Heating rate (^{o}C min^{-1})	Flow rate (cm^{3} min^{-1})	Maize cob					Bean straw				
			Ash (%)	Volatile (%)	Fixed carbon (%)	HHV (MJ kg^{-1})	Energy yield (%)	Ash (%)	Volatile (%)	Fixed carbon (%)	HHV (MJ kg^{-1})	Energy yield (%)
530	15	50	9.69	9.23	81.08	29.95	41.69	15.88	16.61	67.51	24.85	42.91
	15	60	9.37	10.35	80.28	29.25	41.00	15.95	14.87	69.18	24.29	42.02
	20	40	9.93	10.55	79.52	29.26	39.56	14.61	17.73	67.66	24.73	41.96
	20	60	9.82	10.67	79.51	30.45	39.25	17.33	16.95	65.72	24.74	42.89
650	10	40	10.18	6.83	82.99	29.91	38.04	15.94	8.90	75.16	25.73	40.87
	10	50	10.63	9.57	79.80	30.03	39.61	14.27	9.97	75.76	26.14	40.18
	10	60	10.53	7.31	82.16	29.80	39.58	14.66	9.44	75.90	25.70	42.44
	15	40	9.97	6.73	83.30	29.93	37.80	16.92	9.77	73.31	25.62	40.16
	15	50	10.88	7.54	81.58	29.70	37.67	14.39	9.25	76.36	25.53	40.45
	15	60	10.60	7.70	81.70	29.60	37.73	16.60	8.52	74.88	25.95	38.84
	20	50	10.91	6.27	82.82	29.63	37.33	15.41	10.41	74.18	26.08	39.27

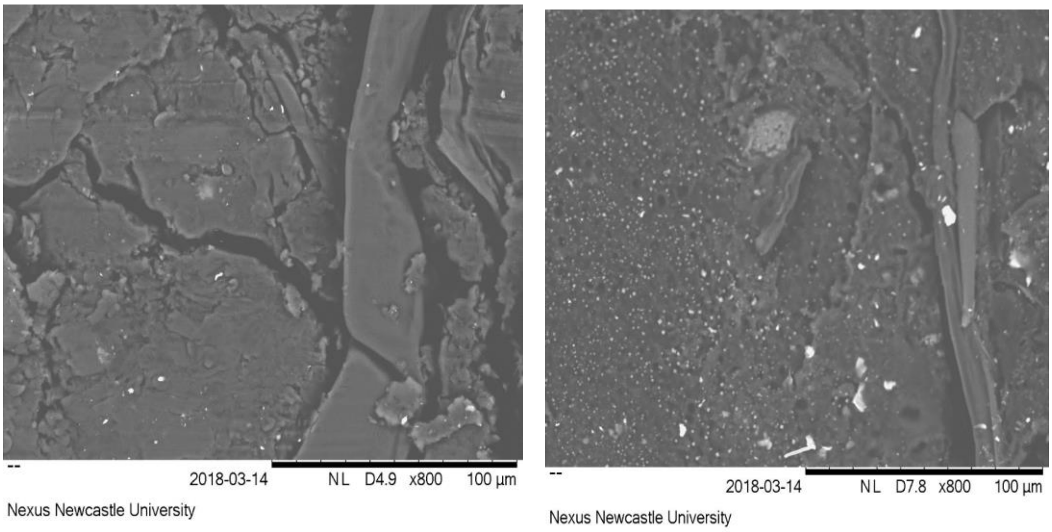
The high heating value (HHV) was 28-30 MJ kg^{-1} for char derived from maize cob briquette and 23-26MJ kg^{-1} for that from bean straw briquette. Increasing pyrolysis temperature from 410°C to 650°C increased HHV of char only by 6-14%. Therefore, the energy yield, (Table 4.4) decreased with pyrolysis temperature due to a higher reduction in char yield (Table 4.1). Other pyrolysis parameters (heating rate and carrier gas flow rate) and briquetting conditions (pressure and temperature) had no impact on HHV and proximate properties. The findings in this study were similar to the work reported by Li et al., (2016) for pinewood sawdust briquettes. The higher HHV of maize cob briquette char when compared to bean straw is likely due to the lower ash content of the maize cob char (Ronsse et al., 2013). The HHV of maize cob briquette char produced from pyrolysis temperatures of 530°C and 650 °C in this study compares well with the calorific value of lignite ($\approx$28 MJ kg^{-1}) (Razuan et al., 2011) and HHV of chars from maize stalk (32-34 MJ kg^{-1}) and rice straw (26-32 MJ kg^{-1}) produced at 600 to 1000 °C (Fu et al., 2011). Increasing maize cob proportion in blended briquettes increased char HHV and fixed carbon content (Table 4.5) due to the lower ash content of maize cob.

Table 4.5: Proximate analysis and high heating value (HHV) of char from bean straw-maize cob blended briquettes (moisture free). Pyrolysis temperature (°C)/carrier gas flow rate (cm^{3} min^{-1})/heating rate (°C min^{-1}) of 650/40/10. Maximum error on proximate anslysis: ±0.47%wt

Bean straw:maize cob ratio	Ash (%wt)	Volatile (%wt)	Fixed carbon (%wt)	HHV (MJ kg^{-1})
25:75	11.82	8.90	79.28	28.84
50:50	13.83	8.81	77.36	28.42
75:25	14.93	7.99	77.08	27.37

The surface area of char derived from maize cob and bean straw briquettes was low at 10.73 m^{2} g^{-1} and 3.29 m^{2} g^{-1} respectively. The surface of maize cob char in this study is low compared to literature (25.67 m^{2} g^{-1}) (Hao et al., 2013). The SEM analysis (Fig 4.6 and Fig 4.7) showed that surface morphology of biochar was strongly dependent on pyrolysis temperature. Compared to briquettes, the surfaces of the chars were rough indicating that the original lignocellulose structures were destroyed. Cracks developed on the surface of chars following pyrolysis most likely due to release of volatiles formed during decomposition. Chars produced at 530 °C had wider cracks compared to those produced at both 410 °C and 650 °C. Above 530 °C, the size of cracks reduced due to collapse of cracks.

(a) Briquette (b) 410 °C



(c) 530 °C (d) 650 °C

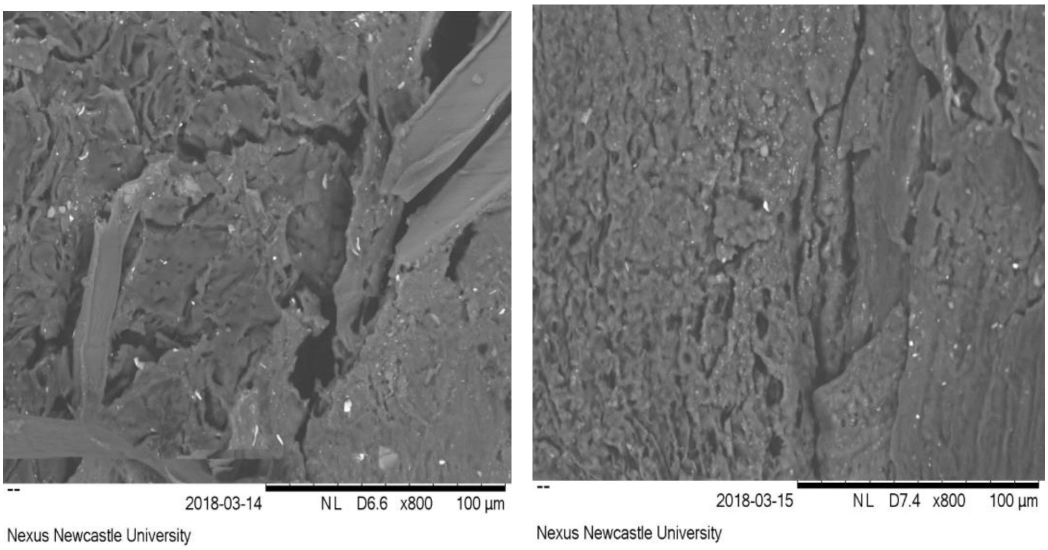
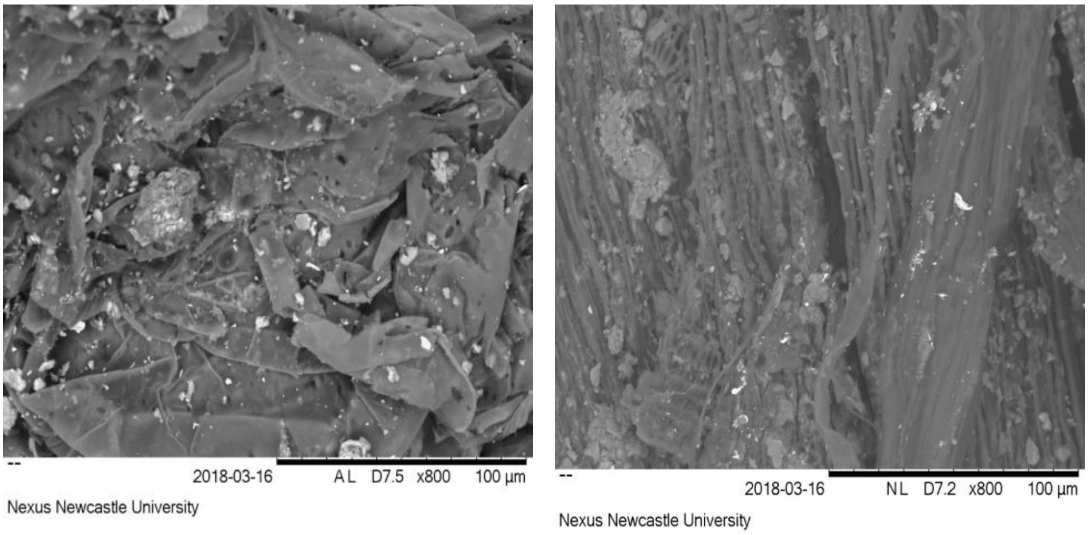


Fig 4.6: SEM images of maize cob briquettes and char produced at pyrolysis temperatures of (a) 410 °C, (b) 530 °C and (c) 650 °C. Maize cob briquettes were produced at a pressure of 200 MPa, moisture of 7.14%, particle size 2.36mm and temperature of 80°C. Char was produced at a carrier gas flow rate of 40 cm^3 min^{-1} and a heating rate of 10°C min^{-1}.

(a) Briquette (b) 410 °C



(c) 530 °C (d) 650 °C

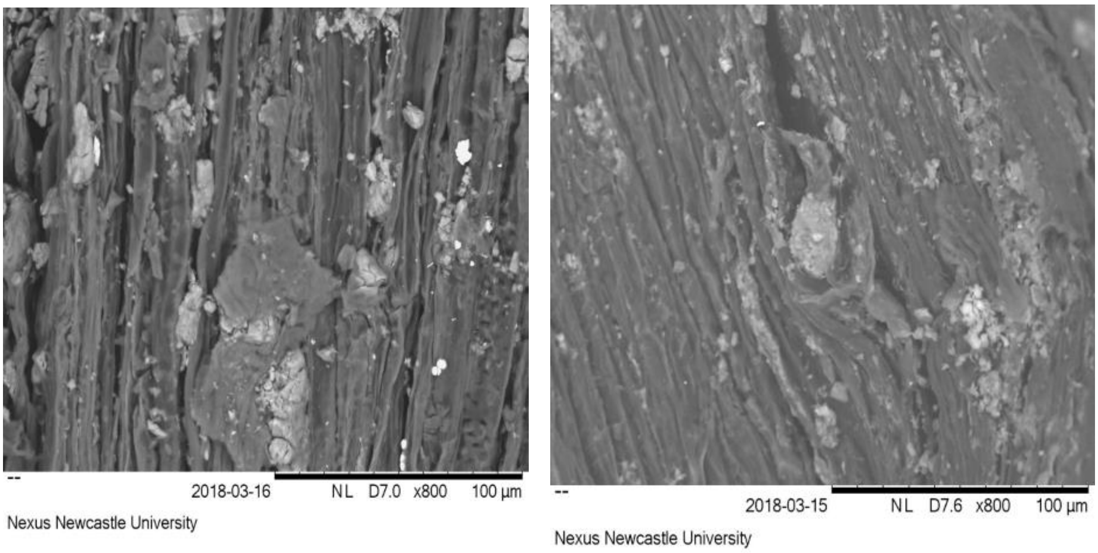


Fig 4.7: SEM images of bean straw briquette and char produced at pyrolysis temperatures of (a) 410 °C, (b) 530 °C and (c) 650 °C. Bean straw briquettes were produced at a pressure of 150 MPa, moisture, 10.63%, particle size <4.0 mm and temperature of 80°C. Char was produced at a carrier gas flow rate of 40cm^3 min^{-1} and a heating rate of 10°C min^{-1}.

For feedstock (maize cob and bean straw), O-H, C-O, C-H, C=C, and C=O are the most common chemical bonds in cellulose, hemicellulose and lignin (Fig 4.8). However, these functional groups were removed or partially removed with increasing pyrolysis temperature (Fig 4.8, Appendix B 8 and Appendix B 9) as a reduction in intensities of O-H (around 3400-3200 cm^{-1}) and C-H (between 3400-3200 cm^{-1}) with increasing temperature. The reduction in O-H is likely due to dehydration of cellulose (Hao et al., 2013). The reduction in the intensity of C-H is an indication of a decrease in aliphaticity of the solid after pyrolysis (Açıkalın et al., 2012). The intensities at 1580 cm^{-1} (ascribed to C=C vibration in aromatic rings) and 876-746 cm^{-1} (indicating aromatic C-H out-of-plane bending vibration) increased with increasing temperature from 410^{o}C to 530^{o}C which indicated an increase in carbonization and aromaticity (Hao et al., 2013). However, the aromaticity decreased (shown by the decrease in the C-H intensities) (Açıkalın et al., 2012) with further increase in temperature to 650^{o}C due to the release of H atoms (Hao et al., 2013). The intensity of the C-H peak at 876-746 cm^{-1} increased with increasing bean straw content in the bean straw-maize cob blended briquettes (Fig 4.9).

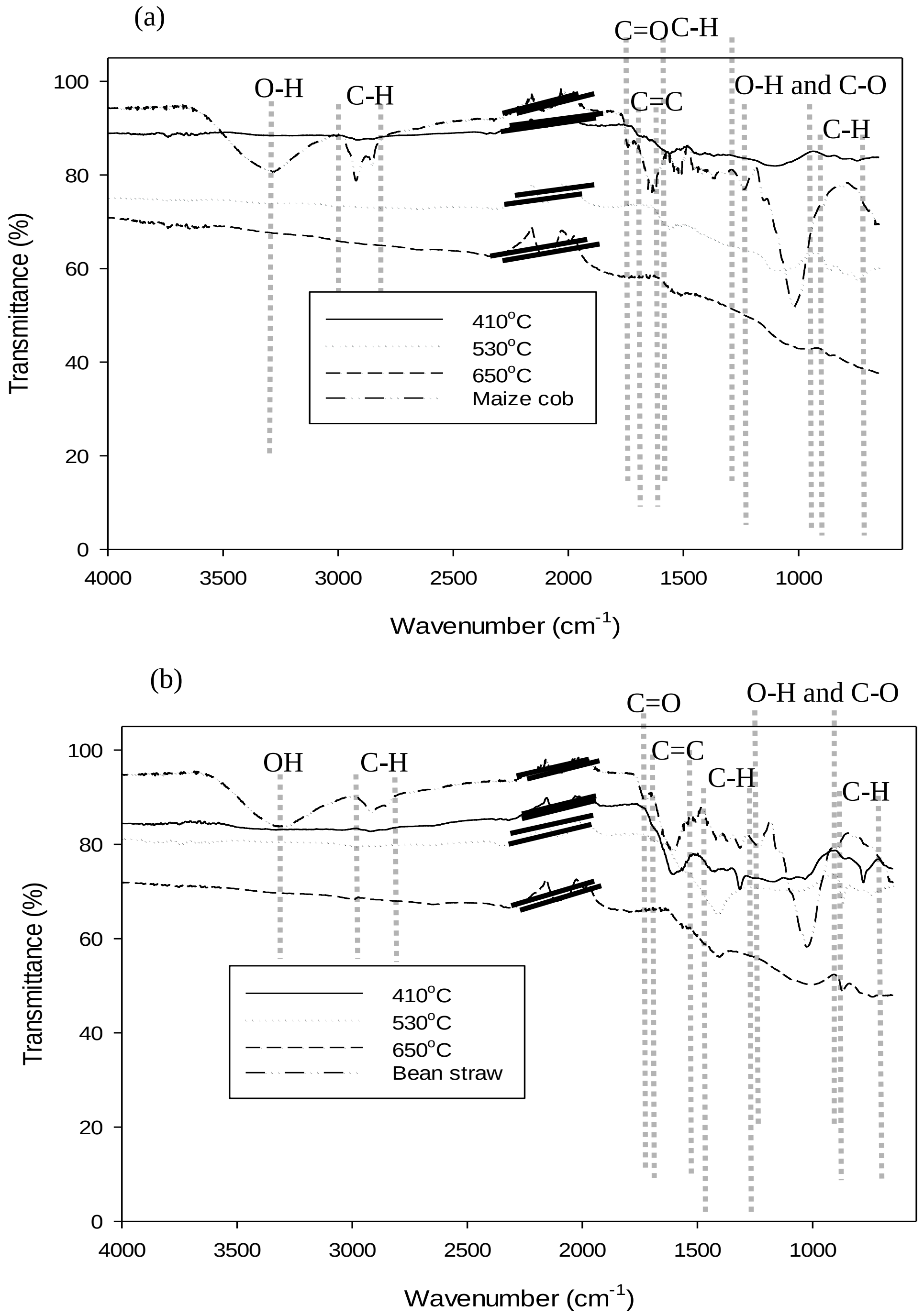


Fig 4.8: FTIR spectra of biochar from (a) maize cob and (b) bean straw briquettes at different pyrolysis temperatures. Maize cob briquettes were produced at a pressure of 200 MPa, moisture of 7.14%, particle size 2.36mm and temperature of 80 °C. Bean straw briquettes were produced at a pressure of 150MPa, moisture, 10.63%, particle size <4.0 mm and temperature of 80°C.

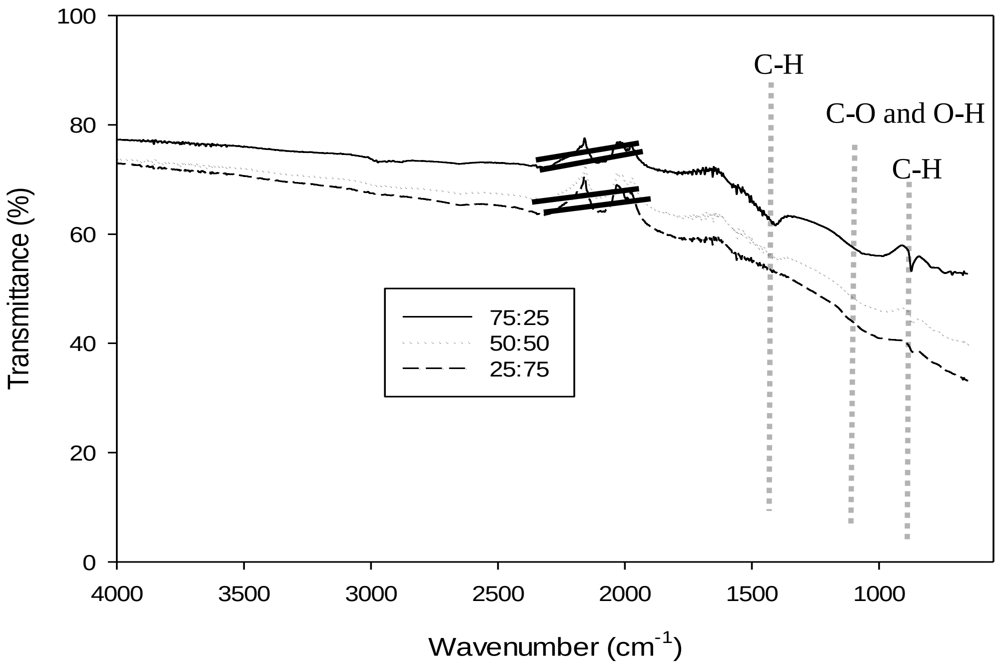


Fig 4.9: FTIR spectra of char from bean straw-maize cob blended briquettes produced at pyrolysis temperature/heating rate/carrier gas flow rate of 650°C/10 °C min^{-1}/40 cm^{3} min^{-1}. Legend: bean straw:maize cob ratio

(b) Bio-oil

Table 4.6 shows the pH, density and water content of the bio-oils from the pyrolysis of maize cob and bean straw briquettes. Bio-oils produced were highly acidic and corrosive with pH values ranging between 3.13-4.31 for maize cob and 2.73-4.39 for bean straw. The low pH could be due to the high content of phenolic compounds (Table 4.7). Bio-oils in this study had density ~1.05 g cm^{-3} and contained up to 73%wt water. The pH and density fall within the range reported in the literature for bio-oil from other biomass materials (Ji-lu, 2007, Park et al., 2012), however, the water content is higher most likely due to variation in particle size (briquette had diameter ~2cm). Increasing particle increases water content in bio-oil due to increased effect of intraparticle dehydration secondary reactions (Garcia-Perez et al., 2008). Both the water content, pH and density were independent of pyrolysis and briquetting conditions studied. Y. Gao et al., (2016) reported that water content of coconut bio-oil increased from 40.31-50.29%wt with increasing temperature from 350°C to 575°C.

Table 4.6: Density, pH and water content of bio-oil from pyrolysis of (a) maize cob briquettes (briquetting conditions: pressure: 200MPa, temperature: 80 ^{o}C, particle size: <2.36mm) and bean straw briquettes (briquetting conditions: pressure: 150MPa, temperature: 80 ^{o}C, particle size: <4mm).

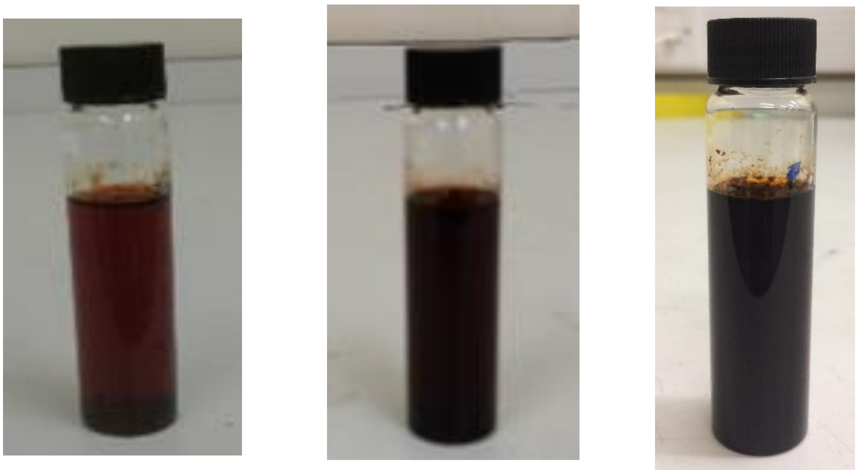
Pyrolysis temperature (^{o}C)	Heating rate (^{o}C min^{-1})	Flow rate (cm^{3} min^{-1})	Maize cob			Bean straw		
			pH	Density (g cm^{-3})	Water content (%wt)	pH	Density (g cm^{-3})	Water content (%wt)
410	10	40	3.75	1.04	69.30	3.48	1.04	68.48
	10	50	3.32	1.04	70.73	3.56	1.04	71.46
	10	60	3.96	1.05	70.33	3.38	1.05	70.17
	15	40	3.13	1.04	70.82	3.64	1.04	69.12
	15	60	3.49	1.04	72.26	3.99	1.04	70.20
	20	50	3.32	1.04	70.83	3.26	1.05	70.87
530	10	40	3.34	1.05	70.10	3.86	1.05	68.31
	10	50	3.83	1.05	69.70	3.56	1.05	69.73
	10	60	3.72	1.05	71.79	3.89	1.04	71.19
	15	50	3.82	1.04	70.86	4.39	1.04	68.32
	15	60	4.31	1.05	71.63	3.70	1.06	69.49
	20	40	3.78	1.04	70.56	3.84	1.04	69.90
	20	60	3.48	1.04	73.30	4.00	1.05	68.49

Pyrolysis temperature (°C)	Heating rate (°C min^{-1})	Flow rate (cm^3 min^{-1})	Maize cob			Bean straw		
			pH	Density (g cm^{-3})	Water content (%wt)	pH	Density (g cm^{-3})	Water content (%wt)
650	10	40	3.70	1.04	70.39	3.52	1.05	68.90
	10	50	3.95	1.05	68.64	3.83	1.04	71.91
	10	60	4.05	1.05	70.91	2.73	1.07	69.06
	15	40	3.96	1.04	72.10	2.87	1.07	69.25
	15	50	3.75	1.04	71.36	4.26	1.04	68.84
	15	60	4.00	1.04	71.00	3.93	1.05	70.87
	20	50	3.76	1.04	72.70	3.91	1.04	68.42

Table 4.7: Composition of bio-oil derived from maize cob and bean straw briquettes at pyrolysis temperature/heating rate/carrier gas flow rate of 650°C/10 °C min^{-1}/40 cm^3 min^{-1}.

Compound	Area (%)	
	Maize cob	Bean straw
Furfural	11.52	8.21
Pentanone 4-Hydroxy-4-Methyl	13.64	8.10
Furanmethanol	11.52	-
Propanone Acetyloxy	3.80	-
2,5-Hexanedione	6.18	6.46
3-Hexene-2,5-dione	-	12.30
2-Hexene-2-One 5- Methyl	6.04	-
Phenol	4.64	3.14
4-Methylphenol	-	0.81
3-Methylphenol	0.59	-
Cyclopentandione 3-Methyl	3.37	5.46
2-Methoxyphenol	1.86	3.03
2-Methoxy-4 Methylphenol	-	2.13
1,2-Benzenediol	2.30	1.85
Glucanpyranose sugar	5.08	3.48
2,6-Dimethoxyphenol	1.19	4.89
3-Hydroxyl 4-Methoxy benzoic acid	-	3.95
D-Allose sugars	5.53	6.30
Hydroquinone-Silyl Ester	-	1.29
Ribopyranose sugar	1.01	2.55
2,6-Dimethoxy-Propanyl phenol	-	1.17
Dimethoxy phenols	-	0.16
Dimethoxy 4 Hydroxyl phenyl acid	-	1.23

Both briquette feedstocks had moisture content <11%, therefore most of the water in the bio-oil from the reactions such as condensation during pyrolysis. The high-water content made ignition impossible to determine the HHV. These bio-oils are of low quality and are therefore not suitable for direct combustion. High water content made these bio-oils unstable as shown by the colour changes (Fig 4.10) which suggests changes in properties of bio-oil with time. These changing properties could make design of an energy system to optimize the use of bio-oil challenging.



(a) First day

(b) 7 days

(c) 30 days

Fig 4.10: Maize cob briquette bio-oil colour change with time. Pyrolysis was carried out at a temperature of 530^{o}C, /heating rate of 10^{o}C min^{-1} and carrier gas flow rate of /40 cm^{3} min^{-1}.

The functional groups in the bio-oil and feedstock were similar (Fig 4.11, Appendix B 10 and Appendix B 11). The spectra for bio-oil obtained at different temperatures were identical which indicates that bio-oil had the same type of compounds irrespective of pyrolysis temperature used. The FTIR spectra show the O-H (stretching between 3200 to 3400cm^{-1}) indicating the presence of water, phenols, acids or alcohols (e.g. furanmethanol, and 3-hydroxyl 4-methoxy benzoic acid). C-H stretching vibration between 2800 and 3000 cm^{-1} and C-H deformation vibration between 1350 and 1475 cm^{-1} which indicates the presence of alkanes (e.g. 2,5 hexandione). The C=O stretching vibration between 1650-1750 cm^{-1} indicates the presence of ketones and aldehydes (e.g. Furfural). The C=C vibrations between 1575 and 1675 cm^{-1} indicates the presence of alkenes and aromatics (3-hexene-2,5-dione, 2-hexene-2-One 5-methyl, 4-methylphenol). The peak around 1300-1000 cm^{-1} shows the presence of C-O and O-H indicating the presence of phenols, alcohols, esters and ethers (e.g. hydroquinone-silyl ester, 2-methoxy-4 methylphenol, 2-methoxyphenol, 2-methoxy-4 methylphenol, 2,6-dimethoxyphenol). The presence of such functional groups were also reported in pistachio shell (Apaydin-Varol et al., 2007), cornelian cherry stone and grape seeds (Alper et al., 2015).

Table 4.7 shows bio-oil contained highly oxygenated compounds mainly furfural, phenolic compounds and sugars, similar to those reported in *Ipomoea carnea* bio-oil (Saikia et al., 2015). An abundance of furfural and phenolic compounds was also reported in bio-oils from corn cob, wheat straw, rice straw and rice husk at pyrolysis temperatures of 400- 450 ^{o}C (Biswas et al., 2017). The bio-oil could be a source of chemical e.g. phenolic compounds are important components of many insecticides and fungicides (Ali et al., 2016), and are also used in organic synthesis e.g. production of phenol formaldehyde resins, dyes and medicines (Cao, 2004). While, furanmethanol is used in production of furan resin (Cao, 2004). Bean straw bio-oil had more phenolic compounds than maize cob bio-oil probably due the higher lignin content in the bean straw (10.2%) as phenols are formed mainly from decomposition of lignin (Salema et al., 2017, Alper et al., 2015).

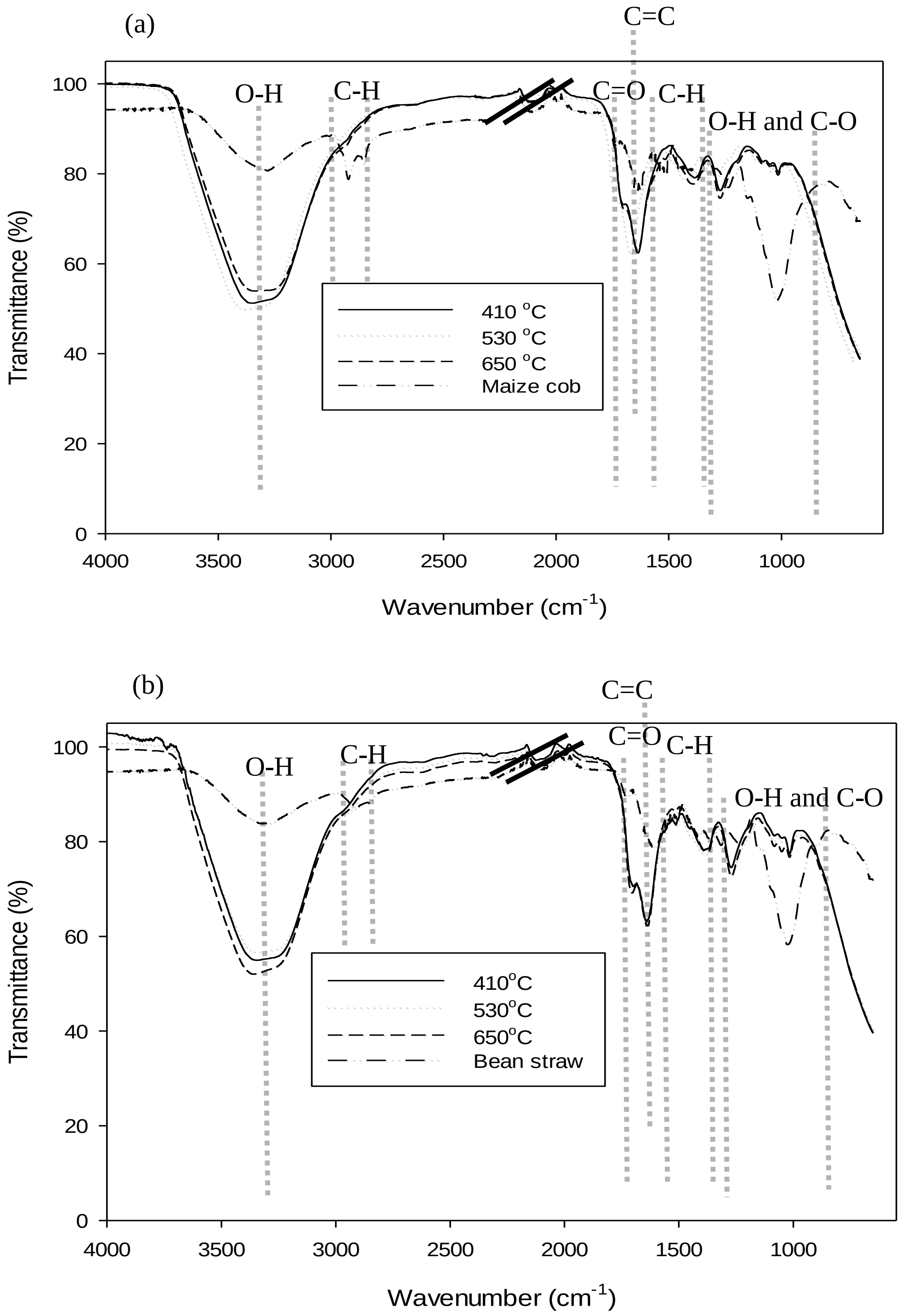


Fig 4.11: FTIR spectra of bio-oil from (a) maize cob and (b) bean straw briquettes. Maize cob briquettes were produced from a pressure of 200 MPa, moisture 7.14%, particle size 2.36mm and temperature of 80 °C. Bean straw briquettes were produced from a pressure of 150MPa, particle size <4mm and temperature of 80°C.

(c) Gas

At temperatures below 400^{o}C, the gas contained mainly CO_2 and CO (Fig 4.12 and Fig 4.13, Appendix B 12) due to decarboxylation and carbonylation of cellulose and hemicellulose (Uzun et al., 2007), which was similar to pyrolysis of corn stover and maize cob ((Mullen et al., 2010) CO evolution from temperature range of 300-650^{o}C was due to decomposition of cellulose, hemicellulose and lignin (Collard and Blin, 2014). A decrease in CO_2 versus temperature was observed in maize cob pyrolysis (Cao, 2004) and cotton straw, rice straw and rice husk (Fu et al., 2011). CH_4 yield increased with increasing temperature and peaked around 550-650^{o}C most likely due to demethylation (Collard and Blin, 2014). Hydrogen was observed at temperatures ≥300^{o}C due to decomposition of lignin (Yang et al., 2007). Though biomass is regarded as CO_2 neutral across its life-cycle, CO_2 removal is required to improve the quality and energy content of the product gas. CO_2 could be a potential carrier gas in torrefaction (Li et al., 2018) or gasification processes.

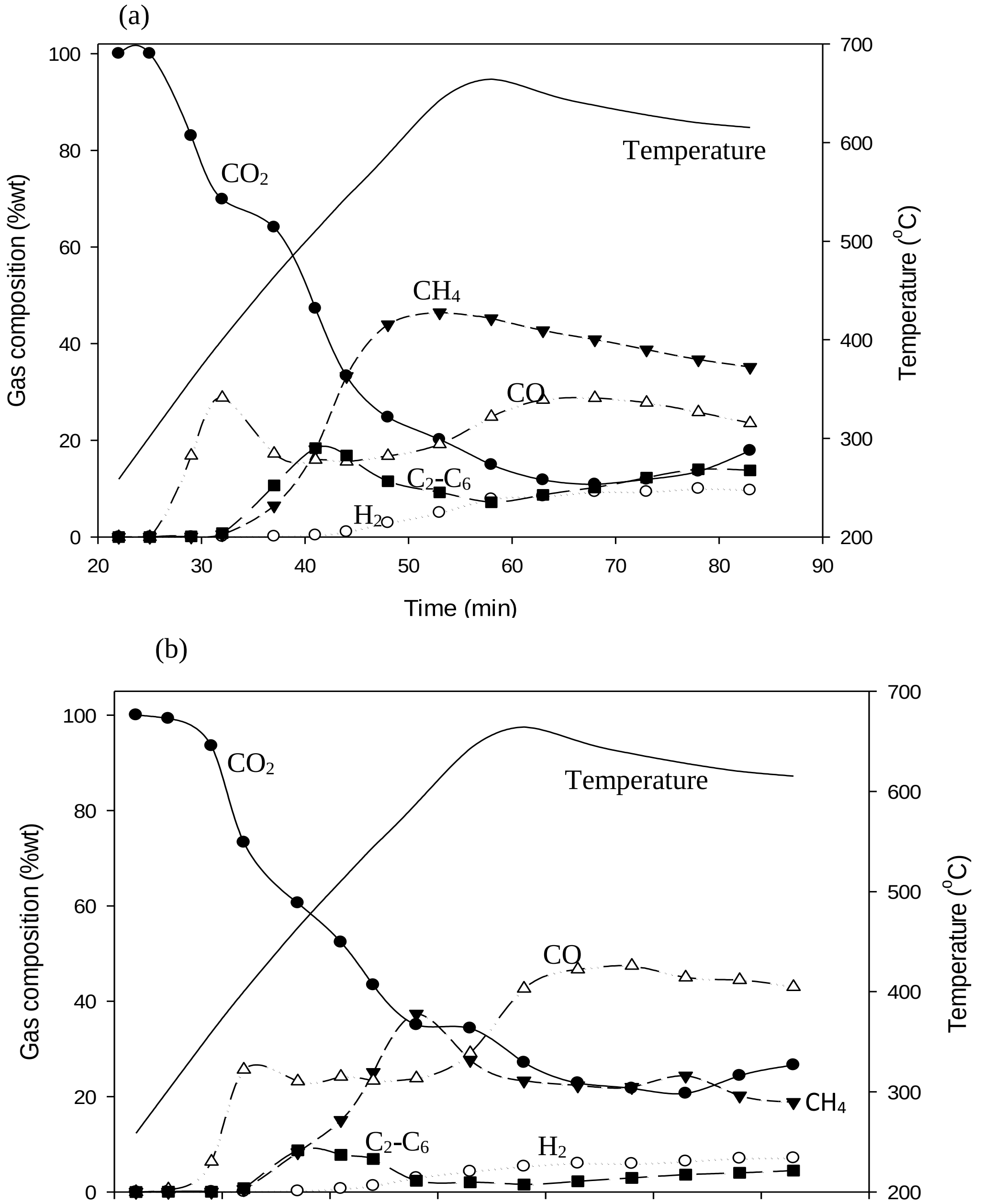
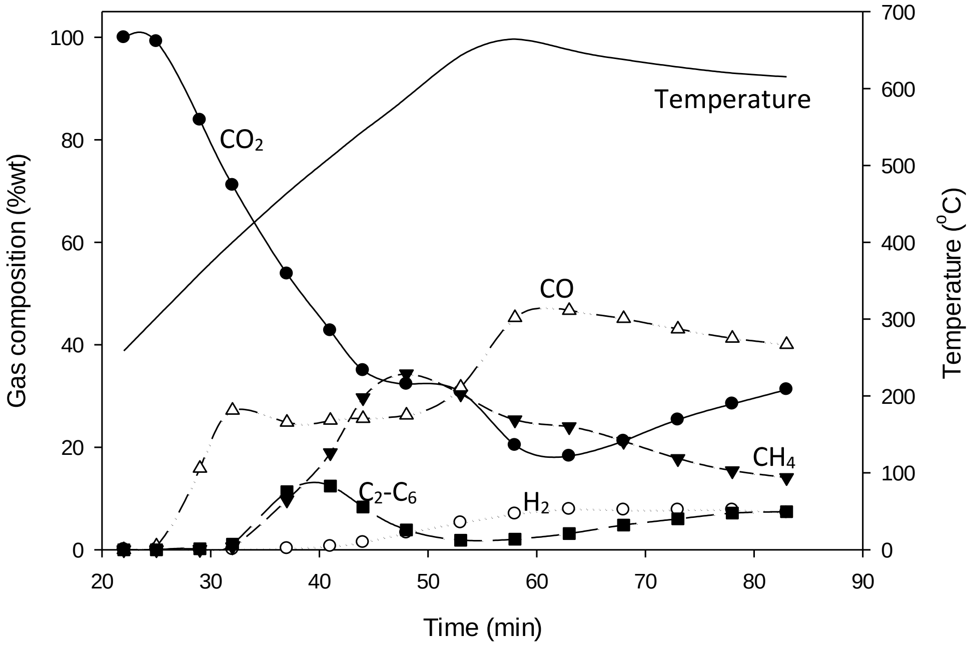


Fig 4.12: Gas composition of (a) maize cob briquettes (briquetting conditions: pressure: 200MPa, temperature: 80 °C and particle size: <2.36mm) and (b) bean straw briquettes (briquetting condition: 150MPa, temperature: 80°C, particle size: <4mm) at pyrolysis temperature/heating rate and carrier gas flow rate of 650°C/10°C min^{-1}/40 cm^3 min^{-1}.

(a) Bean straw-maize cob blend ratio: 25:75



(b) Bean straw-maize cob blend ratio: 75:25

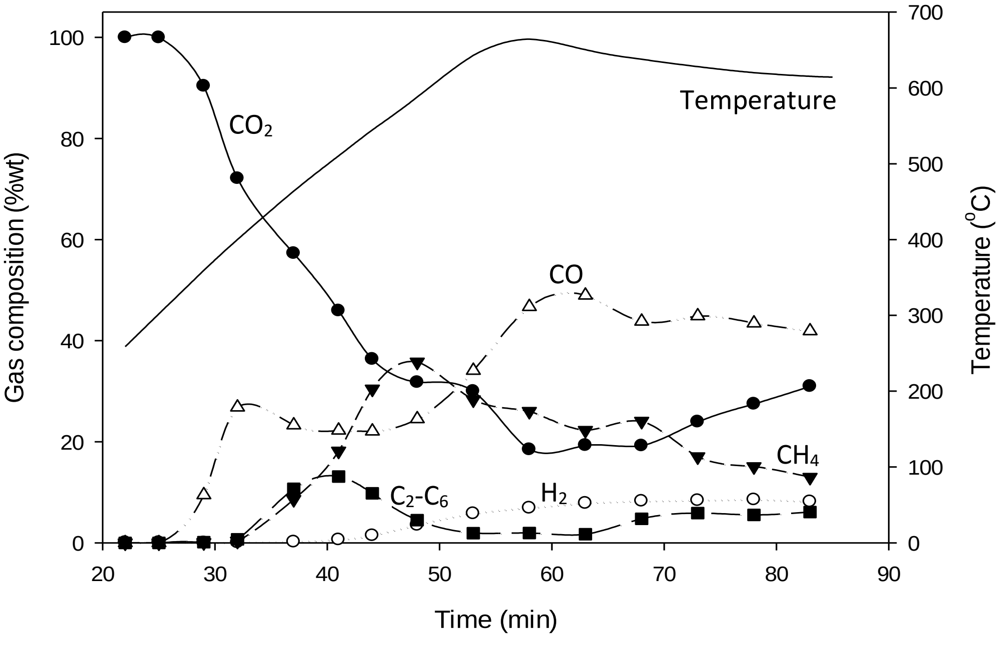


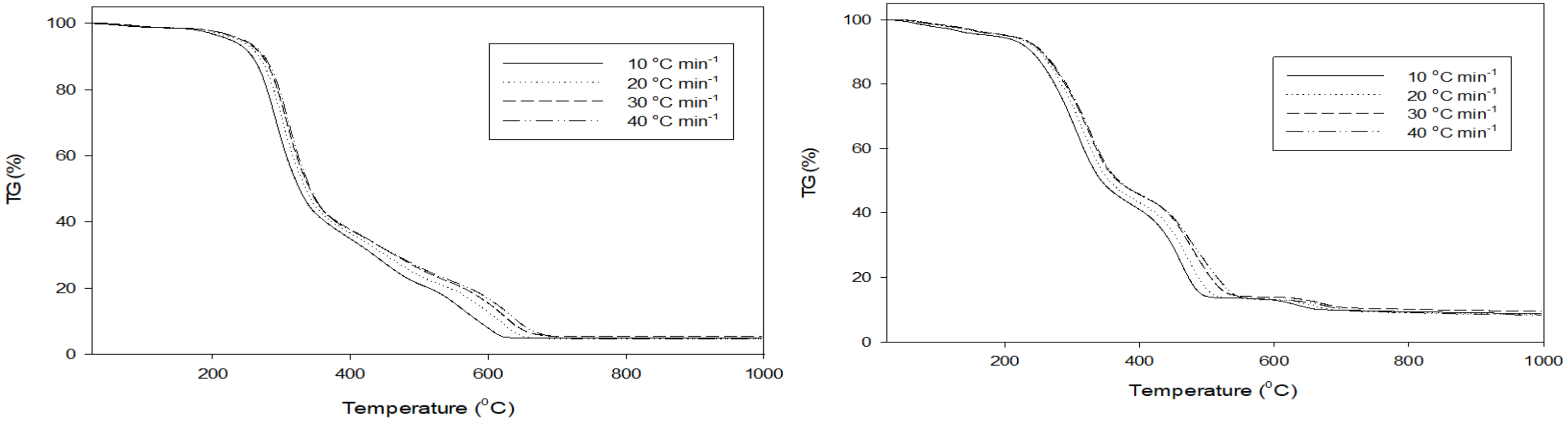
Fig 4.13: Gas composition of bean straw-maize cob blended briquettes at pyrolysis temperature/heating rate/carrier gas flow rate of 650°C/10°C min^{-1}/40 cm^3 min^{-1}. Briquettes were produced from pressure (MPa)/particle size (mm)/temperature (°C) of 150/<4.00/50.

