

**DEVELOPMENT AND CHARACTERISATION OF
HYBRID FUEL BRIQUETTE FROM COAL SLACK
AND TORREFIED WOODY BIOMASS**

By

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CERTIFICATION

This thesis has been read and approved as meeting the requirements of the Department of Mechanical Engineering, Faculty of Engineering and Technology, University of Ilorin, Ilorin, Nigeria for the award of Doctor of Philosophy (Ph.D.) degree.

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DEDICATION

This research work is dedicated to the Almighty God, the giver of insight and inspiration.

It is also dedicated to the living and loving memory of my late younger brother; ADELEKE, Opeyemi Gold. Though you left early to your eternal home, yet your sacrifices were massive for me to complete this work. You are always remembered. Rest on WURAOLAMI.

DECLARATION

I hereby declare that this thesis is a research work carried out by me. It is an original and unpublished work that has not been presented for the award of any degree.

All quotations are distinguished by appropriate quotation marks and the sources of all information are clearly acknowledged by means of appropriate references.

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LIST OF ABBREVIATIONS AND NOTATIONS

Roman letters

A	Pre-exponential factor (min^{-1})
AFT	Ash fusion temperatures ($^{\circ}\text{C}$)
APZ	Active pyrolysis zone
CCS	Cold crushing strength (MPa)
DT	Deformation temperature ($^{\circ}\text{C}$)
E_a	Activation energy (kJ/mol)
EY	Energy yield (%)
FT	Fusion temperature ($^{\circ}\text{C}$)
HFB	Hybrid fuel briquette
HHV	Higher heating value (MJ/kg)
HR	Hybrid ratio
HT	Hemispherical temperature ($^{\circ}\text{C}$)
IRI	Impact resistance index
k	Rate constant of Arrhenius equation
MY	Mass yield (%)
NCV	Net calorific value (MJ/kg)
PPZ	Passive pyrolysis zone
R	Universal gas constant
RI	Reactivity index
RMw	Raw Melina wood
RT	Residence time (minutes)
RTw	Raw Teak wood
SF	Severity factor
ST	Softening temperature ($^{\circ}\text{C}$)
T	Temperature ($^{\circ}\text{C}$)

TT	Torrefaction temperature (°C)
TSI	Tumbling strength index (%)
WRI	Water resistance index (%)

Greek symbols

β	Heating rate (°C/min)
α	Fractional conversion ratio
ρ	Density (g/cm ³)
θ	Bragg's differential angle (°)
λ	Wavelength

ABSTRACT

Nigeria is blessed with over 2.7 billion tonnes of coal and several hectares of forest reserves. However, millions of tonnes of coal slack and wood residues (biomass) generated from coal mining and wood processing respectively, are often discarded as wastes because of near absence of processing. These wastes have enormous potentials as energy sources for both domestic and industrial applications if well processed. Therefore, the aim of this study was to develop and characterise Hybrid Fuel Briquettes (HFB) from lean grade coal fines and torrefied woody biomass using pitch, molasses and starch as binders. The objectives were to: (i) characterise coal fines and woody biomass from Teak (*Tectona grandis*) and Melina (*Gmelina aborea*); (ii) optimise and determine the effect of torrefaction conditions on the combustion properties of the woody biomass; (iii) produce HFB from coal fines and torrefied woody biomass; and (iv) evaluate the mechanical and combustion properties of the HFB.

Teak and Melina woody biomass from Benin, Edo state, and coal from Okaba mine, Kogi state were used in this study. Thermal decomposition studies were carried out on the woody biomass and Okaba coal fines in a STA7300 Thermobalance system. Each of the woody biomass samples of particle sizes 2 and 6 mm, were torrefied at temperature of 240°C and 300°C, for 30 and 60 min residence time and then characterised for their combustion properties. The HFB were produced from the coal fines and torrefied biomass aggregates using the organic binders in a hydraulic press at 14-55 MPa. The briquettes were cured in an inert environment at 200-300°C for 60-120 min. Mechanical and combustion properties of the HFB were evaluated to determine its strength and energy contents, respectively. Phase identification and chemical composition were determined using Fourier Transform Infrared Spectrophotometry, X-ray Diffractometry and X-ray Fluorescence spectrometry. Microstructural and elemental studies were also carried out using Scanning Electron Microscopy and Electron Probe Microanalysis.

The findings of the study were that:

- (i) the woody biomass (Teak and Melina) had Fixed carbon (FC), Volatile Matter (VM), ash, Higher Heating Value (HHV) in the range of 8.92 - 11.73%, 79.26 - 81.42%, 1.73 - 2.15%, 18.39 - 18.72 MJ/kg, respectively, while coal had 66.92% FC, 13.77% VM and HHV of 23.13 MJ/kg;
- (ii) optimised torrefaction conditions of the woody biomass were: particle size, 2 mm; temperature, 260°C; and residence time, 60 min, which resulted in higher FC (41-42%), lower VM (54%) and greater HHV (23 MJ/kg);
- (iii) the best formulation ratio for the HFB (coal and torrefied biomass) production was 97:3 using blend of 8% pitch and 7% molasses under 28 MPa compared with other formulations; and
- (iv) mechanical strength such as drop to fracture (200 times/2m) and cold crushing strength (11 MPa) as well as energy content (24 MJ/kg) of the HFB were higher compared with standards.

The study concluded that the HFB developed has sufficient mechanical strength with desirable combustion properties and thus can be used for energy generation. Therefore, this HFB is recommended for domestic and industrial applications.

CHAPTER 1

INTRODUCTION

1.1 Background

Energy is the bedrock of economic capacity and development of any nation (Koppejan *et al.*, 2012; Mohammed *et al.*, 2013). Since discovery, oil and gas have been largely depended upon as the major energy source in Nigeria. Overdependence of the country on oil and gas sector for foreign exchange earnings as well as generation of energy and power for industrial and domestic purposes has left other sources untapped. However, due to depletion of oil and gas reserves and its fluctuating price in the world market, government is now shifting attention to develop alternative sources of energy for domestic and industrial purposes. In addition, oil and gas are also often produced and delivered at a cost most Nigerian cannot afford. This also necessitates the need to look for more affordable and readily available alternative sources. Nigeria is blessed with other enormous and abundant energy sources such as coal, biomass, solar and wind (Aina *et al.*, 2009).

Coal is an important raw material utilized as sources of energy and reductant in metallurgical industries (Zhong *et al.*, 2017). Nigeria can boast of about 2.7 billion tonnes of coal reserves which are available in 22 coal fields that spread across 13 states of the federation as shown in Figure 1.1 (Nigerian Coal Corporation, 2009; Ofoegbu, 2016; Onuoha, 2016). These reserves have been identified to majorly contain sub-bituminous and lignite family which are lean grade non-coking coals. Exploration/mining, transportation and handling of lean grade coal (Figure 1.2a) inevitably lead to generation of large volume of slack as shown in Figure 1.2b (Massaro *et al.*, 2014; Zarringhalam-Moghaddam *et al.*, 2011). These fines are often discarded as wastes because they are difficult to handle. In addition, their physico-chemical properties do not meet the requirements to successfully function as fuel for energy generation or reductant in direct reduced iron making. Coal fines can easily be

blown away when discarded, thereby polluting the air and nearby water leading to serious environmental problems. However, if these fines are properly processed, they can be useful both as fuel for energy generation and reductant in direct reduced iron (DRI) production.



Figure 1.1: Coal location in Nigeria (Ofoegbu, 2016)

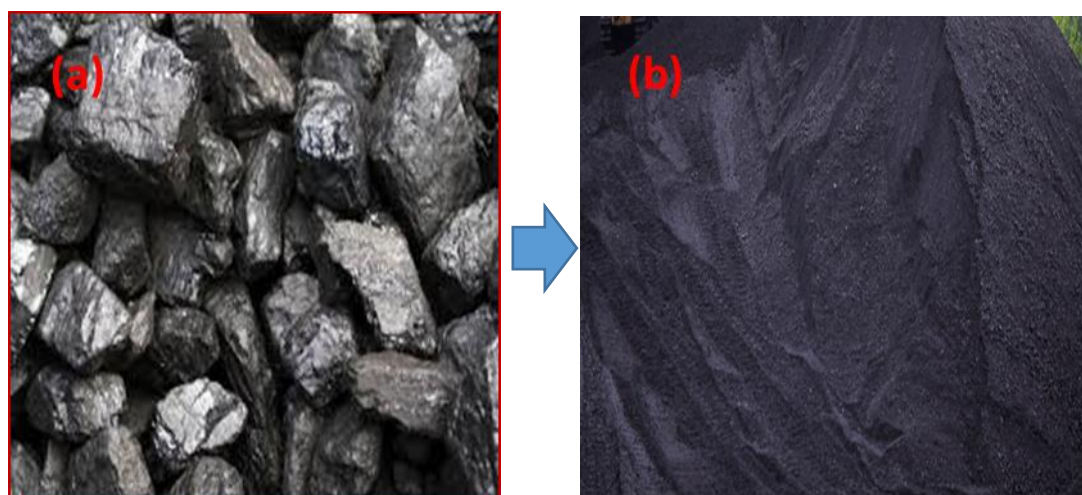


Figure 1.2: (a) Lump coal (b) Coal slack

Another abundant energy source that is readily available and renewable is biomass which can be obtained as wastes from consumption of forest reserves products in Nigeria.

Larger percentage of ever-growing population of the country have resorted to the use of forest wood as sources of fuel for agricultural, domestic and small-scale industrial activities in semi-urban and rural areas. This has led to massive deforestation which has resulted in desertification especially in the Northern part of the country. Flooding, soil erosion and loss of top soil fertility are also some of the consequences of deforestation in the Southern part of the country. Wild life extinction is a further complication and outcome of the dependence on forest wood (Mohammed *et al.*, 2013). Processing of wood for usage in different areas of applications leads to generation of voluminous amount of waste which are often disposed in unhealthy ways such as open burning (Figure 1.3). Dosunmu and Ajayi (2002) estimated the wood wastes generated in Lagos to be 267,436 tons annually while Kuye and Edeh (2013) estimated the agro-forest waste generated annually in Nigeria to be 13 million tons. Rather than felling of trees, wood wastes can be useful as fuel if properly processed for energy generation and DRI production. Biomass has found application in iron making sector for smelting process, feedstock to produce biofuel pellets and co-firing with coal for power generation (Maslejova, 2013; Nathan *et al.*, 2015; Nilsson *et al.*, 2011; Raju & Madhu, 2014; Ståhl & Berghel, 2011). Biomass such as rice husk, palm fibers and shell had been incorporated into briquetting of bituminous coal fines to reduce NO_x and SO_x released during combustion of coal (Blesa *et al.*, 2003a; Zarringhalam-Moghaddam *et al.*, 2011). Thus, biomass can be useful for development of an environmental friendly fuel that reduces the effect of global warming. However, biomass in Nigeria has earned little or no substantial research and industrial attention, thereby making it unexplored and often discarded as wastes.

Based on the advantages of biomass, it has become compelling for Nigeria and other developing nations to research into utilizing biomass wastes available within their domains for energy and metallurgical applications. Teak and Melina wood are common woody biomass species that attract massive utilization in Nigeria, thereby contributing largely to the

waste piles (Okoroigwe, 2015). However, hydrophilic nature, high oxygen content, low energy density and high moisture content (up to 60%) of woody biomass wastes are some of the limitations that must be overcome for their effective utilization for energy generation and DRI making process (Chen and Kuo 2011; Nhuchhen *et al.* 2014). Torrefaction process, an example of thermochemical methods for upgrading biomass, can be used to overcome most of the limitation of biomass.



Figure 1.3: (a) woody biomass waste (b) smoke generated during burning of woody waste.

Torrefaction process is a thermal treatment process where biomass is subjected to temperature range of 200 - 300°C in an inert or nitrogen environment (Lee *et al.*, 2012; Lasode *et al.*, 2014; Chin *et al.*, 2013). This process leads to removal of some hydroxyl groups, thereby impacting hydrophobic condition, improve energy density and grindability of biomass (Prins *et al.* 2006). Torrefaction degree of severity could be light (200 - 230°C), mild (240 - 260°C) or severe (260 - 300°C). Light torrefaction is treatment where hemicellulose is degraded leaving lignin and cellulose unaffected while cellulose is mildly affected under mild torrefaction. Severe torrefaction is characterized by depolymerisation of lignin, cellulose, as well as hemicellulose (Basu, 2013). The influence of torrefaction treatment on biomass varies based on feedstock type, feedstock properties and origin among other factors (Nhuchhen *et al.* 2014; Basu, 2013). There are limited information and research works on torrefaction of

woody biomass of Nigeria origin, thus the present study will first attempt to exclusively explore the process.

Several studies have revealed that briquettes that are suitable for domestic and thermal applications can be developed from coal slack (Mollah *et al.*, 2015; Zarringhalam-Moghaddam *et al.*, 2011). However, coal slack and biomass wastes cannot be used in the form in which they are generated especially in power plant and rotary kiln for power generation and production of DRI, respectively. Therefore, there is need for them to be well processed into briquettes or other solid forms. One of the ways to effectively process these wastes is by densification via briquetting or pelletizing, which can result into useful products suitable as fuel for energy production and iron making processes. However, industrial application of such methods to produce briquettes from lean grade coal slack-biomass wastes that meets metallurgical requirements has not been well established (Benk & Coban, 2011a; Mollah *et al.*, 2015; Taulbee *et al.*, 2009; Zarringhalam-Moghaddam *et al.*, 2011; Zhong *et al.*, 2017). Of recent, Tata steel rotary kiln (Tata Steel, 2017) section reported huge loss and high production cost of DRI due to the menace of large wastes (<3mm) from lean grade coal. It was reported that the briquettes utilized failed to retain their properties at high temperatures (>850°C) possibly due to their low cold crushing strength (<80% CCS of lump coal) resulting from poor binding effects of the binders. The mechanical strength and combustion properties of most briquettes from coal - biomass aggregates reported in the literatures were found to be significantly low (Taulbee *et al.*, 2009; Zarringhalam-Moghaddam *et al.*, 2011). This may be due to inadequate understanding of an effective way to improve the properties of biomass through pre-treatment (torrefaction) and inability to utilize appropriate binders to improve the mechanical strength and combustion properties of the briquettes. Therefore, the aim of the present study is to develop hybrid fuel briquettes with suitable mechanical and combustion

properties from lean grade coal slack and torrefied woody biomass using appropriate organic binders.

1.2 Problem statements

The increase demand for energy resulting from increasing population necessitates the need to intensify efforts in diversifying the narrow energy supply mix. Another current challenge in the country is the need for diversification of sources of power generation to improve our economy and government earnings through exploration of other available natural resources such as coal. Exploration of coal often leads to generation of substantial quantity of waste in the form of coal slack, which is being discarded yearly in million tons. Improper disposal of coal slack could result into environmental pollution apart from the huge economic and energy/metallurgical feedstock raw materials loss. One promising avenue to convert these wastes into useful product is to agglomerate them into briquette. This will not only produce useful fuel but would also offer a near-term and practical means to reduce environmental pollution. Despite previous studies, briquettes of coal-biomass aggregates that meet both energy and metallurgical applications have not been developed.

1.3 Justification of the study

The production of briquettes from coal slack and torrefied wood waste will solve environmental problems and economic wastages associated with their disposal. It will provide readily available and sustainable alternative fuel that can be used for energy generation in homes and industries as well as reductant for iron making through direct reduction route. It will also boost the economy through employment generation and improve government earnings.

1.4 Aim and objectives

The aim of this work was to develop and characterise hybrid fuel briquettes (HFB) from lean grade coal slack and torrefied woody biomass using organic binders. Therefore, the objectives were to:

- i. characterise the coal slack and woody biomass (Teak and Melina);
- ii. carry out thermal decomposition study on the coal and woody biomass;
- iii. optimise and determine the effect of torrefaction conditions on the combustion properties of the woody biomass;
- iv. produce hybrid briquette from coal slack and torrefied biomass using pitch, starch, molasses as well as their blends as binders; and
- v. evaluate the physical, mechanical, combustion and structural properties of the hybrid fuel briquettes.

1.5 Scope of the study

This work was limited to development and characterisation of briquettes from lean grade coal (non-coking coal) and torrefied woody biomass (Teak and Melina) using pitch, starch, molasses as well as their blends as organic binders.

CHAPTER 2

LITERATURE REVIEW

2.1 Coal

Coal can be defined as organic rocklike natural resources. It contains carbon combustible solid visually formed by debris decay ferns, vines, tree and other plants which flourished in swamps millions of years ago. Coal metamorphosed into different types through coalition or lithification process. The different types are peat (precursor of coal), lignite, sub-bituminous, bituminous and anthracites. Anthracite is the highest ranked coal with high carbon content between 80 - 94% (Speight, 2012). Meta-anthracite, anthracite and semi-anthracite are the subgroups of anthracite coal family. Bituminous coal burns with smoky flame and also contains 15 - 20% volatile matter. It is the most abundant variety containing 66 - 80% carbon content. It can also be classified as low-volatile, medium-volatile, high-volatile A, B and C. Sub-bituminous coal is below the bituminous coal on the metamorphosis scale and it is often referred to as black coal. Lignite is the lowest rank of coal with 60 - 65% carbon content. It is different from sub-bituminous because of the higher moisture content and low heating value (Speight, 1994). Sub-bituminous and lignite coal are usually referred to as lean grade coals and constitutes 50% of the world's coal reserves (Nicholls, 2009; Osman *et al.*, 2011).

Sub-bituminous and lignite coals are the most abundant in Nigeria as shown in Table 2.1 which represent the approximate reserves of coal fields across Nigeria. Nigeria coal was first discovered in 1909 near Udi according to Mineral Survey of Southern Nigeria (Ilochi, 2010). The exploration started around 1916 - 1950 and thus Nigeria Coal Corporation was

inaugurated in 1950 (Ilochi, 2010). Coal fields spread over 13 states of the Federation in 22 mines as shown in Table 2.1. There are open cast and underground coal mines. Bituminous coal can be found in Ambasdo and Lafia - Obi mines but the dominant type is the sub-bituminous coal (Nigerian Coal Corporation, 2009). Nigeria coal has been used as source of heat in cement production and as fuel for train (Nwadinigwe, 1982; Okolo & Mkpadi, 2010). However, since discovery of petroleum in 1956, the usage of coal has diminished despite its abundance in the country (Nwadinigwe, 1982; Okolo & Mkpadi, 2010). Fluctuating price of oil and its depleting rate have led to a search for alternative sources of energy and income for the Nation. Adequate exploration and use of coal can bring about economic diversification, improved power generation, possible reduction in the cost of production and thus prices of goods and services. In addition, Ilochi (2010) also reported that the used of coal can bring about;

- improved metallurgical process in the iron and steel sector;
- expansion in industrialization of the economy;
- increase in employment and human resource development;
- increase in national income; and
- reduction in deforestation and prevent desertification especially in the Northern region of Nigeria.

Table 2.2 is the report of proximate, ultimate and calorific value analyses of some coal in Nigeria mines. The fixed carbon are in the range of 21.24 - 58.93% while the calorific values range between 15.82 - 32.93 MJ/kg. The elemental carbon in Nigeria coal from different coal fields ranges between 60 and 83%, indicating that they belong to the family of lignite or sub-bituminous coal. Anthracite has not yet been found in Nigeria, however, the coal types available are suitable for beneficiation (Adekunle *et al.*, 2015; Adeleke & Onumanyi, 2007; Ilochi, 2010; Nyakuma, 2015; Ryemshak & Jauro, 2013).

Table 2.1: Coal mines in Nigeria and the approximate reserves

(Nigerian Coal Corporation, 2009).

S/N. State (mine sites)	Coal type	ER	PR	Mining method/ Depth of coal (m)
ENUGU				
a. Okpara	S.B	100	24	U.G/180
b. Onyeama	S.B	150	40	U.G/180
c. Ezemo	S.B	156	56	O.C/U.G/ 30-45
d. Inyi	S.B	50	20	O.C/U.G/ 25-78
e. Ambasdo	B	1000	N.A	U.G /563
KOGI				
a. Ogboyoga	S.B	427	107	O.C/U.G/ 20- 100
b. Okaba	S.B	250	300	U.G/ 20- 100
c. Okobo	S.B	N.A	N.A	O.C/ NA.
d. Odagbo	S.B	N.A	N.A	O.C/ N.A
DELTA				
a. Ogwashi Azagba	L	250	63	O.C/U.G/ 15- 100
BAUCHI				
a. Daho	S.B	N.A	N.A	U.G/ N.A
b. Kurumu pindosa	S.B	N.A	N.A	U.G/N.A
c. Garin Maigunga	S.B	N.A	N.A	U.G/N.A
KWARA				
a. Janata Koji	S.B	N.A	N.A	U.G/N.A
IMO				
a. Ihioma	L	40	N.A	O.C/U.G/ 20-80
b. Okigwe	S.B	50	N.A	U.G/20-100
BENUE				
a. Owukpa	S.B	75	57	O.C/U.G/10-100
ANAMBRA				
a. Nnewi/Ota	L	30	N.A	U.G/18-38
NASSARAWA				
a. Lafia-Obi	B	156	21-42	U.G/80
EBONYI				
a. Afikpo	S.B	50	N.A	U.G/20-100
PLATEAU				
a. Quindi akwati	S.B	N.A	N.A	U.G/ N.A
EDO				
a. Afuji	S.B	N.A	N.A	U.G/ N.A

ONDO				
a. Ute	S.B	N.A	N.A	U.G/N.A

*L- Lignite coal *N.A- Not available *S.B- Sub-bituminous *B- Bituminous * O.C- Open Cast * U.G- Underground, PR-Proven reserves & ER-Estimated reserves (million tonnes).

Table 2.2: Proximate, ultimate and calorific analysis of coal in some Nigeria mines (db)

Coal mine	VM (%)	FC (%)	MC (%)	AC (%)	C (%)	H (%)	N (%)	S (%)	O (%)	CV (MJ/kg)	Reference
Tai	52.76	26.67	9.61	23.42	79.25	5.58	0.74	2.58	11.95	15.82	R&J, 2013
SJ	30.09	52.26	1.33	17.37	82.51	4.52	1.63	1.31	10.03	27.21	R&J, 2013
Oyeama	23.00	56.90	6.10	14.00	64.30	-	-	0.93	-	21.25	Ilochi, 2010
L-O	32.20	-	-	26.30	-	-	-	2.30	-	-	AO, 2015
Ogboyaga	30.41	54.33	6.93	8.63	78.90	4.10	1.20	0.60	6.60	32.51	A. <i>et al.</i> , 2015
Okaba	32.56	58.13	5.99	3.32	82.80	4.30	2.40	0.60	7.30	32.93	A. <i>et al.</i> , 2015
GM	51.16	22.52	5.28	21.03	61.96	4.42	1.07	0.39	32.16	23.74	N., 2015
Afuze	45.80	21.24	1.97	30.99	72.46	6.07	1.63	1.41	18.43	30.52	N., 2015
Enzimo	32.00	38.00	7.00	23.00	77.4	6.3	6.4	0.8	13.7	21.00	(Sambo, 2009)

*R&J,2013-(Ryemshak & Jauro, 2013), GMG- Gari Maiganga coal mine, SJ-Shankodi Jangwa coal mine, L-O- Lafia-Obi mines, AO, 2015- (Adeleke & Onumanyi, 2007), A. *et al.*, 2015- (Adekunle *et al.*, 2015), N., 2015- (Nyakuma, 2015).

The proximate analysis presented in Table 2.2 are very useful parameters in analysing the potential usage of Nigeria coal for energy generation. Oboirien *et al.* (2018) worked on analysis of clean coal technology in Nigeria for energy generation. The researchers used the proximate analysis of coals from ten different mines to evaluate total electricity generation and CO₂ emissions possible in using clean coal technology in Nigeria. Different clean coal technology such as ultra-supercritical pulverized fuel combustion, supercritical fluidized bed combustion, integrated gasification combined cycle and coal bed methane were studied. It

was concluded that each coal will contribute different fraction in the total potential energy recovery. Coal bed methane yielded the least emission factor (469 g CO₂/kWh) compared to other technology studied. The tendency to further reduce this emission is really possible via co-combustion of coal and biomass.

2.2 Biomass

Biomass are naturally occurring, non-fossil materials which are described as resources of organic origin that are available on renewable, sustainable, clean and recurring bases (Agbor *et al.*, 2014; Basu, 2013). Biomass has also been described as biological materials derived from living organism. It is usually used to describe plant based materials but can equally be applied to animal and vegetable derived materials (Li & Hu, 2003). Unlike fossil fuels, which absorbed CO₂ from the atmosphere many millions of years ago and releases it back to the atmosphere when burnt, biomass maintained a closed carbon cycle with no net increase in atmospheric CO₂. Mostly, biomass are usually replanted and the new ones take up CO₂ from the atmosphere when the previously harvested ones are subjected to combustion (Bapat *et al.*, 1997). Five percent (5%) of biomass present in the world (13.5 billion metric tons) have been mobilized to produce energy while the other 95% are still largely considered as waste (Biomass Energy Centre, 2015). This amount is large enough to provide about 26% of the world's energy consumption, which is equivalent to 6 billion tons of oil. Biomass materials can be classified into five basic categories (Biomass Energy Centre, 2015):

- a. virgin wood: biomass from forestry, arboriculture activities or from wood processing;
- b. energy crop: biomass from high yield crop specifically for energy application;
- c. agricultural residues: these are from agricultural harvesting or processing;
- d. food wastes: these are from food and drink manufacturing, preparation and processing, and post-consumer waste; and

- e. industrial waste and co-products: they are from manufacturing and industrial processes.

Biomass is reported to be the third largest primary energy source after oil, coal and their application for electricity generation globally has risen to 13 TWatts between the year 2000 and 2008 (Evans *et al.*, 2010). Its application is also gaining importance for other purposes such as feedstock in iron smelting process (Chew & Doshi, 2011). This is because biomass is considered carbon neutral; it can significantly reduce net carbon emissions and negative environmental impacts when it replaces coal or other fossil fuels. Thus, it is a clean development mechanism (CDM) for reducing GHG emissions and other pollutants (Li & Hu, 2003). Despite the dominance of fossil fuels for heat and electricity production in many developed countries, sources of biomass exist and continue to be exploited for various forms of energy. van der Stelt *et al.* (2011) estimated that the use of biomass for power generation in 2060 will increase to about 200 exajoules (10^{18} Joules) as against its abysmal level of application in the 1990's. These biomass can also be grouped to be lignocellulosic and non-lignocellulosic in nature.

Lignocellulosic biomass include the non-starch and fibrous part of the plants that are made up of hemicelluloses- $(C_6H_{10}O_5)_m$ and celluloses- $(C_5H_8O_4)_m$ and lignin - $(C_9H_{10}O_3(OCH_3)_{0.9-1.7})_m$ while the non-lignocellulosic materials are the non-cellulosic organic matters which are basically for nutritional purpose (Chen & Kuo, 2011; Foster *et al.*, 2010; Lu *et al.*, 2012; Mohan *et al.*, 2006; Pimchuai *et al.*, 2010). Examples of the latter are protein, sugar, starch and fat contents of any crop (Doelle, 2003). The chemical structure of a typical lignocellulosic biomass is shown in Figure 2.1. To utilize lignocellulosic biomass for proper thermal conversion and energy generation, it is important to understand its components and polymers. Lignin in biomass is a 3-dimentional polymer with C-O-C and C-C linkages and

these varies for different type: angiosperms, gymnosperms and those present in herbaceous or non-woody biomass (Buranov & Mazza, 2008; Rowell, 2005).

Figure 2.1 shows that lignin is a co-polymer of three phenyl propane monomer units such as para-coumaryl, coniferyl and sinapyl alcohols. β -O-4-aryl ether bonds are the most common coupling linkages in the polymerization process of monomers (Pandey & Kim, 2011; Vanholme *et al.*, 2010). Lignin decomposes when subjected to high temperature and that explains why it remains less modified during all the phases of torrefaction (200-300°C). Biomass with higher lignin content yields more solid product during torrefaction and this is due to its various functional groups having different thermal stabilities (Brebü & Vasile, 2009; Yang *et al.*, 2007). Cellulose in itself is crystalline in nature with higher packing density that strengthens biomass structure. Its major link is β -(1 $\rightarrow$ 4)-glucosidic bonds. It contains different hydroxyl group in chain and this make biomass behave as sponge (hydrophilic). Hemicellulose, on the other hand, composes of heteropolysaccharides such as hexoses and pentoses. Xyloglucans, xylans, mannans, glucomannans and β -(1 $\rightarrow$ 3, 1 $\rightarrow$ 4) – glucans are important constituents in the hemicellulose (Pollex *et al.*, 2012; Scheller & Ulvskov, 2010). Biomass with higher cellulose and hemicellulose content contains lower energy content and this is one of the limitations to its usage for energy generation and even metallurgical applications.

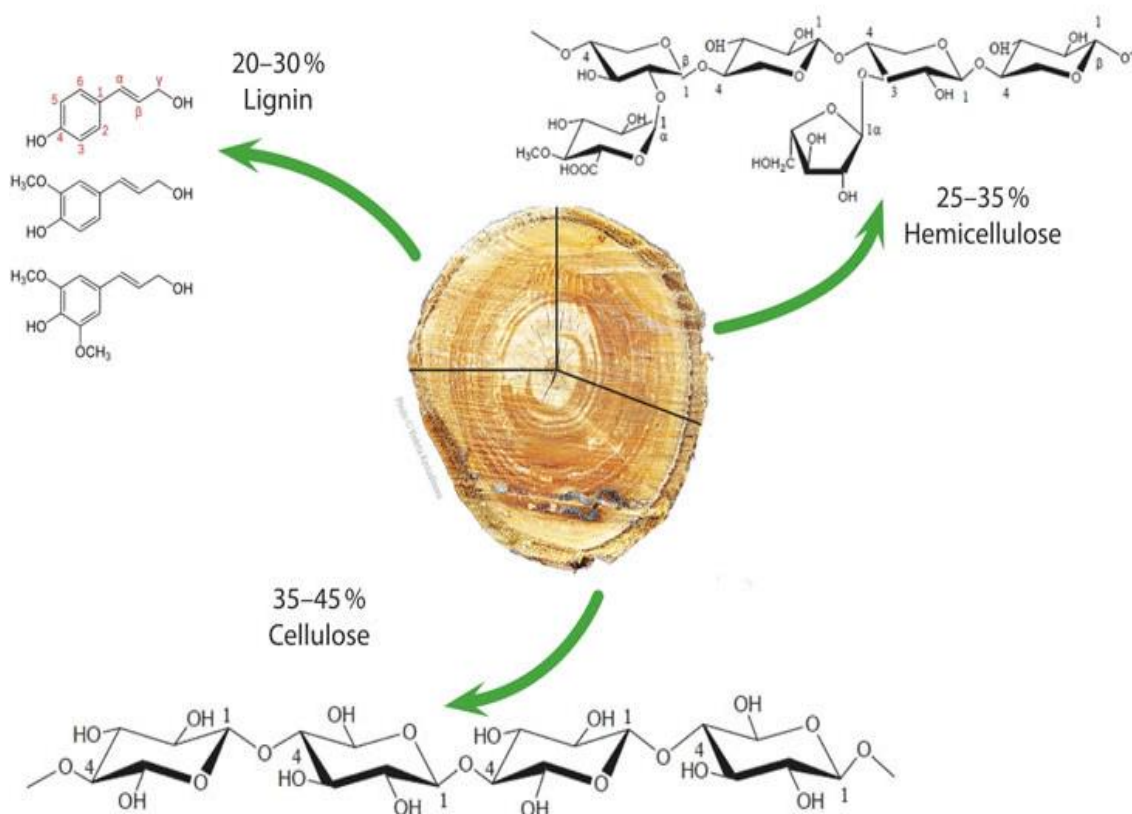


Figure 2.1: Chemical structure of woody lignocellulosic biomass (Helena , 2016)

2.3 Limitation to the use of biomass

According to the Billion-Ton Update report released by the US Departments of Energy (DOE) and Agriculture (USDA) in August 2011, there are more than a billion tons of woody and herbaceous biomass available annually, which can potentially replace about 30% of petroleum consumptions (US Department of Energy, 2011). However, like any other fuel, there are challenges to increasing the use of biomass for energy purposes. Biomass is heterogeneous in nature and differs in terms of chemical, physical and morphological characteristics.

The collection and transportation of dispersed biomass feed stocks are too expensive for bio fuels production (Brown & Mann, 2008). Inherent low energy and bulk densities compared to coal due to high oxygen and moisture contents, are major technical limitations to using biomass as feedstock for bio-energy production which also limits its general and wide

adoption (Arias *et al.*, 2008; Basu, 2013; Medic *et al.*, 2012; Phanphanich & Mani, 2011; Ratte *et al.*, 2011; Tchapda & Pisupati, 2014; Tumuluru *et al.*, 2011; Uemura *et al.*, 2011; van der Stelt *et al.*, 2011; Wannapeera *et al.*, 2011). In order to utilize biomass efficiently, several methods have been developed to upgrade it. A brief comparison of the different thermo-chemical conversions being used for the improvement of biomass is presented in Table 2.3. These include thermo-chemical conversion procedures such as gasification, carbonization, pyrolysis and torrefaction. Production of transportation fuel from biomass through pyrolysis, trans-etherification, fermentation and gasification-based synthesis is also gaining commercial importance. Carbonization is also being used to produce charcoal which is used in many parts of the world as a smokeless fuel. However, continuous use of carbonization process could lead to deforestation. As a better alternative, wood wastes can be harness to serve similar purpose when upgraded via torrefaction process.

Table 2.3: Different thermo-chemical conversion methods (Basu, 2013; Demirbas, 2009)

Process	Temperature (°C)	Pressure (PMa)	Catalyst	Drying
Liquefaction	250-330	5-20	NE	NR
Pyrolysis	300-600	0.1-0.5	NR	NE
Combustion	700-1400	≥0.1	NR	NR but might help
Gasification	500-1300	≥0.1	NR	NE
Torrefaction	200-300	0.1	NR	NE

*NE-Necessary, NR-Not Required,

2.4 Torrefaction

Torrefaction (French word for “roasting”) has been in use since 1930 but it is gaining prominence of recent. It is similar to carbonization that produces solid fuels from biomass but take place in lower temperature region of 200 to 300°C. In any case, this option is also attracting much attention especially in its near term application for upgrading feedstock use

for co-firing biomass in coal-fired power plants and possibly for replacement of coke in metallurgical processes due to its lower energy consumption compared with other process and the ability to produce biochar at maximum mass yield with good quality.

Torrefaction is a thermolysis process where the feedstock is subjected to thermal treatment at a relatively low temperature of 200 - 300°C in the absence or at reduced oxygen level for the purpose of upgrading solid biomass fuel (Basu, 2013; Ciolkosz & Wallace, 2011; Tran *et al.*, 2013). Inert gases such as argon, helium and neon have been employed to create an inert environment but nitrogen is the commonly used carrier gas to provide a non-oxidizing atmosphere in most laboratory tests. Since torrefaction is conducted at conditions similar to those of pyrolysis, torrefaction has also been called mild pyrolysis. As described earlier, raw biomass is characterized by its high moisture content, low energy density, hydrophilic nature and larger volume or low bulk density. Torrefaction has been employed for different biomass by different researchers to improve on some of these drawbacks and the advantage of this process is enormous. These advantages have been summarized in Figure 2.2 (Basu, 2013; Broström *et al.*, 2012; Chen *et al.*, 2015; Demirbas, 2009; van der Stelt *et al.*, 2011).

Torrefaction could be carried out in wet or dry conditions. In wet torrefaction, biomass is subjected to heating in hot compressed water (Yan *et al.*, 2009) while heating is either by a hot inert gas or by direct heating for dry torrefaction. The latter has been the common practice for commercial purposes. Torrefaction could also be pressurized or non-pressurized. Pressurized torrefaction are carried out under an acute flow of pressurized gas while non-pressurized involves gentle flow of gas within the torrefaction chamber (Basu, 2013). The target in all is to improve biomass and reduce cost of improvement. Torrefaction influences biomass based on different degree of treatment process. Chen & Kuo (2011) proposed that torrefaction process could be light, mild or severe. Light torrefaction takes

place at the range of 200 - 240°C in which hemicellulose degradation begins and mild torrefaction is within 240 - 260°C. Cellulose is mildly affected in medium torrefaction and severe torrefaction takes place between 260 - 300°C. Severe torrefaction is characterized by depolymerisation of cellulose, hemicellulose and lignin. However, some group of researchers have also classified the decomposition of biomass polymers into five different stages at different temperatures as shown in Figure 2.3 (Basu, 2013; Bergman *et al.*, 2005; Golova, 1975; Halpern & Patal, 1969; Koukios, 1993; Shafizadeh *et al.*, 1976; Tumuluru *et al.*, 2011).

Decomposition of biomass polymers at temperature between 50 - 120°C (point A) is a non-reactive drying stage where there is a loss in physical moisture in biomass but no change in its chemical composition. Biomass shrinks but may regain its structure if rewetted at point B (120 - 150°C). However, biomass separated out at point B, only in case of lignin that undergoes softening/ glass transition, which make it serve as a binder. Point C (150 - 200°C) is called reactive drying stage resulting in structural deformity of the biomass that cannot be regained upon wetting. This stage initiates breakage of hydrogen and carbon bonds and depolymerisation of hemicellulose. This produces shortened polymers that condense within solid structures. Point D (200 - 250°C) with stage E constitutes torrefaction zone for hemicellulose. This stage is characterized by limited devolatilization and carbonization of solids structure formed in point C. It results in the breakdown of most inter- and intra-molecular hydrogen, Ca-C and Ca-O bonds forming condensable liquids and non-condensable gases. Point E (250 - 300°C) is the higher stage of torrefaction process. Extensive decomposition of hemicellulose into volatiles and solid products takes place. However, lignin and cellulose undergo only a limited amount of devolatilization and carbonization. Biomass cell structure is completely destroyed in this stage making it brittle and non-fibrous.

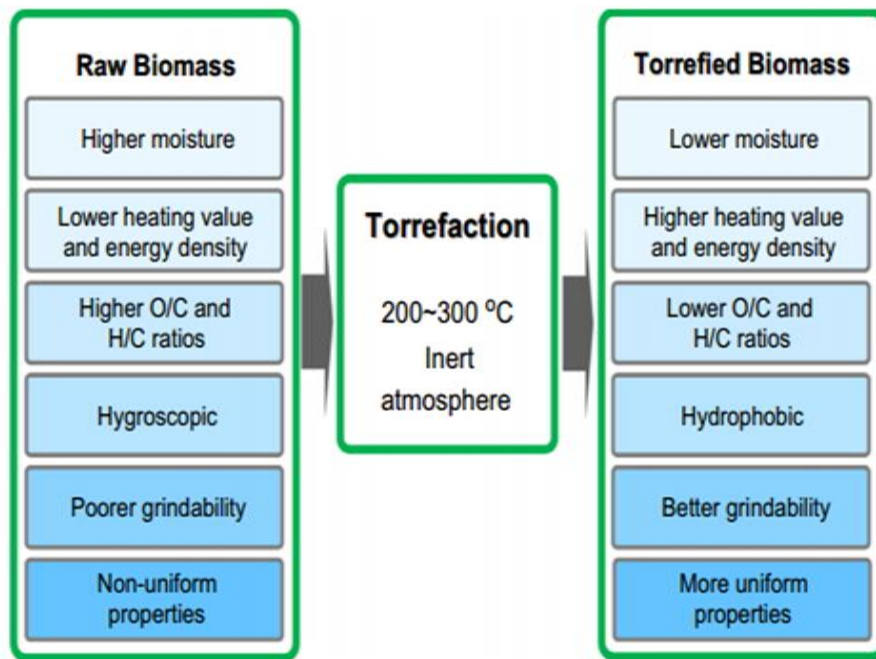


Figure 2.2: Property of biomass before and after torrefaction (Chen & Kuo, 2011).

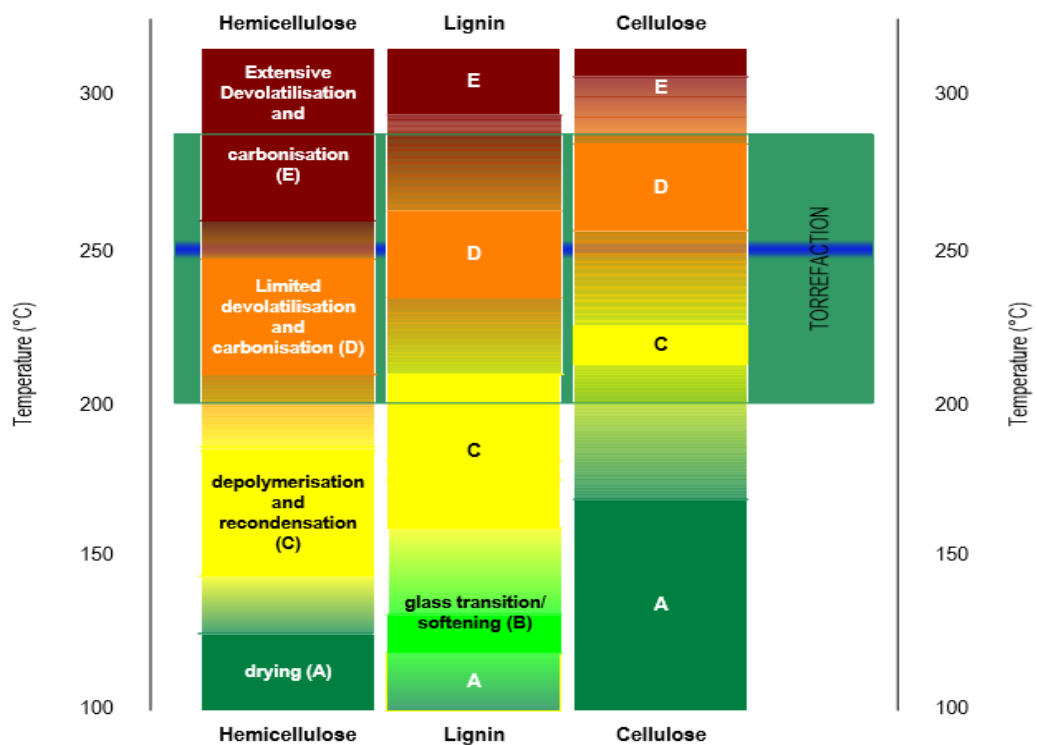


Figure 2.3: Reaction stages in torrefaction (Bergman *et al.*, 1993).

2.4.1 Torrefaction technologies

There are numerous torrefaction reactors that have been in use or under development. The reactor may be classified into different generic group based on heat transfer and solid contact. Few of these technologies with their advantages and disadvantages are discussed in this section (Basu, 2013; Batidzirai *et al.*, 2013; Beekes & Cremers, 2012; Koppejan *et al.*, 2012).

2.4.1.1 Moving Bed Reactor

This is a continuous reactor that consists of an enclosed reactor vessel, where biomass is loaded from the top, and moves down gradually while the torrefaction process takes place as a result of a heat carrying gaseous medium, which enters from bottom to top (Figure 2.4). The reactor does not entail any moving parts. At the reactor bottom, the torrefied product leaves the reactor and is cooled down. At the top of the reactor, gaseous reaction products (volatiles) are removed. The torrefaction process conditions are similar to the other technologies (residence time of 30 - 40 minutes; process temperature of approximately 300°C). Some of the merits of this reactor include:

- relatively simple and low cost;
- high heat transfer;
- high capacity to support large biomass throughput; and
- ability to process biomass with lower density without large disadvantages.

The demerits of this type of reactor are:

- presence of dust particles cause high pressure drops, which can result in automatic reactor shut down;
- limited biomass size and type due to pressure drop;
- temperature distribution is not uniform, especially with indirect heating;

- possibility for channel formation between biomass particles causing unequal torrefaction;
- difficult temperature control; and
- scale-up potential is unproven.

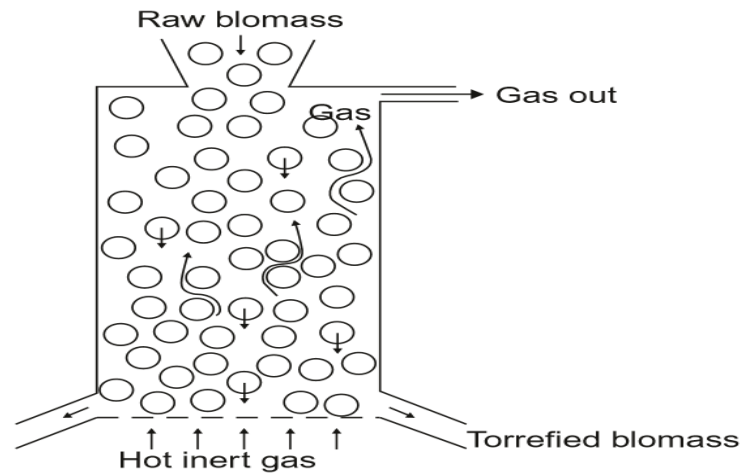


Figure 2.4: A schematic of Moving bed reactor (Basu, 2013).

2.4.1.2 Torbed reactor

In a torbed reactor, a heat carrying medium is blown from the bottom of the bed with high velocity (50 - 80 m/s) past stationary, angled blades. This gives the biomass particles inside the reactor both a vertical and horizontal movement, resulting in toroidal swirls which rapidly heat the biomass particles on the outer walls of the reactor (Figure 2.5). This relatively intense heat transfer enables torrefaction with short residence times (around 80 sec), which results in relatively small reactor sizes. The intense heat transfer could also be used to operate the reactor in a controlled way at elevated temperatures (up to 380°C), resulting in higher loss of volatiles. This technology is flexible in preparing product for different end use markets. However, the process is sensitive to variation in particle size of the feedstock. In summary, the merits are:

- low residence time;
- large throughput due to fast heat transfer and low residence time;

- scale up technology (to 25 t/h);
- no moving parts which implies low maintenance; and
- ability to precisely control product.

Torbed reactor has some demerits and they are:

- high utility fuel demand;
- volumetric reactor capacity is limited;
- high temperature leads to a greater loss of volatiles; and
- risk of tar formation due relatively higher loss of volatile.

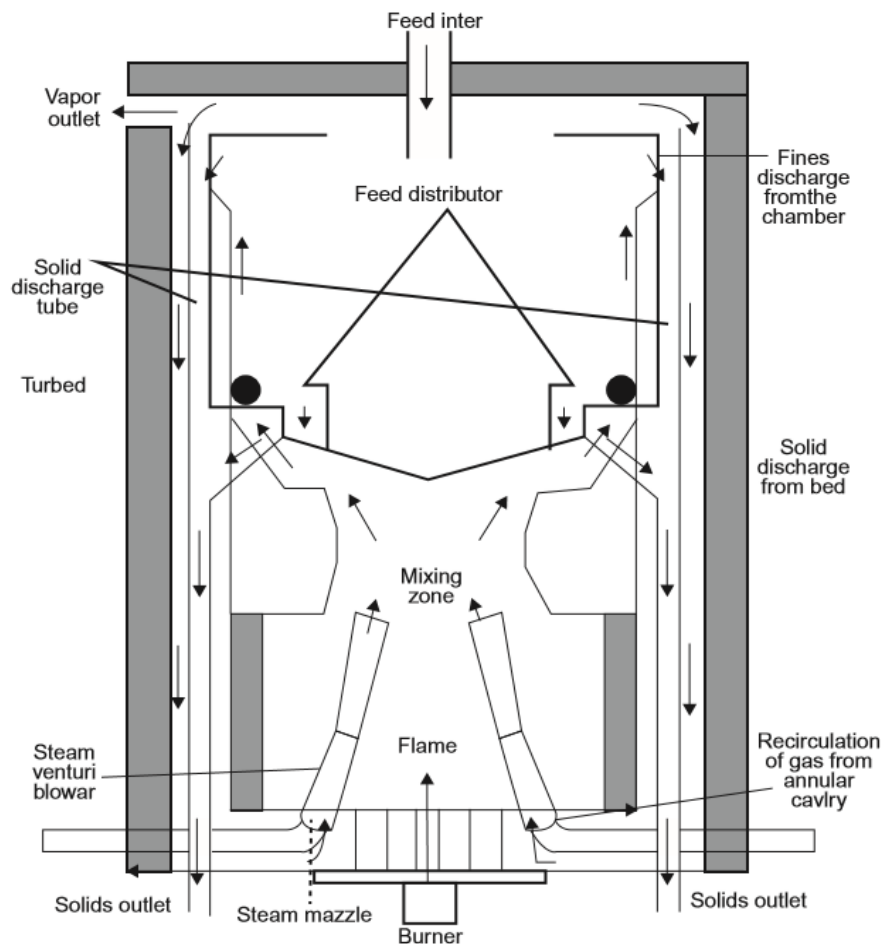


Figure 2.5: Torbed reactor (Basu, 2013)

2.4.1.3 Rotating drum

The rotating drum (Figure 2.6) is a continuous reactor and can be regarded as proven technology for various applications. For torrefaction applications, the biomass in the reactor

can either be directly or indirectly heated using superheated steam or flue gas resulting from the combustion of volatiles. Torrefaction process can be controlled by varying the torrefaction temperature, rotational velocity, length and angle of the drum. The drum rotation causes particles in the bed to mix properly and exchange heat, however, the friction on the wall also increases the fine fraction. Rotating drums have a limited scalability; therefore higher capacities would require modular setup (Basu, 2013; Batidzirai *et al.*, 2013)

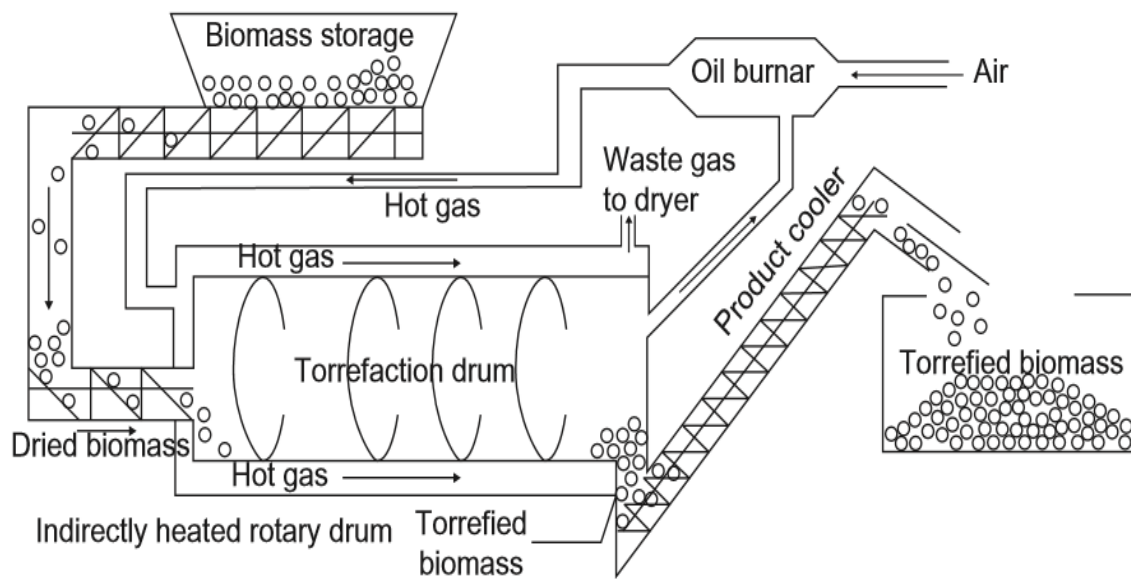


Figure 2.6: Rotary drum reactor (Basu, 2013)

2.4.1.4 Screw or Stationary Shaft

Torrefaction reactor (circular or rectangular cross section) is stationary in this type of reactor, and it could be vertical, horizontal, or inclined (Figure 2.7). The reactor is generally heated from outside to avoid contact with hot gases, though some may have holes for the products of torrefaction to escape. Heat is conducted to the biomass by means of conduction across reactor walls. A rotating screw churns and moves the biomass through the reactor to enhance heat transfer between the wall and the bulk of the biomass and at the same time to move the biomass along its length. The advantages of this type of reactor are:

- relatively cheap reactor;

- better biomass flow;
- ability to take wide range of biomass size; and
- proven technology.

Screw or stationary shaft reactor has the following limitations:

- unequal torrefaction as biomass that touches the reactor wall is heated relatively more and this results in hot spots;
- poor heat exchange because mixing of biomass is limited; and
- limited scaling potential as the ratio of screw surface area/biomass volume is less attractive with larger screws.

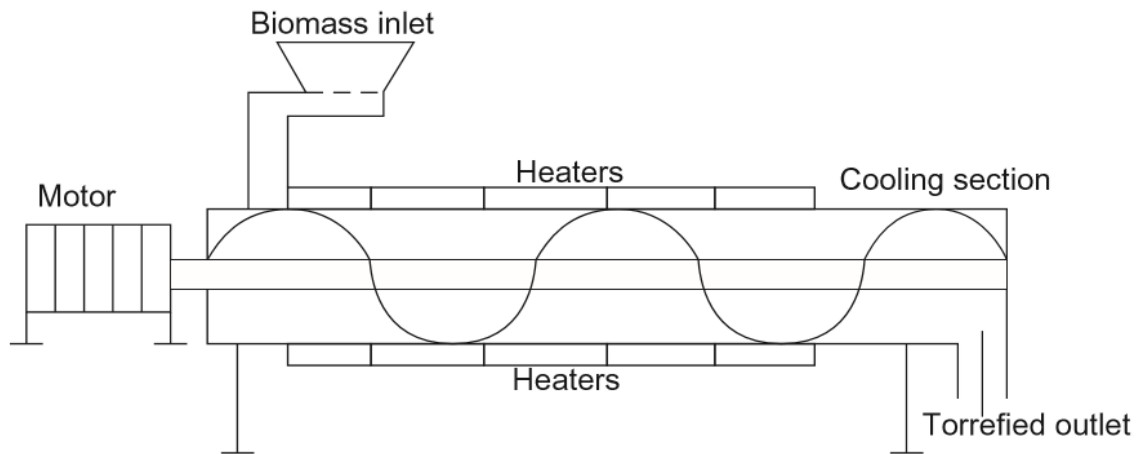


Figure 2.7: Screw or Stationary Shaft (Basu, 2013)

2.4.1.5 Multiple hearth furnace or Herreshoff oven

Herreshoff oven as shown in Figure 2.8 is a continuous reactor, consisting of multiple layers. On every individual layer, a single phase in the torrefaction process takes place. Over the layers, the temperature gradually increases from 220 to 300°C. Biomass enters from the top side of the reactor on a horizontal plate, and is pushed mechanically to the inside. It then falls down through a hole in the plate on a second plate, where biomass is pushed mechanically to the outside, where it falls through another hole and so on. The process is repeated over multiple layers, causing uniform mixing and gradual heating. Heat is applied

per individual reactor layer directly using internal gas burners and steam injection. In the upper reactor layers, biomass first dries, in the lower layers torrefaction takes place.

Herreshoff oven has the following advantages:

- good heat transfer;
- good temperature control;
- ability to take wide range of biomass sizes; and
- scalable technology (7-8 m diameter).

However, the technology is limited based on the following:

- large sized of reactor; and
- heat demand is met through consumption gas combustion making process less sustainable and gas combustible leads to moisture production in the flue gas. This gives a lower efficient combustion of flue gas.

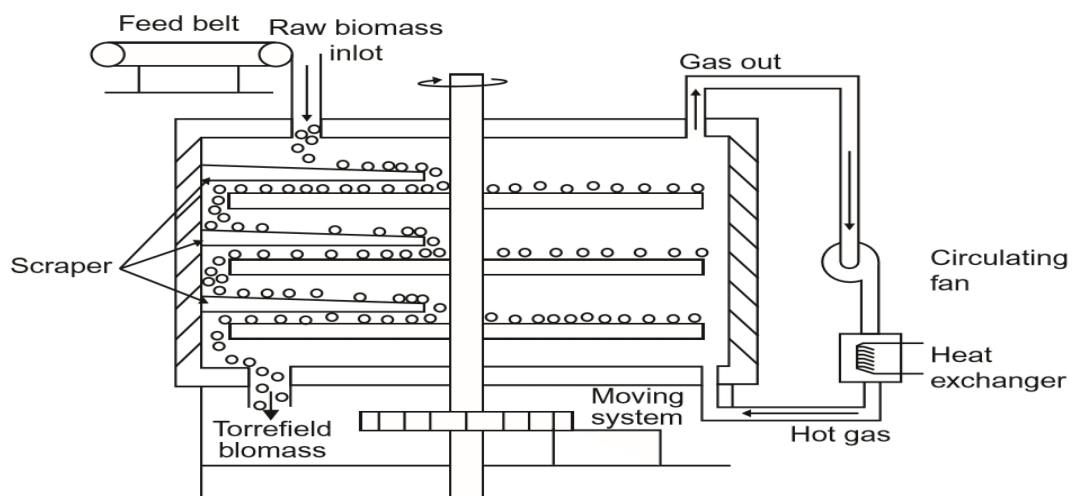


Figure 2.8: Multiple hearth Furnace (Basu, 2013)

2.4.1.6 Belt reactor

The belt dryer can be considered as proven technology for biomass drying applications. While biomass particles are transported using a moving, porous belt, they are directly heated using a hot gaseous medium. In a belt dryer reactor as shown in Figure 2.9, usually multiple belts are placed on top of one another. While biomass particles fall from one

belt on the other, mixing of the particles takes place, resulting in a more homogeneous product. The reactor has the following advantages:

- better temperature control;
- ability to take wide range of biomass sizes;
- relatively low investment costs;
- easy control of residence time through the speed of belt; and
- proven technology for biomass in drying industry.

It is also limited in the following ways:

- system has too many mechanical parts which increases maintenance cost;
- limited upscaling potential since capacity is dependent on the surface area of the belt (other system are volume dependent); and
- the holes in the belt can become clogged with tar and dust causing unequal torrefaction; torrefied product is not homogenous.