4.2.2 Combustion

4.2.2.1 TGA Analysis

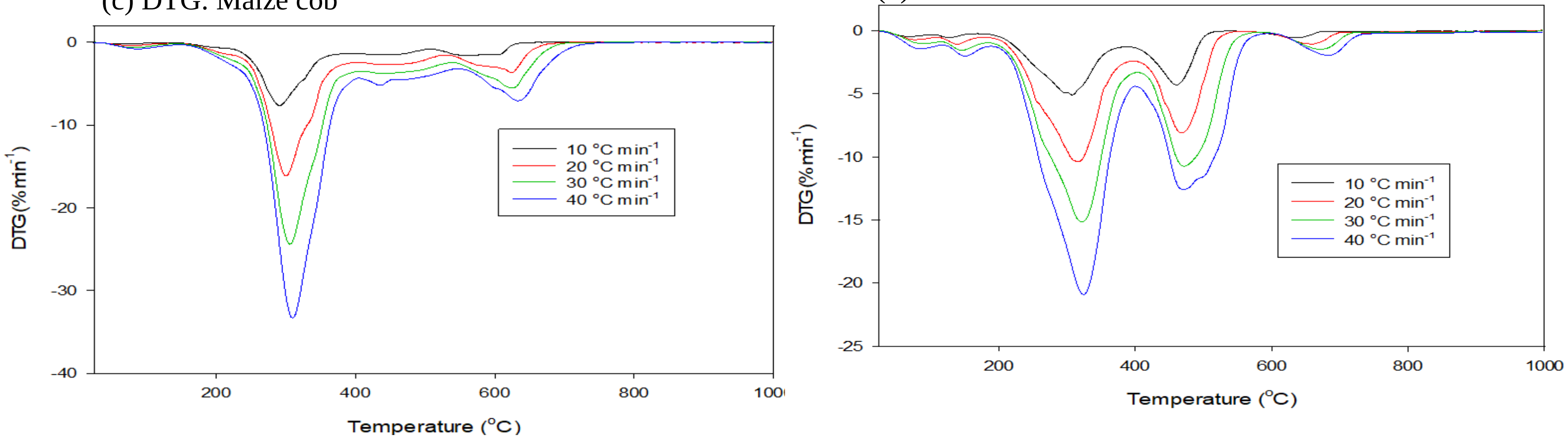
4.2.2.1.1 Combustion of raw maize cob and bean straw

Fig 4.14 a and b show that at a temperature >200°C, a significant reduction in mass up to 403°C for bean straw and 413°C for maize cob. The highest rate of weight loss was due to the release of volatiles which were subsequently oxidized. The slower rate of oxidation of partial decomposed lignin and char occurred at a temperature range of >403-1000°C for bean straw and >413-1000°C for maize cob. The remaining was around 5%wt for maize cob and 8-9 %wt for bean straw (ash content in feedstock). The TG and DTG profiles were similar to those obtained from olive prunings, cotton residue, cardoon, olive kernels and peach kernels (Vamvuka and Sfakiotakis, 2011), empty fruit bunches and palm kernel shell (Ninduangdee et al., 2015). CO_2, CO and H_2O were detected in the gaseous product (Fig 4.15 and Fig 4.16). The impact of varying heating rate on the TGA/DTG and gas profile from combustion of both maize cob and bean straw were identical to during pyrolysis (section 4.2.1.1).



(a) TG: Maize cob

(b) TG: Bean straw



(c) DTG: Maize cob

(d) DTG: Bean straw

Fig 4.14: A comparison of TG and DTG of maize cob and bean straw under air

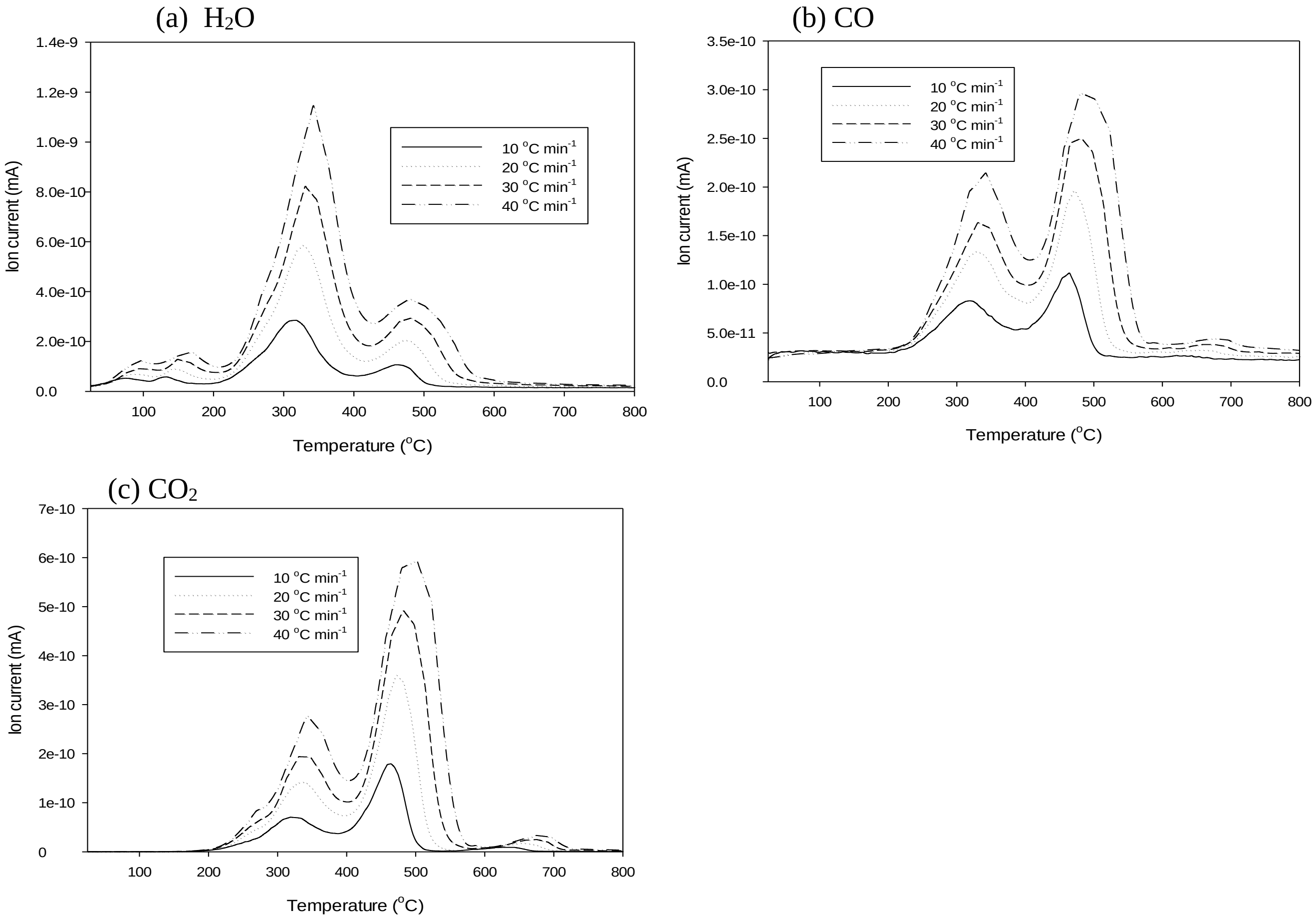
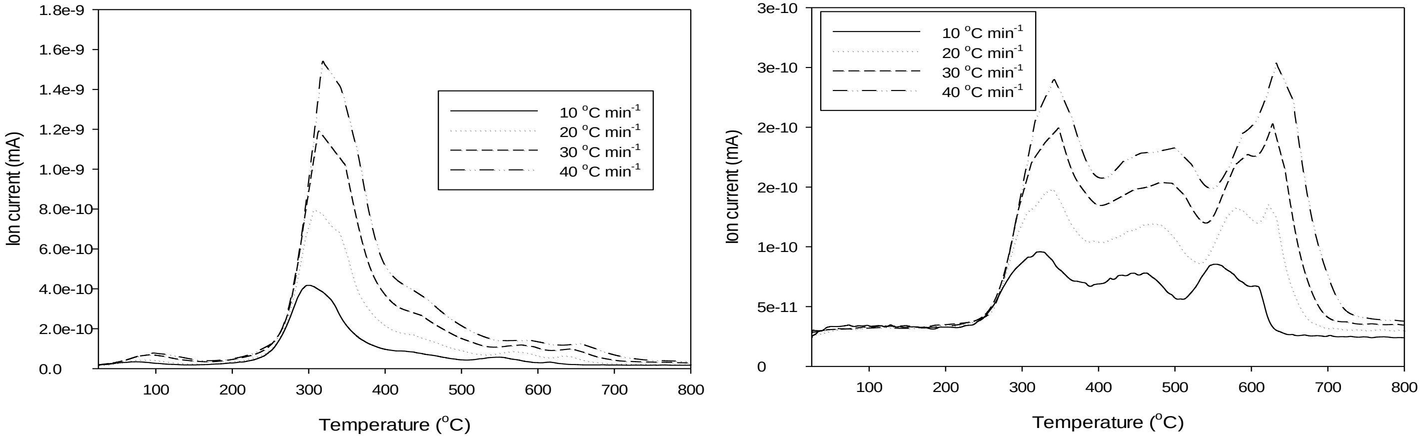


Fig 4.15: Effect of heating rate on yield of (a) H_2O, (b) CO and (c) CO_2 from bean straw in air.

(a) H_2O (b) CO



(c) CO_2

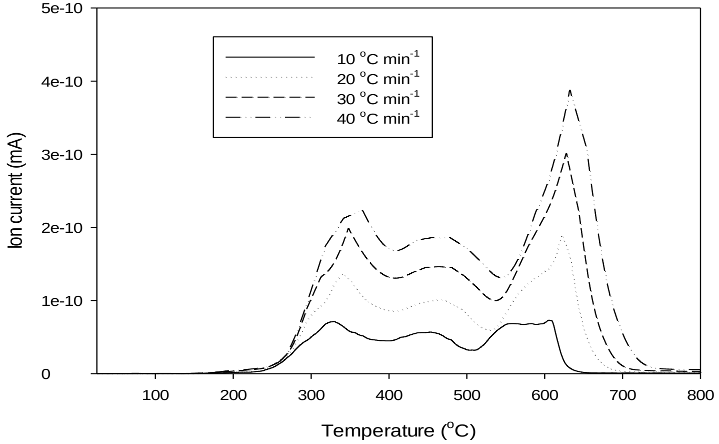


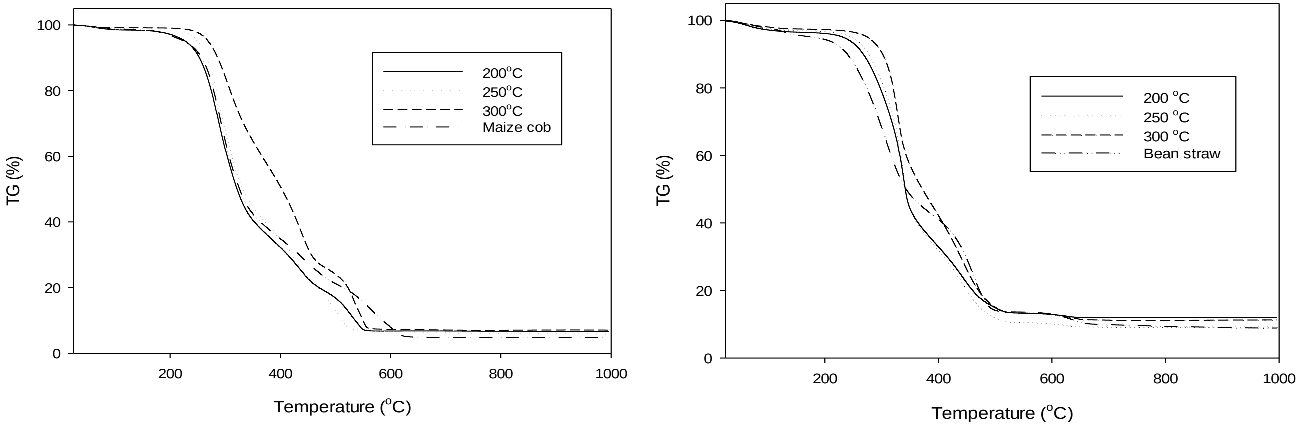
Fig 4.16: Effect of heating rate of yield of (a) H_2O, (b) CO and (c) CO_2 from maize cob in air.

4.2.2.1.2 Combustion of torrefied maize cob and bean straw

Fig 4.17 a and b show the mass loss of torrefied maize cob and bean straw versus temperature range of 25-1000^{o}C. Maize cob torrefaction temperature of 200-250^{o}C had minor effects on the DTG curve during pyrolysis stage (Fig 4.17c) which suggests that the impact of torrefaction on cellulose was minor (Kopczyński et al., 2015). However, torrefied bean straw showed higher rate of degradation during oxidative pyrolysis stage than non-torrefied bean straw (Fig 4.17d). Increasing torrefaction temperature from 200-300^{o}C increased the rate of degradation in the char oxidation stage (Fig 4.17 c and d). A similar trend was reported for torrefied willow within the same temperature range (Kopczyński et al., 2015). The residue (ash) from the combustion of torrefied maize cob and bean straw (torrefaction temperature 200-300^{o}C) ranged between 5.84-7.04% and 9.27-12.27% which was up to 2.31% and 3.40% higher than for non torrefied maize cob and bean straw respectively. In this study, most mass loss which was up to 94.16% and 90.73% during the combustion of torrefied maize cob and bean straw occurred below 598.1^{o}C and 544.4^{o}C respectively.

(a) TG: Torrefied maize cob

(b) TG: Torrefied bean straw



(c) DTG: Torrefied maize cob

(d) DTG: Torrefied bean straw

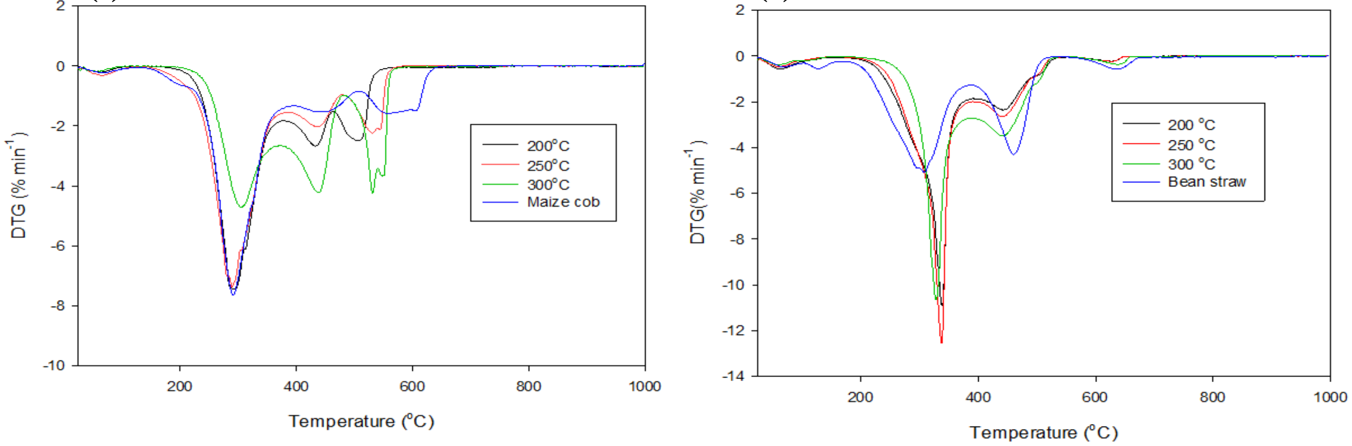
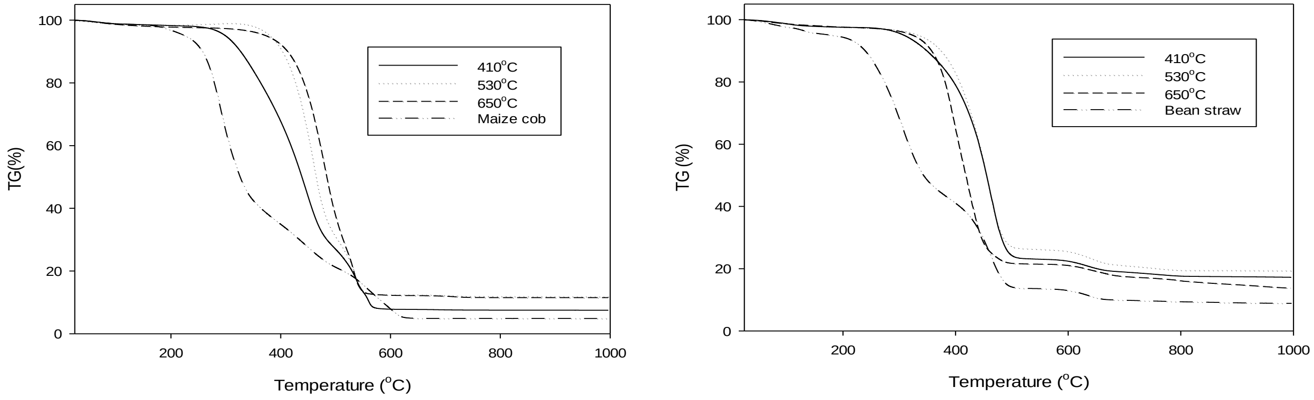


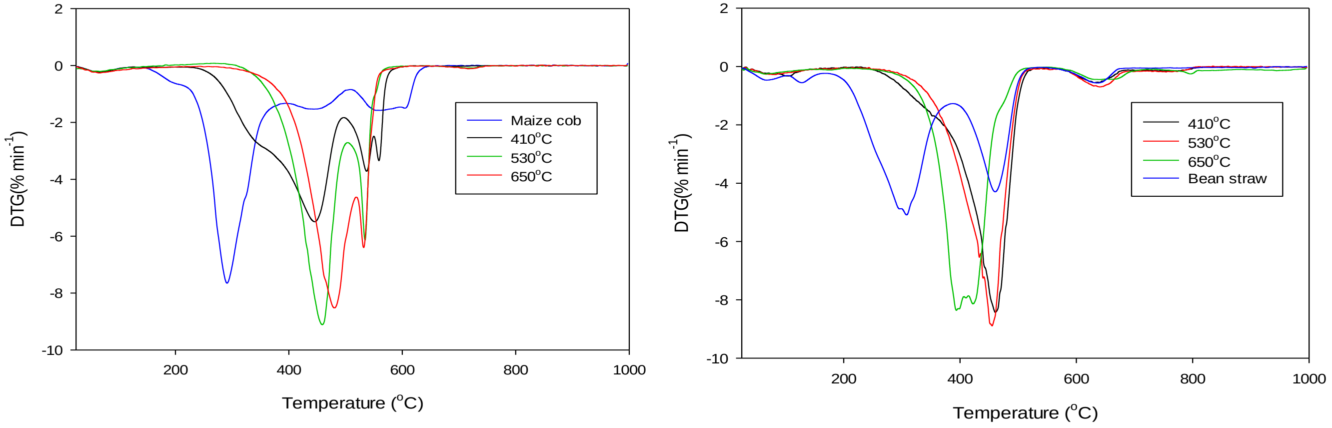
Fig 4.17: TG and DTG curves for torrefied maize cob and bean straw in air

4.2.2.1.3 Combustion of char from pyrolysis of maize cob and bean straw briquettes

The TG and DTG profile (Fig 4.18) of the char and raw material differs which possibly suggests some variations in chemical composition and structure following the pyrolysis process. Unlike raw biomass (feedstock), the TG and DTG profiles of chars show no devolatilization stage except for chars produced at a pyrolysis temperature of 410^{o}C where the devolatilization peak appeared as a weak shoulder on the char decomposition peak (Fig 4.18 c and d). This shows that a large amount of volatiles were released during pyrolysis. However, the appearance of the peak as a weak shoulder corresponding to devolatilization in briquette char at a pyrolysis temperature of 410^{o}C signifies a low degree of carbonization at this temperature compared to higher temperatures of 530-650^{o}C. Fig 4.18 c and d show that char had higher rate of degradation in the char oxidation stage than feedstock. It can be concluded that fixed carbon combustion and oxidative pyrolysis (devolatilization and volatile combustion) were the predominant processes during char and raw biomass combustion respectively which was similar to the study of Yi et al., (2013) for ramie residue i.e. raw and char produced at 500^{o}C. Combustion of maize cob and bean straw char mainly occurred below 649.5^{o}C and 714.4^{o}C where mass loss of up to 90.8% and 80.6% respectively were recorded. The solid residue (ash) was higher than from combustion of raw material (section 4.2.2.1.1), ranging between 7.47-11.82% for maize cob briquette char and 13.72-19.32% for bean straw briquette char.


(a) TG: Maize cob briquette char

(b) TG: Bean straw briquette char


(c) DTG: Maize cob briquette char

(d) DTG: Bean straw briquette char

Fig 4.18: TG and DTG curves for maize cob and bean straw briquette char in air**.**

4.2.2.2 Combustion in a pack bed reactor

Maize cob briquette produced from compacting temperature of 80°C with pressure of 200MPa was tested for combustion in a fixed bed. Fig 4.19 shows that the weight loss was linear within the first 15-75 min of combustion, which was similar for straw, switchgrass and reed canary grass (Khor et al., 2007). The weight loss curve (Fig 4.19) shows a similar trend with the TG

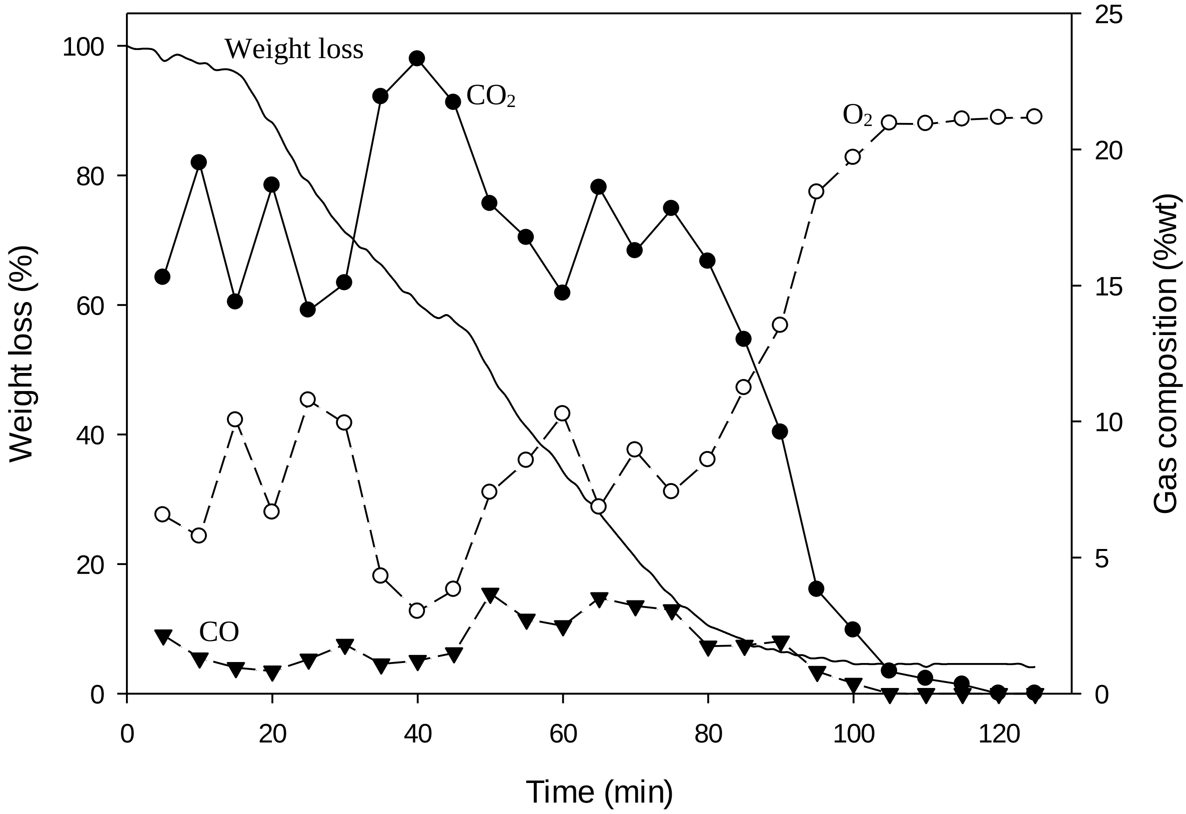


Fig 4.19: Weight loss and gas profile following from the combustion of maize cob briquette produced from a particle size <2.36mm at compacting temperature of 80°C with compacting pressure of 200MPa

The bed temperature profile (Fig 4.20) shows that the ignition front propagates from the top of the bed downwards resulting in an increase in the bed temperature. Heat generated from the ignition source is utilized in drying and devolatilization of briquettes. As shown in (Fig 4.20), the temperature profile does not clearly show any sequential combustion stages (devolatilization and char oxidation) which suggests that char oxidation occurred simultaneously with devolatilization and volatile combustion. This is likely due to a large temperature gradient within large size particles (briquettes) (Castro et al., 2013).

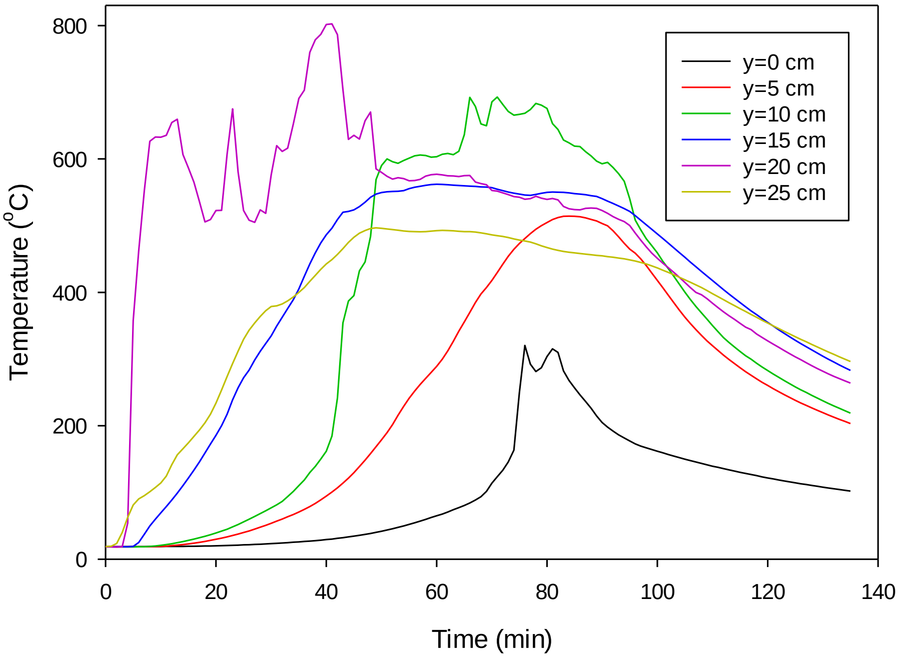


Fig 4.20: Temperature profile from the combustion of maize cob briquettes produced from particle size of <2.36mm at compacting temperature of 80°C with compacting pressure of 200MPa.

Fig 4.20 shows that the bed temperature was higher above the grate, which is a similar trend was observed in straw (Khor et al., 2007) and switchgrass pellet (Gilbert et al., 2009). The maximum temperature acquired in this study was ~800°C and falls within the range of values reported for several materials such as wood pellets, brassica pellet, poplar pellet, refuse-derived fuel pellet, olive stone, almond shell, and pine shavings (Porteiro et al., 2010). The peak temperature provides information about the temperature of the flue gas, while CO_2 and CO composition indicates the degree of conversion of carbon in the biomass material (Castro et al., 2013). The more available oxygen indicates less efficient oxygen consumption in the bed during combustion (Khor et al., 2007). Composition of CO_2 and CO are indicators of the extent of conversion of fuel carbon (Castro et al., 2013). The gaseous product which contains CO_2, CO, H_2, CH_4 and C_2-C_4 is formed during devolatilization (Castro et al., 2013). However, H_2, CH_4 and C_2-C_4 combined were <2% of the total gas product and were therefore not included in the plot (Fig 4.19). The gas composition is not steady, suggesting that the combustion was not stable which could be due to channeling effect. Burning rates defines the mass of maize cob briquettes burnt per unit time, was ~2 g min^{-1}. About 6.35% solid residue (ash) remained after the combustion of the briquette which is high than the residue (4.60-5.38%) corresponding to temperature of ~800^{o}C during combustion in a TGA at varying heating rate from 10-40^{o}C min^{-1}. The ash had a carbon and nitrogen content 4.44% and 0.33% which suggest an incomplete combustion of the fuel.

4.3 Kinetic parameters

Fig 4.21-Fig 4.24 show the regression lines for the FWO and KAS methods. The plots were parallel with high coefficient R^2 >0.94 (Table 4.8 and Table 4.9) suggesting that the order and mechanism of thermal degradation reactions are similar (Nyakuma, 2015). Similar regression plots were reported for melon seed husk (Nyakuma, 2015). The activation energies calculated from both KAS and FWO were conversion dependent, indicating that pyrolysis and combustion of bean straw and maize cob involve multiple reactions (Table 4.8 and Table 4.9). Such variations in activation energies with conversion were reported for soybean straw (Huang et al., 2016), poplar wood (Slopiecka et al., 2012) and smooth cordgrass (Liang et al., 2014). The average activation energies obtained by KAS and FWO in the inert environment were 215.18 and 213.12 kJ mole^{-1} for maize cob and 253.70 kJ mole^{-1} and 250.48 kJ mole^{-1} for bean straw respectively. While the activation energies obtained by KAS and FWO in air were 202.32 kJ mole^{-1} and 202.19 kJ mole^{-1} for maize cob and 164.77 kJ mole^{-1} and 166.51 kJ mole^{-1} for bean straw respectively. The activation energies obtained by the different methods were similar irrespective of biomass material used and the reaction atmosphere. The high level of similarity validates the reliability of calculations and confirms the predictive power of KAS and FWO. For both biomass feedstocks (Table 4.8 and Table 4.9), the activation energy in the inert environment was higher than that in air possibly due to higher heat generated by exothermic reactions (producing CO_2 and H_2O) during combustion. The activation energy of bean straw in air is lower than that of maize cob under the same conditions (Table 4.8 and Table 4.9) which could be due to higher oxygen content in bean straw (47.2%) than maize cob (43.6%) because oxygen bound in a fuel provides a fraction of oxygen required for combustion (Obernberger and Thek, 2004). However, the activation energy of bean straw in He was higher than that of maize cob. The higher the activation energy, the lower the rate of decomposition (Huang et al., 2016). Therefore, these results suggest that bean straw has higher thermal resistance to degradation than maize cob in an inert environment i.e. He. This is likely due to higher lignin content in bean straw (10.2%) than maize cob (1.5%) since the resistance to thermal decomposition of the components is in the order hemicellulose < cellulose < lignin.

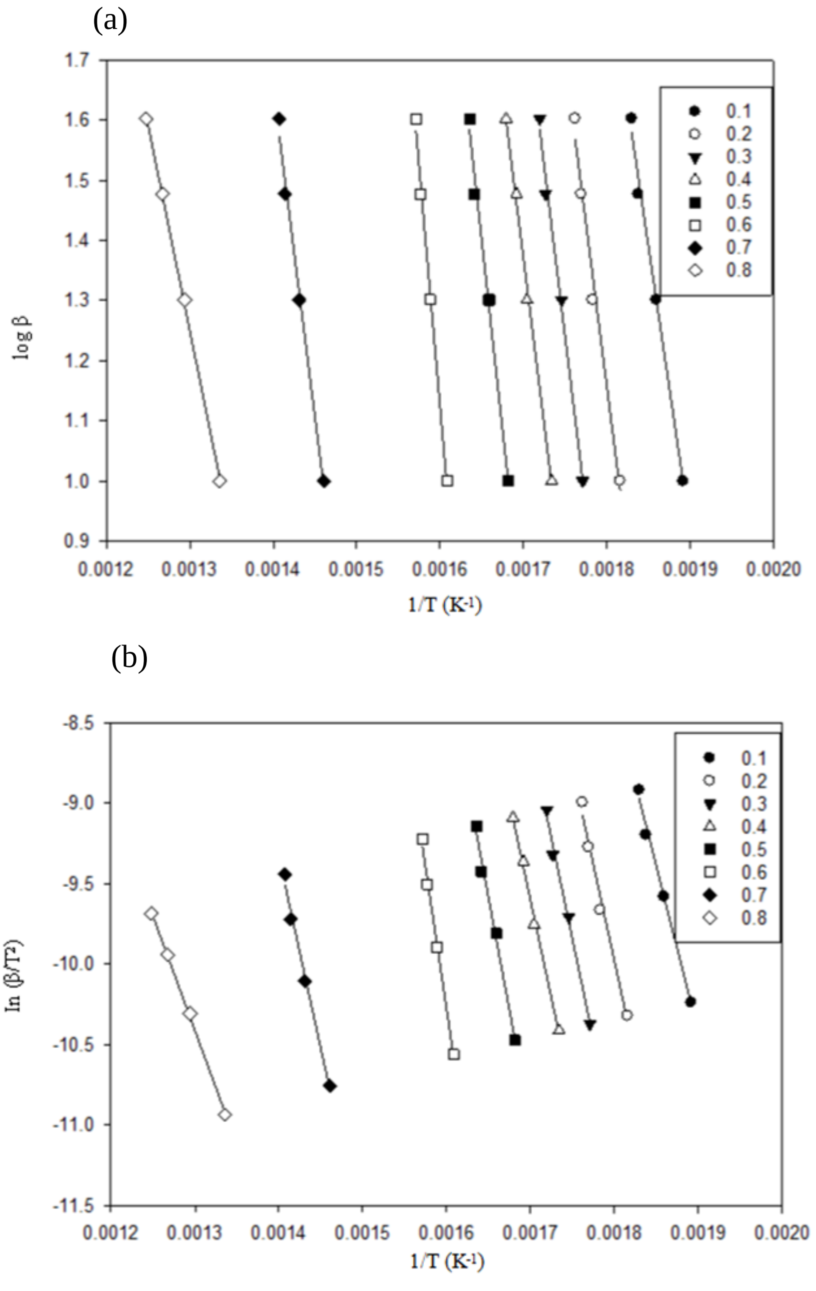


Fig 4.21: Kinetic plots for maize cob using (a) Flynn-Wall-Ozawa and (b) Kissinger-Alkahira-Sunose in air. Legend: conversion

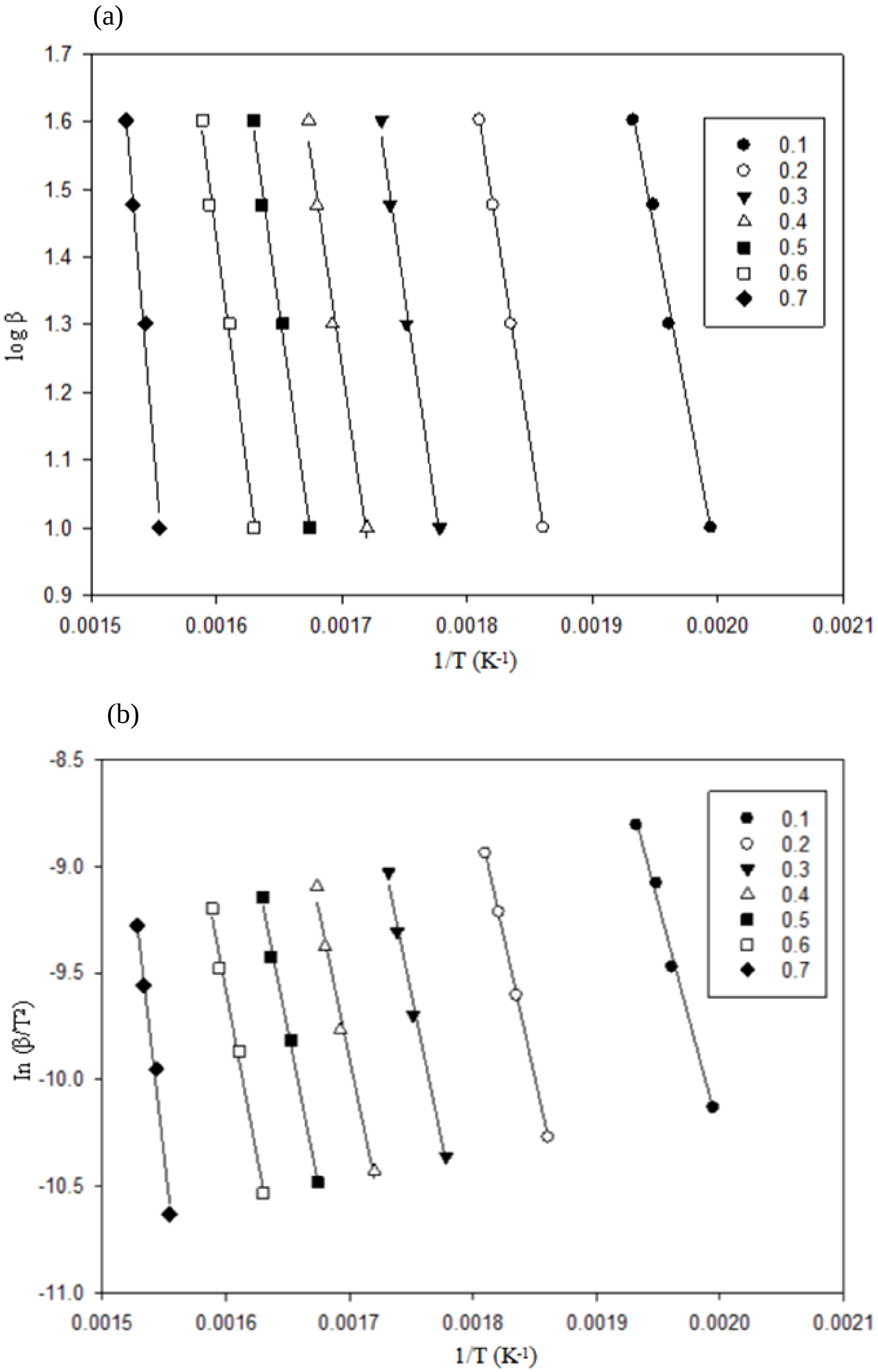


Fig 4.22: Kinetic plots for bean straw using (a) Flynn-Wall-Ozawa and (b) Kissinger-Alkahira-Sunose in He. Legend: conversion

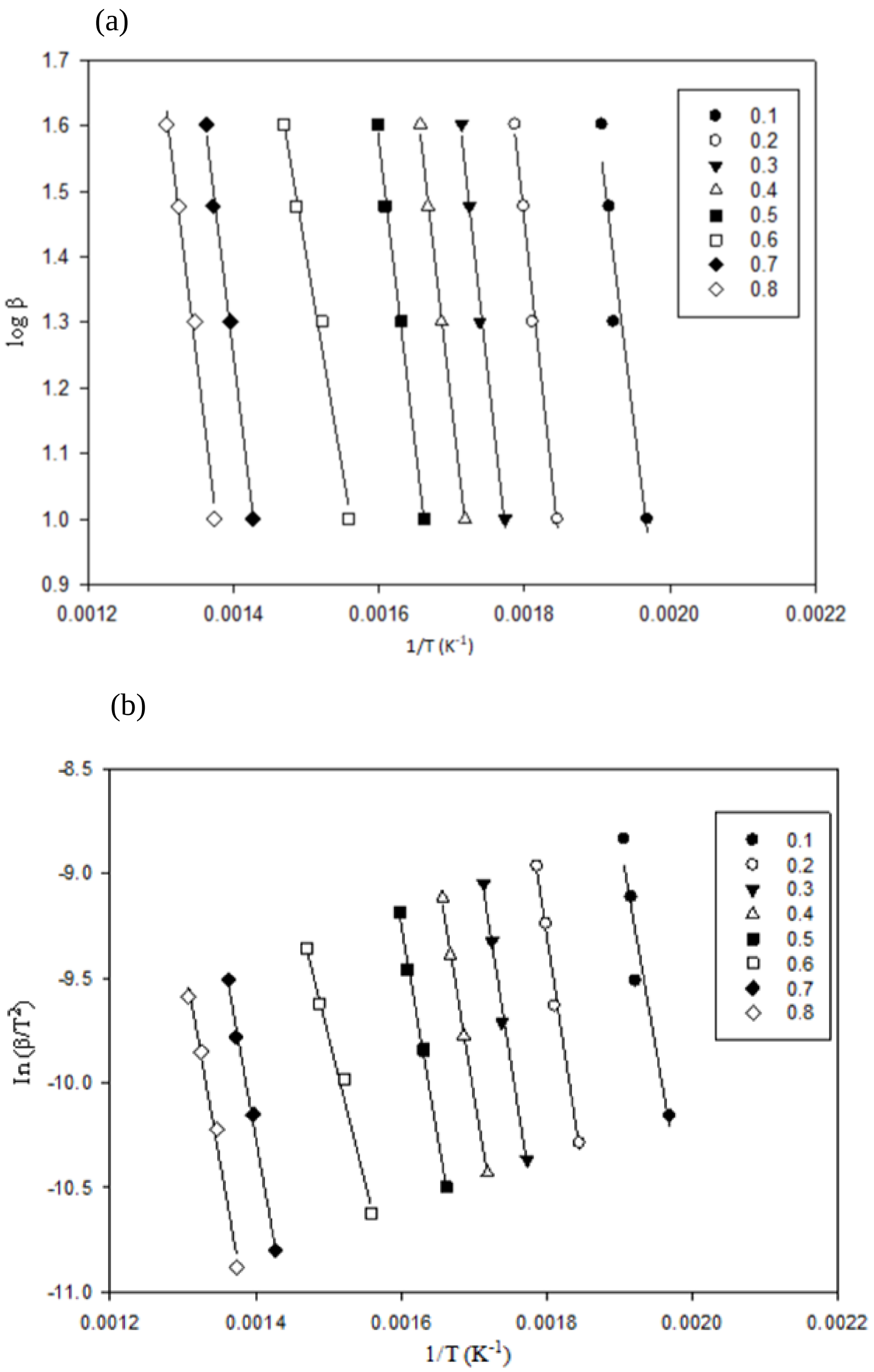


Fig 4.23: Kinetic plot for bean straw using (a) Flynn-Wall-Ozawa and (b) Kissinger-Alkahira-Sunose in air. Legend: conversion

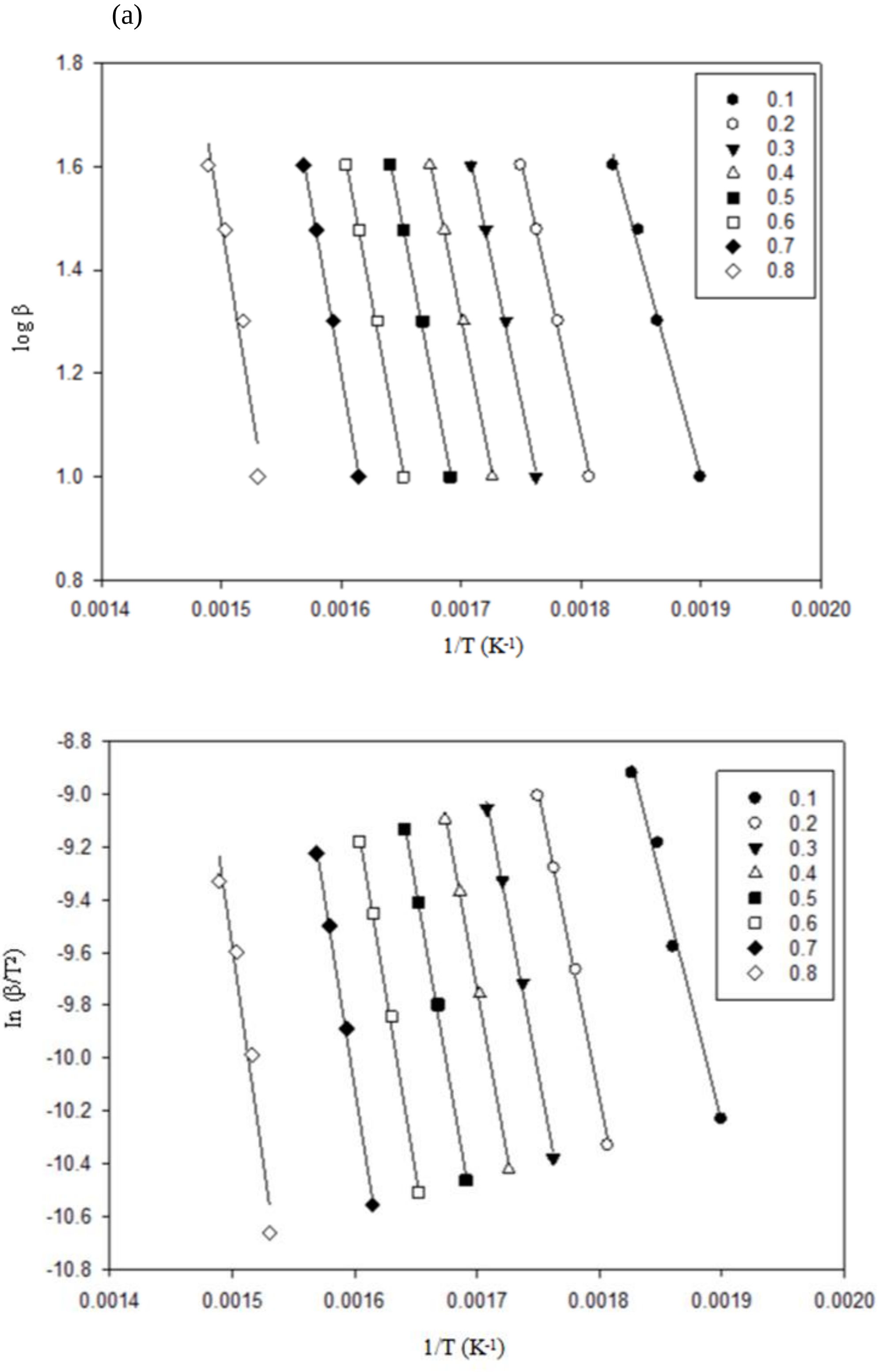


Fig 4.24: Kinetic plot for maize cob using (a) Flynn-Wall-Ozawa and (b) Kissinger-Alkahira-Sunose in He. Legend: conversion

Table 4.8: Activation energy (E) and coefficient of determination (R^2) of maize cob and bean straw in an inert atmosphere (He) using both Flynn-Wall-Ozawa (FWO) and and Kissinger-Alkahira-Sunose (KAS)

Conversion	Maize cob				Bean straw			
	E (kJ mol^{-1})		R^2		E (kJ mol^{-1})		R^2	
	FWO	KAS	FWO	KAS	FWO	KAS	FWO	KAS
0.1	153.56	152.72	0.9915	0.9845	179.59	180.40	0.9930	0.9924
0.2	192.35	192.93	0.9976	0.9974	215.63	217.69	0.9999	0.9999
0.3	202.05	202.89	0.9976	0.9974	230.36	232.78	0.9929	0.9923
0.4	210.55	211.63	0.9976	0.9973	229.89	231.96	0.9877	0.9867
0.5	219.22	220.55	0.9976	0.9973	239.99	242.30	0.9927	0.9921
0.6	229.58	231.19	0.9976	0.9973	252.84	255.56	0.9927	0.992
0.7	240.15	242.10	0.9975	0.9973	405.09	415.20	0.9899	0.9894
0.8	257.52	267.43	0.9425	0.9587	-	-	-	-
Average	213.12	215.18			250.48	253.70		

Table 4.9: Activation energy (E) and coefficient of determination (R^2) of maize cob and bean straw in inert air (80%He + 20% O_2) using Flynn-Wall-Ozawa (FWO) and and Kissinger-Alkahira-Sunose (KAS).

Conversion	Maize cob				Bean straw			
	E (kJ mol^{-1})		R^2		E (kJ mol^{-1})		R^2	
	FWO	KAS	FWO	KAS	FWO	KAS	FWO	KAS
0.1	171.57	171.49	0.9937	0.9930	165.24	165.19	0.9317	0.9251
0.2	197.68	198.60	0.9850	0.9836	188.05	188.59	0.9893	0.9883
0.3	206.44	207.57	0.9938	0.9932	182.10	181.97	0.9919	0.9911
0.4	201.63	202.30	0.9961	0.9957	175.10	174.29	0.9978	0.9976
0.5	228.63	230.41	0.9938	0.9932	169.63	168.18	0.9958	0.9952
0.6	287.10	291.46	0.9952	0.9949	120.16	115.37	0.9883	0.9859
0.7	199.81	198.52	0.9920	0.9911	166.42	163.09	0.9932	0.9922
0.8	124.64	118.21	0.9992	0.9989	165.36	161.49	0.9883	0.9864
Average	202.19	202.32			166.51	164.77		

Pyrolysis and combustion of bean straw and maize cob can be described by kinetic function of the form $(1-\alpha)^n$ where n is the order of reaction and it ranged between 9.0-10.3 and 6.3-13.3 considering both feedstocks in air and He respectively (Table 4.10 and Table 4.11). The n values are relatively constant which suggests that the reaction mechanism is likely independent of heating rate. The order of reaction in this study is comparable to the value reported for pyrolysis of microalgae chlorella vulgaris (n=9) (Chen et al., 2012) and soybean (n=8.19-17.31) (Huang et al., 2016). Fig 4.25-Fig 4.28 show that the experimental (TGA data) and modelled data are in good agreement. The modelled plot was obtained by solving equation 4.2 using MATLAB R2015a.

Table 4.10: Reaction order (n) and pre-exponential factor (A) following pyrolysis in air (80%He +20% O_2) in response to increased heating rate. Activation energy of maize cob and bean straw are 202.26 kJ mol^{-1} and 165.64 kJ mol^{-1} respectively

Heating rate (°C min^{-1})	Maize cob		Bean straw	
	n	A (min^{-1}x10^{17})	n	A(min^{-1}x10^{14})
10	10.0	8.14	9.3	3.00
20	10.1	7.20	9.0	2.73
30	10.2	7.02	9.3	3.27
40	10.3	6.66	9.4	3.38

Table 4.11: Reaction order (n) and pre-exponential factor (A) following pyrolysis in an inert environment (He) in response to increased heating rate. Activation energy of maize cob and bean straw are 214.15 kJ mol^{-1} and 252.09 kJ mol^{-1} respectively

Heating rate (°C min^{-1})	Maize cob		Bean straw	
	n	A (min^{-1}x10^{18})	n	A(min^{-1}x10^{23})
10	6.8	4.83	13.3	3.04
20	6.4	1.83	12.8	2.31
30	6.3	1.09	12.8	1.99
40	6.3	1.02	12.5	2.37

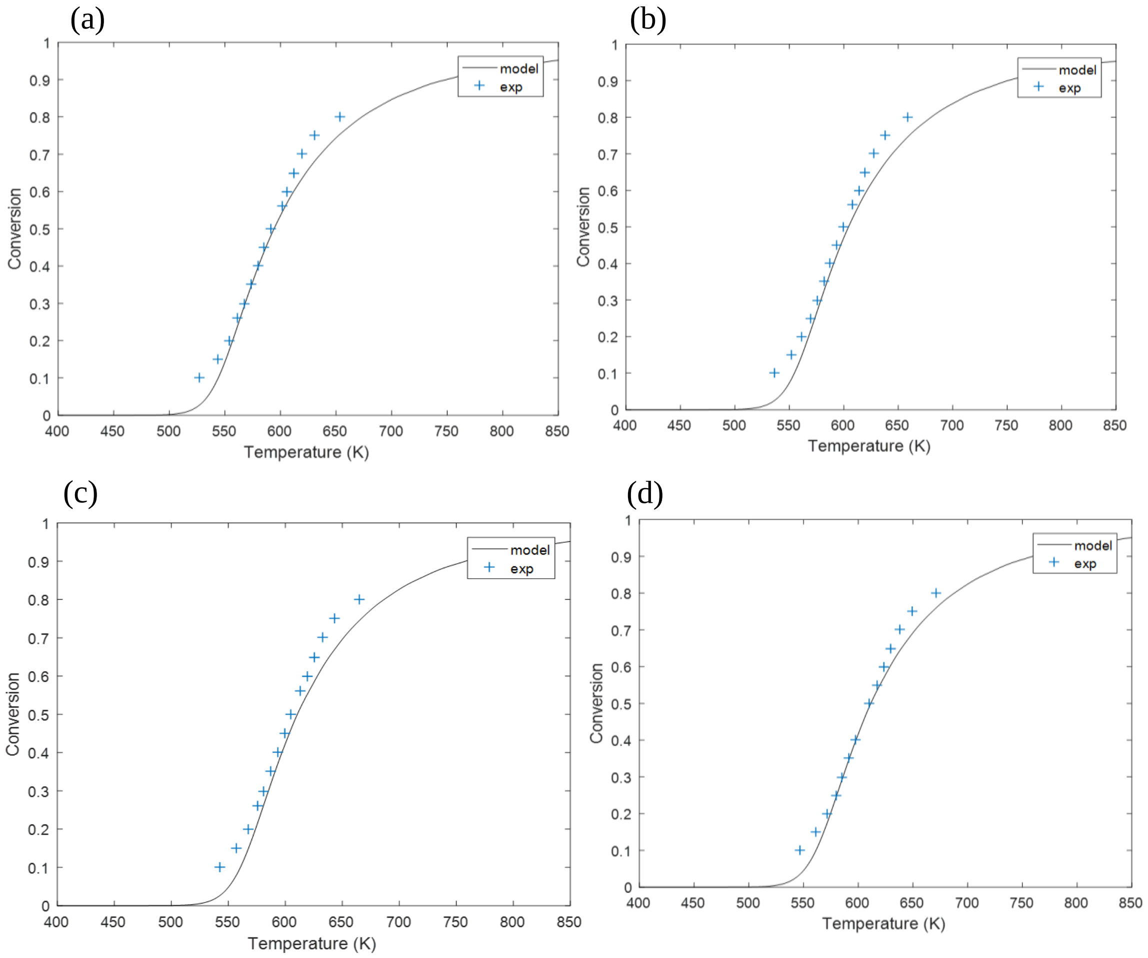


Fig 4.25: Simulation of pyrolysis of maize cob at heating rates of (a) 10 ^{o}C min^{-1} (b) 20 ^{o}C min^{-1} (c) 30 ^{o}C min^{-1} and (d) 40 ^{o}C min^{-1}

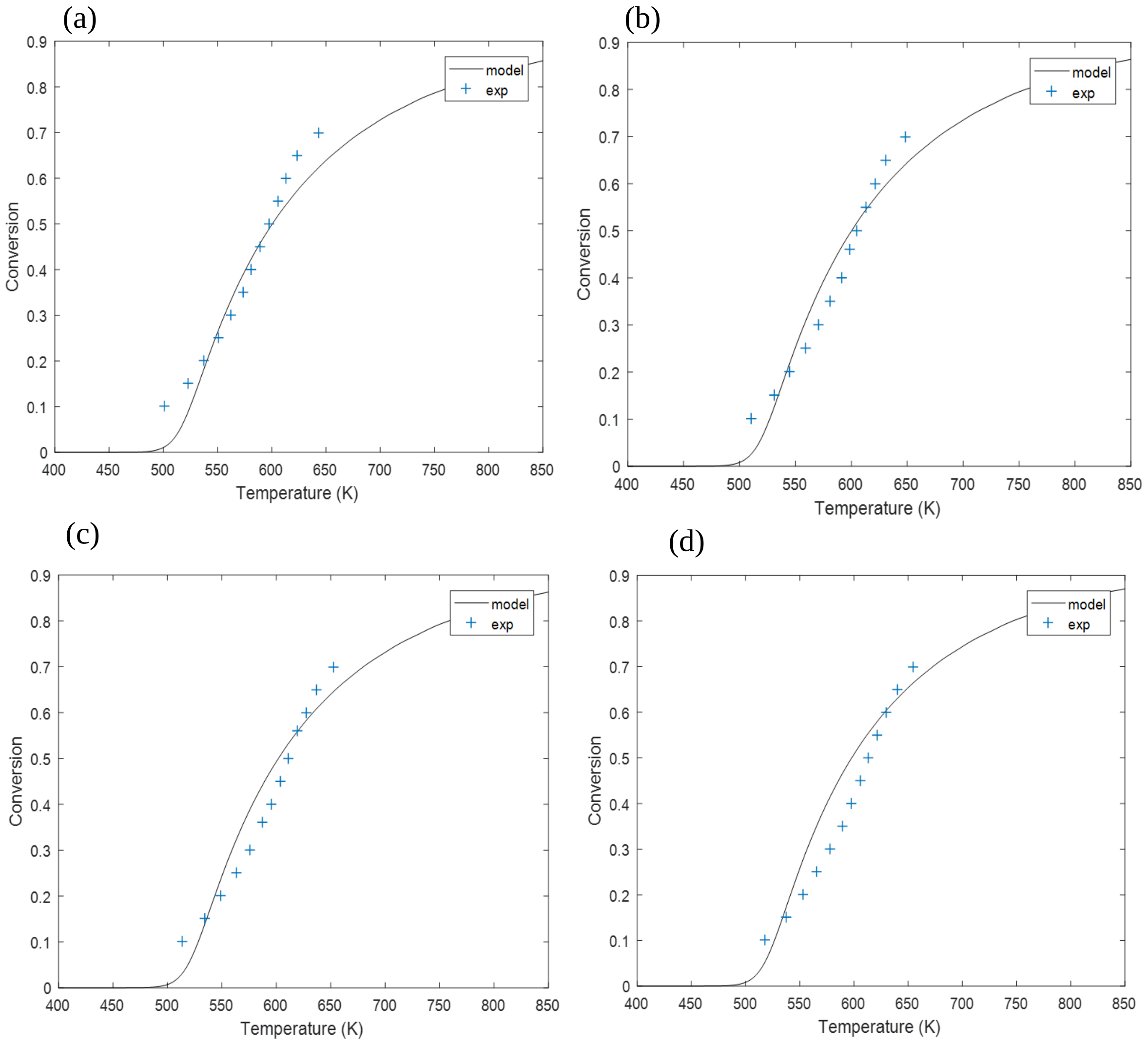


Fig 4.26: Simulation of pyrolysis of bean straw at heating rates of (a) 10 ^{o}C min^{-1} (b) 20 ^{o}C min^{-1} (c) 30 ^{o}C min^{-1} and (d) 40 ^{o}C min^{-1}

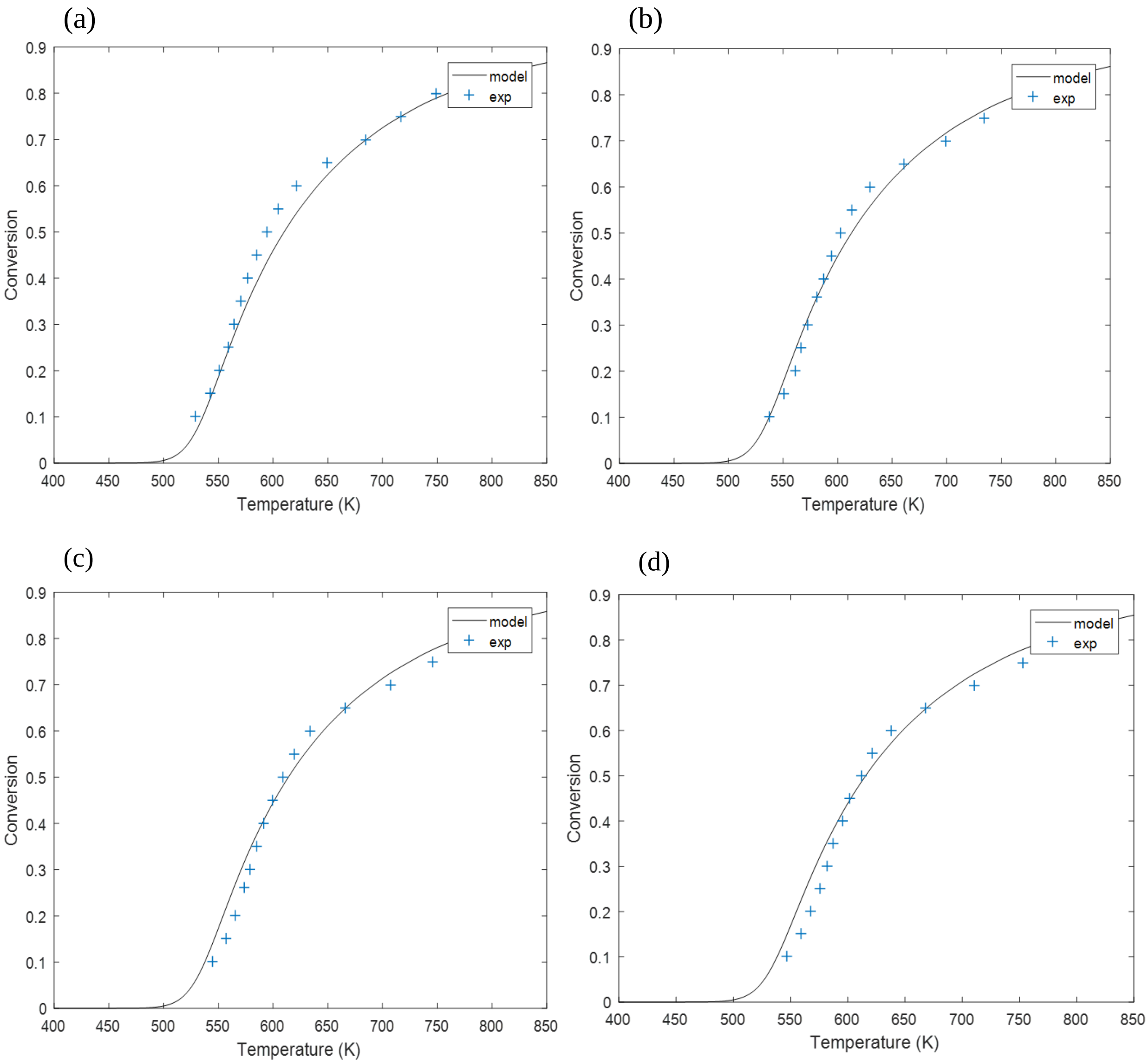


Fig 4.27: Simulation of combustion of maize at heating rates of (a) 10 °C min^{-1} (b) 20 °C min^{-1} (c) 30 °C min^{-1} and (d) 40 °C min^{-1}

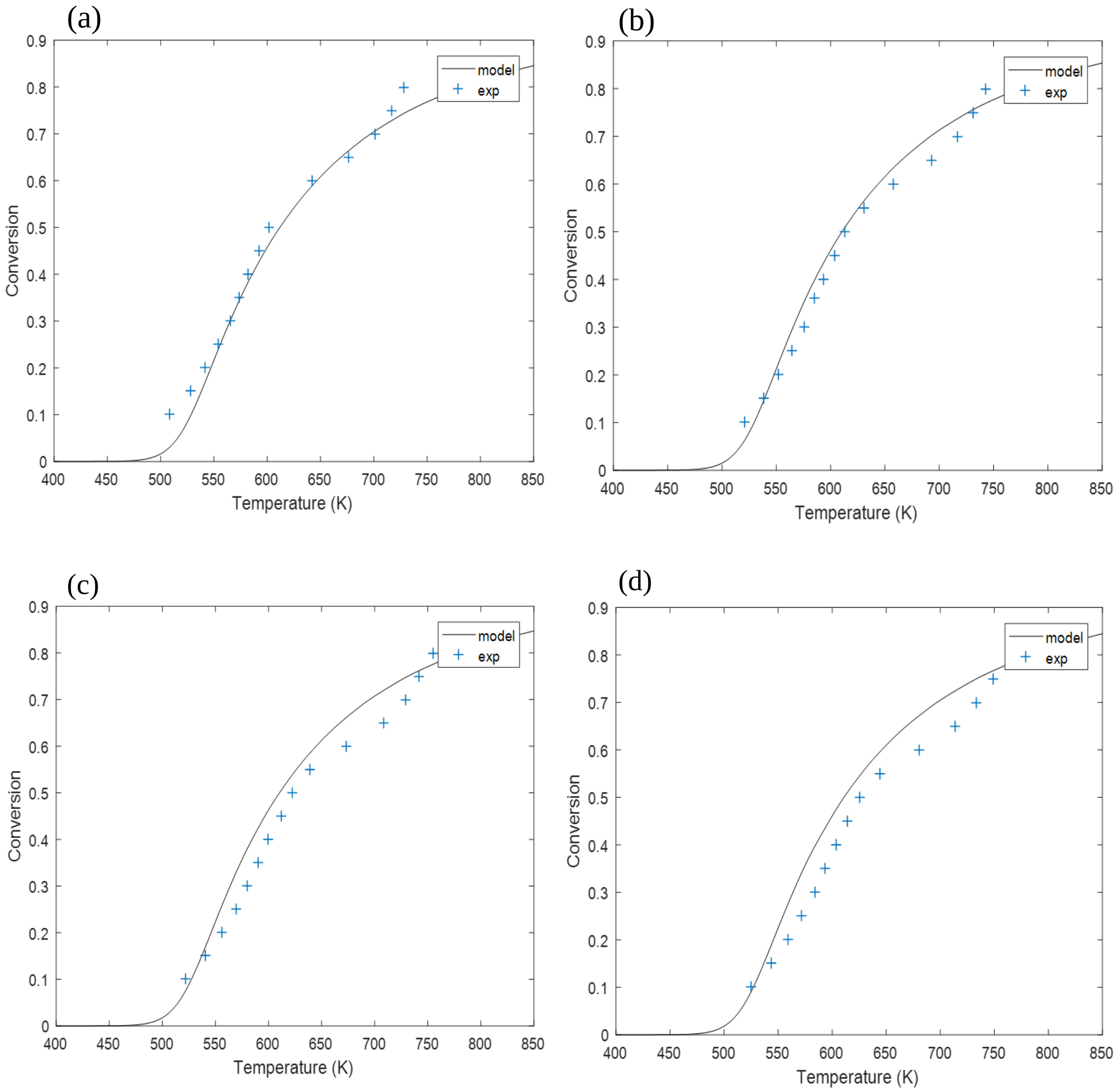


Fig 4.28: Simulation of combustion of bean straw at heating rates of (a) 10 ^{o}C min^{-1} (b) 20 ^{o}C min^{-1} (c) 30 ^{o}C min^{-1} and (d) 40 ^{o}C min^{-1}

4.4 Conclusions

Activation energy changed with conversion which indicates that the combustion and pyrolysis processes involve multiple reactions. The average activation energy of maize cob and bean straw were 202.26 kJ mol^{-1} and 165.64 kJ mol^{-1} in air and 214.15 kJ mol^{-1} and 252.09 kJ mol^{-1} in He respectively. Combustion and pyrolysis kinetic models were developed, and the model and experimental data were in good agreement.

Temperature was the predominant factor that affected yields and properties of pyrolysis products, while heating rate and carrier gas flow rate only had minor impact. Increasing pyrolysis temperature from 410 to 650°C reduced char yields but increased gas and bio-oil yields. Briquetting conditions had no impact on yields and properties of the pyrolysis products. Therefore, briquettes for pyrolysis could be produced from the minimal pressure and/or temperature required for meeting the quality standard in terms of density and mechanical strength to minimize production/energy costs. Increasing maize cob content in a bean straw-maize cob blend significantly increased char fixed carbon content, HHV and bio-oil yield, but gas and char yields and char ash content were reduced.

The slow pyrolysis of briquettes was most suitable for production of solid char, followed by gas; but bio-oil quality was very low due in particular to the high water content. Based on the HHV, char had high HHV which shows its suitability for energy generation unlike bio-oil. Referring to HHV and energy yield, temperature required to produce smokeless fuel (char) was 530°C for pyrolysis of both maize cob and bean straw. The gaseous product contained mainly CO and CO_2 which can be used for heating the process or as carrier gas for gasification and torrefaction. Bio-oil contained furfural, phenolic compounds and sugars and are a potential suitable feedstock for the petrochemical industries. However, the bio-oils were not suitable fuel due to their unstable characteristic, low pH (2-4) and high water content (up to 73%wt).

Chapter 5: General Discussion

Uganda generates large volumes of agricultural and forest residues, with a combined estimated energy potential of ~260PJ annually, with the energy potential of crop residues contributing ~150PJ y^{-1} which accounts for ~50% of total potential energy from biomass residues (Okello et al., 2013b). However, due to limited awareness about the importance of the renewable resources coupled with limited technical capacity within the public domain to invest in renewable energy (MEMD, 2007), these residues are left to decompose in an uncontrollable way and burnt in open air thereby raising environmental concern. Generally, biomass utilization as source of fuel or chemicals is also limited by high moisture content, low energy density, hygroscopic nature, heterogeneity (in terms of size, shape and properties) and low grindability. These challenges can be reduced through briquetting and torrefaction. In this study, maize cob and bean straw briquetting and torrefaction potential were investigated and it was shown that maize cob and bean straw can be transformed into uniform sized feedstock which is easy to handle, transport and store. Briquettes from agricultural residues could provide a suitable alternative to wood fuel and charcoal for energy generation in developing countries. The demands for wood fuel and char in Uganda have been reported to be increasing at a rate of 3% and 6% annually respectively (Okello et al., 2013b). Briquetting of agricultural residues and municipal solid waste (~1500 tons generated daily from the capital city, Kampala) would substitute up to ~6% and ~50% of wood and charcoal consumption in Uganda (Ferguson, 2012). Meanwhile globally, the demand for wood pellet is increasing with an increase from 19.5-28 million tons reported between 2012-2015 (WPAC, 2017). Currently, pellets are produced predominantly from wood (Monedero et al., 2015). However, there is a concern over the sustainability of supplies which might limit the use of wood pellets in the future as demand increases. Furthermore, charcoal dust is a predominant feedstock for briquette production in many developing countries, Uganda inclusive, yet many small-scale producers have limited knowledge about carbonization (Ferguson, 2012). Agricultural residues would therefore provide a clear alternative, especially process based residues like corn cobs which have already been collected from the field. The quality of briquettes is determined in terms of density and mechanical strength which depend on briquetting parameters i.e. compacting pressure and temperature and feedstock characteristics i.e. particle size and moisture content. High density and mechanical strength briquettes are desirable to reduce storage/transportation cost and minimize breakages. Briquettes with high density and mechanical strength required to meet the quality standard could be produced from course ground material (<4mm), compacting pressure of 80°C and (i) moisture content <10% and compacting pressure of 200-250MPa for maize and (ii) moisture content of 10-12% and compacting pressure of 100-250MPa for bean straw. In a hot climatic country like Uganda, agricultural products are left to dry under atmospheric conditions which could reduce the energy input required for feedstock drying. Generally, feedstock/briquettes drying is still a technical challenge in Africa, where sun drying is the predominant method used, though drying space and drying during the rainy season remains a challenge (Mwampamba et al., 2013). Waste heat from process industries e.g. from combined heat and power (CHP) could be used in drying feedstock. The waste heat could also provide heat required for feedstock heating during briquetting through pre-heating particles to the required temperature before briquetting in a mould. Solar dryers could also be used for feedstock drying. Solar drying in Uganda (with a daily mean solar radiation on a horizontal surface estimated at 5.1kWh m^{-2}) could be a viable option (MEMD, 2007). Meanwhile, the range of pressure used in this study (100-250MPa) to produce very high-quality briquettes is likely to be a limitation to large scale briquette production. African countries still have a weak capacity to fabricate briquetting machines (Mwampamba et al., 2013) and access to the fabricated machines remains limited. According to the Global Village Energy Partnership (GVEP) report of 2010, the locally fabricated screw extruder briquetting machines in East Africa cannot effectively compact non-carbonized feedstocks (Ferguson, 2012). Investment in briquetting technologies (roller, screw and piston extruder) is required to improve productivity and diversify feedstock use. According to Obi et al., (2014) the locally fabricated machines in Nigeria are not appropriate for commercial purpose due to their low outputs.

Previous studies (Yank et al., 2016, Yaman et al., 2001) have shown that blending briquettes feedstocks can increase the density and strength of briquettes. Addition of bean straw to maize cob in this study also increased briquette density and mechanical strength and reduced energy requirement (pressure and temperature) compared to maize cob only briquettes. Several agricultural residues could therefore be blended to minimize the use of binders such as wheat, maize flour, molasses and cassava flour which would help address issues associated with food versus field conflict.

Although briquetting increases bulk density and produces uniform size and shape feedstock, some biomass properties such as HHV, grindability and hydrophobicity are not enhanced. In this study, torrefaction temperature of 300°C with a holding time of 30 min was sufficient to produce carbonized feedstocks with similar properties to coal in terms of HHV, fixed carbon and carbon content. The torrefied biomass has higher grindability than the parent biomass which reduces the cost of feedstock grinding (D. Chen et al., 2015). According to Matali et al., (2017) torrefaction reduces biomass moisture adsorption capacity. This increases biomass durability in terms of storage which could be essential in acquiring continuous supply of energy from biomass since biomass, especially agricultural residues are seasonal. Torrefaction at this temperature (300°C) could potentially be carried out using waste heat from other process industries. The waste heat flue gas from process industries has temperature ranging between 250-450°C (Hanning Li et al., 2012) which could provide sufficient energy for the torrefaction process which will enable torrefaction to be integrated with combustion.

Energy required for torrefaction (E), defined as the sum of energy required to dry feedstock (E_d) and torrefy dried feedstock (E_c) was determined following Devanand Maski et al., (2010) method, however, this method excludes the energy consumption during torrefaction at constant temperature. Energy required for feedstock drying (E_d) is the sum of energy required to raise feedstock moisture from room temperature (293K) to 373K, energy require to vaporize moisture (at 373K) and energy required to raise the temperature of dried feedstock from room temperature to 373K (Chen et al., 2017)**.**

$$E_d = \Big((E_w + L_v) \times m_w + (C_{pd} \times (373K - 293K) \times m_d\Big)/\eta \qquad (5.1)$$

Where

$L_v = Latent\ heat\ of\ vaporisation\ of\ water = 2.257\ MJ/kg$

$C_{pd} = specific\ heat\ capacity\ of\ dried\ feedstock.$ The specific heat capacity of maize cob and bean straw used are 1.41 J g^{-1} $^{o}C^{-1}$ (for maize straw) and 1.44 J g^{-1} $^{o}C^{-1}$ (for soybean straw) (Ahn et al., 2009).

$m_w = mass\ of\ moisture\ in\ feedstock:$

$m_d = mass\ of\ dried\ feedstock.$

$\eta = efficiency\ of\ the\ torrefaction\ system = 0.65$ i.e. taking thermal efficiency of rotary kiln

$$E_w = C_{pw} \times (373K - 293K) \qquad (5.2)$$

Where

$C_{pw} = specific\ heat\ capcity\ of\ water = 0.00418\ MJ/kgK$

Energy required to heat biomass to torrefaction temperature T (E_c) is given Equation (5.3) (Chen et al., 2017)

$$E_c = m_d \times C_{pd} \times (T - 373K)/\eta \qquad (5.3)$$

$$E = E_d + E_c \qquad (5.4)$$

The energy required to dry bean straw and maize cob were 0.55MJ kg^{-1} and 3.00 MJ kg^{-1} (including energy required to dry maize cob prior to torrefaction as described in chapter 3, section 3.1.1 materials) (Table 5.1). While the energy required for torrefaction of both dried bean straw and maize cob ranged between 0.19-0.40MJ kg^{-1}. The energy required for feedstock drying is therefore more than the energy requirement for torrefaction dried feedstock which is consistence with literature (Devanand Maski et al., 2010, Chen et al., 2017). The total energy requirement for torrefaction of maize cob and bean straw therefore ranged between 3.19-3.38 MJ kg^{-1} and 0.75-0.95 MJ kg^{-1} respectively.

Table 5.1: Energy requirement for torrefaction of bean straw and maize cob

Torrefaction temperature (°C)	Maize cob		Bean straw	
	Ec (MJ kg^{-1})	E (MJ kg^{-1})	Ec (MJ kg^{-1})	E (MJ kg^{-1})
200	0.19	3.19	0.20	0.75
250	0.29	3.29	0.30	0.85
300	0.38	3.38	0.40	0.95

Slow pyrolysis of briquettes at 530-650°C produced smokeless char (volatile content <20%) with very high quality in terms of high HHV and fixed carbon and low volatile composition compared to briquettes/feedstock. Char is easy to pulverize making it suitable for co-firing with coal. However, briquettes may not be preferred over non-briquetted feedstock for pyrolysis because the bio-oil from briquette had very high water content compared to ~25.3% reported in the literature for loose maize cob (Mullen et al., 2010). This is likely to compromise the economic and environmental benefits of pyrolysis. In addition, the surface area of char obtained from this study is lower than that reported in the literature (Hao et al., 2013). With the undesirable properties of bio-oil (such as low stability and high oxygen and water content (Wang et al., 2018)) which require improvement before applying for energy generation, char could be the desired pyrolysis product in the short run since it could be used directly in a conventional boiler or co-fired with high grade coal. Briquettes could be used as a fuel for providing energy required for pyrolysis. This study revealed that maize cob briquette could be burnt directly in a packed bed reactor for energy generation. As agricultural residues are well distributed globally, and in every parts of Uganda (Okello et al., 2013b), their combustion in small scale plants would be effective because of the low cost of logistics. Fixed bed reactors would be appropriate because they are simple and have low commissioning and operational costs (Porteiro et al., 2010).

The findings of this study could contribute to lessening global warming since briquettes or torrefied agricultural residues could provide alternative fuels to fossil fuel or co-fired with fossil fuel thereby minimizing CO_2 emission. Furthermore, the finding could contribute to reducing the level of wood and charcoal consumption by both rural and urban households, thereby reducing the level at which forest reserves are being depleted. By 2014, 2.3% of Ugandan were still using firewood for lighting while 71.2% and 22.9% were using wood and charcoal respectively for cooking (UBOS, 2016) while, the rate at which Uganda is currently losing forest cover (200,000 hectares annually) has doubled between 1990-2010 i.e. 90,000 hectares annually (Josephat, 2018).

Furthermore, the findings of this study could improve sanitation as the production of briquettes by the local population could help in proper management of agricultural wastes. This could consequently reduce the level of pollution and health related problems and improve the standards of living of the local population. Briquetting/torrefaction could provide opportunitied for the local population to engage in small businesses to employ a section of the population especially in rural areas and increase the household income levels and consequently the Gross Domestic Product. In addition, the results of this study could help the government of Uganda legislate management and control of biomass waste burning, hence, reducing the level of greenhouse gas emissions. In the energy sector, this research will serve as future reference for potential application of bean straw and maize cob for energy generation. Meanwhile, for research community, this study will be used as reference for future study in briquetting, torrefaction, pyrolysis and combustion of agricultural residues. However, successful implementation of this research findings could also be limited by: higher briquetting and torrefaction capital costs, inadequate legal and institutional frameworks to support investment in renewable energy, inadequate standards and quality assurance for both briquette and torrefied biomass and underdeveloped market for both briquette and torrefied biomass. There is still limited knowledge about the potential of briquettes/torrefied agricultural residues as alternative fuel sources. All these limits market and production potential of briquettes/torrefied products and they need sensitization of the public.

Chapter 6: Conclusions and Recommendations

This chapter presents the major conclusions drawn from this study and recommendations for future studies.

6.1 Conclusions

Biomass is an abundant and well distributed resource with the potential of providing alternative source of fuels and chemicals to fossil fuel. However, their high moisture content, low bulk density, low HHV, hygroscopic nature, heterogeneity (in terms of size, shape and properties) and low grindability are still limitations to the above applications. These challenges could be minimized through briquetting and torrefaction. In this study, the impact of briquetting conditions (compacting pressure, temperature, moisture content and particle size) on properties of briquettes were investigated. The quality of briquettes is determined in terms of density and mechanical strength which all depend on briquetting parameters (compacting pressure and temperature) and feedstock characteristics (particle size, moisture content and feedstock blend ratio). High density and mechanical strength briquettes are desirable to reduce storage and transportation costs and minimize breakage during handling, transportation and storage. Increasing pressure and temperature significantly enhanced density and mechanical strength, while an increase in particle size or moisture content significantly lowered density and mechanical strength of briquettes. However, all briquettes satisfied the minimal value of compressive strength 2.56MPa required to minimize breakage during handling, transportation and storage. However, briquettes with very high density and durability could be produced from course particles (<4.00mm), high compacting temperature of 80^{o}C and (i) moisture content <10% and compacting pressure of 200-250MPa for maize cob and (ii) compacting pressure of 100-250 MPa for bean straw. Maize cob-bean straw blending enhanced maize cob briquette density and mechanical strength and reduced energy requirement (pressure and temperature) for maize cob briquetting with an optimum bean staw:maize cob blend ratio of 75:25 producing equally high density briquettes similar to sole bean straw. However, sole bean straw is a preferred substrate over maize cob for briquette production because it produced briquettes with highest density and mechanical strength with a lower energy expenditure (pressure and /temperature). There were strong interactions between briquetting parameters with the moisture x temperature interaction significantly affecting on all the maize cob briquette properties.

While, the pressure × temperature interaction significantly affected density, impact resistance and compressive strength. Briquettes from torrefied feedstock and bio-oil (used as a binder) were of lower qualities than from the raw feedstock. This study further revealed that briquetting of torrefied biomass increased energy requirement for densification/briquetting which was measured in terms of increase in compacting temperature and this signifies an increase in costs of production.

The impact of torrefaction conditions (temperature and holding time) on yields and properties of maize cob and bean straw were also studied. Yields and properties of torrefied product depended on torrefaction conditions and feedstock type. Gas and liquid yields were significantly increased as char yield decreased by increasing torrefaction temperature and holding time. However, temperature was the predominant factor that affected yields and properties of torrefaction products. Torrefaction results in partial decomposition of cellulose, hemicellulose and lignin thereby changing biomass properties. Torrefaction reduced volatile and oxygen compositions and improved carbon, HHV and grindability of the biomass material studied. Torrefaction at temperature of 300°C at holding time of 30 min was enough to produce solid product with similar properties to coal. Based on the properties of the torrefaction products solid < gas < liquid seems to be the order of importance of torrefaction products. Torrefaction liquid product contained mainly water and is acidic. While the gaseous products had mainly CO_2, followed by CO and <1% of H_2 and hydrocarbon combined.

Pyrolysis is a biomass thermochemical conversion method under development stage that is attracting interest because of its potential to produce 3 useful products i.e. char, bio-oil and gas. Yields and properties of pyrolysis product are feedstock and pyrolysis conditions dependent. In this study, temperature was the predominant factor that affected yields and properties of pyrolysis products, but the impact of heating rate and carrier gas flow rates were minor. Furthermore, the impact of briquetting conditions (pressure and temperature) on yields and properties of pyrolysis products were also minor which suggests that all briquettes that meet set quality standards in terms of density and mechanical strength are potential feedstock for pyrolysis. Increasing pyrolysis temperature from 410-650°C reduced char yield and char produced at 530-650°C were smokeless (volatile content <20%) and had very high quality in terms of high HHV and fixed carbon and low volatile composition. However, the qualities of char and bio-oil from pyrolysis of briquettes were low compared those produced from non-briquetted feedstocks reported in literature. The gaseous product requires CO_2 cleaning to improve its quality. While, the bio-oils were acidic, unstable and had high water content.

Combustion and slow pyrolysis kinetic study of bean straw and maize cob in TGA occurred in 3 stages: drying, devolatilization and char degradation. The activation energies of the different agriclutural residues studied varied for the different atmospheres i.e. He and air. The average activation energy of maize cob and bean straw were 202.26 kJ mol^{-1} and 165.64 kJ mol^{-1} in air and 214.15 kJ mol^{-1} and 252.09 kJ mol^{-1} in He respectively. The experimental and model developed data for combustion and pyrolysis were in good agreement. Combustion in packed bed indicates that combustion of briquettes was not stable possibly due to channelling effect.

All the objectives of this study (stated in chapter one, section 1.4) were achieved. These objectives are listed below including the chapters in which each one was achieved:

1. To investigate the effect of briquetting operating parameters on properties of briquettes derived from maize cob and bean straw (chapter three). The optimal briquetting conditions for bean straw, maize cob and bean straw-maize cob blend were obtained.
2. To study the effect of torrefaction operating conditions on torrefaction product yields and properties of maize cob and bean straw (chapter 3). The optimal torrefaction conditions for bean straw and maize cob were determined.
3. To study the effect of pre-treatment conditions on the thermochemical conversion i.e. the case of briquettes (chapter 4). The effect of pyrolysis conditions on yields and properties of pyrolysis products were examined, preferred pyrolysis product and optimal pyrolysis conditions were esterblished.
4. To study the combustion behaviour of torrefied materials using thermogravimetric analysis (chapter 4). The torrefied biomass were tested as feedstock for combustion in a TGA and the effect of torrefaction on combustion characteristics was assessed.
5. To develop pyrolysis and combustion kinetic models for maize cob and bean straw (chapter 4). The activation energies and kinetric functions for combustion and pyrolysis were obtained.

6.2 Recommendations

The following are recommendations for further research:

- Briquetting characteristics of other agricultural residues should be assessed to identify which substrates could be used for energy generation particularly process residues. This would help to diversify feedstocks for briquette production.
- Life-cycle assessment of the briquetting process to determine its contribution to CO_2 emission.
- Net energy value of briquettes from different agricultural materials. This will help in optimizing briquetting conditions while minimizing production costs and providing more information about the appropriate feedstock for briquette production.
- Reducing the energy requirements (pressure and temperature) for briquetting. This is to minimize production and maintenance costs. Different materials could be blended or binders preferably organic binder (agricultural residues) could be used to achieve this.
- Life-cycle assessment of ntorrefaction and optimization of torrefaction temperature and holding time to improve quality of briquettes from torrefied biomass. These will help in assessing the economic viability of torrefaction and its contribution to CO_2 reduction.
- Particulate emissions from combustion of pre-treated agricultural residues to assess the impact of pre-treatment on the combustion efficiency.
- Kinetic studies of pre-treated biomass materials need to be conducted. This could help in optimization of the combustion conditions for pre-treated agricultural residues.

Appendices

Appendix A 1: Publications

A1.1 Briquetting characteristics of bean straw-maize cob blend

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Abstract

Bean straw briquettes exhibited high quality in terms of density, impact resistance and compressive strength. The impact resistance was above 96% for a particle size up to 4mm and pressures as low as 100MPa at a compacting temperature of 80°C. Reducing the compacting temperature required higher pressure and smaller particles to obtain similar quality briquettes. There were strong interactions between briquetting parameters with interaction pressure × temperature significantly affecting both density, impact resistance and compressive strength. Adding bean straw significantly improved the mechanical properties of maize cob briquettes produced at low pressure and from larger particle size. From a practical and energy point of view, a temperature of 80°C should be used for briquetting to reduce energy inputs (pressure and grinding) as this low temperature could be obtained directly from industrial waste heat.

Keywords: Briquette, density, impact resistance, compressive strength, agricultural residues

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1 Introduction

Densification of biomass into briquettes/pellets increases energy density, minimises particulate emissions per unit volume of fuel transported (increases bulk density of fuel) and improves biomass combustion efficiency (uniformity in combustion due to less dust) as well as conveyance efficiencies (less dust and wastage) in commercial energy generation facilities [1-3]. The classification of briquettes and pellets is commonly based on their size i.e. 4.0-10.0 mm diameter and 20-50mm length according to the respective Austrian (ONORM M 7135) and German (DIN 51731) quality standards for wood pellets with 10 - 200 mm diameter and 16 - 400 mm length commonly used for briquettes [4-6].

Properties of briquettes such as ash content, heating value and physical and mechanical properties (i.e. density, durability/impact resistance and compressive strength) directly relate to combustion, transport, handling and storage characteristics. Ash content and heating value are feedstock dependent. However, mechanical properties depend on briquetting conditions (feedstock moisture, particle size, compacting temperature and pressure). With respect to transport, handling and storage, briquettes with high density and mechanical strength are desirable [4, 7, 8]. Compressive strength, i.e. ≥ 2.56 MPa [9] is preferred during transportation and storage [10] while a high durability of over 80 % [11] is required to ensure briquettes/pellets remain intact and reduce the amount of fine particles/dust produced.

Several feedstocks have shown different responses to variation in briquetting variables [4, 12, 13, 7, 14, 15, 16]. The difference in densification characteristics of biomass materials is likely due to variation in their chemical composition which affects their binding properties. Extractives act as lubricants during compression and they prevent strong bond formation by creating a layer between particles [17], whereas lignin improves densification properties due to its thermoplastic behaviour [18]. Meanwhile, the hydroxyl group in hemicellulose and lignin helps in particle bonding through formation of hydrogen bonds [19].

Different biomass materials can be blended to enhance the mechanical properties and the combustion characteristics of briquettes due to changes in the chemical composition. The density of rice husk briquettes was increased from 415.44 - 438.02 kgm^{-3} by adding 0-5% by weight of rice bran [2]. The addition of paper mill waste (up to 30% by weight) to lignite waste improved impact resistance and compressive strength of briquettes [8].

Maize and bean are commonly cultivated crops globally thereby generating large volumes of residues. Highly durable maize cob briquettes (over 95% durability) were produced at high (200 MPa) compacting pressure [20] which could increase the costs and energy requirement for densification. However, no information is available on the densification characteristics of bean straw or a combination of bean straw with maize cob. It is expected that blending maize cob with bean straw could improve maize cob briquetting characteristics at low compacting pressure. This study focussed on analysing the impact of briquetting parameters such as pressure, temperature and particle size and their interactions on the properties of bean straw briquettes. Furthermore, the effects of blending maize cob with bean straw at different ratios on the properties of briquettes were investigated.

2 Materials and Methods

2.1 Materials

Bean straw (10.63±0.88% moisture content) was obtained from Nafferton Farm a research/commercial farm owned and managed by Newcastle University. It was part of an organic crop rotation which was left as residue in the field to dry before being collected and stored under cool/dry conditions prior to use. Maize cobs were kindly provided by Barfoots of Botley Ltd, UK. Maize (supersweet varieties) was harvested at stage R3 (milk stage) across a range of countries (EU and beyond) and stored at 0-5^{o}C for 1-25 days. The maize cobs were a mixture of varieties and are therefore representative of an agricultural processing residue. After the kernels were removed, residual cobs were sent to Newcastle University and stored in a cold room at 6^{o}C prior to briquetting. Residue maize cobs were cut into pieces <5 mm and oven dried at 105^{o}C to a moisture content of 8.62±0.20%. All moisture contents presented in this paper are expressed as % of total fresh weight. Bean straw was manually cut to <2 cm length sections. Both dried maize cobs and bean straw were crushed using a HGBTWTS3 laboratory blender 8010ES and separated using 2.36 and/or 4.00 mm sieves. Table 1 shows properties of the biomass materials. The compositions of the inorganic elements in bean straw and maize cob were determined using inductively coupled plasma (ICP). About 50 mg of each biomass material (bean straw and maize cob) was boiled in Aqua Regia (3 parts hydrochloric acid to 1 part nitric acid) for 24 hr and then evaporated. The residue was brought back into solution with

2ml of concentrated nitric acid and then diluted to 50 ml with pure water and analysed using Inductively Coupled Plasma Masss Sectrometry (ICP-MS).

Table 1: Properties of bean straw and maize cob

Property	Maize cob	Bean straw
Proximate properties (dry basis)		
Ash (%wt)	3.0	6.8
Volatile (%wt)	80.6	69.1
Fixed carbon (%wt)	16.4	24.1
Ultimate properties (dry and ash free)		
C (%)	46.9	43.6
N (%)	2.8	2.6
High heating value (HHV) (MJ/kg)	18.9	17.6
Cellulose (%)	17.7	21.4
Hemicellulose (%)	29.4	19.6
Lignin (%)	1.5	10.2
Extractives (%)	51.4	48.8
Inorganic composition		
B (µg/g)	7.2	102.2
Na (µg/g)	12.9	2523.8
Mg (µg/g)	778.8	1939.8
Al (µg/g)	-	9.3
P (µg/g)	351.8	68.1
K (µg/g)	3854.5	4014.6
Ca (µg/g)	375.4	18047.9
Sc (µg/g)	0.2	0.1
Ti (µg/g)	0.6	0.9
V (µg/g)	0.3	0.3
Cr (µg/g)	2.1	1.1

Mn (µg/g)	13.3	26.6
Fe (µg/g)	-	53.6
Co (µg/g)	-	0.1
Ni (µg/g)	0.6	0.6
Cu (µg/g)	19.0	46.6
Zn (µg/g)	33.7	36.3
Ga (µg/g)	0.2	4.7
As (µg/g)	0.2	-
Rb (µg/g)	1.4	3.6
Sr (µg/g)	1.2	49.5
Mo (µg/g)	0.2	-
Sn (µg/g)	0.4	0.5
Ba (µg/g)	2.8	91.6
Ce (µg/g)	-	0.1
Pb (µg/g)	2.2	2.1

2.2 Briquette preparation

The briquetting machine used had a hollow cylindrical mould, internal diameter of 2 cm and length 12.5 cm as described by [20]. Briquettes were made from bean straw and a bean straw-maize cob blend.