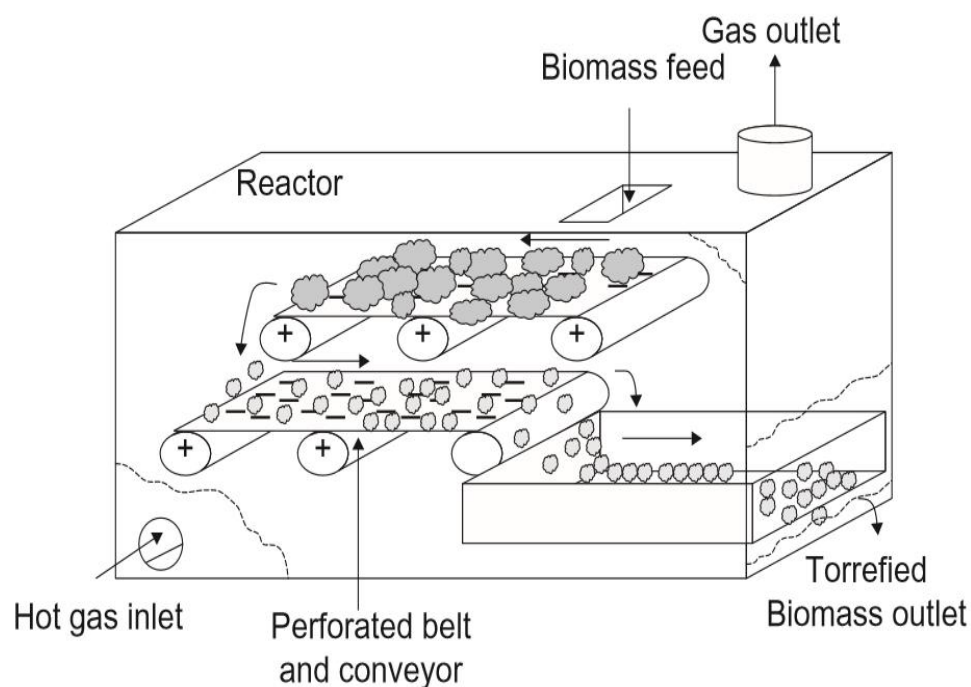


Figure 2.9: Oscillating belt reactor (Basu, 2013)

2.4.1.7 Microwaves Reactor

Microwave irradiation involves electromagnetic wave in the range of 300 MHz to 300 GHz. Typical microwave ovens or microwave reactors work at a frequency of 2.45 GHz (Figure 2.10). The microwave irradiation produces efficient internal heating by direct coupling of microwave energy with the molecules of biomass. The electric component of electromagnetic microwave radiation causes heating by two main mechanisms: dipolar polarization and ionic conduction. The heating depends on the ability of the materials being heated to absorb microwaves and convert it into heat (Basu, 2013; Dhungana *et al.*, 2012; Ren *et al.*, 2012). Metals, for example, reflect microwave, while biomass absorbs it. The advantages of this technology are:

- radiation based heat transfer instead of convection and conduction;
- high heat transfer and fast torrefaction;
- heat transfer less dependent on size of the biomass particle;
- good temperature control; and
- modular.

The demerits are:

- unproven technology for drying or torrefaction of biomass- the effect of rapid heating of biomass is not known;
- electric energy is needed for the process;
- heating of biomass interior is not uniform; and
- requires integration with conventional heaters to achieve uniform heating.

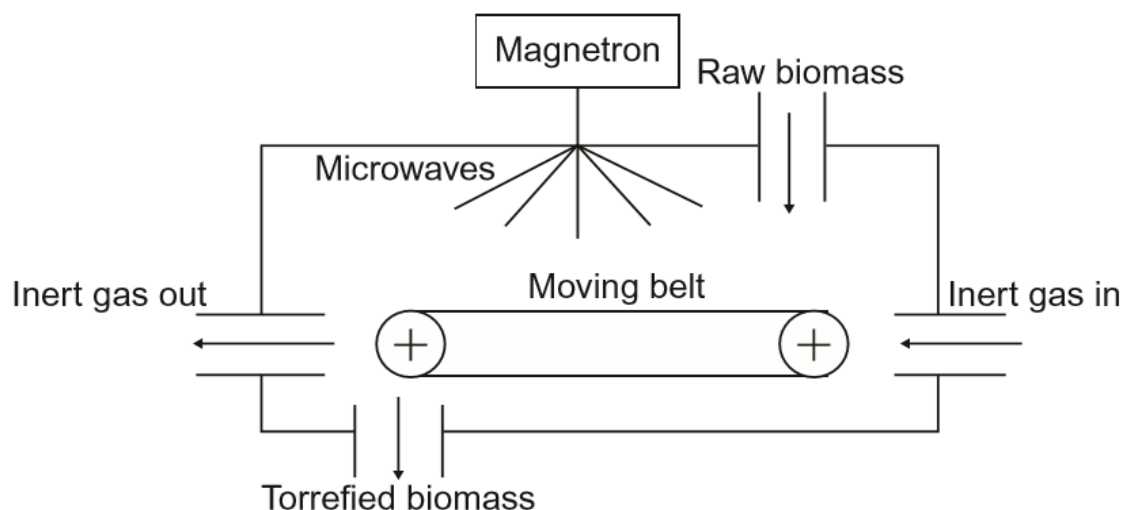


Figure 2.10: Schematic of microwave reactor (Basu, 2013)

2.5 Decomposition kinetics

Lignocellulosic biomass is made up of several chemical constituents and when subjected to thermal treatment, they undergo some form of reaction. This often leads to the liberation of a wide range of volatile species emerging at different rates. Hence, an investigation into thermal stability is a very crucial objective as this gives insight into the reaction mechanism, facilitates the design of decomposition processes and the sizing of reactors (Balogun *et al* 2014; Lasode *et al.*, 2014b; Prins *et al.*, 2006). Thermogravimetric analyses (TGA) is a useful tool in this regard and it can be done with isothermal or non-isothermal measurements. Further analyses of TGA data can provide considerable insights into the kinetics of the processes associated with change in mass. It has also been stated that to any reasonable extrapolation of the effect of thermal treatment on materials necessarily require kinetic parameter evaluation (Vyazovkin *et al.*, 2011).

Kinetic parameter evaluation could be obtained using both isothermal and non-isothermal methods. However, the mass-loss under the warm-up phase is usually unaccounted for in the study of kinetics under isothermal condition. Non-isothermal method can be carried out with model-fitting or model-free (isoconversion) approaches (Lu *et al.*,

2013). To study kinetic of mass loss by non-isothermal method, multiple heating rates has been recommended for its accuracy (White *et al.*, 2011).

Traditionally, in defining the kinetics of a reaction, activation energy (E_a), pre-exponential factor (A) and reaction model, $f(\alpha)$ are evaluated (Vyazovkin *et al.*, 2011). The reaction scheme in any kinetic study is stated in Equation (2.1)



The general form of solid state rate reaction and integral rate law are given in Equations (2.2) and (2.3)

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (2.2)$$

$$g(\alpha) = Kt \quad (2.3)$$

where K = rate constant of Arrhenius equation, and presented in Equation (2.4), t = time, T = Temperature, $f(\alpha)$ = reaction model and $g(\alpha)$ = integral reaction model.

$$K = A e^{-E_a/RT} \quad (2.4)$$

Equations (2.2) and (2.3) can be modified with Equation (2.4) to obtain Equation (2.5)

$$\frac{d\alpha}{dt} = A e^{-E_a/RT} f(\alpha) \quad (2.5)$$

From Equations (2.3) and (2.4), $g(\alpha)$ becomes Equation (2.6)

$$g(\alpha) = A e^{-E_a/RT} t \quad (2.6)$$

A is the pre-exponential factor, E_a is the activation energy, and R is the gas constant. The Arrhenius parameters A and E_a with the reaction model are called kinetic triplet. Under non-isothermal condition, expressing reaction rate as a function of temperature (T) at constant heating rate is possible by utilizing Equation (2.7)

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \frac{dt}{dT} \quad (2.7)$$

where $\frac{d\alpha}{dT}$ is the non-isothermal reaction rate, $\frac{d\alpha}{dt}$ is the isothermal reaction rate and $\frac{dt}{dT}$ is the inverse heating rate ($1/\beta$).

Substituting Equation (2.5) into Equation (2.7) gives the differential form of non-isothermal rate law presented in Equation (2.8):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT} f(\alpha) \quad (2.8)$$

Equation 2.8 then become Equation (2.9) by integration:

$$g(\alpha) = \frac{A}{\beta} \int_0^T e^{-E_a/RT} dT \quad (2.9)$$

Let x replace $\frac{-E_a}{RT}$, Equation (2.9) becomes Equation (2.10) by transforming the limits:

$$g(\alpha) = \frac{AE_a}{\beta RT} \int_x^\infty \frac{e^{-x}}{x^2} dx \quad (2.10)$$

Replacing the integral part of Equation (2.10) with $p(x)$ which is a standard one, we have Equation (2.11):

$$g(\alpha) = \frac{AE_a}{\beta RT} p(x) \quad (2.11)$$

Equation 2.11 has no specific analytical solution but there are so many approximations. The approximation could be based on model-fitting method or model-free method (iso-conversion) as discussed earlier.

Example of non-isothermal model-fitting methods is the C-R method (Coats & Redfern, 1964). It is an integral method that assumes various order of reaction and compares the linearity in each case to select correct order. This method used asymptotic series expansion for approximating the exponential integral in Equation (2.11) and obtained Equation (2.12)

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\left(1 - \frac{2R\bar{T}}{E_a}\right)\right) - \frac{E_a}{RT} \quad (2.12)$$

$\bar{T}$ is the mean experimental temperature and the plot of $\ln\left(\frac{g(\alpha)}{T^2}\right)$ against $\frac{1}{T}$ using Equation (2.12) gives E_a and A from the slope and intercept, respectively. For first order reaction, $g(\alpha) = -\ln(1 - \alpha)$ and $\frac{2R\bar{T}}{E_a}$ is very negligible, Equation (2.12) then becomes Equation (2.13):

$$\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT} \quad (2.13)$$

Therefore, a plot of $\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right)$ against $\frac{1}{T}$ gives a straight line with $\frac{-E_a}{R}$ as slope and $\ln\left(\frac{AR}{\beta E_a}\right)$ as intercept of which A can then be determined. However, model-fitting methods have been reported to have failed in capturing heterogeneous reactions. They are error prone and often lead to significant variations among different fitted models for non-isothermal calculations (Vyazovkin *et al.*, 2011).

Examples of model-free approaches which are commonly employed to describe thermal decomposition kinetics of lignocellulosic biomass are Kissinger-Akahira-Sunose (Akahira & Sunose, 1971; Kissinger, 1957), Friedman (1964), F-W-O (Flynn & Wall, 1966; Ozawa, 1965) and Kim & Agblevor (2007) methods which are expressed in Equations (2.14), (2.15), (2.16) and (2.17) respectively.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE_a}{Rg(\alpha)}\right) - \frac{E_a}{RT} \quad (2.14)$$

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \text{Constant} - \frac{E_a}{RT} \quad (2.15)$$

$$\log\beta = \log\frac{AE_a}{g(\alpha)R} - 2.315 - 0.457\frac{E_a}{RT} \quad (2.16)$$

$$\ln\left(d\alpha/dt\right) = \ln A + n\ln(1-\alpha) - \frac{E_a}{RT} \quad (2.17)$$

The isoconversion methods adopted to investigate the kinetic parameters of thermal decomposition of biomass are the F-W-O and Kim & Agblevor's method for their simplicity and the ease of calculation.

2.6 Briquetting

Briquetting is the agglomeration of fine particles (different or same sizes) by applying pressure on them and compacting into various shapes with or without binding agent. Pressure is applied to coal, biomass or others in a mould so that the particle can articulate/adhere together in a stable manner for subsequent handling. Challenges such as transportation,

disposal, handling, etc faced with the usage of coal fines and biomass can be overcome by agglomerating into briquettes to improve the bulk properties of particulate solids. The objectives and benefits of agglomeration for the utilization of coal and biomass include increased bulk density, improved storage and handling properties, improved flow properties, improved homogeneity of blends, reduced dust losses and improved particle bed heat transfer (Grainger & Gibson, 1981). There are extensive review on agglomeration of coal into briquette and the different technologies/equipment involved in its practice (Osman *et al.*, 2011; Tumuluru *et al.*, 2011b).

There are various types of equipment for coal and biomass densification with technologies ranging from simple to complex devices. The equipment varies in terms of physical size, operating pressure and temperature, power, throughput, feeding device, manual or automatic operation and so on. Pelletizer, hydraulic piston press, mechanical piston press/ram briquetting technology, tabletizer, cuber, roller press, screw extruder, and agglomerator are different types of densification equipment. Brief descriptions of two of these are discussed in this section.

- Piston press/Ram briquetting technology

In developing countries like India, most of the units installed are the reciprocating type where the biomass/coal is pressed in a die by a reciprocating ram at a very high pressure as shown in Figure 2.11 (Grover & Mishra, 1996). Biomass is punched into a die by a reciprocating ram with a very high pressure thereby compressing the mass to obtain a briquette. Briquette produced is usually 60 mm in external diameter. This machine has a 700 kg/h capacity and the power requirement is 25 kW. The ram moves approximately 270 times per minute in this process. It is obvious then that the power consumption in this process is still bearable. Other observable features of this process is that there is less relative motion between the ram and the biomass. Hence, the wear of the ram is considerably reduced and

since the process can easily be used, some operational experience is possibly gained using different types of biomass (Grover & Mishra, 1996; SitiFarhana, 2011).

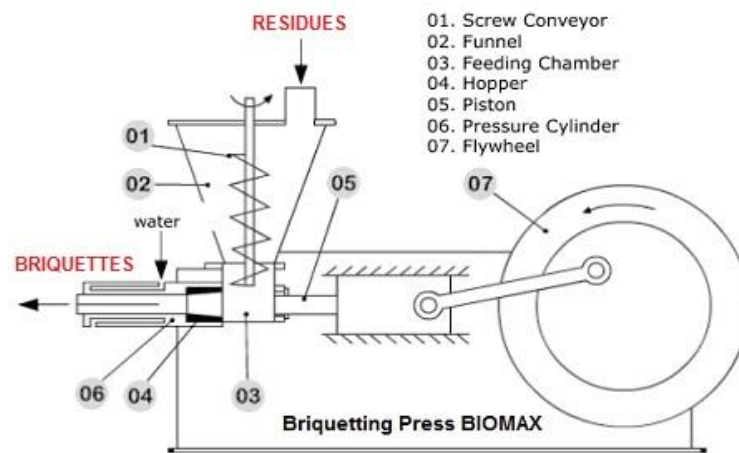


Figure 2.11: A skeletal diagram of piston press (Grover & Mishra, 1996)

- Screw Press Briquetting Technology

In a screw extruder press as shown in Figure 2.12, biomass/coal is extruded continuously by a screw through a heated taper die which is heated externally to reduce the friction. The power consumption in this process is much compared to piston press but exhibit an optimum superior product. Central hole is incorporated in the final briquettes and it is to achieve uniform and efficient combustion. These briquettes can be carbonized so as to further improve on its mechanical properties (Bapat *et al.*, 1997; Grover & Mishra, 1996).

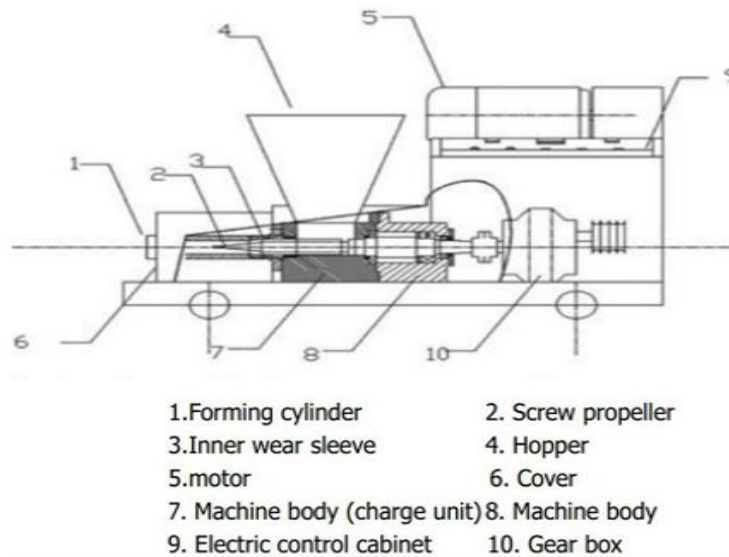


Figure 2.12: Screw press briquetting machine

Briquettes can be useful in the following areas (Basu, 2010; Ilochi, 2010; Tumuluru *et al.*, 2011):

- boilers;
- rotary kiln;
- Food processing industries;
- Textile process houses;
- Agro-products;
- Clay products;
- Domestic;
- Gasification;
- For steam generation;
- Distilleries, bakeries, canteens, restaurants and drying;
- Dyeing, bleaching;
- Tobacco curing, tea drying and oil milling;
- Brick kilns, tile making and pot firing;
- Cooking and water heating; and

- Fuel for gasifiers.

2.6.1 Briquette properties

Dohm (2013) identified the major physical and mechanical properties of coal-biomass briquettes as crushing strength, attriability, water resistance, bulk density, shatter resistance (durability), water content and tensile strength. It was further stated that crushing strength, impact and durability are the most important of these properties and should be the basis of evaluation of briquette's quality required for experimental and industrial coal-biomass briquettes formulations. Other properties are important and should be in detail evaluation based on the requirement of customer or client.

2.6.2 Strength and durability

The strength of bonds between coal and biomass particles in briquettes is the most widely used indicator of its quality (Pietsch, 2002). Crushing strength, attriability and friability are the three parameters that give a signal of the strength of bond. These parameters indicate the extent to which briquettes will degrade during handling, transportation, storage and ultimately usage. Briquette experiences impact, compression and attrition from production to utilization as illustrated in Figure 2.13. The impact force causes briquettes to experience a sudden fracture and breakage into pieces. These forces are encountered when briquettes drop in stock piling at the conveyor transfer points and from bin and chutes. Friability is the term used to describe the tendency of an object to resist impact force. Briquettes can be crushed by compression forces encountered bins, stockpiles and railcars from load applied by other briquettes. Attrition is defined as wearing or grinding down by friction and it is measured by tumbling process. Briquettes are subjected to attrition forces during loading for transportation and unloading point (Dohm, 2013). Different applications also involve briquettes tumbling action such as rotary kiln operations. Drop-shatter test

indicates the extent to which coal lump will break in conventional transit and handling operations and the procedure of its examination is carried out by ASTM D440-07 (2012).

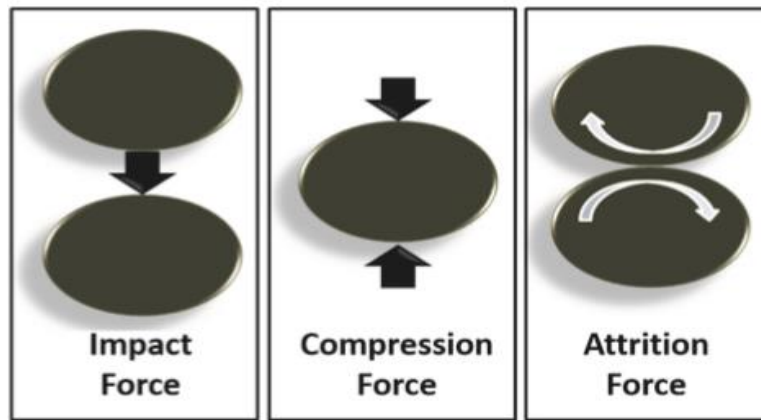


Figure 2.13: Different forces briquettes encounters from production to utilization
(Dohm 2013).

2.6.3 Moisture content

The moisture content is an important parameter because evaporation of moisture from briquette during energy conversion consumes a significant amount of the deliverable energy in a feedstock, therefore, moisture content must be known to properly design a system for minimal energy loss (Basu, 2010; Dohm, 2013).

2.6.4 Bulk density

Density is another important property to consider in briquette production and utilization. It is important when sizing a gasifier and feedstock conveyor to meet desired production. Operation upstream of gasifier such as fuel transportation, bulk handling and storage are directly linked with density (Dohm, 2013). The measurement of mass per unit volume occupied by a group of particle including interstitial volume between particles is the bulk density. Speight (2005) stated that this property can help in understanding processing, storage and transfer equipment at a desired product capacity.

2.6.5 Water resistance

Water uptake that leads to subsequent disintegration of briquettes is a major limitation to the design of lower cost storage and transportation system for co-firing operations. Therefore, water resistance is an important parameter to be considered for production and utilization of briquettes. Dohm (2013) attempted to produce water resistant briquette by coating with paraffin wax, some wood-derived chemical products. It is concluded that briquettes coated with wood-derived chemical product out performed briquettes with no coating and paraffin wax coating.

2.6.6 Elemental composition

The assay of moisture, volatile matter, ash and fixed carbon content of any fuel is referred to as proximate analyses (Basu, 2010). There are various institutional standards for its measurement; example is ASTM, ISO and CEN among others. Volatile matter is the measurement of the condensable and non-condensable vapour (excluding water vapour) produced while heating coal or biomass under specific conditions. Ash content is a measure of the inorganic solid residue remaining after the combustion of coal-biomass under designated conditions. Ash composition also plays a major impact on the occurrence of fouling and slagging within a gasifier. Speight (2012) stated that high alkali-oxide content in ash creates fouling and slagging problems due to reduction of ash melting temperature. It affects the fusibility temperature of coal-biomass briquette (Dohm, 2013). Fixed carbon is also an important parameter in gasification and other area where coal-briquette are being employed. Ultimate analyses of coal-biomass briquette are similar to that of coal and biomass method. It is an assay of elemental composition that is carbon, hydrogen, nitrogen, sulphur and oxygen. It also involves moisture and ash analyses (Basu, 2013).

2.6.7 Combustion properties

Calorific value and ash fusibility are two major thermal properties of briquettes to be considered. Calorific value of a fuel is the heat provided when a unit quantity undergoes complete combustion in the presence of oxygen under predetermined conditions (Speight, 2013). It can be reported as gross calorific (GCV) or net calorific value (NCV). It is also known as higher heating value (HHV). It can be determined using calorimetric by specified ASTM, ISO, CEN standard methods. Ash fusibility is referred to as the softening and melting behaviour of non-combustible mineral residue that is produced during the combustion of briquette (Dohm, 2013). It helps in designing different reactor and kiln for a particular ash removal conditions. The determination of ash fusibility is specified by ASTM D1857–04 (2005). Ash fusion points are measured by observing the behaviour of triangular ash cones formed in a standard mould and subjected to heat in a controlled atmosphere. The observed temperatures vary for different type of materials and these include deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT) and fusion temperature (FT).

2.7 Binder and bonding mechanism

There are various type of binders that have been used in briquetting ranging from organic to inorganic (Pietsch, 2002; Tumuluru *et al.*, 2011b). The different types of binder result in various bonding mechanisms during agglomeration. These mechanisms are: (1) solid bridges; (2) adhesion and cohesion; (3) surface tension and capillary pressure; (4) attraction forces between solid; and (5) interlocking bonds. The mechanism are further divided into subgroups as shown in Figure 2.14. Solid bridges can form between particles by diffusion of atoms and molecules at point of contact as a result of elevated temperature and pressure. Solid bridges are formed when pressure is removed and binder cools. Adhesion and cohesion forces act to bind individual particles when a highly viscous binder such as pitch, molasses

and bitumen is utilized. In this process, adhesion force are present interface between solid particles and binding materials while cohesion forces acts within the binder to strengthen the agglomeration (Pietsch, 2002). Surface tension and capillary forces often improve interparticle bonding in wet agglomerateion process. This is refered to as liquid bridge formation which is a precusor to the formation of solid bridges and this interaction enhances agglomeration strength.

Other forces of attraction within the structure give strength based on molecular, electrical and magnetic interactions. Molecular forces could be van der Waals, free chemcial bonds (valence-forces) and hydrogen bonds. Electrostatic attraction forces form double layer when two particles contact one another due to differnce in electron work factors which induces permanent bonding. Magnetic forces can also contribute to the strength if ferromagnetic particles are present in the agglomerate. Interlocking bonds can form between elongated fibrous materials when particle bend, twist or weave together during agglomeration processes. This phenomena usually produce durable bond similar to that of matrix bonds (Pietsch, 2002). Due to fibrous nature of many biomass materials, interlocking bonds was attributed with the strength of biomass agglomeration.

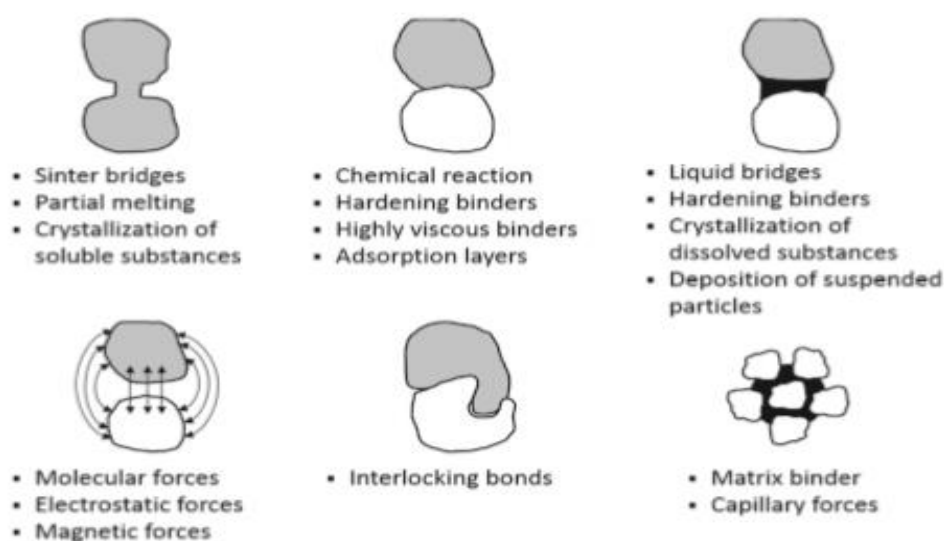


Figure 2.14: Different bonding mechanism (Pietsch, 2002).

2.8 Previous attempts on coal briquettes and bio-coal briquettes

Borowski & Hycnar (2013) worked on utilization of coal fines for production of fuel briquettes. Briquettes were produced using molasses, potato starch, molasses and starch, shredded woody biomass as binders. The briquettes were dried and cured at room temperature for 30 min and for 14 days. They obtained cold crushing strength of 0.52 - 1.42 MPa for briquettes for 30 min and 0.62 - 1.85 MPa after 14 days. The resistant to gravity (shatter resistance) was in the range of 73.3 - 95.1% after 3 drops. The water resistance before briquette disintegrated was 10 - 11 min and the density was 1220 kg/m³. The physical properties of the briquettes still need further improvement for them to be able to effectively function as a fuel. Tosun (2007) also produced clean fuel-magnesia bonded coal briquettes. Turkey lignite coal, magnesia, gypsum, sulphide liquor, sugar waste liquor and CaO were the raw material used in briquetting. The pressure applied was kept constant at 2000 kg/m³ and briquette was cured at 100°C for 2 days. Cold crushing strength of 100 - 900N for various blends of binder was reported for briquettes. The briquette was targeted towards power generation and municipal incineration. The calorific value reported was in the range of 3600 - 5200 kcal/kg for the briquette produced. The mechanical integrity of these briquettes was found to be low and thus needs further work. Nieto-Delgado *et al.* (2014) also worked on the production of anthracite briquettes as fuel to metallurgical coke: full scale performance in a cupola furnace. Briquette was produced from 80 - 95% anthracites fines, 0 - 2% hydrolysed collagen (70°C), 2 - 8% low sulphur lignin from Eucalyptus wood and 0 - 7% silicon. Pressure in the range of 6.9 - 69 MPa was adopted for briquetting. The briquette was dried at ambient temperature for a day and then carbonized at 900°C for 5 min under nitrogen environment. The cold crushing strength obtained was 6.3 MPa for dried briquettes; however, it decreased to 2 - 6 MPa after carbonization. It was reported to be suitable for cupola furnace operations.

Yip *et al.* (2007) worked on pyrolysis of Collie coal briquettes to produce char as a metallurgical reductant. Briquettes were produced without binder and pyrolyzed at 500 - 1400°C with a heating rate of 10°C/min in an inert environment and held at the temperature for 1 h. The cold crushing strength reported for the briquettes were in the range of 6.9 - 14.9 MPa and it was targeted towards metallurgical applications. The use of high temperature for pyrolysis in their work implied that high energy was consumed during the production which may not be economical and thus need for further work. Zhong *et al.* (2016) also worked on xylene activation of coal tar pitch binding characteristics for production of metallurgical quality briquettes from coke breeze. Coal tar pitch and xylene used as binders for briquetting of coke breeze at a pressure of 60 MPa (holding time of 10 s). The briquettes were dried in oven for 3 h and then cured in 1.2 m/s air-flow at 130°C for 1 h. Some briquettes cured at 370°C of N₂ flow (0.5 L/min) for 1 h and then carbonized at 500 - 600°C in an oven for 30 min. The cold crushing strength reported was in the range of 12 - 52 MPa. Briquettes were produced as feedstock for blast furnace with an inference that the briquettes will continue to be strong as temperature increases during usage. It will be expected of coke breeze briquettes as will be compared with non-coking and highly degraded briquettes to have such amount of cold crushing strength. As observed from most previous efforts, the major physical properties required for industrial briquettes are not always detailed in their efforts. Some of the reported physical properties were even obtained after high temperature carbonation especially using coke fines or coke breeze.

2.9 Co-combustion of coal and biomass

Baxter (2005) enumerated the benefits of biomass and coal combustion as low-risk, low-cost, sustainable, renewable energy option that can lead to reduction in net CO₂, SO_x and NO_x along with several societal benefits. However, the challenges of biomass storage, supply, handling, potential increase in corrosion, fly ash, among others were the listed limiting

factors for biomass-coal utilization. Careful selection of operating condition and boiler design were the suggestions for efficient utilization. Demirbas (2004) also discussed combustion characteristics of various biomass fuels such as hazelnut shell, wheat straw, olive husk, spruce wood, wall nut and so on. Comparing co-combustion of biomass with coal showed a reduction in total emissions per unit energy produced. In another study, Demirbaş (2005) endorsed co-combustion of biomass with coal based on the effectiveness in reduction of SO_x, NO_x and ash volume for coal-fired power plant.

Narayanan & Natarajan (2007) also investigated co-firing of bituminous and lignite with bagasse, wood chips, sugar cane trash and coconut shell in an 18.68 MW travelling grate boiler. They reported that wood/coal at 60/40% gave reduction in NO_x emissions better than pure coal combustion. Kwong *et al.* (2007) carried out laboratory scale co-combustion of coal with rice husk and bamboo on different blending ratio. Gaseous pollutant emissions such as CO, CO₂, NO_x and SO_x were reduced. Lu *et al.* (2008) reported that less than 20% of biomass addition to coal in co-combustion yielded little effect on flame stability. Gani *et al.* (2005) studied co-combustion of low-rank coal and sawdust in an electrical heated drop tube furnace and found that biomass can enhance ignition characteristic of low-rank coal due to its high volatile matter. In another study conducted by Yamada *et al.* (2008), abatement of indoor air pollution achieved with coal-biomass household briquettes, comparison was made of the SO₂ emitted from honeycomb-coal briquette and bio-briquettes. It was concluded that bio-briquettes can be used as fuel in order to abate indoor air pollution.

Ilochi (2010) studied the influence of non-woody biomass (ground nut shell and maize cob) on the briquetting of coal from Nigeria. It was reported that bio-coal briquette produced has lower compressive strength and hardness value compared to coal briquette which was due to low amount of binder used and probably the lack of pre-treatment for the biomass used. The burning characteristics of the blend were better than raw coal. However,

applying such briquette in high temperature operations is not visible. Therefore, based on these studies, co-combustion of coal and biomass can substantially reduce greenhouse gas emissions into the atmosphere. Agglomeration of coal slack and biomass upgraded via torrefaction process can therefore bring about proper utilisation of these wastes and also assist in reduction of greenhouse gas emissions that limits the combustion of coal alone. Thus, the aim of the present study is to develop hybrid fuel briquette from coal slack and torrefied biomass using different organic binders. The binders are expected to support the fuel briquette to maintain high mechanical strength and better combustion properties during high temperature operations/applications especially in power plants and metallurgical furnaces.

CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Biomass

Lignocellulosic woody biomass used in this study were Teak (*Tectona grandis*-RTw) and Melina (*Gmelina arborea*-RMw) woods of Benin (Nigeria) origin (6° 20' 17.34" N, 5° 37' 32.70" E). Lumbers were obtained and converted into chips and fines below 6.35 mm using a saw wood cutting machine (Model No: CS33EB) at the National Metallurgical

Laboratory, Jamshedpur, India. The wood chips and fines were sun-dried for five days to remove surface and residual moisture. The wood chips were further pulverized and screened to four different particle sizes (sieve sizes);

- -0.5 mm (represented as 0.5 mm)
- +0.5-2 mm (represented as 2 mm)
- +2-4 mm (represented as 4 mm)
- +4-6.35 mm (represented as 6 mm)

3.1.2 Coal

The lean grade coal used in this study is from Okaba mine (Nigeria: 7° 23' 0" N, 7° 44' 0"E) coal slack. Coal slack less than 3 mm was air-dried, pulverized and screened to obtain particle size below 36 mesh fines at the National Metallurgical Laboratory, Jamshedpur, India.

3.1.3 Binders

The binders used in this study were pitch (BSS 36 mesh), molasses and starch. Pitch and molasses were directly utilized while starch was subjected to gelatinization process before usage. Several proportions of pitch and molasses are also used as blended binders.

3.2 Methods

3.2.1 Thermogravimetric analyses

The thermal degradation and decomposition behavior of biomass and coal were observed with a Thermobalance system (Model No: STA7300). Approximately 6.5 mg of test sample was loaded into the crucible for analysis in the equipment. The experiment was carried out in an inert environment obtained by continuous flow of 100 ml/min of nitrogen. Biomass samples were heated from 30 to 800°C at different heating rates of 5, 10 and 15°C/min while coal was heated up to 1200°C at 5 and 10°C/min. Kim & Agblevor (2007) and F-W-O (Flynn & Wall, 1966; Ozawa, 1965) isoconversion methods were selected to evaluate

kinetic parameters for Melina wood: activation energy (E_a) and pre-exponential factor (A).

In Kim & Agblevor's (2007) method, the rate of fractional weight loss $\left(\frac{d\alpha}{dt}\right)$ is expressed as a function of conversion $f(\alpha) = (1 - \alpha)^n$ to obtain Equation (3.2), where α is the fractional conversion as obtained using Equation (3.1) and n is the reaction order.

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (3.1)$$

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (3.2)$$

where the reaction rate constant k was substituted by Arrhenius expression to obtain Equation (3.3)

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (3.3)$$

Substituting Equation (3.2) into Equation (3.3) and taking the natural logarithm, Equation (3.4) was obtained, thus:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n \ln(1 - \alpha) - \frac{E_a}{RT} \quad (3.4)$$

For different heating rates, corresponding temperature at different conversion ratio were noted and the fractional conversion weight loss from DTG data were also noted. Kinetic parameters (E_a and A) were determined from the plot of $\ln\left(\frac{d\alpha}{dt}\right)$ against $\frac{1}{T}$. The slopes of the isoconversion lines are equivalent to $-\frac{E_a}{R}$ and the intercepts equates to $\ln A(1 - \alpha)^n$ where the reaction was assumed to be first order. Flynn-Wall-Ozawa linearized the temperature integral of Equation (2.11): $g(\alpha) = \frac{AE_a}{\beta RT} p(x)$, using Doyle's approximation (Doyle, 1961) as shown in Equation (3.5)

$$\log p(x) \cong -2.315 + 0.457x \quad (3.5)$$

The logarithm of Equation (2.11): $g(\alpha) = \frac{AE_a}{\beta RT} p(x)$, combined with Equation (3.5) becomes Equation (3.6)

$$\log \beta = \log \frac{AEa}{g(\alpha)R} - 2.315 - 0.457 \frac{Ea}{RT} \quad (3.6)$$

For a particular conversion at heating rates of β_1, β_2 and β_3 , the corresponding temperatures were noted as T_1, T_2 and T_3 . The plot of $\log \beta$ against the inverse of corresponding temperature at a conversion yielded isoconversion lines where E_a as determined from the slope ($-0.457 \frac{Ea}{R}$). Pre-exponential factor was obtained by following ASTM E1641 (2007) standard with the assumption that biomass obeys first order kinetic model.

3.2.2 Design of torrefaction experiment

The experiment was designed based on a 2^k full factorial regression method in Minitab 17 Trial version. Based on the initial thermal study of raw biomass, torrefaction temperature (TT) was set at 240 and 300°C for low and high settings, respectively. The residence time (RT) of samples in the furnace was set as 30 and 60 minutes for low and high settings, respectively (Arteaga-Pérez *et al.*, 2015; Chen & Kuo, 2011). The particle size (PS) of 2 and 6 mm were selected as low and high settings, respectively (Arteaga-Pérez *et al.*, 2015). TT, RT and PS were the independent variables for the experimental design as shown in Table 3.1. Mass Yield (MY), Higher Heating Value (HHV) and Energy Yield (EY) were used as the dependent variables. Factorial linear regressions were calculated in Minitab 17 to estimate the response of the dependent variables. The design was randomized with two replicates for each corner points. Sixteen experimental runs were carried out based on the set conditions and each run was treated as a separate experiment. Severity factor (SF) is a pseudo-first-order reaction that combines TT and RT in one value and provides an approximate indication of the treatment conditions. SF cumulates the effects of temperature and resident time and it was calculated using Equation (3.7) (Lee *et al.* 2012).

$$SF = \log \left(RT \cdot \left(\exp^{TT - T_R / 14.75} \right) \right) \quad (3.7)$$

where T_R - reference temperature that has been adopted to be 100°C as base line for unbounded moisture removal.

Sample identification was based on condition of torrefaction. For example, T or M/240/60/6 represent +4-6.35 mm Teak or Melina wood, torrefied at 240°C for 60 min residence time.

Factorial Regression model development

Full Factorial linear regression models were developed between the dependent variables (MY, HHV and EY) and independent variables (TT, RT and PS) in uncoded formats and were validated via experimentation using the global solution from the response optimizer. In order to validate the regression models, the treatment conditions presented in Table 3.2 were also used for torrefaction experiment.

Table 3.1: Factorial experimental design with three independent and dependent variables in Minitab 17 for Melina wood

		Independent variables			Dependent variables		
Run	Sample ID	TT	RT	PS	MY	HHV	EY
Order		(°C)	(min)	(mm)	(%)	(MJ/kg)	(%)
1	M/240/30/2	240	30	2	-	-	-
2	M/240/30/6	240	30	6	-	-	-

3	M/300/60/6	300	60	6	-	-	-
4	M/300/30/6	300	30	6	-	-	-
5	M/300/60/2	300	60	2	-	-	-
6	M/300/30/2	300	30	2	-	-	-
7	M/240/60/2	240	60	2	-	-	-
8	M/240/60/6	240	60	6	-	-	-
9	M/300/60/6	300	60	6	-	-	-
10	M/300/60/2	300	60	2	-	-	-
11	M/240/60/6	240	60	6	-	-	-
12	M/300/30/6	300	30	6	-	-	-
13	M/240/30/2	240	30	2	-	-	-
14	M/240/30/6	240	30	6	-	-	-
15	M/300/30/2	300	30	2	-	-	-
16	M/240/60/2	240	60	2	-	-	-

Table 3.2: Treatment conditions selected for validation of regression models

S/N	TT (°C)	RT (min)	PS (mm)
1	260	60	2
2	280	60	2
3	300	90	2
4	300	120	2
5	300	60	0.5

6	300	60	4
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Torrefaction experiment

Tubular furnace (KW-Load-SL-No NEC/65 Model) with capacity to supply N₂ was used for the torrefaction process as depicted in Figure 3.1. The setup consisted of a nitrogen cylinder with a pressure regulator valve, a water seal valve, an auto-transformer, and necessary fittings and pipes. An external K-type thermocouple was placed in the center of the sample to monitor temperature variations within the furnace which was displayed on an indicator (Figure 3.1). A water bath to observe the visible flow of gas throughout the experiment was connected to the exhaust pipe of the tubular furnace. An Electronic Analytical and Precision Balance (Sartorius BSA Series: BSA 224S-CW) was used to weigh 46 g of biomass samples for each experiment. The sample was poured into a crucible which was then placed in a tubular furnace and N₂ gas flow was continuous at 2 L/min to maintain an inert environment within the tubular chamber. Heating rate of 12°C/min was employed for the experiment till the desired TT after which it was soaked for each RT. After each RT, the samples were allowed to cool for 4 to 5 minutes in the furnace before it was removed and placed in the desiccator for further cooling. This was done to avoid the oxidation blasting of the torrefied product. Weight loss was calculated using Equation (3.8) and mass yield was also obtained for different set of conditions using Equation (3.9):

$$W_L = (I_w - F_w)/I_w \times 100\% \quad (3.8)$$

$$MY(\%) = 100 - W_L \quad (3.9)$$

where the weight loss (%) is W_L , I_w is the initial weight of the sample (g), F_w is the final weight of the sample after torrefaction (g) and MY represents the mass yield.

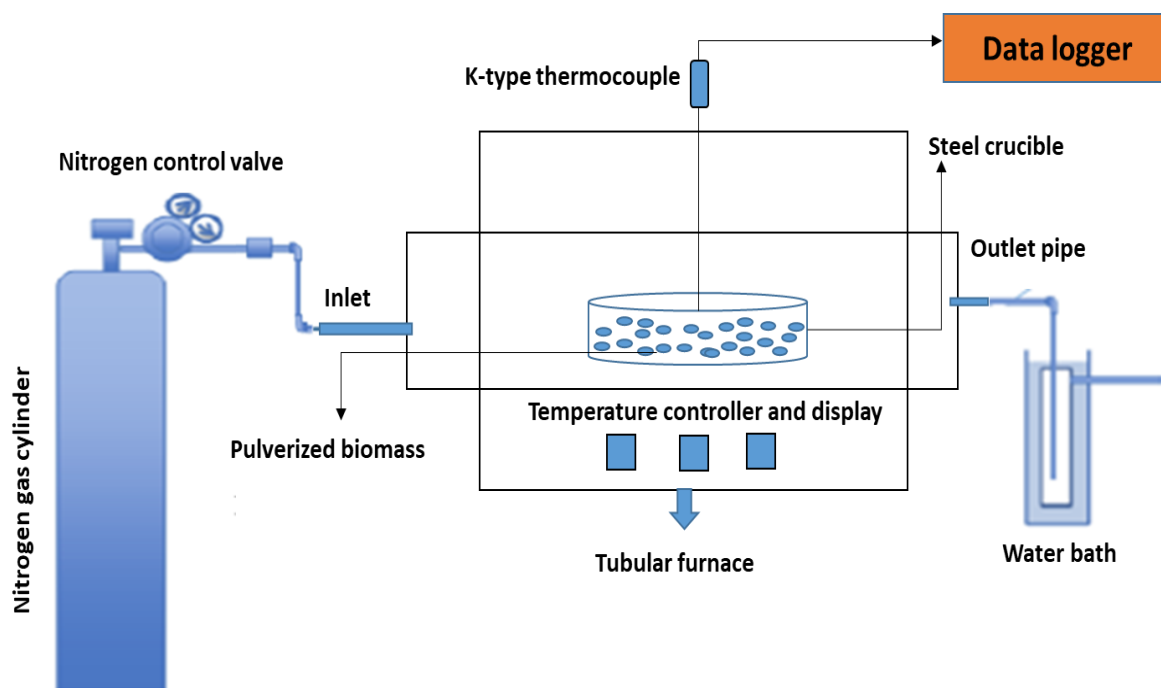


Figure 3.1: Torrefaction setup for optimizing process parameters

Scale-up of torrefaction process (2 kg)

The scale up of torrefaction process was carried out using approximately 2 kg of the woody biomass that is needed for agglomeration. A reactor was designed and fabricated using stainless steel. The reactor was filled with biomass sample ($\cong 2$ kg) and sealed. The reactor was then placed in a salt bath-furnace chamber where the nitrogen gas valve was connected to the inlet and was allowed to flow at 2 L/min to create and maintain an inert environment (Figure 3.2). The exhaust was connected to a water bath in order to observe the continuous flow of the gas and also act as a base for collection of volatiles. Based on the optimized results, the furnace temperature was raised to 260°C and held for 60 min for torrefaction process. The reactor was then removed and allowed to cool down. The sample was weighed to obtain mass yield and weight loss. This process was repeated as many times as possible while the samples were kept in a zip-locked bag in order to accumulate quantity needed for agglomeration. The samples were then pulverized and sieved to obtain particle sizes below 36 mesh for agglomeration.

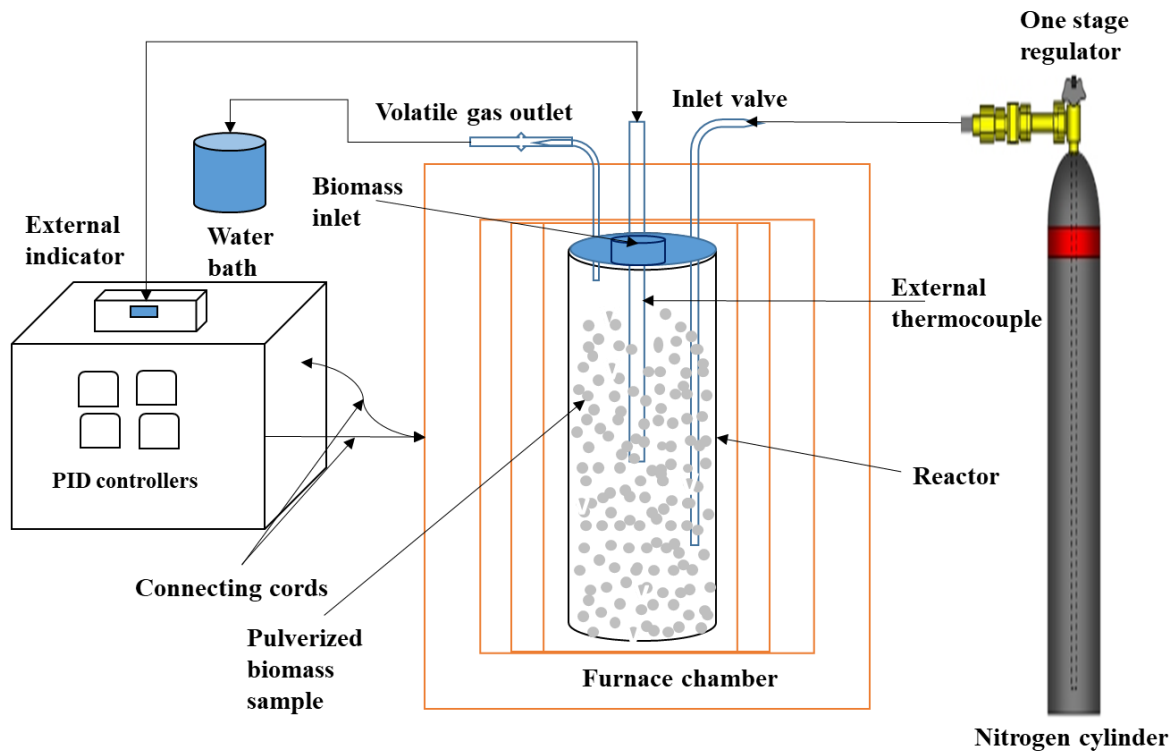


Figure 3.2: Schematic for torrefaction setup for 2 kg-scale sample in a salt-bath furnace

3.3 Combustion properties

The combustion characteristics involves the higher heating value, proximate and ultimate analyses.

3.3.1 Higher Heating Value (HHV) determination

The calorific value (HHV) analysis for the raw biomass, torrefied biomass, coal and pitch was carried out in a Parr 6200 Oxygen Bomb Calorimeter (Model No: A1290DDEE) in accordance with ASTM D5865-04 (2004). The analysis was carried out in duplicates and the average has been reported. Yin (2011), Sheng and Azevedo (2005) and Boie (1953) models in Equations 3.10, 3.11 and 3.12, respectively, were adopted in predicting HHV of raw and torrefied biomass from ultimate analysis;

$$\text{HHV}(\text{MJ/kg}) = 0.2949C + 0.825H \quad (3.10)$$

$$\text{HHV}(\text{MJ/kg}) = -1.3675 + 0.3137C + 0.7009H + 0.0318O \quad (3.11)$$

$$\text{HHV}(\text{MJ/kg}) = 0.3517C + 1.1626H + 0.1047S - 0.1110 \quad (3.12)$$

where C is carbon content (%), H is hydrogen content (%), S is Sulphur content (%) and O is the oxygen content (%).

HHV results were used to obtain the energy yield (EY) after torrefaction in accordance with Equations (3.13) and (3.14):

$$EY = EDR \times MY \quad (3.13)$$

$$EDR = HHV_{\text{Product}} / HHV_{\text{raw biomass}} \quad (3.14)$$

where EDR is energy densification ratio and MY is the mass yield (%).

3.3.2 Proximate analysis

The proximate analysis was carried out in accordance with specified ASTM standards for raw biomass while that of coal and torrefied biomass were carried out according to IS:1350-1(1984) standards for coal and coke. Each analysis was carried out in duplicates on each samples and the average has been reported.

3.3.2.1 Moisture

(a) Raw biomass

Moisture content (MC) was determined according to ASTM E871-82 (2013) standard in an oven (Model No: OF-22G, JESO TECH, Korea). A blank glass crucible was weighed in an Electronic Analytical and Precision Balance (Sartorius BSA Series: BSA 224S-CW) and the weight was recorded as M_t . Approximately 0.5 g of sun-dried sample was placed inside the glass crucible and weighed. The weight was recorded as M_i . The crucible and the sample were placed in the oven at 105°C and removed after 1 h. The final weight, M_f was taken after the crucible and the sample were allowed to cool inside a desiccator. The moisture content, MC was then calculated using Equation (3.15);

$$MC = \frac{M_f - M_t}{M_i - M_t} \times 100\% \quad (3.15)$$

where M_t = weight of empty glass crucible, M_i = weight of glass and sample and M_f is the weight of the container and oven-dried sample.

(b) Torrefied biomass, pitch and coal

The weight, M_1 of blank glass crucible was measured using an Electronic Analytical and Precision Balance (Sartorius BSA Series: BSA 224S-CW). An approximately 1 g of each sample was placed into the crucible and weighed as M_2 (crucible sample). The crucible and the sample was placed in an oven (Model No: OF-22G, JESO TECH, Korea) set at 105°C and allowed to dry for 1 h. The crucible and the oven dried sample were removed and placed in a desiccator for cooling. The crucible and the oven dried sample were weighed and recorded as M_3 . The moisture content was then calculated using Equation (3.16):

$$MC = \frac{M_2 - M_3}{M_2 - M_1} \times 100\% \quad (3.16)$$

where M_1 = weight of crucible (g), M_2 = weight of crucible plus sample (g) and M_3 = weight of crucible plus oven dried sample (g).

Note: The sample is either torrefied biomass, pitch or coal.

3.3.2.2 Volatile matters

(a) Raw biomass

The volatile matter (VM) contents of the raw Tw and Mw were determined in accordance with BS EN 15148 (2009) standard. A blank alumina crucible with tight fitted lid was sintered at 900°C for 7 min, cooled to room temperature in a desiccator. The weight of the sintered blank alumina crucible and the lid was recorded as M_b . Biomass sample of 1 g was weighed into the crucible and the weight of both the covered crucible and the sample was noted as M_d . The covered crucible and its content were then placed in a muffle furnace (Model No: CBFL518C, USA) that was maintained at 900°C for 7 min. After 7 min, the crucible was removed and placed in a desiccator to cool to room temperature. The weight of the crucible and the sample was noted as M_e after cooling. The VM was then calculated using the relation in Equation (3.17);

$$VM(\%) = \left(100 \left(\frac{M_d - M_e}{M_d - M_b} \right) - MC \right) \times \frac{100}{100 - MC} \quad (3.17)$$

where M_b = weight of the empty sintered alumina crucible plus lid (g), M_d = weight of sintered crucible plus lid plus sample before heating, MC = moisture content and M_e = weight of crucible plus lid plus furnace-dried sample.

(b) Torrefied biomass, pitch and coal

An alumina crucible was placed in an Electronic Analytical and Precision Balance (Sartorius BSA Series: BSA 224S-CW) and the weight was recorded as M_o . An approximate 1 g of sample was measured into the crucible and was then covered with a lid. This was done to avoid blasting and combustion of the sample. The weight of the covered crucible and sample was recorded as M_a . Muffle furnace (Model No: CBFL518C, USA) was preheated to 950°C before placing the covered crucible inside for 7 min. The crucible was then removed and allowed to cool in a desiccator and the final weight was noted as M_f . The volatile matter was then calculated using Equation (3.18);

$$VM = \frac{M_a - M_f}{M_a - M_o} \times 100\% \quad (3.18a)$$

$$VM_{db} = VM - MC \quad (3.18b)$$

where M_o = weight of crucible (g), M_a = weight of crucible and the sample (g) and M_f = weight of crucible and the furnace-dried sample. VM_{db} = volatile matter without moisture.

3.3.2.3 Ash content

(a) Raw biomass

The ash content (AC) was carried out in a muffle furnace (Model No: CBFL518C, USA) in accordance with ASTM E1755-01 (2015) standard. Biomass sample (1 g) was placed in a silica crucible and transfer into an oven (Model No: OF-22G, JESO TECH, Korea) for drying at 105°C for 1 h, after which it was removed and placed in a desiccator for cooling. The weight was recorded as M_{od} after cooling. The crucible and sample was then

placed in the muffle furnace up to 585°C and soaked for 3 h. After which it was removed and observed for possible presence of carbon residue. The presence of some carbon residues in the sample necessitated for continuous heating. The crucible and the sample were placed in the furnace for another 1 h till the weight varies to less than 0.3 mg. The final weight of the crucible and sample was recorded as M_{ash} and ash content was calculated using Equation (3.18);

$$AC = \left(\frac{M_{\text{ash}}}{M_{\text{od}}} \right) \times 100\% \quad (3.18)$$

where M_{od} = Initial mass of 105°C dried sample and crucible (g), M_{ash} = mass of ash and crucible (g).

(b) Torrefied biomass, pitch and coal

A muffle furnace (Model No: CBFL518C, USA) was used for ash analysis. A silica crucible was weighed in an Electronic Analytical and Precision Balance (Sartorius BSA Series: BSA 224S-CW) and the weight was noted as M_c . An approximate sample of 1 g was measured into the crucible and both weight recorded as M_s . The crucible and the sample were placed in the muffle furnace set at 815°C. It was allowed to soak for 1 h in the furnace after which it was removed and placed in a desiccator for cooling. The weight of the crucible and the furnace-dried sample were measured and recorded as M_f . The ash content was then calculated using Equation (3.19).

$$AC = \frac{M_f - M_c}{M_s - M_c} \times 100\% \quad (3.19)$$

where M_c = weight of crucible, M_s = weight of crucible and sample and M_f = weight of crucible and furnace-dried sample.

3.3.2.4 Fixed carbon content

The fixed carbon (FC) of the raw biomass, torrefied biomass, pitch and coal was calculated by difference using Equation (3.20).

$$FC = 100 - (MC + AC + VM) \quad (3.20)$$

3.3.3 Ultimate, compositional and SEM analyses

3.3.3.1 Carbon, Hydrogen and Nitrogen (CHN) analysis

The CHN analyses of the raw biomass, torrefied biomass, coal and pitch was carried out in a LECO-CHN628 Analyzer (Model No: 622-000-000, SN-12357) using ASTM D5373 (2016) standard. Oven-dried sample (105°C for 1 h) of 0.5g was weighed and encapsulated in a thin foil to fit into the Assay Carousel Stackable 30POS that served as holder for the sample in the LECO-CHN628 Analyzer. The sample was transfer into the purge chamber directly above the combustion furnace already at 1300°C. The combustion process of the sample, reduction of the output gases and display of result took close to 7 min for each analysis. The result was displayed in percentage mass on computer screen as analyzed by windows-based CHN628Series software connected with the equipment

3.3.3.2 Sulphur analysis

Sulphur analysis was carried out in a LECO S-144DR Sulphur Determinator (Model No: 606-000-300, SN-477) using ASTM D4239-11 (2011) standard. Oven-dried sample (105°C for 1 h) of an approximate value of 0.1 g was weighed into a silica boat crucible. The silica boat crucible was then pushed into the tubular furnace already heated to 1350°C where combustion of the sample took place. Sulphur detector then detect the quantity of sulphur present in percentage mass and the result was analyzed using S-144DR software connected with the equipment. Oxygen content for the raw biomass, torrefied biomass coal and pitch was calculated by difference that is $100 - (C + H + N + S + \text{Ash})$.

3.3.3.3 Compositional analyses

Compositional analysis was carried out by gravimetric method as reported by Ayeni *et al.* (2015) and it is detailed below.

Determination of extractives content

Dried raw biomass of 2.5 g was loaded into a cellulose thimble of Soxhlet extractor. With the Soxhlet extractor set up, 150 mL of acetone was used as solvent for extraction. Residence times for the boiling and rising stages were carefully adjusted to 70°C and 25 min respectively on the heating mantle for a 4 h run period. After extraction, the sample was air dried at room temperature for five minutes. Constant weight of the extracted material was achieved in a conventional oven at 105°C. The %(w/w) of the extractives content was evaluated as the difference in weight between the raw extractive-laden biomass and extractive-free biomass.

Hemicellulose: 1 g of extracted dried biomass was transferred into a 250 mL Erlenmeyer flask. 150 mL of 500 mol/m³ NaOH was added. The mixture was boiled for 3.5 h with distilled water. It was filtered after cooling through vacuum filtration and washed until neutral pH was attained. The residue was dried to a constant weight at 105°C in a conventional oven. The difference between the sample weight before and after this treatment is the hemicellulose content (%w/w) of dry biomass (Ayeni *et al.*, 2015).

Lignin: 0.3 g of dried extracted raw biomass was weighed in glass test tubes and 3 mL of 72% H₂SO₄ was added. The sample was kept at room temperature for 2 h with careful shaking at 30 min interval for complete hydrolysis. After the initial hydrolysis, 84 mL of distilled water was added. The second step of hydrolysis was made to occur in an autoclave for 1 h at 121°C. The slurry was then cooled at room temperature. Hydrolysates were filtered through vacuum using a filtering crucible. The acid insoluble lignin was determined by drying the residues at 105°C while monitoring weight change. The acid soluble lignin fraction was determined by measuring the absorbance of the acid hydrolyzed samples at 320 nm (UV-VIS spectrophotometer). The lignin content was calculated as the summation of acid insoluble lignin and acid soluble lignin.

Cellulose: The cellulose content (%w/w) was calculated by difference, assuming that extractives, hemicellulose, lignin, ash, and cellulose are the only components of the entire biomass.

3.3.3.4 SEM analyses

Morphology observation of raw and torrefied biomass was carried out in a Tabletop microscope (T-1000 model, Japan).

3.4 Briquette production

The briquette production process was carried out based on the layout shown in Figure 3.3. Raw materials used were in accordance with the typical formulation shown on Tables 3.3 and 3.4 for the total briquette weight.

Table 3.3: Formulation of briquette with individual binders
(Percentage of total briquette weight)

Hybrid ratio	Coal (%)	Torrefied biomass (%)	Binders (%)	Water (%)
97:3	97	3	3-20	10
95:5	95	5	3-20	10
90:10	90	10	3-20	10
85:15	85	15	3-20	10
80:20	80	20	3-20	10

Table 3.4: Formulation for blended binder in 97:3 hybridization ratio
(Percentage of total briquette weight)

Hybrid ratio	Binders (%)				
	Coal (%)	Torrefied biomass (%)	Pitch	Molasses	Water (%)
97:3	97	3	5	5	10
97:3	97	3	8	7	10
97:3	97	3	10	5	10
97:3	97	3	5	10	10

Representatively, 8P-7M for blended binder composition implied that 8% pitch and 7% molasses were added as part of the total briquette weight as shown in Table 3.4. Similarly, 90:10 HR is a tag for hybrid ratio where coal fine is 90% and torrefied biomass is 10% of the total briquette weight. Four different particle size distributions were adopted to evaluate the influence of coal slack sizes on briquette production: -BSS 36 mesh, -BSS 72 mesh, -BSS 100 mesh and -BSS 150 mesh. The blends of coal fines, torrefied biomass, binder and water were thoroughly mixed together to obtain homogeneity. Briquetting of 25 g of the blends was carried out in a 25 mm internal diameter cylindrical steel die under a hydraulic press as shown Figure 3.4. The load used was in the range of 14 - 55 MPa for briquette production. Briquettes of various configurations and hybrid ratios were produced. Briquettes were cured at room temperature and then further cured in muffle furnace (inert condition) at the temperature range of 200 - 300°C for a residence time of 30 - 120 minutes. The briquettes were allowed to cool in a desiccator after removal from the furnace and were placed in zip locked bags for further characterizations.

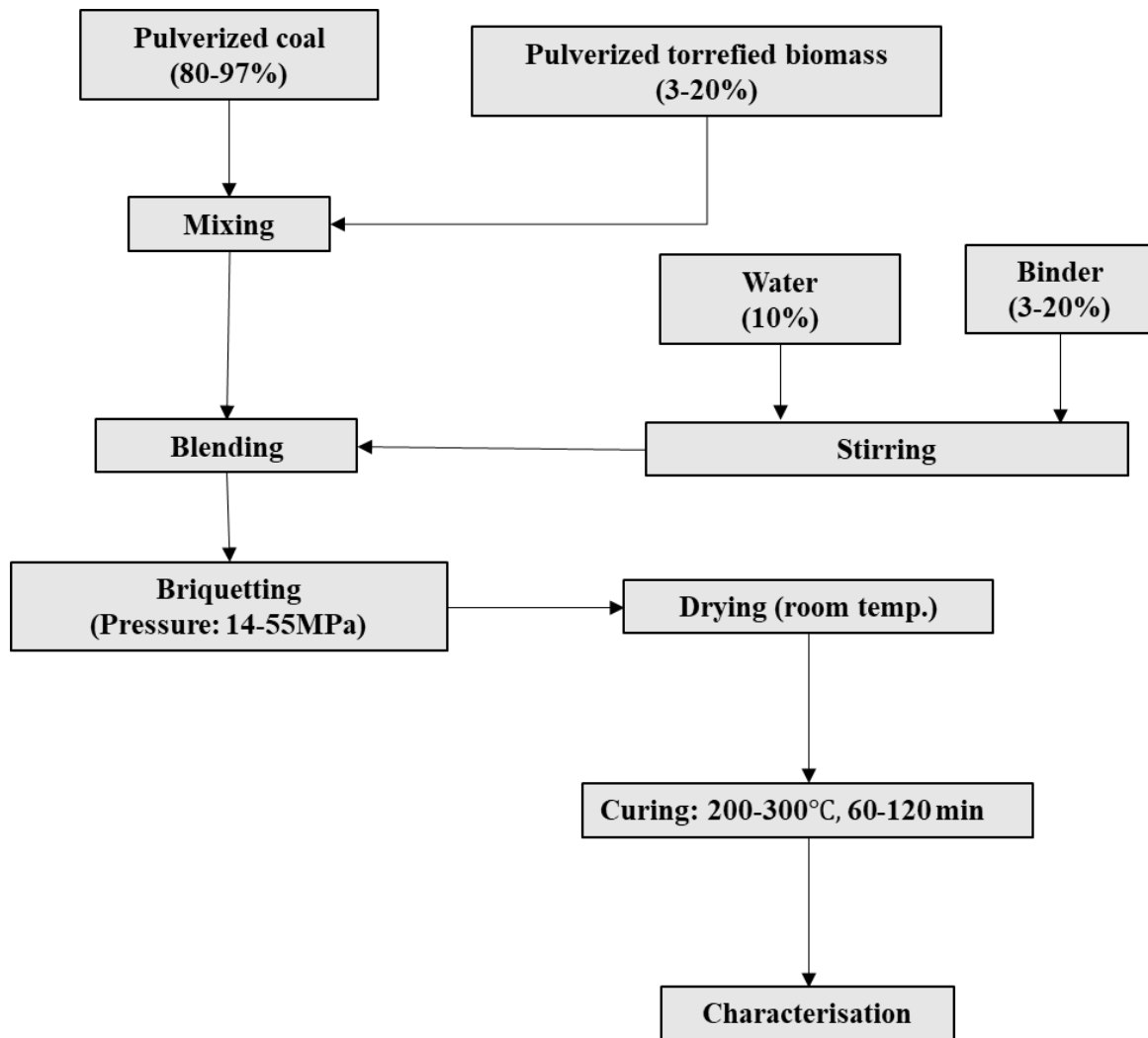


Figure 3.3: Production layout for hybrid fuel briquette



Figure 3.4: Briquetting machine and its components

3.5 Evaluation of briquette properties

3.5.1 Physical and Mechanical properties

(a) Bulk density

The height, diameter and mass of green briquettes were measured and recorded in order to calculate the green density. The measurement were repeated after the briquettes were cured in order to obtain the dry density. The density was calculated as a ratio of mass to volume for each briquettes. The volume of the samples was calculated using Equation (3.21).

$$V = \pi r^2 h \quad (3.21)$$

where V is the volume (cm^3), r is the radius of the cylindrical samples (cm) and h is the height (cm). The density (ρ) was then obtained using Equation (3.22);

$$\rho = \frac{M}{V} \quad (3.22)$$

(b) Impact resistance and drop tests

In order to measure the resistance of the hybrid fuel briquettes to size degradation when subjected to different kind of forces, drop and shatter tests were carried out on the briquettes in accordance with previously reported and widely accepted methods (Blesa *et al.*, 2001; Richard, 1990; Thoms *et al.*, 1999). Drop test involves averaging the results of 3-6 single drop tests. Briquette sample was repeatedly dropped from a stationary height of 2 m onto a concrete floor until it fractured. The average number of drops it took the briquette to fracture into pieces and the average number of pieces the briquettes broke into were recorded. The impact resistance index was then calculated based on the relation in Equation (3.23).

$$IRI = \frac{100 \times \text{Average no of drops}/2\text{m}}{\text{Average no pieces}} \quad (3.23)$$

(c) Cold crushing strength (CCS)

Cold crushing strength (compressive strength) was carried out in a universal mechanical testing machine (Figure 3.5) operated in a compression mode (10 kN Hounsfield apparatus) as applicable for coke and briquettes (Richard, 1990; Thoms *et al.*, 1999; Yip *et al.*, 2007). Each briquette was placed between the crushing jaws and allowed to have a tight contact with pressure head at 0.5 mm/s strain rate. The maximum crushing load (M_f) which the briquettes can withstand before cracking or breaking was recorded and repeated twice for each sample. The average was used to calculate CCS in accordance with Equation (3.24). D is the bottom circular diameter of the briquettes.

$$CCS = \frac{4M_f}{\pi D^2} \quad (3.24)$$

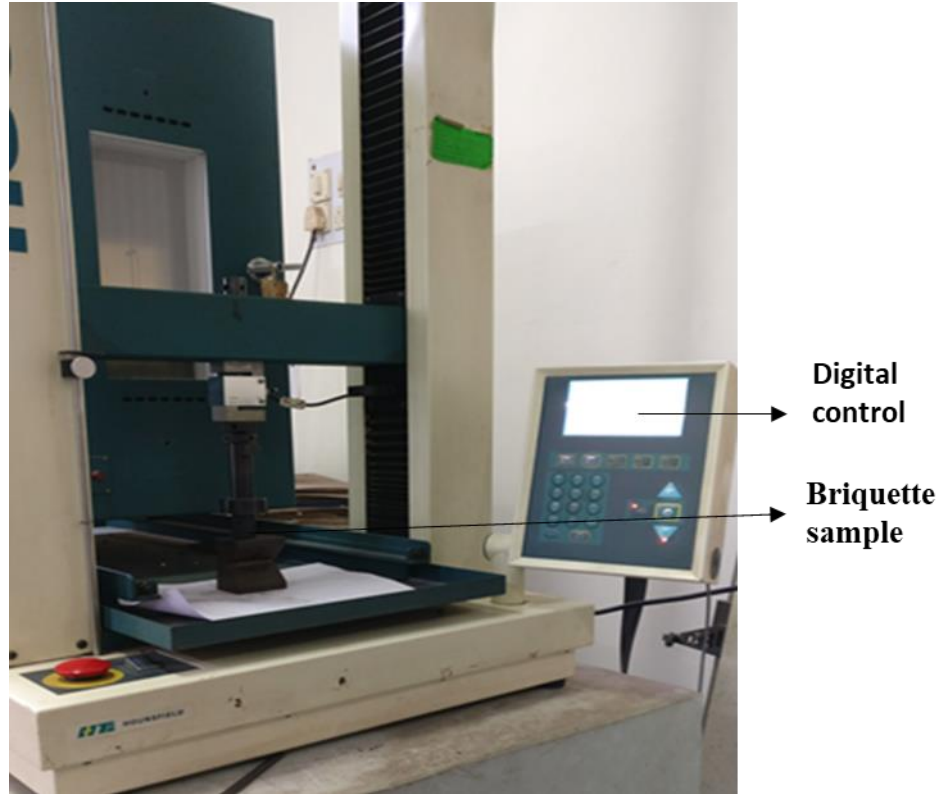


Figure 3.5: Hydraulic mechanical testing machine loaded with briquette sample

(d) Water Resistance

A simple immersion-in-water test on a single briquette was adopted for resistance against absorption of water and disintegration in accordance with modified Richard's method (Richard's 1990). Briquette of a known weight (W_1) was immersed in a cylindrical glass containing 220 ml water at $30 \pm 2^\circ\text{C}$ for 30 minutes after which it was removed and cleaned to remove water on its surface and reweighed (W_2). Relative change in weight of the briquettes was measured and percentage water absorbed was calculated using Equation (3.25) from which WRI (%) was evaluated with Equation (3.26);

$$\% \text{ of water absorbed} = \frac{W_2 - W_1}{W_1} \times 100 \quad (3.25)$$

$$\text{WRI (\%)} = 100 - \% \text{ water gained} \quad (3.26)$$

(e) Tumbling test

Some briquette samples were selected based on the initial physical properties to observe abrasion resistance of the briquette after curing and high temperature exposure. For

high temperature exposure, briquettes were placed in the furnace, heated to 1200°C and held for 2 h after which it was adopted for tumbling test. Tumbling strength test was carried out in accordance with modified Ueki *et al.*'s (2014) mini-laboratory method for briquette. The setup was made of stainless steel tubular vessel of 40 mm inner diameter, a length of 200 mm and a belt system for rotation as shown in Figure 3.6. Three to four briquette samples of known initial weight W_0 were placed in the steel tube and rotated at a speed of 30 rpm for 20 minutes. The sample was removed after tumbling and screened on a 3.15 mm size sieve. The +3 mm particles of the sample were weighed and used to calculate tumbling strength index in accordance with Equation (3.27) (Ueki *et al.*, 2014);

$$TSI_{+3mm} = \frac{W_{+3mm}}{W_0} \times 100 \quad (3.27)$$

where TSI_{+3mm} is the tumbling strength index (%), W_{+3mm} and W_0 are the weight of +3mm particle size and initial samples.

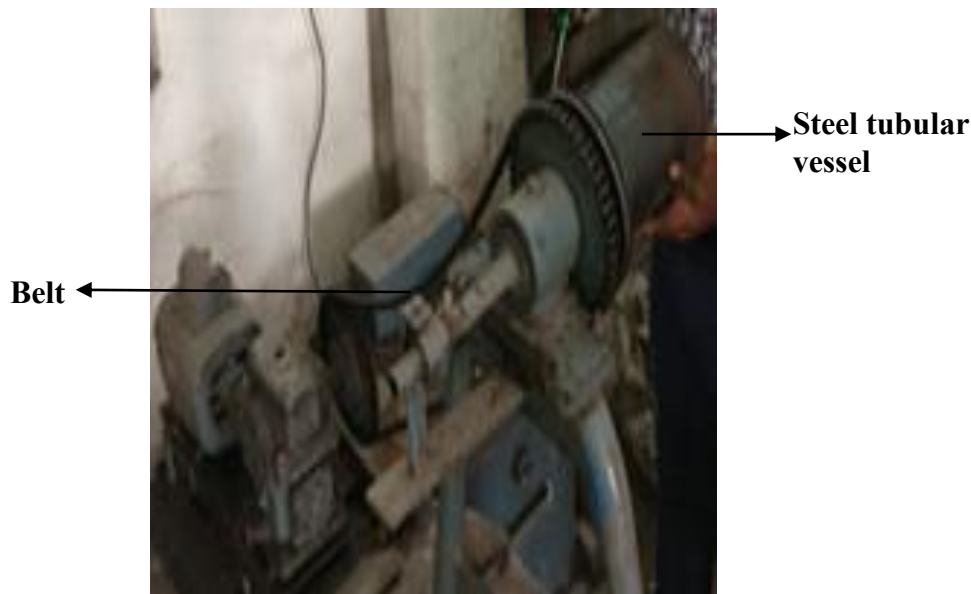


Figure 3.6: Tumbling index experimental setup

3.5.2 Ash Fusion Test (AFT)

Ashing of pulverized coal and some selected briquette samples was carried out in a muffle furnace at 815°C for 3 h. AFT was carried out in accordance with ASTM D 1857-04

standard (2005). 1 g of the ash was mixed with dextrin solution to be formable into cone in shape plate. The formed cones were allowed to dry for 4 - 5 min in the sample holder. The AFT (AF700) furnace was purge with N₂ and O₂ gases (50/50) at 2.2 - 2.5 L/min. At 400°C, the sample was placed in the furnace while the process was monitored with an AFT700 software to evaluate the initial deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT) and final fusion temperature (FT).

3.5.3 Phase Identification

X-ray diffraction (XRD) method was used to identify phases present in the ashes of raw coal and hybrid fuel briquettes samples. Powdered samples were scanned at 2 θ from 10 - 90° using Cu-K α radiation filtered with Ni (λ of 1.5426 Å) at the scan rate of 0.02sec/step in an X-ray power Diffractometer (D8 Discover, Bruker, Germany). The principle of X-ray diffraction is based on x-rays scattering by lattice atoms acting as grating. In accordance with Bragg's law, parallel beams of x-ray of wavelength λ are incident on a set of crystal planes of interplanar spacing, d , at an angle θ and the constructively scattered x-rays provides the corresponding XRD pattern based on the Equation (3.28);

$$n\lambda = 2d\sin\theta \quad (3.28)$$

where n is the order of diffraction, λ is the wavelength of X-ray, d is the distance between two planes (interplanar distance) and θ is the Bragg's diffraction angle. Phases present in pulverized raw coal, biomass, biochar and briquettes samples were determined by JCPDF (Joint committee power diffraction file) software with standard XRD patterns of various elements and compound of powder samples.

3.5.4 Ash Analyses

The ash compositional analysis of selected samples was carried out using X-ray fluorescence (XRF) spectrometer (Bruker S8 TIGER model). Briquette ash of 8 g was thoroughly mixed with 2 g of wax (binder). The mixture was made into pellet of 34 mm

diameter (1 mm thick). The sample was then placed in sample holder and transfer into the XRF for analyses. Spectra plus launcher was used to collect ash compositions.

3.5.5 Combustion analyses

Selected briquette samples were subjected to proximate, ultimate and higher heating value (HHV) analyses. This was done to evaluate the influence of briquetting procedure and binders on the thermal properties of the coal slack. The briquette sample was pulverized and sieved to particle size below 72 mesh and subjected to similar procedure discussed in section 3.3.

3.5.6 Fourier Transform Infrared spectrophotometry

Fourier Transform Infrared spectrophotometry (FTIR) spectrophotometry was used to characterize the functional groups present in the raw biomass, torrefied biomass, raw coal, pitch and some briquette samples. An approximately 2 mg of samples with dry KBr (potassium bromide) powder, approximately 300 mg, were weighed into an agate mortar for pulverization and mixed until the samples dispersed into each other. The powder mixture was molded by pressing into a transparent disc for 10 min using a tablet machine. The discs were analyzed by FTIR and the spectra were recorded in the range of $4000 - 400 \text{ cm}^{-1}$ at a resolution of 4cm^{-1} .

3.5.7 Microstructural and elemental studies

The microstructural and elemental studies of few hybrid fuel briquettes were carried out using scanning electron microscope (SEM) and electron probe microanalyzer (EPMA) equipped with EDX (energy dispersive x-ray spectroscopy). Hybrid fuel briquettes of 2 mm x 10 mm cylinder were placed in carbon coater and vacuumed to 1.5 Torr for degassing and removal of dust particles before been used for microanalyses. The SEM study was carried out at 15 keV and at a vacuum of 10^{-6} Torr using Nova Nano SEM 430. EPMA characterization was performed at a similar operating condition to SEM via JEOL 8230 model. SEM images

were taken at different magnifications for comparison. EDX was used to do point and bulk elemental analyses of the briquettes. Elemental mapping of few samples were also carried out to see their distribution in the briquettes.

3.5.8 Reactivity test

Reactivity of some briquette sample was carried out based on ASTM D5341M-14 (2014). 200 g of +19 mm -21 mm briquettes samples were placed in reaction vessel (Inconel tube) which was purged for 5 min at 5 to 10 L/min of N₂ before loading the vessel into the furnace. The reaction vessel was placed into the furnace and heated to 1100°C in the atmosphere of N₂ gas within 30 min. The samples were soaked at 1100°C for 10 min in N₂ gas. Thereafter, CO₂ gas was introduced into the furnace at a flow rate of 5.0 L/min and the samples were soaked for 120 min. After exactly 120 min exposure to CO₂, the gas source was switched back to N₂ at 5 to 10 L/min for 5 min to purge the reactor vessel of CO₂. Subsequently, the reaction vessel was removed from the furnace and the sample was allowed to cool to temperature of 100°C. After cooling, the briquettes samples were weighed and the reactivity index (RI) was calculated based on the relation in Equation (3.29);

$$RI = \frac{A-B}{A} \times 100 \quad (3.29)$$

where A is the original test sample weight before reaction and B is the sample weight after reaction in CO₂.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterisation of the woody biomass, coal and binders

The raw woody biomass, Melina (RMw) and Teak (RTw), were characterised along with coal and pitch samples and the results are discussed in this section. The proximate analysis include the moisture content, volatile matter, ash content and fixed carbon while the CHNSO contents were determined through ultimate analysis. The calorific value were determined and presented as higher heating value (HHV).

4.1.1 Proximate, ultimate and HHV analyses of the woody biomass

The proximate, ultimate and higher heating value (HHV) analyses for the woody biomass are presented in Table 4.1. The moisture content of RMw and RTw are within the range of 7.01 - 10.43 % obtained for tropical woody biomass, and are higher than the range of 5.74 - 6.31% for non-woody biomass (Balogun, 2014). High moisture content of the woody biomass is considered as a disadvantage for its effective utilization as feedstock for combustion or gasification process (Basu, 2013). Thus, the need for its removal/reduction to the barest minimum level through torrefaction process.

The volatile matter (VM) content of the RMw and RTw ranges from 79 - 81% and it is higher than the 13.77% obtained for coal and 73.99% of pitch. Basu (2013) revealed that woody biomass usually contains VM (dry basis) > 80%. The VM shows the amount of condensable and non-condensable vapour that will be released when the fuel is heated. High VM in woody biomass and pitch implied that higher vapour will be released during their combustion as against coal (Tables 4.1 and 4.2). High VM of the woody biomass is a huge disadvantage to its usefulness (Ayse, 2010; Basu, 2010; Zhong *et al.*, 2017). The high VM often leads to fast combustion, smoke formation and also make biomass hydrophilic in nature

(Basu, 2013; Tumuluru *et al.*, 2011). Therefore, some degree of devolatilization becomes paramount before adopting biomass as feedstock for combustion and gasification processes.

The inorganic content of the woody biomass is very low compared with the lean grade coal used in this study as shown in Table 4.2. The ash content, which is 2.15% for RMw and 1.73% for RTw, are higher than 0.3% obtained for Eucalyptus wood (Arteaga-Pérez *et al.*, 2015) and 1.11% obtained for Bayan wood (Chen & Kuo, 2010). However, the ash contents are lower than 2.70 and 4.20% obtained for Beach and Birch woods, respectively (Wei *et al.*, 2017). Therefore, the ash contents of the woody biomass are within reasonable amount (<5%) that is useful for energy generation based on the previous findings and recommendations (Wei *et al.*, 2017).

The fixed carbon (FC) contents of the woody biomass (8.72% - 11.75%) are significantly low compared with that of the lean grade coal (66.92%) as shown in Table 4.2. Though, on a general perspective, biomass contains low fixed carbon (Basu, 2013). The FC obtained in the present study are in trend with 10 - 12% obtained for willow wood (Bridgeman *et al.*, 2008) and 8.98% obtained for *Ficus Benjamina* (Chen & Kuo, 2010). The effect of low FC of the biomass is reflective in its HHV as shown in Table 4.1. The HHV of the woody biomass is lower than that of lean grade coal and can also be traced to their low carbon contents (Table 4.2).

The carbon (47%), hydrogen (6 - 7%), nitrogen (0.38 - 0.39%) and sulphur contents (0.24 - 0.26%) of RMw and RTw are similar to those of tropical wood in previous studies (Arteaga-Pérez *et al.*, 2015; Balogun, 2014; Chen & Kuo, 2010). The low sulphur and nitrogen contents are pointers that woody biomass can be useful for briquette production with low probability of emission of voluminous greenhouse gases. The oxygen content of the woody biomass is higher compared with coal and pitch as shown in Tables 4.1 and 4.2. This could lead to low fuel ratio in the woody biomass compared with the lean grade coal. It is

therefore expedient to upgrade the woody biomass before its utilization as feedstock in the briquette production to reduce the moisture, the volatile matter and the oxygen content and improve the higher heating value.

Table 4.1: Proximate, ultimate and higher heating value analyses of the raw woody biomass

Samples	Proximate analysis (%)				Ultimate analysis (%)					HHV (MJ/kg)
	MC	VM	AC	FC	C	H	N	S	O	
Melina	7.52	81.42	2.15	8.92	47.09	6.65	0.38	0.24	43.54	18.39
Teak	7.23	79.26	1.73	11.73	47.84	6.09	0.39	0.26	43.69	18.72

4.1.2 Proximate, ultimate and HHV analyses of the coal

The proximate, ultimate and higher heating value (HHV) analyses of the coal and pitch used in this study are presented in Table 4.2. The moisture content (MC) of the coal is 1.37% and this is similar to 1.33% that was reported for coal in Shankodi Jangwa mine, in Nigeria (Ryemshak & Jauro, 2013) as shown in Table 4.2. The moisture content is however, lower than 6.10% reported for coal from Oyeama's mine (Ilochi, 2010) as shown in Table 4.2. The low moisture content of the coal is of great advantage when using it as a feedstock in the production hybrid fuel briquette.

The volatile matter (VM) content of the coal is lower than 30.09% and 23.00% reported for coal from Shankodi Jangwa (Ryemshak & Jauro, 2013) and Oyeama's mine (Ilochi, 2010), respectively. The coal falls in the range of sub-bituminous family which are referred to as lean grade (Speight, 2012). The volatile matters of the coal is far lower than that of the woody biomass (Table 4.1) and this implied that there will be lower smoke during its combustion. The low VM also shows that the lean grade coal is hydrophobic in nature

compared with the woody biomass and thus, will impact this property to the hybrid fuel briquette.

Lean grade coals have high ash content that can be as high as 50% as reported by Speight (1994). The ash content of the coal in the present study is similar to coal from Shankodi Jangwa's mine and a little higher than coal from Oyeama's mine as shown in Table 4.2. The ash content of the coal is lower compared with 20.42% ash content of Gari Maiganga coal (Ryemshak & Jauro, 2013) and 30.00% of Afuze coal (Nyakuma, 2015) of Nigeria origin. This suggests that the coal can be representatively used on the basis of ash content as feedstock in the production of hybrid fuel briquette.

Fixed carbon is the carbonaceous material in the coal which is left after volatile materials are driven off (Speight, 2012). The fixed carbon (FC) content of the coal is 66.92% and this is higher than what was reported for coals from Shankodi Jangwa's and Oyeama's mines as shown in Table 4.2. The fixed carbon of the coal is higher than those of the woody biomass as shown in Table 4.1. The FC of the present coal makes it suitable for the production of hybrid fuel briquettes along with upgraded biomass.

The HHV of the coal in this study is higher compared with those of woody biomass (Table 4.1) and this can be traced to their carbon and fixed carbon contents. The HHV of the coal in this study compares well with coal from Oyeama's and Shankodi Jangwa's mine as shown in Table 4.2. This shows that the coal in the present study can potentially serve as feedstock for the production of hybrid fuel briquette.

Coal is majorly classified based on its carbon content into various family or group. The coal in the present study belongs to the low-volatile sub-bituminous or lignite family with carbon content ranging from 66 - 80% (Speight, 1994). They are often referred to as lean grade coal and this is the most abundant family available in Nigeria mines. Lean grade coal generates high volume of slack which are often discarded as waste though contains

considerably high amount of carbon (Taulbee *et al.*, 2009). The low sulphur and nitrogen contents in the present coal are similar to the previous studies as shown in Table 4.2. This implied that along with the woody biomass, there will be significant reduction in the emission of oxides of sulphur and nitrogen when used for energy generation.

Table 4.2: Proximate, ultimate and higher heating value analyses of coal and pitch

Samples	Proximate analysis (%)				Ultimate analysis (%)					HHV (MJ/kg)
	MC	VM	AC	FC	C	H	N	S	O	
Coal	1.37	13.77	17.94	66.92	73.43	2.51	1.31	0.71	22.04	23.13
Pitch	0.18	73.99	0.95	24.88	89.17	7.43	0.30	0.50	2.60	39.73
Pitch ⁺⁺	-	72.71	0.06	27.23	92.23	4.81	1.07	-	1.38	-
SJ*	1.33	30.09	17.37	52.26	82.51	4.52	1.63	1.31	10.03	27.21
Oyeama**	6.10	23.00	14.00	56.90	64.30	-	-	0.93	-	21.25

*SJ-Shankodi Jangwa coal mine (Ryemshak & Jauro, 2013),**Ilochi (2010) ⁺⁺Zhong *et al.* (2017)

4.1.3 Proximate, ultimate and HHV analyses of the binders

Due to the difficulty encountered as a result of lower melting point of starch and the liquid nature of molasses during characterisation, only pitch was subjected to characterisation. The proximate, ultimate and higher heating value analyses of pitch are presented in Table 4.2. Pitch is a by-product of the destructive distillation of coal into char or coke and it is a complex mixture of poly-aromatic with good cohesive nature (Zhong *et al.*, 2017). The moisture content of the pitch is 0.18% and this is a positive sign of the possible low moisture contribution to the hybrid fuel briquette when used as feedstock. The volatile matter of the pitch is 73.99%. Pitch with volatile matter above 72% was described to be of average quality (Zhong *et al.*, 2017). The ash content of the pitch in the present study is higher than pitch from previous study as shown in Table 4.2. However, the FC is lower and

this implied that the pitch considered as binder for the production of the hybrid fuel briquette is also of average quality.

The carbon content of the pitch is lower than what was reported for coal-tar pitch in previous study as shown in Table 4.2. The hydrogen content of the pitch is higher while the nitrogen content is lower compared with that of coal-tar pitch reported by Zhong *et al.* (2017). The characterisation generally depicts that the pitch is a lean grade type with average quality. However, it can be used effectively as binder for the hybrid fuel briquette production based on its good cohesive nature.

4.2 Thermal decomposition

Thermal decomposition study was carried out to understand the weight loss mechanism of both the lean grade coal and woody biomass under non-isothermal conditions and the results are discussed in this section. Thermal decomposition study of the lean grade coal was carried out basically to understand the temperature at which it begins to experience massive weight loss while that of woody biomass was to obtain significant preliminary information in preparation for torrefaction process. Kinetic parameters (activation energy and pre-exponential factor) of Melina wood were also determined to comprehend the behavioral pattern under pyrolysis process especially torrefaction temperature range.

4.2.1 Thermal decomposition of the lean grade coal

The thermogravimetric curves of the lean grade coal which show the weight loss pattern in nitrogen environment at different heating rate are presented in Figure 4.1. The weight loss pattern of the lean grade coal is similar to the woody biomass (Figure 4.2). However, massive weight loss terminated at 800 - 900°C, which reflected a typical characteristic of a lean grade non-coking coal (Speight, 2012). Figure 4.1 shows that coal begins to have massive weight loss around 318°C. This implied that exposure of coal to a temperature higher than 318°C will bring about massive volatile loss. Thus, to produce

briquettes from the lean grade coal, lower temperature range where the weight loss will be limited to bounded and unbounded moisture loss must be employed during its curing. Figure 4.1 served as the basis on which curing conditions for the briquettes were set. To have a briquette with good mechanical integrity from lean grade coal, low temperature curing (200 - 300°C) under a protected environment that is deficient of oxygen was needed.

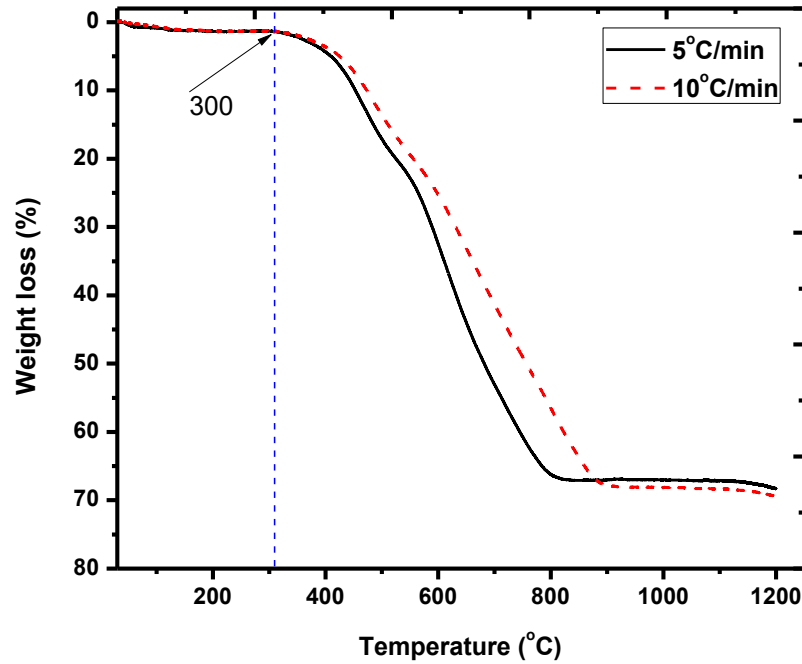


Figure 4.1: Thermogravimetric curves of coal slack at 5 and 10°C/min heating rates

4.2.2 Thermal decomposition of the woody biomass

Figure 4.2 shows the thermogravimetric curves (TG) while Figure 4.3 represent the first derivative thermogravimetric curves (DTG) at different heating rates for Melina and Teak woods. The TG curves (Figure 4.2a and 4.2b) show an initial sharp weight loss (up to 9%) below 110°C for both Teak and Melina woods which resulted from evaporation of unbounded moisture (Zanatta *et al.*, 2016). This stage was followed by reactive drying phase (below 200°C) where there was minimal weight loss as a result of loss of bounded moisture (water of crystallization) and light volatile organic compounds (VOCs) (Balogun *et al.*, 2014).

Active pyrolysis zone (APZ), where significant weight loss occurred resulting from degradation of the wood polymers, then follows. The APZ was between 240 - 350°C and has been described with a wide spectrum of volatile release due to degradation of hemicellulose, cellulose and lignin which are the polymers of biomass (Balogun *et al.*, 2014; Burhenne *et al.*, 2013). There was no appreciable weight loss after 520°C and this stage has been characterized to tends towards residual fixed carbon and ash in woody biomass (Burhenne *et al.*, 2013).

The DTG curves which are mirrors of TG curves show the first peak with a characteristic shoulder that spanned from 30 to 110°C and it basically depicts unbounded moisture loss (Figure 4.3a and 4.3b). The second major peak with characteristic shoulder spanned from 200 to 520°C for both Melina and Teak wood and has been ascribed to cellulose decomposition (Balogun *et al.*, 2014). However, the maximum DTG peak temperature at different heating rates ranged between 318 - 336°C for Melina wood and 345 - 363°C for Teak wood, and this is attributed to cellulose degradation (Balogun *et al.*, 2014). After the maximum DTG peak, the decomposition continues until around 520°C after which it nearly sustained a constant trend. This signifies continuation of cellulose degradation and lignin decomposition (Zanatta *et al.*, 2016).

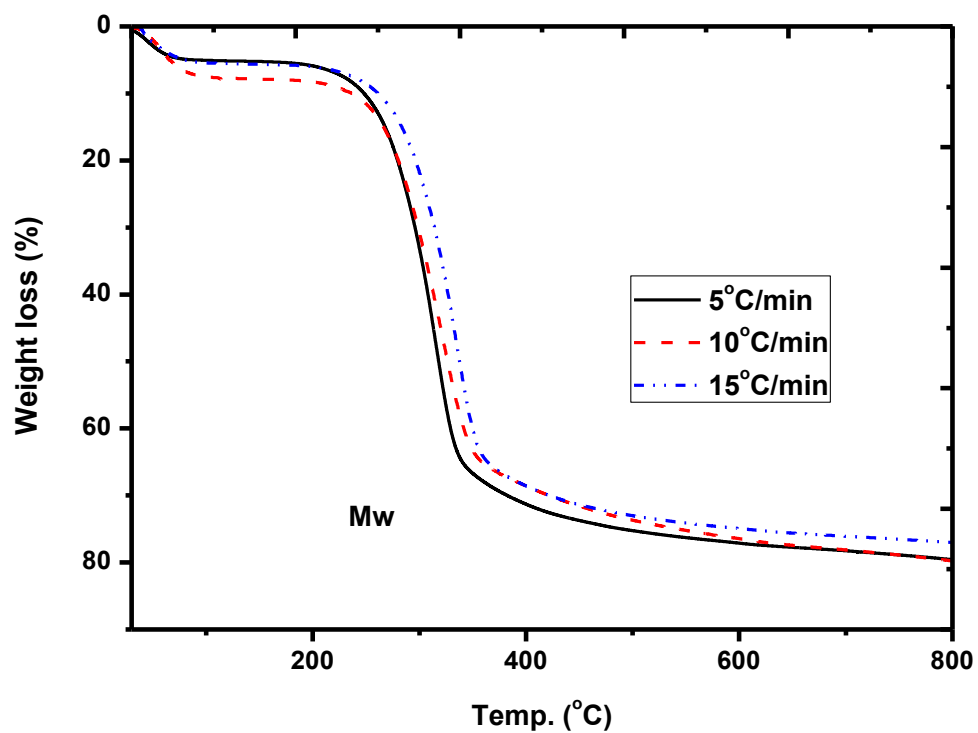


Figure 4.2a: TG curves for Melina wood at different heating rates

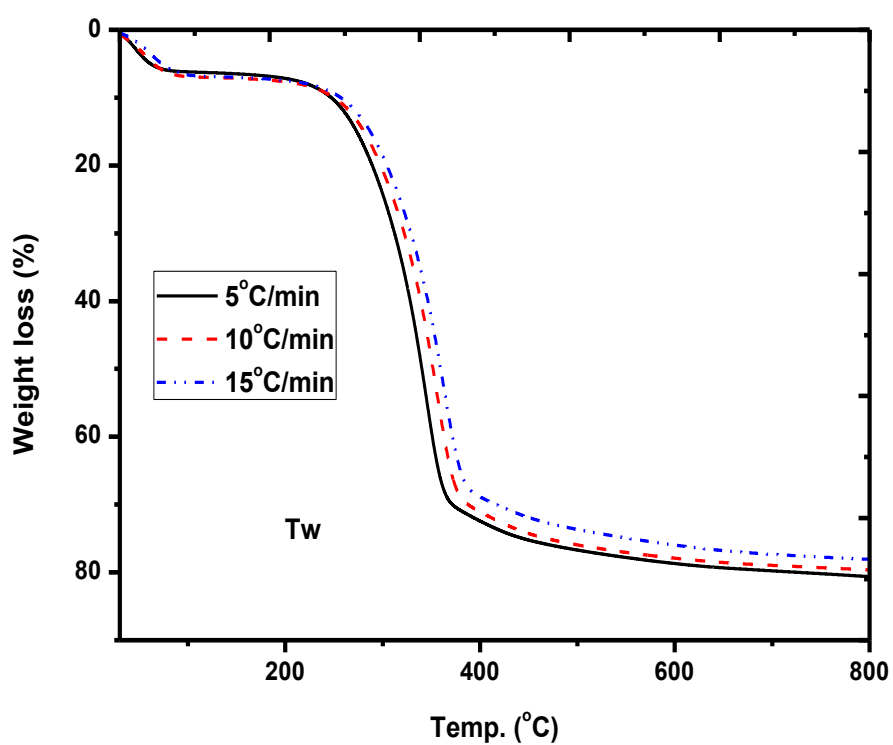


Figure 4.2b: TGA curves for Teak wood at different heating rates

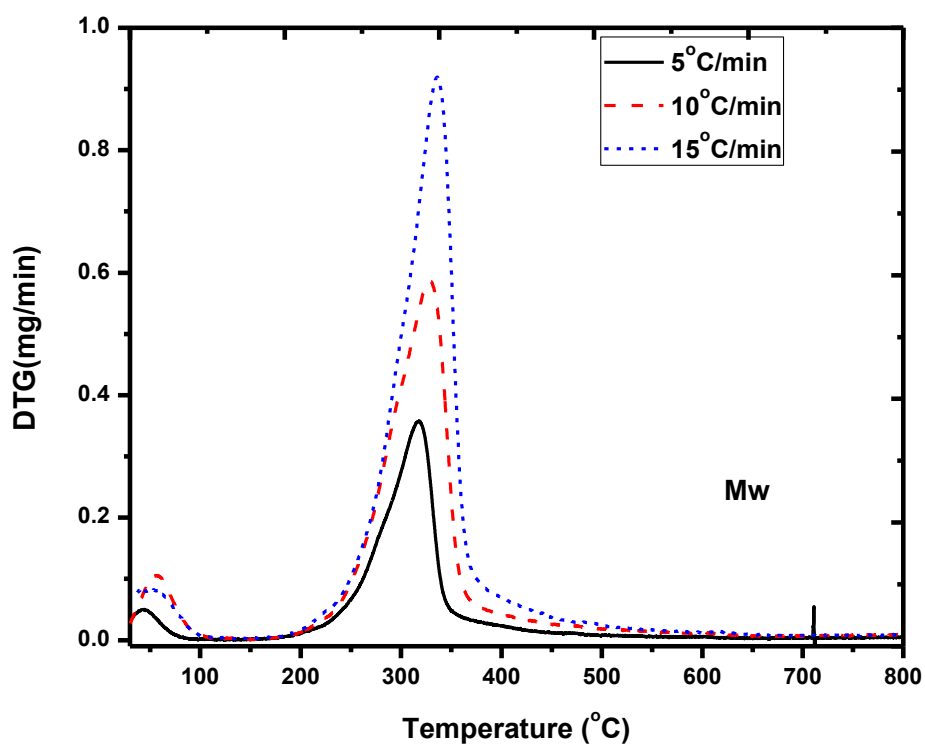


Figure 4.3a: DTG curves for Melina wood at different heating rates

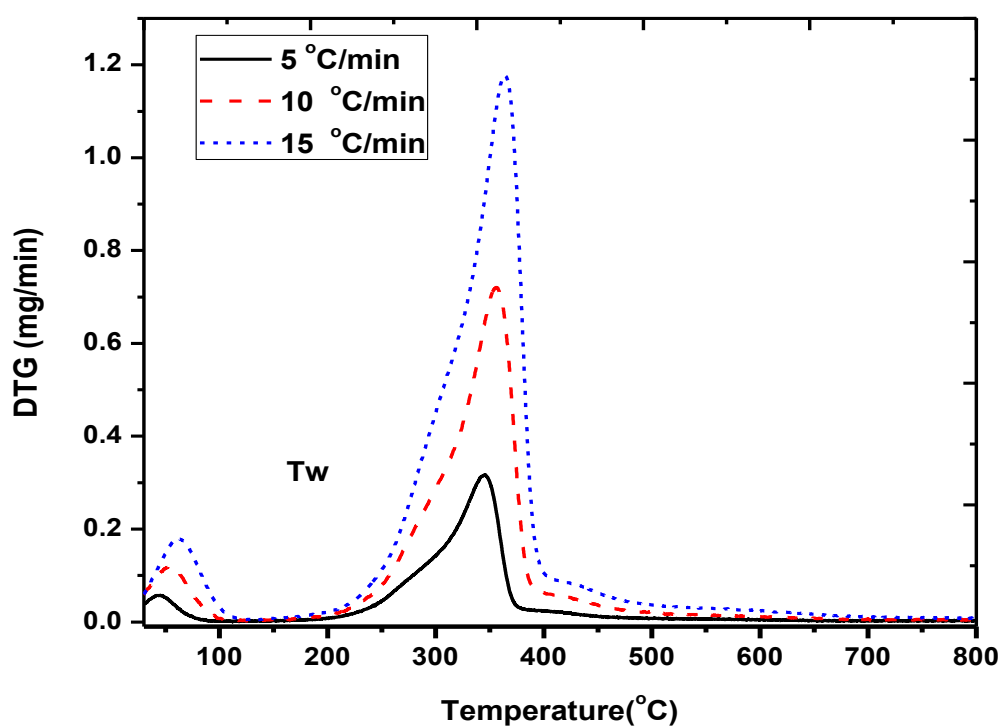


Figure 4.3b: DTG curves for Teak wood at different heating rates

Table 4.3 shows the influence of heating rates on devolatilization parameters during decomposition of both Melina and Teak woods. The heating rate does not affect the temperature where devolatilization commence for both biomass samples, T_{onset} . However, T_{onset} for Teak wood is a little higher compared with that of Melina wood. The temperature at which maximum loss occurred (T_{peak}) increased as the heating rate increases and this was similar for the T_{offset} which describes the termination of degradation of cellulose. The temperature at which the weight loss of the sample remained relatively unchanged (T_{burnout}) also increased as the heating rate increases. These results follow a similar trend for T_{onset} , T_{peak} , T_{offset} and T_{burnout} observed by El-Sayed & Mostafa (2015) for bagasse and cotton stock.

Table 4.3 also shows that maximum cellulose decomposition (DTG_{peak}) increased from 0.3577 to 0.9194 mg/min at 5 to 15°C/min heating rate for Melina wood. It also increased from 0.3165 to 1.1770 mg/min at 5 to 15°C/min heating rate for Teak wood. This result is in agreement with the observation of Williams and Ahmad (2000), who demonstrated that the maximum weight loss rate shifted to higher temperature when TG/DTG was used to investigate the pyrolysis of oil-shale and lignocellulosic biomass. The maximum conversion at T_{peak} (α_{max}) was higher at 5°C/min with 49.96% for Melina wood and 67.87% for Teak wood compared to 48.55% and 67.04 % at 15°C/min for Melina and Teak wood, respectively. It implied that at low heating rate, the transfer of heat is encouraged by mass diffusion mechanism that facilitated more mass loss. This is similar to the observation of Balogun *et al.* (2014) for thermal decomposition of Teak wood. They reported that 55% mass loss was obtained at 5 K/min compared to 48% at 35 K/min heating rate.

The secondary pyrolysis zone (PPZ) is the region where further degradation of hemicellulose, cellulose and lignin continues. This begins at 350°C until the T_{offset} for the different heating rates was reached. Bu *et al.* (2016) attributed this stage to continuous devolatilization with charring.

Table 4.3: Influence of heating rates on devolatilization parameters of the woody biomass during decomposition

Sample	β (°C)	T _{onset} (°C)	T _{peak} (°C)	DTG _{peak} (mg/min)	T _{offset} (°C)	$\alpha_{\max}$ (%)	T _{burnout} (°C)
Melina wood	5	191	318	0.3577	444	49.96	560
	10	197	326	0.4706	502	49.91	607
	15	197	336	0.9194	504	48.55	645
Teak wood	5	197	345	0.3165	463	67.87	496
	10	198	356	0.7208	507	67.81	548
	15	199	363	1.1770	516	67.04	631

The differential thermal analysis (DTA) curves in Figure 4.4 is a successful tool applied for quantification of heat energy required for phase transition, oxidation, decomposition, adsorption and desorption (El-Sayed & Mostafa, 2015). Figure 4.3 shows an initial endothermic effect at 110°C in phase 1 which was immediately followed by an exothermic effect within the same zone below 200°C. The exothermic effect continued at torrefaction temperature range between 200 - 300°C (phase 2) and it has been attributed to hemicellulose and cellulose decomposition. The maximum exothermic effect was observed in phase 3 (between 300 - 400°C) which is more pronounced for Teak wood than Melina. This is attributed to maximum cellulose decomposition and continued lignin degradation (Kok & Özgür, 2013). Generally, based on the thermograms in Figure. 4.4, it can be concluded that the highest heat energy consumption for the thermal decomposition and degradation lies below 400°C at every heating rate, which implied that the process required less external energy consumption as a result of heat been released after the reaction becomes more exothermic.

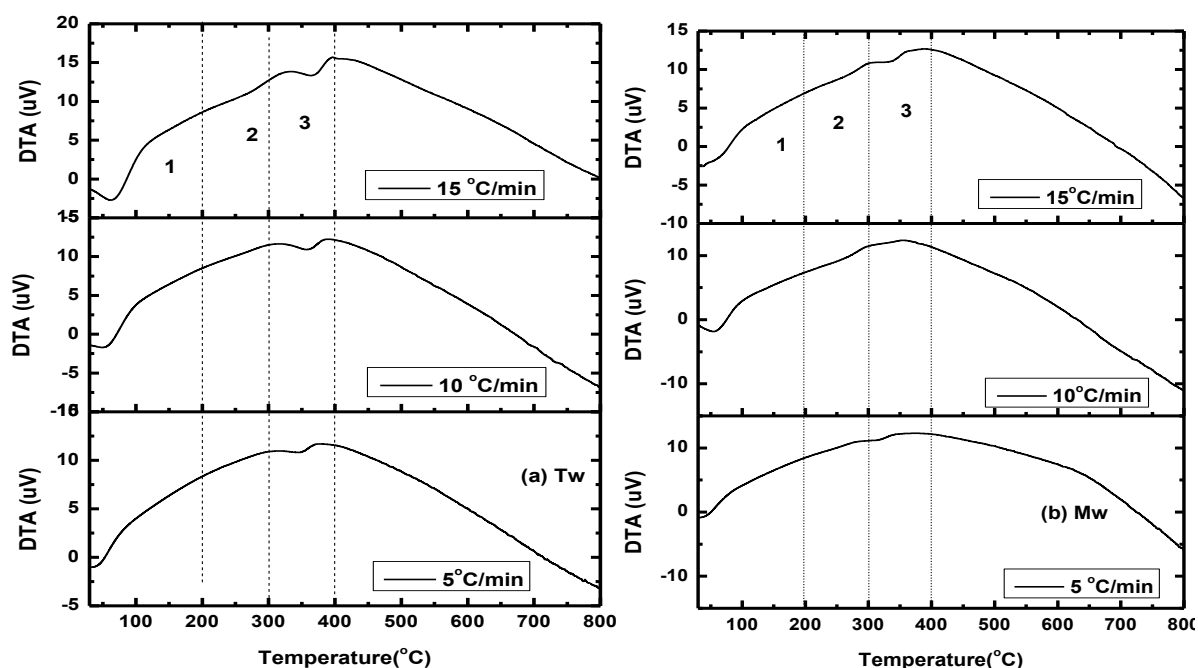


Figure 4.4: DTA curves at different heating rates (a) Teak wood (b) Melina wood

4.2.3 Kinetic parameters for Melina wood

Figures 4.5a and 4.5b represent the isoconversion lines which was derived from Equations 3.4 and 3.6. Fractional ratios of 0.1 to 0.95 were considered in this study since lower fractional conversions represent basic dehydration and unbounded moisture evolution stage (Balogun *et al.*, 2014; Burhenne *et al.*, 2013). Figures 4.6a and 4.6b are the plots of activation energy against fractional conversion and temperature for K-M and F-W-O-M, respectively. As the temperature increases slowly, the activation energy varies for the fractional conversion. Notably, the two isoconversion methods follow a similar pattern. However, the activation energy values obtained using K-M were higher compared to F-W-O-M at every fractional conversion. The difference is due to the mathematical methods of calculation (Vyazovkin *et al.*, 2014). The activation energy fluctuates between 41.21 kJ/mol to 558 kJ/mol for K-M and 15.15 kJ/mol to 161.9 kJ/mol for F-W-O-M within the APZ and PPZ of the decomposition process.

For torrefaction temperature range between 200 and 300°C, there was sharp variations in the activation energy as the conversion ratios increased for both isoconversion methods.

The variation has been explained to be due to biomass heterogeneity in which specific polymers behave differently during devolatilization of reacting pyrolysis compounds (Balogun *et al.*, 2014). The progression of depolymerisation could also influence this variation. From conversion of 0.4 to 0.7 which is within the temperature of 300 - 340°C, the activation energy was nearly constant mainly because of cellulose decomposition. As the reaction progresses and the fractional conversion increases from 0.7 to 0.85, a rise in activation energy which later drops at fractional conversion of 0.9 was observed as a result of lignin decomposition. The temperature increase led to formation of carbon-rich material as a result of higher devolatilization, covalent bond, different functional group of biomass forming higher polymer or aromatization of side chains (El-Sayed & Mostafa, 2015). Similar fluctuation in the activation energy from the beginning to the end of thermal decomposition was obtained for Teak wood by Balogun *et al.* (2014) for both FWO and Starink's isoconversion methods adopted in their study. Therefore, it is noteworthy to state that the values of activation energy for these isoconversion methods depend on the mathematical calculation approach but the trend of fluctuation is important to understand the process of decomposition of the wood polymers.

Due to the fluctuating activation energy during APZ, different reactions were going on which include de-hydroxylation, dehydration of bounded moisture, carbonization among other reactions as reported by Liu *et al.* (2011). However, sufficient energy required for lignin decomposition could be obtained with low temperature input under 400°C as a result of the process being exothermic in nature. Continuous supply of external temperature input is not important for further decomposition because activation energy (E_a) drops after 80% conversion around 350°C.

The thermal decomposition of Melina wood was slow on a general basis at APZ due to high pre-exponential factor as shown in Table 4.4. The results obtained from isoconversion

can be reliable especially for the APZ because of the correlation factors (R^2) which were as high as unity (1) at some conversion ratios. In the torrefaction zone (APZ) which is of paramount interest to this study, the activation energy fluctuates with two minimum and one maximum peaks as shown in Figures 4.6a and 4.6b. This significantly shows hemicellulose and cellulose decomposition. It was followed with an increase in activation which has been attributed to commencement of lignin degradation (El-Sayed & Mostafa, 2015).

Consequently, in designing an industrial reactor for the application/pre-treatment of Melina wood (biomass) in bioenergy production, sufficient thermal decomposition and product formation especially carbon-rich solid residue can be obtained at lower temperature, which implied low energy consumption. In addition, desired extent of devolatilization and rate at which it takes place depending on the end use of biomass can be monitored via the decomposition study.

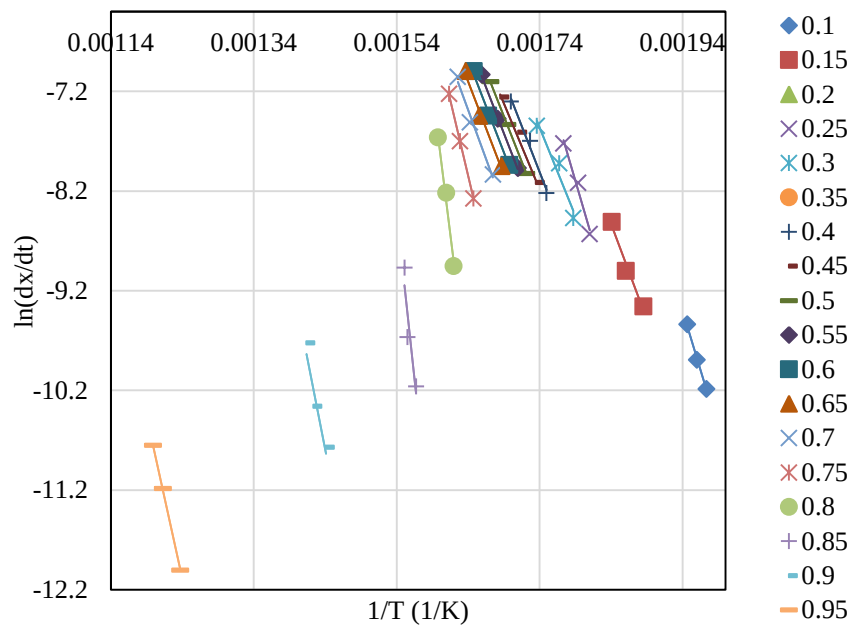


Figure 4.5a: Plot of $\ln(dx/dt)$ against $1/T$ according to K-M isoconversion method to obtain activation energy (E_a) at various conversions (APZ and PPZ).

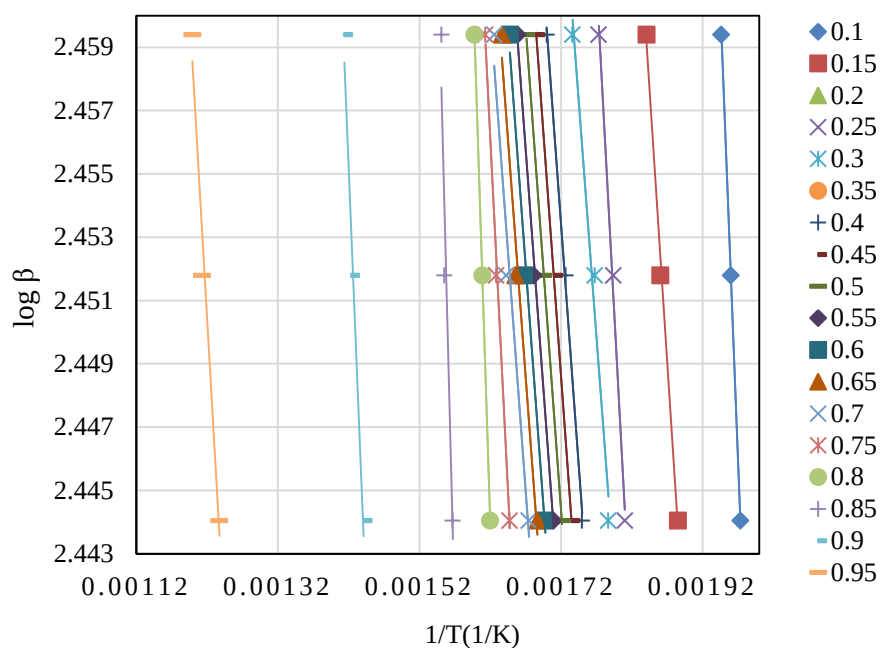


Figure 4.5b: Plot of $\log \beta$ against $1/T$ according to F-W-O-M to obtain activation energy (E_a) at various conversions (APZ and PPZ).