(a) Bean straw

The impact of briquetting parameters: temperature (20-80°C), particle size (<2.36 mm and <4.00 mm i.e. the sieve sizes which were available) and pressure (100, 150, 200, 250MPa i.e. within the range of pressures used for briquetting several biomass materials [21, 22]) and their interactions on density, impact resistance and compressive strength of bean straw briquettes were studied using a 2 level factorial experimental design, considering 3 replicates of the corner points and a midpoint (Table 2). The maximum compacting temperature (80°C) used in this study was near the glass transition temperature of maize cob (80°C) and bean straw (70°C) because compacting around glass transition temperature aids plastic deformation which is essential in the formation of permanent bonds between particles [23]

Table 2: Design of experiment for statistical analysis of the effects of pressure (MPa), particle size (mm) and temperature (^{o}C) on properties of briquette. Midpoint: pressure/particle size/temperature of 175/3.18/50

Pressure (MPa)	Particle size (mm)	Temperature (^{o}C)
250	2.36	80
250	2.36	80
100	2.36	80
100	4.00	80
100	4.00	20
100	2.36	80
250	4.00	20
100	2.36	20
100	4.00	80
250	4.00	80
250	4.00	80
250	2.36	20
100	2.36	20
100	2.36	20
100	4.00	20
175	3.18	50
250	4.00	20
100	2.36	80
250	4.00	20
100	4.00	80
250	2.36	20
250	2.36	80
100	4.00	20
250	4.00	80
250	2.36	20

(b) Maize cob-bean straw blend

Briquetting of bean straw-maize cob blend was conducted after the analysis of bean straw briquetting characteristics. Pre-determined quantities of crushed bean straw and maize cob (both of particle size <4.00 mm) were mixed in the ratios of 100:0, 75:25, 50:50, 25:75 and 0:100 bean straw:maize cob on a weight basis; stirred to obtain a uniform mixture and immediately briquetted. The effect of bean straw:maize cob blend on briquetting properties was assessed. Bean straw-maize cob mixtures were compressed at compacting pressure/temperature of 200MPa/80^{o}C (i.e. the optimal pressure/temperature identified for both bean straw and maize cob) or 150MPa/50^{o}C (i.e. to assess the possibility of minimising the energy requirement) and a particle size of <4.00mm which was optimal for both maize cob [20] and bean straw.

About 7g of ground bean straw or bean straw-maize cob mixture at the desired composition as described above was fed inside the mould and manually compressed using a 10 tonne Hydraulic Bench Press (Clarke CSA10BB). A dwell time (i.e. duration for which particles under compression remain under maximum/required compacting pressure during briquetting) of 20s was chosen for all experiments to minimise briquette relaxation [7, 24] that may have negative impacts on briquette properties. Briquettes were stored in an air tight container at room temperature (approximately 20^{o}C) for 7 days to allow stabilisation [25] prior to analysis of their properties (density, impact resistance and compressive strength).

2.5 Briquette characterisation

Moisture, ash, volatile matter and fixed carbon content of bean straw and maize cob-bean straw briquettes were determined according to BS 1016-6 standard. Ultimate analysis was carried out using an elementar vario macro cube to determine percentage of carbon and nitrogen. High heating value (HHV) was determined using a CAL2K ECO bomb calorimeter. Scanning electron microscopy (SEM) analysis was carried out using a TM3030 Hitachi Microscope. Differential Scanning Calorimetry (DSC) analysis was carried out (DSC Q20 model) to identify glass transition temperature to determine the range of compacting temperatures to be used in the briquetting experiments. Analysis of neutral detergent fibre (NDF) was carried out by enzymatic gravimetry, while acid detergent lignin (ADL) and acid detergent fibre (ADF) were analysed using an Ankom 220 analyser. The composition of cellulose, hemicellulose and lignin were subsequently determined [26].

Cellulose = Neutral detergent fiber (NDF) – Acid detergent lignin (ADL) (1)

Hemicellulose = Neutral detergent fiber (NDF) – Acid detergent fiber (ADF) (2)

Lignin = Acid detergent lignin (ADL) (3)

Density= mass/volume was determined using the stereometric method which allows briquettes being used for thermo-chemical applications to remain dry [27]. For impact resistance, a briquette was released 4 times from a height of 1.85 m to fall freely under gravity onto a metallic plate to determine impact resistance according to the method of Ndindeng et al [28]. Percentage residual weight of briquettes was determined after each drop. The remaining piece with the highest weight was taken as the residue and used for the next drop. Impact resistance was defined as the percentage residual weight after the 4th drop.

Compressive strength was determined via both the cleft and simple pressure tests using a Tinius Olsen H50KS compressing machine. Briquettes were placed between two flat parallel surfaces with surface area greater than the briquette. Briquettes were placed horizontally for the cleft test and vertically for the simple pressure test. An increasing load was then applied to compress briquettes at a rate of 1 mm min^{-1} until the briquette failed/cracked. The ultimate load at the point where the briquette cracks, F was used to calculate the compressive strength using Equations (4) and (5).

$$Compressive\ strengt, \sigma = F/A \tag{4}$$

$$Compressive\ strength, \sigma = F/l \tag{5}$$

Where *A* and *l* are the cross-sectional area (m^2) and length (m) of briquettes.

The physical and mechanical properties of briquettes such as density, impact resistance and compressive strength are presented as mean values of 6 samples/briquettes. The impact of pressure, moisture content, particle size and temperature and their interactions on density, impact resistance and compressive strength of briquettes were analysed using Minitab 17 at a significance level of α=0.05, based on the design of experiment in Table 2.

3 Results and discussion

3.1 Density of bean straw briquettes

Density is an important property that directly relates to the energy to volume ratio of briquettes [4] and is key in determining the handling, transportation (reducing logistic costs), ignition and combustion characteristics [29]. However, increasing density reduces porosity thereby reducing air circulation, hence reducing combustion rate [9]. The extent of this impact is feedstock and briquetting condition (such as pressure, temperature and particle) dependent. In this study, density of bean straw briquettes ranged between 886.0-1123.3 kg m^{-3} with variation in the briquetting parameters studied. The lowest density of 886 kgm^{-3} was produced at a low compacting temperature of 20 ^{o}C with a large particle size <4mm and a low pressure of 100MPa whereas the highest density (1063.0-1123.3kg m^{-3}) was produced at both tested particle sizes (<2.36 mm and <4.00mm), pressure ≥ 150MPa and high temperature (50-80^{o}C). All briquettes produced at low pressures (100-150 MPa) and low temperature (20 ^{o}C) together with those at medium pressure (200 MPa), low temperature (20 ^{o}C) and large particle size (<4.00 mm) had density below 1000 kg m^{-3} which falls below the range 1000-1400 kg m^{-3} as required by the German Standard DIN 51731. Irrespective of the compacting pressure and particle size, all briquettes produced at a high compacting temperature (80 ^{o}C) had density >1000 kg m^{-3}. Density increased with increasing temperature and pressure, though, it was maximised at particle size of <3.18mm (Fig 1a). Although particle size had a small effect, temperature and pressure were the predominant factors affecting density which agreed well with findings on tropical hardwood sawdust briquettes using a pressure range of 10-50 MPa [13]. However, Rhén et al [15] reported that under compacting pressure of 46-114 MPa, density of spruce pellets was predominantly affected by temperature (26-144 ^{o}C) and moisture (6.3-14.7 %). Increasing temperature above 50^{o}C had little effect on density (Fig 1a), indicating that briquetting temperature of 50-80 ^{o}C could be used to produce high density briquettes.

All briquetting variables and their interactions had significant impact ($P<0.05$) on density (Fig 2a; Table 3) except for the particle size x temperature interaction. Particle size had a significant impact only at low compacting temperature (20 ^{o}C) and compacting pressure of 100-200 MPa, where density decreased with an increase in particle size (Fig 3a), most likely due to high resistance to plastic deformation of particles at this temperature and range of pressure. Therefore, high pressure (250 MPa) is required to crush and bind large particles (<4.00mm) together, producing equally high-density briquettes as particles size <2.36mm. At low compacting temperature (20 ^{o}C), density increased with increasing compacting pressure (100-250MPa) (Fig 3a). This trend is consistent with results reported in the literature for briquettes from waste paper and wheat straw [4], palm kernel cake pellet [30], beech sawdust [21] and neem powder and sawdust [31]. The increasing trend in density with increasing compacting temperature (Fig 3a) within the range of temperatures used (20-80 ^{o}C) agrees well with findings on pellets produced from several biomass feedstocks e.g. spruce, birch, reed canary grass (room temperature to 80 ^{o}C) [17] wheat straw and wheat straw extract pellets (30-100 ^{o}C) [32]. Furthermore, Razuan et al [30] also reported an increasing trend in density of palm kernel cake pellets (average particle size 2 mm and moisture 7.9%) as temperature was increased from 20 to 100 ^{o}C, however, further increasing temperature above 100 ^{o}C, reduced the density and compressive strength. Similarly, Gilbert et al [33] obtained highest density and strength of switchgrass pellets at 100 ^{o}C in an operating temperature range of 14-125 ^{o}C.

Table 3: Analysis of variance for bean straw briquette density

	Degrees of freedom	Sum of squares	Mean sum of squares	F-value	P-value
Pressure (*p*)	1	93900	93900.1	2081.85	0.000
Particle size (*s*)	1	728	728.2	16.14	0.001
Temperature (*t*)	1	50729	50728.8	1124.70	0.000
$p \times s$	1	330	330.0	7.32	0.016
$p \times t$	1	1438	1438.4	31.89	0.000
$s \times t$	1	39	38.5	0.85	0.369
$p \times s \times t$	1	713	712.9	15.80	0.001
Error	16	722	45.1		
Total	24	149678			

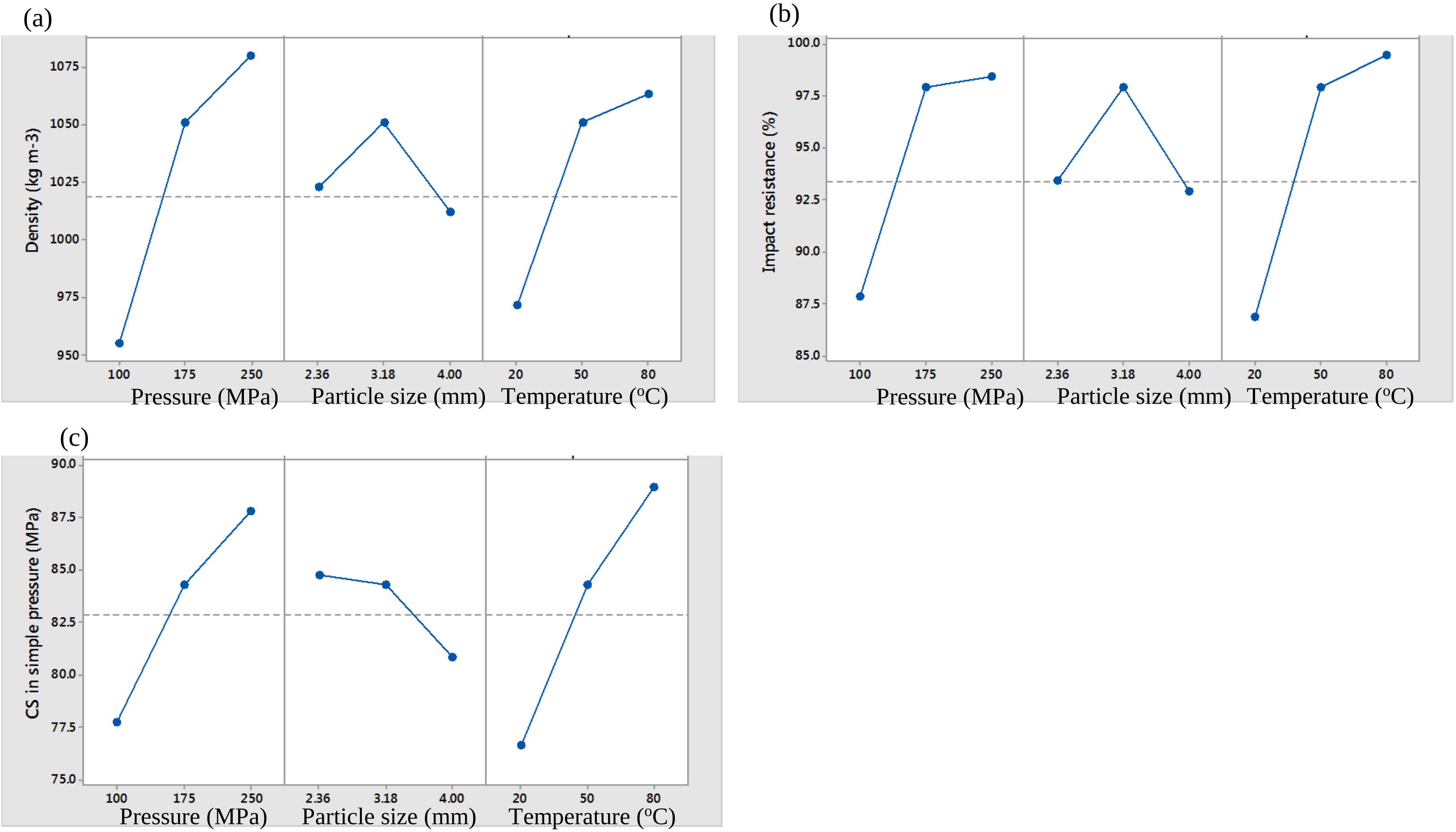

Fig 1: Effects of briquetting parameters: pressure, particle size and temperature on (a) density, (b) impact resistance and (c) compressive strength (CS) of bean straw briquette.

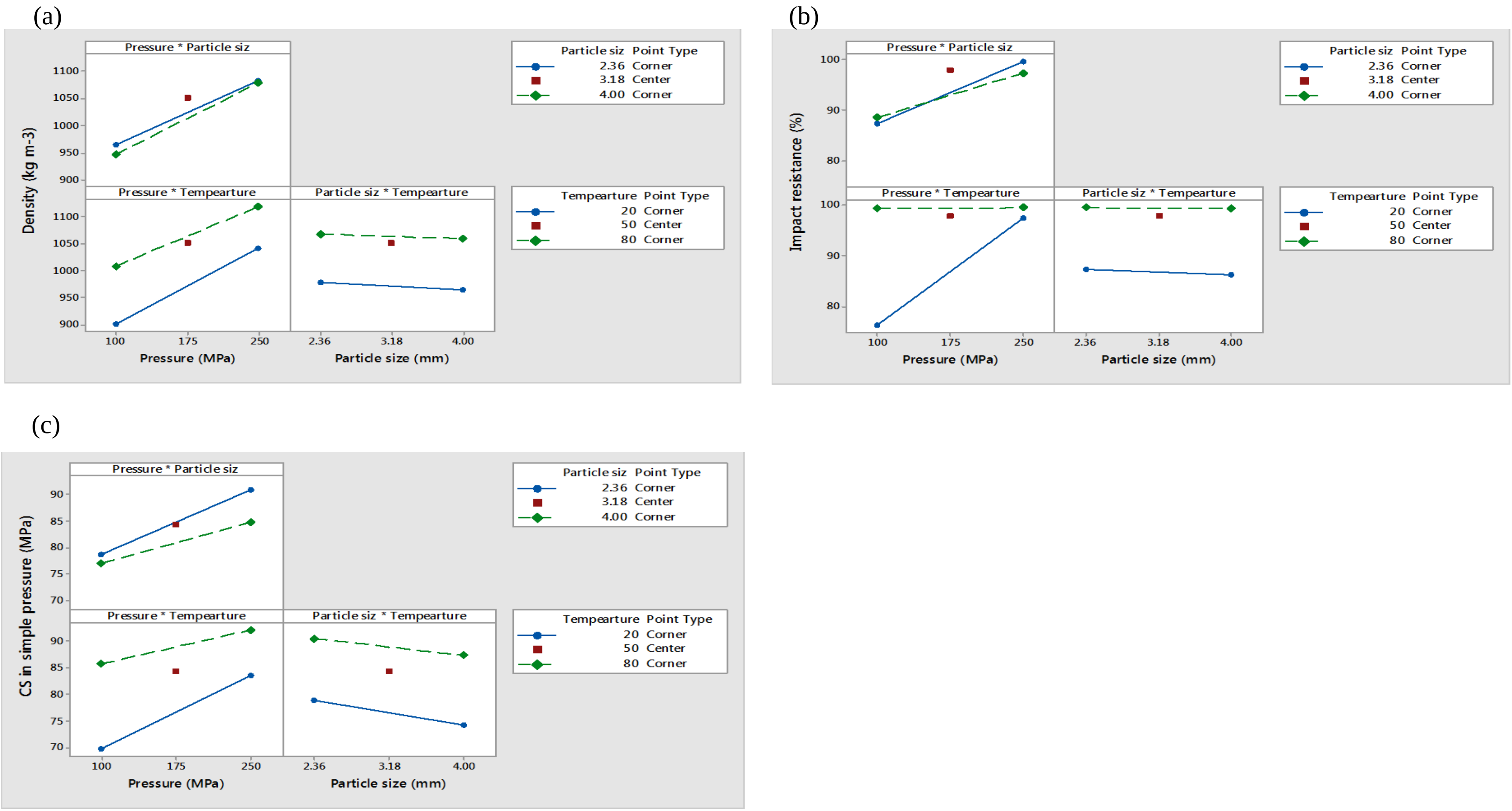

Fig 2: Interaction effects of briquetting parameters: pressure, moisture content, particle size and temperature on (a) density, (b) impact resistance and (c) compressive strength (CS) of bean straw briquette. Red square represents the mid-point.

3.2 Impact resistance of bean straw briquettes

Impact resistance is a measure of durability of briquettes which defines the tendency of a briquette to produce dust or break when it is subjected to a destructive force. It is an indicator of mechanical strength [34] where briquettes with high impact resistance/durability are desirable to minimise breakage and dust formation during transport and conveying. Impact resistance of >80% is required for handling and transportation efficiency [34, 35]. In this study, the impact resistance of bean straw briquettes was well above 80% (up to 99.8% in some cases), except for briquettes derived from a low compacting pressure of 100MPa, with small particles (<2.36mm) and at a low temperature (20 °C) (Fig 3b). These briquettes lost more than 20% of their weight and therefore are less resistant to the destructive forces experienced during transport and handling. The large amount of fine particles and dust (>20%) generated could potentially cause disturbance to boiler feed systems, lead to reduced efficiency of combustion and increase the risks of fire and explosion during transport, handling and storage [36]. All bean straw briquettes produced at high temperature (80 °C) and high compacting pressure (200-250MPa) had high impact resistance with <2.5 % dust/fine particles generated and are therefore highly durable and satisfy European Standard Committee CEN/TC335 (for solid biofuels) for durability. These highly durable briquettes (impact resistance >97.5%) would also help minimise health related problems resulting from fine particles/dust [37].

For bean straw, temperature and pressure were found to be the predominant factors (Fig 1b) affecting impact resistance whereas particle size in the range tested had little effect. Increasing pressure and temperature from 175-250MPa and 50-80°C respectively had little impact (Fig 1b). However, according to Castellano et al., [18], increasing particle size from 2mm to 4mm decreased the durability of pine, oat, triticale and rice straw briquettes but had no influence on that of *Eucalyptus camaldulensis* and Pyrenean oak briquettes. Similarly, under compacting pressures of 1.5MPa [3], increasing particle size from <1.41mm to 1.41-3.17mm significantly decreased the durability of larch pellets but had no impact on the durability of tulipwood pellets. The authors found that increasing compacting temperature (120-180 °C) significantly increased the durability of pellets from both feedstocks. From previous studies [20], impact resistance of maize cob briquettes at a moisture content range of 7-17% was significantly reduced by increasing particle size from <2.36-<4mm. From all of the aforementioned studies, it can be concluded that the effect of particle size is feedstock dependent.

There was a significant ($P< 0.05$) pressure x temperature interaction on impact resistance (Fig 2b; Table 4). At low compacting temperature (20 °C), impact resistance increased with increasing pressure from 100-200 MPa and remained constant with further increments to 250 MPa (Fig 3b). This indicates that maximum inter-particle bonding was achieved at compacting pressure ranging between 200-250MPa at 20°C. Rajaseenivasan et al [31] also observed an increasing trend in impact resistance of neem powder and sawdust briquettes when pressure was increased from 7 to 33 MPa. Increasing compacting temperature (20-80 °C) significantly increased impact resistance (Fig 3.b) at low compacting pressures (100-150MPa) and at 80 °C. At the high temperature of 80°C, impact resistance was independent of compacting pressure and particle size.

Table 4: Analysis of variance for bean straw briquette impact resistance

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	670.98	670.984	61.94	0.000
Particle size (*s*)	1	1.76	1.760	0.16	0.692
Temperature (*t*)	1	953.82	953.820	88.06	0.000
$p \times s$	1	18.55	18.550	1.71	0.209
$p \times t$	1	662.55	662.550	61.17	0.000
$s \times t$	1	1.35	1.354	0.12	0.728
$p \times s \times t$	1	9.00	9.004	0.83	0.375
Error	16	173.31	10.832		
Total	24	2512.88			

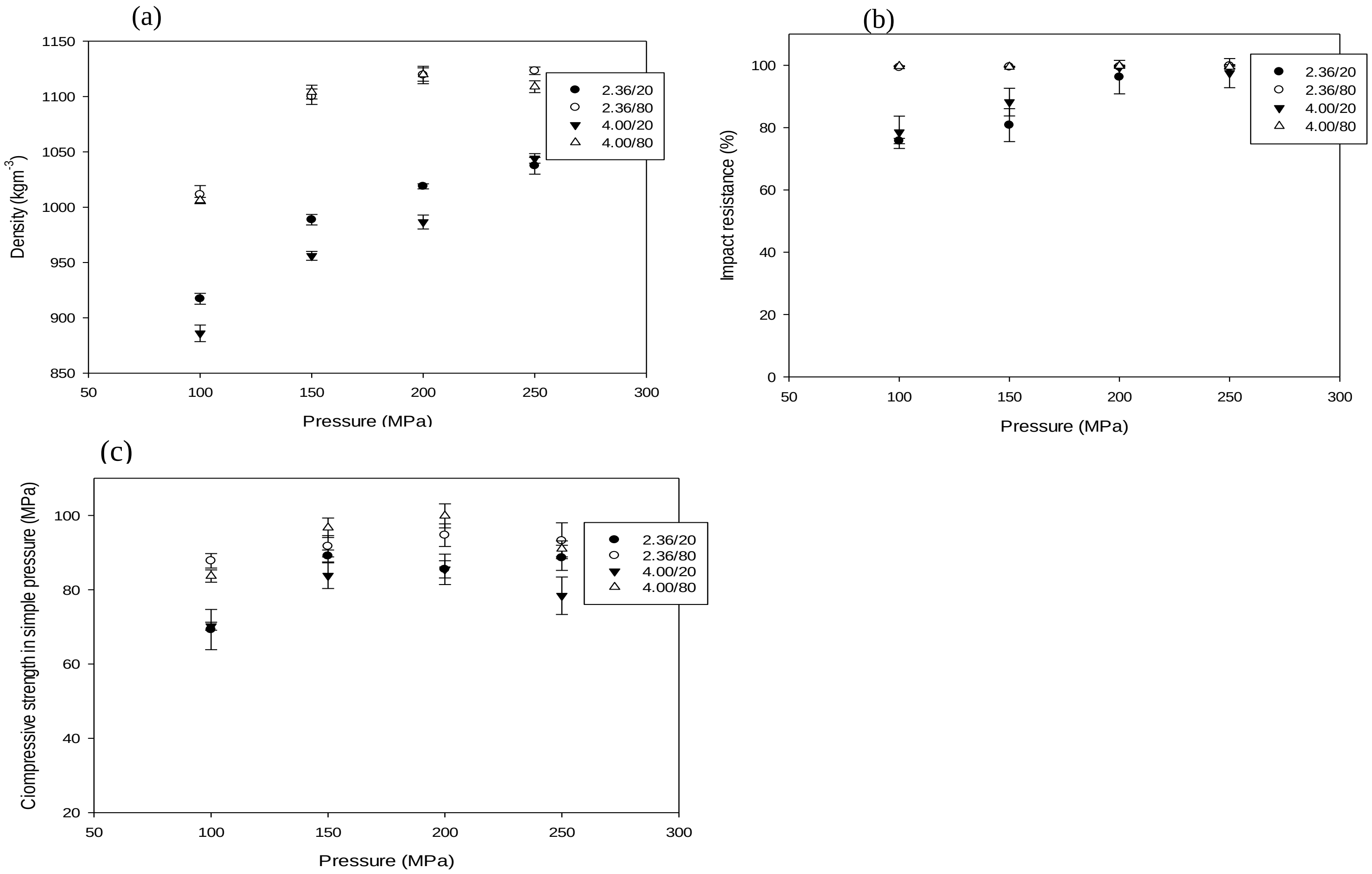

Fig 3: Effect of compacting conditions (temperature, pressure) and feedstock particle size (legend: particle size (mm)/ compacting temperature (^{o}C)) on briquette (a) density, (b) impact resistance and (c) compressive strength of bean straw briquette

3.3 Compressive strength of bean straw briquettes

Compressive strength is the maximum load that a briquette can withstand before it breaks. It is used to estimate the compressive stress resulting from the weight of the top briquettes on lower briquettes during storage, transport and handling [38]. It is also a measure of mechanical strength, therefore the higher the value the better. In this study, compressive strength was measured by both the in cleft and simple pressure tests. This study revealed a strong positive correlation between compressive strength in cleft and simple pressure (data not shown) which agreed well with previous findings [20] and therefore, only data for compressive strength in simple pressure, referred to as compressive strength (CS) hereafter, are presented. CS ranged between 69.3-99.9 MPa with variations in briquetting parameters. All briquettes had CS much higher the minimum recommended value i.e. > 2.56 MPa, [9] for efficient transport, storage and handling with minimal breakage.

Temperature and pressure were the predominant factors affecting CS (Fig 1c). It was reported [13] that pressure (10-50 MPa) was the predominant factor affecting CS of tropical hardwood sawdust briquettes (i.e. *C. pentandra*, *T. scleroxylon*, *A. robusta*, *T. superba*, *P. Africana*, and *C. mildbreadii*) made from particles <3.35 mm with a moisture content of 11.46%. Moisture (6.3-14.7 %) and temperature (26-144 ^{o}C) predominantly affected CS of spruce pellets under compacting pressures 46-114 MPa [15]. While moisture content (between 2 and 14 %) was the predominant factor affecting CS of birch, spruce and reed canary grass pellets produced from compacting pressures of 200-400MPa and a particle size of <1.00mm [17]. Such variations can be attributed to variations in feedstock properties and briquetting parameters used in the different studies.

Compressive strength increased with increasing pressure and temperature whereas it decreased significantly (P<0.05) with increasing particle size (Fig 1c and Table 5). Mechanical strength and density depend on the strength of inter-particle bonds which are affected by particle size, compacting pressure and temperature. Small particles have large surface areas thereby helping to form strong bonds (with and without solid bridges) between particles during briquetting [39]. In bonding without solid bridges, solid particles are attracted to each other by actions of short-range forces such as molecular (van der Waal's forces, hydrogen bridge and valence force i.e. free chemical bond) and electrostatic forces. Valence and Van der Waals' forces can contribute to bonding when seperation between particles are about 10 Å and 0.1µm respectively [40, 20]. Bonding by action of electrostatic force occurs due to the presence of excess charge which may by created from grinding and inter-particle friction [40]. Therefore, the forces contributing to bonding become less effective for large pore sizes, thereby weakening the briquettes. During bonding by solid brigde formation application of high pressure and temperature cause diffusion of molucules from one particle to another. Solid brigdes can also be formed as a result of chemical reactions and solification of melted components [40, 41]. These observations are in agreement with studies on maize cob under particle size (<2.36-<4.00 mm) with compacting pressure of 150-250MPa [20] and pine with particle size of 0.5-4.0 mm and pressure of 31-318 MPa [42]. However, it contradicts Zhang and Guo [43] where for varying caragana korshinskii kom particle sizes (0.16-5.0 mm), minimum briquette CS (62.16 MPa) was obtained at a particle size <0.16 mm under a compacting pressure and temperature of 10-170 MPa and 70-150 ^{o}C. These differences in results confirm the need to analyse variations in briquettes properties on an individual feedstock basis.

Pressure x temperature and pressure x particle size x temperature interactions significantly affected compressive strength ($P<0.05$, Fig 2c; Table 5). Irrespective of the compacting temperature, compressive strength increased with increasing pressure (100-150MPa) but remained relatively constant with further increments in pressure up to 250 MPa. Increasing pressure squeezes natural binder components out of biomass particles and also causes plastic and elastic deformation of particles thereby reducing void spaces between particles and increasing inter-particle bonding by solid bridge formation, increasing contact areas (which increase short range forces such as molecular and electrostatic forces) and through mechanical interlocking, consequently increasing both density and strength [13, 44, 43, 14].

Compressive strength increased with increasing temperature for the tested range of compacting pressures (Fig 3c). The highest, increment of 27% was observed at low pressure i.e. 100 MPa and particle size <2.36 mm when temperature was increased from 20-80 ^{o}C, most likely due to high particle resistance to deformation at low pressure (100 MPa) and temperature (20 ^{o}C). Temperature minimises relaxation and improves the degree of densification by: (i) softening biomass particles, consequently aiding plastic deformation upon compression and increasing the inter-particle bonding through mechanical interlocking and (ii) facilitating the release of natural binders such as lignin, cellulose and hemicellulose which form solid bridges upon cooling thereby increasing the mechanical strength and density [33, 41]. Natural binders such as lignin and hemicellulose can undergo plastic deformation or be squeezed out of particles during compression at temperatures near the glass transition tempearture [23] which was 70 ^{o}C in this study. Increasing temperature (from 20-80 ^{o}C) not only improved briquette density and mechanical strength but also reduced the briquetting pressure required, which can potentially reduce production costs by directly minimising the energy required for compression. The use of high pressure is associated with high electrical energy consumption and high wear and tear of briquetting equipment [45]. Heat softens biomass particles, reduces friction between particles and the mould, thereby minimising costs of depreciation, repair and maintenance resulting from wear and tear [45].

The increasing trend in compressive strength with increasing pressure or temperature agreed well with trends reported for palm oil mill residue briquettes (pressure 3-11MPa) [9], torrefied switchgrass [33] and hazelnut shell charcoal (particle size of >2.0 mm, pressure of 800 MPa, using 6.5-18.0 %wt pyrolysis oil as a binder) [46].

Table 5: Analysis of variance for bean straw briquette compressive strength

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	606.01	606.015	47.79	0.000
Particle size (*s*)	1	92.04	92.042	7.26	0.016
Temperature (*t*)	1	907.74	907.740	71.59	0.000
$p \times s$	1	32.20	32.202	2.54	0.131
$p \times t$	1	83.63	83.627	6.60	0.021
$s \times t$	1	3.23	3.227	0.25	0.621
$p \times s \times t$	1	61.44	61.440	4.85	0.043
Error	16	202.87	12.680		
Total	24	1991.40			

3.4 Bean straw-maize cob blended briquettes

Density, impact resistance and compressive strength of bean straw-maize cob mix briquettes ranged between 949.3-1154.2 kgm^{-3}, 63.2-99.8%, and 30.5-99.6 MPa respectively with variations in the bean straw:maize cob blend ratio of 0:100% by weight. All briquettes satisfied the German Standard DIN 51731 with density 1000-1400 kgm^{-3} except for bean straw:maize cob blend ratio of 0:100 under a low compacting pressure of 150 MPa and a temperature of 50 ^{o}C which produced briquettes with the lowest density i.e. 949.3 kgm^{-3}. These briquettes also had the lowest impact resistance (63.2%) which did not attain the minimum recommended value of 80%. However, all other briquettes had both impact resistance and compressive strength above the minimum values of 80% and 2.36 MPa required to minimise breakage and dust formation.

Blend ratio had no effect on impact resistance at high pressure and temperature of 200MPa/80^{o}C (Table 6). However, at a low compacting pressure/temperature of 150MPa/50^{o}C, impact resistance was reduced by ~36% as maize cob content increased from 75-100%. Although increasing maize cob content from 0-75% reduced density by <5%, CS decreased by 47-49% (Table 6). This is most likely due to higher resistance of maize cobs to plastic deformation. From scanning electron microscopy (SEM) imaging (Fig 4), maize cob is highly porous compared to bean straw which could have increased resistance to plastic deformation thereby increasing the energy requirement (high pressure) to minimise separation between and within (pores) particles. During briquetting, pressure causes particles to first rearrange to form closely packed mass and secondly to elastically and plastically deform when pressure increases. During plastic and elastic deformation, particles move and fill void spaces which increases contact area, consequently increasing both density and strength [44, 14]. Lastly, volume is significantly reduced, resulting in the density of the material approaching the true density of the component ingredients. By the end of this stage, the deformed/broken particles cannot change position because of a decreased number of cavities [44]. Sole bean straw and a bean straw:maize cob blend ratio of 75:25 by weight were the best substrates for producing briquettes with high density and mechanical strength (Table 6). Blending improved both the density and mechanical strength of maize cob briquettes but these properties were lower when compared with bean straw only briquettes. The optimal bean straw:maize cob blend ratio was 75:25 producing equally high density briquettes as sole bean straw.

Scanning electron microscopy (SEM) images (Fig 4) of briquettes which were broken from the middle in a direction perpendicular to the axis of the cylindrical briquettes shows that bonding in bean straw is strongly enhanced by mechanical interlocking while for maize cobs bonding was mainly by solid bridge formation. Application of high pressure and/or temperature during densification results in diffusion of molecules at the point of contact from one particle to another, thus forming solid bridges while fibrous or bulky particles interlock to form mechanical interlocking bonds [41]. Particles of corn stover and switchgrass briquettes/pellets are bonded mainly by solid brigdes resulting from natural binders i.e. mainly lignin and protein [40]. Variations in the bonding mechanism are likely to be due to differences in the nature of biomass materials and in particular the more fibrous nature of the bean straw. During compression, interlocking bonds are formed [41] with increasing strength and density. As the proportion of maize cob content was increased, the extent of bond formation by mechanical interlocking was reduced (Fig 4), most likely due to maize cob particles only filling the void spaces between the fibrous bean straw particles. The reduction in the extent of bonding by mechanical interlocking could explain the reduced strength and density of bean straw briquettes with increasing content of maize cob in the blend. In addition, variations in lignin content (maize cob 1.5% and bean straw 10.2% (Table 1)) coud have also caused a difference in densification characteristics of these materials since high lignin content provides better densification properties [1]. Maize cob has lower lignin content than bean straw therefore, increasing maize cob composition would lower the lignin content of the blend thereby reducing density and strength of resulting briquettes. A decreasing trend in density of briquettes was observed by increasing corn stover content from 0-100% in corn stover:peanut shell blends [47]. Increasing palm kernel shell content from 0-10% reduced sawdust briquette density from 420 to 380 kg m^{-3} and durability from 64.74 to 32.28%. However, further increasing palm kernel content to 50% increased density and durability to 480kg m^{-3} and 73.40% respectively [48]. Blending bamboo with rice straw in the ratio of 5:0-0:5 by weight (i.e. bamboo : rice straw) reduced density of sole bamboo (1250 kgm^{-3}) and sole rice straw (1350 kgm^{-3}) pellets (to around 1000-1100kg m^{-3}), however, durability was maximised (99.03%) with a blend ratio of 2:3 [49].

Bean straw ash content was about double that of maize cob (Table 1). Inorganic elements determine formation of deposits, fly ash emissions and ash melting point during combustion [50]. Potassium (K), sodium (Na), silicon (Si) and aluminium (Al) decrease the ash melting point while calcium (Ca) and magnesium (Mg) increase the ash melting point. Furthermore, increasing K content increases aerosol formation during combustion and hence fouling inside boilers and increased particulate emissions [51, 50]. Variations in the effect of the inorganics elements on ash melting point are likely due to variation in their melting temperatures. Generally, the composition of the inorganic elements was higher in bean straw than in maize cob (Table 1). This demonstrates the variability in biomass properties which may indicate requirement for varying optimal conditions for processing different biomass materials for energy. Ca, K, Na, and Mg were the dominant inorganic elements in bean straw while K, Mg, Ca and phosphorous (P) were the dominant inorganic elements in maize cob. Mullen et al [26] also reported that the inorganic fraction of maize cob was predominantly K which in this study was is over 3 times the concentrations of Ca and Mg combined which is likely to lower the ash melting point of maize cob. While the high Ca concentration in bean straw is likely to increase the ash melting point of bean straw. The K concentration is high in both bean straw and maize cob which may increase aerosol formation during combustion and hence fouling inside the boiler and increased particulate emissions [51]. However, the content of the alkali metal (K and Na) may be reduced by leaching these biomass materials with water [50]. The content of heavy metals such as As, Cr, Cu, Pb and Zn were determined as a requirement by the German standard DIN 51731. The concentrations of heavy metals in both maize cob and bean straw were within the acceptable limits by the German standard DIN 51731 i.e. As <0.8mg/kg, Cr < 8mg/kg, Pb < 100mg/kg and Zn < 100mg/kg, except Cu > 5mg/kg. Heavy metal content is required to be as low as possible as it affects ash quality and particle emissions [51]. Therefore, fuel ash content has to be minimised for process efficiency [51]. In this study, increasing maize cob content in the blend: (i) increased briquette volatile composition due to higher volatile content in maize cobs compared to bean straw and (ii) reduced ash and fixed carbon content (Table 7). Blending had a higher impact on ash content than on volatile and fixed carbon contents. Increasing maize cob content from 25-50% did not result in a significant change in HHV (17-17.9 MJ kg^{-1}), fixed carbon and volatile contents. The high heating values (HHV) of the bean straw-maize cob blend in the current study are comparable with that of switchgrass (17.3 MJ kg^{-1}) [33], peanut shells (17.55 MJ kg^{-1}) and coconut fiber (17.74 MJ kg^{-1}), but higher than those of sawdust (14.99 MJ kg^{-1}), rice husk (14.77 MJ kg^{-1}) and palm fibre (16.84 MJ kg^{-1}) [24] which means from the same amount of fuel, more energy can be generated from the blend.

Table 6: Effect of blending ratio (bean straw:maize cob) on density, impact resistance and compressive strength of briquettes

Bean straw:maize cob ratio (wt:wt)	Pressure: 200 MPa and temperature: 80 °C			Pressure: 150 MPa and temperature: 50 °C		
	Density (kg m^{-3})	Impact resistance (%)	CS (MPa)	Density (kg m^{-3})	Impact resistance (%)	CS (MPa)
100:0	1153.2	99.8	99.6	1063.0	99.8	92.6
75:25	1154.2	99.4	83.6	1052.9	99.5	69.0
50:50	1126.5	99.6	65.4	1038.1	97.7	56.5
25:75	1114.4	99.4	52.4	1019.0	98.6	47.5
0:100	1018.4	99.8	40.4	949.3	63.2	30.5

Table 7: Effect of blending ratio (bean straw:maize cob) on proximate properties of briquettes and HHV

Bean straw:maize cob ratio (wt:wt)	Ash (%)	Volatile (%)	Fixed carbon (%)	HHV (MJ kg^{-1})
75:25	5.4	76.9	17.7	17.0
50:50	4.5	77.5	18.0	17.9
25:75	3.0	79.9	17.1	17.3

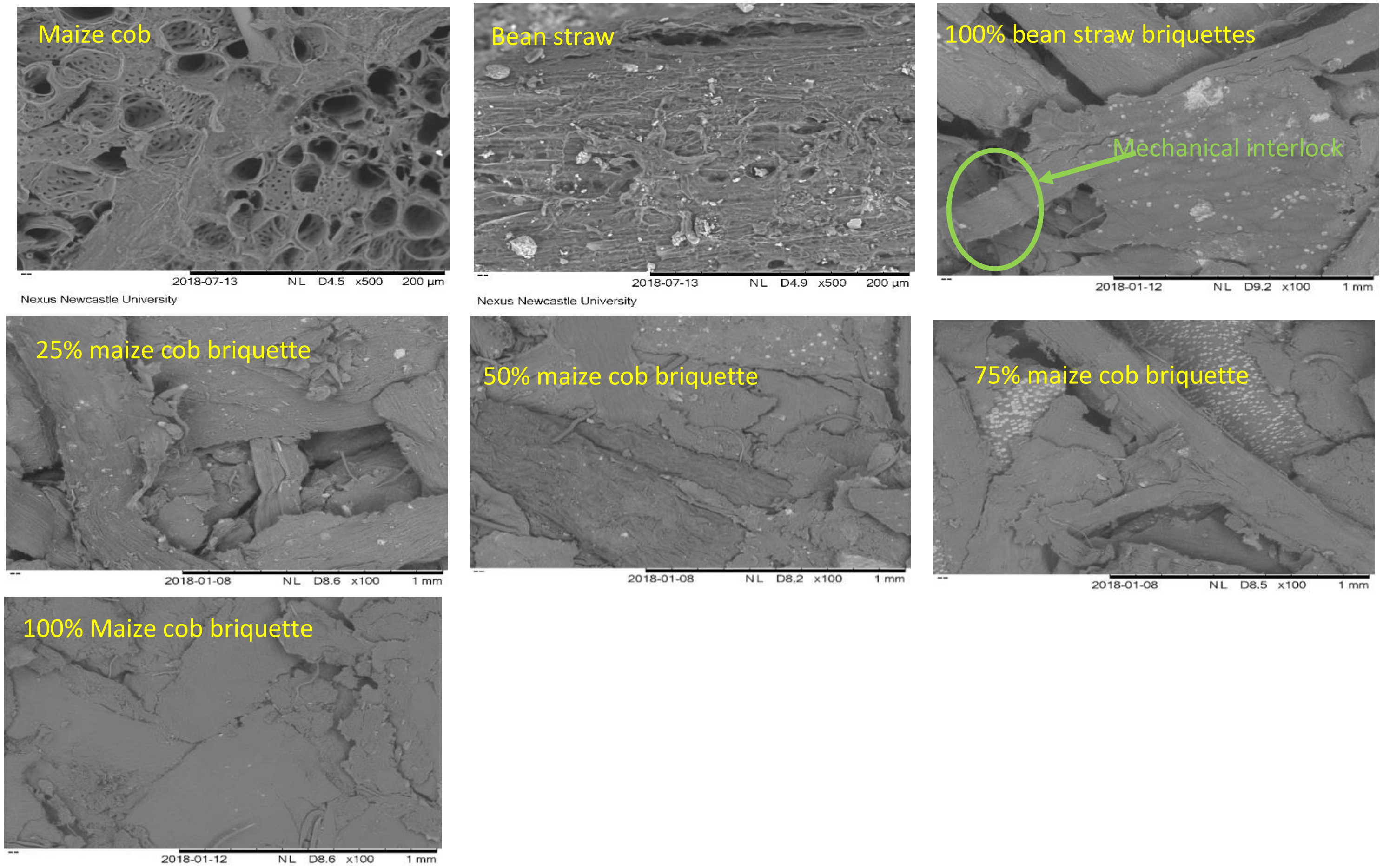

Fig 4: Bonding in bean straw:maize cob briquettes produced at compacting pressure of 200MPa with a moisture content of 10.63% for bean straw and 8.62% for maize cobs

4 Conclusions

This study revealed that increasing pressure and temperature improved bean straw briquette density and mechanical strength. However, particle size had little impact at compacting pressure/temperature of 250MPa/20^{o}C and at compacting temperature of 80^{o}C irrespective of compacting pressure tested. All bean straw briquettes at pressure 100-200MPa and temperature of 80^{o}C satisfied the German Standard DIN 51731 (density 1000-1400 kg m^{-3}). Strong interactions were observed between briquetting parameters with interaction pressure × temperature significantly affecting density, impact resistance and compressive strength. Blending of bean staw:maize cob enhanced briquette characteristics with an optimum 75:25 (wt:wt) ratio producing equally high density briquettes similar to sole bean straw. However, sole bean straw produced briquettes with highest density and mechanical strength with a lower energy expenditure (pressure and /temperature) and therefore is a preferred substrate over maize cob for briquette production.

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References

[1] R.I. Muazu, J.A. Stegemann, Effects of operating variables on durability of fuel briquettes from rice husks and corn cobs, Fuel Process. Technol. 133 (2015) 137–145.

[2] A. Yank, M. Ngadi, R. Kok, Physical properties of rice husk and bran briquettes under low pressure densification for rural applications, Biomass Bioenergy. 84 (2016) 22–30.

[3] S. min Lee, B.J. Ahn, D.H. Choi, G.-S. Han, H.-S. Jeong, S.H. Ahn, I. Yang, Effects of densification variables on the durability of wood pellets fabricated with Larix kaempferi C. and Liriodendron tulipifera L. sawdust, Biomass Bioenergy. 48 (2013) 1–9.

[4] A. Demirbaş, Physical properties of briquettes from waste paper and wheat straw mixtures, Energy Convers. Manag. 40 (1999) 437–445.

[5] A. Amaya, N. Medero, N. Tancredi, H. Silva, C. Deiana, Activated carbon briquettes from biomass materials, Bioresour. Technol. 98 (2007) 1635–1641.

[6] J.O. Chaney, Combustion characteristics of biomass briquettes, University of Nottingham, 2010. http://eprints.nottingham.ac.uk/11732/ (accessed February 10, 2016).

[7] V. Panwar, B. Prasad, K.L. Wasewar, Biomass residue briquetting and characterization, J. Energy Eng. 137 (2010) 108–114.

[8] S. Yaman, M. Sahan, H. Haykiri-Acma, K. Sesen, S. Kucukbayrak, Fuel briquettes from biomass–lignite blends, Fuel Process. Technol. 72 (2001) 1–8.

[9] H.M. Faizal, Z.A. Latiff, M.A. Wahid, A.N. Darus, Physical and combustion characteristics of biomass residues from palm oil mills, New Asp. Fluid Mech. Heat Transf. Environ. Mastorakis NE V Mlad. Z Bojkovic Eds Wiley N. Y. USA ISBN. (2010) 978–960.

[10] T.U. Onuegbu, O. Ikechukwu Martin, N.O. Ilochi, U.E. Ekpunobi, A.S. Ogbuagu, Enhancing the Properties of Coal Briquette Using Spear Grass (Imperata Cylindrica), Leonardo J. Sci. 17 (2010) 47–58.