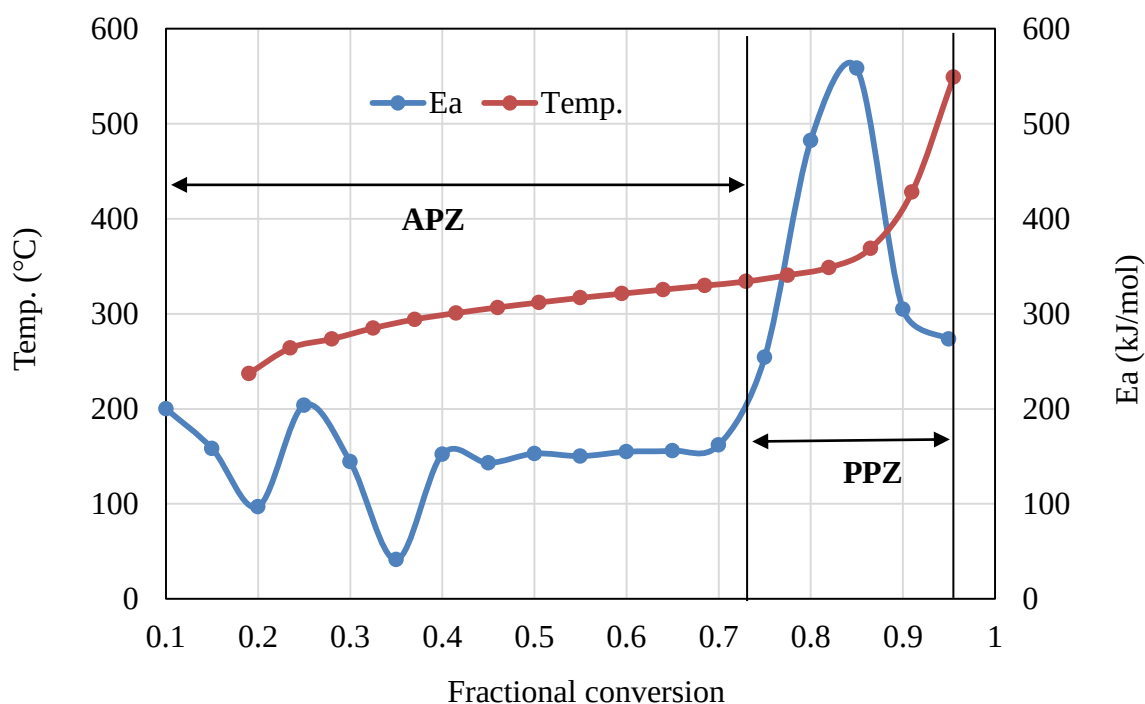


Figure 4.6a: Activation energy against fractional conversion for different temperature obtained via K-M.

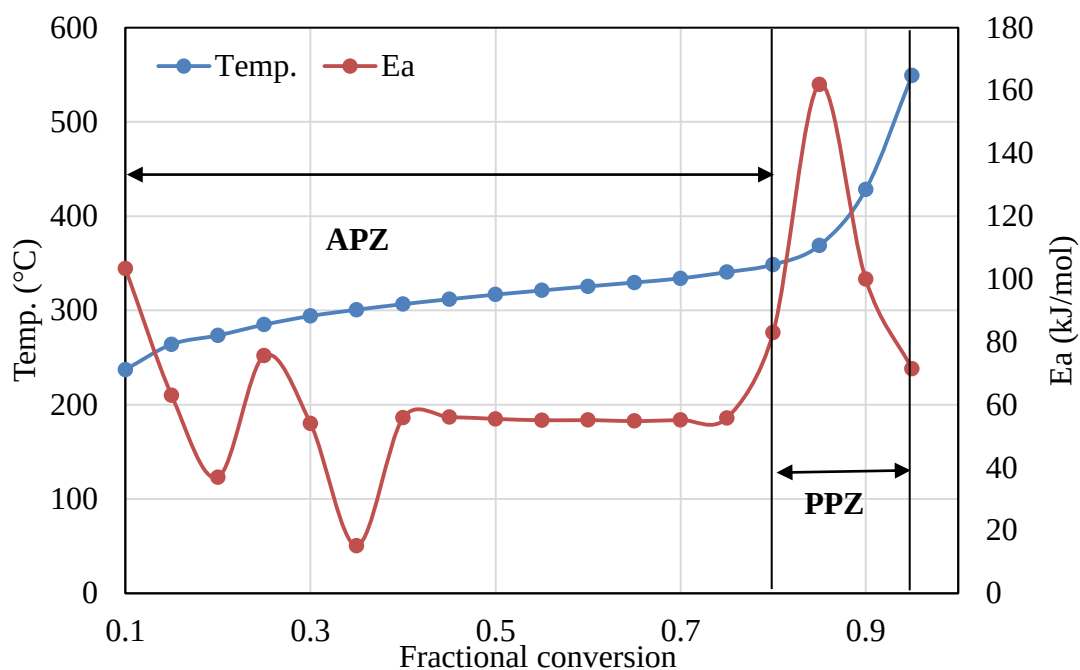


Figure 4.6b: Activation energy against fractional conversion for different temperature obtained via F-W-O-M.

Table 4.4: Pre-exponential factor for different conversion and respective correlation factors (R^2) for the linear fitting shown in Figures 4.5a and 4.5b

α	K-M		F-W-O-M	
	A (/min)	R^2	A (/min)	R^2
0.10	1.74E+16	0.9969	2.13E+10	1.0000
0.15	3.70E+11	0.9768	1.30E+07	0.9968
0.20	7.98E+14	0.9860	1.20E+05	0.9854
0.25	3.50E+15	0.9860	4.70E+08	0.9950
0.30	1.56E+10	0.9413	2.10E+06	0.9803
0.35	8.65E+03	0.9661	1.60E+02	0.9929
0.40	3.80E+10	0.9844	3.10E+06	0.9976
0.45	5.27E+09	0.9880	3.30E+06	0.9998
0.50	3.66E+10	1.0000	5.10E+06	0.9993

0.55	4.17E+10	0.9989	1.80E+06	0.9963
0.6	4.73E+10	0.9934	3.50E+06	0.9885
0.65	5.34E+10	0.9892	1.90E+06	0.9826
0.70	1.51E+11	0.9815	2.70E+06	0.9712
0.75	7.54E+18	0.9999	2.10E+06	0.9591
0.80	4.45E+37	0.9887	7.80E+09	97420
0.85	1.22E+42	0.8707	5.67E+12	0.9311
0.90	1.78E+19	0.9216	1.11E+10	0.9758
0.95	5.73E+13	0.9996	2.30E+08	0.9774

4.3 Torrefaction of woody biomass using full factorial experimental design

Full factorial experimental design was used for torrefaction of the woody biomass (Melina and Teak) in order to obtain conditions that will be best suited to improve the properties of the woody biomass to give high mass yield, HHV and energy yield in readiness for application in briquetting. Each of the woody biomass was subjected to separate experimental design. It is imperative to note that thermal decomposition study gave gainful insight into the weight loss behaviour and reaction mechanism that biomass undergoes during pyrolysis, however, it is expedient to understand the influence of other torrefaction parameters such as particle size and residence time on the woody biomass. Therefore, the influence of variation of parameters such as temperature, residence time and particle size on mass yield (MY), higher heating value (HHV) and energy yield (EY) of the woody biomass during torrefaction was obtained.

The full factorial experimental design was further used for the optimization of the torrefaction parameters (temperature, residence time and particle size) to obtain optimum torrefaction conditions in order to have high energetic yields (MY, HHV and EY). Typical

Pareto plots, Normal plot, Main effect and interaction plots of torrefaction parameters on the energetic yields are presented in the Figures A1-5. To predict energetic yields of the woody biomass from torrefaction parameters, linear factorial regression models were developed using the experimental design and are discussed in this section.

4.3.1 Melina wood

The experimental design and the severity factor (SF) used for torrefaction of Melina wood (RMw) are presented in Table 4.5, which is the design interface of the MINITAB 17 used for the optimization process. The energetic yields (MY, HHV and EY) were the responses (dependent variables) from the set parameters are also presented in Table 4.5.

Table 4.5: Factorial experimental design with three independent and dependent variables in Minitab 17 for RMw

Independent variables					Dependent variables		
Run	TT	RT	PS	SF	MY	HHV	EY
Order	(°C)	(min)	(mm)		(%)	(MJ/kg)	(%)
1	240	30	2	5.60	77.17	21.18	88.88
2	240	30	6	5.60	79.21	20.75	89.38
3	300	60	6	7.67	44.75	25.86	62.93
4	300	30	6	7.37	47.96	26.12	68.12
5	300	60	2	7.67	42.52	27.04	62.52
6	300	30	2	7.37	40.34	28.26	61.99
7	240	60	2	5.90	81.18	21.08	93.05
8	240	60	6	5.90	66.33	22.37	80.69
9	300	60	6	7.67	57.39	22.23	69.37
10	300	60	2	7.67	38.07	29.11	60.26
11	240	60	6	5.90	77.98	21.15	89.68

12	300	30	6	7.37	41.85	27.83	63.33
13	240	30	2	5.60	76.85	21.7	90.68
14	240	30	6	5.60	78.87	21.32	91.44
15	300	30	2	7.37	40.16	27.07	59.12
16	240	60	2	5.90	78.54	20.86	89.09

*TT-Torrefaction temperature, PS- particle size, RT- residence time, EY- energy yield, MY- mass yield, SF-severity factor and HHV-higher heating value.

4.3.1.1 Main and interactions effects of torrefaction parameters on energetic yields

Mass yield is the quantity of solid residue that remains after torrefaction. It depicts much information about biomass and torrefaction process itself. It determines the energy yield of biomass. Energy yield is an important response for torrefaction. In the course of torrefaction, energy-lean volatiles, moisture and gases are released from biomass, taking up certain quantity of resident energy in biomass (Shinya, 2008). For Melina wood, the mass and energy yields decreased with increase in torrefaction temperature as shown in Figure 4.7a.

The HHV of torrefied biomass increased with increase in temperature. The influence of temperature was more pronounced than resident time and particle size on mass yield, HHV and energy yield during torrefaction. Low torrefaction temperature (TT) setting (240°C) gave high mass yield but progressing towards 300°C, the mass yield drastically decreased and this implied that for maximum mass yield, torrefaction must be carried out at low temperature settings. However, biomass torrefaction at low temperature gave low HHV due to minimum degradation of hemicellulose and cellulose contents of biomass. Similar observation was made for energy yield (EY) as residence time (RT) and particle size (PS) had negligible effects on these responses.

Figure 4.7b shows that navigating from low to high setting of RT, the yield relatively remains constant. However, a change in PS has slight effect on MY indicating that its effect cannot be totally neglected (Figure 4.7c). By implication, temperature has tenacious influence on MY and EY which showed that TT is a major torrefaction parameter to be considered as it influenced HHV more compared to PS and RT as shown in Figure 4.7. Advancing from low to high TT setting, HHV yield drastically increased which is as a result of severe devolatilization thereby yielding more C-C bonds rather than O-H bonds that dominates hemicellulose in biomass (Basu *et al.*, 2014). The observation in the present study is in agreement with the result of Chin *et al.* (2013b) during optimization of torrefaction conditions for high energy density solid bio fuel from biomass and fast growing species in Malaysia.

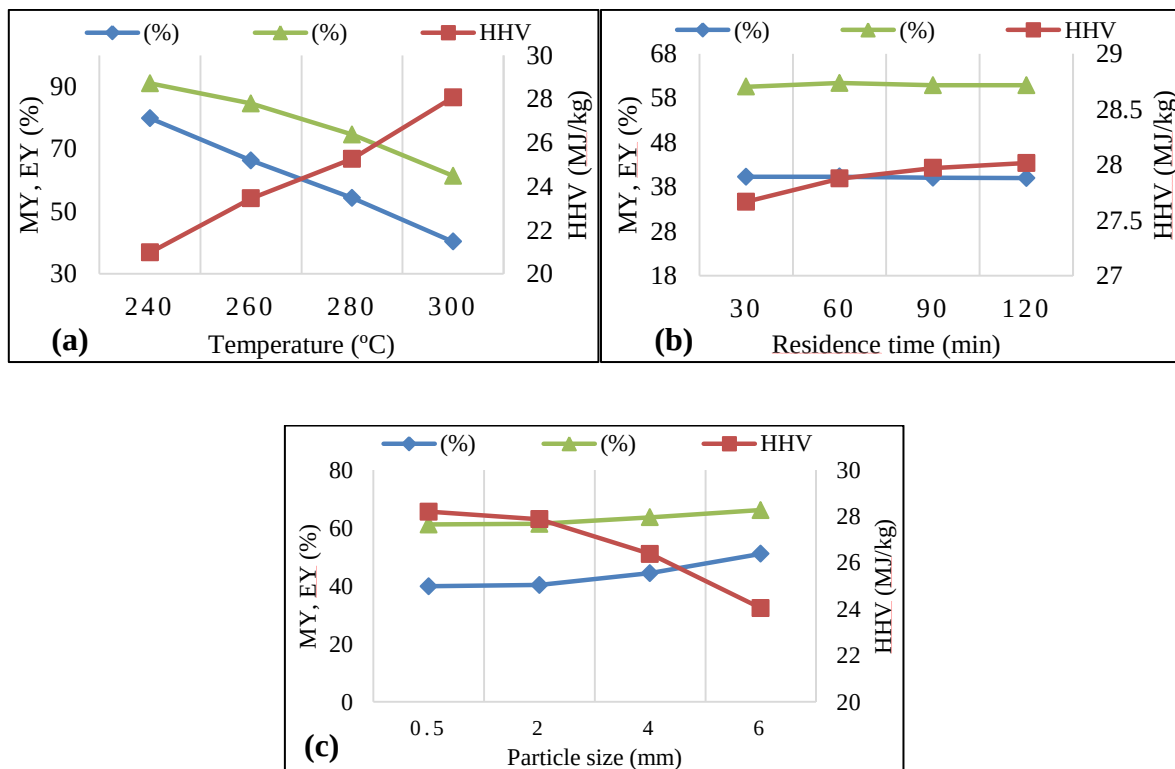


Figure 4.7: (a) Influence of variation of TT at constant RT= 60 min and PS = 2mm on MY, HHV and EY of Melina wood (b) Influence of variation of RT at constant TT=300°C and PS

=2 mm on MY, HHV and EY of Melina wood (c) Influence of variation of PS at constant TT=300°C and RT= 60 min on MY, HHV and EY of Melina wood.

4.3.1.2 Factorial regression models and response optimizer

The results of the analysis of variance (ANOVA) are presented in Tables A1-A3 (Appendix). For α -level of 0.05, Tables A1-A3 showed that only TT effect was significant for torrefaction of lignocellulosic biomass compared with RT and PS because the p-values were zeros (0) and is lower than the threshold significance level (0.05) compared to 2-way and 3-way interactions. To fit the responses function and experimental data, factorial linear regression was performed and the relatively high R^2 and adjusted R^2 values for MY (Equation 4.1), HHV (Equation 4.2) and EY (Equation 4.3) showed that the factorial regression models are well correlated with the actual data. The R^2 obtained from full factorial regression method (FFRM) for these linear models at 95% confidence level were 0.962, 0.9189 and 0.9628 for MY, HHV and EY, respectively. The R^2 of the linear models for energy yield and HHV in this study are higher than the 0.8500 and 0.8880 reported by Lee *et al.* (2012) for quadratic models developed using surface response method during torrefaction of mixed soft woods. Thus, the linear models show good correlation with actual data than quadratic models and are recommended for prediction of energetic yields of tropical woody biomass.

$$MY (\%) = 177.6 - 0.456 TT + 16.179PS - 0.0551 TT * PS \quad (4.1)$$

$$HHV (MJ / kg) = 9.8 + 0.054 TT - 4.63 PS + 0.018 TT * PS \quad (4.2)$$

$$EY (\%) = 205.9 - 0.5 TT + 1.9 PS - 0.0007 TT * PS \quad (4.3)$$

Figure 4.8 represents the plots of predicted versus actual responses (predicted at 95% confidence level- α of 0.05). The correlation factor (R^2) for the plots were 0.9620, 0.9196 and 0.9677 for MY, HHV and EY respectively. The relatively high values obtained for correlation factors implied that the linear models are valid for prediction of the output of torrefaction of lignocellulosic biomass in terms of mass yield, HHV and energy yield. The

response optimizer in MINITAB 17 was used for maximum set goal of MY, HHV and EY and it gave TT of 260 °C, RT of 60 min and PS of 2 mm as the global solution of the independent variables. The predicted responses were 66.67% for MY, 23.33 MJ/kg for HHV and 81.17% for EY and the desirability were close to the weight value set (unity/1).

Global solution obtained from the factorial regression models was validated using the set conditions of 260°C TT, 60 min RT and 2 mm PS in a torrefaction experiment. Mass yield of 66.33 %, HHV of 23.45 MJ/kg and EY of 84.58% were obtained and these were very close to the global solution responses. The result suggests that the models can correctly predict mass yield, higher heating value and energy yield of lignocellulosic biomass in Nigeria and tropical regions without the need for higher order term inform of quadratic or polynomial functions.

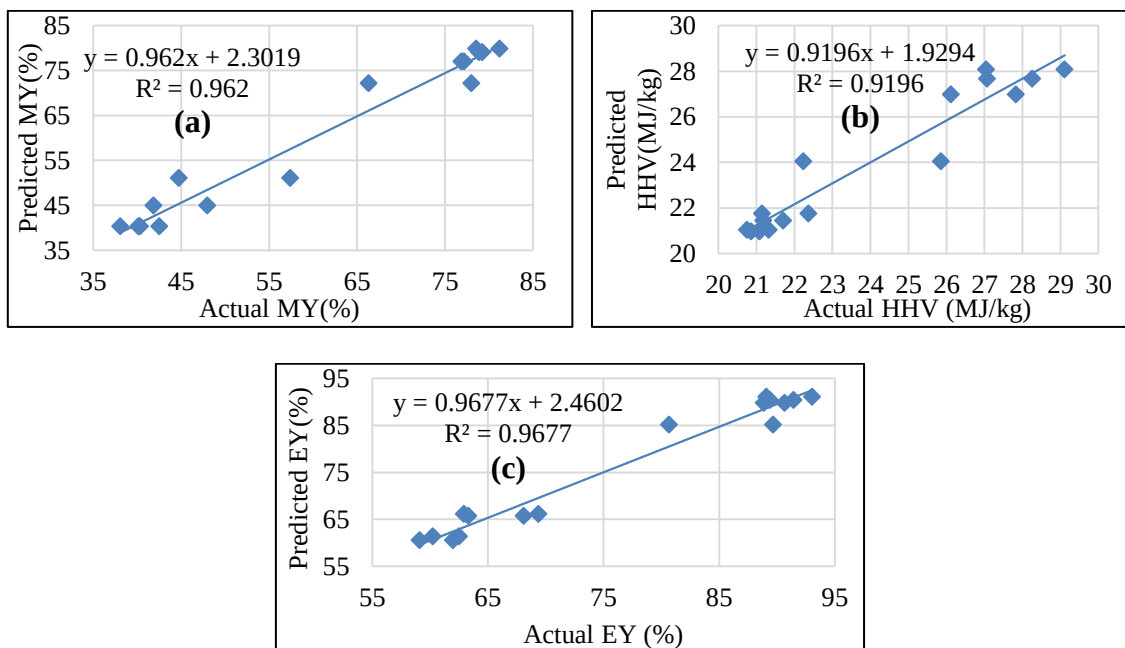


Figure 4.8: Predicted versus actual response plots for Melina wood (a) MY (%) (b) EY (%) and (c) HHV (MJ/kg)

4.3.2 Teak wood

The experimental design and the severity factor (SF) used for torrefaction of Teak wood (RTw) are presented in Table 4.6, which is the design interface of the MINITAB 17

used for the optimization process. The energetic yields (MY, HHV and EY) which were the responses (dependent variables) from the set parameters are also presented in Table 4.6.

4.3.2.1. Main and interactions effects of torrefaction parameters on energetic yields

Analyzing the factorial design, significance of torrefaction parameters and their interactions on mass yield, HHV and energy yield were identified at 0.05 α -level. Figure 4.9 shows that TT has the largest influence on mass yield and this is similar to the observation for Melina wood. Mass yield is the quantity of biochar obtained after torrefaction and it dropped as the temperature increase from low (240°C) to high (300°C) set. The mass yield dropped from an average of 76% to 44% as TT was increased. Residence time and PS studies adopted in this work do not have significant impact on the mass yield. The ANOVA result (Table A4) shows that TT has p-values less than 0.05 α -level while RT and PS has p-values >> greater. The 2-ways and 3-ways interactions between the factors were not also significant since the p-values are >> greater than 0.05 α -level (Table A4). It implied that TT has the largest effect in determining the mass yield during torrefaction of lignocellulosic biomass.

Table 4.6: Factorial experimental design with three independent and dependent variables in Minitab 17 for RTw

Independent variables					Dependent variables		
Run	TT	RT	PS	SF	MY	HHV	EY
Order	(°C)	(min)	(mm)		(%)	(MJ/kg)	(%)
1	300	60	2	5.90	50.32	25.96	69.78
2	240	60	2	5.90	81.62	21.86	95.31
3	240	60	6	5.90	79.76	20.73	88.32
4	240	60	2	7.67	80.58	21.69	93.36
5	300	60	6	5.59	48.26	25.23	65.78

6	240	30	6	7.37	83.03	20.84	92.43
7	300	30	6	5.59	49.67	25.19	66.84
8	240	30	2	5.59	84.89	20.48	92.87
9	240	30	2	7.37	81.18	21.43	92.93
10	300	30	2	7.67	47.91	25.94	66.39
11	300	60	2	5.90	57.69	26.46	81.54
12	240	60	6	7.37	82.29	21.09	92.71
13	300	30	6	7.37	56.48	25.88	78.08
14	300	30	2	7.67	43.24	26	60.06
15	300	60	6	5.59	58.48	25.98	81.16
16	240	30	6	7.67	85.27	20.55	93.61

Although, the significance of torrefaction parameters on energy yield is reminiscent of MY where TT has the dominant influence (Figure 4.9, Table A6), TT and PS main effects are significant HHV of torrefaction of biomass. TT has the largest influence with P-value of 0.000 which is lower than 0.05 α -level as against 0.024 for PS as shown in Table A5. Increasing temperature led to a strident increase in HHV of biomass. The interactions of these factors were found to be insignificant (p-value >> greater than 0.05 α -level). The trend obtained for temperature influence is similar to the observation of Chin *et al.* (2013). They reported that resident time has minimal influence on energy density (HHV) of biomass compared with temperature during torrefaction process. It was also observed that lower temperature led to lower hemicellulose loss and thus was considered to have minimal effect on oil palm and fast growing species in Malaysia. Further effort to also observe the role of particle size was carried out in this study and it was observed that within the range below

6.35 mm particle sizes, there was no pronounced contribution of particle size variation for mass and energy yield; however, a minimum effect existed for HHV of torrefied product.

4.3.2.2 Analyses of factorial linear regression

To fit the responses function and experimental data, factorial linear regression was carried out. The R^2 and adjusted R-squares for mass yield were 0.9686 and 0.9412, respectively as shown in Table A3. Equation 4.4 represents the predicted mass yield for torrefied biomass in an uncoded units. This model was significant at 95% confidence level with p-value < 0.05 α -level as shown in Table A4.

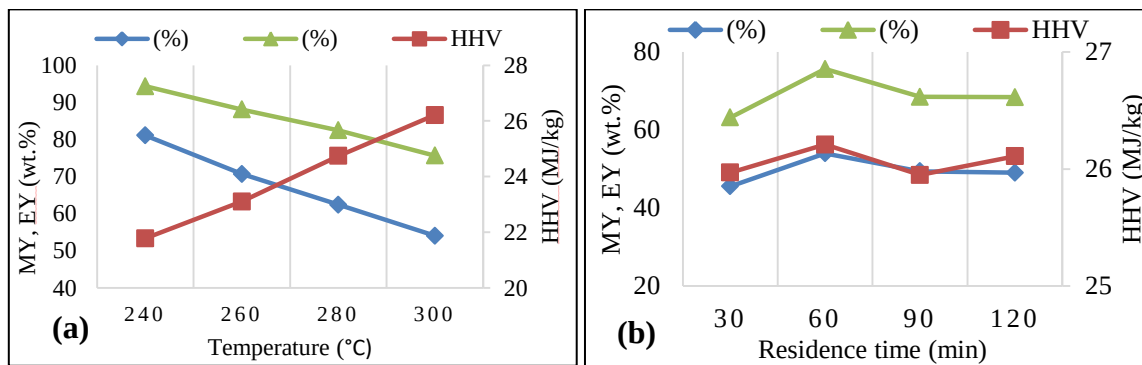
$$MY (\%) = 301.8 - 0.91TT - 1.89RT - 12.8 PS + 0.0077 TT * RT + 0.056 TT * PS$$

(4.4)

The R-square and adjusted R-square for HHV were 0.9669 and 0.9755, respectively (Table A5) and this showed that there was a good correlation between the predicted and actual data. Equation 4.5 represents the predicted higher heating value for lignocellulosic biomass and it was significant at 95% confidence level.

$$HHV (MJ/kg) = -3.64 + 0.0983 TT + 0.70 PS - 0.00254TT * PS$$

(4.5)



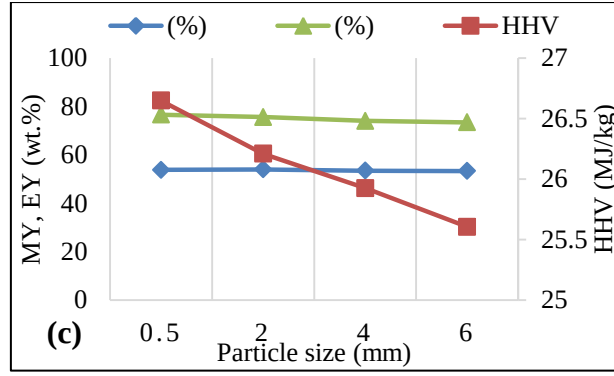


Figure 4.9: (a) Influence of variation of TT at constant RT= 60 min and PS = 2 mm on MY, HHV and EY of Teak wood (b) Influence of variation of RT at constant TT = 300°C and PS =2 mm on MY, HHV and EY of Teak wood (c) Influence of variation of PS at constant TT = 300°C and RT= 60 min on MY, HHV and EY of Teak wood.

Energy yield indicates the amount of preserved energy in torrefied biomass (Lee *et al.*, 2012). The R-square of 0.8755 and adjusted R-square of 0.8722 (Table A6) were obtained for the model and this indicates significant correlation with the actual data. Equation 4.6 is the predicted energy yield for the torrefied biomass. Compared with the linear regression models developed for Melina wood, the R-squares of those of Teak wood are closer for all the responses that is MY, HHV and EY as shown in Table A6. The R-squares obtained for the linear regression model of the HHV of Teak wood is higher than 0.8973 obtained for as quadratic regression employed to correlate torrefaction temperature and time influence on HHV yield during torrefaction of Macaranga species by Chin *et al.* (2013a).

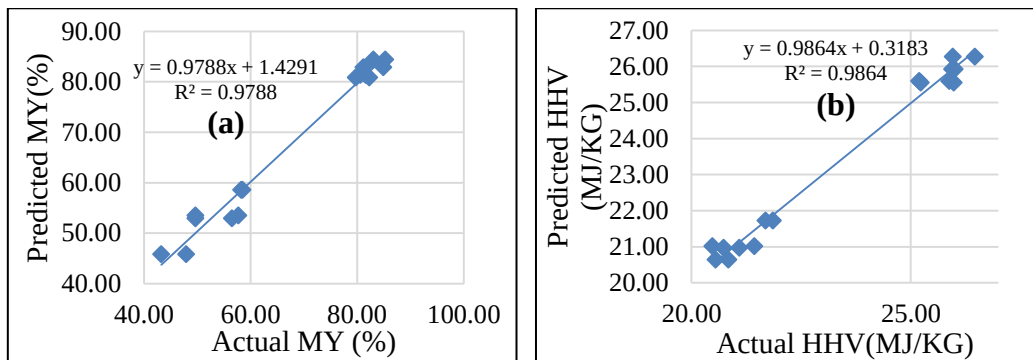
$$EY (\%) = 285 - 0.815 TT - 1.84 RT - 15.5 PS + 0.0082TT * RT + 0.069TT * PS \quad (4.6)$$

4.3.2.3 Response optimizer

Figure 4.10 shows the plots of predicted versus actual responses for Teak wood (predicted at 95% confidence level- α of 0.05). The correlation factor (R^2) for the plots were 0.9780, 0.986 and 0.918 for MY, HHV and EY respectively. The relatively high values obtained for correlation factors implied that the linear models are valid for prediction of the

output of torrefaction of lignocellulosic biomass in terms of mass yield, HHV and energy yield. For a single point solution in order to obtain maximum mass yield, HHV and energy yield, response optimization was carried out. Global solution (optimized condition) that was obtained for maximum set goal of MY, HHV and EY using Minitab17 response optimizer were at TT of 260°C, RT of 60 minutes and PS of 2 mm. The predicted responses were 73.31% for MY, 23.19 MJ/kg for HHV and 88.35% for EY at a composite desirability of approximately 0.89 which was closed to the weighted value set (unity).

Global solution as obtained from the factorial regression models was validated using the set conditions: TT of 260°C ;, RT of 60 min; and PS of 2 mm for a confirmatory experiment. Mass yield of 70.20 %, HHV of 23.10 MJ/kg and EY of 88.07% were obtained and these were in close agreement with the global solution responses.



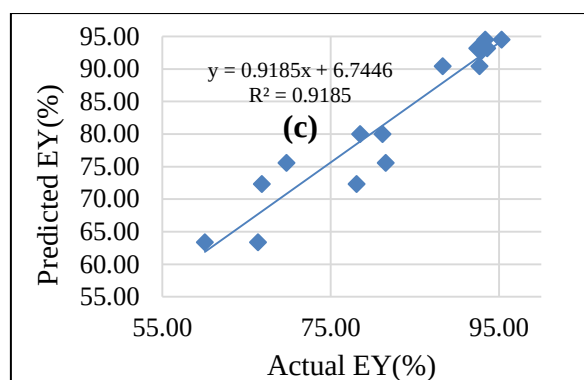


Figure 4.10: Predicted versus. actual plots for Teak wood (a) MY (%) (b) EY (%) and (c) HHV (MJ/kg)

4.4 Characterisation of biochar produced from Melina and Teak wood using torrefaction process

Biochar is the solid residue after torrefaction process of the raw woody biomass. The sample's colour change, ultimate analysis, proximate analysis, higher heating value and surface morphology were employed to evaluate the influence of torrefaction process on the woody biomass under different conditions.

4.4.1 Colour change after torrefaction process

The colours of Melina (RMw) and Teak (RTw) wood with some of the torrefied samples under different conditions are presented in Figure 4.11. The biochar produced from torrefaction process was different in colour from the RTw and RMw. The woody biomass (RTw and RMw) that were subjected to mild torrefaction at 240°C irrespective of residence time and particle size changed from light brown (Figure 4.11a and d) to dark brown products (Figure 4.11c and f) while severely torrefied samples yielded black products (Figure 4.11b and e). This implied that the loss of volatiles and moisture were high under severe (300°C) torrefaction. The change in colour signals the degree of conversion of RTw and RMw to biochar, and it is an indicator that thermal degradation has led to transformation of hemicellulose, cellulose and lignin (White & Dietersberger, 2001).

Sundqvist (2004) treated wood biomass surface thermally with absorption, reflection and scattering phenomenon of visible light incident (380 - 800 nm) and reported that formation of different chemophoric groups such as carbonyls, hydroxyls, methoxyls and phenolic compounds with the ability to absorb visible light incident are responsible for the dark colour in biomass. The dark brown colour of mildly torrefied Teak and Melina woods may be due to the formation of aldehydes and phenols (Aydemir *et al.*, 2012). Severe torrefaction led to loss of hydrophilic and oxygenated compounds resulting from the destruction of intra- and inter- molecular C-O and C-H bonds and this directly results into the formation of black hydrophobic compounds (Pach *et al.* 2002; Tumuluru *et al.* 2011; Na *et al.* 2013; Nhuchhen *et al.* 2014).



Figure 4.11: Colours of; (a) raw Melina wood (b) severely torrefied Melina wood (c) mildly torrefied Melina wood (d) raw Teak wood (e) severely torrefied Teak wood and (f) mildly torrefied Teak wood.

4.4.2 Ultimate contents

The ultimate analysis of the biochar (Table 4.7) are compared with that of raw biomass (Table 4.1) in this section. The carbon content of the biochar produced at both mild and severe torrefaction conditions were higher than that of the raw woody biomass (Table 4.1). However, biochar produced from severe conditions, at various residence time and

particle size has higher carbon content in the range of 63 - 72% compared with 52 - 56% for mild condition at various residence time and particle size. The carbon contents of the biochar were enhanced by both mild and severe torrefaction conditions. This is as result of thermal decomposition that led to breaking of different polymer chain, thereby liberating oxygen, hydrogen and water leaving carbon-rich residues (Du *et al.*, 2014).

The hydrogen content in the raw woody biomass (6 - 7%) presented in Table 4.1 dropped to 4 - 5% for biochar produced under both mild and severe torrefaction conditions (Table 4.7) because of dehydration (loss of bounded water and unbounded water). The hydrogen content in severe condition was lower than that of mild condition for both woody biomass. The nitrogen (N) and sulphur (S) contents remain in the range of 0.2 - 0.4% for both raw woody biomass and biochar. This implied that biochar from torrefied wood samples as well as raw biomass will generate lower quantity of SO_x and NO_x emissions when utilized as fuel.

The oxygen content of the biochar was lower compared with 43.69% of raw Teak and 43.54% of Melina woods (Table 4.1). The range of oxygen content of the biochar produced under mild conditions is 37 - 38% compared to 19 - 29% under severe conditions. The reduction in oxygen content within the elemental matrix of biochar is as a result of dehydration reaction which gives room for the loss of water vapour and other light volatile organic compounds. Formation of CO and CO₂ at higher degree in severe condition compared with mild condition is also responsible for lower oxygen content (Prins *et al.*, 2006). High oxygen content in biomass reduces its heating value, thereby making it an undesirable lean grade fuel (Du *et al.*, 2014). Oxygen content of the biochar produced under severe conditions is higher than 11.36% reported for bituminous coal by Gamgoum *et al.* (2016) but at par with 29.59% of low volatile coal reported by Du *et al.* (2014).

Biochar produced from severe conditions has carbon and oxygen contents in the range of lean grade coal (Table 4.2). This makes biochar (torrefied woody biomass) a suitable feedstock that would partially or totally serve as a substitute for coal in thermal and metallurgical applications.

4.4.3 H/C and O/C atomic ratios

The ability to produce heat and generate electricity is what distinguish various fuel from one another (Gamgoum *et al.*, 2016). A useful tool of comparison of these fuels is the H/C (hydrogen/carbon) and O/C (oxygen/carbon) atomic ratios diagram. The lower the H/C and O/C atomic ratios, the greater the energy content of such fuel feedstock (Basu, 2013). The H/C and O/C atomic ratios of raw Teak (RTw) and raw Melina (RMw) compared to various forms of solid fuel are illustrated on the *van Krevelen* diagram (Figure 4.12). The H/C and O/C atomic ratios of RTw is slightly lower than that of RMw. The H/C and O/C of RMw are 1.68 and 0.69, respectively, while the H/C and O/C of RTw are 1.52 and 0.69, respectively. These ratios were observed to be higher than other type of fuels such as petcoke, anthracite, bituminous coal and so on as shown in Figure 4.12 (Jones *et al.* 2006; Basu 2013).

The high H/C and O/C atomic ratios may be responsible for the low HHV of the raw Teak and Melina woods. This corresponds to the observation of Basu (2013) on HHV of wood biomass reducing from 20.5 MJ/kg to 15 MJ/kg when the O/C atomic ratio increased to 1.03 from 0.86. Torrefaction process carried out at severe (300°C) conditions led to higher reduction in H/C and O/C atomic ratios compared to mild torrefaction condition as shown in Figure 4.12. Oxygen content of RTw and RMw were reduced under different torrefaction conditions due to series of decomposition reactions such as dehydration that favours the formation of more C-C and C-H and destruction of C-O and H-O bonds (Gamgoum *et al.*, 2016).

The O/C atomic ratio for biochar from severe torrefaction condition is in the range of 0.23 - 0.39 while the H/C atomic ratio is in the range of 0.76 - 1.27. The range of 0.45 - 0.58 O/C and 1.21 - 1.37 H/C atomic ratios were observed for mildly torrefied biomass. A similar reduction from > 0.6 to ≤ 0.3 was observed by Balogun (2014) for O/C atomic ratio of different woody and non-woody biomass. As revealed on the van Krevelen diagram (Figure 4.12), the H/C and O/C atomic ratios of biochar from severe torrefaction conditions tend towards those of the lean grade coals (sub-bituminous and lignite). Thus, it can be adopted for thermal and metallurgical applications.

Table 4.7: Ultimate analyses of biochar produced under different torrefaction conditions

	Samples	C (%)	H (%)	N (%)	S (%)	O (%)
Mild conditions	T/240/60/6	54.67	6.01	0.36	0.21	37.28
	M/240/60/6	55.53	5.92	0.27	0.22	36.26
	T/240/60/2	54.78	5.95	0.36	0.22	37.11
	M/240/60/2	53.86	6.03	0.20	0.20	38.35
	T/240/30/6	53.29	6.06	0.35	0.20	38.98
	M/240/30/6	52.41	5.95	0.25	0.20	39.79
	T/240/30/2	53.94	5.92	0.25	0.21	38.12
	M/240/30/2	54.87	5.92	0.22	0.21	37.25
	M/300/60/6	63.19	5.62	0.28	0.19	29.08
Severe conditions	T/300/60/6	63.02	5.26	0.42	0.19	29.24
	T/300/60/2	63.99	5.29	0.35	0.22	27.51
	M/300/60/2	72.04	4.74	0.33	0.20	19.67
	T/300/30/6	64.23	5.31	0.44	0.19	27.88
	M/300/30/6	69.54	5.09	0.30	0.20	22.84
	T/300/30/2	67.73	4.80	0.46	0.23	23.70
	M/300/30/2	70.24	4.86	0.38	0.22	22.08

*T/300/30/2 represent Teak wood (2 mm particle size) treated under severe condition (300°C) for residence time of 30 min * M/300/30/2 represent Melina wood (2mm particle size) treated under severe condition (300) for residence time of 30 min.

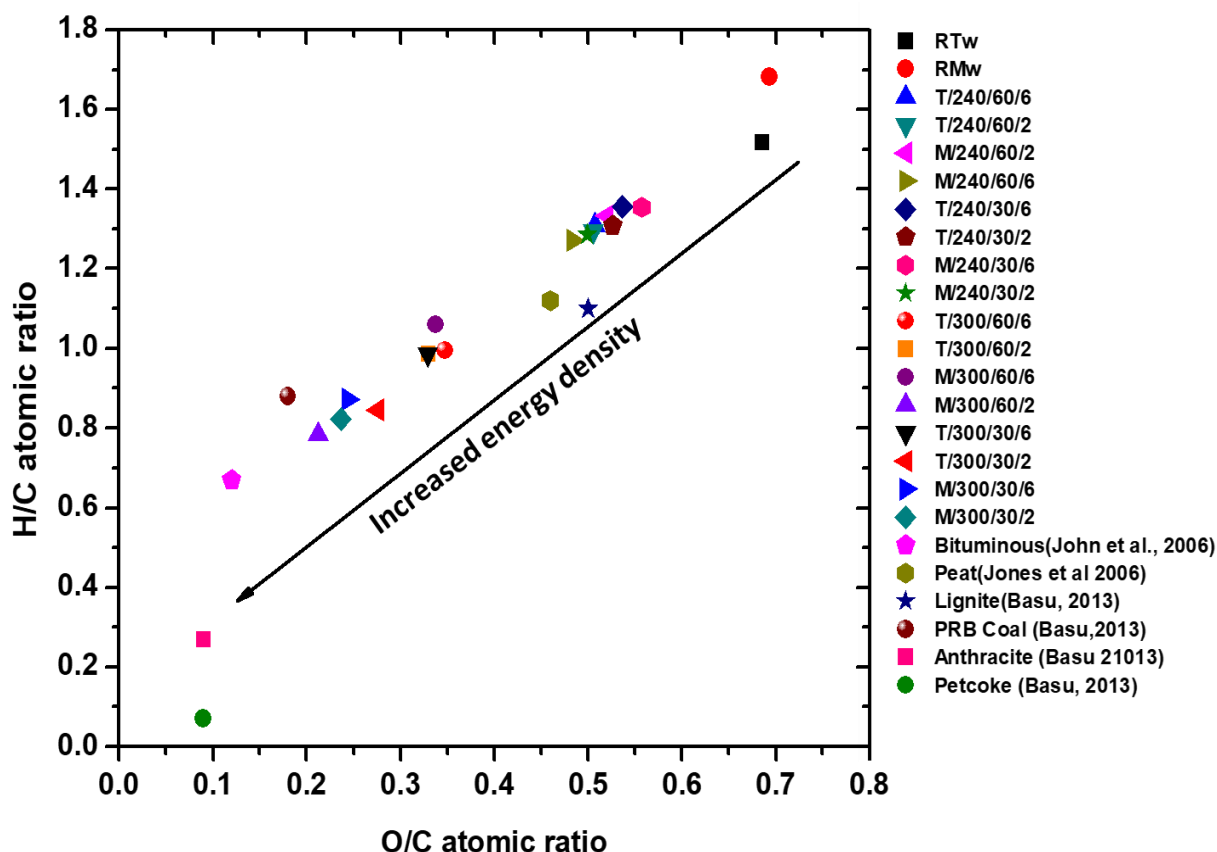


Figure 4.12: Comparison of H/C and O/C atomic ratios of the raw and torrefied biomass in this study with some other solid fossil fuels.

4.4.4 Proximate contents

The proximate contents of biochar presented in Table 4.8 are compared to that of raw woody biomass (Table 4.1) in this section. The moisture content (MC) reduced from the range of 7 - 8% for raw woody biomass (Table 4.1) to 2 - 3% for biochar (Table 4.8). Moisture loss is due to dehydration and it contributes to the total weight loss of biomass. The reduced moisture content in the biochar compared to the raw woody biomass makes it more desirable as feedstock in energy generation since it will consume less energy to dehydrate (Basu, 2013).

The volatile matters (VM) of the biochar are generally lower than the 79.26% of RTw and 81.42% of RMw (Table 4.1). The VM of the biochar produced from mild torrefaction conditions are in the range of 70.39 - 77.01% as shown in Table 4.8. Conversely, the VM of

the biochar from RMw produced under severe conditions reduced to 34.64 - 44.39% against the 42.55 - 48.48% for RTw (Table 4.8). This implied that the conversion of complex polymers into smaller monomers and that of smaller monomers into condensable and non-condensable volatile gases (VM) was minimal under mild torrefaction conditions (Basu, 2013). The results also showed that RMw released more condensable and non-condensable products compared with RTw. The devolatilization rate of the woody biomass has direct impact on the fixed carbon of their biochar (Basu, 2013).

The fixed carbon of the biochar was generally higher than the 8.92% and 11.73% of Melina wood (RMw) and Teak wood (RTw), respectively. The fixed carbon (FC) obtained for biochar produced under severe torrefaction conditions was higher compared with that of biochar produced under mild conditions for both woody biomass. Biochar produced from RMw has higher FC compared with RTw at every conditions as shown in Table 4.8. The highest FC obtained was 58.17% for RMw under severe condition (300°C), which could be due to its VM, being the lowest. This observation indicates that there is inverse relationship between fixed carbon and volatile matter of a woody biomass. That is, high fixed carbon content indicates low volatile matter. High fixed carbon is essential for biochar utilization in energy production (Almeida *et al.*, 2010).

The ash represents the mineral content of biomass and it is in the range of 1 - 3% for the raw biomass (Table 4.1) and biochar (Table 4.8). There was no significant difference in the ash content of the raw woody biomass and that of the biochar, indicating that torrefaction at different conditions has relatively no significant effect on the ash content. This result agrees with the observation of Nhuchhen *et al.* (2014), which stated that ash as non-combustible material could remain constant or increase because it is not driven off via torrefaction. High ash content is not desirable in biochar for utilization in gasifiers. It will cause decrease in operation throughput and increase operating cost (Mehmood *et al.*, 2012).

The ash content in the biochar are generally low and thus can be effectively utilized as feedstock for energy generation.

The moisture and the VM contents of the woody biomass decreased while the fixed carbon increased after severe torrefaction at 300°C compared with the mild torrefaction (240°C). The loss of VM and higher FC are signals to improve mass yield, HHV and energy yield during torrefaction process. Higher loss in VM implied that there will be low mass and energy yields while the HHV increases. High HHV is desirable for the biochar, however, the maximum energetic yields were obtained for both woody biomass at the optimum torrefaction temperature of 260°C (Figure 5A).

Table 4.8: Proximate analysis of biochar under different torrefaction conditions

	Sample	MC (%)	VM (%)	Ash (%)	FC (%)
Mild conditions	T/240/60/6	3.13	74.87	1.82	20.19
	M/240/60/6	3.03	71.70	2.20	23.07
	T/240/60/2	3.22	74.98	1.79	20.02
	M/240/60/2	3.01	71.89	2.22	22.89
	T/240/30/6	3.73	77.01	2.00	17.27
	M/240/30/6	3.07	72.70	2.18	22.06
	T/240/30/2	3.80	75.65	1.78	18.78
	M/240/30/2	3.00	70.39	2.20	24.42
	M/300/60/6	2.73	48.02	2.05	47.21
Severe conditions	T/300/60/6	2.76	37.87	2.20	57.18
	T/300/60/2	2.56	47.08	2.05	48.32
	M/300/60/2	2.53	34.64	2.29	60.55
	T/300/30/6	2.73	48.48	1.78	47.02
	M/300/30/6	2.51	44.39	2.21	50.90
	T/300/30/2	2.56	42.55	2.03	52.87
	M/300/30/2	2.47	37.15	2.23	58.17

4.2.5 Fuel ratio and higher heating value

Another useful parameter to determine the quality of a fuel is the ratio of its fixed carbon to volatile matter, that is, fuel ratio (Nhuchhen and Afzal, 2017). The fuel ratio of the raw biomass compared with the biochar are presented in Figure 4.13. It can be observed that the fuel ratios of biochar produced under both severe and mild torrefaction conditions are higher than those of raw woody biomass. This resulted from the loss of volatile matters of the

raw biomass during torrefaction process. Biochar from Melina wood has the highest fuel ratio of 1.75 under severe (300°C) torrefaction compared to 0.11 of the raw Melina wood. Similarly, a fuel ratio of 1.24 was obtained at 300°C for biochar of Teak wood compared to 0.15 of the raw biomass. The lower fuel ratio of the raw woody biomass indicates that it has higher reactivity than biochar produced after torrefaction. The increase in fixed carbon led to an increase in fuel ratio which implied that combustion of biochar will be stable than that of the raw woody biomass (Suresh *et al.*, 2012). The fuel ratios of Melina wood were higher than those of Teak wood and this was due to the higher loss in volatile matter content in Melina compared with Teak wood as shown in Table 4.8. In addition, the fuel ratios of the biochar were higher at 300°C compared with 240°C which was due to higher devolatilization.

Figure 4.14 represents the comparison of higher heating value (HHV) obtained experimentally with some models developed based on ultimate characteristics as stated in Equations (3.12 - 3.14). The HHV of biochar under both the mild and severe torrefaction was better than that of raw woody biomass. The HHV of biochar from Teak and Melina woody biomass range between 22 and 28 MJ/kg under severe conditions while that of biochar produced from mild conditions slightly varied from 20 to 21 MJ/kg. Lasode *et al.* (2014) also obtained up to 27 MJ/kg for HHV from tropical woody biomass after torrefaction process.

Nhuchhen and Afzal (2017) stated that while existing models such as Yin (2011), Sheng and Azevedo (2005), and Boie (1953) can be effective in predicting HHV of biomass, these models are limited as they fail to be potent in the prediction of HHV of biochar. In an attempt to confirm the opinion of Nhuchhen and Afzal (2017), efforts were made to compare the HHV results obtained using such models. For the raw woody biomass, predicted HHV deviates by 4%, 4.2% and 2% using Yin (2011), Sheng and Azevedo (2005), and Boie (1953) models, respectively. Based on its least deviation, Boie model is well suited for raw woody biomass. However, the deviation became extremely large when same models were employed

to predict the HHV of biochar. The predicted HHVs were compared with the measured HHV, and the deviations were 13.8%, 11.9% and 4.77% for Yin (2011), Sheng and Azevedo (2005) and Boie (1953) models, respectively. This implied that prediction of the HHV of biochar is still open to further studies, and thus, calorimetry still remain the best method to obtain HHV of biochar. The improvement in HHV for biochar is traceable to the improvement in fixed carbon content which resulted from lower O/C and H/C atomic ratios. With 22% improvement in HHV for mild conditions and 55% for severe conditions, the biochar from Melina and Teak woods are suitable for the production of pellets and bio-coal briquettes that is useful as fuel.

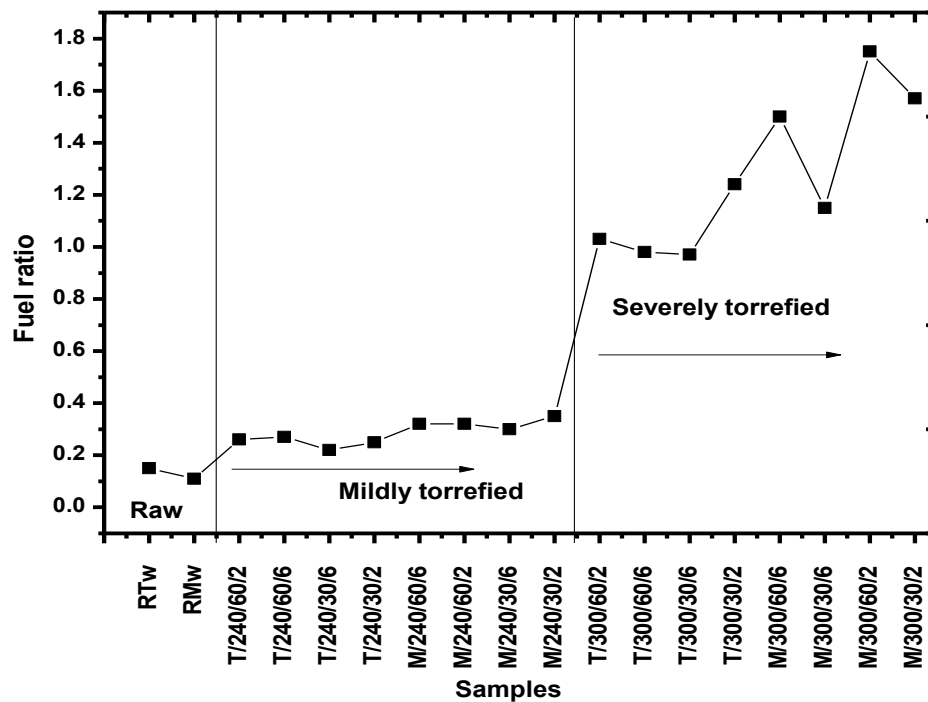


Figure 4.13: Fuel ratios of raw biomass compared with torrefied biomass samples

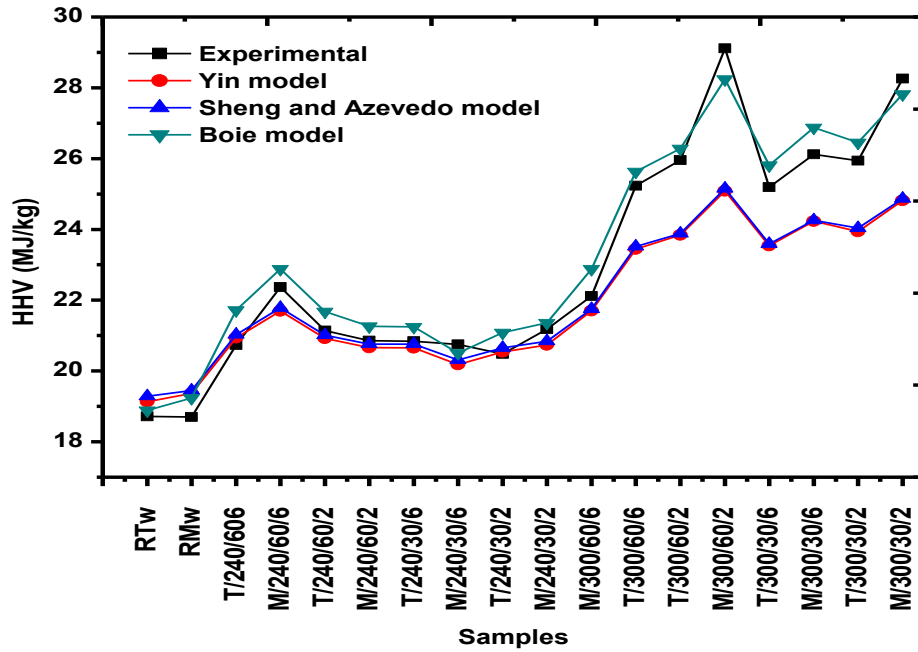


Figure 4.14: Comparison between experimental and predicted values of HHV for raw woody biomass and biochar.

4.2.6 Influence of severity factor on weight loss and the rise in higher heating value

The weight loss by the woody biomass during torrefaction has direct implication on the higher heating value (HHV) as discussed in section 4.2.5. For further emphasis on the influence of torrefaction parameters on the increment in higher heating value (HHV_{rise}), severity factor that combined the effects of both temperature and residence time was used to vividly observe the weight loss trend along with HHV_{rise} as shown in Figure 4.15. HHV_{rise} was obtained by subtracting the HHV of raw biomass from that of torrefied samples ($HHV_{rise} = HHV_{torrefied\ sample} - HHV_{raw\ sample}$).

Figure 4.15a shows that Melina wood (RMw) experienced higher weight loss compared to Teak wood (RTw). The HHV_{rise} followed a similar trend to the weight loss based on the severity factor: higher weight loss implied higher HHV_{rise} (Figure 4.15 a and b). The HHV_{rise} of RMw was better than that of RTw (Figure 4.15b). The weight loss ranges from 20.89 to 60.02% for RMw and 16.90 to 51.74 % for RTw. The result obtained in the

present study is in agreement with the reports of Lee *et al.* (2012) and Medic *et al.* (2012) which stated that an increase in combined severity factor during biomass pre-treatment processes leads to massive loss in weight for biomass. Therefore, it is expected that with the increase of pre-treatment severity factor, low mass yield will be obtained for torrefaction of tropical lignocellulosic biomass. The HHV_{rise} may be due to the removal of lean energy content and light volatiles that voluminosely dominate the hemicellulose, thereby, leaving energy-rich contents of cellulose and lignin in biochar (Eisenhuber *et al.*, 2013). Generally, torrefaction process led to tremendous improvement in HHV of the woody biomass.

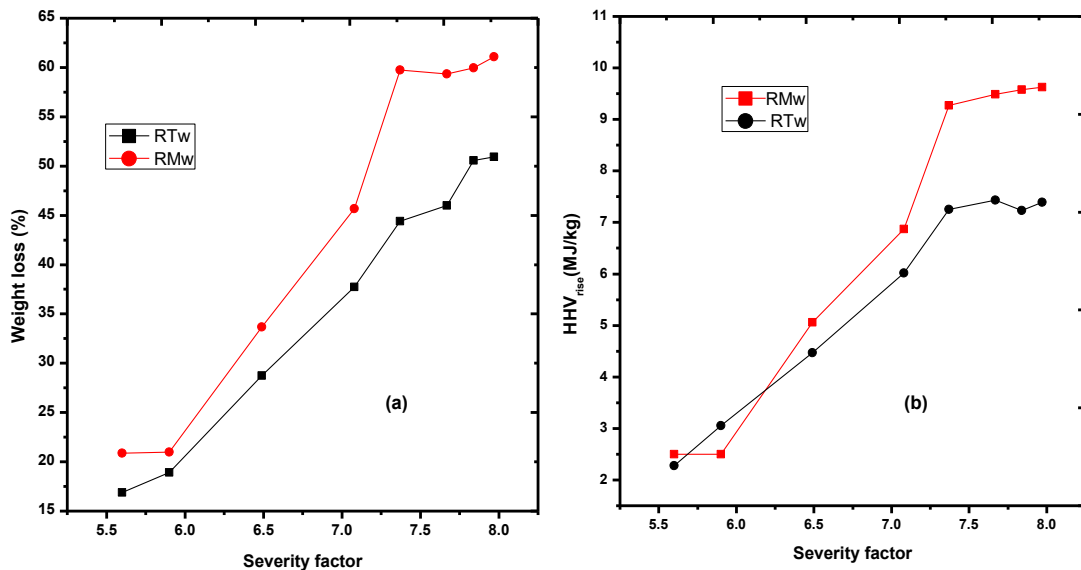


Figure 4.15: The influence of severity factor on (a) weight loss (b) HHV_{rise}
(particle size = 2 mm)

4.2.7 Surface morphology of raw woody biomass and biochar

The micrographs of raw Melina (RMw) and Teak (RTw) compared with some of their biochar are presented in Figures 4.16 - 4.18 and discussed in this section. The fibrous nature of biomass is seen on the micrographs of RMw and RTw with varied arrangement (Figure 4.16). This fibrous nature makes the grindability of raw woody biomass samples difficult. Spongy-form structure can also be observed in the micrographs of both raw woody biomass. This structure forms the basis for its hydrophilic nature that makes it absorbs moisture from

the surroundings (Basu, 2010). The micrographs obtained after torrefaction at mild and severe conditions are similar to each other, with presence of pores across the surfaces of both the Melina and Teak woody biomass. Therefore, torrefaction condition can be said to have no significant influence on the morphological structure of the woody biomass. There were no clear features in term of pores on the micrographs of the raw woody biomass at higher magnification due to charging effect and therefore the micrographs were taken at X180 magnification (Figure 4.16). However, micro, macro and mesopores are seen in the micrographs of biochar (Figures 4.17 - 4.18).

Biochar produced at 240°C are filled with more tissue that were not devolatilized leading to fewer pores observed on Figures 4.17a and 4.18a. This implied that the grindability enhancement will be low compared to biochar produced at 300°C. As can be seen on Figures 4.17b and 4.18b, the morphology of the biochar of RMw and RTw featured a honey-comb-like structure with cylindrical holes connected by some large holes. The pattern of arrangement is similar to what was obtained for high pyrolysis of empty fruit bunch and rice husk biochar by Claoston *et al.* (2014). The arrangement of pores enhances the grindability output at 300°C (Mohan *et al.*, 2006). Higher level of crack formation and shrinkages were observed at the surface of the severely torrefied samples. This could be due to higher volatile loss in both Melina and Teak wood during torrefaction.

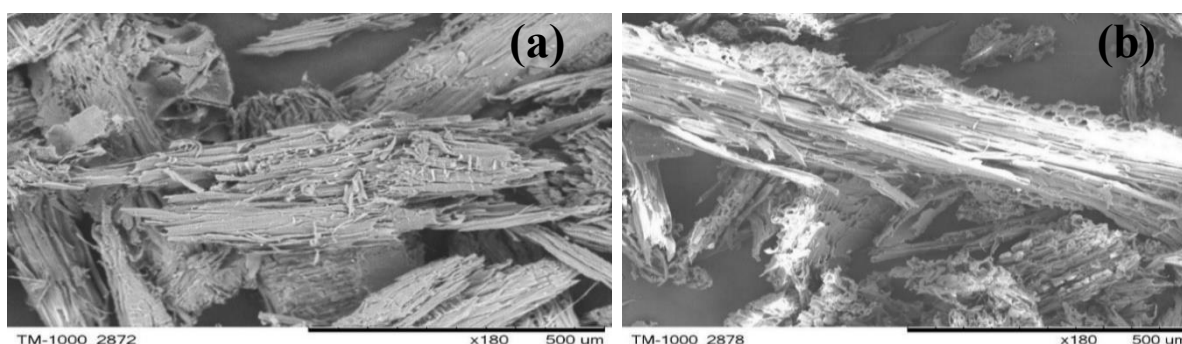


Figure 4.16: Micrographs of the raw woody biomass (a) RMw and (b) RTw

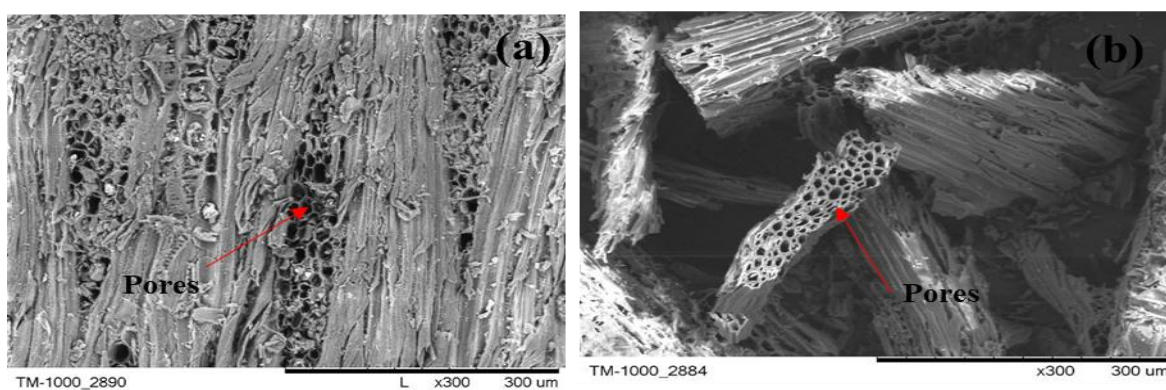


Figure 4.17: Micrographs of biochar (a) T/240/60/6 and (b) T/300/30/6

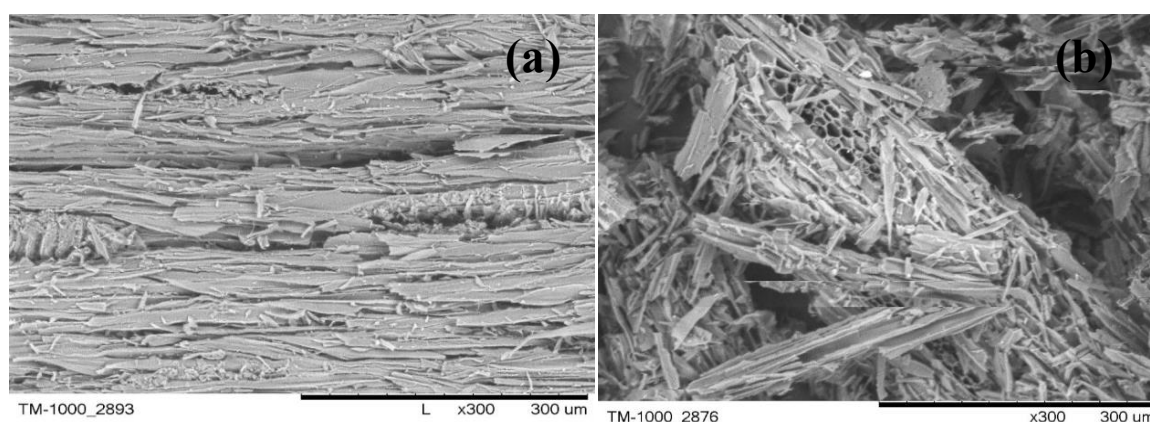


Figure 4.18: Micrographs of biochar (a) M/240/60/6 and (b) M/300/30/6

4.4 Properties of biochar produced using the optimized conditions

The properties of biochar produced using mild and severe torrefaction conditions showed that torrefaction led to the improvement of woody biomass. However, the desired to have optimum mass yield, higher heating value and energy yield led to parametric optimization as discussed in section 4.3. The optimized conditions (TT of 260°C; RT of 60 min; and PS of 2 mm) based on mass yield, HHV and energy yield was adopted for torrefaction of the both Melina and Teak wood in order to obtain sufficient amount of biochar required for production of the hybrid fuel briquette. The biochar produced at the optimized conditions was then characterized and compared with raw woody biomass and some other torrefaction conditions. The proximate, ultimate, higher heating value (HHV) and

compositional analyses of the biochar produced using optimized conditions compared with raw woody biomass and some other conditions are presented in Table 4.9.

Generally, the moisture content (MC) and volatile matter (VM) of the biochar decreased in order of torrefaction temperature compared with the raw woody biomass as shown in Table 4.9. The higher the torrefaction temperature, the lower the MC and VM compared with the raw woody biomass. Conversely, the fixed carbon and HHV of biochar also increased as the temperature increases from 240 to 300°C as shown in Table 4.9. There was no notable difference in the ash content in since torrefaction does not have any effect on biomass ash. The woody biomass have higher improvement based on proximate analyses at 300°C as against the optimum conditions and 240°C (Table 4.9). However, the resulting mass yield and the possible energy yield are very low due to higher loss of some energy-lean and rich components of the woody biomass at 300°C. Therefore, a balance of energetic yields and proximate contents was obtained at the optimum torrefaction conditions in order to have quality amount of biochar required for hybrid fuel briquettes.

The effect of torrefaction on the ultimate contents of the biochar produced at the optimum conditions show that it is better than biochar produced at 240°C, but low in quality compared with that of 300°C. In general, the carbon (C) content increased along with reduction of the oxygen (O) and hydrogen (H) contents as shown in Table 4.8. Based on the ultimate analysis, biochar with high energetic yield having an improved ultimate contents compared with the raw woody biomass and biochar produced at 240°C is a good feedstock for the production of hybrid fuel briquette.

The composition analysis of only the raw woody biomass and biochar produced at the optimum conditions was carried out due to the nature of the test and its costs. The hemicellulose and cellulose compositions of both woody biomass were reduced while there was an increment in the lignin content as shown in Table 4.9. This indicated that torrefaction

process led to a loss of hemicellulose and cellulose while enhancing lignin. Melina wood had an acute rise in lignin compared with Teak wood due to higher loss in cellulose-based components as shown in Table 4.9. Thus, there is higher tendency that the hybrid fuel briquette produced from the blend of coal and Melina wood will possess better mechanical integrity due to the bonding strength of lignin (Pandey & Kim, 2011). The properties of the biochar were better than raw woody biomass and are comparable to that of lean grade coal that was characterized in the present study (Tables 4.2 and 4.9) and those that are been used as feedstock for briquetting and direct reduced iron production (Maslejova, 2013). The biochar produced at the optimum torrefaction conditions were used in briquetting process.

4.5 Production and characterisation of hybrid fuel briquette

Hybrid fuel briquette (HFB) was produced from the biochar obtained using optimized conditions, the lean grade coal, and binders (pitch, molasses and starch). The blend of pitch and molasses (15%) with various ratios was also used as binder. Biochar of Melina wood and lean grade coal were used to produce the HFB that was used to study the influence of various parameters. Variation in particle sizes and pressure have specific roles in developing briquettes and while other factors were fixed, they were varied. Particle size was fixed in the range below each specific sieve sizes adopted. The formulation used for particle size and pressure variation study was 95% lean grade coal: 5% biochar (15% binder content). The results presented in this session are the hybrid fuel briquettes produced from coal slack and Melina wood while that of Teak wood was presented for comparison. Typical examples of green and cured HFB produced in this study are presented in Figure 4.19.

Five major physical and mechanical properties that serve as litmus to establish the integrity and quality of a fuel briquette are density, water resistance, impact resistance, drop to fracture and cold crushing strength (Richard, 1990; Thoms *et al.*, 1999). The evaluation of these properties revealed the influence of processing pressure, particle size, binder types and

percentage composition, influence of hybrid formulation and curing conditions on the hybrid fuel briquette and these are discussed in this session.

Table 4.9: Proximate, ultimate, higher heating value and compositional analyses of biochar produced using optimized condition compared with raw woody biomass and some other conditions.

		RM _w	RM _w *	RM _w **	RM _w ***	RT _w	RT _w *	RT _w **	RT _w ***
Proximate analysis (%)	MC	7.52	2.68	3.01	2.53	7.23	2.74	3.22	2.56
	VM	81.42	54.09	71.89	34.64	79.26	54.2	74.98	47.08
	AC	2.15	2.17	2.22	2.29	1.73	1.78	1.79	2.05
	FC	8.92	41.06	22.89	60.55	11.73	41.28	20.02	48.32
Ultimate analysis (%)	C	47.09	66.05	53.86	72.04	47.84	60.4	54.78	63.99
	H	6.65	5.18	6.03	4.74	6.09	5.67	5.95	5.29
	N	0.38	0.36	0.20	0.33	0.39	0.35	0.36	0.35
	S	0.24	0.22	0.20	0.20	0.26	0.21	0.22	0.22
	O	43.54	26.02	38.35	19.67	43.69	31.56	37.11	27.51
CV	HHV(MJ/kg)	18.39	23.46	21.08	29.11	18.72	23.63	21.69	26.46
Composition (%)	Hemi-C	6.50	0.80	-	-	5.60	1.10	-	-
	Cellulose	53.10	29.40	-	-	62.40	41.00	-	-
	Lignin	28.20	54.50	-	-	16.90	46.20	-	-
	Extractives	10.47	13.13	-	-	13.75	9.92	-	-

*Optimized condition (260°C - 60 min -2 mm), ** 240°C - 60 min-2 mm, ***300°C - 60 min - 2 mm, CV-calorific value.

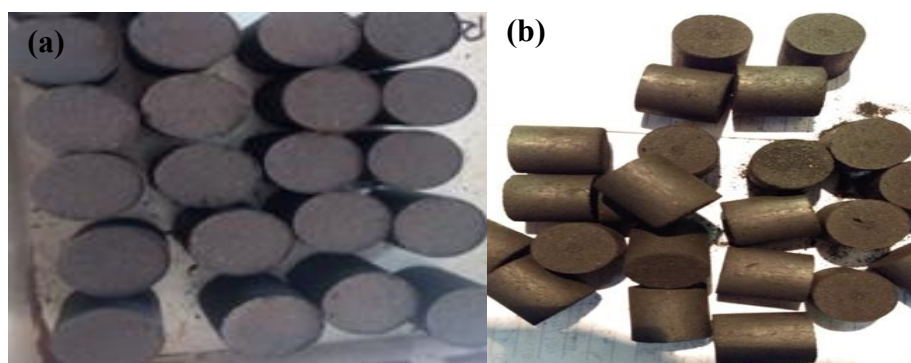


Figure 4.19: Hybrid fuel briquettes using blended binder (8%pitch-7%molasses)

(a) green (b) cured

4.5.1 Physical and mechanical properties of the HFB

4.5.1.1 Bulk density

The influence of particle size variation on the density of briquettes is shown in Figure 4.20. The initial density of the HFB while varying the particle sizes was in the range of 1.46 - 1.55 g/cm³. There was a drop in density of the HFB to a range of 1.26 to 1.34 g/cm³ after they were cured. This was as a result of possible removal of moisture and some light volatile matters from the briquettes. Variation in the curing conditions also have a slight influence on the density of the briquettes. Increasing the severity of curing causes more shrinkage and loss of volatile matter. Similarly, increasing pressure led to more reduction in size of the HFB while the weight remain constant, thereby leading to an increase in initial density of the green briquette. The density was reduced after curing with no clearly defined variation under different conditions under 14 MPa pressure as shown in Figure 4.21. However, at 28 MPa briquetting pressure, increasing curing caused a further reduction in density. There was no consistent effect of curing conditions after 28 MPa where all lies in the range of 1.25 to 1.35 g/cm³. This could be as result of different degrees of moisture evolution from the HFB and devolatilization of the raw materials.

Pitch-bonded briquettes have the lowest range of density compared to other binders as shown in Figure 4.22 and was reduced under all curing condition sets. Increasing the

proportion of torrefied biomass reduced the density of the hybrid fuel briquette produced from both blended and individual binders (Figures 4.23 and 4.24). As observed for other factors under consideration, the density of briquette generally reduced after curing. The effect of curing condition can easily be identified when different blended binder ratios were used as shown in Figure 4.24. The severe the curing condition, the lower the density, which is traditionally traceable to the evolution of moisture and low temperature volatiles in briquette raw materials (Blesa *et al.*, 2003). Density of green briquette range from 1.40 - 1.60 g/cm³ and it was reduced to a range of 1.12 to 1.38 g/cm³ for all blended binders and hybrid ratios. The density (1.18-1.32 g/cm³) of the briquette developed after curing is higher than the blast furnace coke (0.87 g/cm³) as reported by Mori *et al.* (2011). The range is a reminiscent of formed coke produced from Victorian brown coal by Mollah *et al.* (2015). This suggests that the pore volume of a typical blast furnace coke is higher than that of the briquette produced in this study.

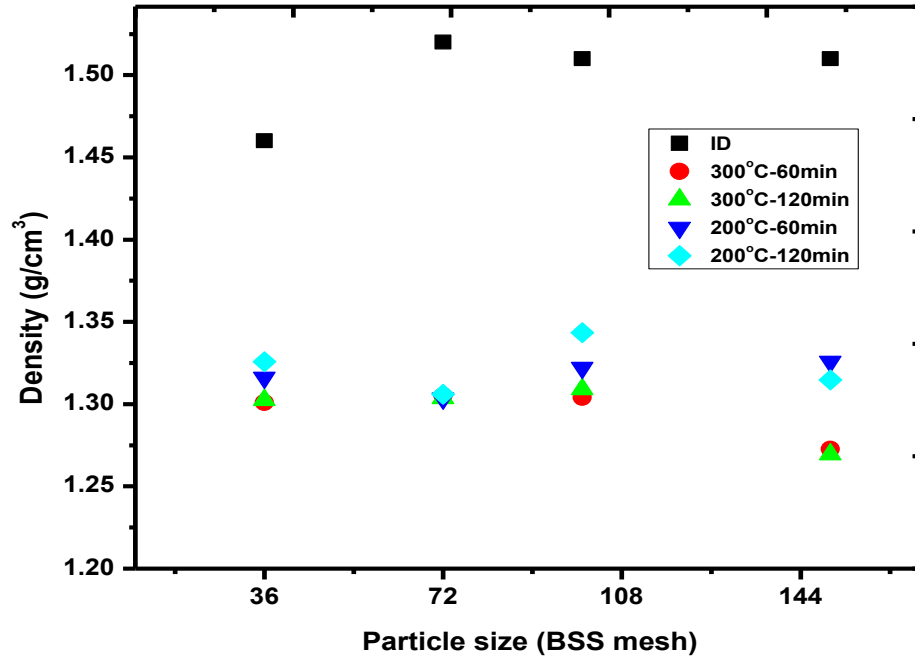


Figure 4.20: Influence of particle size variations on the density of briquettes under different curing conditions.

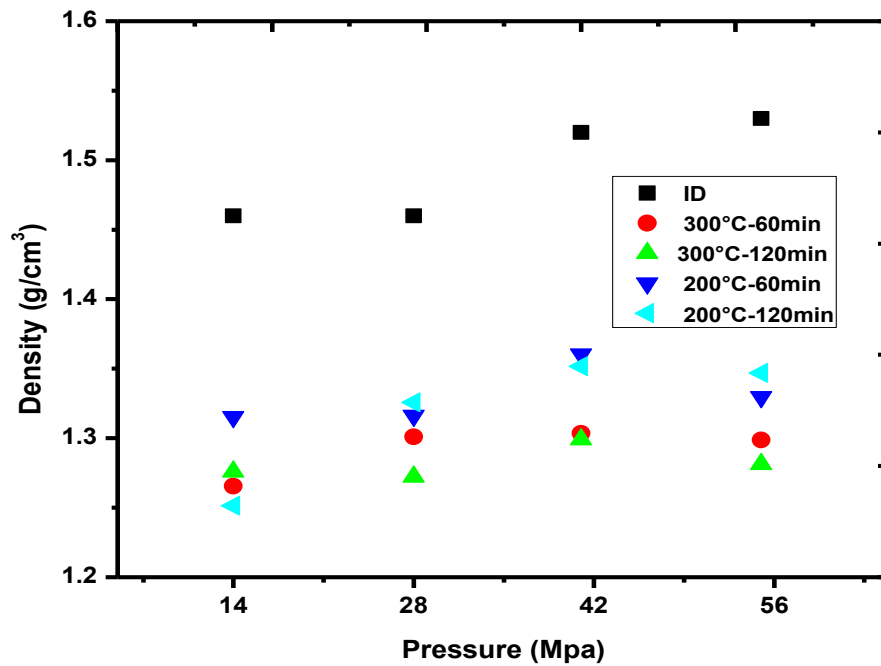


Figure 4.21: Effect of pressure variations on the density of briquettes under different curing conditions.

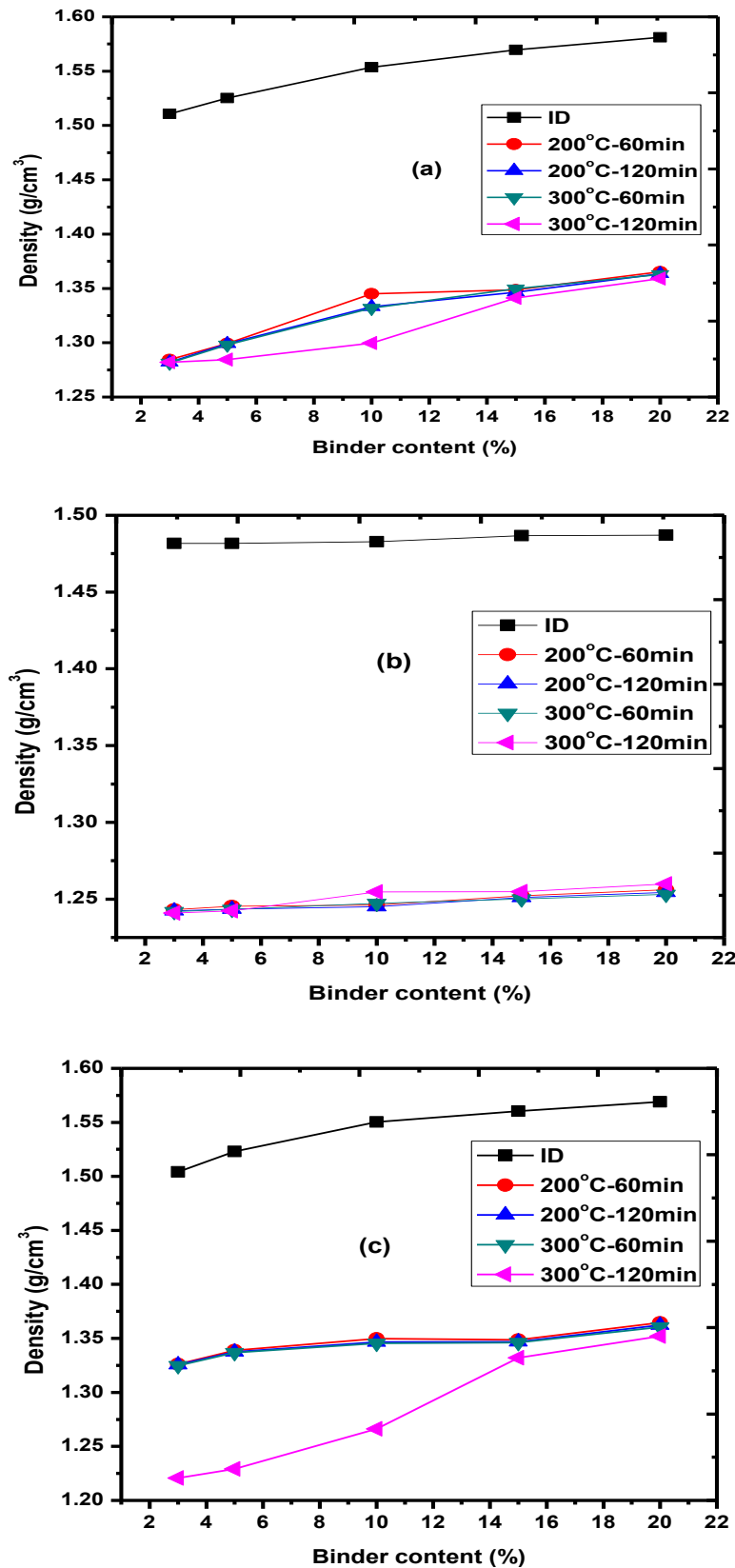


Figure 4.22: Influence of binder variations on density of HFB using 95:5HR at different curing conditions (a) Molasses (b) Pitch (c) Starch

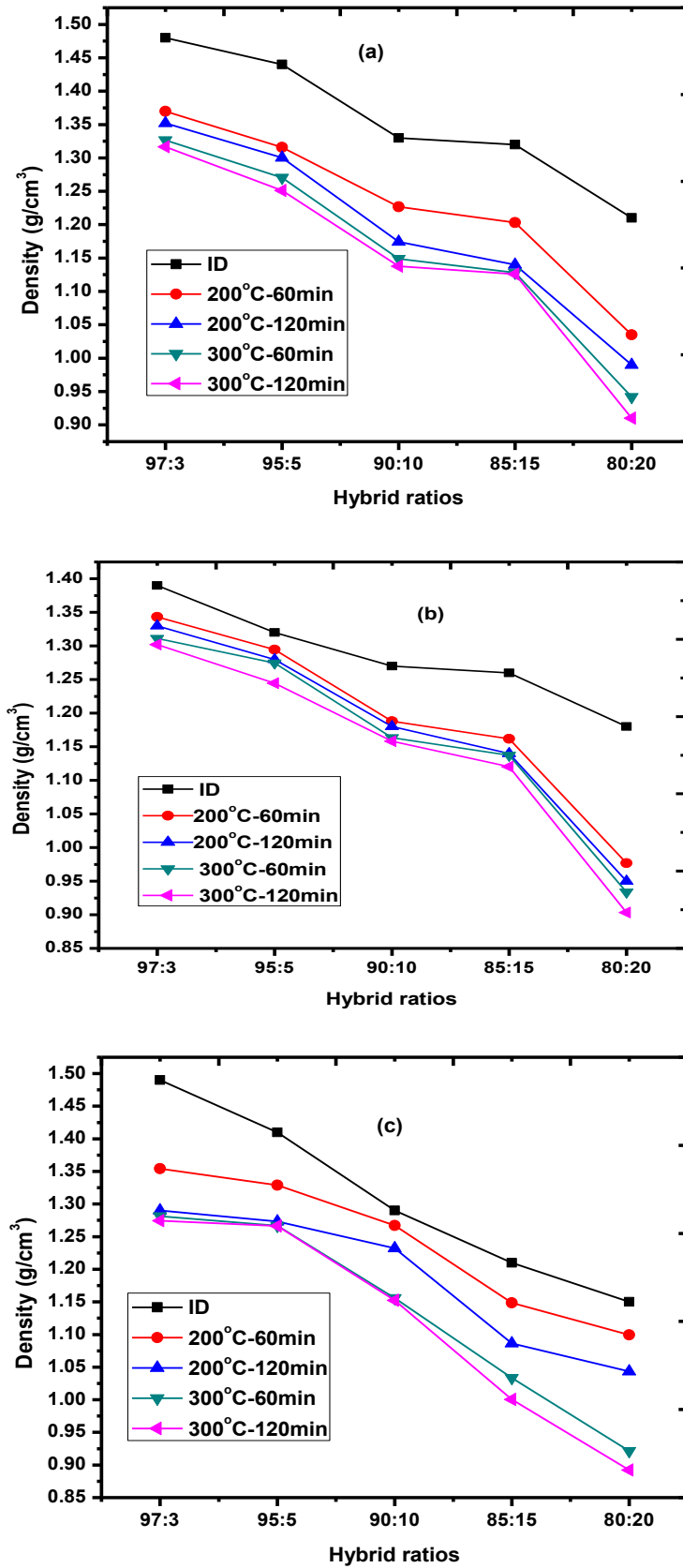


Figure 4.23: Impact of hybrid ratios on the density of HFB using separate binder (a) Molasses

(b) Pitch (c) Starch

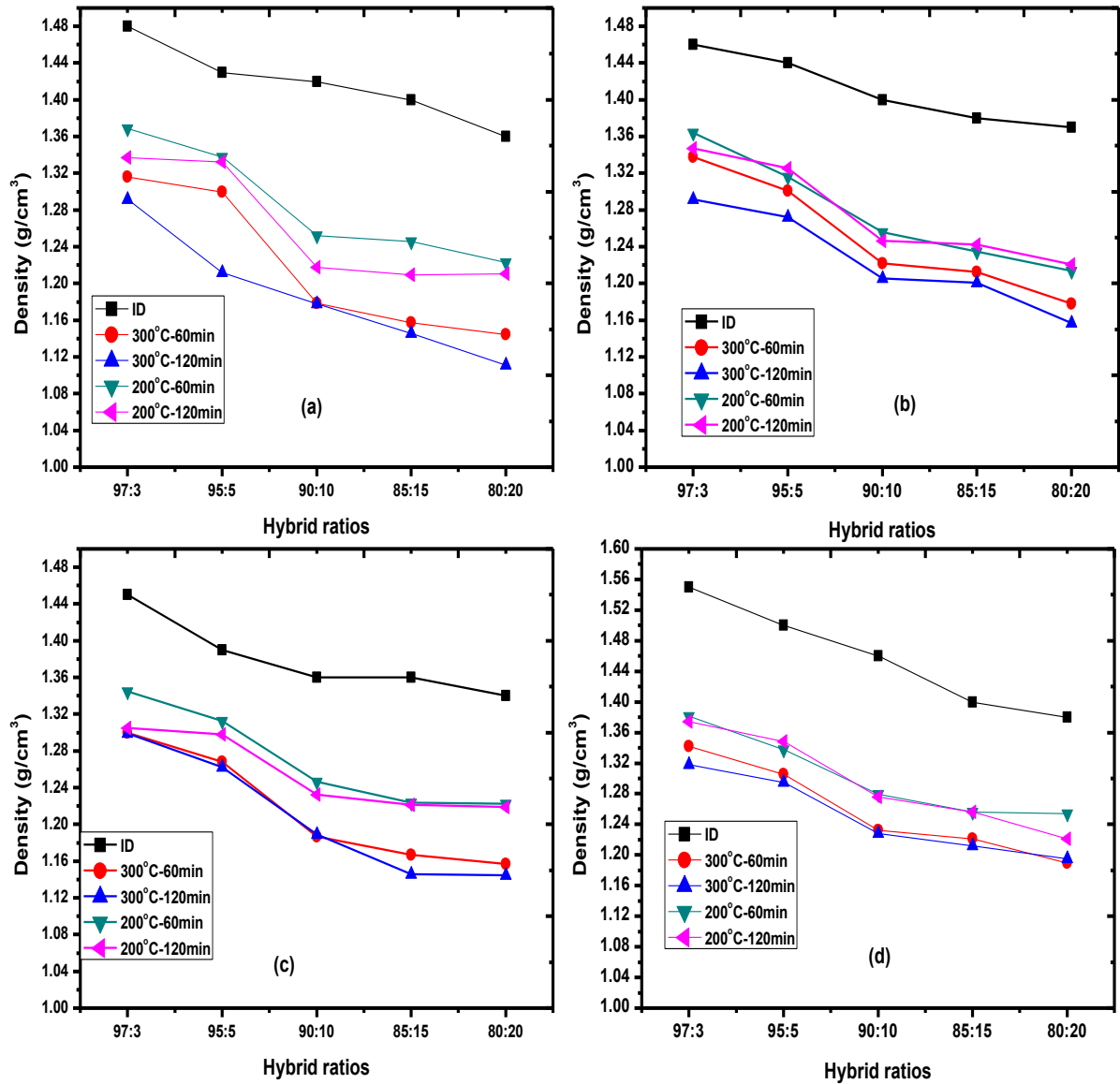


Figure 4.24: Influence of hybrid ratios on the density of HFB at different curing conditions using blended binder (a) 5P-5M (b) 8P-7M (c) 10P-5M (d) 5P-10M

4.5.1.2 Drop to fracture number

The drop to fracture is a twin test with impact resistance that measures the friability of the hybrid fuel briquettes. Friability is referred to as the tendency of a briquette to resist impact forces. Briquette can suddenly break into small pieces from a sudden impact force. The drop to fracture number (times/2m) required to break briquettes into pieces are shown in Figures 4.25 - 4.29 based on parametric variations. Figure 4.25 shows that as the particle size

became finer, there was a decline in the drop to fracture number as particle becomes contain more. The highest value was obtained at particle size below 36 mesh with 176 (times/2m) drop number. Significantly, increasing severity of curing lowered the number of drops the briquettes can withstand before breakage. Moisture and light volatile in briquettes produced from finer particle might experience difficulty to evolve due to closer particle distance resulting from higher surface area and thereby causing their forceful liberation (Huko *et al.*, 2015). The evolution can possibly create some undesirable crack within the briquettes which can later be ultimately responsible for lower drop to fracture number.

The effect of pressure variation on the drop to fracture number is also presented in Figure 4.26. The highest drop to fracture number was obtained with 28 MPa. Briquetting below and above 28 MPa yielded lesser drop to fracture number. The interactions of different raw materials and the effect of curing conditions may be responsible for this behaviour. Zhong *et al.* (2017) briquetted coal with high pressure of 60 MPa, cured it at 370°C and then carbonize at 600°C. The highest drop to fracture number recorded for the briquette was 57 time/2m. Evidently, the HFB in the present study were produced using lesser amount of energy in terms of pressure and yet possessed high resistance to fracture. An increase in the severity of curing from 200 to 300°C yielded lesser drop to fracture number. Increase in severity of curing i.e. curing at higher temperatures may lead to internal crack formations resulting from evolution of moisture and light volatiles within the bulk of the briquette. These crack sites could weaken the HFB when subjected to drop to fracture test.

The influence of different types of binder on drop to fracture number of the HFB is shown in Figure 4.27. The drop to fracture number is in the order of starch< molasses<pitch. Pitch-bonded briquettes were better off at 300°C-60 min curing condition while molasses gave the best drop to fracture number at 200°C-60 min. This implied that HFB can be produced from molasses by lowering the curing severity while a moderate curing severity

will produce durable HFB from pitch binder. Increasing the binder percentage composition in the briquettes resulted in increase in drop to fracture number for both pitch-bonded and molasses-bonded briquettes. However, for starch, there was no much change in drop to fracture number and this response is similar to previous study (Ikelle & Joseph, 2014). Figure 4.28 represent the effect of hybrid ratios and individual binders (10%) on the drop to fracture number of the HFB. At every curing conditions, pitch-bonded briquettes have the highest drop to fracture number. It can also be seen that the drop to fracture number decreased with an increase in the percentage quantity of the torrefied wood. This could be as a result of devolatilization as the quantity of torrefied biomass increased.

The best drop to fracture strength was obtained with a 3 - 5% torrefied wood biomass addition to coal fines. The HFB produced from the blended binders however have higher drop to fracture number compared with individual binders. The performance of pitch and molasses when blended at every curing conditions are shown in Figure 4.29. The highest drop to fracture number was 224 times/2m for HFB produced from 97:3 HR, while the addition of up to 20% torrefied wood yielded 35 - 60 times/2m at all the curing conditions. The more the proportion of torrefied biomass in the aggregates, the higher the devolatilization rate of the briquettes. This could create more pores within the briquette and thus weakens it. The drop to fracture strengths of most of the hybrid fuel briquette produced with blended binders in this study are higher compared with 57 times/2m reported by Zhong *et al.* (2017) for briquettes produced from the blend of 13% pitch-2% molasses. This indicated that some of the HFB produced in the present study have better impact resistance and good friability property. Therefore, it is recommended that hybrid fuel briquettes to be used for energy generation and metallurgical application should possess higher drop to fracture strength above 100 times/2m.

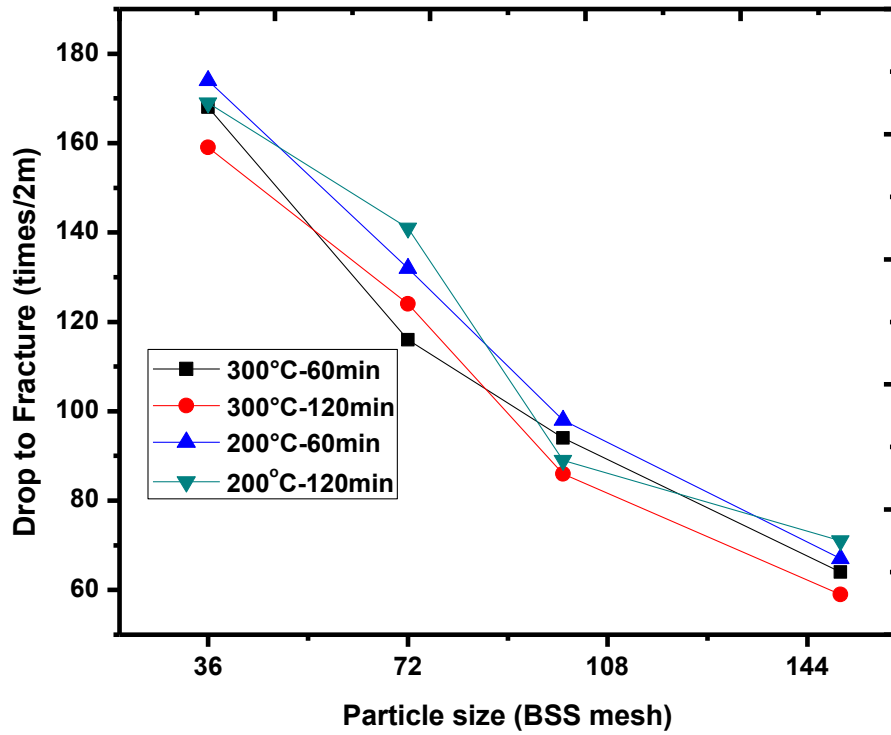


Figure 4.25: The drop to fracture number for HFB (95:5HR) while varying particle size under different curing conditions.

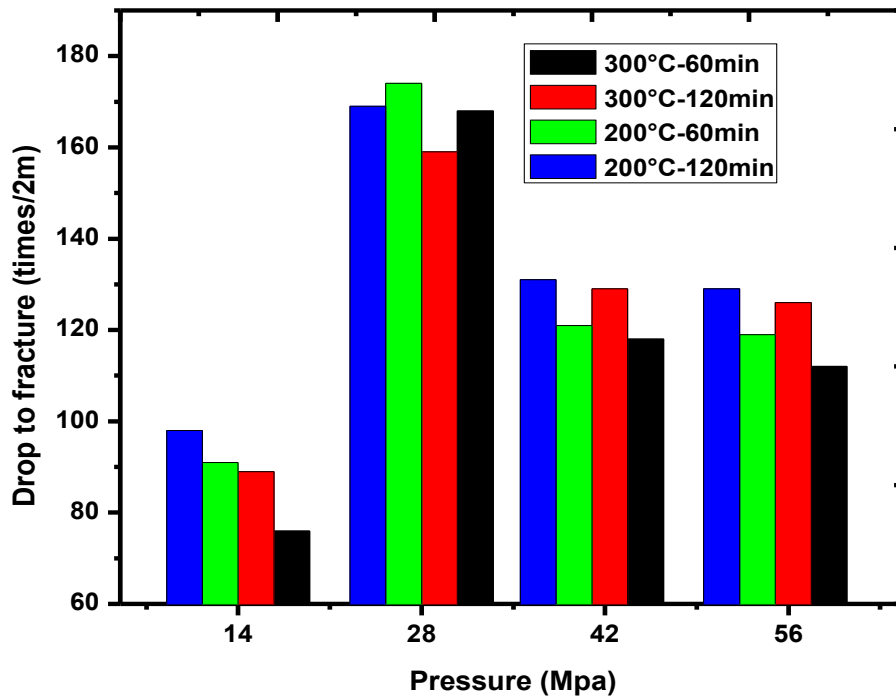


Figure 4.26: Effect of pressure variations on drop to fracture number of HFB (95:5HR) under different curing conditions.

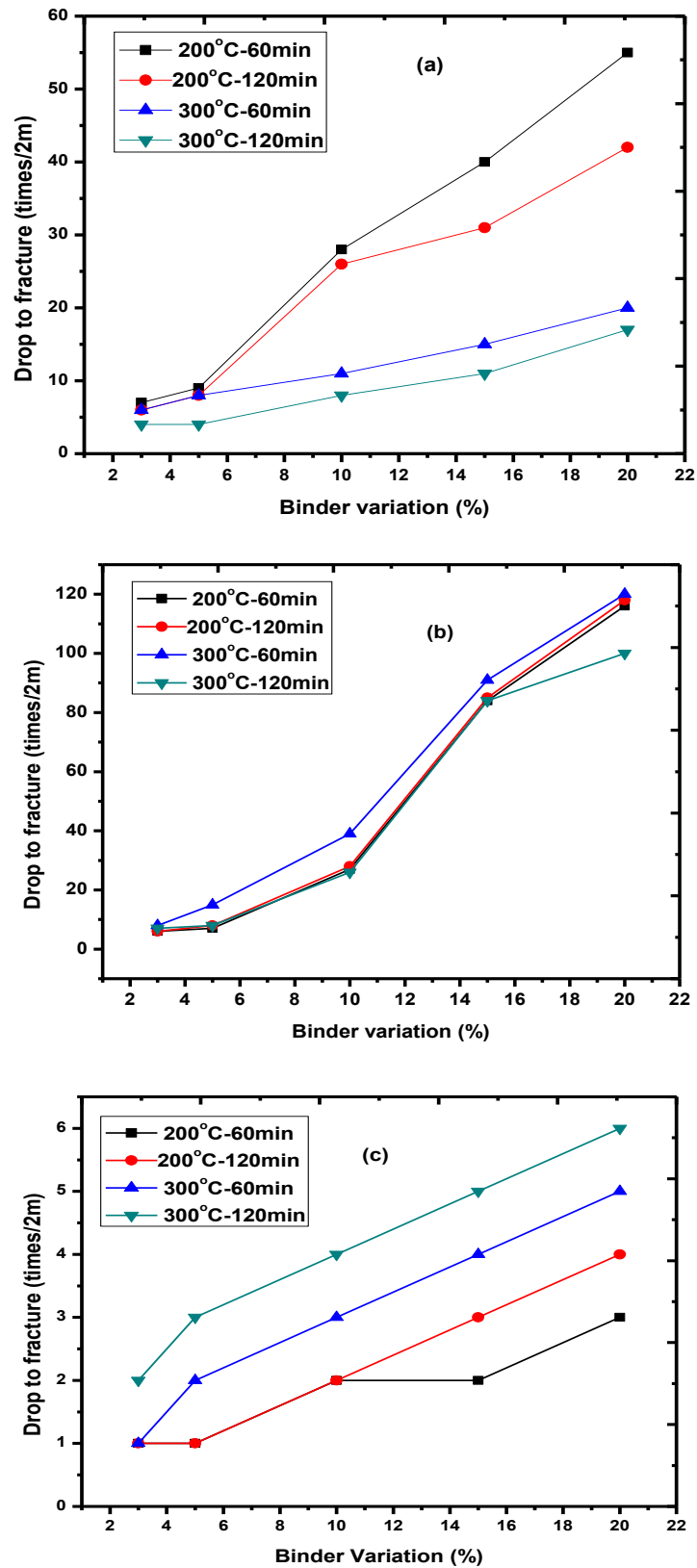


Figure 4.27: Influence of binder variations on drop to fracture number of HFB (95:5HR) at different curing conditions (a) Molasses (b) Pitch (c) Starch

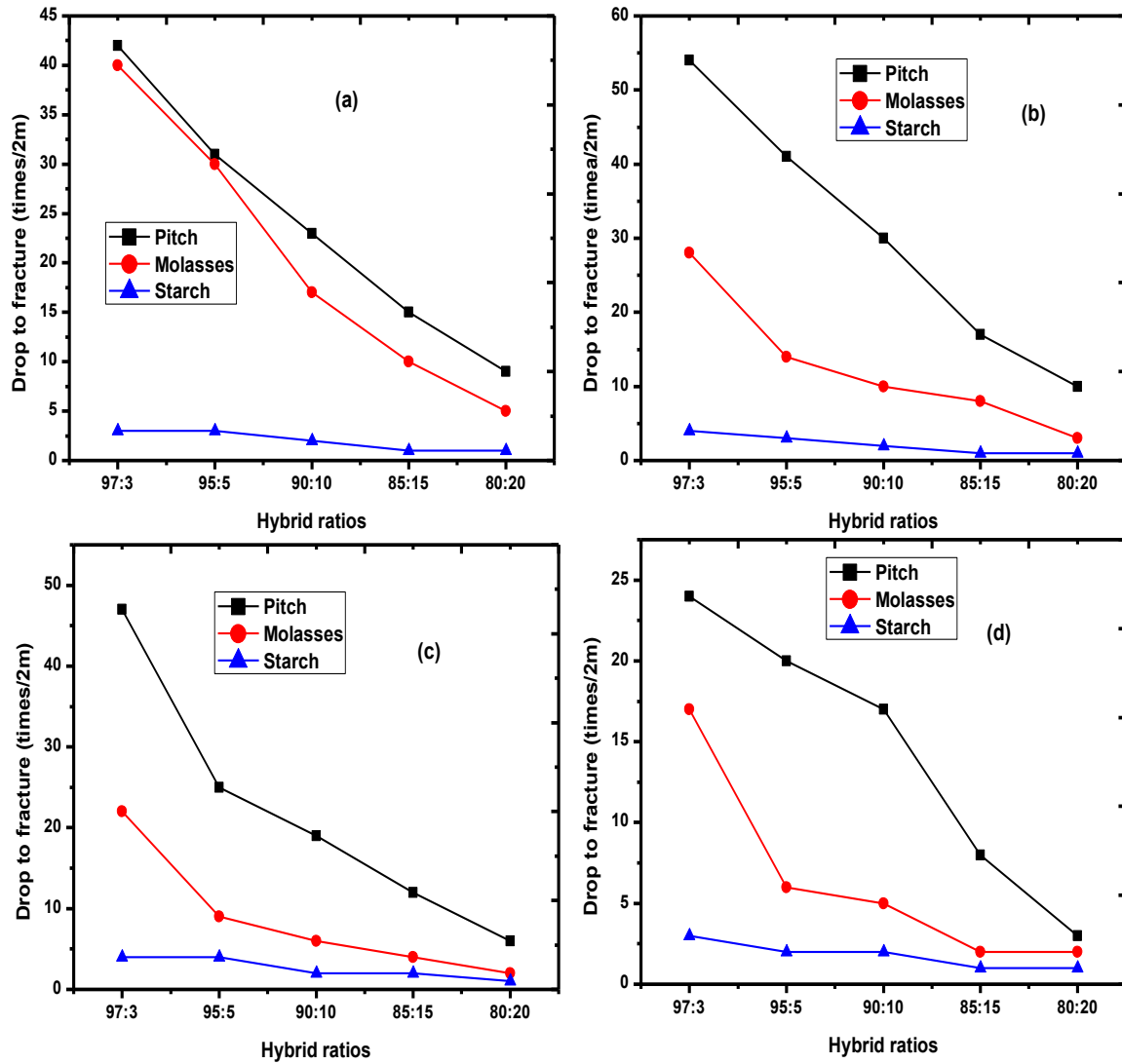


Figure 4.28: Impact of hybrid ratios on drop to fracture number of the HFB (95:5 HR) using separate binder (10%) at different curing conditions (a) 200°C-60 min (b) 200°C-120 min (c) 300°C-60 min (d) 300°C-120 min.

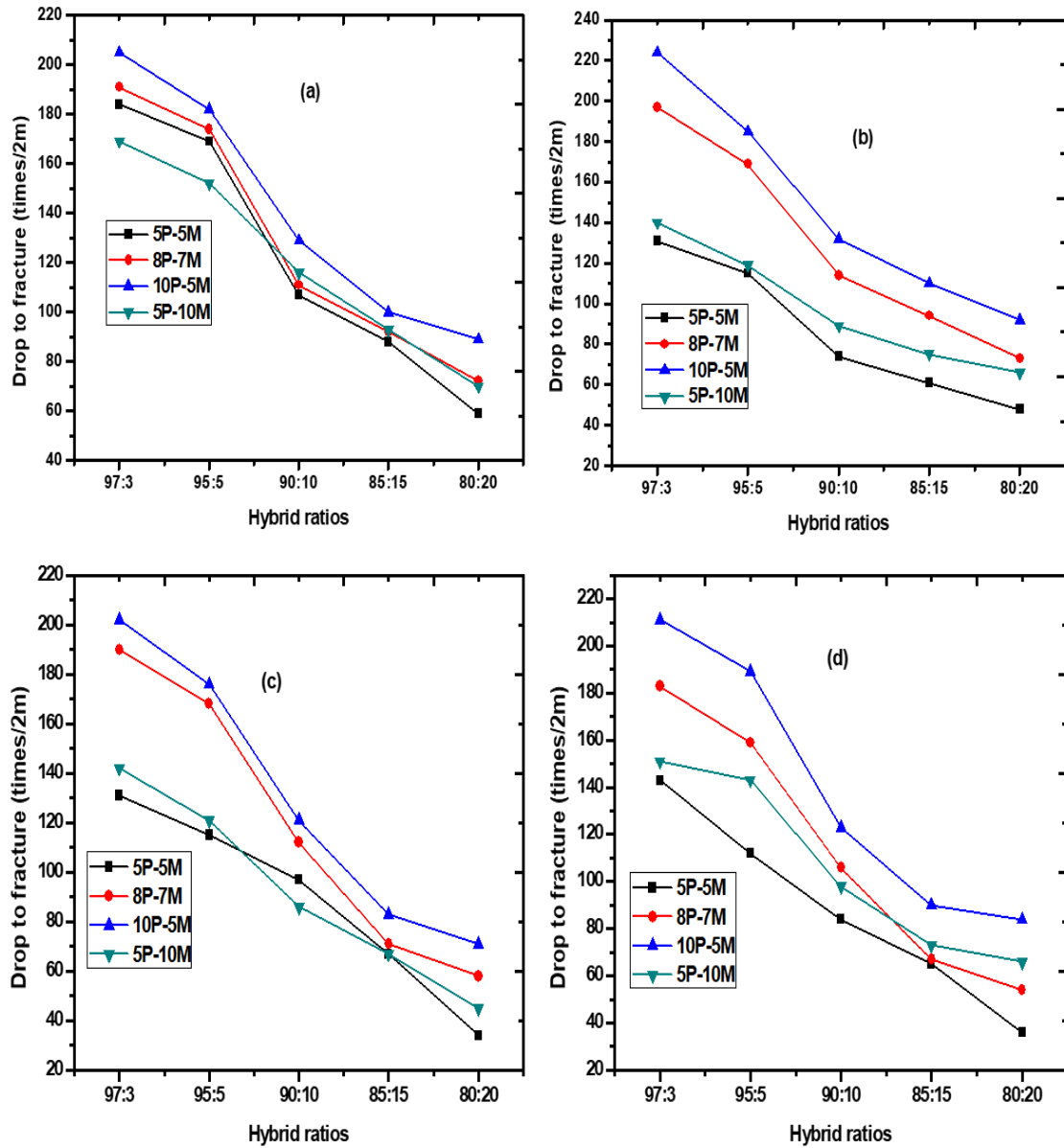


Figure 4.29: Effect of hybrid ratios on the drop to fracture number of HFB using blended binder at different curing conditions (a) 200°C-60 min (b) 200°C-120 min (c) 300°C-60 min (d) 300°C-120 min.

4.5.1.3 Impact resistance index

The impact resistance indices of the hybrid fuel briquettes are presented in Figures 4.30 to 4.34 based on different parametric variations. The influence of particle size and pressure variation are shown in Figures 4.30 and 4.31, respectively. Figure 4.30 shows that the impact resistance index (IRI) decreased as the particle size becomes finer. The finer the

particle sizes, the higher the surface area and thus more contact between different particles within the briquettes. This may lead to smaller interstitial distance between the different particles within the briquettes that does not allow easy evolution of moisture and volatiles during curing (Kashaninejad *et al.*, 2014), thereby making the briquette relatively weak. Hybrid fuel briquettes produced with 28 MPa have the highest IRI compared with other pressure used as shown in Figure 4.31. Pitch-bonded briquettes have the highest IRI compared with molasses and starch-bonded briquettes at all the percentage content as shown in Figure 4.32. It was also observed that pitch-bonded briquettes have higher IRI at 300°C - 60 min compared with curing conditions while the IRI for molasses-bonded briquette was higher at 200°C-60 min curing condition. Starch-bonded briquettes have the lowest IRI which was in the range of 25 to 250 at all its percentage content. This depicts that the bonding strength of particles to particles using starch was weak under different curing conditions and thus are not recommended for usage during the production of hybrid fuel briquette.

Figure 4.33 shows the influence of hybrid ratios on the IRI of HFB using separate binders. The figure revealed that the IRI of the HFB decreased as the proportion of the torrefied biomass in the hybrid ratios increased at fixed binder content (10%). The impact resistance was generally low at 10% percentage binder content with the highest value of 1330. From Figure 4.33, starch-bonded briquettes have the lowest impact resistance index compared with pitch and molasses bonded briquettes at every hybrid ratio. This behaviour is similar to what was observed for the drop to fracture number of the starch-bonded briquettes. This implied that apart from being able to sustain few drops before fracture, the briquette crumbled to more particles compared with briquettes produced with other binders. Figure 4.34 shows the IRI of hybrid fuel briquettes produced with blended binders at various curing conditions. From Figure 4.34, HFB produced with 8%pitch-7%molasses and 10%pitch-5%molasses gave the highest IRI at every curing conditions. However, at 200°C-120 min,

HFB produced with 10%pitch-5%molasses has the highest IRI value. This is similar for the drop to fracture number where HFB produced with 10%pitch-5%molasses has the highest value (Figure 4.29a). This may be due to pitch coking process that continued within the HFB during curing, thus leading to more strength that can sustain impact force. The IRI of the HFB produced in this study range from 1110 to 7500 and it is far higher than 50 proposed for briquettes of industrial application by Richard (1990) and Thoms *et al.* (1999). Lázaro *et al.* (2007) and Blesa *et al.* (2003) also obtained IRI in neighbourhood of 1000 and also proposed it as benchmarks of briquettes to be used for industrial and domestic applications. However, the present study shows that it is possible to obtain briquettes with higher IRI values, which implies better mechanical strength and ability to withstand impact as well as other stress during operations. Hence, briquettes to be used as feedstock in power plant and rotary kiln for energy generation and DRI making process, respectively, should have IRI above 2000.

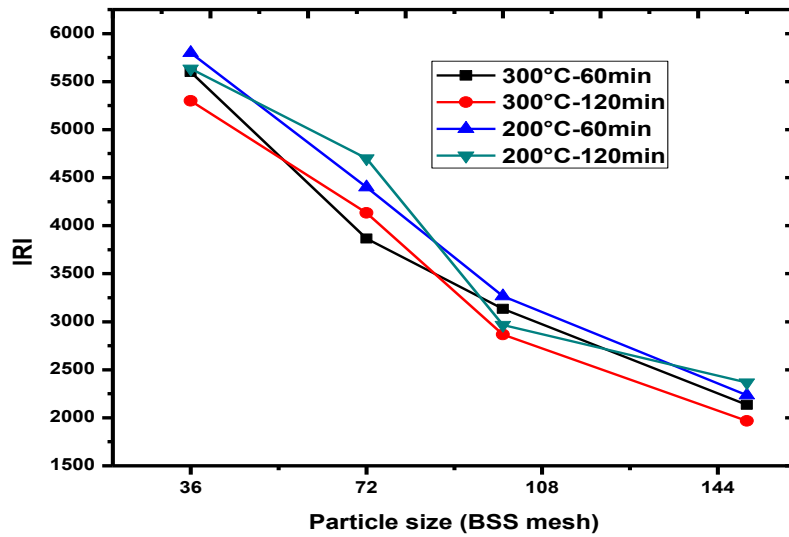


Figure 4.30: Influence of particle size variations on impact resistance index (IRI) of HFB (95:5HR) under different curing conditions.

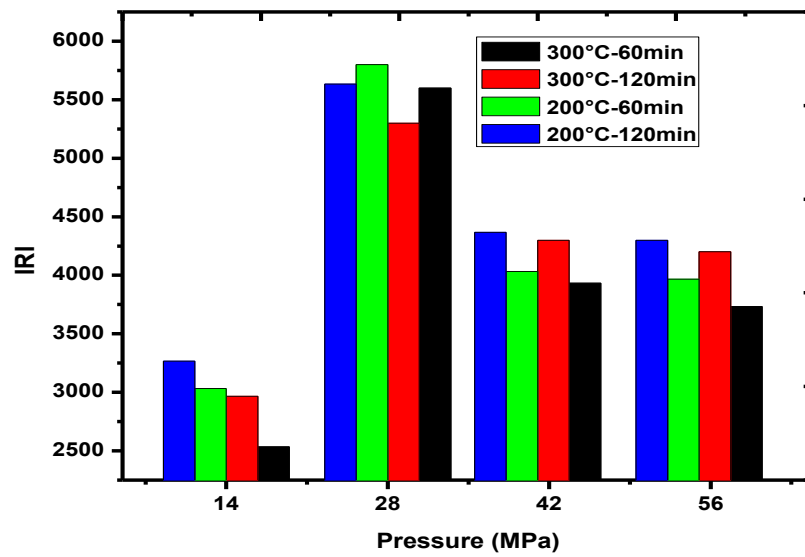


Figure 4.31: Effect of pressure variations on IRI of HFB (95:5HR) under different curing conditions.