[11] O.O. Fasina, Physical properties of peanut hull pellets, Bioresour. Technol. 99 (2008) 1259–1266.

[12] S. Yaman, M. Sahan, H. Haykiri-acma, K. Sesen, S. Kucukbayrak, Production of fuel briquettes from olive refuse and paper mill waste, Fuel Process. Technol. 68 (2000) 23–31.

[13] J.S. Mitchual, K. Frimpong-Mensah, N.A. Darkwa, Effect of species, particle size and compacting pressure on relaxed density and compressive strength of fuel briquettes, Int. J. Energy Environ. Eng. (2013) 1–6.

[14] M.T. Carone, A. Pantaleo, A. Pellerano, Influence of process parameters and biomass characteristics on the durability of pellets from the pruning residues of Olea europaea L., Biomass Bioenergy. 35 (2011) 402–410.

[15] C. Rhén, R. Gref, M. Sjöström, I. Wästerlund, Effects of raw material moisture content, densification pressure and temperature on some properties of Norway spruce pellets, Fuel Process. Technol. 87 (2005) 11–16.

[16] J.S. Tumuluru, L.G. Tabil, Y. Song, K.L. Iroba, V. Meda, Impact of process conditions on the density and durability of wheat, oat, canola, and barley straw briquettes, BioEnergy Res. 8 (2015) 388–401.

[17] Y. Huang, M. Finell, S. Larsson, X. Wang, J. Zhang, R. Wei, L. Liu, Biofuel pellets made at low moisture content – Influence of water in the binding mechanism of densified biomass, Biomass Bioenergy. 98 (2017) 8–14.

[18] J.M. Castellano, M. Gómez, M. Fernández, L.S. Esteban, J.E. Carrasco, Study on the effects of raw materials composition and pelletization conditions on the quality and properties of pellets obtained from different woody and non woody biomasses, Fuel. 139 (2015) 629–636.

[19] H. Li, X. Liu, R. Legros, X.T. Bi, C. Jim Lim, S. Sokhansanj, Pelletization of torrefied sawdust and properties of torrefied pellets, Appl. Energy. 93 (2012) 680–685.

[20] D.K. Okot, P.E. Bilsborrow, A.N. Phan, Effects of operating parameters on maize COB briquette quality, Biomass Bioenergy. 112 (2018) 61–72.

[21] P. Križan, M. Matú, Ľ. Šooš, J. Beniak, Behavior of Beech Sawdust during Densification into a Solid Biofuel, Energies. 8 (2015) 6382–6398.

[22] A. Demirbas, A. Sahin-Demirbas, Briquetting Properties of Biomass Waste Materials, Energy Sources. 26 (2004) 83–91.

[23] N. Kaliyan, R.V. Morey, Densification characteristics of corn cobs, Fuel Process. Technol. 91 (2010) 559–565.

[24] O.C. Chin, K.M. Siddiqui, Characteristics of some biomass briquettes prepared under modest die pressures, Biomass Bioenergy. 18 (2000) 223–228.

[25] P. Wilaipon, The Effects of Briquetting Pressure on Banana-Peel Briquette and the Banana Waste in Northern Thailand, Am. J. Appl. Sci. 6 (2009) 167–171.

[26] C.A. Mullen, A.A. Boateng, N.M. Goldberg, I.M. Lima, D.A. Laird, K.B. Hicks, Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis, Biomass Bioenergy. 34 (2010) 67–74.

[27] F. Rabier, M. Temmerman, T. Bohm, H. Hartmann, P. Daugbjergjensen, J. Rathbauer, J. Carrasco, M. Fernandez, Particle density determination of pellets and briquettes, Biomass Bioenergy. 30 (2006) 954–963.

[28] S.A. Ndindeng, J.E.G. Mbassi, W.F. Mbacham, J. Manful, S. Graham-Acquaah, J. Moreira, J. Dossou, K. Futakuchi, Quality optimization in briquettes made from rice milling by-products, Energy Sustain. Dev. 29 (2015) 24–31.

[29] O.A. Sotannde, A.O. Oluyege, G.B. Abah, Physical and combustion properties of briquettes from sawdust of Azadirachta indica, J. For. Res. 21 (2010) 63–67.

[30] R. Razuan, K.N. Finney, Q. Chen, V.N. Sharifi, J. Swithenbank, Pelletised fuel production from palm kernel cake, Fuel Process. Technol. 92 (2011) 609–615.

[31] T. Rajaseenivasan, V. Srinivasan, G. Syed Mohamed Qadir, K. Srithar, An investigation on the performance of sawdust briquette blending with neem powder, Alex. Eng. J. 55 (2016) 2833–2838.

[32] W. Stelte, C. Clemons, J.K. Holm, J. Ahrenfeldt, U.B. Henriksen, A.R. Sanadi, Fuel Pellets from Wheat Straw: The Effect of Lignin Glass Transition and Surface Waxes on Pelletizing Properties, BioEnergy Res. 5 (2012) 450–458.

[33] P. Gilbert, C. Ryu, V. Sharifi, J. Swithenbank, Effect of process parameters on pelletisation of herbaceous crops, Fuel. 88 (2009) 1491–1497.

[34] H. Haykiri-Acma, S. Yaman, S. Kucukbayrak, Production of biobriquettes from carbonized brown seaweed, Fuel Process. Technol. 106 (2013) 33–40.

[35] C. Antwi-Boasiako, B.B. Acheampong, Strength properties and calorific values of sawdust-briquettes as wood-residue energy generation source from tropical hardwoods of different densities, Biomass Bioenergy. 85 (2016) 144–152.

[36] M. Temmerman, F. Rabier, P. Jensen, H. Hartmann, T. Bohm, Comparative study of durability test methods for pellets and briquettes, Biomass Bioenergy. 30 (2006) 964–972.

[37] M.F. Zainuddin, S. Rosnah, M.M. Noriznan, I. Dahlan, Effect of Moisture Content on Physical Properties of Animal Feed Pellets from Pineapple Plant Waste, Agric. Agric. Sci. Procedia. 2 (2014) 224–230.

[38] M. Matúš, P. Križan, L. Šooš, J. Beniak, Effects of Initial Moisture Content on the Physical and Mechanical Properties of Norway Spruce Briquettes, World Acad. Sci. Eng. Technol. Int. J. Environ. Chem. Ecol. Geol. Geophys. Eng. 9 (2015) 1156–1162.

[39] S.A. Rahaman, P.A. Salam, Characterization of cold densified rice straw briquettes and the potential use of sawdust as binder, Fuel Process. Technol. 158 (2017) 9–19.

[40] N. Kaliyan, R.V. Morey, Natural binders and solid bridge type binding mechanisms in briquettes and pellets made from corn stover and switchgrass, Bioresour. Technol. 101 (2010) 1082–1090.

[41] N. Kaliyan, R. Vance Morey, Factors affecting strength and durability of densified biomass products, Biomass Bioenergy. 33 (2009) 337–359.

[42] P. Križan, Research of factors influencing the quality of wood briquets, Acta Montan. Slovaca-ISSN. (2007) 1335–1788.

[43] J. Zhang, Y. Guo, Physical properties of solid fuel briquettes made from Caragana korshinskii Kom, Powder Technol. 256 (2014) 293–299.

[44] J.S. Tumuluru, C.T. Wright, J.R. Hess, K.L. Kenney, A review of biomass densification systems to develop uniform feedstock commodities for bioenergy application, Biofuels Bioprod. Biorefining. 5 (2011) 683–707.

[45] P.D. Grover, S.K. Mishra, Biomass briquetting: technology and practices, Food and Agriculture Organization of the United Nations, 1996. http://wgbis.ces.iisc.ernet.in/energy/HC270799/RWEDP/acrobat/fd46.pdf (accessed March 11, 2017).

[46] A. Demirbaş, Properties of charcoal derived from hazelnut shell and the production of briquettes using pyrolytic oil, Energy. 24 (1999) 141–150.

[47] C. Gong, D. Lu, G. Wang, T. Tabil, D. Wang, Compression characteristics and energy requirement of briquettes made from a mixture of corn stover and peanut shells, BioResources. 10 (2015) 5515–5531.

[48] O.F. Obi, Evaluation of the physical properties of composite briquette of sawdust and palm kernel shell, Biomass Convers. Biorefinery. 5 (2015) 271–277.

[49] Z. Liu, X. Liu, B. Fei, Z. Jiang, Z. Cai, Y. Yu, The properties of pellets from mixing bamboo and rice straw, Renew. Energy. 55 (2013) 1–5.

[50] A.I. Moreno, R. Font, J.A. Conesa, Physical and chemical evaluation of furniture waste briquettes, Waste Manag. 49 (2016) 245–252.

[51] I. Obernberger, G. Thek, Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour, Biomass Bioenergy. 27 (2004) 653–669.

A.1.2 Effects of operating parameters on maize cob briquette quality

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Abstract

Briquetting is considered as one of the pre-treatment methods available for producing uniform sized and moisture content feedstock which is easy to handle, transport and store. The quality of briquettes in terms of density and durability depends on the physical and chemical properties of the feedstock and briquetting conditions. In this study, the effect of compacting pressure, temperature, moisture content, and particle size on the properties of briquettes for thermochemical applications were investigated. It was found that density, impact resistance, and compressive strength significantly increased with increasing compacting temperature (20-80 °C) and compacting pressure (150-250 MPa). However, increasing moisture content and particle size had a negative impact on briquette quality. The results showed that there was a strong interaction between briquetting parameters with the interaction between moisture and temperature significantly affecting both briquette density and mechanical strength. Briquettes with high density and durability/mechanical strength required to meet quality certification standards could be obtained with course ground material (< 4mm) from relatively low moisture content feedstock (7-8%) with pressure of 200-250MPa and a compacting temperature of 80°C.

Keywords: Briquette quality, density, impact resistance, compressive strength, maize cob, agricultural residues

1 Introduction

Biomass for energy generation has attracted much attention because it is an abundant resource [1] and CO_2 neutral [2, 3]. According to the World Energy Council [4], biomass contributes 14% out of the 18% of global energy supply from renewables and contributes 10% of total global energy consumption. It is the predominant source of energy in developing countries e.g. over 80% in sub-Saharan Africa, which is mainly used for cooking [5]. Biomass is heterogeneous in terms of size, shape and composition and has low bulk density (e.g. about 4 times lower than the bulk density of diesel) [6], leading to difficulties in handling, storage and transport. Densification of biomass into briquettes/pellets increases bulk density from 40-200 kgm^{-3} to 450-800 kgm^{-3} [5, 7] and produces a high energy feedstock with uniform moisture, shape and size which makes it suitable for storage and transportation with potential uses in combustion, pyrolysis and gasification [8]. Densification minimises particulate emissions per unit solid fuel transported and improves biomass combustion efficiency as well as conveyance efficiencies (less dust and wastage and lower labour cost) in commercial energy generation facilities [9, 10]. The classification of briquettes and pellets is commonly based on their sizes e.g. 4.0-10.0 mm diameter and 20-50mm length according to the respective Austrian (ONORM M 7135) and German (DIN 51731) quality standards for pellets [11, 12] with 10 - 200 mm diameter and 16 - 400 mm length commonly used for briquettes [13-16].

Due to the increase in the share of renewable energy required to achieve national government targets, the demand for densified products increased from 7 to 19 million tonnes for the period 2006–2012 [17]. However, shortage of feedstock and sustainability of supply for wood pellet production provides a major challenge especially in the rapidly growing EU pellet market with an urgent need to broaden the feedstock range by using agricultural residues and other sources of biomass e.g. municipal solid waste. Briquetting can be preferred over pelleting for agricultural residues because it can accommodate feedstock with large particle sizes and high moisture content [18], which in turn reduces the energy input in pre-processing of feedstock (grinding and drying). It was reported [19] that the energy required for grinding corn stover decreased 3 fold when increasing particle size from 0.8 mm to 3.2 mm at a moisture content of 6-12%.

In transport, handling and storage briquettes with high density and mechanical strength are desirable [20]. High density is desired to reduce transport and storage costs [21-23], with high compressive strength, i.e. ≥2.56 MPa [24] preferred to prevent breakages [25]. Durability of over 80 % [26] is reported to ensure briquettes/pellets remain intact during transport/storage and reduce the amount of fine particles/dust produced [7]. Ensuring moisture content of feedstocks between 5-22 % has been reported to facilitate stable compaction of several feedstocks such as wood, alfalfa, lignite, wheat straw and waste paper [20, 22, 27, 28].

Particle size for producing briquettes can be varied from 0.1 to 6 mm depending on type of feedstock [29-34]. However, Ahmed et al [35] also reported that particle size of 6-8 mm together with 13-15% in powder form was recommended to enhance briquette durability by increasing interlockages and minimising spaces between particles [7]. Although pellets have been studied intensively with certified quality standards available (e.g. Austrian ONORM M 7135, Swedish SS 187120, German DIN 51731 and DIN EN 15270 and European Standard Committee CEN/TE 335), very little work has been done on briquetting of agricultural residues and the only standards available for briquettes are for wood. Pellet standards therefore have often been used to determine agricultural residue briquette quality. Previous studies [21, 24, 30, 36] showed that briquette properties were strongly dependent upon moisture content, particle size, temperature, compacting pressure and type of feedstock. However, the findings are case-specific and the results are variable. Increasing compacting pressure for mango and eucalyptus leaf [21] from 30 to 100 MPa increased the density from 600 to 1100kgm^{-3}. Similarly increasing pressure from 3 to 11MPa increased the density of palm oil mill residues from 950 to 1010 kgm^{-3} [24]. Density of tropical hard wood briquettes decreased when particle size was increased from $<$1mm to 2-3.35mm, however, there was a weak positive correlation between compressive strength and particle size [36]. The effect of moisture content varies depending on feedstock such that impact resistance (as measured by shatter index) of paper mill briquette increased from 36227 to 168875 when moisture content was increased from 5 % to 15 % and maximum compressive strength of 1299 kgcm^{-2} was reported at a moisture content of 9 % [30].

To date, interactions between different briquetting parameters (compacting pressure, moisture content, particle size and compacting temperature) on properties of briquettes have not been studied. Therefore, fully understanding how chemical composition and physical properties impact upon briquette product quality is essential. The literature shows that low pressures (5-31 MPa) [9, 34], used in the compaction of maize residues resulted in the production of low density ($<$ 1000 kgm^{-3}) briquettes which did not meet the German Standard DIN 51731 (1-1.4 gcm^{-3}). Kaliyan and Morey [33] produced maize cob briquettes at a pressure of 150 MPa and reported that density and durability were significantly affected by, moisture content (10 and 20 %), pre-heating temperature (25 and 85 ^{o}C) and particle size (mean particle diameter 0.85 and 2.81 mm), however, the impact of pressure and the interactions between briquetting parameters were not analysed. In this study, the effect of briquetting conditions (pressure, moisture, particle size and temperature) and their interactions on the properties of maize cob briquettes was investigated. The findings from this study have clear potential globally as maize is one of the major crops grown globally but particularly in sub-Saharan Africa regions where a large amount (~7 million tonnes) produced annually [37] are either burnt in open air (without heat recovery) or are dumped to decompose in uncontrollable ways. Converting residue cobs into energy would not only contribute to reducing greenhouse gas emissions but also to a more sustainable waste management strategy.

2 Materials and Methods

2.1 Material

Maize cobs were kindly provided by Barfoots of Botley Ltd, UK. Maize (supersweet varieties) was harvested at Stage R3 (milk stage) of maturity in Senegal, Morocco, United State of America, South Africa, Greece, Germany, United Kingdom, France and Spain and stored at 0-5^{o}C for 1-25 days. Waste cobs were sent to Newcastle University and stored in a cold room at 6^{o}C prior to briquetting. The waste maize cobs are representative of material that would be used in processing rather than the production of corn cobs grown to maturity as would be the case for many developing countries including Africa. Residue maize cobs were cut into pieces $<$ 5 mm and oven dried at 105^{o}C for 2-8 hours to obtain a range of moisture contents. All moisture contents presented in this paper are on a % wet basis. Dried maize cobs were crushed using a HGBTWTS3 laboratory blender 8010ES and separated using 2.36 and 4.00 mm sieves to study the effects of particle size.

2.2 Briquette preparation

A machine fabricated with a hollow cylindrical mould, internal diameter of 2 cm and length 12.5 cm was adapted from the work of Zafari and Kianmehr [28]. The mould was fitted inside two 150W band heaters connected to a temperature controller and was insulated with Fortaglas for operator safety and to reduce heat loss.

About 7g of ground maize cob was fed inside the mould and then manually compressed using a 10 tonne Hydraulic Bench Press (Clarke CSA10BB). A dwell time (i.e. duration for which particles under compression remain under maximum compacting pressure during briquetting) of 20s was chosen for all experiments to minimise briquette relaxation [21, 29] which could have negative impacts on briquette properties (density, impact resistance and compressive strength). The effects of temperature (20-80°C), moisture content, (7-17%) particle size ($<$ 2.36 mm and $<$4.00 mm) and pressure (150, 200, 250MPa i.e. within the range of pressures used for briquetting several biomass materials [23, 38, 39]) and their interactions were studied using a 2-level factorial design of experiment. Briquettes were stored in an air tight container at room temperature (approximately 20°C) for 7 days to allow stabilisation [40] prior to analysis of their properties (density, impact resistance and compressive strength).

2.3 Briquette characterisation

Moisture, ash, volatile matter and fixed carbon content of maize cobs and briquettes were determined according to ASTM D3173, ASTM D3174, ASTM D3175 and ASTM D3172 standards respectively. Ultimate analysis was carried out using a Carlo Erba 1108 Elemental Analyser to determine percentage of carbon, hydrogen and nitrogen. High heating value (HHV) was determined using a CAL2K ECO bomb calorimeter. Scanning electron microscopy (SEM) analysis was carried out using a TM3030Hitachi Microscope. Differential Scanning Calorimetry (DSC) analysis was carried out using a DSC Q20 model to identify the range of compacting temperatures to be used in the briquetting experiments. Analysis of neutral detergent fibre (NDF) was carried out by enzymatic gravimetry, while acid detergent lignin (ADL) and acid detergent fibre (ADF) were analysed using an Ankom 220 analyser. The composition of cellulose, hemicellulose and lignin were subsequently determined [41]:

$$\text{Cellulose} = \text{Neutral detergent fibre (NDF)} - \text{Acid detergent lignin (ADL)} \qquad (1)$$

$$\text{Hemicellulose} = \text{Neutral detergent fibre (NDF)} - \text{Acid detergent fibre (ADF)} \quad (2)$$

$$\text{Lignin} = \text{Acid detergent lignin (ADL)} \quad (3)$$

Density was determined using the stereometric method which allows briquettes to be used for thermo-chemical applications to remain dry [42]. Height and diameter of a briquette was measured using a digital vernier calliper (error: ± 0.005 mm) to determine volume. For impact resistance, a briquette was released 4 times from a height of 1.85 m to fall freely under gravity onto a metallic plate to determine impact resistance [43]. Percentage residual weight of briquettes was determined after each drop. The remaining piece with the highest weight was taken as the residue and used for the next drop. Impact resistance was defined as the percentage residual weight after the 4th drop. Compressive strength was determined via both the cleft and simple pressure tests using a Tinius Olsen H50KS compressing machine. Briquettes were placed between two flat parallel surfaces with surface area greater than the briquette. Briquettes were placed horizontally for the cleft test and vertically for the simple pressure test. An increasing load was then applied to compress briquettes at a rate of 1 mm/min until the briquette failed/cracked. The ultimate load at the point where the briquette cracks, F was used to calculate the compressive strength using Equations (4) and (5). An average of 3 measurements for each test were carried out.

$$\text{Compressive strength } \sigma = F/A \quad (4)$$

$$\text{Compressive strength, } \sigma = F/l \quad (5)$$

Where A and l are the cross-sectional area (m^2) and length (m) of briquettes.

The physical and mechanical properties of briquettes such as density, impact resistance and compressive strength are presented as mean values of at least 6 samples/briquettes. Minitab 17 statistical software was used to analyse the impact of the variables and their interactions on density, impact resistance and compressive strength of briquettes. Statistical analysis was carried out at a significance level of $\alpha = 0.05$.

3 Results and Discussion

3.1 Characteristics of maize cobs

Fresh maize cobs used in this study had high moisture content (73.9 ± 0.74%), which is much higher than in other work e.g. 30.3 % [44]. The high moisture content is likely due to the use of fresh maize cobs which were harvested at early stage of maturity (R3 i.e. milk stage) and also stored at 0-5^{o}C prior to analysis. They cannot be used directly for briquetting according to European Standard Committee CEN/TC 335 for solid fuels as the moisture content in briquettes is required to be 5-15%. In addition, high moisture feedstock/products are prone to fungal decomposition during transportation and storage [27] and poor combustion properties such as low heat output, low combustion temperature, and long fuel residence time in the combustion chamber [17]. Therefore, these fresh maize cobs must be dried/partly dried prior to being briquetted. Maize cob (Table 1) had high volatiles (~76%) and low ash content (3.2%), which agreed well with other work [45, 46]. Fresh maize cobs had a similar high heating value to that of woody materials and anthracite.

Table 1: Properties of fresh maize cobs (dry basis)

Property	Mazie cob
Proximate analysis	
Ash (%wt)	3.2 (± 0.03)
Volatiles (%wt)	76.1 (± 0.70)
Fixed carbon (%wt)	20.7 (± 0.70)
Ultimate analysis	
C (%)	46.9 (± 0.01)
H (%)	8.1 (± 0.39)
N (%)	2.8 (± 0.06)
O (%) by difference	42.2 (± 0.33)
High heating value (HHV) (MJ/kg)	18.9 (± 0.07)

Differential scanning calorimetry analysis was carried out to identify the range of compacting temperatures to be used in the briquetting experiments. An endothermic peak was observed at 100.9 °C associated with a loss of moisture, but no transition steps were observed (Fig 1). The non-visibility of the glass transition temperature could be due to interference from the moisture endothermic peak [47], as the glass transition step is likely to overlap with the moisture endothermic peak area.

A maximum compacting temperature of 80°C was therefore chosen for this study based on the glass transition temperature of 79.2°C identified for corn stover [48]. Furthermore, compacting at high temperatures i.e. ≥100°C is undesirable because it not only requires high energy input which in turn reduces energy efficiency but also reduces compressive strength of briquettes due to the evaporation of water which makes them brittle [49]. A certain amount of moisture is required to reduce friction between particles and the mould during compaction and to enhance the force of attraction between particles [27].

Two exothermic peaks at 283.78°C and 337.73°C observed in the DSC thermo-gram (Fig.1) could be due to the decomposition of hemi-cellulose, cellulose, and lignin [50]. The lignin, cellulose and hemicellulose composition identified in this study were 1.5%, 47.1 % and 29.4% respectively with the remaining 22.0% likely to be extractives (e.g. protein, starch, oil and sugar). A low lignin content in this study compared to much higher levels (3-15 %) observed by other researchers, [33, 41, 51, 52] could be due to the analysis method used in this study of which the acid detergent lignin (ADL) only gives a partial value of total lignin content [33].

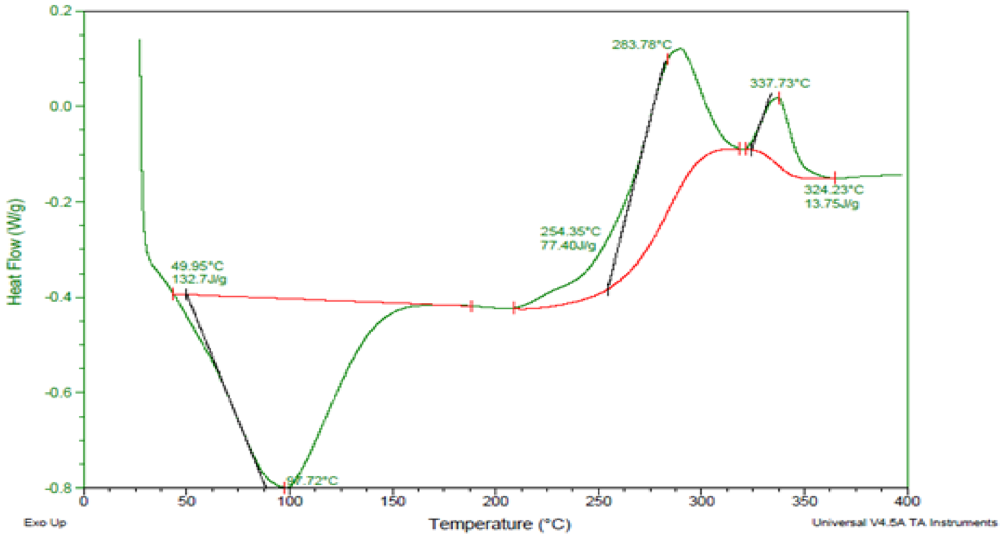


Fig 1: Differential scanning calorimetry (DSC) thermo-gram of maize cobs at 7.14 % moisture content

3.2 Density

Briquette density ranged between 516 kgm^{-3} and 1058.2 kgm^{-3} from variations in briquetting parameters used in this study. The lowest density of 516 kgm^{-3} was obtained with a low temperature (20 ^{o}C), a high moisture content (16.94 %) and a particle size $<$4.0 mm, the density of all other treatment combinations being $>$700 kgm^{-3}. With the exception of where a high compacting pressure (250 MPa), small particle size ($<$2.36 mm) and a high temperature (80 ^{o}C) were used, all briquettes produced from the high moisture content of 16.94 % had a density less than 1000 kgm^{-3} (Fig 5) which falls below the range of 1-1.4 gcm^{-3} required to meet the German Standard DIN 51731. Highest density briquettes (1054.4-1058.2 kgm^{-3}) were produced from particle size of $<$2.36 mm, moisture content of 7.14 % and pressure of 200-250 MPa Under these conditions density remained relatively constant likely due to a reduction in original void spaces between particles and an increase in inter-particle bonding at high pressures i.e. > 200 MPa. This trend is consistent with results reported for briquettes from palm oil mill residues [24] and pine [32]. Density increased with increasing compacting pressure and temperature but decreased with increasing particle size and moisture content (Fig 2a). Moisture content and pressure were the predominant factors affecting briquette density. However, Zhang and Guo [38] found that particle size (0.16-5 mm) and moisture content of 5-17 % were the predominant factors that affected density of caragana korshinskii kom briquettes within a range of compacting temperatures of 70-150 ^{o}C and compacting pressure of 10-170 MPa. Rhén et al [53] reported that density of spruce pellet was predominantly affected by moisture content (6.3-14.7 %) and compacting tempearture (26-144 ^{o}C) for particle size of $<$3.15 mm and compacting pressure of 46-114 MPa. A similar observation was reported [54] on density of olive tree pruning residue pellets produced from various particle size ranges $<$1 mm to $<$4 mm, moisture content of 5-20 %, compacting temperature of 60-150 ^{o}C and pressure of 71-176 MPa. Variable results for factors affecting briquette density are likely due to variation in feedstock properties in addition to which many of the comparative studies have mainly focused on the effects of single factors rather than looking at the interaction among them.

All interactions (Table 2) had significant impact on density ($P<0.05$) except the interaction between moisture and particle size. Briquettes produced at around 17 % moisture content and pressure <250 MPa (Fig 5) had a density below the German Standard (DIN 51731) for pellets (1-1.4 gcm^{-3}) regardless of particle size and compacting temperature. This is likely due to the incompressibility of water that prevents particles from being completely flattened at high moisture content. Furthermore, the low briquette density could have been attributed to a reduction in briquette weight or an increase in briquette volume upon drying and stabilising. It was also observed that a high proportion of large cracks (Fig. 4) were formed in briquettes produced at high moisture content i.e. 16.94 %. Matúš et al. [27] also reported appearance of cracks on spruce briquettes produced at a moisture content above 16.5 % with 2.56, 12.69, 35.92, 26.06 and 27.77 % of particles $<$0.50, 0.5-$<$1.00, 1.00-$<$2.00, 2.00-$<$4.00 and $>$4.00 mm in sizes. Increasing compacting pressure to 250 MPa and reducing particle size ($<$2.36 mm) could increase the density into the standard range ~ 1,000 kgm^{-3} but this will increase the energy requirement for producing briquettes.

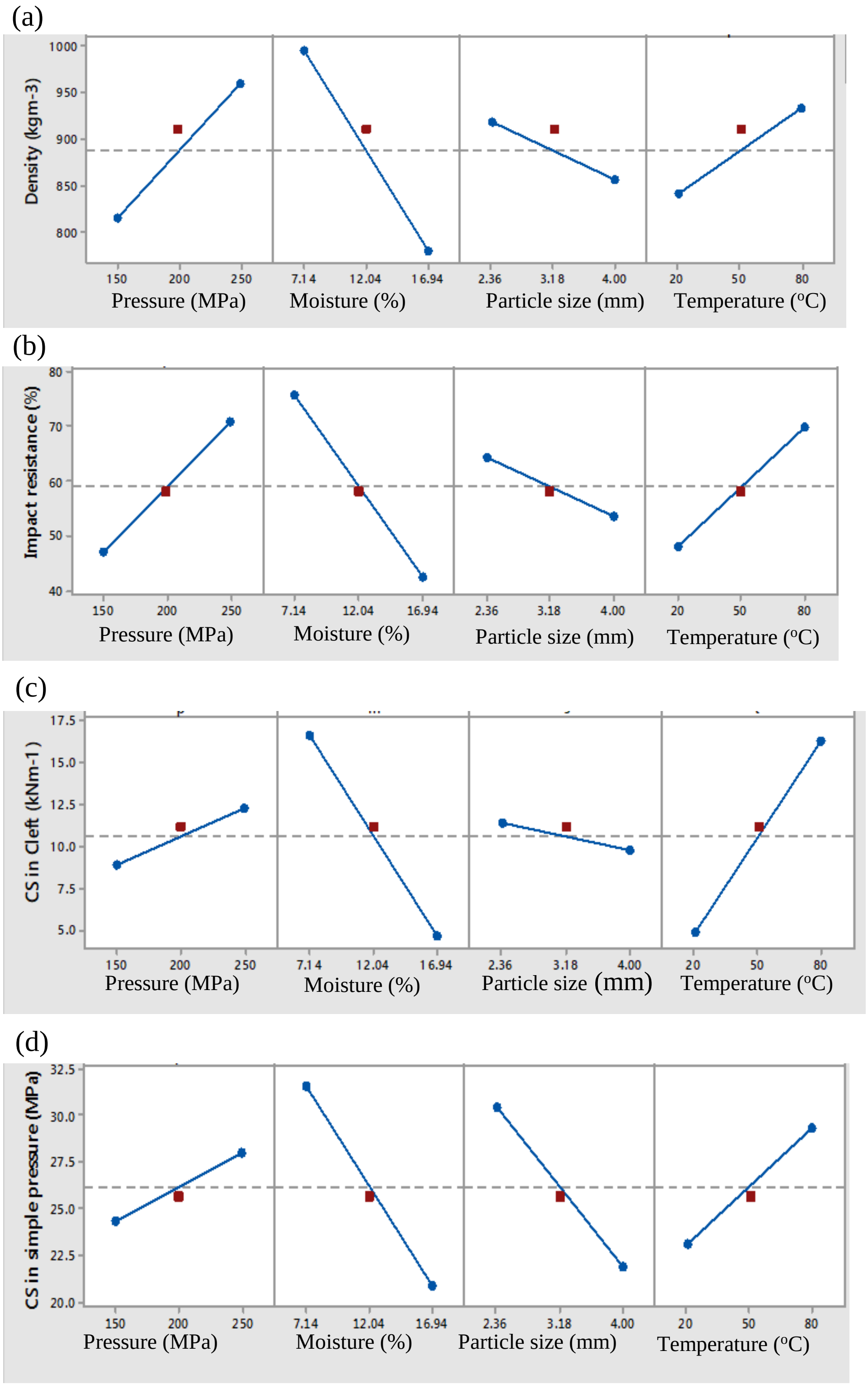


Fig 2: Effects of briquetting parameters: pressure, moisture content, particle size and temperature on (a) density, (b) impact resistance, (c) compressive strength (CS) in cleft and (d) compressive strength in simple pressure. Red square represents the mid-point.

Table 2: Analysis of variance: Response variable: Briquette density

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	253650	253650	6274.78	0.000
Moisture content (*m*)	1	559678	559678	13845.27	0.000
Particle size (*s*)	1	45418	45418	1123.54	0.000
Temperature (*t*)	1	101393	101393	2508.26	0.000
$p \times m$	1	28145	28145	696.24	0.000
$p \times s$	1	37772	37772	934.40	0.000
$p \times t$	1	2997	2997	74.15	0.000
$m \times s$	1	87	87	2.14	0.153
$m \times t$	1	23069	23069	570.69	0.000
$s \times t$	1	14971	14971	370.35	0.000
$p \times m \times s$	1	414	414	10.23	0.003
$p \times m \times t$	1	1552	1552	38.38	0.000
$p \times s \times t$	1	9377	9377	231.97	0.000
$m \times s \times t$	1	3200	3200	79.15	0.000
$p \times m \times s \times t$	1	385	385	9.52	0.004
Error	32	1294	40		
Total	48	1083917			

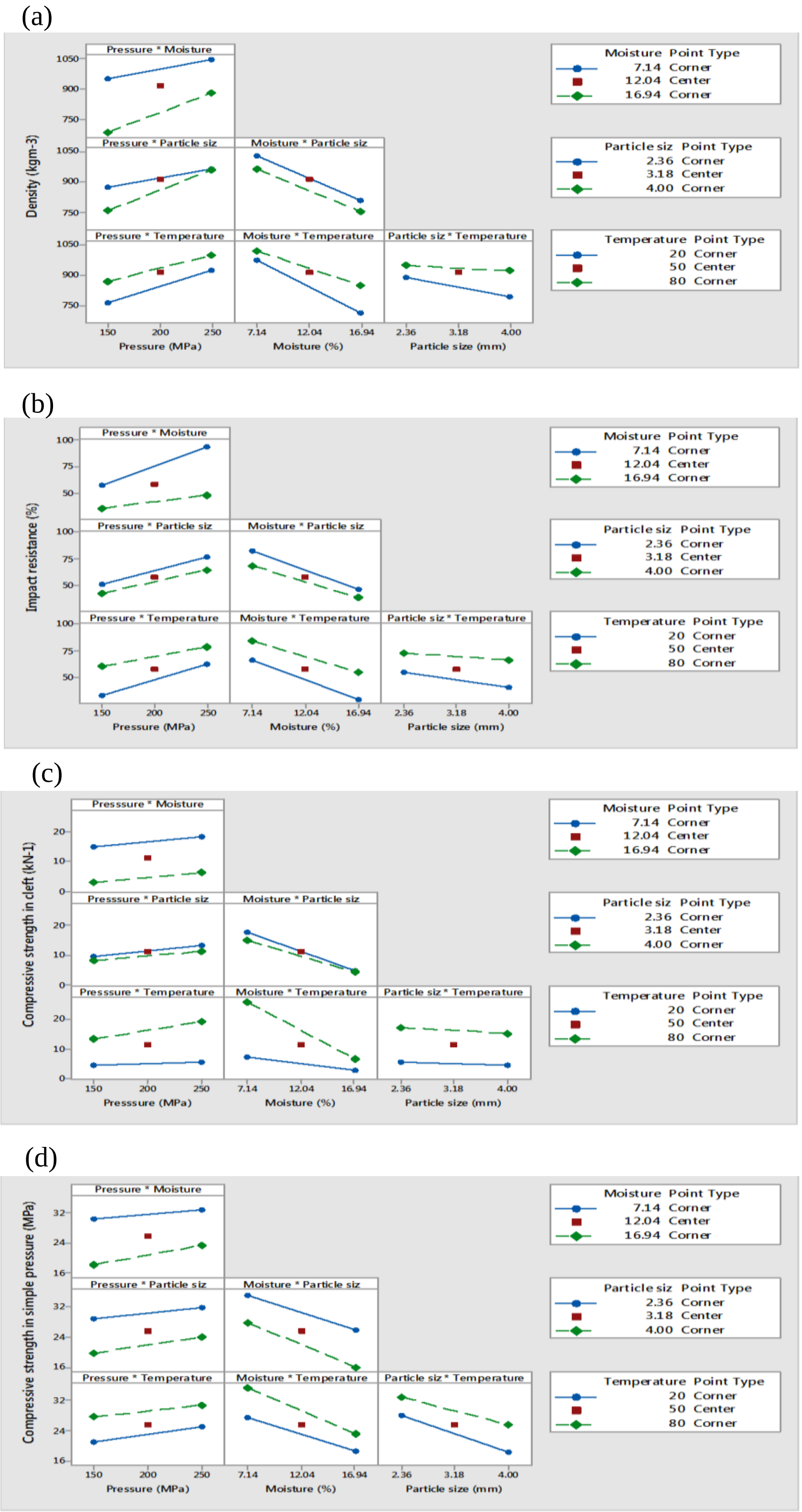


Fig 3: Interaction effects of briquetting parameters: pressure, moisture content, particle size and temperature on (a) density, (b) impact resistance, (c) compressive strength (CS) in cleft and (d) compressive strength in simple pressure. Red square represents the mid-point.

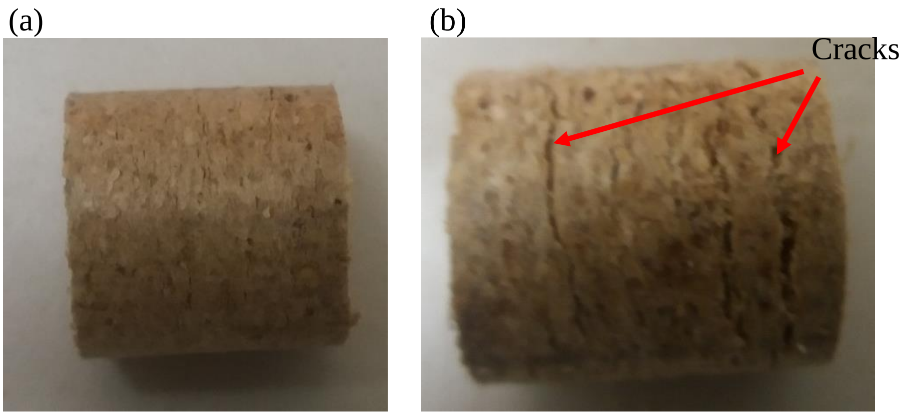


Fig. 4: Briquette produced from pressure of 200 MPa, compacting temperature of 80 ^{o}C and particle size of $<$2.36 mm at moisture content of (a) 7.14% and (b) 16.94 %.

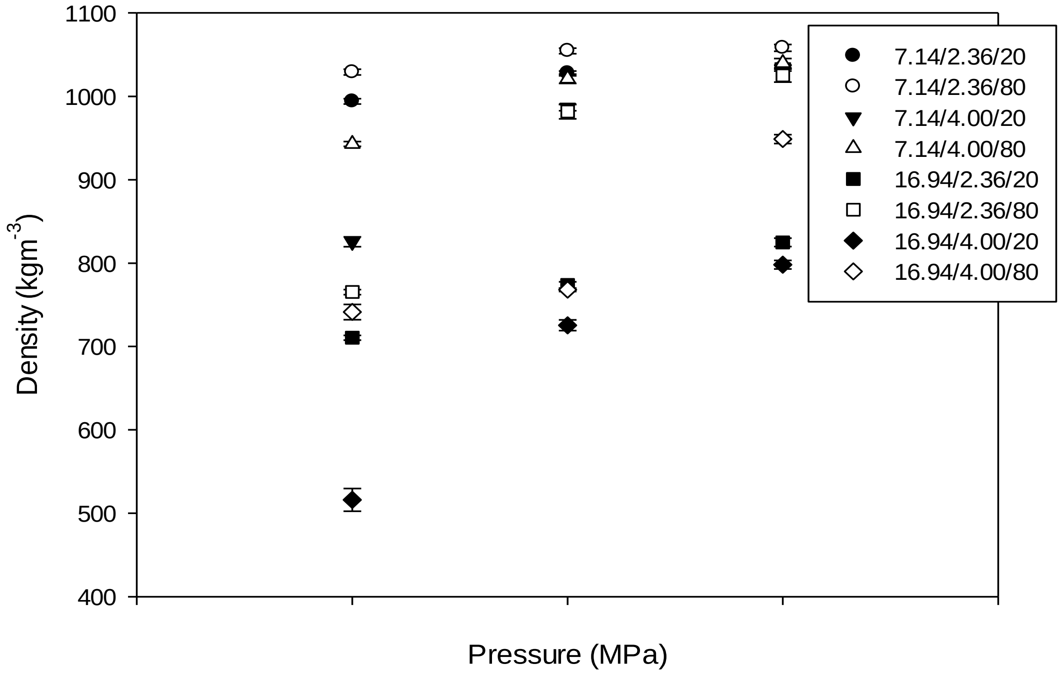


Fig 5: Effect of pressure on briquette density (legend: particle size (mm)/ moisture content (%)/ compacting temperature (^{o}C))

At low moisture content (7.14 %), for small particle size $<$2.36 mm, compacting pressure and temperature had little effect on density. Density only increased by less than 4 % when pressure was increased from 150 MPa to 200 MPa and remained almost constant with a further increase to 250 MPa. However, at a moisture content of 7.14 % for a particle size $<$4 mm, a significant increase in density (~20 %) was observed when increasing pressure from 150 MPa to 200 MPa; but with only a slight further increase of ~5 % as pressure was increased to 250 MPa. In addition, compacting temperature had a great effect at 150 MPa (~14 % increase). In contrast, at high moisture content (17 %), increasing pressure and temperature significantly increased density for both particle sizes which was probably due to the combined effect of high pressure and heat softening the particles and evaporating moisture. Therefore, with maize cob feedstock at moisture content 7.14-10%, high density briquettes could be produced at either 150 MPa/80 ^{o}C or 200 MPa/20 ^{o}C for particle size $<$2.36 mm but for particle size $<$4 mm a pressure $>$200 MPa was required. At high moisture content (16.94 %), only a particle size $<$ 2.36 mm could provide briquettes with a density ≥ 1000 kgm^{-3} and this was under conditions of high pressure and temperature i.e. 250 MPa and 80 ^{o}C.

3.3 Impact resistance

Impact resistance is a measure of durability of briquettes which defines their tendency to produce dust or break when subjected to a destructive force. It is an indicator of the mechanical strength of briquettes [55], therefore its value should be as high as possible. In this study, impact resistances ranged from 17.7 % to 99.8 % with variations in the briquetting parameters used. Within all ranges of briquetting parameters studied, impact resistance was increased in response to increased pressure and temperature, but was reduced with an increase in moisture content and particle size (Fig 2b). The optimal moisture content and pressure identified in this study compares well with the optimal moisture content (7.5 %) and pressure (200 MPa) required to produce olive waste briquettes with high impact resistance [30]. At high temperature and pressure, moisture evaporates and increases the rate of heat transfer within biomass particles. However, very high moisture prohibits complete flattening of particles which lowers inter-particle bonds [7], causing less stable and weak briquettes. Application of temperature and pressure causes diffusion of molecules thus reducing void space and forming solid bridges which increases bonding between particles and hence the strength of briquettes. The results agreed well with previous studies for paper mill waste briquettes (prepared in a pressure range of 150-250 MPa and moisture content of 9 % [30] and mango and eucalyptus leaf briquettes (pressure of 30-100 MPa and moisture content of 8.6 % and 7.9 % respectively [21]). However, they disagreed with the findings for pulping residue and spruce sawdust briquettes [23] where impact resistance increased as moisture content was increased from 7 to 15 %. The variations are likely due to variation in the range of optimal moisture contents used for the different feedstocks.

At a fixed compacting temperature of 20 ^{o}C, impact resistances of briquettes prepared at high moisture content (16.94 %) and particle size $<$4.0 mm were not influenced by compacting pressure (likely due to the incompressibility of water) and remained around 20 %. Decreasing particle size to $<$2.36mm had little effect on impact resistance at low compacting pressures but led to a significant increase at 250 MPa. This could be due to the heat generated at high compacting pressure enhancing the release of water within small particles, helping the binding process. Impact resistance was almost 3 fold higher at 150 MPa when temperature was increased to 80 ^{o}C most likely due to solid bridge formation, however, particle size had no impact. There were significant interactions ($p<0.05$) between briquetting parameters on impact resistance (Table 3; Fig 3b) except for the: pressure x particle size, moisture content x particle size x temperature and pressure x moisture content x particle size x temperature interactions. Under high pressure and temperature, low molecular weight components become binding elements of particles whereas at high temperature and pressure, moisture evaporates and increases the rate of heat transfer within biomass particles [56].

Table 3: Analysis of variance: Response variable: Impact resistance

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	6821.1	6821.1	360.74	0.000
Moisture content (*m*)	1	13293.4	13293.4	703.03	0.000
Particle size (*s*)	1	1342.0	1342.0	88.12	0.000
Temperature (*t*)	1	5794.8	5794.8	306.47	0.000
$p \times m$	1	1666.2	1666.2	88.12	0.000
$p \times s$	1	21.6	21.6	1.14	0.293
$p \times t$	1	357.5	357.5	18.91	0.000
$m \times s$	1	109.2	109.2	5.78	0.022

$m \times t$	1	195.2	195.2	10.32	0.003
$s \times t$	1	233.2	233.2	12.33	0.001
$p \times m \times s$	1	181.0	181.0	9.57	0.004
$p \times m \times t$	1	125.5	125.5	6.63	0.015
$p \times s \times t$	1	144.9	144.9	7.66	0.009
$m \times s \times t$	1	21.9	21.9	1.16	0.290
$p \times m \times s \times t$	1	66.3	66.3	3.50	0.070
Error	32	605.1	18.9		
Total	48	30979.3			

At low moisture content (7.14 %) and particle size (<2.36 mm) increasing compacting temperature from 20 ^{o}C to 80 ^{o}C significantly increased impact resistance i.e. from 50 % to 80 % at 150 MPa. However, there was no effect of temperature on impact resistance at higher compacting pressures >200 MPa (Fig 6). For larger particle size (<4 mm), compacting temperature had a significant effect resulting in high impact resistance (>80 %) but only at high pressure (200 MPa-250 MPa) when a compacting temperature of 20 ^{o}C was used. Impact resistance increased significantly ($P < 0.05$) with an increase in pressure from 150 to 200MPa, but was unchanged above 200 MPa.

Briquettes with high impact resistance/durability are desirable to minimise breakage and dust formation during transporting and conveying. Up to now, there are no certified standards for biomass briquettes, however, other researchers [55, 57] have reported that impact resistance of 80 - 90 % or over 90 % is required for better handling and transportation. However, very high-quality briquettes (with impact resistance above 95%) were obtained at (i) small particle size (<2.36 mm), low moisture content (7.14 %) and high pressure (>200 MPa) and (ii) high particle size (<4.00 mm), low moisture content (7.14 %), high temperature (80 ^{o}C) and high pressure > 200 MPa. These briquettes lost only < 3.5 % of their weight after shattering and are therefore durable thus satisfying the European Standard Committee CEN/TC 335 (durability >95 %) and are also suitable for transportation, storage and handling with minimal breakage and dust generation.

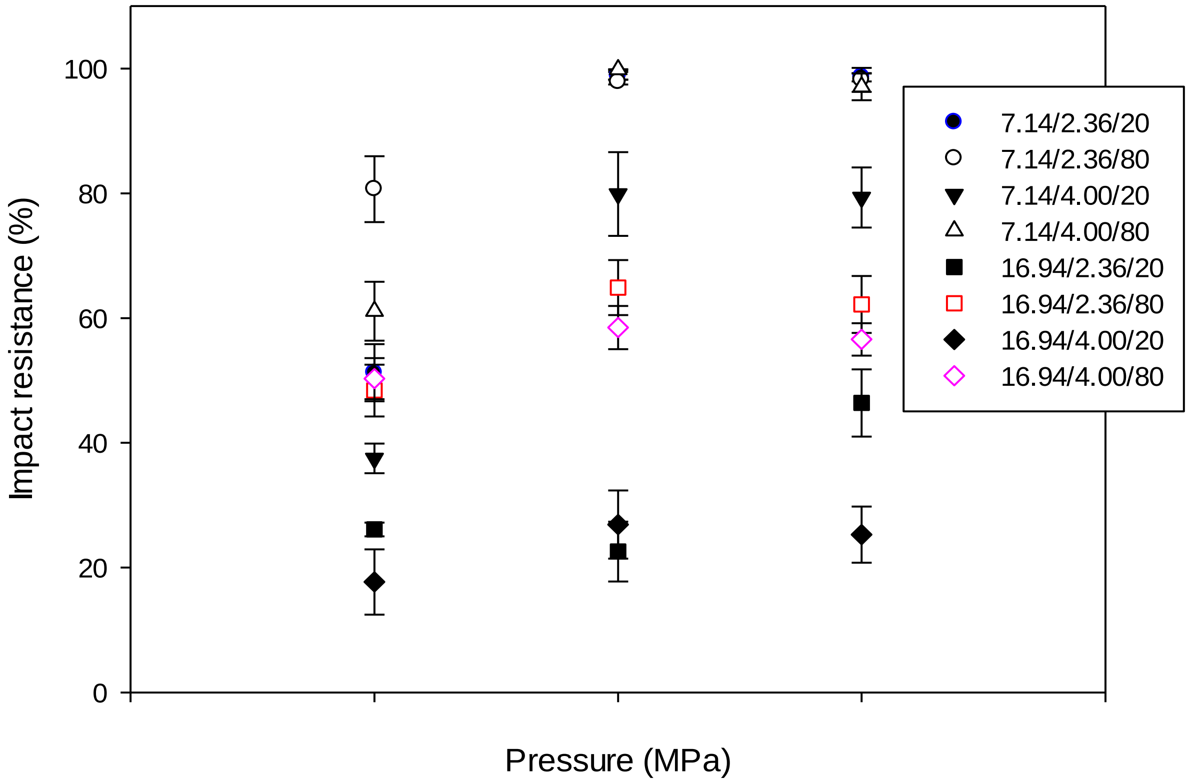


Fig 6: Effect of compacting conditions (temperature, pressure) and feedstock properties (moisture content, particle size) (legend: particle size (mm)/ moisture content (%)/ compacting temperature (^{o}C))

3.4 Compressive strength (CS)

Compressive strength is the maximum load that a briquette can withstand before it breaks [58]. It is used to estimate the compressive stress resulting from the weight of the top briquettes on the lower briquettes during storage, transport and handling. Compressive strength (CS) tests were performed via both cleft and simple pressure tests. These two tests have been used independently [9, 13, 53, 59] to determine compressive strength of briquettes and it was found from this study (data not presented) that there was a strong positive correlation between the two tests.

Moisture content and compacting temperature were the dominant factors affecting compressive strength in cleft whilst simple pressure was mainly affected by moisture content and particle size i.e. simple pressure decreased with increasing moisture content and particle size (Fig 2c and 2d). The compressive strength (between 75 and 120 MPa) of pine briquettes increased with an increase in compacting pressure in the range of 31 - 318 MPa but was reduced with an increase in particle size i.e. 0.5 - 4.0 mm [32]. Compressive strength of hazelnut shell briquettes produced from particle size of 2-4 mm, moisture content of 8.7 % with pyrolysis oil from hazelnut shell and some wood as binder (6.5-18.0 %) increased (from around 11 to 38 MPa) when compacting pressure was increased from 300 to 800 MPa [13]. However, the effect of moisture content found in this study contradicts with others. For example, for lupin seed with an average particle size of 0.5 mm, compressive strength of briquettes increased with moisture content from 9.5 % to 15.0 % [60]. A 30% increase in compressive strength of olive refuse briquette was observed when moisture content was increased from 5 % to 15 % [30] using a compacting pressure of 200 MPa and particle size of $<$0.250mm. An increase in compressive strength of pulping reject briquettes from 13.0 to 37.2 MPa was reported when moisture and compacting pressure were increased from 7 % to 18 % and 300 MPa to 800 MPa respectively [23].

Both compressive strength in cleft and simple pressure increased significantly ($P < 0.05$) when pressure was increased from 150 MPa to 200 MPa but with no further increase at higher pressures. One can argue that an increase in compacting pressure is associated with an increase in interparticle bonds resulting from an increase in cohesion force [36]. However, above the optimal compacting pressure, in this case 200 MPa, the phenomenon of dilation occurs, producing cracks in briquettes and consequently weakens them [61]. Interaction plots (Fig 3c and d) shows that there were significant interactions (Table 4 and 5) on compressive strength in cleft (Table 4) for all variables with the exception of: pressure x moisture, pressure x particle size, pressure x particle size x temperature, moisture x particle size x temperature and, pressure x moisture x particle size x temperature. For compressive strength in simple pressure all variables showed significant interactions with the exception of particle size x temperature and, pressure x moisture x particle size x temperature (Table 5).

Table 4: Analysis of variance: Response variable: Compressive strength in cleft.

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (p)	1	138.38	138.38	427.15	0.000
Moisture content (m)	1	1722.01	1722.01	5315.51	0.000
Particle size (s)	1	32.18	32.18	99.32	0.000
Temperature (t)	1	1549.28	1549.28	4782.33	0.000
$p \times m$	1	0.00	0.00	0.01	0.940
$p \times s$	1	1.05	1.05	3.24	0.081
$p \times t$	1	73.26	73.26	226.14	0.000
$m \times s$	1	17.64	17.64	54.46	0.000
$m \times t$	1	654.90	654.90	2021.56	0.000
$s \times t$	1	1.44	1.44	4.43	0.043
$p \times m \times s$	1	11.70	11.70	36.12	0.000
$p \times m \times t$	1	29.93	29.93	92.37	0.000
$p \times s \times t$	1	0.01	0.01	0.02	0.900
$m \times s \times t$	1	1.11	1.11	3.43	0.073
$p \times m \times s \times t$	1	0.11	0.11	0.34	0.564
Error	32	10.37	0.32		
Total	48	4243.70			

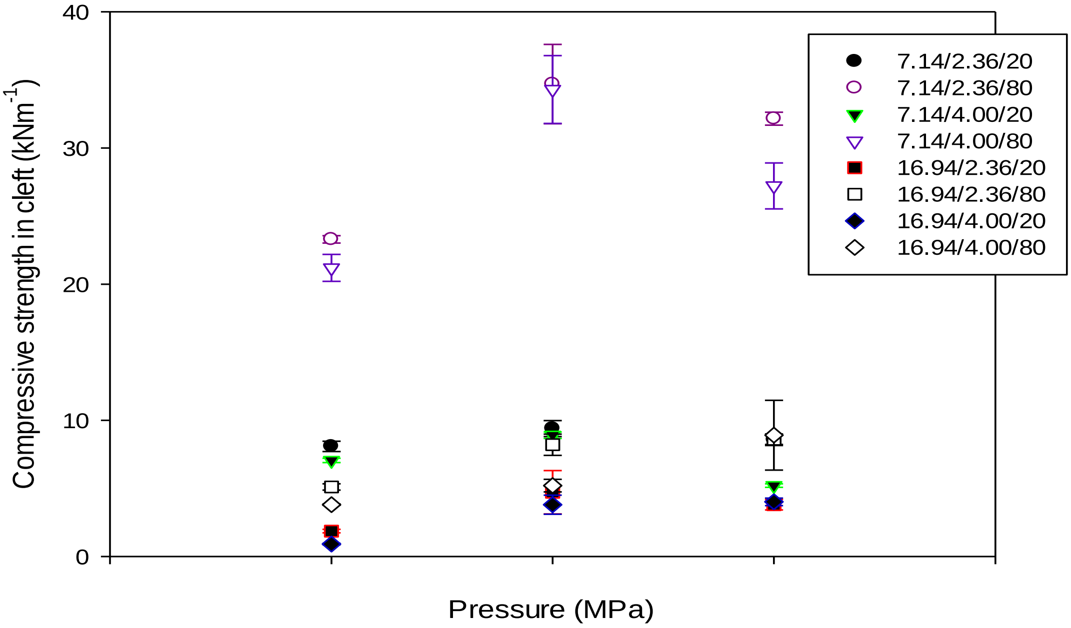
Table 5: Analysis of variance: Response variable: Compressive strength in simple pressure.

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	161.33	161.33	125.76	0.000
Moisture content (*m*)	1	1376.02	1376.02	1072.57	0.000
Particle size (*s*)	1	884.08	884.08	689.12	0.000
Temperature (*t*)	1	466.25	466.25	363.43	0.000
$p \times m$	1	23.80	23.80	18.55	0.000
$p \times s$	1	7.36	7.36	5.74	0.023
$p \times t$	1	2.08	2.08	1.62	0.212
$m \times s$	1	21.60	21.60	16.84	0.000
$m \times t$	1	32.34	32.34	25.21	0.000
$s \times t$	1	16.80	16.80	13.10	0.001
$p \times m \times s$	1	31.04	31.04	24.20	0.000
$p \times m \times t$	1	13.87	13.87	10.81	0.002
$p \times s \times t$	1	19.25	19.25	15.01	0.000
$m \times s \times t$	1	7.21	7.21	5.62	0.024
$p \times m \times s \times t$	1	0.70	0.70	0.55	0.465
Error	32	41.05	1.28		
Total	48	3105.07			

It is recommended [24] that the minimum compressive strength in simple pressure for briquettes is 2.56 MPa to enable storage, transportation and handling with minimum breakage. Compressive strength in simple pressure of all briquettes in this study was above the recommended value (Fig. 7b). The smallest value of 10 MPa was obtained at large particle size ($<$4 mm), with low compacting pressure and temperature (150 MPa and 20 ^{o}C) and high moisture content (16.94 %).

At a compacting temperature of 20 ^{o}C, compressive strength in cleft was below 10 kNm^{-1} for all moisture content and particles size variations studied (Fig.7a). Increasing compacting pressure from 150 to 200 MPa resulted in more than 100% increase in compressive strength in cleft for particle size $<$4 mm and high moisture content but had little impact where small particle size $<$2.36 mm and low moisture content were used. Increasing pressure increased compressive strength because particles undergo plastic and elastic deformation, thereby increasing contact areas of particles which in turn filling void spaces and increasing inter-particle bonds [38, 54]. High compacting pressure could also crush large size particles, leading to increased densification [62]. During briquetting, pressure causes particles to rearrange to form closely packed mass and then to elastically and plastically deform when pressure increases. During the plastic and elastic deformation, particles move and fill void spaces which increases contact area, consequently increasing both density and strength [18], [54] [18, 54]. According to Kers [31] and Antwi-Boasiako and Acheampong [57], too much moisture in the feedstock leaves cracks/void space in briquettes due to the escape of moisture within the briquette. The formation of cracks/void spaces makes briquettes more porous thereby reducing their strength and density. Therefore, a minimum amount of moisture in a feedstock is required to act as a binding/catalyst to release low molecular mass products which binds particles together thereby improving briquette strength. However, low moisture content is associated with low rate of heat transfer between particles and therefore the requirement for high compacting pressure [56]. In addition, moisture is responsible for bringing interfacial forces and capillary pressure into play to increase forces of attraction between particles [27].

(a)



(b)

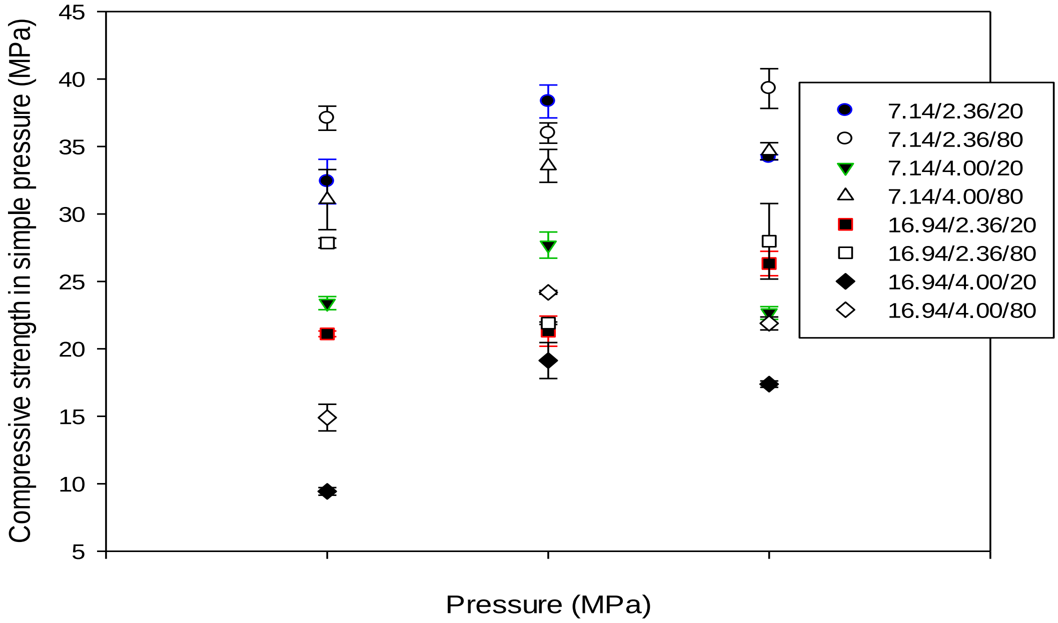


Fig 7: Effect of briquetting conditions (temperature, pressure) and feedstock properties (particles size, moisture content) on compressive strength in (a) cleft, (b) simple pressure (legend: particle size (mm)/ moisture content (%)/ compacting temperature (^{o}C))

At a compacting temperature of 80 ^{o}C, the effect of compacting pressure was highly significant both with high and low moisture content feedstocks. An increasing temperature releases natural binders such as lignin, cellulose and hemicellulose which form solid bridges upon cooling [49, 62, 63] thereby increasing strength and density. A scanning electron microscopy (SEM) image (Fig 8) of a briquette which was broken from the middle in a direction perpendicular to the axis of the cylindrical briquettes showed a relatively smooth surface and particles which were flattened to form a layer. The layer observed in the SEM image could have resulted from solid bridge formation as no evidence of mechanical interlock was observed. Application of high pressure and/or temperature during densification results in diffusion of molecules at the point of contact from one particle to another, thus forming solid bridges [7]. Particles of corn stover and switchgrass briquettes/pellets are bonded mainly by solid brigdes resulting from natural binders i.e. mainly lignin and protein [14]. Natural binders can be squeezed out of particles at temperatures near the glass transistion temperature (80 ^{o}C for maize cob) and improve particle bonding through formation of solid bridges on cooling [7]. An increase in temperature also results in evaporation of water from the particles of biomass under compression and since water is uncompressible, the density of the briquette is increased.

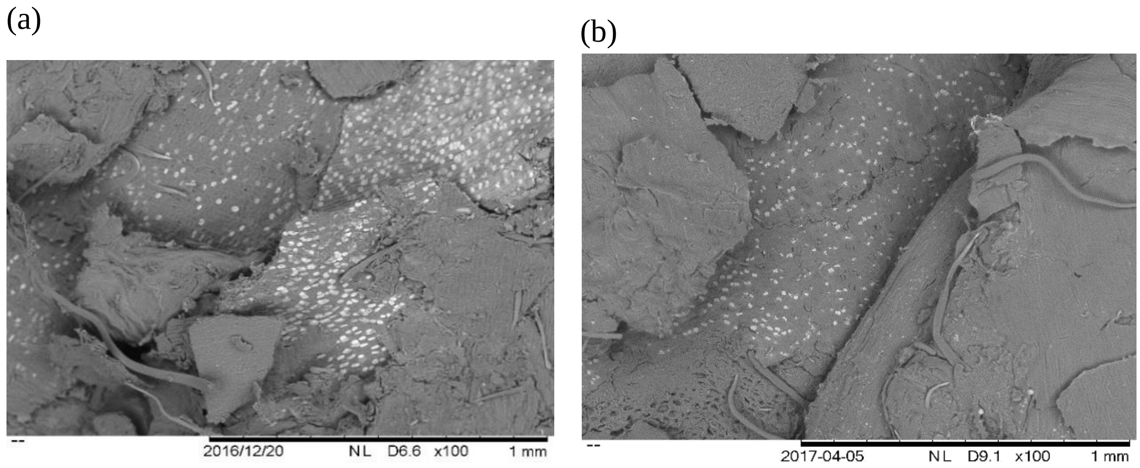


Fig 8: SEM image of broken briquette perndicular to the axis of the cylindrical briquette from crused maiez cob of 2.36 mm seive size, (a) compacting pressure of 250 MPa, compacting tempearture of 80 ^{o}C, moisture content of 7.14 % (b) compacting pressure of 150 MPa, compacting tempearture of 20 ^{o}C, moisture content of 16.94 %.

At a fixed pressure, small particles are more densely packed than large particles [43]. In addition, they have large surface area of contact which helps to create strong inter-particle bonding, while large particles cause cracks which reduces density and strength [28]. The larger surface area of small particles also facilitates better heat transfer (necessary for strong bond formation) between particles thereby improving density and strength [54]. High porosity would lower both density and strength. Valence and Van der Waals' forces can contribute to bonding when seperation between particles are about 10 Å and 0.1µm respectively [14]. Therfore, the forces contributing to bonding become less effective for large pore sizes, thereby weakening the briquettes.

4 Conclusions

Briquettes properties are an important character to meet the increasing demand for biomass feedstocks, enabling long-term handling, storage and transport. In this study, an increase in compacting pressure and temperature and a decrease in moisture content and particle size increased density, impact resistance and compressive strength of corn cob briquettes. The results showed that compacting pressure of 150MPa led to low quality and is not suitable for briquette production regardless of the other parameters used in briquetting process. Pressure ≥ 200MPa and temperature had no effect on properties of briquettes made from low moisture content ($<$10 %), or small particle size ($<$2.36mm) maize cob. However, by increasing compacting temperature up to 80°C, the particle size could be increased without trading off any durability properties. This is because temperature releases components such as lignin, cellulose and hemicellulose which act as binders. Compressive strength in simple pressure was in the recommended range (≥ 2.56MPa) for all tested conditions. There was a strong interaction between briquetting parameters and the interaction between moisture and temperature significantly affected all the briquette properties studied most likely because moisture accelerates heat transfer between maize cob particles which ease elastic and plastic deformation during compression and also facilitates the release of natural binders.

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References

[1] R. Yin, R. Liu, Y. Mei, W. Fei, X. Sun, Characterization of bio-oil and bio-char obtained from sweet sorghum bagasse fast pyrolysis with fractional condensers, Fuel. 112 (2013) 96–104.

[2] H. Long, X. Li, H. Wang, J. Jia, Biomass resources and their bioenergy potential estimation: A review, Renew. Sustain. Energy Rev. 26 (2013) 344–352.

[3] W.-H. Chen, J. Peng, X.T. Bi, A state-of-the-art review of biomass torrefaction, densification and applications, Renew. Sustain. Energy Rev. 44 (2015) 847–866.

[4] World Energy Council, World Energy Resources, 2016. www.worldenergy.org (accessed September 29, 2017).

[5] C. Okello, S. Pindozzi, S. Faugno, L. Boccia, Development of bioenergy technologies in Uganda: A review of progress, Renew. Sustain. Energy Rev. 18 (2013) 55–63.

[6] R. A. Ghaly, J. B. Pyke, A. E. Ghal, Physical and Thermochemical Properties of Uncontaminated and Diesel-Contaminated Peat, Energy Sources. 21 (1999) 433–451.

[7] N. Kaliyan, R. Vance Morey, Factors affecting strength and durability of densified biomass products, Biomass Bioenergy. 33 (2009) 337–359.

[8] P. Adapa, L. Tabil, G. Schoenau, Compaction characteristics of barley, canola, oat and wheat straw, Biosyst. Eng. 104 (2009) 335–344.

[9] R.I. Muazu, J.A. Stegemann, Effects of operating variables on durability of fuel briquettes from rice husks and corn cobs, Fuel Process. Technol. 133 (2015) 137–145.

[10] M.F. Zainuddin, S. Rosnah, M.M. Noriznan, I. Dahlan, Effect of Moisture Content on Physical Properties of Animal Feed Pellets from Pineapple Plant Waste, Agric. Agric. Sci. Procedia. 2 (2014) 224–230.

[11] I. Obernberger, G. Thek, Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour, Biomass Bioenergy. 27 (2004) 653–669.

[12] A. García-Maraver, V. Popov, M. Zamorano, A review of European standards for pellet quality, Renew. Energy. 36 (2011) 3537–3540.

[13] A. Demirbaş, Properties of charcoal derived from hazelnut shell and the production of briquettes using pyrolytic oil, Energy. 24 (1999) 141–150.

[14] N. Kaliyan, R.V. Morey, Natural binders and solid bridge type binding mechanisms in briquettes and pellets made from corn stover and switchgrass, Bioresour. Technol. 101 (2010) 1082–1090.

[15] A. Amaya, N. Medero, N. Tancredi, H. Silva, C. Deiana, Activated carbon briquettes from biomass materials, Bioresour. Technol. 98 (2007) 1635–1641.

[16] J.O. Chaney, Combustion characteristics of biomass briquettes, University of Nottingham, 2010. http://eprints.nottingham.ac.uk/11732/ (accessed February 10, 2016).

[17] T. Miranda, I. Montero, F. Sepúlveda, J. Arranz, C. Rojas, S. Nogales, A Review of Pellets from Different Sources, Materials. 8 (2015) 1413–1427.

[18] J.S. Tumuluru, C.T. Wright, J.R. Hess, K.L. Kenney, A review of biomass densification systems to develop uniform feedstock commodities for bioenergy application, Biofuels Bioprod. Biorefining. 5 (2011) 683–707.

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

[20] A. Demirbas, A. Sahin, Evaluation of biomass residue 1. Briquetting waste paper and wheat straw mixtures, Fuel Process. Technol. 55 (1998) 175–183.

[21] V. Panwar, B. Prasad, K.L. Wasewar, Biomass residue briquetting and characterization, J. Energy Eng. 137 (2010) 108–114.

[22] S. Yaman, M. Sahan, H. Haykiri-Acma, K. Sesen, S. Kucukbayrak, Fuel briquettes from biomass–lignite blends, Fuel Process. Technol. 72 (2001) 1–8.

[23] A. Demirbas, A. Sahin-Demirbas, Briquetting Properties of Biomass Waste Materials, Energy Sources. 26 (2004) 83–91.

[24] H.M. Faizal, Z.A. Latiff, M.A. Wahid, A.N. Darus, Physical and combustion characteristics of biomass residues from palm oil mills, New Asp. Fluid Mech. Heat Transf. Environ. Mastorakis NE V Mlad. Z Bojkovic Eds Wiley N. Y. USA ISBN. (2010) 978–960.

[25] T.U. Onuegbu, O. Ikechukwu Martin, N.O. Ilochi, U.E. Ekpunobi, A.S. Ogbuagu, Enhancing the Properties of Coal Briquette Using Spear Grass (Imperata Cylindrica), Leonardo J. Sci. 17 (2010) 47–58.

[26] O.O. Fasina, Physical properties of peanut hull pellets, Bioresour. Technol. 99 (2008) 1259–1266.

[27] M. Matúš, P. Križan, L. ’ubomír Šooš, J. Beniak, Effects of Initial Moisture Content on the Physical and Mechanical Properties of Norway Spruce Briquettes, World Acad. Sci. Eng. Technol. Int. J. Environ. Chem. Ecol. Geol. Geophys. Eng. 9 (2015) 1156–1162.

[28] A. Zafari, M.H. Kianmehr, Factors affecting mechanical properties of biomass pellet from compost, Environ. Technol. 35 (2014) 478–486.

[29] O.C. Chin, K.M. Siddiqui, Characteristics of some biomass briquettes prepared under modest die pressures, Biomass Bioenergy. 18 (2000) 223–228.

[30] S. Yaman, M. Sahan, H. Haykiri-acma, K. Sesen, S. Kucukbayrak, Production of fuel briquettes from olive refuse and paper mill waste, Fuel Process. Technol. 68 (2000) 23–31.

[31] J. Kers, P. Kulu, A. Aruniit, V. Laurmaa, P. Križan, L. Šooš, ü Kask, Determination of physical, mechanical and burning characteristics of polymeric waste material briquettes, Est. J. Eng. 16 (2010) 307.

[32] P. Križan, Research of factors influencing the quality of wood briquets, Acta Montan. Slovaca-ISSN. (2007) 1335–1788.

[33] N. Kaliyan, R.V. Morey, Densification characteristics of corn cobs, Fuel Process. Technol. 91 (2010) 559–565.

[34] S. Mani, L.G. Tabil, S. Sokhansanj, Specific energy requirement for compacting corn stover, Bioresour. Technol. 97 (2006) 1420–1426.

[35] S.A. Ahmed, A. Kumari, K. Mandavgane, A Review on Briquettes as an Alternative Fuel, Int. J. Innov. Eng. Technol. 3 (2014) 139–144.

[36] J.S. Mitchual, K. Frimpong-Mensah, N.A. Darkwa, Effect of species, particle size and compacting pressure on relaxed density and compressive strength of fuel briquettes, Int. J. Energy Environ. Eng. (2013) 1–6.

[37] R. Suleiman, K. Rosentrater, B. Chove, Periodic Physical Disturbance: An Alternative Method for Controlling Sitophilus zeamais (Maize Weevil) Infestation, Insects. 7 (2016) 51.

[38] J. Zhang, Y. Guo, Physical properties of solid fuel briquettes made from Caragana korshinskii Kom, Powder Technol. 256 (2014) 293–299.

[39] P. Križan, M. Matú, Ľ. Šooš, J. Beniak, Behavior of Beech Sawdust during Densification into a Solid Biofuel, Energies. 8 (2015) 6382–6398. doi:10.3390/en8076382.

[40] P. Wilaipon, The Effects of Briquetting Pressure on Banana-Peel Briquette and the Banana Waste in Northern Thailand, Am. J. Appl. Sci. 6 (2009) 167–171.

[41] C.A. Mullen, A.A. Boateng, N.M. Goldberg, I.M. Lima, D.A. Laird, K.B. Hicks, Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis, Biomass Bioenergy. 34 (2010) 67–74.

[42] F. Rabier, M. Temmerman, T. Bohm, H. Hartmann, P. Daugbjergjensen, J. Rathbauer, J. Carrasco, M. Fernandez, Particle density determination of pellets and briquettes, Biomass Bioenergy. 30 (2006) 954–963.

[43] S.A. Ndindeng, J.E.G. Mbassi, W.F. Mbacham, J. Manful, S. Graham-Acquaah, J. Moreira, J. Dossou, K. Futakuchi, Quality optimization in briquettes made from rice milling by-products, Energy Sustain. Dev. 29 (2015) 24–31.

[44] V.. Umogbai, H.. Iorter, Experimental Evaluation of the Performance of a Prototype Solar Dryer Box, Afr. J. Food Sci. Technol. 4 (2013) 110–115.

[45] A. Shah, M.J. Darr, D. Dalluge, D. Medic, K. Webster, R.C. Brown, Physicochemical properties of bio-oil and biochar produced by fast pyrolysis of stored single-pass corn stover and cobs, Bioresour. Technol. 125 (2012) 348–352.

[46] C. Du, J. Wu, D. Ma, Y. Liu, P. Qiu, R. Qiu, S. Liao, D. Gao, Gasification of corn cob using non-thermal arc plasma, Int. J. Hydrog. Energy. 40 (2015) 12634–12649.

[47] H.A. Ruiz, M.A. Cerqueira, H.D. Silva, R.M. Rodríguez-Jasso, A.A. Vicente, J.A. Teixeira, Biorefinery valorization of autohydrolysis wheat straw hemicellulose to be applied in a polymer-blend film, Carbohydr. Polym. 92 (2013) 2154–2162.

[48] C. Karunanithy, Y. Wang, K. Muthukumarappan, S. Pugalendhi, Physiochemical Characterization of Briquettes Made from Different Feedstocks, Biotechnol. Res. Int. 2012 (2012) 1–12.

[49] P. Gilbert, C. Ryu, V. Sharifi, J. Swithenbank, Effect of process parameters on pelletisation of herbaceous crops, Fuel. 88 (2009) 1491–1497.

[50] A. Sharma, V. Pareek, D. Zhang, Biomass pyrolysis—A review of modelling, process parameters and catalytic studies, Renew. Sustain. Energy Rev. 50 (2015) 1081–1096.

[51] M. Jahirul, M. Rasul, A. Chowdhury, N. Ashwath, Biofuels Production through Biomass Pyrolysis —A Technological Review, Energies. 5 (2012) 4952–5001.

[52] S. Satimanont, A. Luengnaruemitchai, S. Wongkasemjit, Effect of temperature and time on dilute acid pretreatment of corn cobs, Int. J. Chem. Biol. Eng. 6 (2012) 333–337.

[53] C. Rhén, R. Gref, M. Sjöström, I. Wästerlund, Effects of raw material moisture content, densification pressure and temperature on some properties of Norway spruce pellets, Fuel Process. Technol. 87 (2005) 11–16.

[54] M.T. Carone, A. Pantaleo, A. Pellerano, Influence of process parameters and biomass characteristics on the durability of pellets from the pruning residues of Olea europaea L., Biomass Bioenergy. 35 (2011) 402–410.

[55] H. Haykiri-Acma, S. Yaman, S. Kucukbayrak, Production of biobriquettes from carbonized brown seaweed, Fuel Process. Technol. 106 (2013) 33–40.

[56] M. Adzic, R. Savic, Cooling of wood briquettes, Therm. Sci. 17 (2013) 833–838.

[57] C. Antwi-Boasiako, B.B. Acheampong, Strength properties and calorific values of sawdust-briquettes as wood-residue energy generation source from tropical hardwoods of different densities, Biomass Bioenergy. 85 (2016) 144–152.

[58] B. Rubio, M.T. Izquierdo, E. Segura, Effect of binder addition on the mechanical and physicochemical properties of low rank coal char briquettes, Carbon. 37 (1999) 1833–1841.

[59] B. Lela, M. Barišić, S. Nižetić, Cardboard/sawdust briquettes as biomass fuel: Physical–mechanical and thermal characteristics, Waste Manag. 47 (2016) 236–245.

[60] D. Andrejko, J. Grochowicz, Effect of the moisture content on compression energy and strength characteristic of lupine briquettes, J. Food Eng. 83 (2007) 116–120.

[61] G.C. Wakchaure, I. Mani, Effect of binders and pressures on physical quality of some biomass briquettes, J. Agric. Eng. 46 (2009) 24–30.

[62] H. Yumak, T. Ucar, N. Seyidbekiroglu, Briquetting soda weed (Salsola tragus) to be used as a rural fuel source, Biomass Bioenergy. 34 (2010) 630–636.

[63] L.S. Nikolaisen, P.D. Jensen, Biomass feedstocks: categorisation and preparation for combustion and gasification, in: Biomass Combust. Sci. Technol. Eng., Elsevier, 2013: pp. 36–57. http://linkinghub.elsevier.com/retrieve/pii/B9780857091314500030 (accessed February 10, 2016).

Appendix A 2: Design of experiment for statistical analysis of the effect of torrefaction conditions on yield of torrefaction products. Mid-point: temperature (^oC)/holding time (min) of 250/45

Temperature (^oC)	Holding time (min)
300	0
200	0
200	90
200	0
250	45
300	90
300	90
200	90
300	0

Appendix A 3: Proximate analysis (BS 1016-6)

A 3.1 Moisture content (MC)

Weigh an empty crucible (mass M_1) and gradually add 1 g of a sample (to the nearest 0.1mg) and record the weight of the crucible and the sample (mass M_2). Gently tab the crucible to evenly spread the sample over the bottom of the crucible and oven dried the sample at 105-110^{o}C for 1 hour. Cool the crucible in a desiccator and reweigh (mass M_3). Moisture content, MC is calculated from Equation (A.1).

$$MC = \frac{M_2 - M_3}{M_2 - M_1} \times 100\% \qquad (A.1)$$

A 3.2 Percentage volatile matter (PVM)

Weigh an empty crucible (mass M_1) and gradually add 1 g of a sample (to the nearest 0.1mg) and record weight of the crucible and the sample (mass M_2). Heat the sample in the absence of oxygen in a furnace at a temperature of 925°C for 7 min. Cool the residue in a desiccator and reweigh (mass M_3). Percentage volatile matter (PVM) is computed from Equations (A.2).

$$PVM = \frac{M_2 - M_3}{M_2 - M_1} \times 100 - MC \qquad (A.2)$$

A 3.3 Percentage ash content (PAC)

Weigh an empty crucible (mass M_1) and gradually add 1 g of a sample (to the nearest 0.1mg) and record the weight of the crucible and the sample (mass M_2). Gently tab the crucible to evenly spread the sample over the bottom of the crucible. Heat the sample in the absence of oxygen in a furnace at a temperature of 750°C for 1 hour. Cool the residue (ash) to room temperature in a desiccator, and reweighed (mass M_3). Ash content is computed from Equations (A.3).

$$PAC = \frac{M_3 - M_1}{M_2 - M_1} \times 100 \qquad (A.3)$$

A 3.4 Percentage of fixed carbon (PFC)

PFC is calculated by difference using Equation (A.4).

$$\mathrm{PFC} = 100 - \mathrm{PAC} - \mathrm{MC} - \mathrm{PVM} \qquad (A.4)$$

Appendix A 4: Design of experiment for statistical analysis of the effects of pressure (MPa), particle size (mm) and temperature (°C) on properties of bean straw briquette. Midpoint: pressure/particle size/temperature of 175/3.18/50

Pressure (MPa)	Particle size (mm)	Temperature (°C)
250	2.36	80
250	2.36	80
100	2.36	80
100	4.00	80
100	4.00	20
100	2.36	80
250	4.00	20
100	2.36	20
100	4.00	80
250	4.00	80
250	4.00	80
250	2.36	20
100	2.36	20
100	2.36	20
100	4.00	20
175	3.18	50
250	4.00	20
100	2.36	80
250	4.00	20
100	4.00	80
250	2.36	20
250	2.36	80
100	4.00	20
250	4.00	80
250	2.36	20

Appendix A 5: Design of experiment for statistical analysis of the effects of pressure (MPa), moisture content (%), particle size (mm) and temperature (ºC) on properties of maize cob briquette. Midpoint: pressure/moisture content/particle size/temperature of 200/12.04/3.18/50

Pressure (MPa)	Moisture content (%wt)	Particle size (mm)	Temperature (ºC)
250	7.14	4.00	20
250	16.94	4.00	80
250	16.94	2.36	20
150	7.14	2.36	80
250	16.94	2.36	20
250	16.94	4.00	20
150	16.94	4.00	20
150	7.14	4.00	20
150	16.94	2.36	80
150	16.94	4.00	80
150	16.94	2.36	80
150	16.94	2.36	20
250	16.94	2.36	80
250	7.14	4.00	80
250	16.94	2.36	80
150	7.14	4.00	20
250	16.94	4.00	20
150	7.14	4.00	80
150	7.14	2.36	20
250	7.14	4.00	80
150	7.14	2.36	80
250	7.14	4.00	20
150	7.14	2.36	80
150	7.14	4.00	80

150	16.94	4.00	20
250	7.14	2.36	20
150	7.14	4.00	20
150	16.94	2.36	20
250	16.94	2.36	20
250	7.14	4.00	20
150	16.94	2.36	20
250	7.14	2.36	80
150	7.14	2.36	20
150	16.94	4.00	80
250	16.94	4.00	80
150	16.94	2.36	80
250	7.14	2.36	20
150	16.94	4.00	20
250	7.14	2.36	80
150	7.14	2.36	20
250	7.14	4.00	80
150	7.14	4.00	80
250	7.14	2.36	80
200	12.04	3.18	50
250	7.14	2.36	20
250	16.94	4.00	20
250	16.94	4.00	80
150	16.94	4.00	80
250	16.94	2.36	80

Appendix A 6: Analysis of variance for maize cob briquette density

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	253650	253650	6274.78	0.000
Moisture content (*m*)	1	559678	559678	13845.27	0.000
Particle size (*s*)	1	45418	45418	1123.54	0.000
Temperature (*t*)	1	101393	101393	2508.26	0.000
$p \times m$	1	28145	28145	696.24	0.000
$p \times s$	1	37772	37772	934.40	0.000
$p \times t$	1	2997	2997	74.15	0.000
$m \times s$	1	87	87	2.14	0.153
$m \times t$	1	23069	23069	570.69	0.000
$s \times t$	1	14971	14971	370.35	0.000
$p \times m \times s$	1	414	414	10.23	0.003
$p \times m \times t$	1	1552	1552	38.38	0.000
$p \times s \times t$	1	9377	9377	231.97	0.000
$m \times s \times t$	1	3200	3200	79.15	0.000
$p \times m \times s \times t$	1	385	385	9.52	0.004
Error	32	1294	40		
Total	48	1083917			

Appendix A 7: Analysis of variance for bean straw briquette density

	Degrees of freedom	Sum of squares	Mean sum of squares	F-value	P-value
Pressure (*p*)	1	93900	93900.1	2081.85	0.000
Particle size (*s*)	1	728	728.2	16.14	0.001
Temperature (*t*)	1	50729	50728.8	1124.70	0.000
p × *s*	1	330	330.0	7.32	0.016
p × *t*	1	1438	1438.4	31.89	0.000
s × *t*	1	39	38.5	0.85	0.369
p × *s* × *t*	1	713	712.9	15.80	0.001
Error	16	722	45.1		
Total	24	149678			

Appendix A 8: Analysis of variance for impact resistance of maize cob briquettes

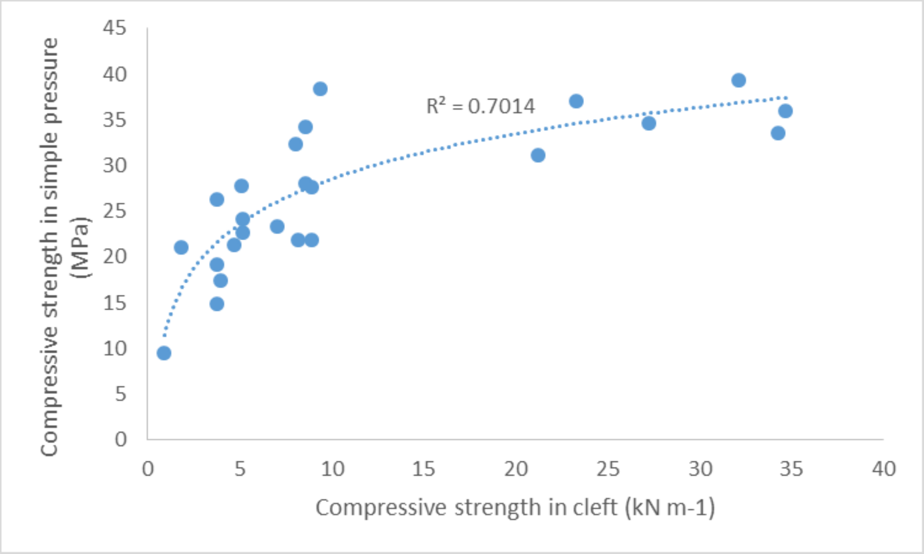
	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	6821.1	6821.1	360.74	0.000
Moisture content (*m*)	1	13293.4	13293.4	703.03	0.000
Particle size (*s*)	1	1342.0	1342.0	88.12	0.000
Temperature (*t*)	1	5794.8	5794.8	306.47	0.000
$p \times m$	1	1666.2	1666.2	88.12	0.000
$p \times s$	1	21.6	21.6	1.14	0.293
$p \times t$	1	357.5	357.5	18.91	0.000
$m \times s$	1	109.2	109.2	5.78	0.022
$m \times t$	1	195.2	195.2	10.32	0.003
$s \times t$	1	233.2	233.2	12.33	0.001
$p \times m \times s$	1	181.0	181.0	9.57	0.004
$p \times m \times t$	1	125.5	125.5	6.63	0.015
$p \times s \times t$	1	144.9	144.9	7.66	0.009
$m \times s \times t$	1	21.9	21.9	1.16	0.290
$p \times m \times s \times t$	1	66.3	66.3	3.50	0.070
Error	32	605.1	18.9		
Total	48	30979.3			

Appendix A 9: Analysis of variance for impact resistance of bean straw briquettes

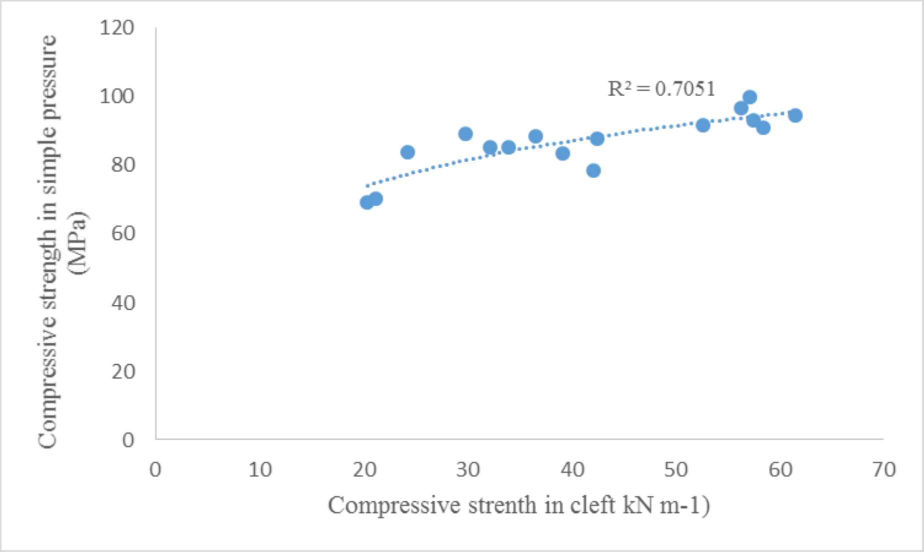
	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	670.98	670.984	61.94	0.000
Particle size (*s*)	1	1.76	1.760	0.16	0.692
Temperature (*t*)	1	953.82	953.820	88.06	0.000
$p \times s$	1	18.55	18.550	1.71	0.209
$p \times t$	1	662.55	662.550	61.17	0.000
$s \times t$	1	1.35	1.354	0.12	0.728
$p \times s \times t$	1	9.00	9.004	0.83	0.375
Error	16	173.31	10.832		
Total	24	2512.88			

Appendix A 10: Correlation between compressive strength in cleft and simple pressive for (a) maize cob (b) bean straw briquettes.

(a)



(b)



Appendix A 11: Analysis of variance for compressive strength in cleft of maize cob briquettes.

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	138.38	138.38	427.15	0.000
Moisture content (*m*)	1	1722.01	1722.01	5315.51	0.000
Particle size (*s*)	1	32.18	32.18	99.32	0.000
Temperature (*t*)	1	1549.28	1549.28	4782.33	0.000
$p \times m$	1	0.00	0.00	0.01	0.940
$p \times s$	1	1.05	1.05	3.24	0.081
$p \times t$	1	73.26	73.26	226.14	0.000
$m \times s$	1	17.64	17.64	54.46	0.000
$m \times t$	1	654.90	654.90	2021.56	0.000
$s \times t$	1	1.44	1.44	4.43	0.043
$p \times m \times s$	1	11.70	11.70	36.12	0.000
$p \times m \times t$	1	29.93	29.93	92.37	0.000
$p \times s \times t$	1	0.01	0.01	0.02	0.900
$m \times s \times t$	1	1.11	1.11	3.43	0.073
$p \times m \times s \times t$	1	0.11	0.11	0.34	0.564
Error	32	10.37	0.32		
Total	48	4243.70			

Appendix A 12: Analysis of variance for compressive strength in simple pressure of maize cob briquettes.