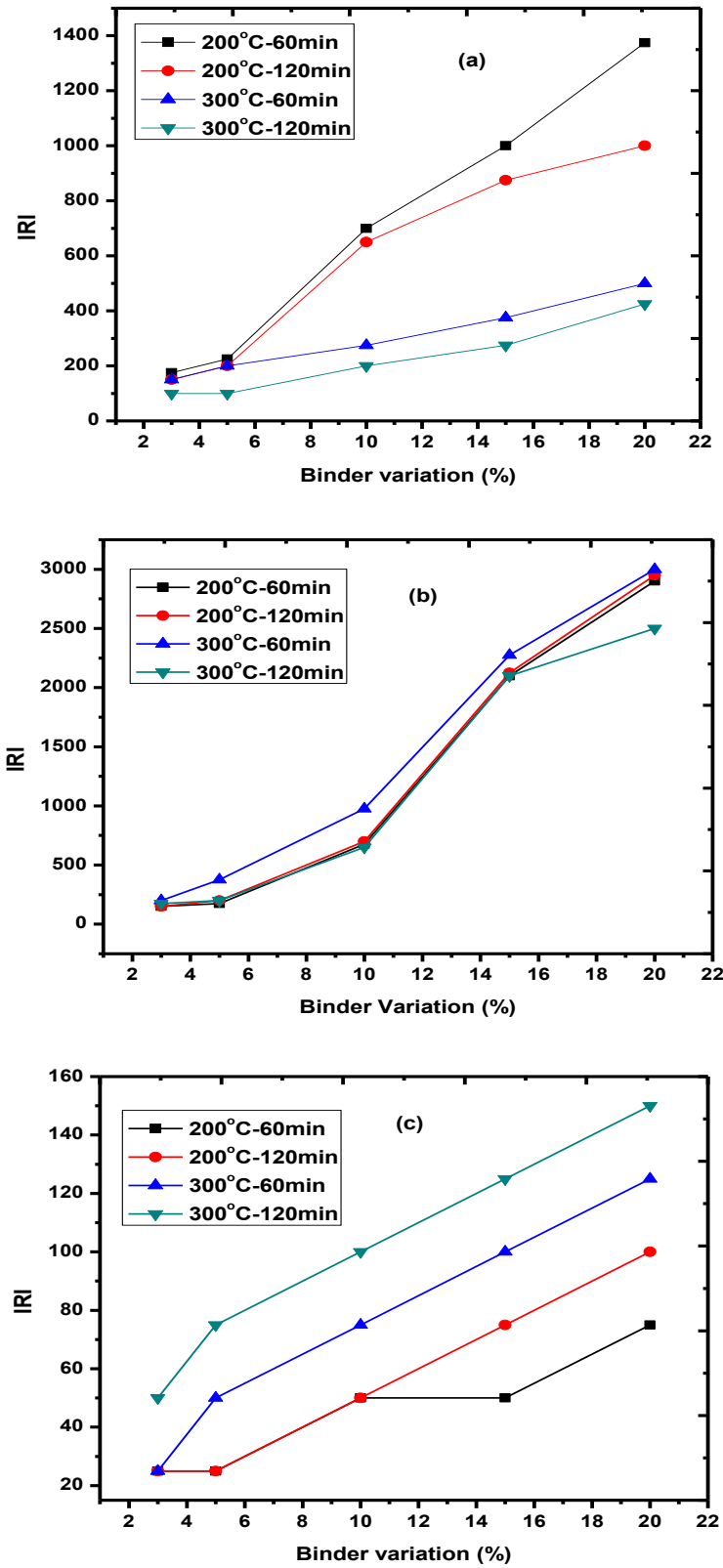


Figure 4.32: The impact of binder variations on IRI of HFB (95:5HR) at different curing conditions (a) Molasses (b) Pitch (c) Starch

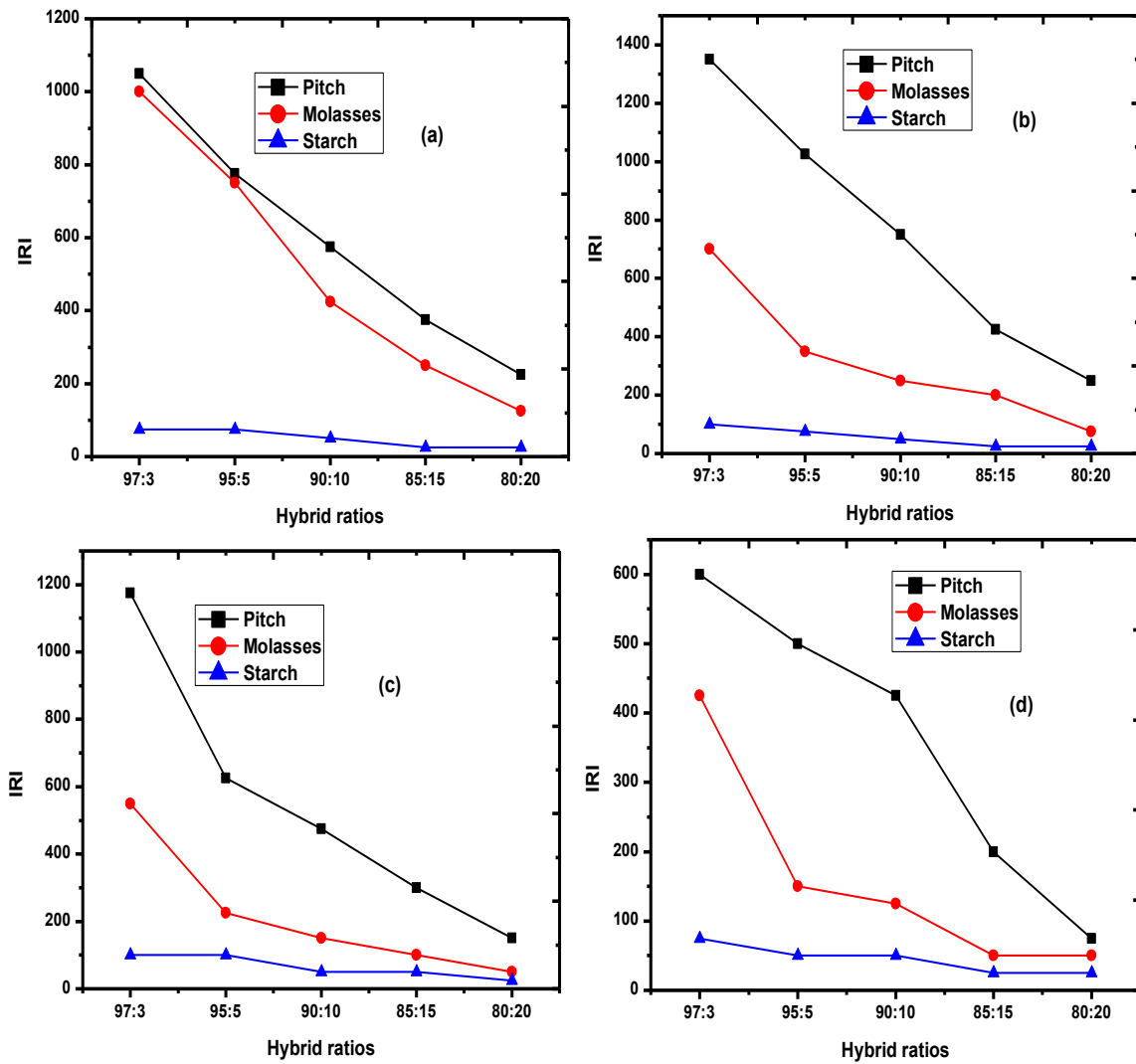


Figure 4.33: Influence of hybrid ratios on IRI of the HFB (95:5 HR) using individual binders (10%) at different curing conditions (a) 200°C-60 min (b) 200°C-120 min (c) 300°C-60 min (d) 300°C-120 min.

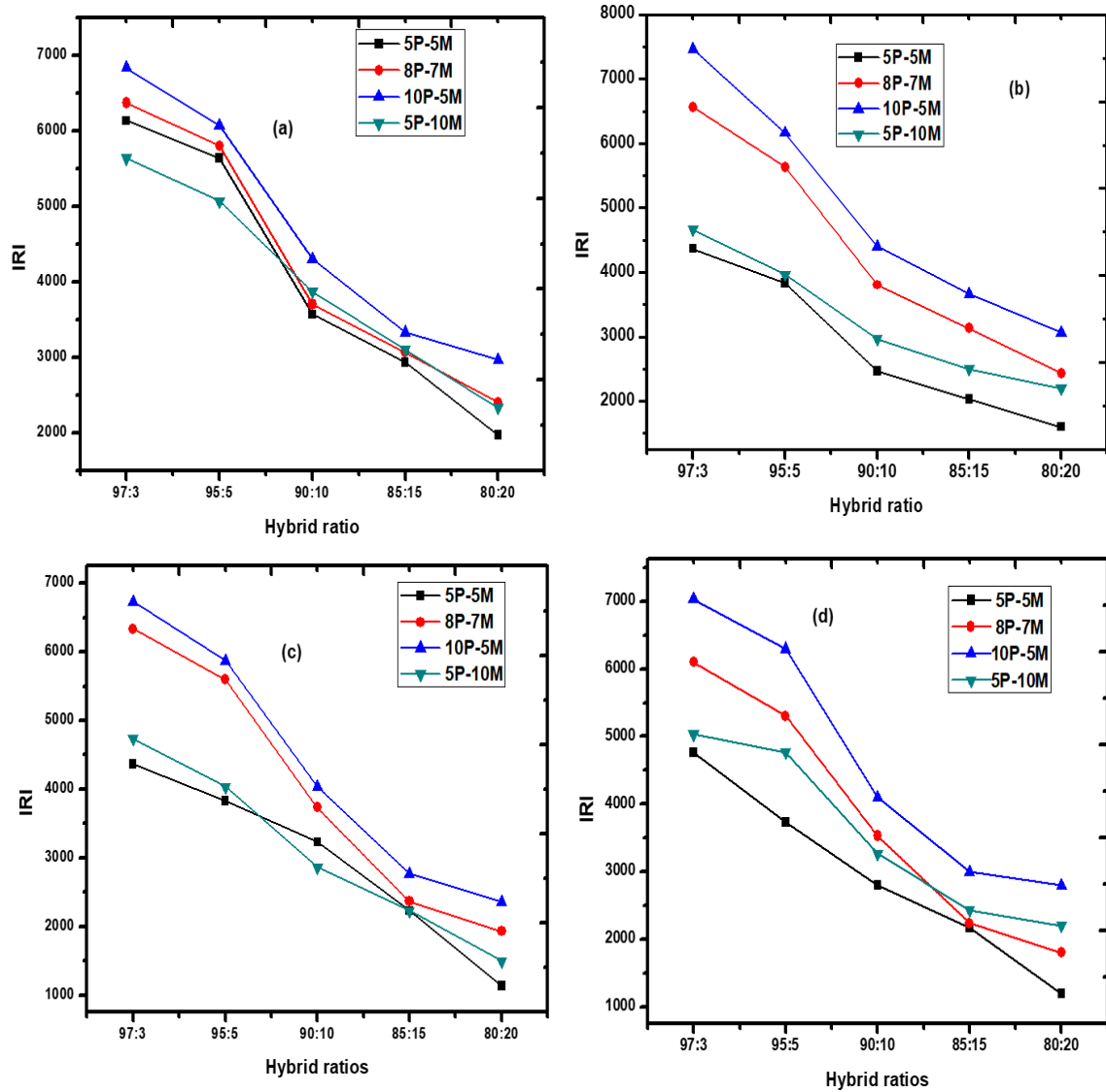


Figure 4.34: Influence of hybrid ratios on IRI of HFB using blended binder at different curing conditions (a) 200°C-60 min (b) 200°C-120 min (c) 300°C-60 min (d) 300°C-120 min.

4.5.1.4 Cold crushing strength

The cold crushing strength of the hybrid fuel briquettes based on different parametric variations are presented in Figures 4.35 - 4.39. The influence of particle sizes and pressure variation on cold crushing strength (CCS) of the HFB are presented in Figures 4.35 and 4.36, respectively. Particle of -36 BSS mesh and pressure of 28 MPa gave the best CCS and this is similar for other mechanical properties (IRI and drop to fracture). The increase in binder content led to an improved CCS of the briquettes as shown in Figure 4.37 and this may

generally be due to formation of stronger bond due to excess binder content within the particles interstitial spaces. It is observed that the CCS of pitch-bonded briquettes increases with an increase of curing time at 300°C, whereas the CCS of molasses-bonded decreased. HFB produced with starch binder at all percentage content gave the lowest CCS under all curing conditions. The lower CCS of the HFB may be due to more aliphatic bonding strength of starch compared with molasses and pitch as observed by Shibani (2011). Molasses-bonded briquettes gave the highest CCS even at 10% as a result of its initial viscous behaviour compared with other binders (Zhong *et al.*, 2016). The behaviour of molasses was also reported to be similar to that of phenolic resin when used as binder in coal briquette (Benk & Coban, 2011b).

Figure 4.38 shows the influence of hybrid ratios at 10% binder contents on the CCS of HFB. The CCS of the HFB decreased as torrefied biomass content increased under every curing conditions. This implied that more torrefied biomass weakens the HFB and it may be due to higher rate of devolatilization. The influence of the blended binder and hybrid ratios on the CCS of the HFB are presented in Figure 4.39. It was observed that the hybrid fuel briquettes produced with 5%pitch-10%molasses gave the highest CCS (11.50 MPa) compared to others as shown in Figure 4.39. This is due to more molasses content which contributed higher bonding strength in the interstitial particle distance within the briquette. Hybrid fuel briquettes produced with 10 - 20% molasses, 8%pitch-7%molasses and 5%pitch-10% molasses have higher CCS than the lower limit of the mechanical strength (6.9 MPa) for conventional coke reported by Yip *et al.* (2007). It is also very interesting to note that the CCS of all the hybrid fuel briquettes produced in this study were higher than proposed benchmarks of 350 kPa (Richard, 1990; Thoms *et al.*, 1999) and 847.50 kPa (Zarringhalam-Moghaddam, *et al.*, 2011) reported as per the requirement of useful briquettes for domestic and industrial

applications. Therefore, CCS above 11 MPa is recommended for briquette to be used as feedstock for energy generation and DRI making processes.

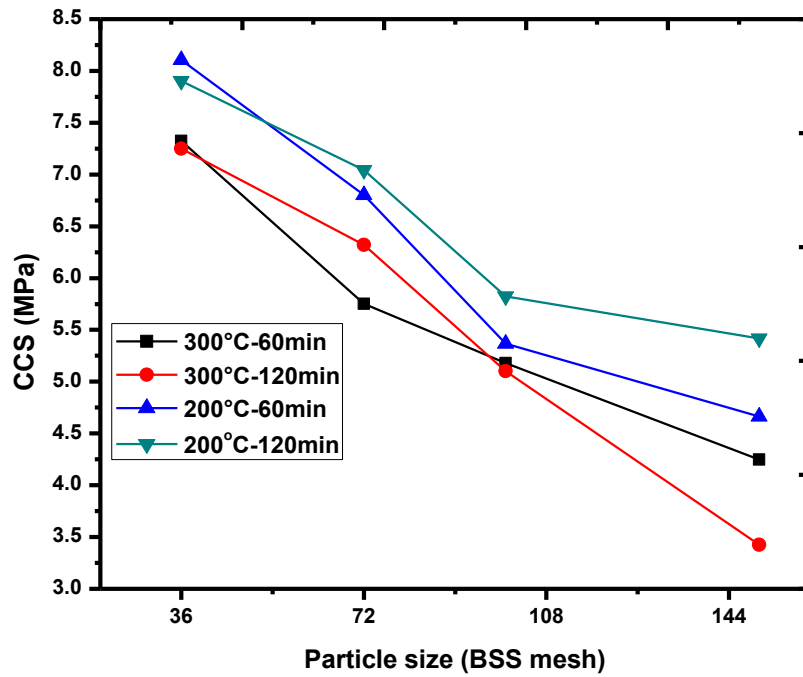


Figure 4.35: The effect of particle size variations on CCS of HFB (95:5HR) under different curing conditions.

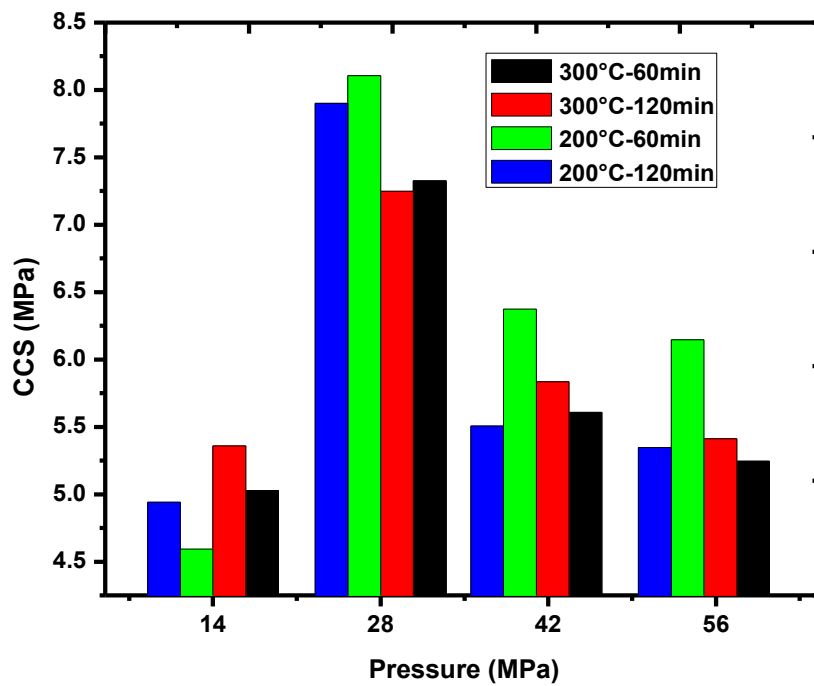


Figure 4.36: Influence of pressure variations on CCS of HFB (95:5HR) under different curing conditions.

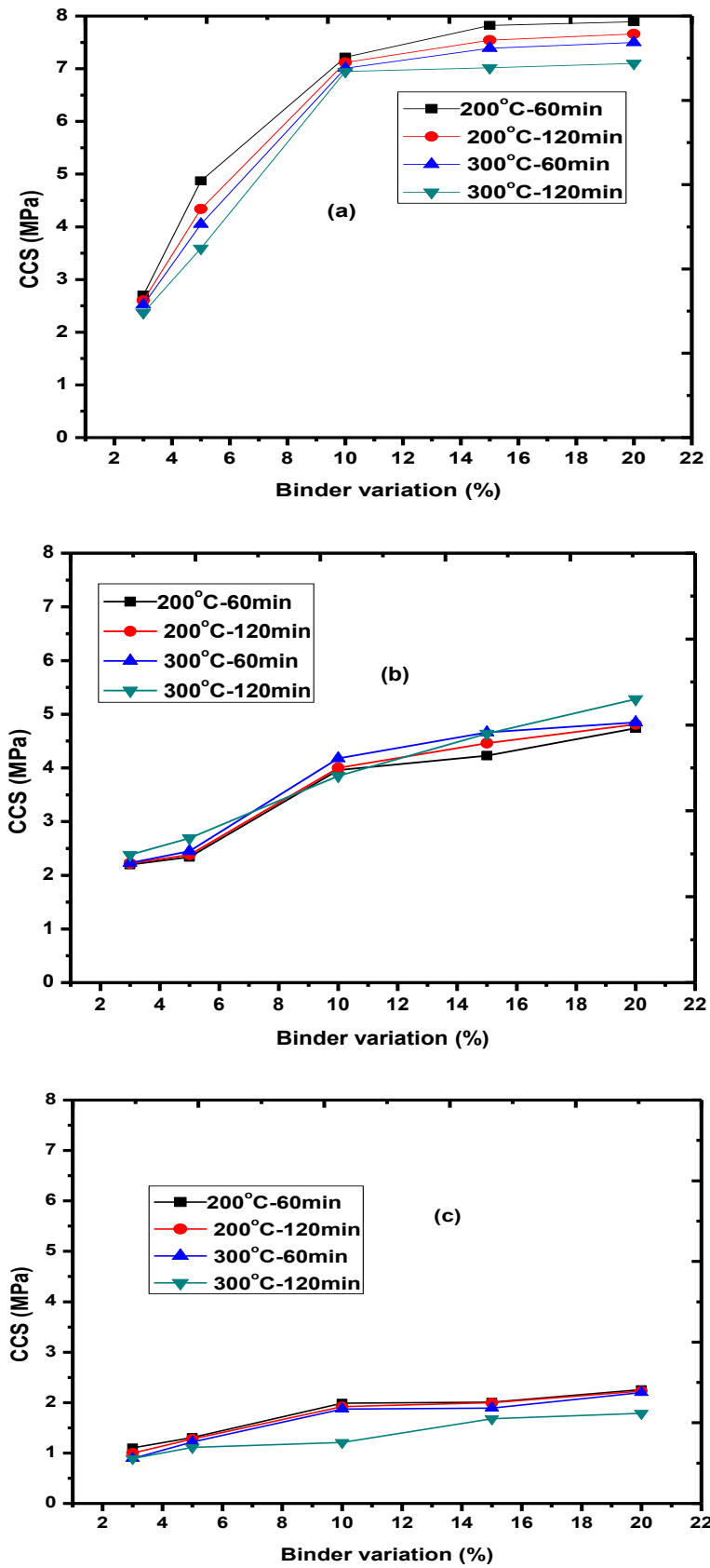


Figure 4.37: Influence of variation in binder content on the CCS of HFB (95:5HR) at different curing conditions (a) Molasses (b) Pitch (c) Starch

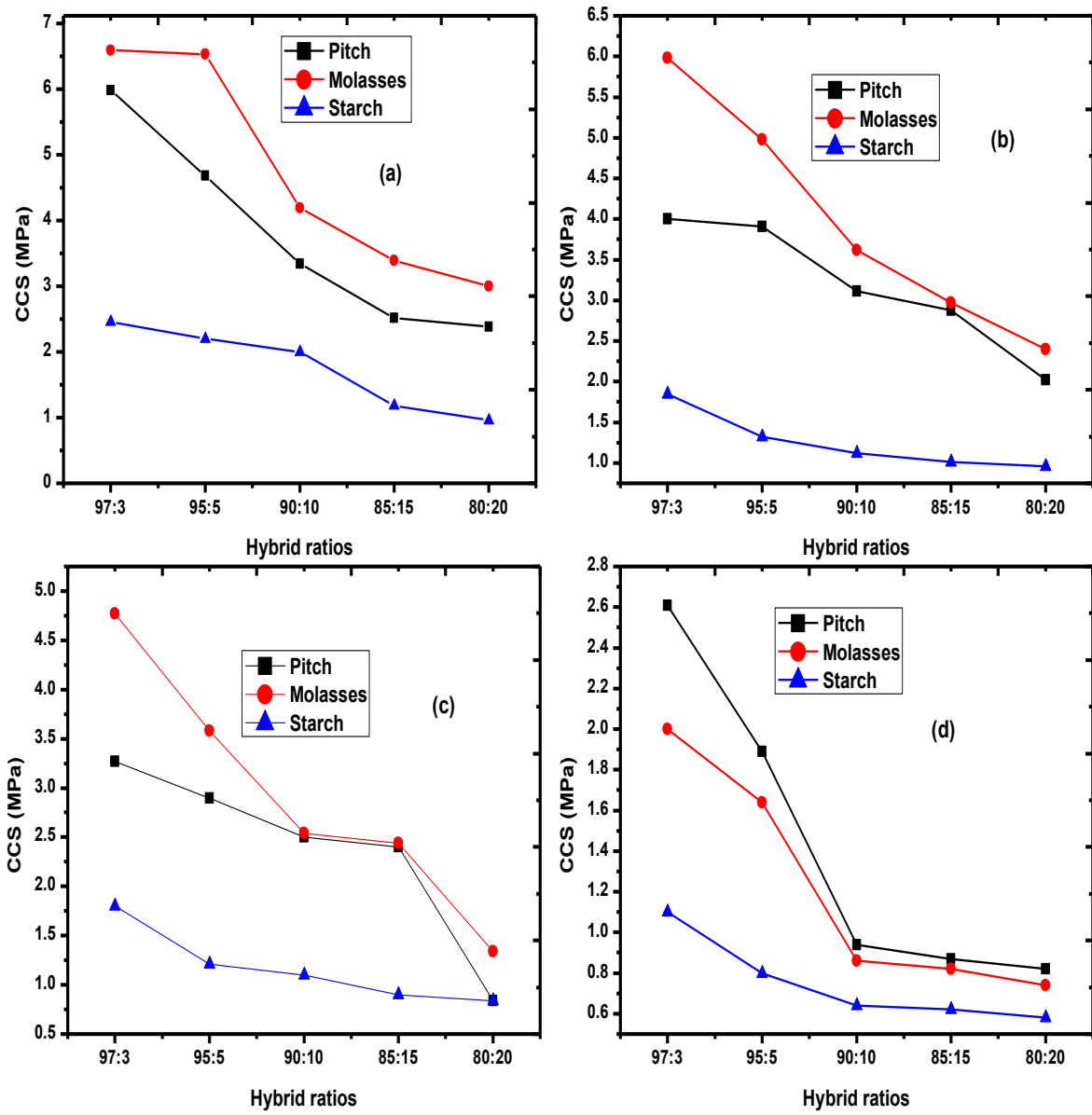


Figure 4.38: The effect of hybrid ratios on CCS of the HFB (95:5 HR) using separate binders (10%) at different curing conditions (a) 200°C-60 min (b) 200°C-120 min (c) 300°C-60 min (d) 300°C-120 min

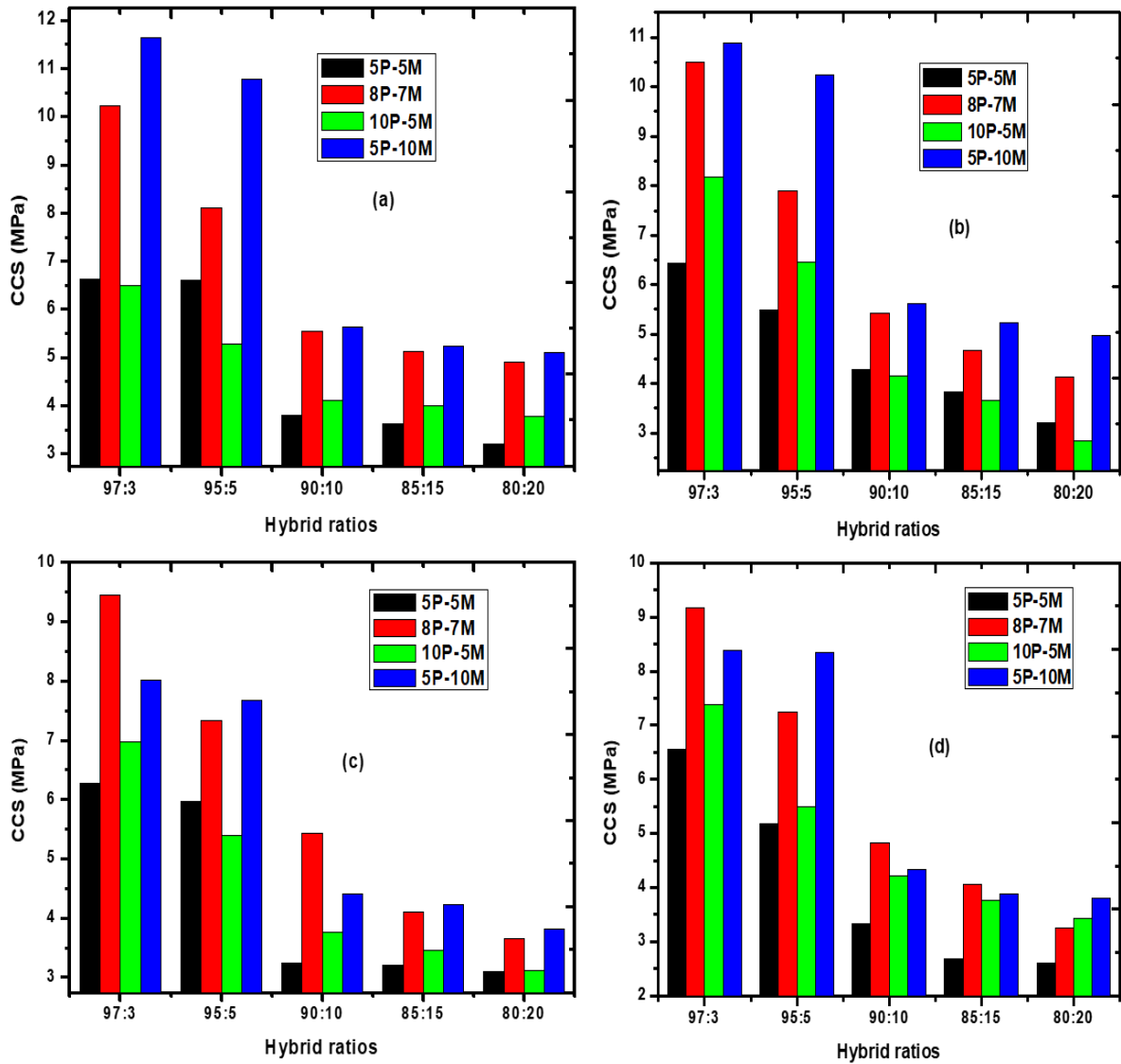


Figure 4.39: Influence of hybrid ratios on CCS of HFB using blended binder at different curing conditions (a) 200°C-60 min (b) 200°C-120 min (c) 300°C-60 min (d) 300°C-120 min.

4.5.1.5 Water resistance

The water resistance index (WRI) of the hybrid fuel briquettes based on different parametric variations are presented in Figures 4.40 - 4.44. WRI indicates the resistance of briquettes to water especially during transportation in an open wagon or trucks and on outdoor stockpiling (Richard, 1990). It has been reported that briquettes with a reasonable $WRI > 95\%$ has good water resistance (Richard, 1990; Thoms *et al.*, 1999).

Figures 4.40 and 4.41 represent the influence of particle size and pressure variations on the WRI of the HFB (95:5HR) using blended binder ratios (8%pitch-7%molasses) under different curing conditions. The briquettes produced from all applied pressure and particle sizes have WRI above 97%. HFB produced with finer sizes gave lower strength (CCS and IRI) and the reason was attributed to possible crack formation and more pores within it. These pores and cracks may permits more intake when exposed to water which may responsible for lower WRI compare with HFB produced from -36BS mesh.

Pitch-bonded briquettes failed to meet the required 95% WRI at 3 - 5% but surpassed it at 10% and above as shown in Figure 4.42. The WRI of molasses-bonded briquettes were below 95% except when its content was above 15% under every curing conditions as shown in Figure 4.42. The HFB produced with starch at all percentage content failed to meet 95% WRI at every curing conditions as shown in Figure 4.42. Figure 4.43 shows the influence of hybrid ratios on WRI of the HFB using separate binders. Figure 4.43 also shows that as the proportion of torrefied biomass increased in the HFB, the WRI decreased. It can also be observed that only pitch-bonded briquettes have WRI well above 95% at the hybrid ratios of 97:3 and 95:5. This may be due to the nature of molasses and starch which are hydrophilic materials coupled with the degree of crack formed that could allow capillary action when the HFB were soaked in water (Benk & Coban, 2011b).

Briquettes produced with the blended binders under every curing condition have higher WRI than the required 95% as shown in Figure 4.44. It can also be observed that increase in torrefied biomass content lowered the WRI but not below the desirable limit (95%). This is probably due to the firm interaction between the blend of binders and torrefied biomass as well as coal particle, thereby producing closely packed HFB. Thus, the blend of pitch and molasses is recommended to be used as binder for the production of HFB in order to obtain higher water resistance property.

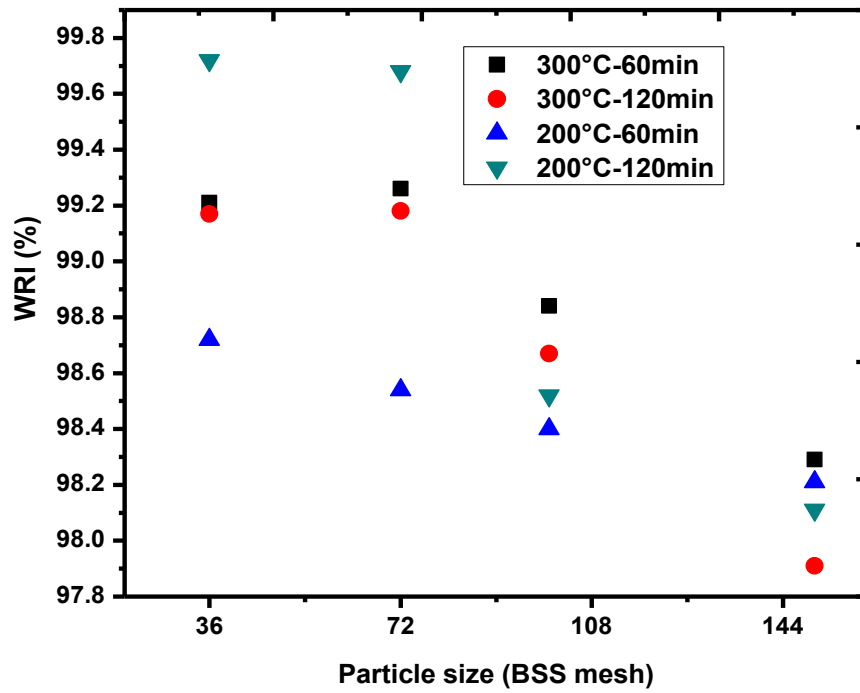


Figure 4.40: Effect of particle size variations on WRI of HFB (95:5HR) under different curing conditions.

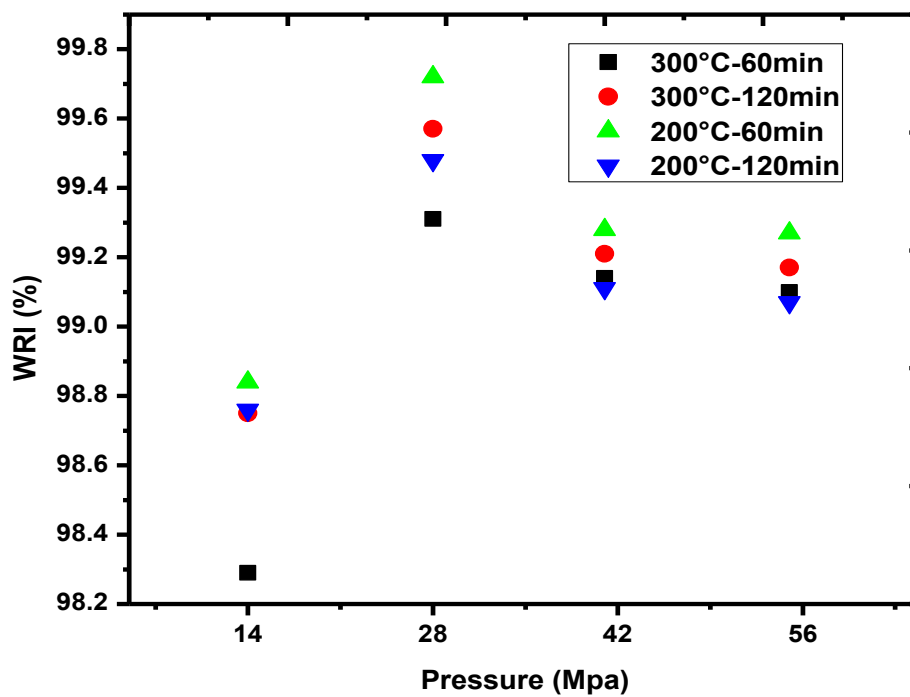


Figure 4.41: Influence of pressure variations on water resistance index (WRI) of HFB (95:5HR) under different curing conditions.

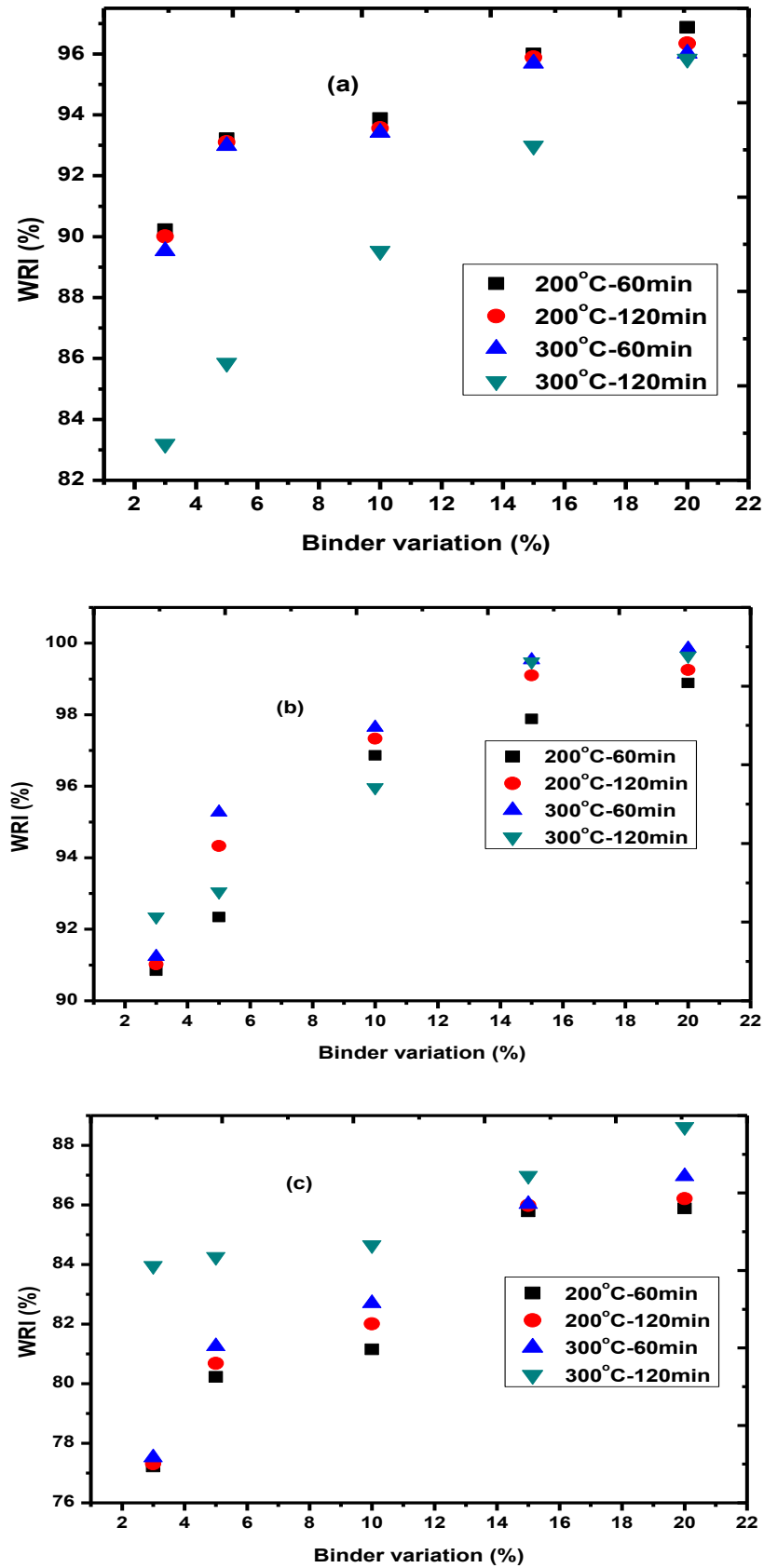


Figure 4.42: Impact of variation in binder content on the WRI of HFB (95:5HR) at different curing conditions (a) Molasses (b) Pitch (c) Starch

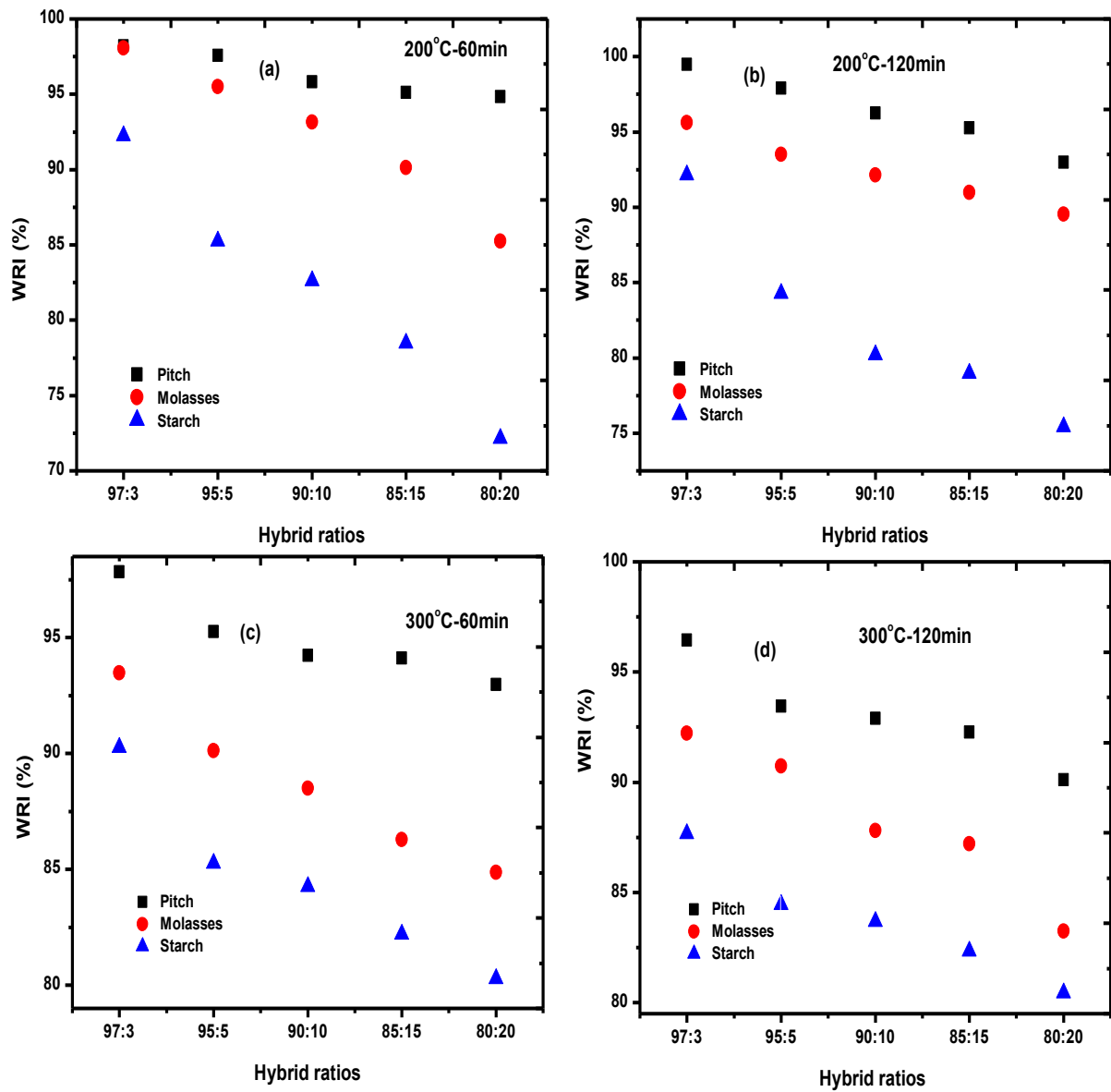


Figure 4.43: Influence of hybrid ratios on WRI of the HFB using separate binder (10%) at different curing conditions (a) 200°C-60 min (b) 200°C-120 min (c) 300°C-60 min (d) 300°C-120 min.

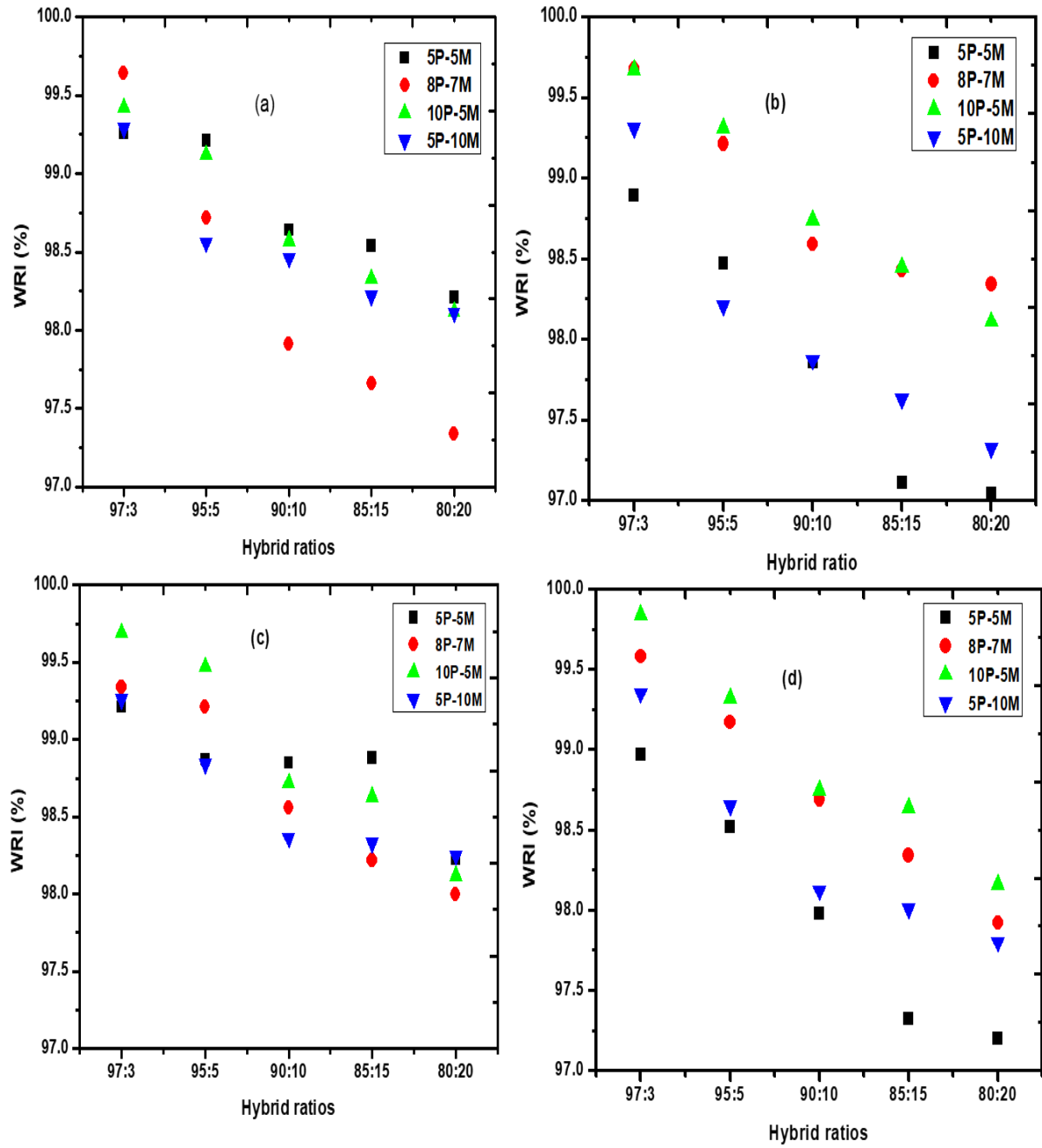


Figure 4.44: Influence of hybrid ratios on WRI of HFB using blended binder at different curing condition (a) 200°C-60 min (b) 200°C-120 min (c) 300°C-60 min (d) 300°C-120 min.

4.5.1.6 Tumbling strength index and reactivity index

The tumbling strength which is measured via the TSI_{+3mm} is also referred to as attrition strength. The tumbling strength index of selected hybrid fuel briquettes (97:3HR) produced from different blended binder ratios under various curing conditions are presented in Figure 4.45. The tumbling strength index of all the hybrid fuel briquettes were higher than the 95% recommended for briquettes to be used in domestic and industrial applications reported Richard (1990) and Thoms *et al.* (1999). However, 8% pitch-7% molasses and 5% pitch-10% molasses gave the highest TSI_{+3mm} at every curing conditions. The TSI_{+3mm} of HFB produced with 8% pitch-7% molasses and 5% pitch-10% molasses that are higher than other blend ratios may be as a result of the strong bond formed within the briquette due to more molasses content. It further revealed that the more aromatic bond present in molasses which affected other mechanical properties (IRI, drop to fracture and CCS) also contributed to the attrition strength. This implied that the hybrid fuel briquettes will generate less fines under attrition or tumbling force during transportation and utilization. The tumbling strength index obtained for the hybrid fuel briquettes in the present study are higher than 55.5% obtained for molasses-bonded briquettes in a previous study (Taulbee *et al.*, 2009).

The TSI_{+3mm} of HFB (97:3HR) produced from different blended binder ratios after being subjected to treatment at 1200°C are compared with cured (room temperature) samples and presented in Figure 4.46. The TSI_{+3mm} of HFB produced from the lean grade non-coking coal was carried out to mimic the coke strength after reduction (CSR) of coke. The CSR of a good coke must be higher than 65% resulting from low reactivity index (coke reactivity index) which must be between 20 - 25% (Holuszko *et al.*, 2017; Nieto-Delgado *et al.*, 2014). In the normal coke strength after reduction (CSR) test meant for coke, the CSR projects the strength of the coke under high temperature and similarly the TSI_{+3mm} used in the present study projects that the HFB has sufficient strength at high temperature. It was observed that

the TSI_{+3mm} of the HFB drastically reduced from the range of 95.5 - 98.3% for the cured to 62 - 77% for the 1200°C treated samples. This is traceable to the high reactivity (observed from reactivity index: RI) of the HFB which is higher than 54% as shown in Figure 4.47. The high reactivity meant that there was higher loss of volatiles and some carbon content from the HFB (Machado *et al.*, 2010). This was more pronounced in the HFB with more torrefied biomass content (Figure 4.47). The high temperature TSI_{+3mm} may not be required if the HFB were to be used in thermal operations. However, in a rotary kiln where fuel usually undergoes regular turning, high tumbling index became critical. Thus, this properties becomes very important for fuel that will be used as feedstock in production of DRI and other related furnaces. It is therefore recommended that fuel to be used for metallurgical operations should have tumbling index above 95%.

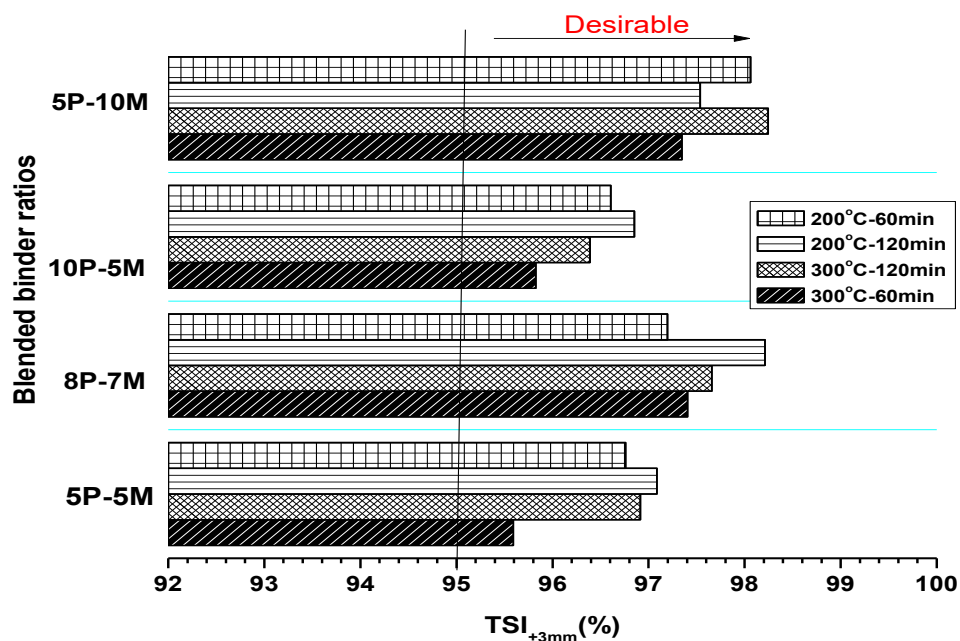


Figure 4.45: Tumbling strength index of hybrid fuel briquettes (97:3HR) produced with blended binder at different curing conditions showing the desirable TSI_{+3mm} line.

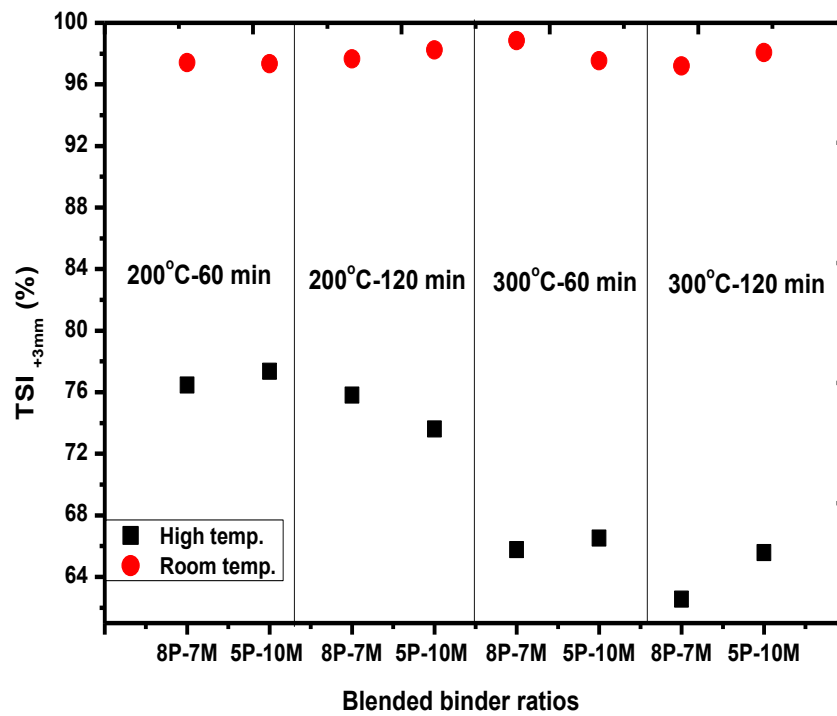


Figure 4.46: Effect of blended binder ratios on TSI_{+3mm} at different curing conditions under different tumbling test conditions

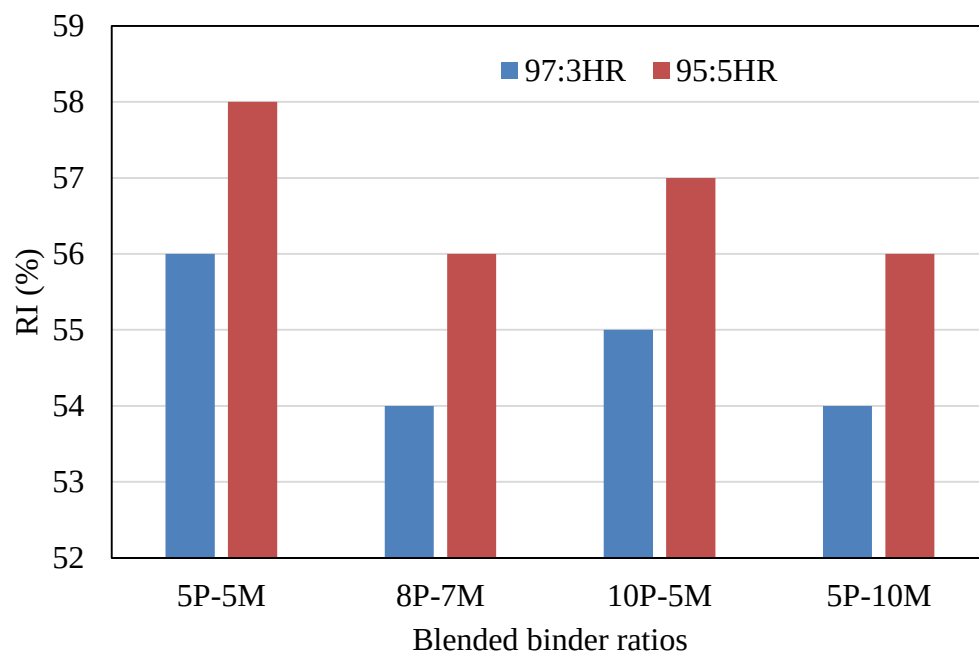


Figure 4.47: Reactivity index (RI) of selected hybrid fuel briquette samples cured at 200°C-60 min

4.5.1.7 Comparison between the properties of coal-Teak blend and coal-Melina blend HFB

The physical and mechanical properties of hybrid fuel briquettes produced from coal and torrefied Melina wood blend (coal-Mw blend) at the optimum hybrid ratios (97:3 and 95:5) using 8%pitch - 7%molasses and 5%pitch - 10%molasses blended binder ratios are compared with that of coal and torrefied Teak wood blend (coal-Tw blend) as shown in Figures 4.48 - 4.52. The densities of HFB of coal-Tw were in the range of 1.28 - 1.40 g/cm³ compared to 1.27 - 1.38 g/cm³ for coal-Mw as shown in Figure 4.48. The density of HFB of coal - Tw blend were a little higher than HFB of coal-Mw blend which may be due to more VM in the torrefied Tw. The densities of the HFB produced from both coal-Tw and coal-Mw blends decreased with increase in severity of curing conditions. This was due to higher loss of moisture and light volatile matters within the briquettes. The densities were generally within the range of 1.19-1.40 g/cm³ reported for lump coal to be used in thermal application by Tchapda & Pisupati (2014).

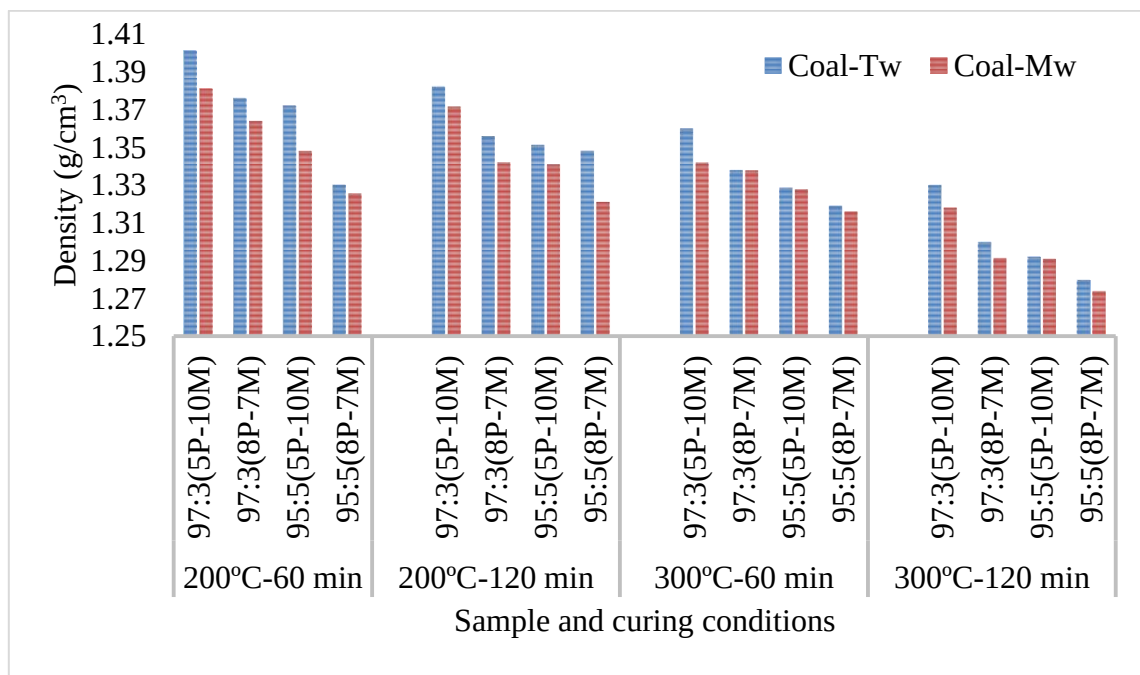


Figure 4.48: Comparison of the density of HFB produced from coal-Tw and coal-Mw blends under different curing conditions using blended binders.