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	161.33	161.33	125.76	0.000
Moisture content (*m*)	1	1376.02	1376.02	1072.57	0.000
Particle size (*s*)	1	884.08	884.08	689.12	0.000
Temperature (*t*)	1	466.25	466.25	363.43	0.000
$p \times m$	1	23.80	23.80	18.55	0.000
$p \times s$	1	7.36	7.36	5.74	0.023
$p \times t$	1	2.08	2.08	1.62	0.212
$m \times s$	1	21.60	21.60	16.84	0.000
$m \times t$	1	32.34	32.34	25.21	0.000
$s \times t$	1	16.80	16.80	13.10	0.001
$p \times m \times s$	1	31.04	31.04	24.20	0.000
$p \times m \times t$	1	13.87	13.87	10.81	0.002
$p \times s \times t$	1	19.25	19.25	15.01	0.000
$m \times s \times t$	1	7.21	7.21	5.62	0.024
$p \times m \times s \times t$	1	0.70	0.70	0.55	0.465
Error	32	41.05	1.28		
Total	48	3105.07			

Appendix A 13: Analysis of variance for compressive strength in cleft of bean straw briquettes

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	1915.31	1915.31	391.28	0.000
Particle size (*s*)	1	5.04	5.04	1.03	0.325
Temperature (*t*)	1	2223.37	2223.37	454.21	0.000
p × *s*	1	27.73	27.73	5.67	0.030
p × *t*	1	4.00	4.00	0.82	0.379
s × *t*	1	26.46	26.46	5.41	0.034
p × *s* × *t*	1	0.06	0.06	0.01	0.913
Error	16	78.32	4.89		
Total	24	4298.47			

Appendix A 14: Analysis of variance for compressive strength in simple pressure of bean straw briquettes

	Degree of freedom	Sum of square	Mean sum of square	F-value	P-value
Pressure (*p*)	1	606.01	606.015	47.79	0.000
Particle size (*s*)	1	92.04	92.042	7.26	0.016
Temperature (*t*)	1	907.74	907.740	71.59	0.000
p × *s*	1	32.20	32.202	2.54	0.131
p × *t*	1	83.63	83.627	6.60	0.021
s × *t*	1	3.23	3.227	0.25	0.621
p × *s* × *t*	1	61.44	61.440	4.85	0.043
Error	16	202.87	12.680		
Total	24	1991.40			

Appendix A 15: Torrefied bean straw. Holding time: 30 min

(a) 200°C

(b) 250°C

(c) 300°C

Appendix A 16: Analysis of Variance for char yield from torrefaction of maize cob

	Degrees of freedom	Sum of squares	Mean sum of squares	F-Value	P-value
Temperature (T)	1	1541.79	1541.79	714.02	0.000
Holding time (H)	1	33.70	33.70	15.61	0.017
T×H	1	44.65	44.65	20.68	0.010
Error	4	8.64	2.16		
Total	8	1646.56			

Appendix A 17: Analysis of Variance for liquid yield from torrefaction of maize cob

	Degrees of freedom	Sum of squares	Mean sum of squares	F-Value	P-value
Temperature (T)	1	539.890	539.890	468.03	0.000
Holding time (H)	1	8.040	8.040	6.97	0.058
T×H	1	16.474	16.474	14.28	0.019
Error	4	4.614	1.154		
Total	8	571.416			

Appendix A 18: Analysis of Variance for gas yield from the torrefaction of maize cob

	Degrees of freedom	Sum of squares	Mean sum of squares	F-Value	P-value
Temperature (T)	1	256.851	256.851	349.00	0.000
Holding time (H)	1	8.841	8.841	12.01	0.026
T×H	1	6.864	6.864	9.33	0.038
Error	4	2.944	0.736		
Total	8	282.675			

Appendix A 19: Analysis of Variance for the char yield from the torrefaction of bean straw

	Degrees of freedom	Sum of squares	Mean sum of squares	F-Value	P-value
Temperature (T)	1	464.363	464.363	1494.75	0.000
Holding time (H)	1	62.440	62.440	200.99	0.000
T×H	1	13.390	13.390	43.10	0.003
Error	4	1.243	0.311		
Total	8	547.256			

Appendix A 20: Analysis of Variance for the liquid yield from the torrefaction of bean straw

	Degrees of freedom	Sum of squares	Mean sum of squares	F-Value	P-value
Temperature (T)	1	155.320	155.320	1193.74	0.000
Holding time (H)	1	16.445	16.445	126.39	0.000
T×H	1	10.557	10.557	81.14	0.001
Error	4	0.520	0.130		
Total	8	183.006			

Appendix A 21: Analysis of Variance for the gas yield from the torrefaction of bean straw

	Degree of freedom	Sum of square	Mean sum of square	F-Value	P-value
Temperature (T)	1	70.152	70.152	65.74	0.001
Holding time (H)	1	9.835	9.835	9.22	0.039
T×H	1	1.240	1.240	1.16	0.342
Error	4	4.269	1.067		
Total	8	94.805			

Appendix B 1: Design of experiment for analysis of the impact of pyrolysis conditions on yields of pyrolysis products

Pyrolysis temperature (ºC)	Heanting rate (ºC min^{-1})	Carrier gas flow rate (cm^3 min^{-1})
530	15	50
410	10	50
410	15	40
650	15	60
650	15	40
650	10	50
410	20	50
530	20	60
530	10	60
530	10	40
410	15	60
530	20	40
530	15	50
530	15	50
650	20	50

Appendix B 2: Analysis of Variance for bio-oil yield from pyrolysis of bean straw briquette. Briquetting conditions: pressure (MPa)/particle size (mm) and temperature (°C) of 150/<4.00/80

	Degree of freedom	Sum of square	Mean square	F-Value	P-Value
Temperature (T)	1	17.2872	17.2872	30.84	0.003
Heating rate (H)	1	0.1013	0.1013	0.18	0.689
Carrier gas flow rate (F)	1	0.1860	0.1860	0.33	0.590
T×T	1	0.5215	0.5215	0.93	0.379
H×H	1	1.0601	1.0601	1.89	0.228
F×F	1	0.1142	0.1142	0.20	0.671
T×H	1	2.9241	2.9241	5.22	0.071
T×F	1	0.0324	0.0324	0.06	0.820
H×F	1	3.2400	3.2400	5.78	0.061
Error	5	2.8030	0.5606		
Total	14	28.0957			

Appendix B 3: Analysis of Variance for char yield from pyrolysis of bean straw briquette. Briquetting conditions: pressure (MPa)/particle size (mm) and temperature (°C) of 150/<4.00/80

	Degree of freedom	Sum of square	Mean square	F-Value	P-Value
Temperature (T)	1	125.928	125.928	369.53	0.000
Heating rate (H)	1	0.016	0.016	0.05	0.836
Carrier gas flow rate (F)	1	0.026	0.026	0.08	0.792
T×T	1	2.203	2.203	6.47	0.052
H×H	1	0.075	0.075	0.22	0.659
F×F	1	0.540	0.540	1.59	0.264
T×H	1	0.005	0.005	0.01	0.909
T×F	1	0.449	0.449	1.32	0.303
H×F	1	0.096	0.096	0.28	0.618
Error	5	1.704	0.341		
Total	14	131.262			

Appendix B 4: Analysis of Variance for gas yield from pyrolysis of bean straw briquette. Briquetting conditions: pressure (MPa)/particle size (mm) and temperature (°C) of 150/<4.00/80

	Degree of freedom	Sum of square	Mean square	F-Value	P-Value
Temperature (T)	1	49.9001	49.9001	84.79	0.000
Heating rate (H)	1	0.1985	0.1985	0.34	0.587
Carrier gas flow rate (F)	1	0.0722	0.0722	0.12	0.740
T×T	1	4.8548	4.8548	8.25	0.035
H×H	1	0.5664	0.5664	0.96	0.372
F×F	1	0.1603	0.1603	0.27	0.624
T×H	1	2.6896	2.6896	4.57	0.086
T×F	1	0.2401	0.2401	0.41	0.551
H×F	1	2.2201	2.2201	3.77	0.110
Error	5	2.9426	0.5885		
Total	14	63.8380			

Appendix B 5: Analysis of Variance for char yield from pyrolysis of maize cob briquette. Briquetting conditions: pressure (MPa)/particle size (mm)/moisture content (%wt)/temperature (ºC) of 200/<2.36/7.14/80

	Degree of freedom	Sum of square	Mean square	F-Value	P-Value
Temperature (T)	1	124.189	124.189	47.06	0.001
Heating rate (H)	1	3.302	3.302	1.25	0.314
Carrier gas flow rate (F)	1	0.106	0.106	0.04	0.849
T×T	1	14.812	14.812	5.61	0.064
H×H	1	0.051	0.051	0.02	0.895
F×F	1	0.949	0.949	0.36	0.575
T×H	1	0.226	0.226	0.09	0.782
T×F	1	0.990	0.990	0.38	0.567
H×F	1	2.265	2.265	0.86	0.397
Error	5	13.196	2.639		
Total	14	160.710			

Appendix B 6: Analysis of Variance for bio-oil yield from pyrolysis of maize cob briquette. Briquetting conditions: pressure (MPa)/particle size (mm)/moisture content (%wt)/temperature (ºC) of 200/<2.36/7.14/80

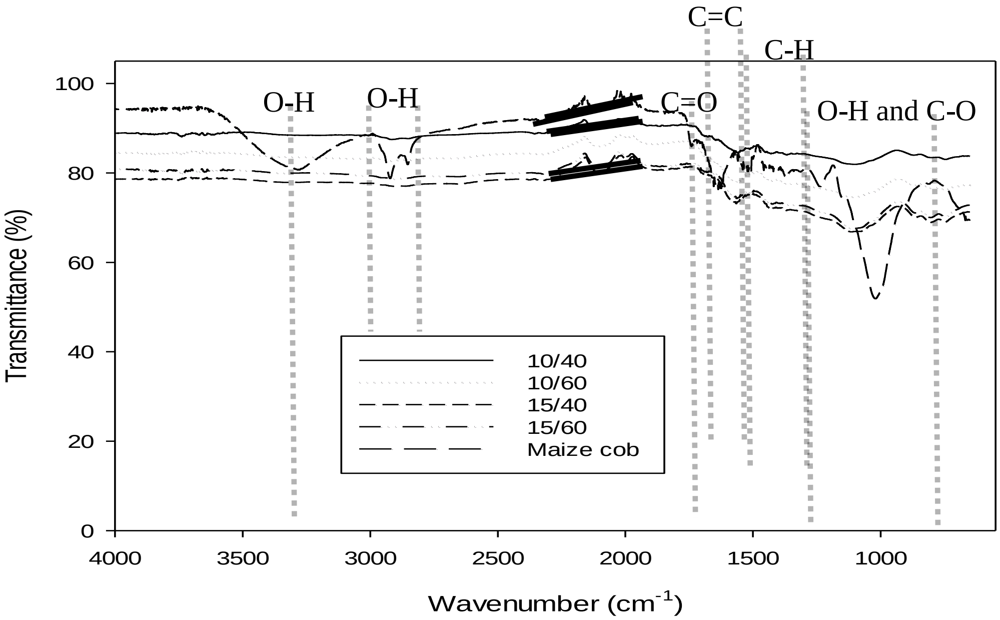
	Degree of freedom	Sum of square	Mean square	F-Value	P-Value
Temperature (T)	1	15.9612	15.9612	10.33	0.024
Heating rate (H)	1	0.0221	0.0221	0.01	0.910
Carrier gas flow rate (F)	1	1.0952	1.0952	0.71	0.438
T×T	1	1.8700	1.8700	1.21	0.321
H×H	1	0.0394	0.0394	0.03	0.879
F×F	1	0.1452	0.1452	0.09	0.772
T×H	1	0.4489	0.4489	0.29	0.613
T×F	1	0.0009	0.0009	0.00	0.982
H×F	1	0.0144	0.0144	0.01	0.927
Error	5	7.7290	1.5458		
Total	14	27.4528			

Appendix B 7: Analysis of Variance for gas yield from pyrolysis of maize cob briquette. Briquetting conditions: pressure (MPa)/particle size (mm)/moisture content (%wt)/temperature (ºC) of 200/<2.36/7.14/80

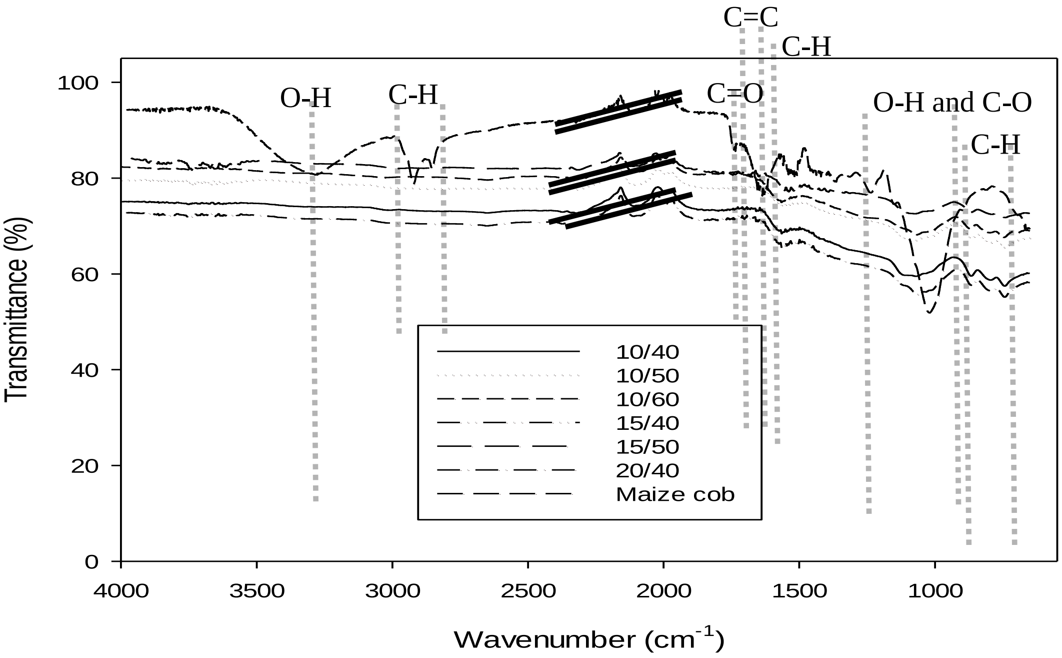
	Degree of freedom	Sum of square	Mean square	F-Value	P-Value
Temperature (T)	1	51.1060	51.1060	18.73	0.008
Heating rate (H)	1	3.8642	3.8642	1.42	0.287
Carrier gas flow rate (F)	1	0.5202	0.5202	0.19	0.681
T×T	1	6.1563	6.1563	2.26	0.193
H×H	1	0.1807	0.1807	0.07	0.807
F×F	1	0.3520	0.3520	0.13	0.734
T×H	1	1.3110	1.3110	0.48	0.519
T×F	1	1.0506	1.0506	0.39	0.562
H×F	1	2.6406	2.6406	0.97	0.370
Error	5	13.6411	2.7282		
Total	14	80.9938			

Appendix B 8: FTIR spectra of char from pyrolysis of maize cob briquettes (briquetting conditions: pressure: 200MPa, moisture: 7.14%, particle size: <2.36mm and temperature: 80^{o}C)

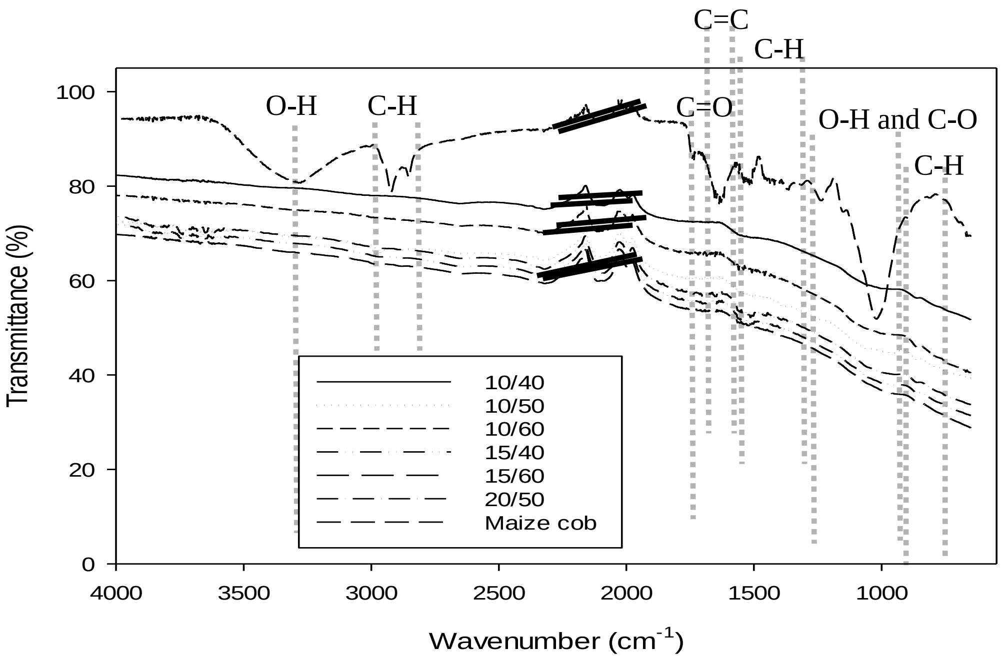
B 8.1: Pyrolysis temperature: 410 ^{o}C



B 8.2: Pyrolysis temperature: 530 ^{o}C

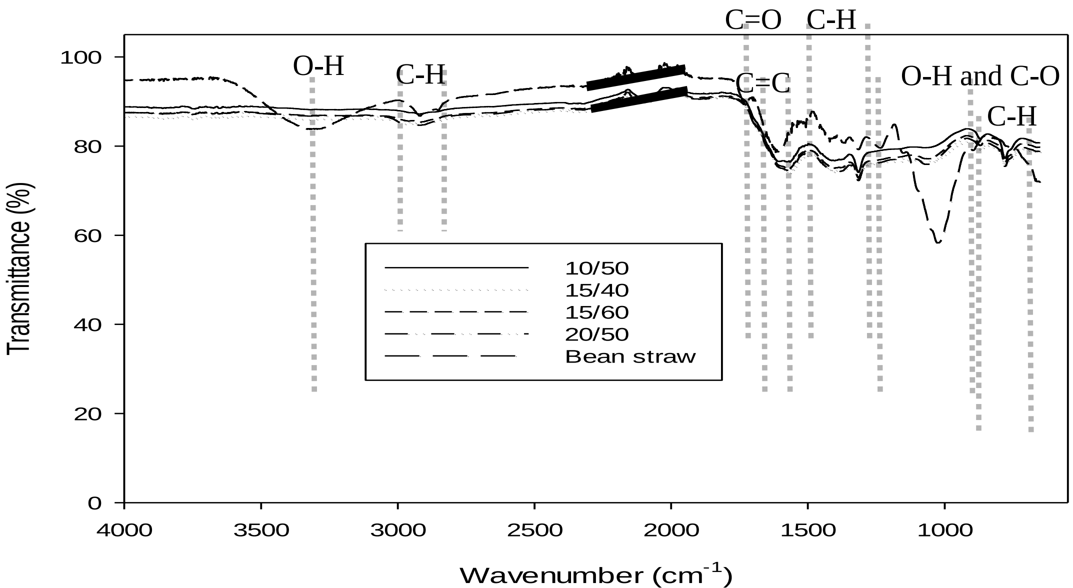


B 8.3: Pyrolysis temperature: 650°C

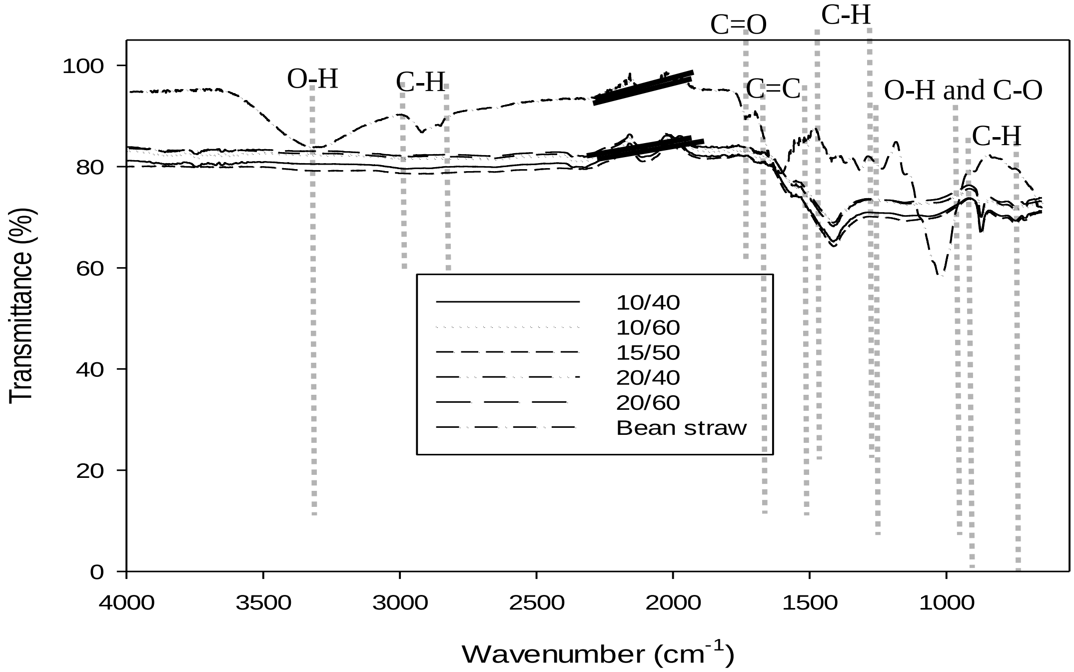


Appendix B 9: FTIR spectra of char of bean straw briquette char (briquetting conditions: pressure: 150MPa, moisture: 10.63%, particle size: <4mm and temperature: 80°C)

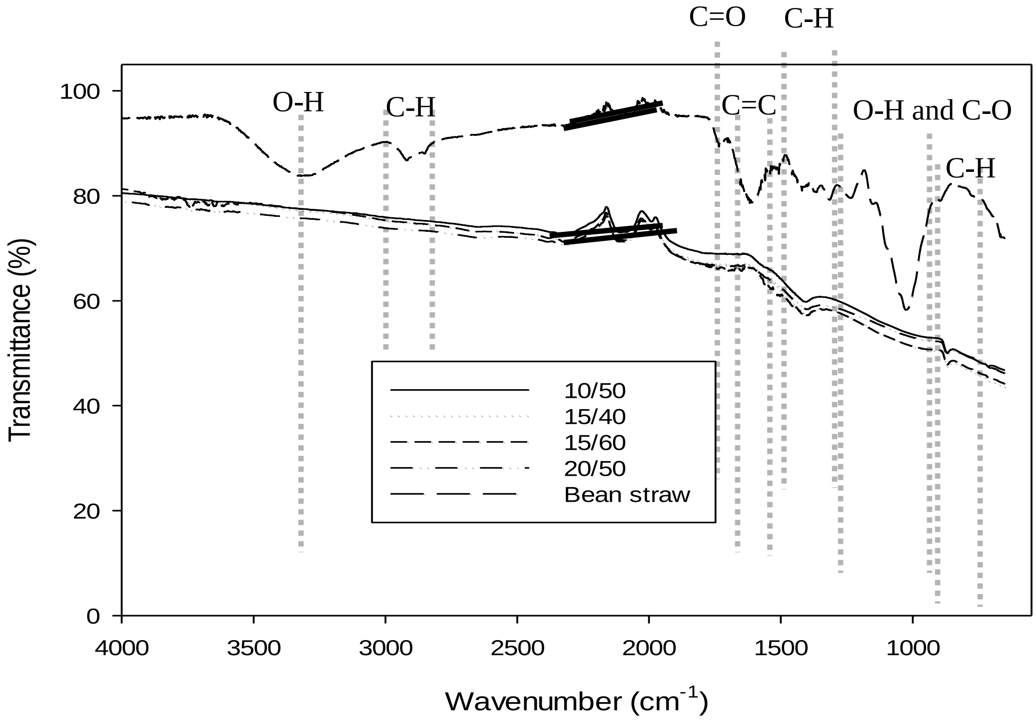
B 9.1: Pyrolysis temperature: 410°C



B 9.2: Pyrolysis temperature: 530^{o}C

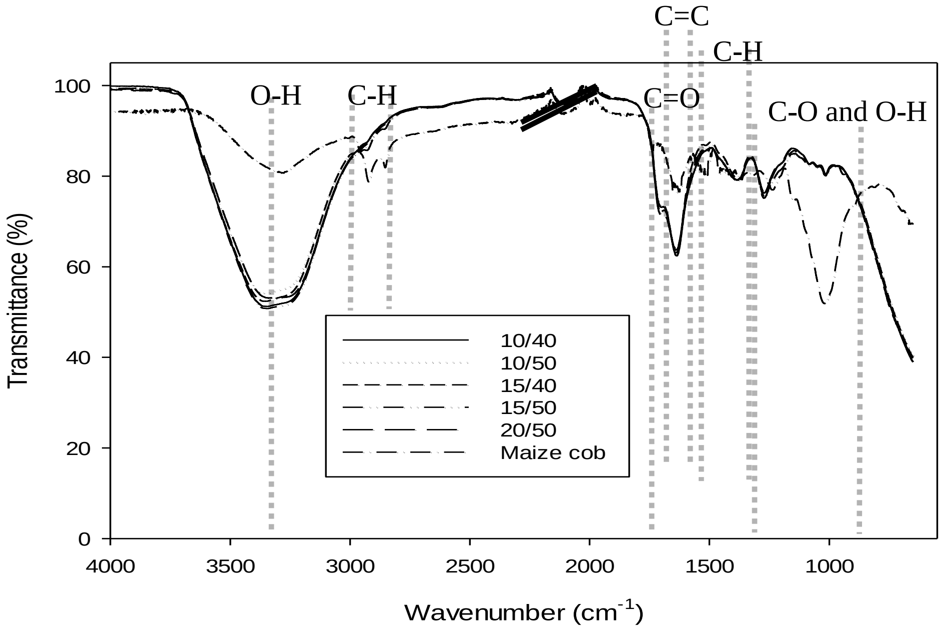


B 9.3: Pyrolysis temperature: 650^{o}C

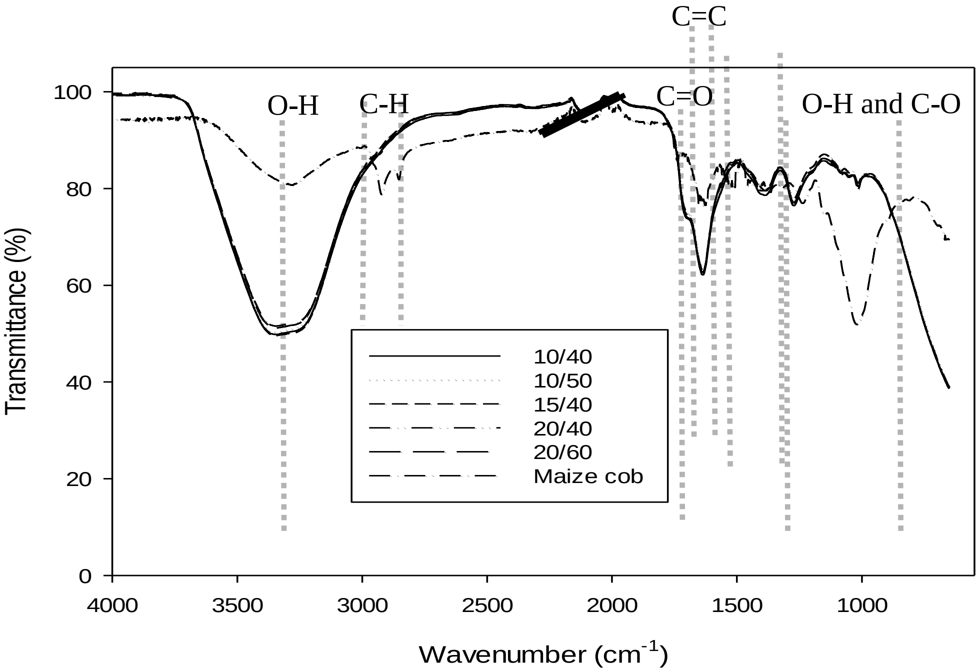


Appendix B 10: FTIR spectra of bio-oil from pyrolysis of maize cob briquette (briquetting conditions: pressure: 200MPa, moisture: 7.14%, particle size: <2mm and temperature: 80^{o}C)

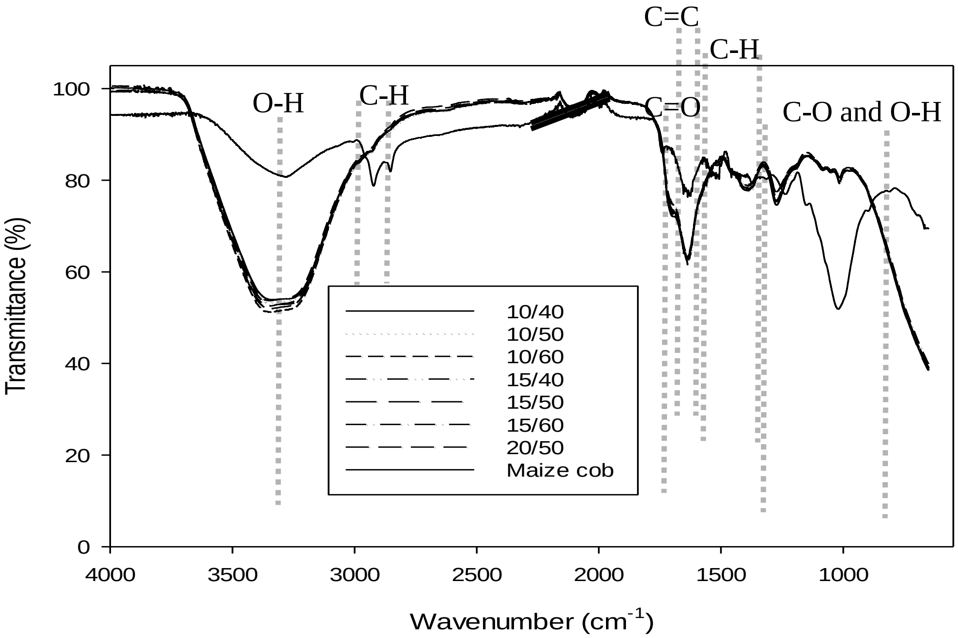
B 10.1: Pyrolysis temperature: 410^{o}C



B 10.2: Pyrolysis temperature: 530^{o}C

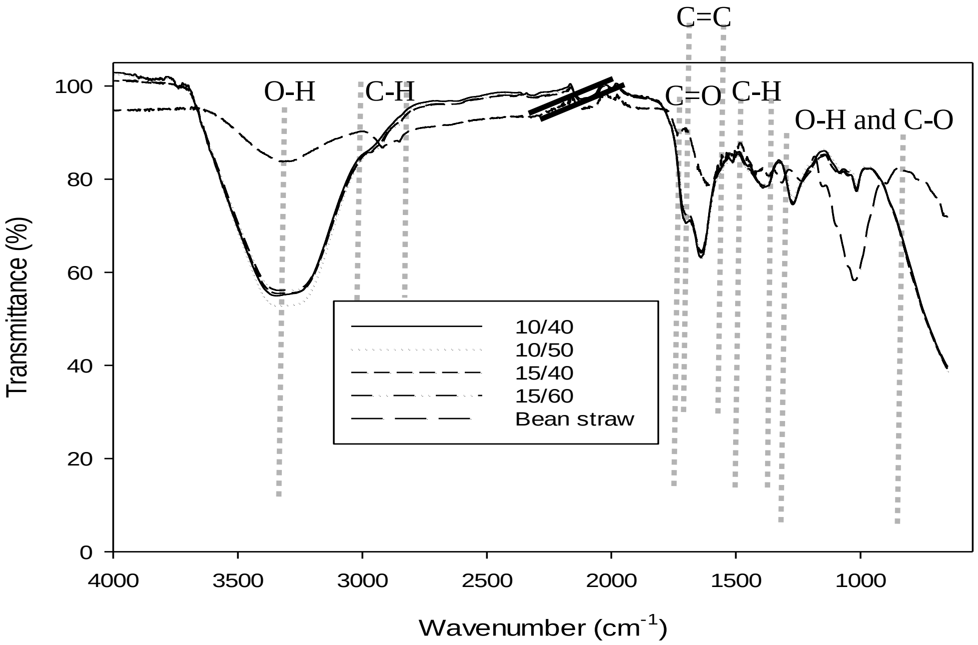


B 10.3: Pyrolysis temperature: 650°C

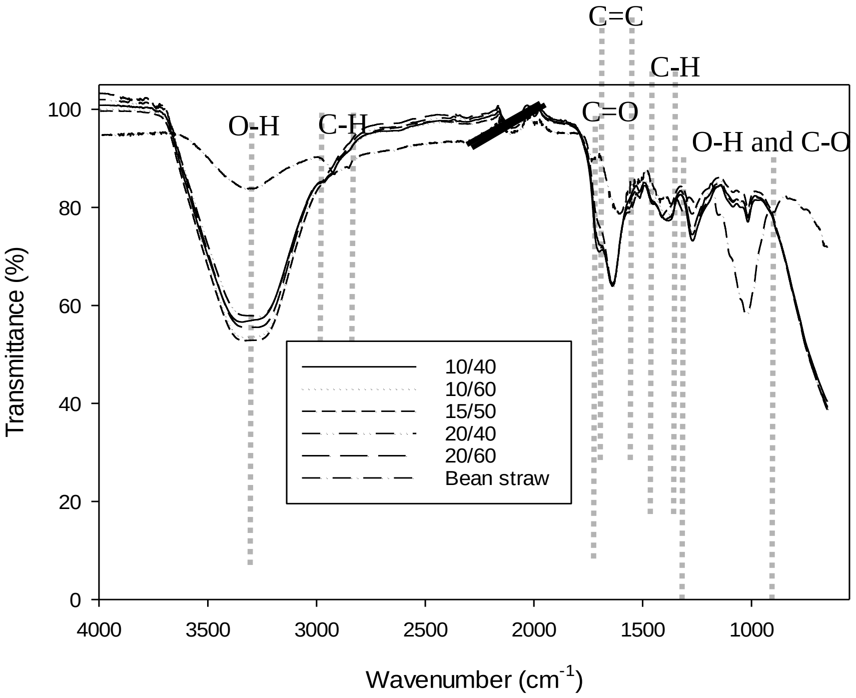


Appendix B 11: FTIR spectra of bio-oil from pyrolysis bean straw briquettes (briqurtting conditions: pressure: 150MPa, moisture: 10.63%, particle size: <4.00mm and temperature: 80°C)

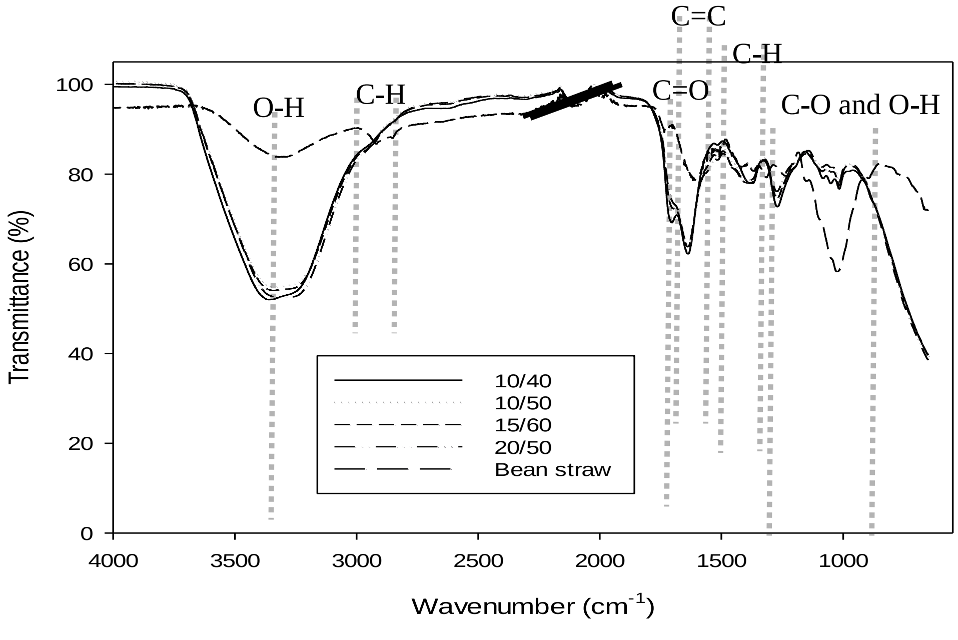
B 11.1: Pyrolysis temperature: 410°C



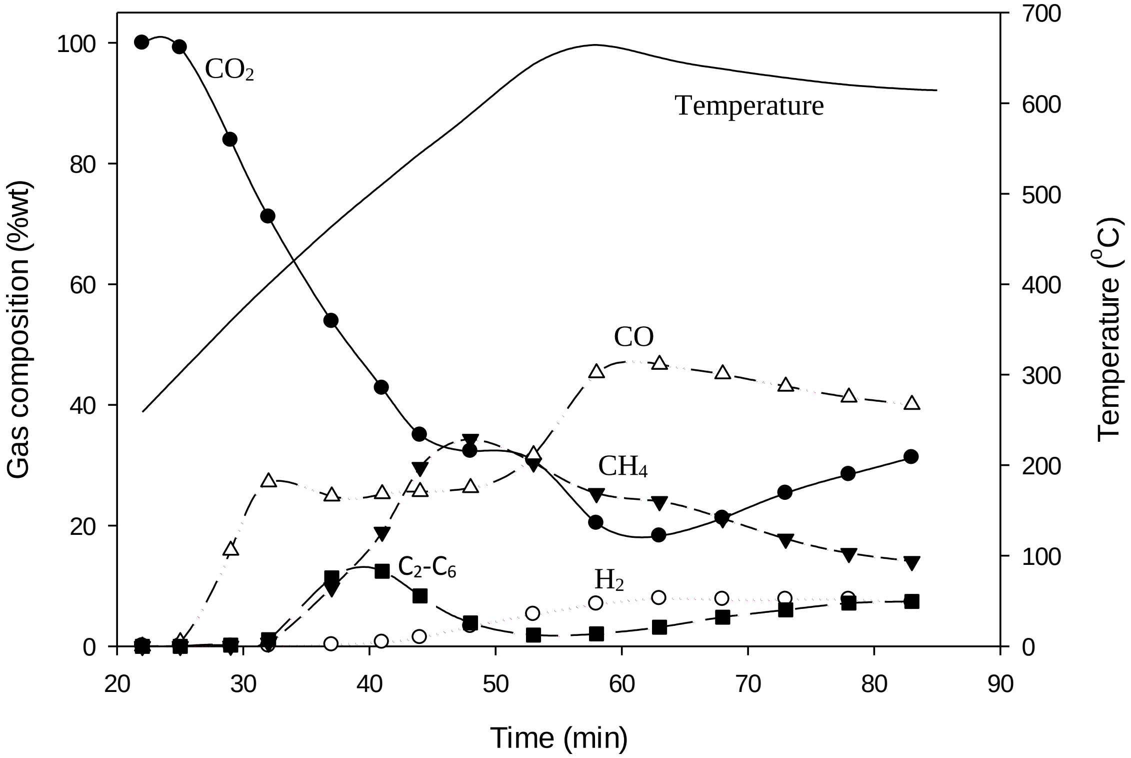
B 11.2: Pyrolysis temperature: 530°C



B 11.3: Pyrolysis temperature: 650°C



Appendix B 12: Gas composition of bean straw-maize cob blended briquettes at pyrolysis/heating rate and carrier gas flow rate of 650°C/10°C min^{-1}/40 cm^3 min^{-1}. Bean straw: maize cob blend ratio of 50:50 (briquetting condition: pressure: 150MPa, particle size: <4mm and temperature: 80°C)



References

Açıkalın, K., Karaca, F., Bolat, E., 2012. Pyrolysis of pistachio shell: Effects of pyrolysis conditions and analysis of products. Fuel 95, 169–177.

Adapa, P., Tabil, L., Schoenau, G., 2009. Compaction characteristics of barley, canola, oat and wheat straw. Biosyst. Eng. 104, 335–344.

Adzic, M., Savic, R., 2013. Cooling of wood briquettes. Therm. Sci. 17, 833–838.

Agbor, V.B., Cicek, N., Sparling, R., Berlin, A., Levin, D.B., 2011. Biomass pretreatment: Fundamentals toward application. Biotechnol. Adv. 29, 675–685.

Agrawal, A., Chakraborty, S., 2013. A kinetic study of pyrolysis and combustion of microalgae Chlorella vulgaris using thermo-gravimetric analysis. Bioresour. Technol. 128, 72–80.

Ahmad, M.S., Mehmood, M.A., Al Ayed, O.S., Ye, G., Luo, H., Ibrahim, M., Rashid, U., Arbi Nehdi, I., Qadir, G., 2017. Kinetic analyses and pyrolytic behavior of Para grass (Urochloa mutica) for its bioenergy potential. Bioresour. Technol. 224, 708–713.

Ahmed, S.A., Kumari, A., Mandavgane, K., 2014. A Review on Briquettes as an Alternative Fuel. Int. J. Innov. Eng. Technol. 3, 139–144.

Ahn, H.K., Sauer, T.J., Richard, T.L., Glanville, T.D., 2009. Determination of thermal properties of composting bulking materials. Bioresour. Technol. 100, 3974–3981.

Alakangas, E., Valtanen, J., Levlin, J., 2006. CEN technical specification for solid biofuels—Fuel specification and classes. Biomass Bioenergy 30, 908–914.

Ali, N., Saleem, M., Shahzad, K., Hussain, S., Chughtai, A., 2016. Effect of operating parameters on production of bio-oil from fast pyrolysis of maize stalk in bubbling fluidized bed reactor. Pol. J. Chem. Technol. 18.

Alper, K., Tekin, K., Karagöz, S., 2015. Pyrolysis of agricultural residues for bio-oil production. Clean Technol. Environ. Policy 17, 211–223.

Al-Wabel, M.I., Al-Omran, A., El-Naggar, A.H., Nadeem, M., Usman, A.R.A., 2013. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes. Bioresour. Technol. 131, 374–379.

Amaya, A., Medero, N., Tancredi, N., Silva, H., Deiana, C., 2007. Activated carbon briquettes from biomass materials. Bioresour. Technol. 98, 1635–1641.

Andrejko, D., Grochowicz, J., 2007. Effect of the moisture content on compression energy and strength characteristic of lupine briquettes. J. Food Eng. 83, 116–120.

Angın, D., 2013. Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. Bioresour. Technol. 128, 593–597.

Antwi-Boasiako, C., Acheampong, B.B., 2016. Strength properties and calorific values of sawdust-briquettes as wood-residue energy generation source from tropical hardwoods of different densities. Biomass Bioenergy 85, 144–152.

Apaydin-Varol, E., Pütün, E., Pütün, A.E., 2007. Slow pyrolysis of pistachio shell. Fuel 86, 1892–1899.

Asadullah, M., Rahman, M.A., Ali, M.M., Rahman, M.S., Motin, M.A., Sultan, M.B., Alam, M.R., 2007. Production of bio-oil from fixed bed pyrolysis of bagasse. Fuel 86, 2514–2520.

Ateş, F., Pütün, E., Pütün, A.E., 2004. Fast pyrolysis of sesame stalk: yields and structural analysis of bio-oil. J. Anal. Appl. Pyrolysis 71, 779–790.

Aziz, N.S. binti A., Nor, M.A. bin M., Manaf, S.F. binti A., Hamzah, F., 2015. Suitability of Biochar Produced from Biomass Waste as Soil Amendment. Procedia - Soc. Behav. Sci. 195, 2457–2465.

Azizi, K., Keshavarz Moraveji, M., Abedini Najafabadi, H., 2018. A review on bio-fuel production from microalgal biomass by using pyrolysis method. Renew. Sustain. Energy Rev. 82, 3046–3059.

Bach, Q.-V., Skreiberg, Ø., 2016. Upgrading biomass fuels via wet torrefaction: A review and comparison with dry torrefaction. Renew. Sustain. Energy Rev. 54, 665–677.

Bach, Q.-V., Tran, K.-Q., Skreiberg, Ø., Khalil, R.A., 2014. Effects of CO2 on Wet Torrefaction of Biomass. Energy Procedia 61, 1200–1203.

Bach, Q.-V., Tran, K.-Q., Skreiberg, Ø., Trinh, T.T., 2015. Effects of wet torrefaction on pyrolysis of woody biomass fuels. Energy 88, 443–456.

Barta-Rajnai, E., Wang, L., Sebestyén, Z., Barta, Zs., Khalil, R., Skreiberg, Ø., Grønli, M., Jakab, E., Czégény, Z., 2017. Effect of Temperature and Duration of Torrefaction on the Thermal Behavior of Stem Wood, Bark, and Stump of Spruce. Energy Procedia 105, 551–556.

Bartocci, P., Bidini, G., Asdrubali, F., Beatrice, C., Frusteri, F., Fantozzi, F., 2018. Batch pyrolysis of pellet made of biomass and crude glycerol: Mass and energy balances. Renew. Energy 124, 172–179.

Basu, P., 2010. Pyrolysis and Torrefaction, in: Biomass Gasification Design Handbook. Elsevier, pp. 65–96.

Bhutto, A.W., Qureshi, K., Harijan, K., Abro, R., Abbas, T., Bazmi, A.A., Karim, S., Yu, G., 2017. Insight into progress in pre-treatment of lignocellulosic biomass. Energy 122, 724–745.

Biswas, B., Pandey, N., Bisht, Y., Singh, R., Kumar, J., Bhaskar, T., 2017. Pyrolysis of agricultural biomass residues: Comparative study of corn cob, wheat straw, rice straw and rice husk. Bioresour. Technol. 237, 57–63.

Bridgwater, A.V., 2012. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy 38, 68–94.

Bridgwater, A.V., Meier, D., Radlein, D., 1999. An overview of fast pyrolysis of biomass. Org. Geochem. 30, 1479–1493.

Cao, Q., 2004. Pyrolytic behavior of waste corn cob. Bioresour. Technol. 94, 83–89.

Carone, M.T., Pantaleo, A., Pellerano, A., 2011. Influence of process parameters and biomass characteristics on the durability of pellets from the pruning residues of Olea europaea L. Biomass Bioenergy 35, 402–410.

Castro, Z.S., Gauthier-Maradei, P., Hernández, H.E., 2013. Effect of particle size and humidity on sugarcane bagasse combustion in a fixed bed furnace 26, 73–85.

Chaney, J.O., 2010. Combustion characteristics of biomass briquettes. University of Nottingham.

Chang, S., Zhao, Z., Zheng, A., He, F., Huang, Z., Li, H., 2012. Characterization of Products from Torrefaction of Sprucewood and Bagasse in an Auger Reactor. Energy Fuels 26, 7009–7017.

Chen, C., Ma, X., He, Y., 2012. Co-pyrolysis characteristics of microalgae Chlorella vulgaris and coal through TGA. Bioresour. Technol. 117, 264–273.

Chen, D., Gao, A., Ma, Z., Fei, D., Chang, Y., Shen, C., 2018. In-depth study of rice husk torrefaction: Characterization of solid, liquid and gaseous products, oxygen migration and energy yield. Bioresour. Technol. 253, 148–153.

Chen, D., Zheng, Z., Fu, K., Zeng, Z., Wang, J., Lu, M., 2015. Torrefaction of biomass stalk and its effect on the yield and quality of pyrolysis products. Fuel 159, 27–32.

Chen, L., Xing, L., Han, L., 2009. Renewable energy from agro-residues in China: Solid biofuels and biomass briquetting technology. Renew. Sustain. Energy Rev. 13, 2689–2695.

Chen, W.-H., Liu, S.-H., Juang, T.-T., Tsai, C.-M., Zhuang, Y.-Q., 2015. Characterization of solid and liquid products from bamboo torrefaction. Appl. Energy 160, 829–835.

Chen, Yen-Hau, Chang, C.-C., Chang, C.-Y., Yuan, M.-H., Ji, D.-R., Shie, J.-L., Lee, C.-H., Chen, Yi-Hung, Chang, W.-R., Yang, T.-Y., Hsu, T.-C., Huang, M., Wu, C.-H., Lin, F.-C., Ko, C.-H., 2017. Production of a solid bio-fuel from waste bamboo chopsticks by torrefaction for cofiring with coal. J. Anal. Appl. Pyrolysis 126, 315–322.

Chew, J.J., Doshi, V., 2011. Recent advances in biomass pretreatment – Torrefaction fundamentals and technology. Renew. Sustain. Energy Rev. 15, 4212–4222.

Chhabra, V., Shastri, Y., Bhattacharya, S., 2016. Kinetics of Pyrolysis of Mixed Municipal Solid Waste-A Review. Procedia Environ. Sci. 35, 513–527.

Chin, O.C., Siddiqui, K.M., 2000. Characteristics of some biomass briquettes prepared under modest die pressures. Biomass Bioenergy 18, 223–228.

Chin Yee Sing, M. Shiraz Aris, 2013. A Study of Biomass Fuel Briquettes from Palm Oil Mill Residues. Asian J. Sci. Res. 6, 537–545.

Choi, H.S., Choi, Y.S., Park, H.C., 2012. Fast pyrolysis characteristics of lignocellulosic biomass with varying reaction conditions. Renew. Energy 42, 131–135.

Chou, C.-S., Lin, S.-H., Lu, W.-C., 2009. Preparation and characterization of solid biomass fuel made from rice straw and rice bran. Fuel Process. Technol. 90, 980–987.

Choudhury, N.D., Chutia, R.S., Bhaskar, T., Kataki, R., 2014. Pyrolysis of jute dust: effect of reaction parameters and analysis of products. J. Mater. Cycles Waste Manag. 16, 449–459.

Colin, B., Dirion, J.-L., Arlabosse, P., Salvador, S., 2017. Quantification of the torrefaction effects on the grindability and the hygroscopicity of wood chips. Fuel 197, 232–239.

Collard, F.-X., Blin, J., 2014. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. Renew. Sustain. Energy Rev. 38, 594–608.

Czajczyńska, D., Nannou, T., Anguilano, L., Krzyżyńska, R., Ghazal, H., Spencer, N., Jouhara, H., 2017. Potentials of pyrolysis processes in the waste management sector. Energy Procedia 123, 387–394.

Damartzis, Th., Vamvuka, D., Sfakiotakis, S., Zabaniotou, A., 2011. Thermal degradation studies and kinetic modeling of cardoon (Cynara cardunculus) pyrolysis using thermogravimetric analysis (TGA). Bioresour. Technol. 102, 6230–6238.

Danjuma, M.N., Maiwada, B., Tukur, R., 2013. Disseminating Biomass Briquetting Technology in Nigeria: A case for Briquettes Production Initiatives in Katsina State. Int. J. Emerg. Technol. Adv. Eng. 3, 12–20.

Debdoubi, A., El amarti, A., Colacio, E., Blesa, M.J., Hajjaj, L.H., 2006. The effect of heating rate on yields and compositions of oil products from esparto pyrolysis. Int. J. Energy Res. 30, 1243–1250.

Deepak, K.B., Jnanesh, N.A., 2015. Investigation of Areca Leaves as a Biomass Fuel by the Method of Briquetting. IPASJ Int. J. Mech. Eng. IIJME 3, 1–7.

Demiral, İ., Eryazıcı, A., Şensöz, S., 2012. Bio-oil production from pyrolysis of corncob (Zea mays L.). Biomass Bioenergy 36, 43–49.

Demirbaş, A, 1999. Physical properties of briquettes from waste paper and wheat straw mixtures. Energy Convers. Manag. 40, 437–445.

Demirbaş, Ayhan, 1999. Properties of charcoal derived from hazelnut shell and the production of briquettes using pyrolytic oil. Energy 24, 141–150.

Demirbas, A., Arin, G., 2002. An Overview of Biomass Pyrolysis. Energy Sources 24, 471–482.

Demirbas, A., Sahin-Demirbas, A., 2004. Briquetting Properties of Biomass Waste Materials. Energy Sources 26, 83–91.

Devanand Maski, Matthew Darr, Robert Anex, 2010. Torrefaction of Cellulosic Biomass Upgrading - Energy and Cost Model, in: 2010 Pittsburgh, Pennsylvania, June 20 - June 23, 2010. Presented at the 2010 Pittsburgh, Pennsylvania, June 20 - June 23, 2010, American Society of Agricultural and Biological Engineers.

Donar, Y.O., Çağlar, E., Sınağ, A., 2016. Preparation and characterization of agricultural waste biomass based hydrochars. Fuel 183, 366–372.

Du, C., Wu, J., Ma, D., Liu, Y., Qiu, P., Qiu, R., Liao, S., Gao, D., 2015. Gasification of corn cob using non-thermal arc plasma. Int. J. Hydrog. Energy 40, 12634–12649.

Electricity Regulatory Authority (ERA), 2018a. Annual Report 2016-2017. Electrcity Regulatory Authority, Kampala, Uganda.

Electricity Regulatory Authority (ERA), 2018b. Energy generated to national grid. Kampala, Uganda.

El-Sayed, S.A., Khairy, M., 2015. Effect of heating rate on the chemical kinetics of different biomass pyrolysis materials. Biofuels 6, 157–170.

Emerhi, E. A, 2011. Physical and combustion properties of briquettes produced from sawdust of three hardwood species and different organic binders. Adv. Appl. Sci. Res. 2, 236–246.

Faizal, H.M., Latiff, Z.A., Wahid, M.A., Darus, A.N., 2010. Physical and combustion characteristics of biomass residues from palm oil mills. New Asp. Fluid Mech. Heat Transf. Environ. Mastorakis NE V Mlad. Z Bojkovic Eds Wiley N. Y. USA ISBN 978–960.

Ferguson, H., 2012. Briquette Businesses in Uganda. Potential Briquette Enterp. GVEP Internation, London.

Fu, P., Yi, W., Bai, X., Li, Z., Hu, S., Xiang, J., 2011. Effect of temperature on gas composition and char structural features of pyrolyzed agricultural residues. Bioresour. Technol. 102, 8211–8219.

Gai, C., Zhang, Y., Chen, W.-T., Zhang, P., Dong, Y., 2013. Thermogravimetric and kinetic analysis of thermal decomposition characteristics of low-lipid microalgae. Bioresour. Technol. 150, 139–148.

Gao, P., Zhou, Y., Meng, F., Zhang, Y., Liu, Z., Zhang, W., Xue, G., 2016. Preparation and characterization of hydrochar from waste eucalyptus bark by hydrothermal carbonization. Energy 97, 238–245.

Gao, Y., Yang, Y., Qin, Z., Sun, Y., 2016. Factors affecting the yield of bio-oil from the pyrolysis of coconut shell. SpringerPlus 5, 333.

García-Maraver, A., Popov, V., Zamorano, M., 2011. A review of European standards for pellet quality. Renew. Energy 36, 3537–3540.

Garcia-Maraver, A., Rodriguez, M.L., Serrano-Bernardo, F., Diaz, L.F., Zamorano, M., 2015. Factors affecting the quality of pellets made from residual biomass of olive trees. Fuel Process. Technol. 129, 1–7.

Garcia-Perez, M., Wang, X.S., Shen, J., Rhodes, M.J., Tian, F., Lee, W.-J., Wu, H., Li, C.-Z., 2008. Fast Pyrolysis of Oil Mallee Woody Biomass: Effect of Temperature on the Yield and Quality of Pyrolysis Products. Ind. Eng. Chem. Res. 47, 1846–1854.

Gilbert, P., Ryu, C., Sharifi, V., Swithenbank, J., 2009. Effect of process parameters on pelletisation of herbaceous crops. Fuel 88, 1491–1497.

Gong, C., Lu, D., Wang, G., Tabil, T., Wang, D., 2015. Compression characteristics and energy requirement of briquettes made from a mixture of corn stover and peanut shells. BioResources 10, 5515–5531.

Goyal, H.B., Seal, D., Saxena, R.C., 2008. Bio-fuels from thermochemical conversion of renewable resources: A review. Renew. Sustain. Energy Rev. 12, 504–517.

Grover, P.D., Mishra, S.K., 1996. Biomass briquetting: technology and practices. Food and Agriculture Organization of the United Nations.

Guizani, C., Jeguirim, M., Valin, S., Limousy, L., Salvador, S., 2017. Biomass Chars: The Effects of Pyrolysis Conditions on Their Morphology, Structure, Chemical Properties and Reactivity. Energies 10, 796.

Hamidul Islam, Md., Mosharraf Hossain, Md., Abdul Momin, Md., 2014. Development of Briquette from Coir Dust and Rice Husk Blend: An Alternative Energy Source. Int. J. Renew. Energy Dev. IJRED 3.

Hao, F., Zhao, X., Ouyang, W., Lin, C., Chen, S., Shan, Y., Lai, X., 2013. Molecular Structure of Corncob-Derived Biochars and the Mechanism of Atrazine Sorption. Agron. J. 105, 773.

Haykiri-Acma, H., Yaman, S., Kucukbayrak, S., 2013. Production of biobriquettes from carbonized brown seaweed. Fuel Process. Technol. 106, 33–40.

Heo, H.S., Park, H.J., Dong, J.-I., Park, S.H., Kim, S., Suh, D.J., Suh, Y.-W., Kim, S.-S., Park, Y.-K., 2010a. Fast pyrolysis of rice husk under different reaction conditions. J. Ind. Eng. Chem. 16, 27–31.

Heo, H.S., Park, H.J., Park, Y.-K., Ryu, C., Suh, D.J., Suh, Y.-W., Yim, J.-H., Kim, S.-S., 2010b. Bio-oil production from fast pyrolysis of waste furniture sawdust in a fluidized bed. Bioresour. Technol. 101, S91–S96.

Hosseini Koupaie, E., Dahadha, S., Bazyar Lakeh, A.A., Azizi, A., Elbeshbishy, E., 2018. Enzymatic pretreatment of lignocellulosic biomass for enhanced biomethane production-A review. J. Environ. Manage.

Hu, Q., Shao, J., Yang, H., Yao, D., Wang, X., Chen, H., 2015. Effects of binders on the properties of bio-char pellets. Appl. Energy 157, 508–516.

Hu, S., Jiang, L., Wang, Y., Su, S., Sun, L., Xu, B., He, L., Xiang, J., 2015. Effects of inherent alkali and alkaline earth metallic species on biomass pyrolysis at different temperatures. Bioresour. Technol. 192, 23–30.

Huang, X., Cao, J.-P., Zhao, X.-Y., Wang, J.-X., Fan, X., Zhao, Y.-P., Wei, X.-Y., 2016. Pyrolysis kinetics of soybean straw using thermogravimetric analysis. Fuel 169, 93–98.

Huang, Y., Finell, M., Larsson, S., Wang, X., Zhang, J., Wei, R., Liu, L., 2017. Biofuel pellets made at low moisture content – Influence of water in the binding mechanism of densified biomass. Biomass Bioenergy 98, 8–14.

Idris, S.S., Rahman, N.A., Ismail, K., 2012. Combustion characteristics of Malaysian oil palm biomass, sub-bituminous coal and their respective blends via thermogravimetric analysis (TGA). Bioresour. Technol. 123, 581–591.

IEA, B., 2007. International Energy Agency (IEA) Annual 2006. UPDATE 2, 7.

Imam, T., Capareda, S., 2012. Characterization of bio-oil, syn-gas and bio-char from switchgrass pyrolysis at various temperatures. J. Anal. Appl. Pyrolysis 93, 170–177.

International Energy Agency (IEA), 2018a. Global Energy and CO2 Status Report 2017.

International Energy Agency (IEA), 2018b. Renewables 2018: Market analysis and forecast from 2018 to 2023. Internal Energy Agency.

Jahirul, M., Rasul, M., Chowdhury, A., Ashwath, N., 2012. Biofuels Production through Biomass Pyrolysis —A Technological Review. Energies 5, 4952–5001.

Jeguirim, M., Limousy, L., Dutournie, P., 2014. Pyrolysis kinetics and physicochemical properties of agropellets produced from spent ground coffee blended with conventional biomass. Chem. Eng. Res. Des. 92, 1876–1882.

Ji-lu, Z., 2007. Bio-oil from fast pyrolysis of rice husk: Yields and related properties and improvement of the pyrolysis system. J. Anal. Appl. Pyrolysis 80, 30–35.

Johansson, L.S., Tullin, C., Leckner, B., Sjövall, P., 2003. Particle emissions from biomass combustion in small combustors. Biomass Bioenergy 25, 435–446.

Josephat, M., 2018. Deforestation In Uganda: Population Increase, Forests Loss And Climate Change. Environ. Risk Assess. Remediat. 02.

Joshi, Y., Di Marcello, M., de Jong, W., 2015. Torrefaction: Mechanistic study of constituent transformations in herbaceous biomass. J. Anal. Appl. Pyrolysis 115, 353–361.

Kaliyan, N., Morey, R.V., 2010a. Natural binders and solid bridge type binding mechanisms in briquettes and pellets made from corn stover and switchgrass. Bioresour. Technol. 101, 1082–1090.

Kaliyan, N., Morey, R.V., 2010b. Densification characteristics of corn cobs. Fuel Process. Technol. 91, 559–565.

Kaliyan, N., Vance Morey, R., 2009. Factors affecting strength and durability of densified biomass products. Biomass Bioenergy 33, 337–359.

Kan, T., Strezov, V., Evan J., T., 2016. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. Renew. Sustain. Energy Rev. 57, 1126–1140.

Karkania, V., Fanara, E., Zabaniotou, A., 2012. Review of sustainable biomass pellets production – A study for agricultural residues pellets' market in Greece. Renew. Sustain. Energy Rev. 16, 1426–1436.

Karunanithy, C., Wang, Y., Muthukumarappan, K., Pugalendhi, S., 2012. Physiochemical Characterization of Briquettes Made from Different Feedstocks. Biotechnol. Res. Int. 2012, 1–12.

Kers, J., Kulu, P., Aruniit, A., Laurmaa, V., Križan, P., Šooš, L., Kask, ü, 2010. Determination of physical, mechanical and burning characteristics of polymeric waste material briquettes. Est. J. Eng. 16, 307.

Khor, A., Ryu, C., Yang, Y., Sharifi, V.N., Swithenbank, J., 2007. Straw combustion in a fixed bed combustor. Fuel 86, 152–160.

Klinghoffer, N.B., Castaldi, M.J., 2013. Gasification and pyrolysis of municipal solid waste (MSW), in: Waste to Energy Conversion Technology. Elsevier, pp. 146–176.

Kong, L., Xiong, Y., Tian, S., Li, Z., Liu, T., Luo, R., 2013. Intertwining action of additional fiber in preparation of waste sawdust for biofuel pellets. Biomass Bioenergy 59, 151–157.

Kopczyński, M., Plis, A., Zuwała, J., 2015. Thermogravimetric and kinetic analysis of raw and torrefied biomass combustion. Chem. Process Eng. 36, 209–223.

Križan, P., 2007. Research of factors influencing the quality of wood briquets. Acta Montan. Slovaca-ISSN 1335–1788.

Križan, P., Matú, M., Šooš, Ľ., Beniak, J., 2015. Behavior of Beech Sawdust during Densification into a Solid Biofuel. Energies 8, 6382–6398.

Lee, S. min, Ahn, B.J., Choi, D.H., Han, G.-S., Jeong, H.-S., Ahn, S.H., Yang, I., 2013. Effects of densification variables on the durability of wood pellets fabricated with Larix kaempferi C. and Liriodendron tulipifera L. sawdust. Biomass Bioenergy 48, 1–9.

Lela, B., Barišić, M., Nižetić, S., 2016. Cardboard/sawdust briquettes as biomass fuel: Physical–mechanical and thermal characteristics. Waste Manag. 47, 236–245.

Leontiev, A., Kichatov, B., Korshunov, A., Kiverin, A., Medvetskaya, N., Melnikova, K., 2018. Oxidative torrefaction of briquetted birch shavings in the bentonite. Energy 165, 303–313.

Li, A., Liu, H.-L., Wang, H., Xu, H.-B., Jin, L.-F., Liu, J.-L., Hu, J.-H., 2016. Effects of Temperature and Heating Rate on the Characteristics of Molded Bio-char. BioResources 11.

Li, Hanning, Chen, Q., Zhang, X., Finney, K.N., Sharifi, V.N., Swithenbank, J., 2012. Evaluation of a biomass drying process using waste heat from process industries: A case study. Appl. Therm. Eng. 35, 71–80.

Li, Hui, Liu, X., Legros, R., Bi, X.T., Jim Lim, C., Sokhansanj, S., 2012. Pelletization of torrefied sawdust and properties of torrefied pellets. Appl. Energy 93, 680–685.

Li, L., Wang, G., Wang, S., Qin, S., 2013. Thermogravimetric and kinetic analysis of energy crop Jerusalem artichoke using the distributed activation energy model. J. Therm. Anal. Calorim. 114, 1183–1189.

Li, S.-X., Chen, C.-Z., Li, M.-F., Xiao, X., 2018. Torrefaction of corncob to produce charcoal under nitrogen and carbon dioxide atmospheres. Bioresour. Technol. 249, 348–353.

Liang, Y., Cheng, B., Si, Y., Cao, D., Jiang, H., Han, G., Liu, X., 2014. Thermal decomposition kinetics and characteristics of Spartina alterniflora via thermogravimetric analysis. Renew. Energy 68, 111–117.

Lim, J.S., Abdul Manan, Z., Wan Alwi, S.R., Hashim, H., 2012. A review on utilisation of biomass from rice industry as a source of renewable energy. Renew. Sustain. Energy Rev. 16, 3084–3094.

Liu, Q., Chmely, S.C., Abdoulmoumine, N., 2017. Biomass Treatment Strategies for Thermochemical Conversion. Energy Fuels 31, 3525–3536.

Liu, Z., Hoekman, S.K., Balasubramanian, R., Zhang, F.-S., 2015. Improvement of fuel qualities of solid fuel biochars by washing treatment. Fuel Process. Technol. 134, 130–135.

Liu, Z., Liu, X., Fei, B., Jiang, Z., Cai, Z., Yu, Y., 2013. The properties of pellets from mixing bamboo and rice straw. Renew. Energy 55, 1–5.

Long, H., Li, X., Wang, H., Jia, J., 2013. Biomass resources and their bioenergy potential estimation: A review. Renew. Sustain. Energy Rev. 26, 344–352.

Malmgren, A., Riley, G., 2012. Biomass Power Generation, in: Comprehensive Renewable Energy. Elsevier, pp. 27–53.

Mamvura, T.A., Pahla, G., Muzenda, E., 2018. Torrefaction of waste biomass for application in energy production in South Africa. South Afr. J. Chem. Eng. 25, 1–12.

Mandø, M., 2013. Direct combustion of biomass, in: Biomass Combustion Science, Technology and Engineering. Elsevier, pp. 61–83.

Mani, S., Tabil, L.G., Sokhansanj, S., 2006. Specific energy requirement for compacting corn stover. Bioresour. Technol. 97, 1420–1426.

Mani, T., Murugan, P., Abedi, J., Mahinpey, N., 2010. Pyrolysis of wheat straw in a thermogravimetric analyzer: Effect of particle size and heating rate on devolatilization and estimation of global kinetics. Chem. Eng. Res. Des. 88, 952–958.

Martín-Lara, M.A., Ronda, A., Zamora, M.C., Calero, M., 2017. Torrefaction of olive tree pruning: Effect of operating conditions on solid product properties. Fuel 202, 109–117.

Matali, S., Rahman, N.A., Idris, S.S., Yaacob, N., 2017. Combustion properties, water absorption and grindability of raw/torrefied biomass pellets and Silantek coal. Presented at the ADVANCED MATERIALS FOR SUSTAINABILITY AND GROWTH: Proceedings of the 3rd Advanced Materials Conference 2016 (3rd AMC 2016), Langkawi, Malaysia, p. 100005.

Matúš, M., Križan, P., Šooš, L., Beniak, J., 2015. Effects of Initial Moisture Content on the Physical and Mechanical Properties of Norway Spruce Briquettes. World Acad. Sci. Eng. Technol. Int. J. Environ. Chem. Ecol. Geol. Geophys. Eng. 9, 1156–1162.

Mei, Y., Che, Q., Yang, Q., Draper, C., Yang, H., Zhang, S., Chen, H., 2016. Torrefaction of different parts from a corn stalk and its effect on the characterization of products. Ind. Crops Prod. 92, 26–33.

Meng, X., Sun, R., Ismail, T.M., Zhou, W., Ren, X., Zhang, R., 2018. Parametric studies on corn straw combustion characteristics in a fixed bed: Ash and moisture content. Energy 158, 192–203.

Meng, X., Sun, R., Ismail, T.M., Zhou, W., Ren, X., Zhang, R., 2017. Parametric studies on corn combustion characteristics in a fixed bed: Primary air flow rate and different corn lengths. Appl. Therm. Eng. 126, 702–716.

Ministry of Energy and Mineral Development (MEMD), 2007. The Renewable Energy Policy for Uganda. Minist. Energy Miner. Dev. Kampala Uganda 1–128.

Miranda, T., Montero, I., Sepúlveda, F., Arranz, J., Rojas, C., Nogales, S., 2015. A Review of Pellets from Different Sources. Materials 8, 1413–1427.

Mitchual, J.S., Frimpong-Mensah, K., Darkwa, N.A., 2013. Effect of species, particle size and compacting pressure on relaxed density and compressive strength of fuel briquettes. Int. J. Energy Environ. Eng. 1–6.

Mohamed, A.R., Hamzah, Z., Daud, M.Z.M., Zakaria, Z., 2013. The Effects of Holding Time and the Sweeping Nitrogen Gas Flowrates on the Pyrolysis of EFB using a Fixed–Bed Reactor. Procedia Eng. 53, 185–191.

Mohammed, T.I., Olugbade, T.O., 2015. Burning Rate of Briquettes Produced from Rice Bran and Palm Kernel Shells. Int. J. Mater. Sci. Innov. 3, 68–73.

Mohan, D., Pittman, C.U., Steele, P.H., 2006. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. Energy Fuels 20, 848–889.

Monedero, E., Portero, H., Lapuerta, M., 2015. Pellet blends of poplar and pine sawdust: Effects of material composition, additive, moisture content and compression die on pellet quality. Fuel Process. Technol. 132, 15–23.

Moreno, A.I., Font, R., Conesa, J.A., 2016. Physical and chemical evaluation of furniture waste briquettes. Waste Manag. 49, 245–252. Muazu, R.I., Stegemann, J.A., 2015. Effects of operating variables on durability of fuel briquettes from rice husks and corn cobs. Fuel Process. Technol. 133, 137–145.

Mullen, C.A., Boateng, A.A., 2008. Chemical Composition of Bio-oils Produced by Fast Pyrolysis of Two Energy Crops †. Energy Fuels 22, 2104–2109.

Mullen, C.A., Boateng, A.A., Goldberg, N.M., Lima, I.M., Laird, D.A., Hicks, K.B., 2010. Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis. Biomass Bioenergy 34, 67–74.

Mwampamba, T.H., Owen, M., Pigaht, M., 2013. Opportunities, challenges and way forward for the charcoal briquette industry in Sub-Saharan Africa. Energy Sustain. Dev. 17, 158–170.

My, G., H, B., L, E.M., A, M., A, A., K, E. harfi, A, H., 2017. Utilization of Starink Approach and Avrami Theory to Evaluate the Kinetic Parameters of the Pyrolysis of Olive Mill Solid Waste and Olive Mill Wastewater. J. Adv. Chem. Eng. 07.

Mythili, R., Venkatachalam, P., 2015. Product Yield and Characteristics of Char. Energy Sources Part Recovery Util. Environ. Eff. 37, 2632–2638.

Naik, S.N., Goud, V.V., Rout, P.K., Dalai, A.K., 2010. Production of first and second generation biofuels: A comprehensive review. Renew. Sustain. Energy Rev. 14, 578–597.

Ndindeng, S.A., Mbassi, J.E.G., Mbacham, W.F., Manful, J., Graham-Acquaah, S., Moreira, J., Dossou, J., Futakuchi, K., 2015. Quality optimization in briquettes made from rice milling by-products. Energy Sustain. Dev. 29, 24–31.

Ngusale, G.K., Luo, Y., Kiplagat, J.K., 2014. Briquette making in Kenya: Nairobi and peri-urban areas. Renew. Sustain. Energy Rev. 40, 749–759. https://doi.org/10.1016/j.rser.2014.07.206

Nhuchhen, D., Basu, P., Acharya, B., 2014. A Comprehensive Review on Biomass Torrefaction. Int. J. Renew. Energy Biofuels 1–56.

Nikolaisen, L.S., Jensen, P.D., 2013. Biomass feedstocks: categorisation and preparation for combustion and gasification, in: Biomass Combustion Science, Technology and Engineering. Elsevier, pp. 36–57.

Ninduangdee, P., Kuprianov, V.I., Cha, E.Y., Kaewrath, R., Youngyuen, P., Atthawethworawuth, W., 2015. Thermogravimetric Studies of Oil Palm Empty Fruit Bunch and Palm Kernel Shell: TG/DTG Analysis and Modeling. Energy Procedia 79, 453–458.

Nocera, F., Gagliano, A., Patania, F., Bruno, M., Scirè, S., 2016. Slow pyrolysis kinetics of apricots stones by thermogravimetric analysis, in: Renewable Energy Congress (IREC), 2016 7th International. IEEE, pp. 1–6.

Nunes, L.J.R., Matias, J.C.O., Catalão, J.P.S., 2014. Mixed biomass pellets for thermal energy production: A review of combustion models. Appl. Energy 127, 135–140.

Nyakuma, B.B., 2015. Thermogravimetric and Kinetic Analysis of Melon (Citrullus colocynthis L.) Seed Husk Using the Distributed Activation Energy Model. Environ. Clim. Technol. 15, 77–89.

Obernberger, I., Brunner, T., Barnthaler, G., 2006. Chemical properties of solid biofuels—significance and impact. Biomass Bioenergy 30, 973–982.

Obernberger, I., Thek, G., 2004. Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. Biomass Bioenergy 27, 653–669.

Obi, O.F., 2015. Evaluation of the physical properties of composite briquette of sawdust and palm kernel shell. Biomass Convers. Biorefinery 5, 271–277.

Obi, O.F., Adeboye, B.S., Aneke, N.N., 2014. Biomass briquetting and rural development in Nigeria. Int J Sci Env. Technol 3, 1043–1052.

Obi, O.F., Okongwu, K.C., 2016. Characterization of fuel briquettes made from a blend of rice husk and palm oil mill sludge. Biomass Convers. Biorefinery 6, 449–456.

Ogunjobi, K.J., Lajide, L. (Eds.), 2013. Characterisation of Bio-Oil and Bio-Char from Slow-Pyrolysed Nigerian Yellow and White Corn Cobs. J. Sustain. Energy Environ. 4, 77–84.

Okello, C., Pindozzi, S., Faugno, S., Boccia, L., 2013a. Development of bioenergy technologies in Uganda: A review of progress. Renew. Sustain. Energy Rev. 18, 55–63.

Okello, C., Pindozzi, S., Faugno, S., Boccia, L., 2013b. Bioenergy potential of agricultural and forest residues in Uganda. Biomass Bioenergy 56, 515–525.

Oladeji, J.T., 2015. Theoretical Aspects of Biomass Briquetting: A Review Study. J. Energy Technol. Policy 5, 72–81.

Onay, O., Kockar, O.M., 2003. Slow, fast and flash pyrolysis of rapeseed. Renew. Energy 28, 2417–2433.

Özçimen, D., Ersoy-Meriçboyu, A., 2010. Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials. Renew. Energy 35, 1319–1324.

Özçimen, D., Karaosmanoğlu, F., 2004. Production and characterization of bio-oil and biochar from rapeseed cake. Renew. Energy 29, 779–787.

Pahla, G., Ntuli, F., Muzenda, E., 2018. Torrefaction of landfill food waste for possible application in biomass co-firing. Waste Manag. 71, 512–520.

Panwar, V., Prasad, B., Wasewar, K.L., 2010. Biomass residue briquetting and characterization. J. Energy Eng. 137, 108–114.

Park, Y.-K., Yoo, M.L., Lee, H.W., Park, S.H., Jung, S.-C., Park, S.-S., Kim, S.-C., 2012. Effects of operation conditions on pyrolysis characteristics of agricultural residues. Renew. Energy 42, 125–130.

Peng, W., Wu, Q., Tu, P., 2000. Effects of temperature and holding time on production of renewable fuels from pyrolysis of Chlorella protothecoides. J. Appl. Phycol. 147–152.

Phan, A.N., Ryu, C., Sharifi, V.N., Swithenbank, J., 2008. Characterisation of slow pyrolysis products from segregated wastes for energy production. J. Anal. Appl. Pyrolysis 81, 65–71.

Porteiro, J., Patiño, D., Collazo, J., Granada, E., Moran, J., Miguez, J.L., 2010. Experimental analysis of the ignition front propagation of several biomass fuels in a fixed-bed combustor. Fuel 89, 26–35.

Poudel, J., Ohm, T.-I., Lee, S.-H., Oh, S.C., 2015a. A study on torrefaction of sewage sludge to enhance solid fuel qualities. Waste Manag. 40, 112–118.

Poudel, J., Ohm, T.-I., Oh, S.C., 2015b. A study on torrefaction of food waste. Fuel 140, 275–281.

Prasityousil, J., Muenjina, A., 2013. Properties of Solid Fuel Briquettes Produced from Rejected Material of Municipal Waste Composting. Procedia Environ. Sci. 17, 603–610.

Pütün, A.E., Uzun, B.B., Apaydin, E., Pütün, E., 2005. Bio-oil from olive oil industry wastes: Pyrolysis of olive residue under different conditions. Fuel Process. Technol. 87, 25–32.

Rabier, F., Temmerman, M., Bohm, T., Hartmann, H., Daugbjergjensen, P., Rathbauer, J., Carrasco, J., Fernandez, M., 2006. Particle density determination of pellets and briquettes. Biomass Bioenergy 30, 954–963.

Rahaman, S.A., Salam, P.A., 2017. Characterization of cold densified rice straw briquettes and the potential use of sawdust as binder. Fuel Process. Technol. 158, 9–19.

Raheem, A., Wan Azlina, W.A.K.G., Taufiq Yap, Y.H., Danquah, M.K., Harun, R., 2015. Thermochemical conversion of microalgal biomass for biofuel production. Renew. Sustain. Energy Rev. 49, 990–999.

Rajaseenivasan, T., Srinivasan, V., Syed Mohamed Qadir, G., Srithar, K., 2016. An investigation on the performance of sawdust briquette blending with neem powder. Alex. Eng. J. 55, 2833–2838.

Raveendran, K., Ganesh, A., 1996. Heating value of biomass and biomass pyrolysis products. Fuel 75, 1715–1720.

Razuan, R., Finney, K.N., Chen, Q., Sharifi, V.N., Swithenbank, J., 2011. Pelletised fuel production from palm kernel cake. Fuel Process. Technol. 92, 609–615. 8

Recari, J., Berrueco, C., Abelló, S., Montané, D., Farriol, X., 2014. Effect of temperature and pressure on characteristics and reactivity of biomass-derived chars. Bioresour. Technol. 170, 204–210.

Rehrah, D., Bansode, R.R., Hassan, O., Ahmedna, M., 2016. Physico-chemical characterization of biochars from solid municipal waste for use in soil amendment. J. Anal. Appl. Pyrolysis 118, 42–53.

Rhén, C., Gref, R., Sjöström, M., Wästerlund, I., 2005. Effects of raw material moisture content, densification pressure and temperature on some properties of Norway spruce pellets. Fuel Process. Technol. 87, 11–16.

Ronsse, F., van Hecke, S., Dickinson, D., Prins, W., 2013. Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. GCB Bioenergy 5, 104–115.

Rosillo-Calle, F., Peter de Groovt, Sarah L. Hemstock, Jeremy Woods, 2007. The biomass handbook: bioenergy for sustainable environment. TJ International Ltd, Padstrow, UK.

Roy, M.M., Corscadden, K.W., 2012. An experimental study of combustion and emissions of biomass briquettes in a domestic wood stove. Appl. Energy 99, 206–212.

Rubio, B., Izquierdo, M.T., Segura, E., 1999. Effect of binder addition on the mechanical and physicochemical properties of low rank coal char briquettes. Carbon 37, 1833–1841.

Ruiz, H.A., Cerqueira, M.A., Silva, H.D., Rodríguez-Jasso, R.M., Vicente, A.A., Teixeira, J.A., 2013. Biorefinery valorization of autohydrolysis wheat straw hemicellulose to be applied in a polymer-blend film. Carbohydr. Polym. 92, 2154–2162.

Rukthong, W., Thanatawee, P., Sunphorka, S., Piumsomboon, P., Chalermsinsuwan, B., 2015. Computation of Biomass Combustion Characteristic and Kinetic Parameters by using Thermogravimetric Analysis. Eng. J. 19, 41–57.

Ryu, C., Yang, Y.B., Khor, A., Yates, N.E., Sharifi, V.N., Swithenbank, J., 2006. Effect of fuel properties on biomass combustion: Part I. Experiments—fuel type, equivalence ratio and particle size. Fuel 85, 1039–1046.

Saber, M., Nakhshiniev, B., Yoshikawa, K., 2016. A review of production and upgrading of algal bio-oil. Renew. Sustain. Energy Rev. 58, 918–930.

Saikia, P., Gupta, U.N., Barman, R.S., Kataki, R., Chutia, R.S., Baruah, B.P., 2015. Production and Characterization of Bio-Oil Produced from Ipomoea carnea Bio-Weed. BioEnergy Res. 8, 1212–1223.

Salema, A.A., Afzal, M.T., Bennamoun, L., 2017. Pyrolysis of corn stalk biomass briquettes in a scaled-up microwave technology. Bioresour. Technol. 233, 353–362.

Samuel Tusingwire, 2013. Investigation of the thermal energy potential of some biomass residues as a potential domestic energy source. Mbarara University of Science and Technology, Uganda.

Samuli, R., Henrik, H., Tiina, M., Kaisa, K., Sanna, S., 2014. Wood chip drying in connection with combined heat and power or solar energy in Finland. EPJ Web Conf. 9.

Sánchez, M.E., Lindao, E., Margaleff, D., Martínez, O., Morán, A., 2009. Pyrolysis of agricultural residues from rape and sunflowers: Production and characterization of bio-fuels and biochar soil management. J. Anal. Appl. Pyrolysis 85, 142–144.

Şensöz, S., Can, M., 2002. Pyrolysis of Pine (Pinus Brutia Ten.) Chips: 1. Effect of Pyrolysis Temperature and Heating Rate on the Product Yields. Energy Sources 24, 347–355.

Şensöz, S., Kaynar, İ., 2006. Bio-oil production from soybean (Glycine max L.); fuel properties of Bio-oil. Ind. Crops Prod. 23, 99–105.

Shah, A., Darr, M.J., Dalluge, D., Medic, D., Webster, K., Brown, R.C., 2012. Physicochemical properties of bio-oil and biochar produced by fast pyrolysis of stored single-pass corn stover and cobs. Bioresour. Technol. 125, 348–352.

Shankar, N.S., Prakash, D.J., Nagabhushan, E., 2012. Studies onBriquetting and Characterization of Coke Oven Sludge. Int. J. Eng. Trends Technol. 3, 698–701.

Shariff, A., Noor Mohamed, N., Lau, A., Ali Azwan Mohd, M., 2016. A comparative study on biochar from slow pyrolysis of corn cob and cassava wastes. World Acad. Sci. Eng. Technol. Int. J. Biotechnol. Bioeng. 10, 767–771.

Sharma, A., Pareek, V., Zhang, D., 2015. Biomass pyrolysis—A review of modelling, process parameters and catalytic studies. Renew. Sustain. Energy Rev. 50, 1081–1096. https://doi.org/10.1016/j.rser.2015.04.193

Shen, J., Wang, X.-S., Garcia-Perez a, M., Mourant, D., Rhodes, J.M., Li, C.-Z., 2009. Effects of particle size on the fast pyrolysis of oil mallee woody biomass. Fuel 88, 1810–1817.

Shi-Xiang Zhao, Na Ta, Xu-Dong Wang, 2017. Effect of Temperature on the Structural and Physicochemical Properties of Biochar with Apple Tree Branches as Feedstock Material. Energies 10, 1293.

Slopiecka, K., Bartocci, P., Fantozzi, F., 2012. Thermogravimetric analysis and kinetic study of poplar wood pyrolysis. Appl. Energy 97, 491–497.

Sotannde, O.A., Oluyege, A.O., Abah, G.B., 2010. Physical and combustion properties of briquettes from sawdust of Azadirachta indica. J. For. Res. 21, 63–67.

Stelte, W., Clemons, C., Holm, J.K., Ahrenfeldt, J., Henriksen, U.B., Sanadi, A.R., 2012. Fuel Pellets from Wheat Straw: The Effect of Lignin Glass Transition and Surface Waxes on Pelletizing Properties. BioEnergy Res. 5, 450–458.

Stolarski, M.J., Szczukowski, S., Tworkowski, J., Krzyżaniak, M., Gulczyński, P., Mleczek, M., 2013. Comparison of quality and production cost of briquettes made from agricultural and forest origin biomass. Renew. Energy 57, 20–26.

Suhartini, S., Hidayat, N., Wijaya, S., 2011. Physical properties characterization of fuel briquette made from spent bleaching earth. Biomass Bioenergy 35, 4209–4214.

Suliman, W., Harsh, J.B., Abu-Lail, N.I., Fortuna, A.-M., Dallmeyer, I., Garcia-Perez, M., 2016. Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties. Biomass Bioenergy 84, 37–48.

Tabil, L., Adapa, P., Kashaninejad, M., 2011. Biomass feedstock pre-processing–part 1: pre-treatment, in: Biofuel's Engineering Process Technology. InTech.

Temmerman, M., Rabier, F., Jensen, P., Hartmann, H., Bohm, T., 2006. Comparative study of durability test methods for pellets and briquettes. Biomass Bioenergy 30, 964–972.

Toscano, G., Pizzi, A., Foppa Pedretti, E., Rossini, G., Ciceri, G., Martignon, G., Duca, D., 2015. Torrefaction of tomato industry residues. Fuel 143, 89–97.

Tumuluru, J.S., Tabil, L.G., Song, Y., Iroba, K.L., Meda, V., 2015. Impact of process conditions on the density and durability of wheat, oat, canola, and barley straw briquettes. BioEnergy Res. 8, 388–401.

Tumuluru, J.S., Wright, C.T., Hess, J.R., Kenney, K.L., 2011. A review of biomass densification systems to develop uniform feedstock commodities for bioenergy application. Biofuels Bioprod. Biorefining 5, 683–707.

Uemura, Y., Omar, W.N., Tsutsui, T., Yusup, S.B., 2011. Torrefaction of oil palm wastes. Fuel 90, 2585–2591.

Uganda Bureau of Statistics (UBOS), 2016. The National Population and Housing Census 2014- Main Report. Kampala, Uganda.

Umogbai, V.I., Iorter, H.A., 2013. Experimental Evaluation of the Performance of a Prototype Solar Dryer Box. Afr. J. Food Sci. Technol. 4, 110–115.

Uzun, B.B., Pütün, A.E., Pütün, E., 2007. Composition of products obtained via fast pyrolysis of olive-oil residue: Effect of pyrolysis temperature. J. Anal. Appl. Pyrolysis 79, 147–153.

Vamvuka, D., Sfakiotakis, S., 2011. Combustion behaviour of biomass fuels and their blends with lignite. Thermochim. Acta 526, 192–199.

Wakchaure, G.C., Mani, I., 2011. Thermal and Storage Characteristics of Biomass Briquettes with Organic Binders. J. Agric. Eng. 48, 43–53.

Wang, S., Lin, H., Ru, B., Dai, G., Wang, X., Xiao, G., Luo, Z., 2016. Kinetic modeling of biomass components pyrolysis using a sequential and coupling method. Fuel 185, 763–771.

Wang, Y., Wu, Q., Dai, L., Zeng, Z., Liu, Y., Ruan, R., Fu, G., Yu, Z., Jiang, L., 2018. Co-pyrolysis of wet torrefied bamboo sawdust and soapstock. J. Anal. Appl. Pyrolysis 132, 211–216.

Wannapeera, J., Fungtammasan, B., Worasuwannarak, N., 2011. Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass. J. Anal. Appl. Pyrolysis 92, 99–105.

Wei, L., Xu, S., Zhang, L., Zhang, H., Liu, C., Zhu, H., Liu, S., 2006. Characteristics of fast pyrolysis of biomass in a free fall reactor. Fuel Process. Technol. 87, 863–871.

Werther, J., Saenger, M., Hartge, E.-U., Ogada, T., Siagi, Z., 2000. Combustion of agricultural residues. Prog. Energy Combust. Sci. 27.

White, J.E., Catallo, W.J., Legendre, B.L., 2011. Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies. J. Anal. Appl. Pyrolysis 91, 1–33.

Widell, H., 2013. Industrial-scale biomass combustion plants: engineering issues and operation, in: Biomass Combustion Science, Technology and Engineering. Elsevier, pp. 225–277.

Wilaipon, P., 2009. The Effects of Briquetting Pressure on Banana-Peel Briquette and the Banana Waste in Northern Thailand. Am. J. Appl. Sci. 6, 167–171.

Williams, A., Jones, J.M., Ma, L., Pourkashanian, M., 2012. Pollutants from the combustion of solid biomass fuels. Prog. Energy Combust. Sci. 38, 113–137.

Wolf, J.P., Dong, 2013. Biomass combustion for power generation: an introduction, in: Biomass Combustion Science, Technology and Engineering. Elsevier, pp. 3–8.

World Energy Council, 2016. World Energy Resources 2016.

WPAC, 2017. Global pellet market outlook in 2017. Wood Pellet Association of Canada.

Yaman, S., 2004. Pyrolysis of biomass to produce fuels and chemical feedstocks. Energy Convers. Manag. 45, 651–671.

Yaman, S., Sahan, M., Haykiri-Acma, H., Sesen, K., Kucukbayrak, S., 2001. Fuel briquettes from biomass–lignite blends. Fuel Process. Technol. 72, 1–8.

Yaman, S., Sahan, M., Haykiri-acma, H., Sesen, K., Kucukbayrak, S., 2000. Production of fuel briquettes from olive refuse and paper mill waste. Fuel Process. Technol. 68, 23–31.

Yang, H., Huang, L., Liu, S., Sun, K., Sun, Y., 2016. Pyrolysis process and characteristics of products from sawduct briquettes. BioResources 11, 2438–2456.

Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86, 1781–1788.

Yanik, J., Kornmayer, C., Saglam, M., Yüksel, M., 2007. Fast pyrolysis of agricultural wastes: Characterization of pyrolysis products. Fuel Process. Technol. 88, 942–947.

Yank, A., Ngadi, M., Kok, R., 2016. Physical properties of rice husk and bran briquettes under low pressure densification for rural applications. Biomass Bioenergy 84, 22–30.

Yi, Q., Qi, F., Cheng, G., Zhang, Y., Xiao, B., Hu, Z., Liu, S., Cai, H., Xu, S., 2013. Thermogravimetric analysis of co-combustion of biomass and biochar. J. Therm. Anal. Calorim. 112, 1475–1479.

Yip, K., Wu, H., Zhang, D., 2007. Pyrolysis of Collie Coal Briquettes To Produce Char as a Metallurgical Reductant †. Energy Fuels 21, 419–425.

Yorgun, S., Yıldız, D., 2015. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization. J. Anal. Appl. Pyrolysis 114, 68–78.

Yumak, H., Ucar, T., Seyidbekiroglu, N., 2010. Briquetting soda weed (Salsola tragus) to be used as a rural fuel source. Biomass Bioenergy 34, 630–636.

Zafari, A., Kianmehr, M.H., 2014. Factors affecting mechanical properties of biomass pellet from compost. Environ. Technol. 35, 478–486.

Zainuddin, M.F., Rosnah, S., Noriznan, M.M., Dahlan, I., 2014. Effect of Moisture Content on Physical Properties of Animal Feed Pellets from Pineapple Plant Waste. Agric. Agric. Sci. Procedia 2, 224–230.

Zhang, J., Guo, Y., 2014. Physical properties of solid fuel briquettes made from Caragana korshinskii Kom. Powder Technol. 256, 293–299.

Zhang, L., Xu, C. (Charles), Champagne, P., 2010. Overview of recent advances in thermo-chemical conversion of biomass. Energy Convers. Manag. 51, 969–982.

Zhang, S., Dong, Q., Zhang, L., Xiong, Y., Liu, X., Zhu, S., 2015. Effects of water washing and torrefaction pretreatments on rice husk pyrolysis by microwave heating. Bioresour. Technol. 193, 442–448.

Zhang, X., Xu, M., Sun, R., Sun, L., 2006. Study on Biomass Pyrolysis Kinetics. J. Eng. Gas Turbines Power 128, 493.

Zheng, A., Zhao, Z., Chang, S., Huang, Z., Wang, X., He, F., Li, H., 2013. Effect of torrefaction on structure and fast pyrolysis behavior of corncobs. Bioresour. Technol. 128, 370–377.

Zheng, Y., Pan, Z., Zhang, R., 2009. Overview of biomass pretreatment for cellulosic ethanol production. Biol Eng 2, 18.