Figure 4.49 shows the comparison between the drop to fracture numbers of HFB produced from coal-Tw and coal-Mw blends using different curing conditions. The drop to fracture numbers of 97:3HR using 8%pitch - 7%molasses blended binder ratios were higher than all other formulations at every curing conditions for both coal-Tw and coal-Mw blends. The drop to fracture number of the HFB of coal-Mw blends were a little higher than that of coal-Tw at every blended ratios and curing conditions. This may be due to higher lignin content of Melina wood as shown in Table 4.9. Lignin as a binder improves the bonding strength within the coal-Melina blend compared with coal-Teak blend. The drop to fracture generally ranges between 118 and 197 times/2m for the HFB examined. This is much higher than 77 time/2m that was obtained for briquettes produced from coke breeze using xylene activated coal-tar pitch binder by Zhong *et al.* (2016) and 57 time/2m of the briquettes produced from high volatile coal by Zhong *et al.* (2017).

The impact resistance index of the HFB produced from coal-Tw and coal-Mw blends presented in Figure 4.50 shows that the coal-Mw blend has the highest impact resistance compared with coal-Tw blend. This may be due to the influence of higher lignin content in the biochar of Melina along with other organic binders compared with lower lignin content in the biochar of Teak as shown in Table 4.9. The range of the IRI of the HFB was 2950 to 6500 and this is far superior to IRI of 1000 that were obtained for coal briquettes produced in previous studies using molasses and other organic binders (Blesa *et al.*, 2003; Mayoral *et al.*, 2001) and much more higher than the proposed 50 IRI value for briquettes that can be used for domestic and industrial purposes (Thoms *et al.*, 1999).

Figure 4.51 compares the CCS of HFB produced from coal-Tw and coal-Mw blends using different curing conditions. The CCS of HFB produced from coal-Mw blends were higher than those of coal-Tw blends. This similarly shows the influence of higher lignin in biochar of Melina wood compared with that of Teak wood (Table 4.9). The 5%pitch-10%

molasses blended binder ratio gave 11.46 MPa which was the highest CCS when HFB were cured at 200°C. HFB produced from 8% pitch-7% molasses blended binder ratio has better CCS when cured at 300°C. The CCS result is reminiscence of the influence of molasses and pitch in HFB when used as individual binder. At 200°C, the water and moisture of molasses evaporated and could have left sufficient amount of oxygen bridges along with wood lignin and pitch to form strong bond within the coal particles. However, more molasses devolatilization at 300°C as against continuous coking of pitch could be responsible for the decrease in CCS of HFB produced from 5% pitch-10% molasses blended binder ratios (Zhong *et al.*, 2016).

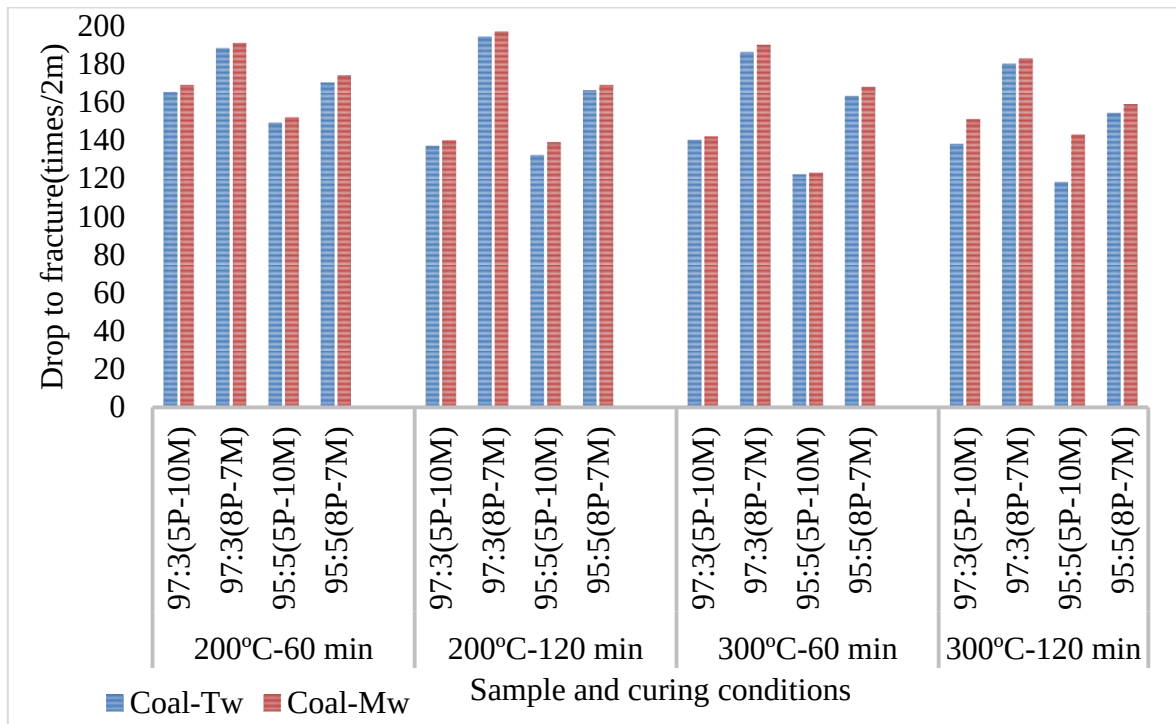


Figure 4.49: Comparison of the drop to fracture number of HFB produced from coal-Tw and coal-Mw blends under different curing conditions using blended binders.

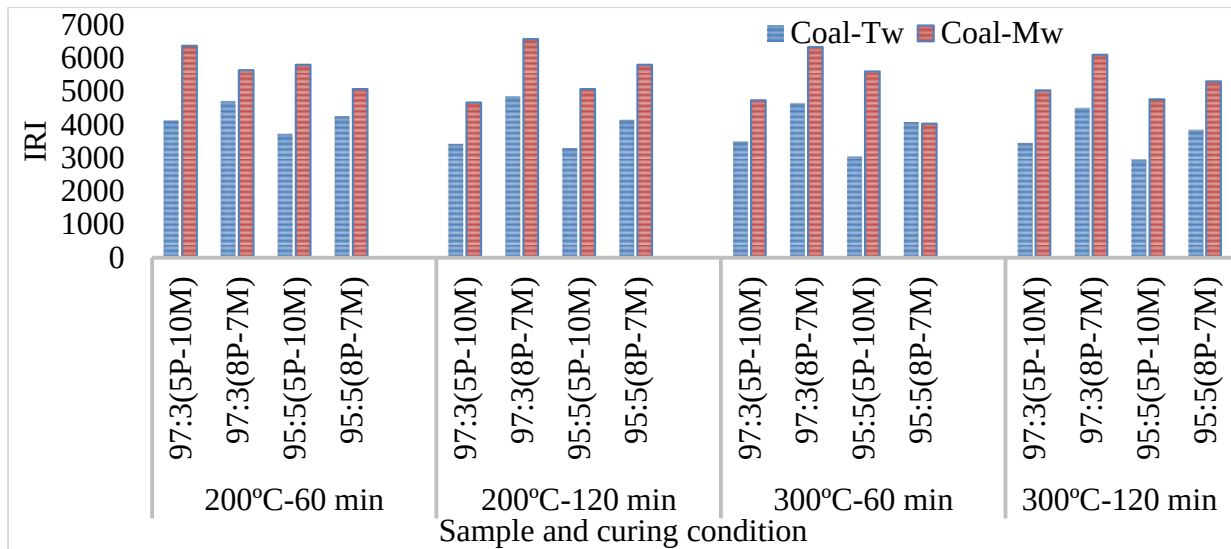


Figure 4.50: Comparison of the IRI of HFB produced from coal-Tw and coal-Mw blends under different curing conditions using blended binders

Water resistance index (WRI) of the HFB produced from coal-Tw and coal-Mw blends are presented in Figure 4.52. HFB produced from coal-Mw blends have higher WRI than coal-Tw blends at every curing condition. The WRI ranges from 97.8 to 99.67% and are generally higher than the 95% recommended for briquettes to be used domestically and industrially (Mayoral *et al.*, 2001; Zarringhalam-Moghaddam *et al.*, 2011).

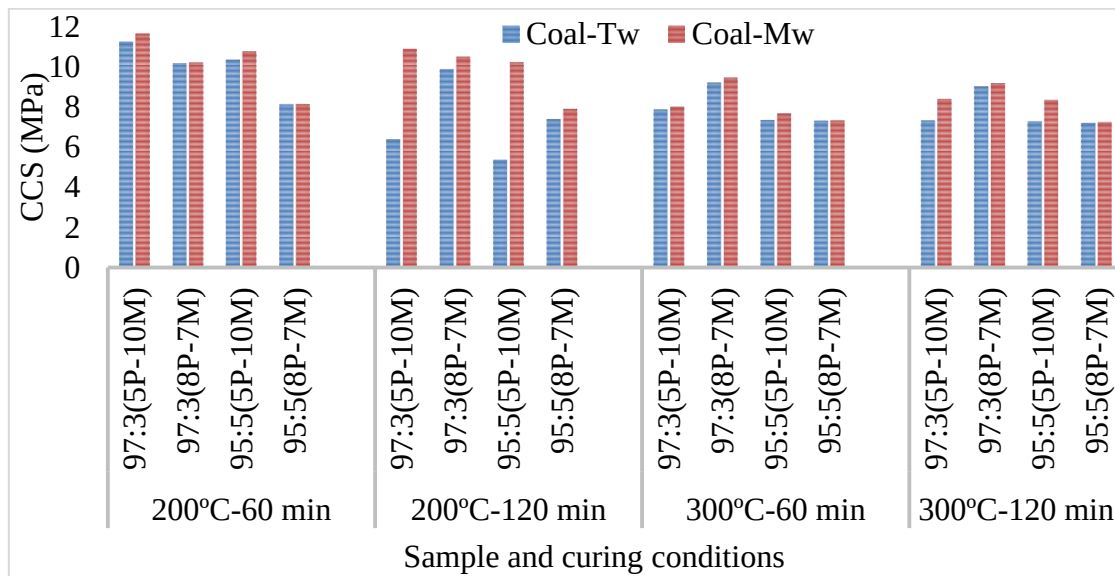


Figure 4.51: Comparison of the CCS of HFB produced from coal-Tw and coal-Mw blends under different curing conditions using blended binders.

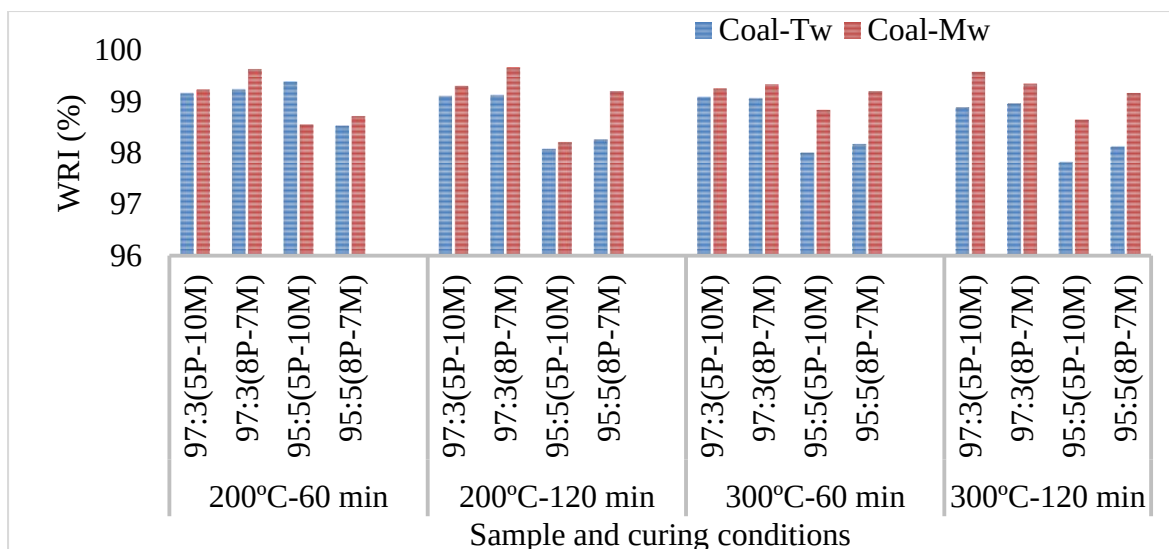


Figure 4.52: Comparison of the WRI of HFB produced from coal-Tw and coal-Mw blends under different curing conditions using blended binders.

4.5.2 Combustion properties

4.5.2.1 Proximate contents

The proximate contents of the hybrid fuel briquettes produced from coal-Melina blends are presented in Figures 4.53 to 4.56 at different hybridization ratios and curing conditions. Figure 4.53 shows the proximate content of hybrid fuel briquettes (90:10HR) produced using pitch and molasses separately. The difference in the effect of pitch and molasses as binders on the proximate contents was minimal as shown in Figure 4.53. Fixed carbon (FC) in the range of 64.34 - 64.64%, ash contents (AC) in the range of 18.66 to 18.72%, VM in the range of 13.89 - 14.20% and moisture content (MC) in the range of 2.75 - 2.84% were obtained for different hybrid ratios of molasses-bonded briquettes. Similarly, FC in the range of 65.01 - 65.13%, AC in the range of 18.16 - 18.21%, VM in the range of 14.21 - 14.30 and MC in the range of 2.45 - 2.53% were obtained for different hybrid ratios of pitch-bonded briquettes. The results of the proximate contents of the HFB show that there was a little contribution to the AC and VM contents of the lean grade coal by the torrefied biomass and organic binder. The AC content of the woody biomass and organic binders as

shown in Tables 4.1 and 4.2 are very low and thus will contribute little to that of the HFB. Similarly, the woody biomass was initially devolatilized which implied reduction in its VM content. The devolatilization process continues under curing of the HFB and therefore, a little addition to the initial VM of the lean grade coal.

The proximate content of HFB produced with the blend of pitch and molasses at different ratios of 97:3, 95:5 and 90:10 are presented in Figures 4.54 to 4.56. The ash content was around 18.01 - 18.11% for all the HFB and this was a little higher than 17.84% in the raw coal. The MC of the HFB at 200°C were in the range of 2.10 - 3.0% while those cured at 300°C were lower in the range of 1.54 to 1.70%. This could be as a result of increase severity of curing from 200 to 300°C that impacted more hydrophobic properties on the HFB (Bergman *et al.*, 2005). The VM of HFB cured at 200°C were in the range of 15 - 17% while those cured at 300°C were in the range of 14 - 15%. An increase in the proportion of torrefied biomass and organic binders gave a little increment in VM content of the HFB. This is due to the higher percentage of VM present in torrefied biomass and organic binder than the lean grade coal. The increase in FC of the HFB as the severity of curing increased from 200 to 300°C at both residence time was minimal. The FC was in the range of 64 - 68% which is similar to the lean grade coal used for the production of the HFB.

The proximate contents of the HFB (Figures 4.53 - 4.56) generally fall in the range of coal lump recommended for thermal applications (Speight, 2012; Tumuluru *et al.*, 2011a). Savolainen (2003) reported that Russian coal (MC = 9 - 11%, VM = 26 - 29% and ash = 9 - 11%) and Polish coal (MC = 9 - 13%, VM = 31 - 34% and ash = 12 - 15%) with Pine sawdust were suitable for co-firing in thermal plant. Gurbuz-Beker *et al.* (1998) also reported that Siberian sub-bituminous coal briquettes with MC of 2.5%, VM of 19% and FC of 72.91% was suitable as fuel in thermal application even though the briquettes were not water resistant (dispersed after 20 min of immersion in water). Comparatively, the HFB in the present study

have good proximate contents that does not deteriorate due to briquetting process. Thus, the HFB can be used as feedstock in thermal application domestically and industrially.

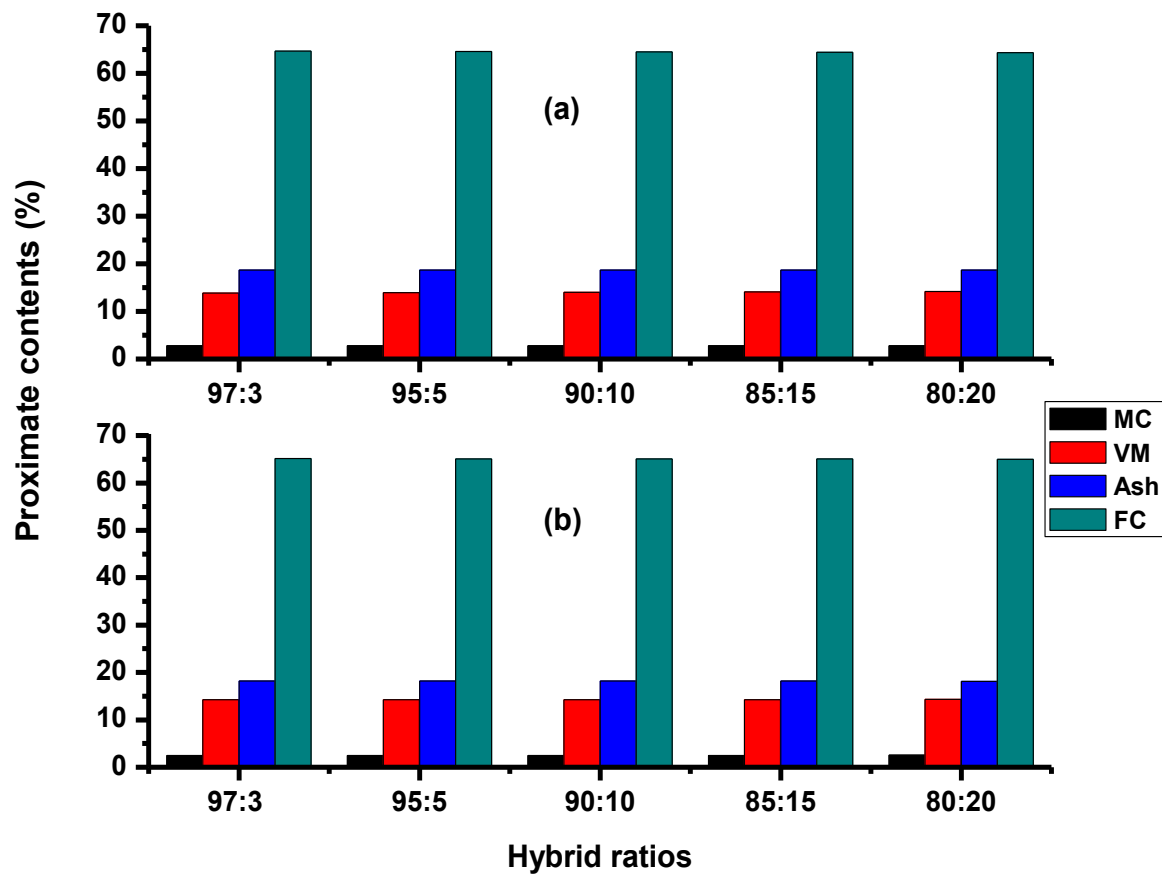


Figure 4.53: Proximate contents of HFB produced using separate binder (10%) (a) Molasses
(b) Pitch

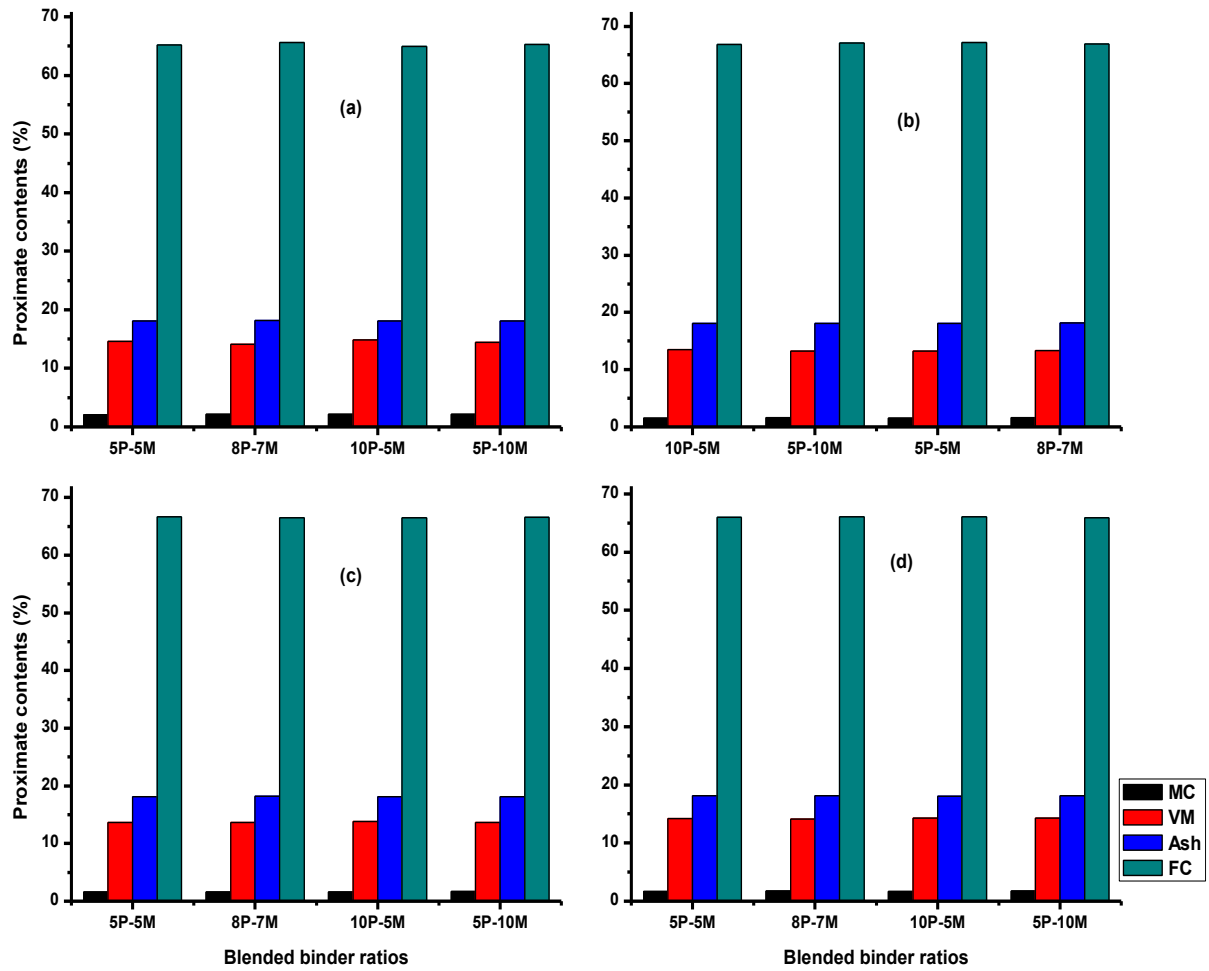


Figure 4.54: Influence of blended binder ratios on the proximate contents of HRB (97:3HR) at different curing conditions (a) 200°C-60 min (b) 300°C-60 min (c) 300°C-120 min (d) 200°C-120 min.

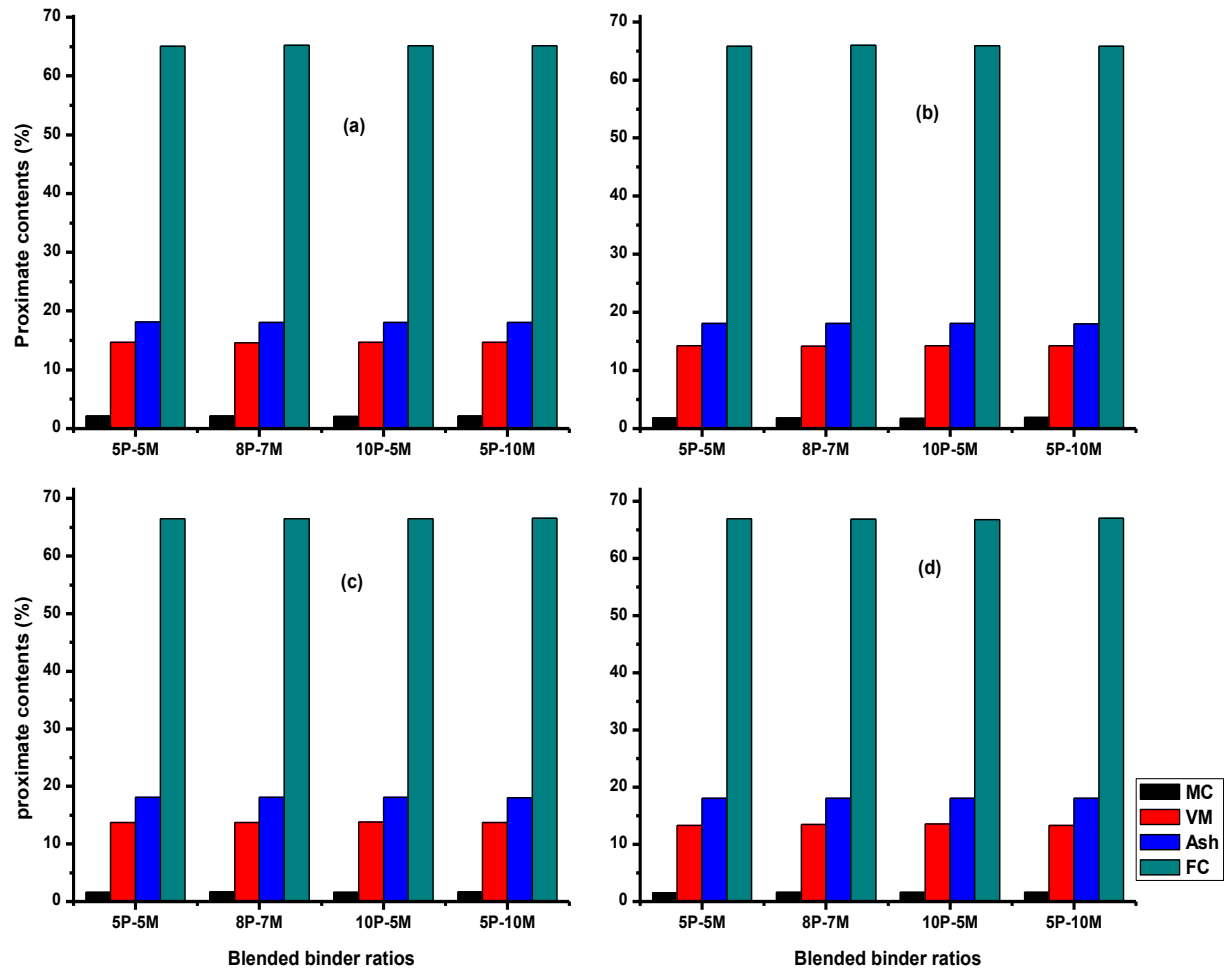


Figure 4.55: Influence of blended binder ratios on the proximate contents of HRB (95:5HR) at different curing conditions (a) 200°C-60 min (b) 300°C-60 min (c) 300°C-120 min (d)

200°C-120 min.

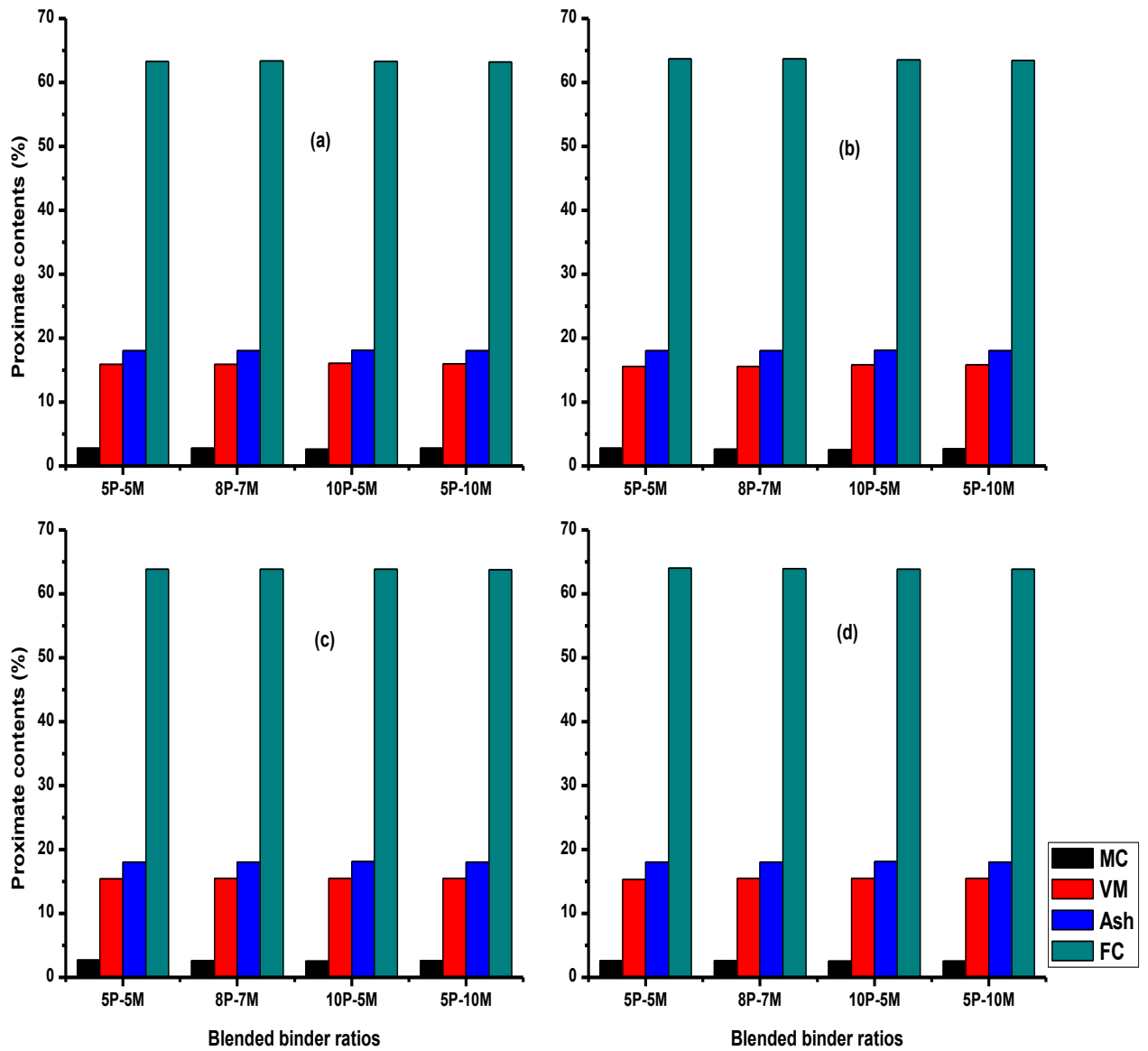


Figure 4.56: Influence of blended binder ratios on the proximate contents of HRB (90:10HR) at different curing conditions (a) 200°C-60 min (b) 300°C-60 min (c) 300°C-120 min (d) 200°C-120 min.

4.5.2.2 Ultimate contents

The elemental compositions (ultimate contents) of selected HFB samples are presented in Tables 4.10 - 4.13. The elemental composition of HFB produced from different hybridization ratios using individual binder (pitch and molasses) are reported in Table 4.10. The carbon contents range from 74 to 76% which is just a little higher than 73% for the lean grade coal. The hydrogen content (H) and oxygen (O) were <2.6 and <22%, respectively. The sulphur (S) and nitrogen (N) contents were <1% for all the HFB and this is suitable for thermal generation without any need for further beneficiation to reduce environmental pollution that may arise from its combustion (Speight, 2012; Yu, Tahmasebi *et al.*, 2013). There was a little variation in the elemental compositions of the HFB compared with the lean grade coal and this could be as a result of the response of individual raw materials to curing process. Lean grade coal was used for the production of the HFB and it has the tendencies along with other organic components to liberate low molecular weight during curing (Speight, 2012; 2013). Therefore, the elemental compositions are as a result of contributions from each constituents of the HFB after curing. The trend of elemental compositions obtained for HFB produced from individual binders of pitch and molasses are similar to the HFB produced from their blends as shown in Tables 4.11 - 4.13. A minor increment (1 - 2%) in the carbon content carbon was observed in the HFB as the severity of curing increased for all blended binder ratios which is the direct implication of reduction in oxygen (O) content resulting from loss of bounded and unbounded moisture.

Table 4.10: Ultimate analyses of HFB produced from different hybrid ratios using molasses and pitch separately (cured at 300°C-60min)

Curing conditions	Hybrid ratios	C (%)	H (%)	N (%)	S (%)	O (%)
300°C-60 min (Molasses)	97:3	74.32	2.50	0.98	0.77	21.43
	95:5	74.45	2.51	0.96	0.76	21.32
	90:10	74.45	2.53	0.95	0.74	21.33
	85:15	74.54	2.56	0.93	0.74	21.23
	80:20	74.47	2.58	0.90	0.72	21.33
300°C-60 min (Pitch)	97:3	74.65	2.48	0.93	0.73	21.21
	95:5	74.56	2.50	0.92	0.73	21.29
	90:10	74.58	2.52	0.92	0.72	21.26
	85:15	75.54	2.53	0.92	0.72	20.29
	80:20	75.54	2.57	0.91	0.72	20.26

Table 4.11: Ultimate contents of HFB (97:3HR) using blended binder at different curing conditions

Curing conditions	Blended binder ratios	C (%)	H (%)	N (%)	S (%)	O (%)
200°C-60 min	5P-5M	74.23	2.2	0.96	0.72	21.89
	8P-7M	74.54	2.21	0.94	0.72	21.59
	10P-5M	74.55	2.20	0.95	0.73	21.57
	5P-10M	74.54	2.23	0.94	0.74	21.55
200°C-120 min	5P-5M	74.33	2.19	0.95	0.72	21.81
	8P-7M	74.56	2.20	0.94	0.73	21.57
	10P-5M	74.46	2.20	0.95	0.73	21.66
	5P-10M	74.58	2.22	0.93	0.74	21.53
300°C-60 min	5P-5M	74.67	2.16	0.93	0.72	21.52
	8P-7M	74.68	2.16	0.93	0.72	21.51
	10P-5M	74.66	2.15	0.94	0.73	21.52
	5P-10M	74.70	2.17	0.92	0.73	21.48
300°C-120 min	5P-5M	75.43	2.15	0.93	0.72	20.77
	8P-7M	75.25	2.15	0.89	0.73	20.98
	10P-5M	75.23	2.14	0.91	0.73	20.99
	5P-10M	75.34	2.16	0.92	0.73	20.85

Table 4.12: Ultimate contents of HFB (95:5HR) using blended binder at different curing conditions

Curing conditions	Blended binder ratios	C (%)	H (%)	N (%)	S (%)	O (%)
200°C-60 min	5P-5M	74.21	2.34	0.92	0.71	21.82
	8P-7M	74.23	2.35	0.91	0.72	21.79
	10P-5M	74.24	2.34	0.91	0.72	21.79
	5P-10M	74.23	2.36	0.91	0.73	21.77
200°C-120min	5P-5M	74.33	2.32	0.92	0.71	21.72
	8P-7M	74.33	2.32	0.91	0.72	21.72
	10P-5M	74.36	2.33	0.90	0.72	21.69
	5P-10M	74.28	2.34	0.91	0.73	21.74
300°C-60 min	5P-5M	75.05	2.30	0.91	0.73	21.01
	8P-7M	75.02	2.31	0.90	0.72	21.05
	10P-5M	75.11	2.31	0.89	0.73	20.96
	5P-10M	75.00	2.32	0.90	0.73	20.95
300°C-120 min	5P-5M	75.44	2.28	0.90	0.72	20.66
	8P-7M	75.36	2.27	0.91	0.71	20.75
	10P-5M	75.21	2.27	0.91	0.72	20.89
	5P-10M	75.45	2.28	0.92	0.73	20.62

Table 4.13: Ultimate contents of HFB (90:10HR) using blended binder ratios at different curing conditions

Curing conditions	Blended binder ratios	C (%)	H (%)	N (%)	S (%)	O (%)
200°C-60 min	5P-5M	73.56	2.48	0.90	0.72	22.34
	8P-7M	73.53	2.48	0.91	0.73	22.35
	10P-5M	73.67	2.49	0.90	0.72	22.22
	5P-10M	73.23	2.51	0.91	0.73	22.62
200°C-120 min	5P-5M	73.45	2.48	0.91	0.71	22.45
	8P-7M	74.10	2.47	0.90	0.72	21.81
	10P-5M	73.28	2.47	0.89	0.70	22.66
	5P-10M	73.23	2.50	0.90	0.71	22.66
300°C-60 min	5P-5M	73.20	2.45	0.91	0.72	22.72
	8P-7M	73.21	2.44	0.90	0.71	22.74
	10P-5M	73.20	2.44	0.91	0.72	22.73
	5P-10M	73.22	2.46	0.91	0.72	22.69
300°C-120 min	5P-5M	73.23	2.43	0.90	0.72	22.72
	8P-7M	73.23	2.43	0.91	0.72	22.71
	10P-5M	73.20	2.45	0.91	0.72	22.72
	5P-10M	73.22	2.46	0.91	0.71	22.70

4.5.2.3 Higher heating value

An important factor that determines the quality of any solid fuel including coal is the higher heating value (HHV). It determines the potential of energy in coal and that of the HFB (Speight, 2012). The HHV of selected hybrid fuel briquettes based on different curing conditions and hybrid ratios are presented in Figures 4.57 to 4.60. The HHV of the hybrid fuel briquette showed a little improvement over that of the lean grade coal (23.13 MJ/kg) (Table 4.2). It can be observed that the HHV of molasses-blended briquettes are lower compared to pitch-bonded briquettes as shown in Figure 4.57. An increase in the proportion of torrefied biomass in the HFB gave a slight improvement in the HHV for individual binders (Figure 4.57). The HHV of the HFB produced from blend of pitch and molasses binder was in the range of 24 - 25 MJ/kg for all hybridization ratios and it is within the range for sub-bituminous coal (Speight, 1994). However, there was a little increment in the HHV as the proportion of torrefied biomass increased in the HFB and this could be as a result of continuous carbonization experienced by the biomass. As shown in Figures 4.58 to 4.60, an increase in the proportion of pitch in the blend of both binders gave higher HHV compared to an increased molasses content. This is probably due to the heating value of pitch as it continues to coke within the hybrid fuel briquette matrix.

HFB produced from 8% pitch-7% molasses and 10% pitch-5% molasses blended binder ratios gave higher HHV compared with 5% pitch-5% molasses and 5% pitch-10% molasses blended ratios. This could be as a result of the coking tendencies of pitch during curing compared with the devolatilization of molasses (Sharma *et al.*, 2002). The influence of curing conditions can further be observed from Figures 4.57 - 4.59. A higher curing severity (300°C) gave a higher HHV compared with those cured at 200°C for different residence time. This could be as a result of a minor loss of volatiles from the torrefied biomass and the

organic binders. The HHV of the selected HFB showed a 10% increment compared with the lean grade coal.

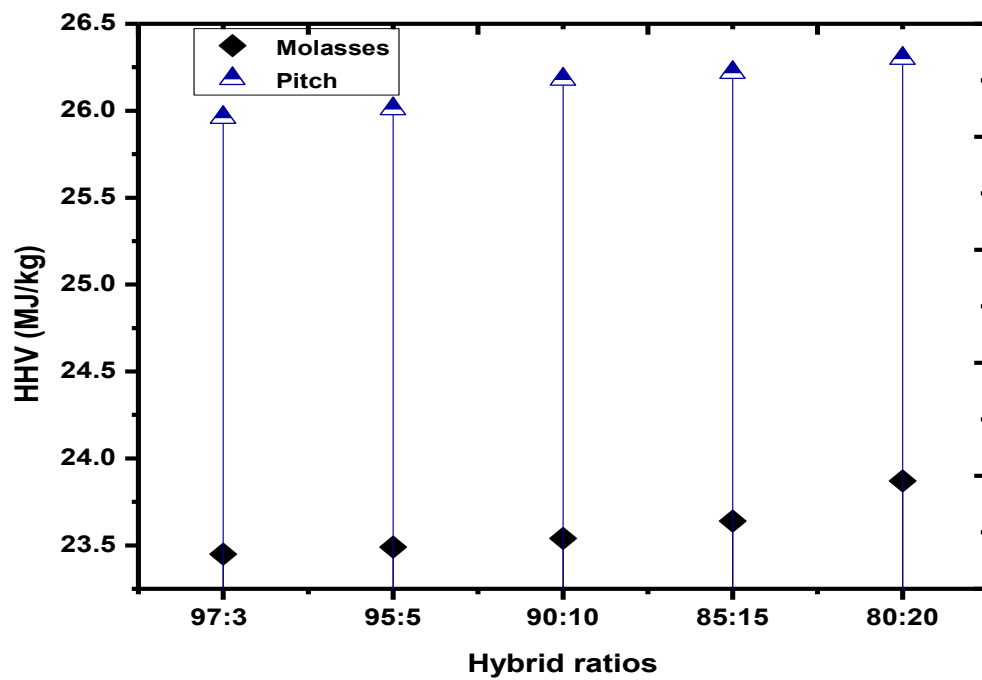


Figure 4.57: Influence of hybrid ratios on higher heating value of HFB (95:5HR) produced with pitch and molasses separately at 300°C-60 min.

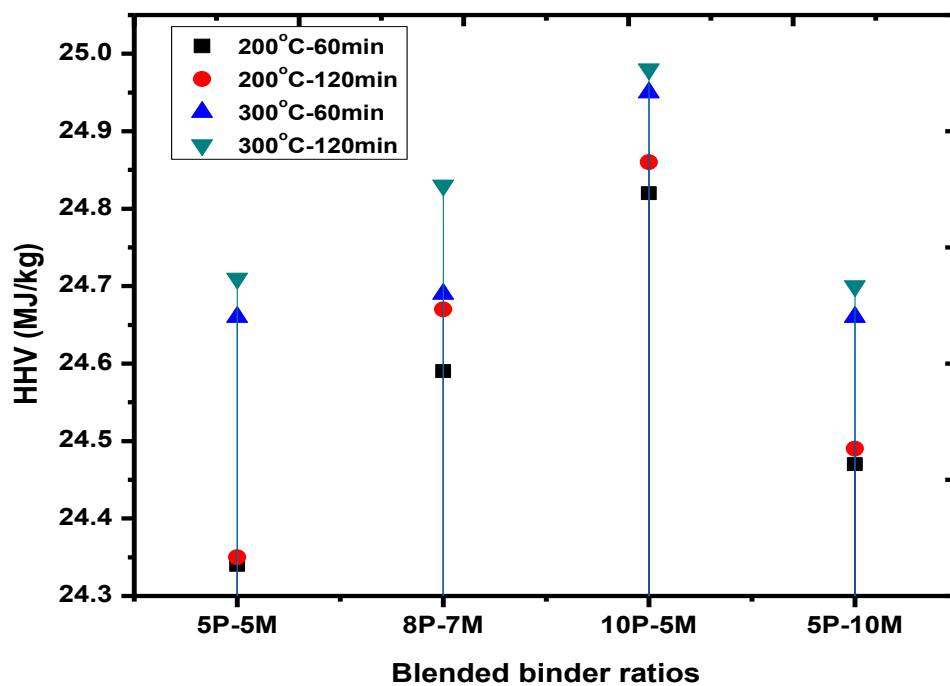


Figure 4.58: Influence of blended binder ratios on higher heating value (HHV) of the HFB (97:3HR) using different curing conditions.

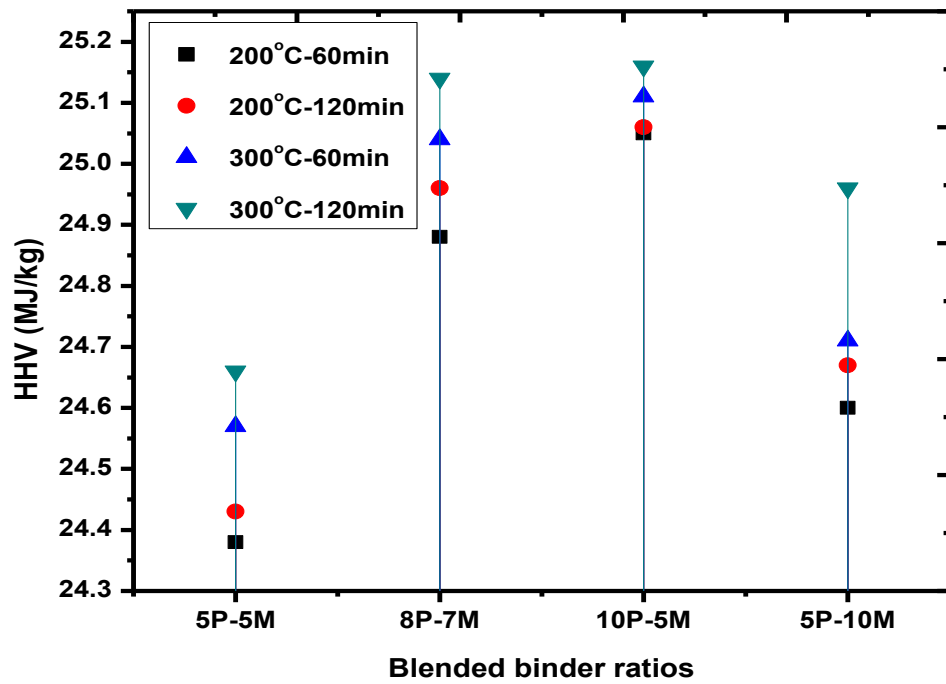


Figure 4.59: Influence of blended binder ratios on higher heating value (HHV) of the HFB (95:5HR) using different curing conditions.

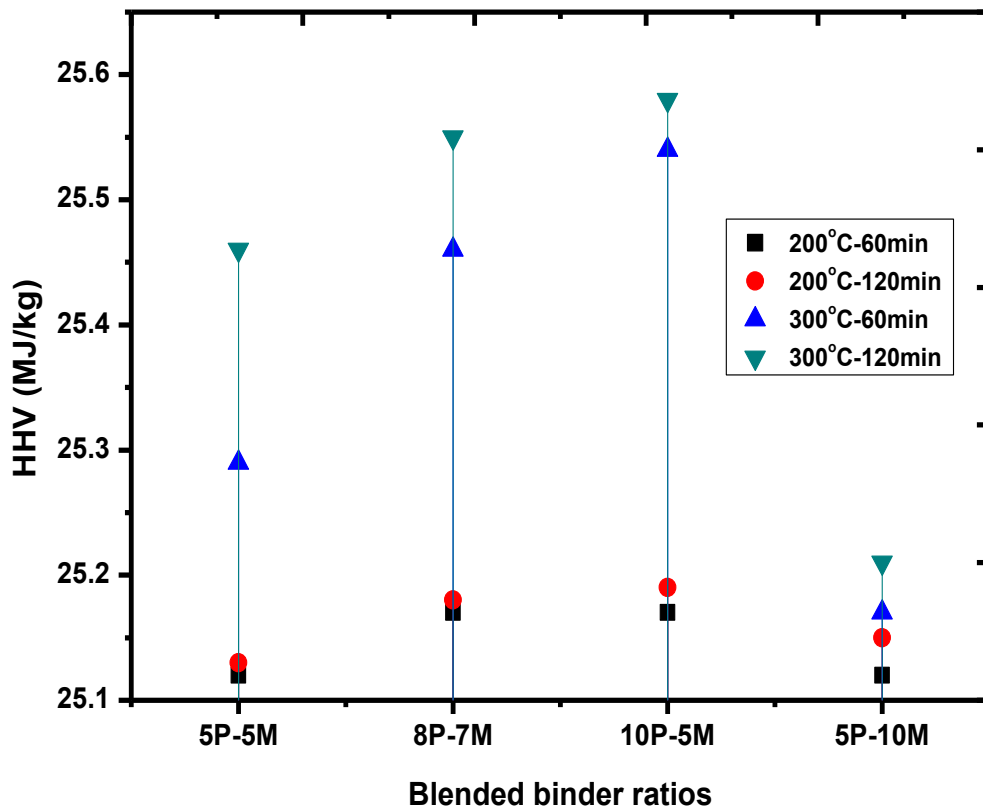


Figure 4.60: Influence of blended binder ratios on higher heating value (HHV) of the HFB (90:10HR) using different curing conditions.

4.5.2.4 Ash analyses

The major mineral phases present in the ashes of raw coal and HFB are shown in the diffractogram (XRD pattern) on Figures 4.61 - 4.65. The XRD patterns of the ashes of raw coal and HFB showed similar mineral compositions. It mainly indicates the presence of Quartz (Q), Mullite (M) and Hematite (H). Kaolinite (K) and Anatase (A), the lower temperature oxides of titanium were also observed through XRD. Some of the peaks in the patterns was identified via the JCPD file and previous studies (Mishra *et al.*, 2016a; Mishra *et al.*, 2016b). The XRD patterns at all the different hybridization ratios of the HFB were similar. The additions of torrefied biomass and different organic binders (different ratios) does not alter the mineral compositions of the ash in the hybrid fuel briquettes. This may be as a result of the low ash content of the torrefied biomass and the organic binders. Quartz (Q) was seen as the major mineral phase in all the XRD patterns (Figures 4.61 - 4.65).

Phase transformation does not evolve in the ash of the hybrid fuel briquette samples and this could be as a result of low temperature curing used in the briquetting process. An increase in the curing temperature of the hybrid fuel briquettes to $>400^{\circ}\text{C}$ could lead to mineral phase transformations where kaolinite (K) may be oxidized to form different oxides (Mishra *et al.*, 2016). Identification of some other minerals by XRD only in a multi-component system such as coal and the hybrid fuel briquettes is difficult to detect due to peak overlapping (Sharma *et al.*, 2014). However, the presence of other mineral phases inform of oxides were clearly detected and quantified using XRF as shown in Table 4.14. The composition of the major oxides found in the raw coal and HFB ashes are SiO_2 (57 - 58%), Al_2O_3 (19 - 21%), Fe_2O_3 (8 - 9%), K_2O , MgO and CaO (2 - 3%), Na_2O (0.2%) and TiO_2 (1 - 2%). The presence of ZnO and CuO were very small in ppm. The presence of these oxides in

the coal and HFB has been reported in previous studies on characterization of coal ash (Mishra *et al.*, 2016; Mishra *et al.*, 2016; Naya, 2013; Sharma *et al.*, 2014). The presence of these oxides in different ratios serves as indices for different coal ash behaviours such as slagging, fouling and abrasion.

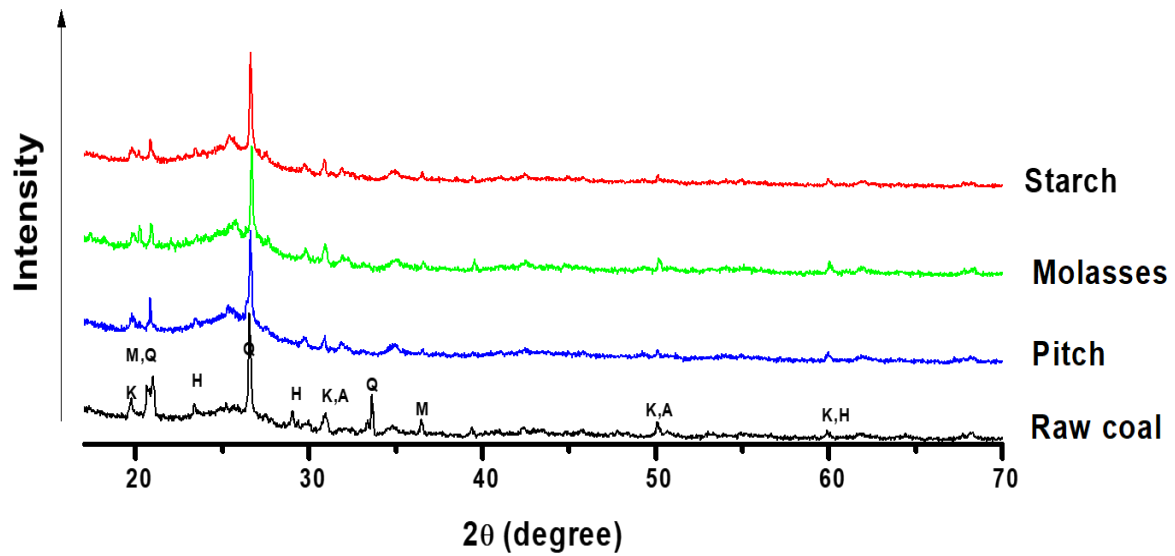


Figure 4.61: Diffractograms of raw coal and HFB produced from 95:5 HR using individual binders cured at 300°C for 60 min

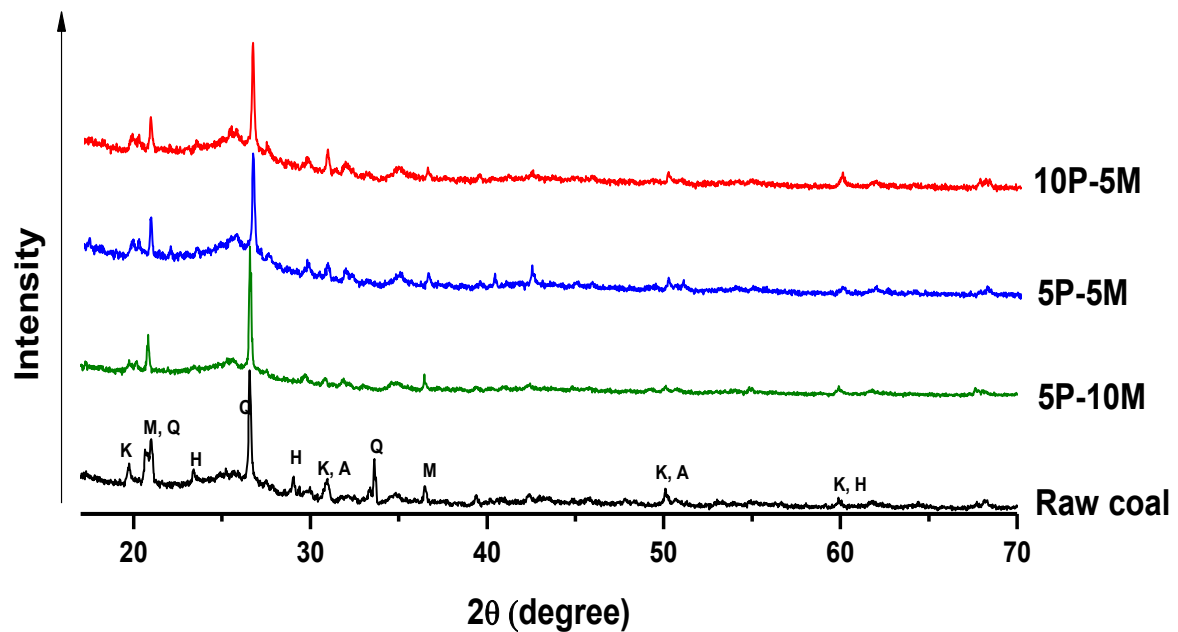


Figure 4.62: Diffractograms of raw coal and HFB produced from 95:5 HR using blended binders cured at 200°C for 60 min

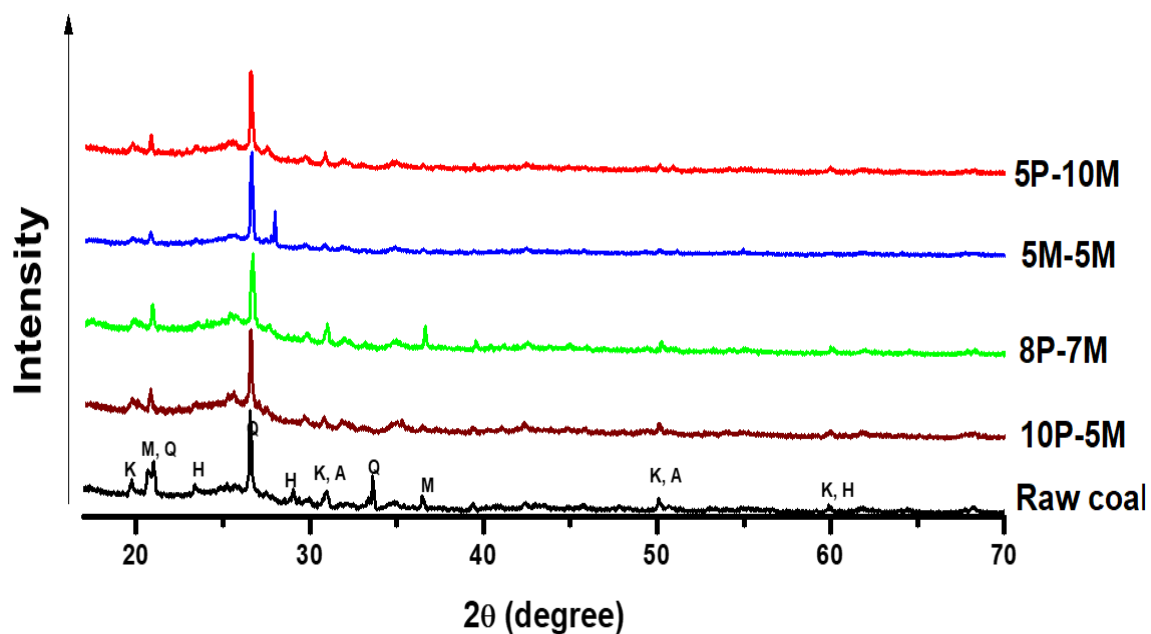


Figure 4.63: Diffractograms of raw coal and HFB produced from 97:3 HR using blended binders cured at 300°C for 60 min.

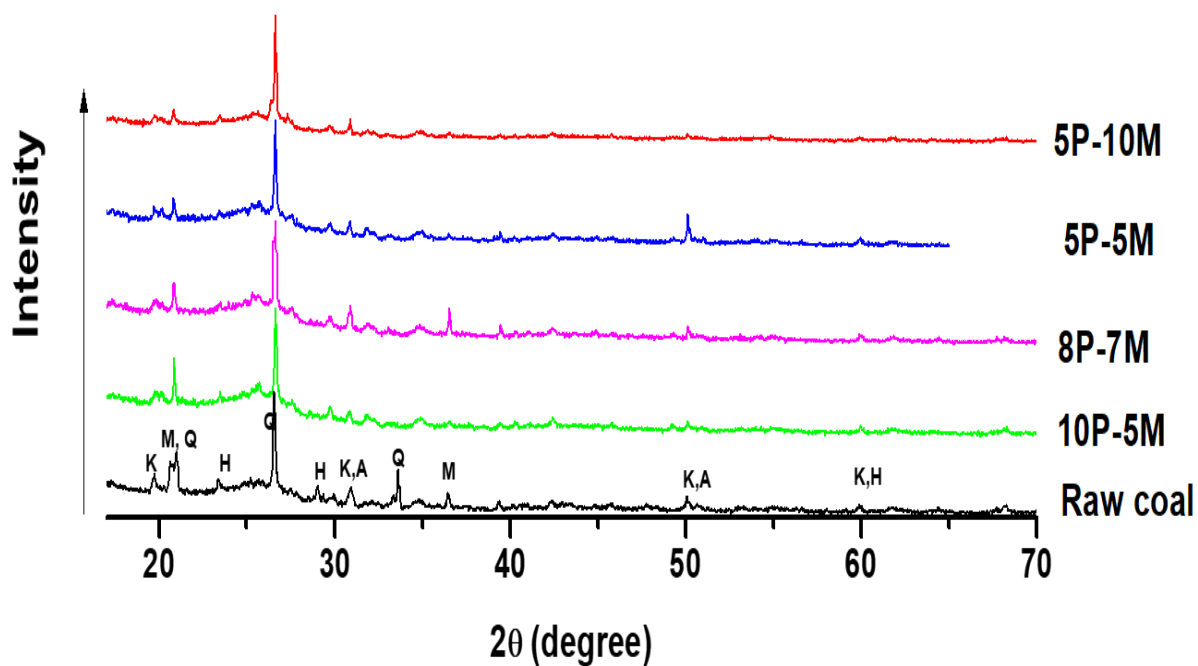


Figure 4.64: Diffractograms of raw coal and HFB produced from 97:3 HR using blended binders cured at 200°C for 60 min.

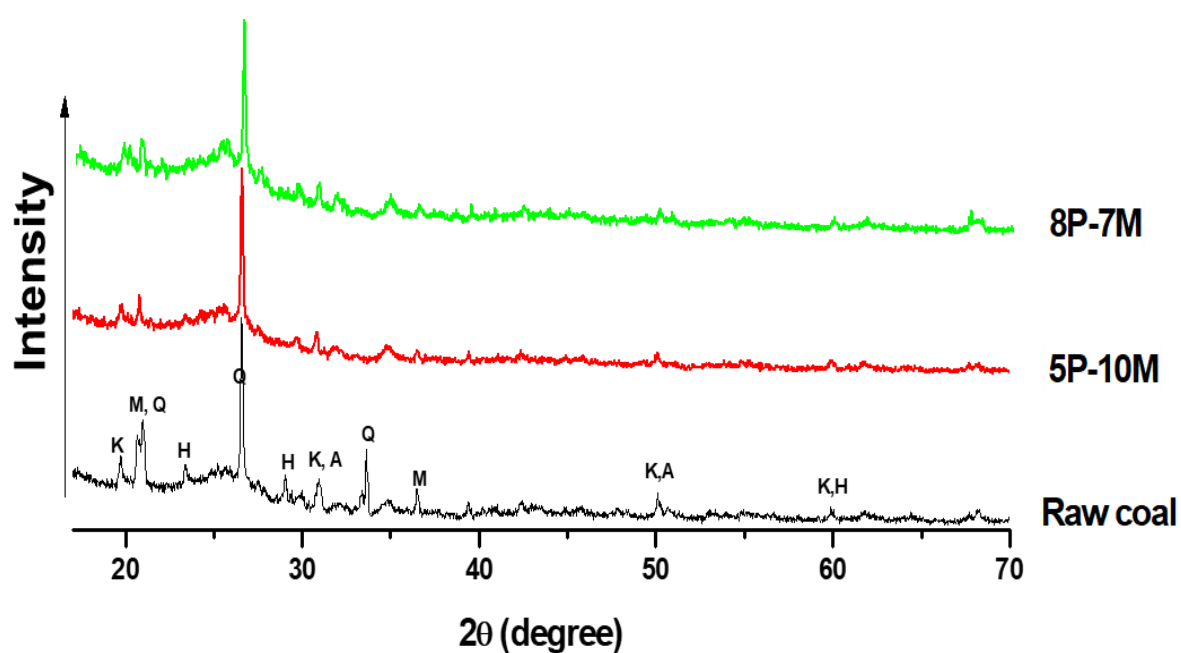


Figure 4.65: Diffractograms of raw coal and HFB produced from 90:10HR using blended binders cured at 200°C for 60 min

Table 4.14: Ash composition of raw coal and HFB cured at 200°C for 60 min

Ash compositions											
	Samples	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	CaO	Na ₂ O	TiO ₂	ZnO	CuO
		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(ppm)	(ppm)
Binder ratios	Raw coal	58.00	19.97	8.26	2.04	2.07	2.56	0.21	1.26	0.02	0.01
	HFB (97:3)										
	5P-5M	58.30	19.72	8.41	2.19	2.08	2.4	0.23	1.59	0.02	0.01
	8P-7M	58.50	20.53	8.61	2.21	1.83	2.74	0.21	1.62	0.02	0.01
	10P-5M	57.60	19.08	8.67	2.43	1.92	2.95	0.22	1.61	0.02	0.01
	5P-10M	58.00	19.83	8.29	2.24	2.00	2.64	0.21	1.59	0.02	0.01
	HFB (95:5)										
Binder ratios	5P-5M	57.50	19.82	8.35	2.14	2.06	2.6	0.21	1.62	0.02	0.01
	8P-7M	57.36	19.86	8.32	2.14	2.01	2.81	0.22	1.61	0.02	0.01
	10P-5M	58.21	19.90	8.35	2.07	2.09	2.81	0.22	1.59	0.02	0.01
	5P-10M	58.24	20.50	8.42	2.07	2.03	2.82	0.22	1.56	0.02	0.01
	HFB (90:10)										
Binder ratios	5P-5M	58.32	19.63	8.25	2.01	2.06	2.78	0.21	1.63	0.02	0.01
	8P-7M	58.86	19.76	8.22	2.14	2.01	2.67	0.20	1.61	0.02	0.01
	10P-5M	58.21	19.90	8.30	2.16	2.1	2.61	0.20	1.60	0.02	0.01
	5P-10M	58.24	19.80	8.32	2.09	2.03	2.66	0.21	1.54	0.02	0.01

Based on the XRF analyses carried out on different samples, no significant differences can be observed in the ash composition of raw coal and HFB. This is obvious with the ash fusion temperature (AFT) results for different hybridization ratios shown on Table 4.15. The deformation temperature (DT) ranges from 1200 - 1250°C for coal and HFB ashes while the softening temperatures (ST) are from 1240 - 1290°C. The hemispherical temperature (HT) and fusion temperature (FT) range from 1270 - 1300°C and 1300 - 1350°C, respectively. There was a little drop each of DT, HT, ST and FT of raw coal compared with the HFB ash. The ash fusion temperature do not exceed 1350°C for the FT compared with FT of >1500°C obtained for Meghalaya coal which is a sub-bituminous type (Sharma *et al.*, 2014). This point to the nature of the raw coal as lean grade compared with Meghalaya coal which was reported to be a higher grade coal. The AFTs of raw coal and HFB largely depend upon the oxide ratios of the ashes. A brief description of the important oxide ratios are discussed as follows:

a. Silica-Alumina ratios ($\text{SiO}_2/\text{Al}_2\text{O}$)

The silica-alumina ratio is an important parameter that affects the flow properties of coal ash slag and it is negatively correlated with DT, ST and FT (Mishra *et al.*, 2016). Silica-alumina ratio (abrasion potential) presented in Table 4.16 ranges from 2.8 - 3.01 for raw coal and HFB. This is a little higher than 2.01 - 2.86 reported for PCB coal by Mishra *et al.* (2016a). This signifies the presence of coarse-grained non-spherical quartz which can sustain the ash as solid until 1600°C (Reifenstein, 1999; Shibaoka, 1972). However, the presence of other basic oxides in the coal and HFB lowers the softening and melting points of the ashes to 1350°C. The trend of inorganic matters in the coal ash is reminiscence of the HFB ash and this depicts that there is a little contribution from the addition of torrefied biomass, pitch and molasses to the inorganic matters in the HFB since they are basically organic materials.

**Table 4.15: Ash fusion temperatures of raw coal compared with HFB cured
at 200°C-60 min**

	Samples	DT (°C)	ST (°C)	HT (°C)	FT (°C)
	Raw coal	1250	1290	1300	1350
	HFB (97:3)				
Binder ratios	5P-5M	1240	1260	1290	1320
	8P-7M	1230	1240	1280	1300
	10P-5M	1240	1250	1290	1330
	5P-10M	1240	1250	1270	1310
	HFB (95:5)				
Binder ratios	5P-5M	1240	1250	1290	1340
	8P-7M	1230	1260	1280	1330
	10P-5M	1240	1240	1280	1340
	5P-10M	1230	1260	1280	1330
	HFB (90:10)				
Binder ratios	5P-5M	1200	1250	1270	1300
	8P-7M	1210	1250	1280	1310
	10P-5M	1230	1240	1290	1320
	5P-10M	1220	1240	1270	1310

Table 4.16: Oxide ratios of coal and HFB cured at 200°C-60 min

	Samples	Silica/Alumina	Basic/Acidic	Silica ratio	Slagging factor	Fouling factor
	Raw coal	2.90	0.19	0.82	0.14	0.43
	HFB (97:3)					
Binder ratios	5P-5M	2.96	0.19	0.82	0.14	0.46
	8P-7M	2.85	0.19	0.82	0.14	0.47
	10P-5M	3.02	0.21	0.81	0.15	0.55
	5P-10M	2.92	0.19	0.82	0.14	0.47
	HFB (95:5)					
Binder ratios	5P-5M	2.90	0.19	0.82	0.14	0.46
	8P-7M	2.89	0.20	0.82	0.14	0.46
	10P-5M	2.93	0.19	0.81	0.14	0.45
	5P-10M	2.84	0.19	0.81	0.14	0.44
	HFB (90:10)					
Binder ratios	5P-5M	2.97	0.19	0.82	0.14	0.43
	8P-7M	2.98	0.19	0.82	0.14	0.44
	10P-5M	2.93	0.19	0.82	0.14	0.46
	5P-10M	2.94	0.19	0.82	0.14	0.44

b. Silica ratio ($\text{SiO}_2 / (\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO})$)

These oxides ratio is applied to predict coal ash slagging performance (Mishra *et al.*, 2016; Song *et al.*, 2009). A good coal must have high silica ratio ≥ 0.78 which implied that it will be hard to fuse (Mishra *et al.*, 2016). The silica ratio of both raw coal and HFB ashes are > 0.81 as presented in Table 4.16. The silica ratios obtained are similar to that of Prajapara coal which showed positive correlation to DT and FT, and was considered as good coal (Mishra *et al.*, 2016). Thus, the silica ratios of the presented study shows that the HFB will perform well during slagging.

c. Basic/ Acid ratio $((\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}) / (\text{SiO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3))$

The ratio of the basic to acidic oxides is also considered as an index for slagging behaviour (Lawrence *et al.*, 2008). The basic/acidic (ratio) has been reported to have negative correlation with FT and DT (Mishra *et al.*, 2016). Coal with basic/acidic (B/A) ≥ 0.4 is grouped to be low melting ash while $B/A \leq 0.11$ are considered to be very good coal for thermal and metallurgical applications. The B/A of the ashes of raw coal and HFB are in the range of 0.19 - 0.20. This indicates that slag formation will not be highly favoured during the use of the HFB.

d. Slagging factors (B/A*Sulphur)

The slagging factor of the ash of coal and HFB ranges from 0.13 to 0.14. This is lower than slagging factor of 0.6 recommended for coal that has low slagging potential (McLennen *et al.*, 2000). On a general basis, the slagging factor of the HFB ash was similar to that of the raw coal, which indicates that the addition of torrefied biomass, pitch and molasses to raw

coal did not increase its slagging potential. Thus, the slagging potential of the HFB totally depends on the mineral composition of the raw coal.

e. Fouling factor ($B/A \cdot (Na_2O + K_2O)$)

The tendency of coal to pollute the environment by smelling or generation of foul odours is usually determined by the fouling factor. The fouling factor (FF) of the HFB ashes (0.44 - 0.55) were a little higher compared to that of raw coal (0.43). The FF results of the present study are similar to FF of < 0.45 which were obtained for Prajapara coal (Mishra *et al.*, 2016) and Meghalaya coal (Sharma *et al.*, 2014) that were reported to have low fouling factor. The low FF indicates that the HFB has low potential to fouling. Based on the oxides ratios (Table 4.16), the ashes of HFB behaved similarly to that of raw coal used for its production. It is worthy to note that the ashes of HFB does not have high tendency for clinker formation, slagging and fouling during its conversion process such as combustion and gasification (Mishra *et al.*, 2016).

4.5.3 Structural characterization

4.5.3.1 Fourier transform infrared spectroscopy (FTIR) results

Figure 4.66 shows the spectra of raw materials adopted for briquette production. The FT-IR spectra of hybrid fuel briquettes produced from different conditions compared with raw coal are presented in Figures 4.67 to 4.69. The spectra of $3300 - 3700 \text{ cm}^{-1}$ zone is attributed to the stretch vibration of phenolic hydroxyl group (Li & Zhu, 2014; Speight, 1994). The peak at 3434 cm^{-1} did not appear significantly in raw coal as shown in Figure 4.66 and this implied that the raw coal contains lower proportion of phenolic hydroxyl group. The spectra in the range of $2800 - 2975 \text{ cm}^{-1}$ and 1375 cm^{-1} that appeared in pitch is deformation vibration of C-H in aliphatic carbon ($-CH_3$) and $-C(CH_3)_2$, respectively. The 2915 cm^{-1} peak is also present in treated Melina (Mw) and Teak (Tw). The relative intensity of peak at 2915

cm^{-1} decreases and nearly disappears in the hybrid fuel briquette samples. This may be due to curing process that easily liberate the aliphatic group from pitch.

From Figure 4.66, the peak at 1600 cm^{-1} that is observed from treated biomass and pitch is not present in the FT-IR spectra of raw coal. The peak has been attributed to the presence of aromatic ring ($\text{C}=\text{C}$) in biomass and pitch (Speight 1994). The peak 1597 cm^{-1} is attributed to condensed aromatic ring ($\text{C}=\text{C}$) while $760 - 870\text{ cm}^{-1}$ is assigned to out of plane vibration of aromatic CH_3 groups (Speight 1994). In addition, the spectra $1000 - 1300\text{ cm}^{-1}$ was assigned to phenolic $\text{C}-\text{O}$ or $-\text{OH}$ of water functional group. The spectra are present in raw coal but the intensity drops in the hybrid fuel briquette samples (Figures 4.68 - 4.69). Though, the nature of coal suggestively makes the spectra complex for individual compound analysis, however, the hybrid fuel briquettes samples shows the presence of aromatic $\text{C}=\text{C}$ bonds and phenolic OH group. Zhong *et al.* (2017) established that along with $\text{C}=\text{C}$ group, oxygen bridges due to the presence of large oxygen containing functional groups makes coal particles to form firm and strong briquettes. The hybrid fuel briquettes have the tendency to keep its structure and the strength will further improve with temperature during utilization as pitch completes its coking process. Wood polymer (lignin) also has a wide range of temperature stability and therefore can continuously bring about strength as briquettes are fed into kiln for metallurgical applications.

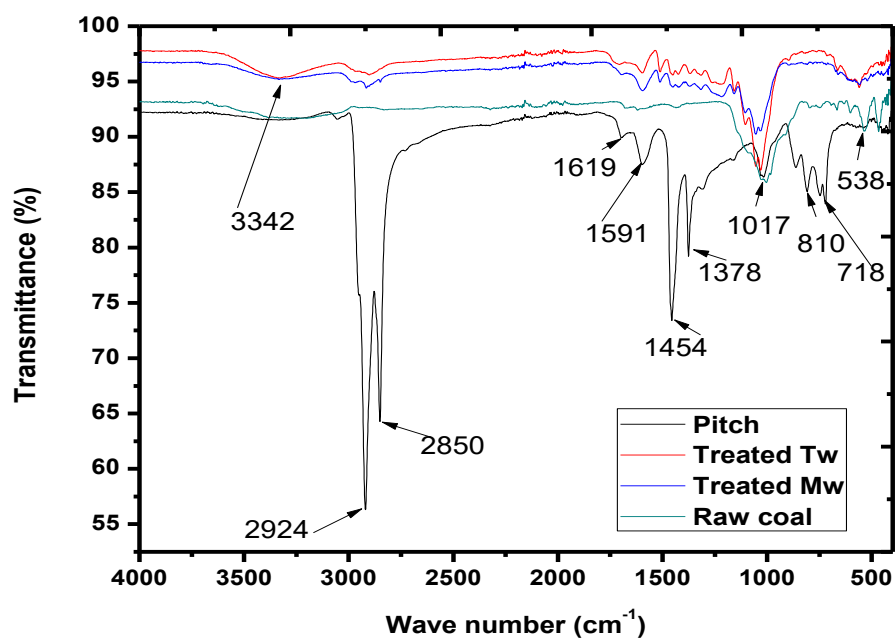


Figure 4.66: FT-IR spectra of raw materials used for hybrid fuel briquette production

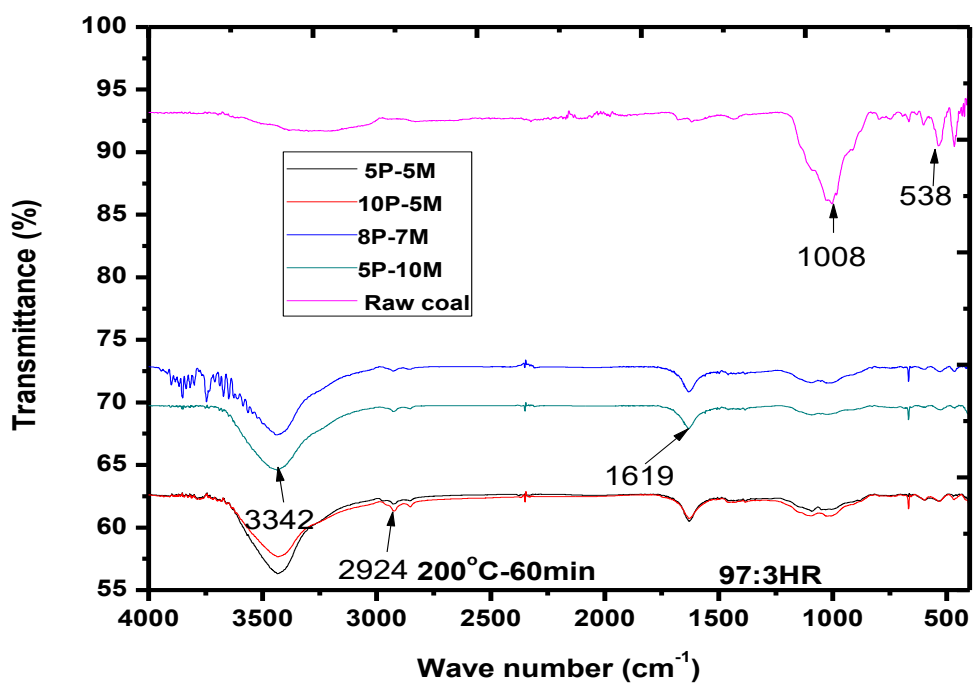


Figure 4.67: FT-IR spectra of hybrid fuel briquettes (97:3HR) from different blended binder ratios compared with that of raw coal

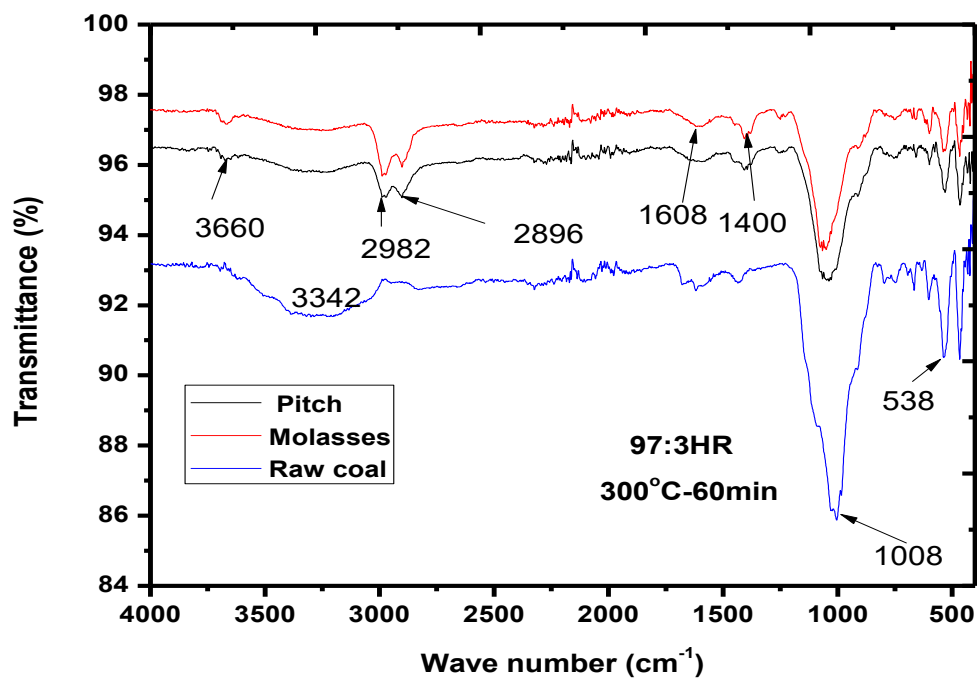


Figure 4.68: FT-IR spectra of hybrid fuel briquettes (97:3HR) from individual binder (pitch and molasses) compared with that of raw coal

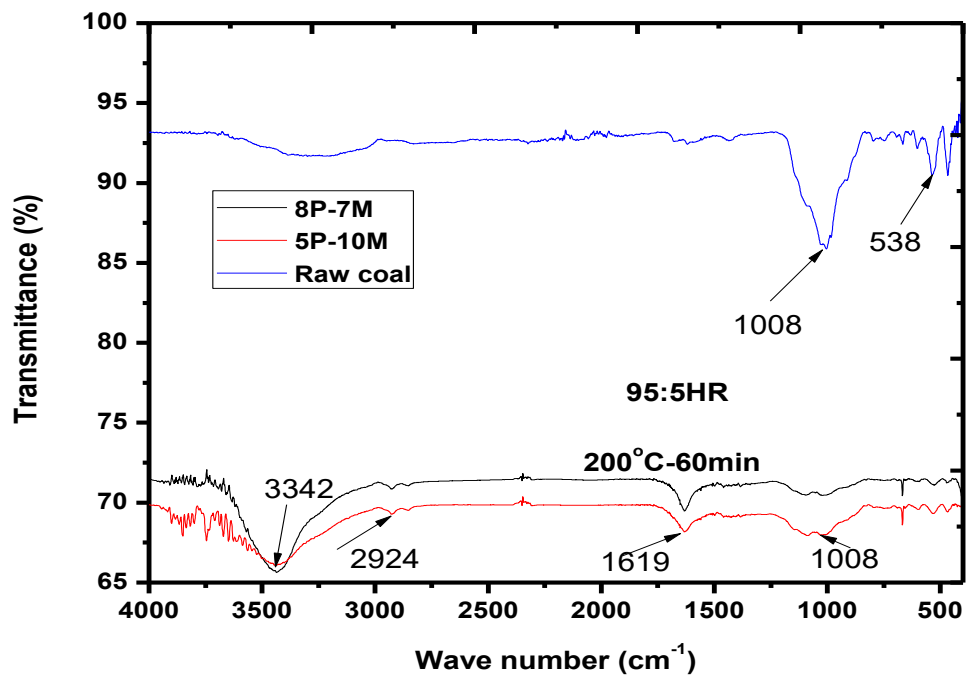


Figure 4.69: FT-IR spectra of hybrid fuel briquettes (95:5HR) from different blended binder ratios compared with that of raw coal.

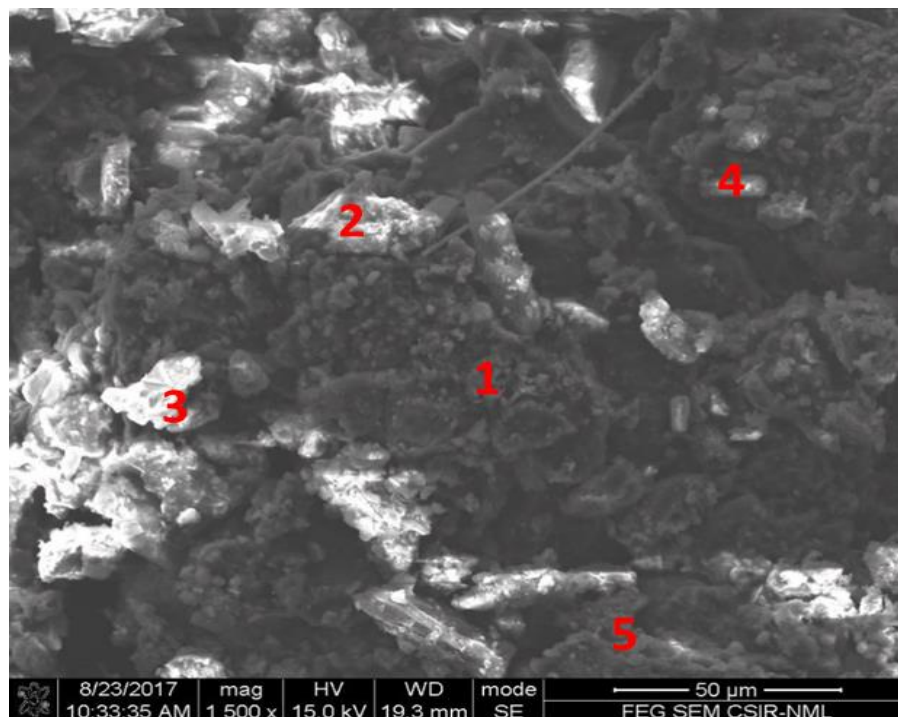
4.5.3.2 SEM-EDX/EPM analyses

Figure 4.70 is the SEM image of hybrid fuel briquettes (95:5HR) produced from the blend of 5%pitch-5%molasses. Figure 4.70 shows a granular fissures along with some fibrous appearances which may be torrefied biomass. The spectrum analyses (EDX) on Figure 4.70 shows that point 1 contained high carbon content compared to other points (2 - 5). It also shows that there were variations of different element across the hybrid fuel briquette (point 1 - 5). This could be because the HFB comprises of different organic materials. However, the carbon content were above 73% for the points examined and this validates the overall amount of carbon obtained from the ultimate analyses. Though, the bonding mechanism between the materials could not be established, the charging effect observed on the HFB could be as a result of oxygen bridges which can help in strengthening the briquettes (Zhong *et al.*, 2017).

Figure 4.71 represents the SEM image of HFB (97:3HR) produced from the blend of 8%pitch-7%molasses. It consists of irregular grainy surface though more compact than what was observed in Figure 4.70. The dominant element in the HFB is carbon with little variation at points 1 - 5 examined as shown on the energy spectra (Figure 4.71). Similar microstructure was observed on the SEM image of the HFB (97:3HR) when subjected to a more severe curing condition as shown in Figure 4.72. However, a grainier and cemented coal particles can be observed when HFB produced from the blend of 8%pitch-7% molasses was cured at 200°C for 120 min (Figure 4.73). The energy spectra also show that it majorly contains carbon along with other element such as oxygen, aluminium and silicon.

The microstructure of the HFB produced from 97:3HR using 5%pitch-10%molasses (cured at 200°C for 60 min) revealed granular surface that were more homogenous and closely packed (Figure 4.74). This may be the reason why the HFB (97:3HR) produced using 5%pitch-10%molasses have higher strength compared with others. However, similar to what was obtained for its ultimate analyses, the energy spectra at points 1-5 show reduction in

carbon content compared with others. The SEM images obtained for the different HFB examined show similar structures such as granular surface, irregular arrangement and charging effects observed for briquettes produced from high volatile coal (Zhong *et al.*, 2017). The structures of the HFB produced from different blended binder ratios are similar to each other and it contains primarily carbon, oxygen and small amount of trace element such as iron (Fe), silicon (Si), calcium (Ca) and aluminium (Al).



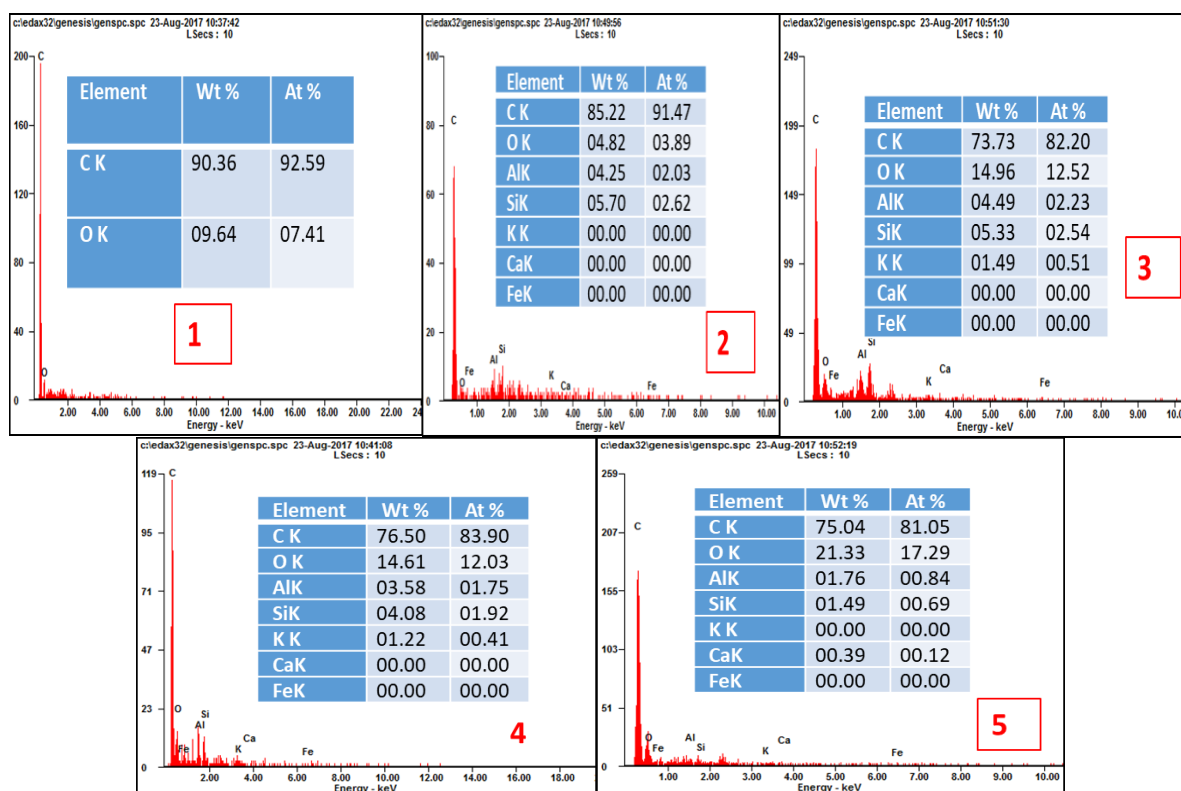
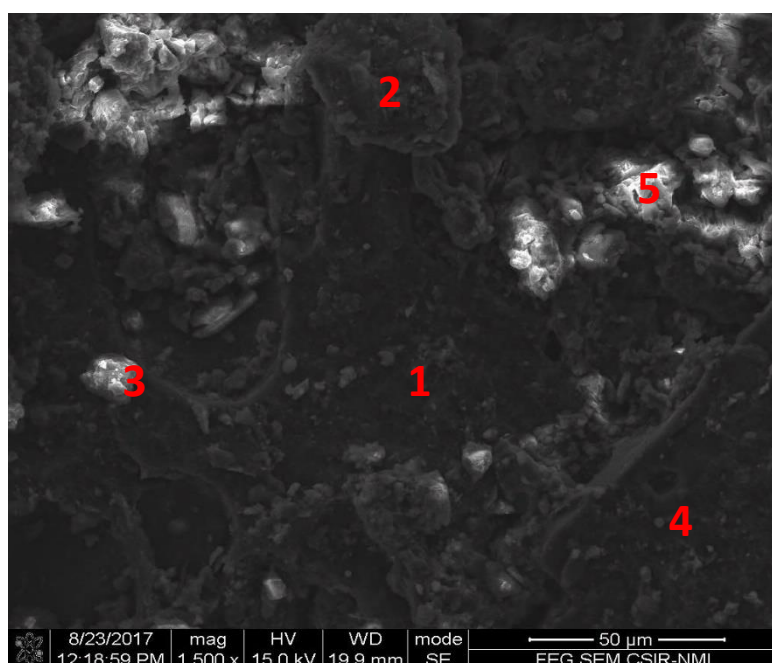


Figure 4.70: SEM image and EDX point analyses of HFB (95:5HR) produced from blend of 5% pitch-5% molasses and cured at 200°C-60min



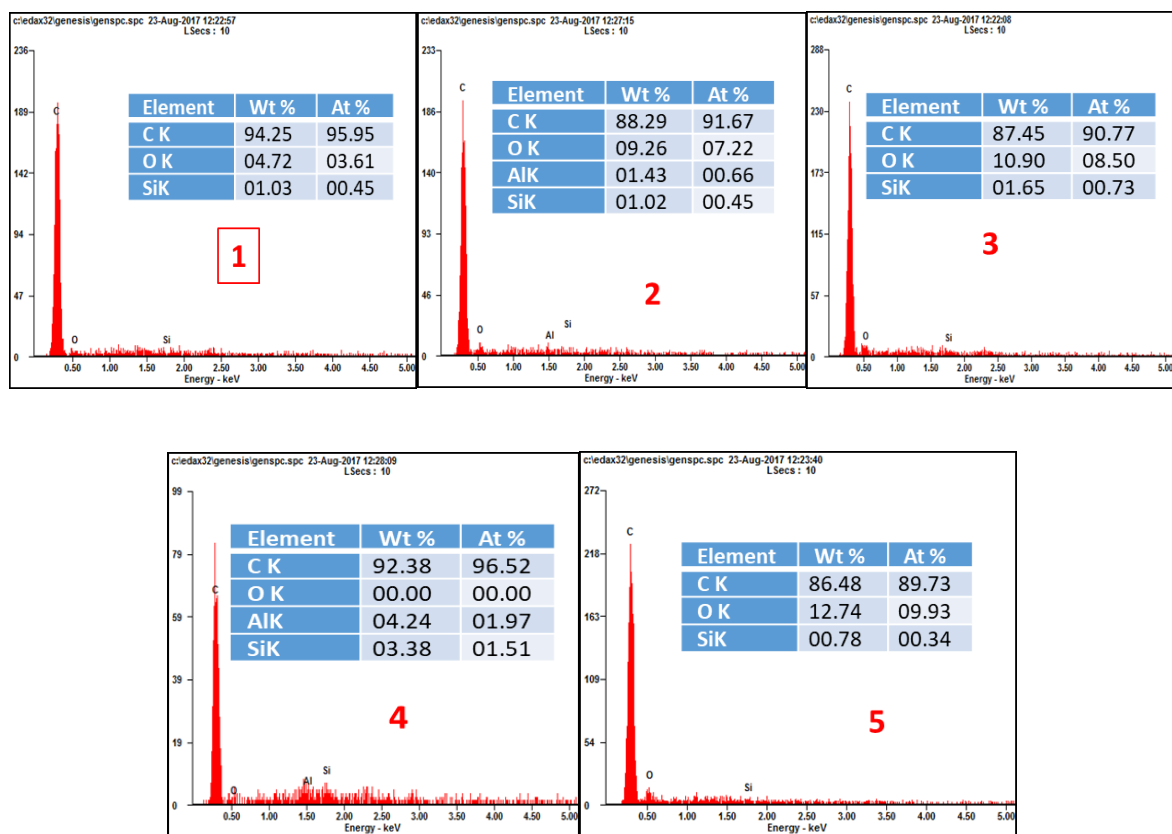
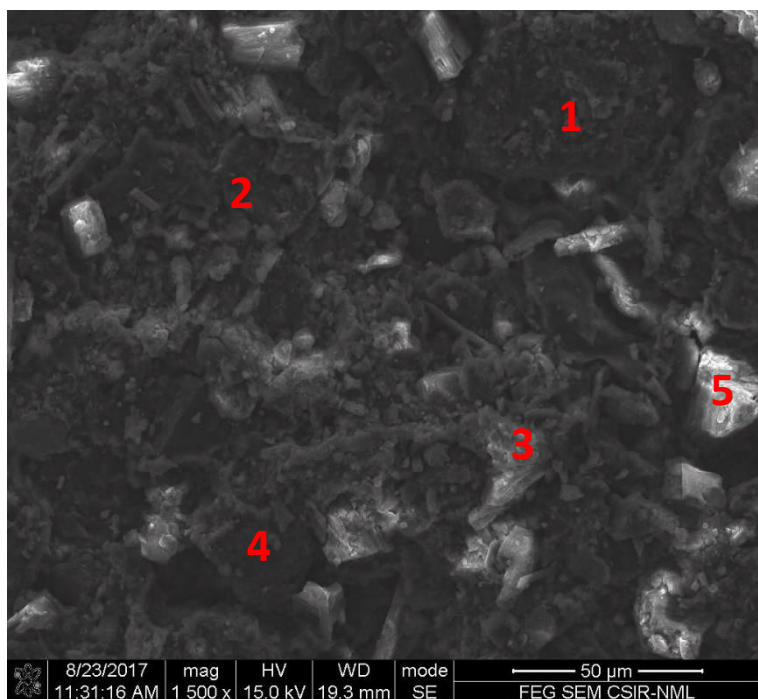


Figure 4.71: SEM image and EDX point analyses of HFB (97:3HR) produced from blend of 8% pitch-7% molasses and cured at 200°C-60min.



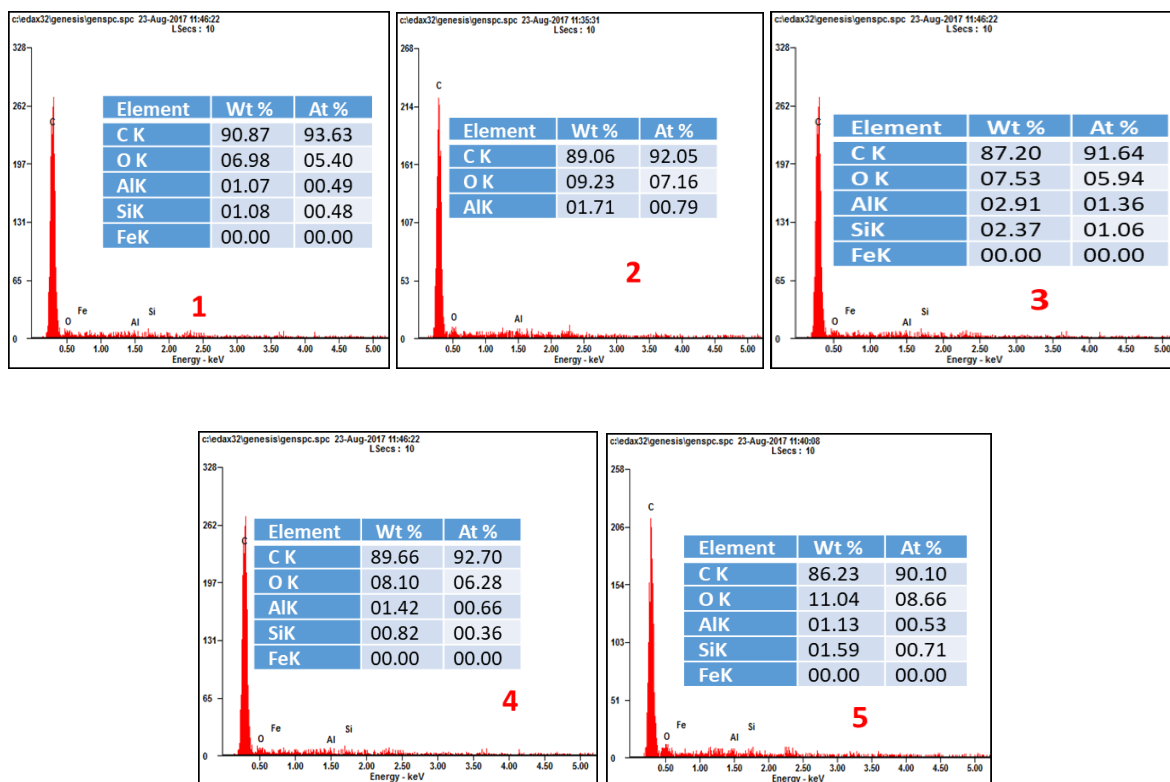
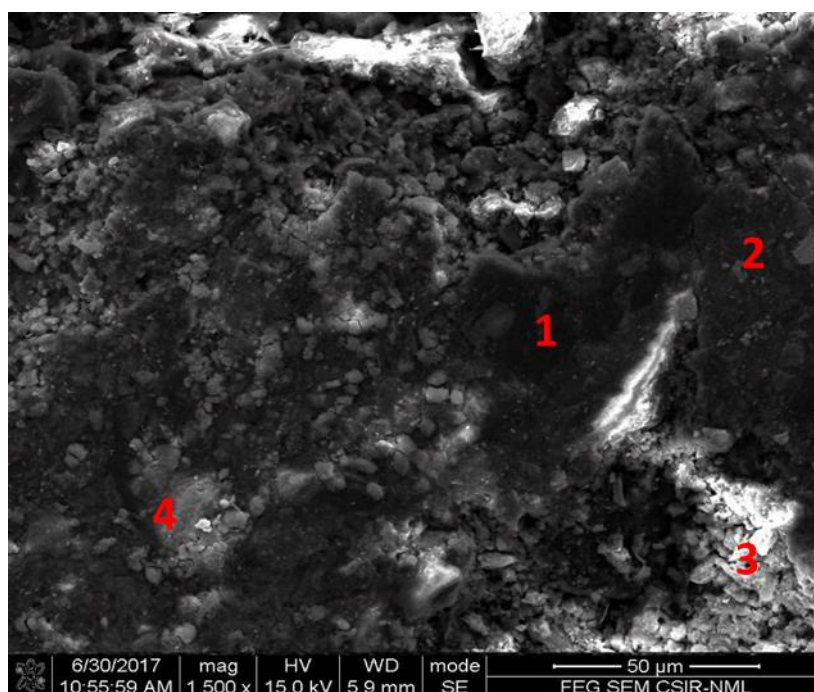


Figure 4.72: SEM image and EDX point analyses of HFB (97:3HR) produced from blend of 8% pitch-7% molasses and cured at 300°C-60min.



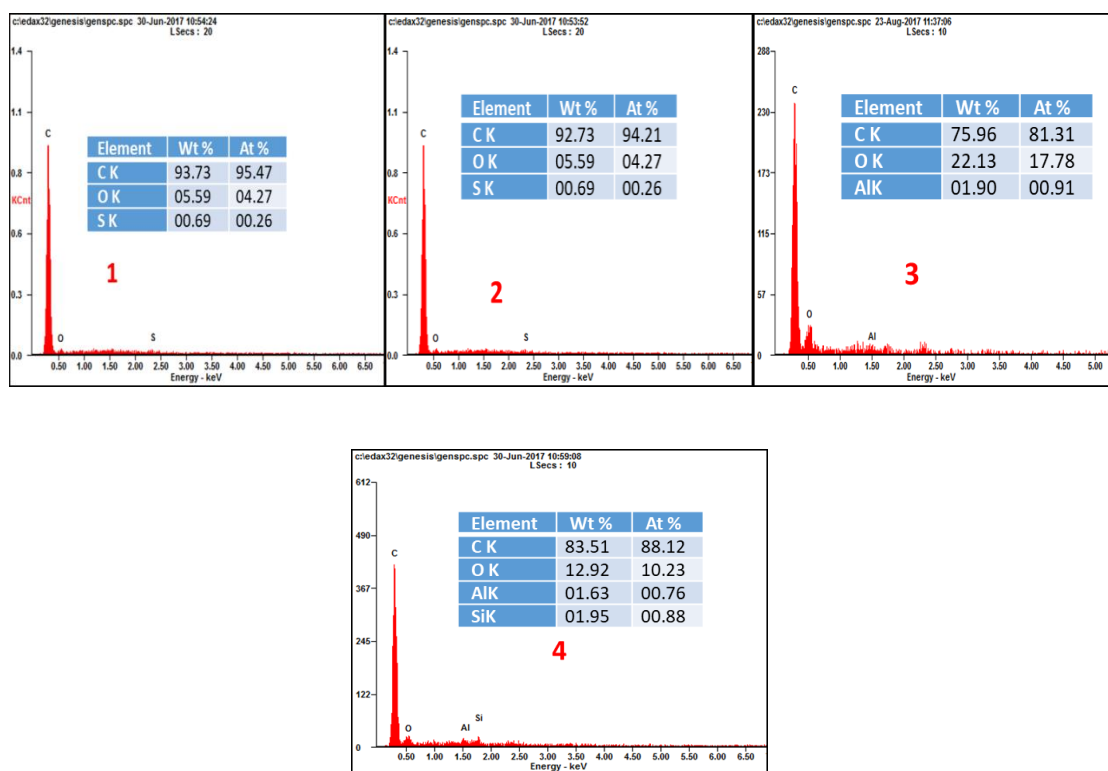
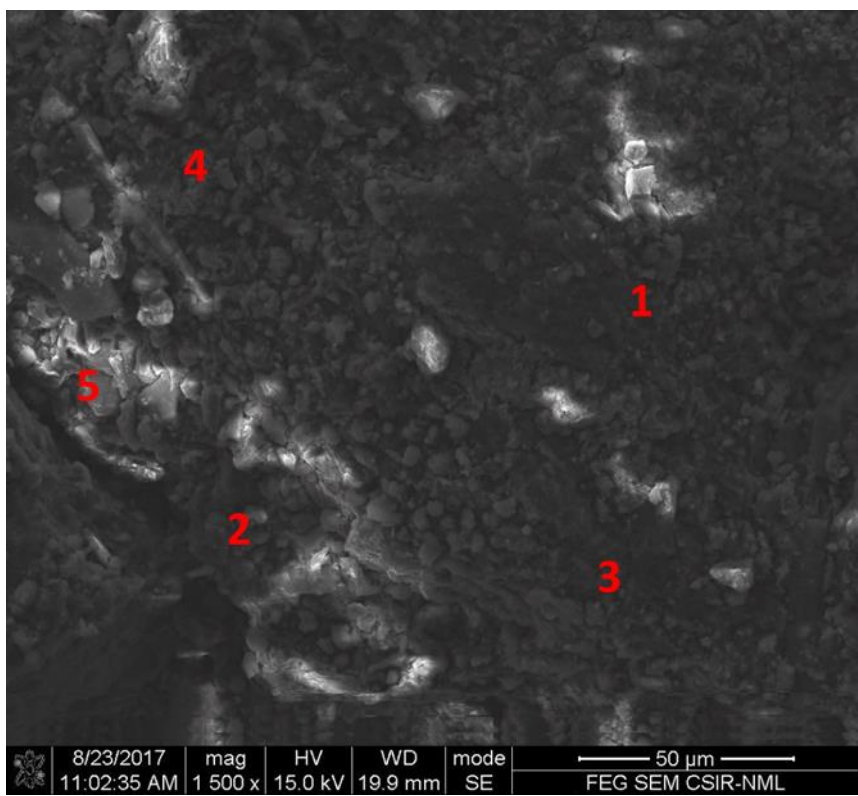


Figure 4.73: SEM image and EDX point analyses of HFB (97:3HR) produced from blend of 8% pitch-7% molasses and cured at 200°C-120min.



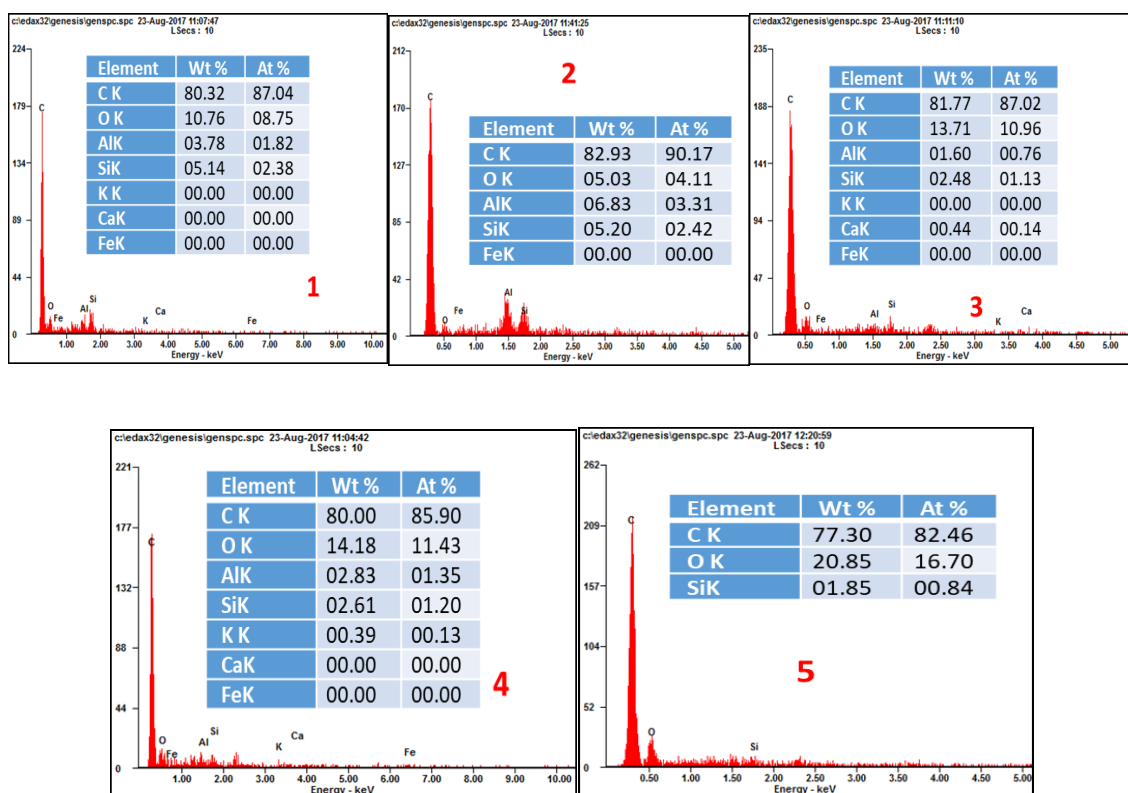
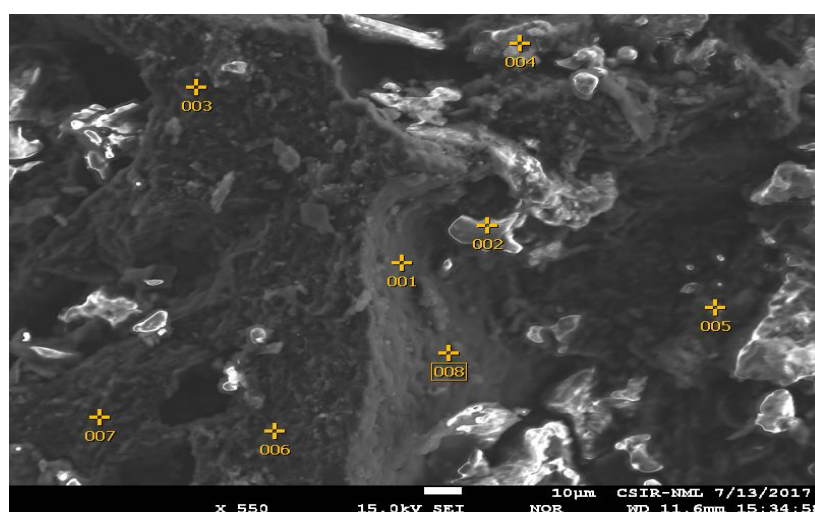


Figure 4.74: SEM image and EDX point analyses of HFB (97:3HR) produced from blend of 5% pitch-10% molasses and cured at 200°C-60min.

The spatial distribution of elements in HFB (97:3HR) produced from 8% pitch-7% molasses cured at 200°C for 60 min was also examined using electron probe microanalysis (EPMA) and the image is shown in Figure 4.75. Elemental mapping of the HFB are also presented in Figure 4.76. Figure 4.75 shows granular surface with charging effects which could be as a result of the presence of oxygen bridges. The oxygen bridges could contribute to further strengthen of the coal-torrefied biomass particle bond along with other bonding mechanisms within the briquette. Figure 4.75 also shows that carbon is the foremost element present in the HFB along with oxygen. However, the presence of iron (Fe), silicon (Si), aluminum (Al) and sulfur (S) though with variations from point to point could also be observed on the EDX spectrum.

The elemental mapping analyses shown in Figure 4.76 revealed that carbon dominates the entire surface with moderate distribution. Oxygen (O), silicon (Si) and aluminum (Al)

could also be observed to disperse well at the surface of the HFB examined. The presence of other trace elements such magnesium (Mg), potassium (K), calcium (Ca) and iron (Fe) generally dispersed well and does not just concentrate at a point on the surface of the briquette. These ash-forming elements were connected with the organic matrix of the the HFB as they dispersed well along with carbon as shown in Figure 4.76. The ash behaviour of the HFB was affected by the presence of calcium, magnesium and iron. These element elements forms different oxides (Table 4.16) that lowered the ash fussion temperature of the HFB (Table 4.15).



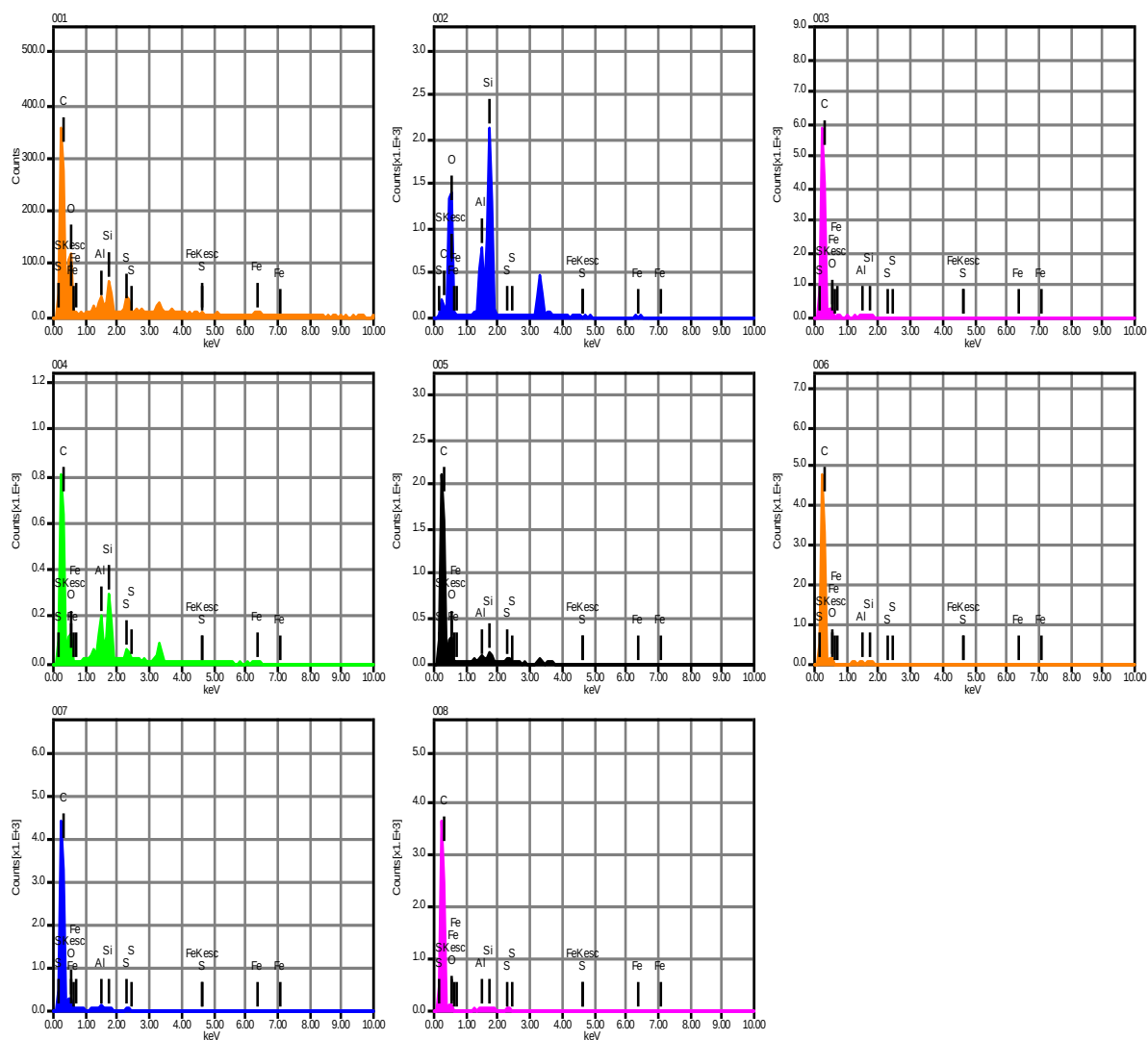


Figure 4.75: EPMA image and point analyses for HFB (97:3HR) produced from 8% pitch-7% molasses cured at 200°C for 60 min.

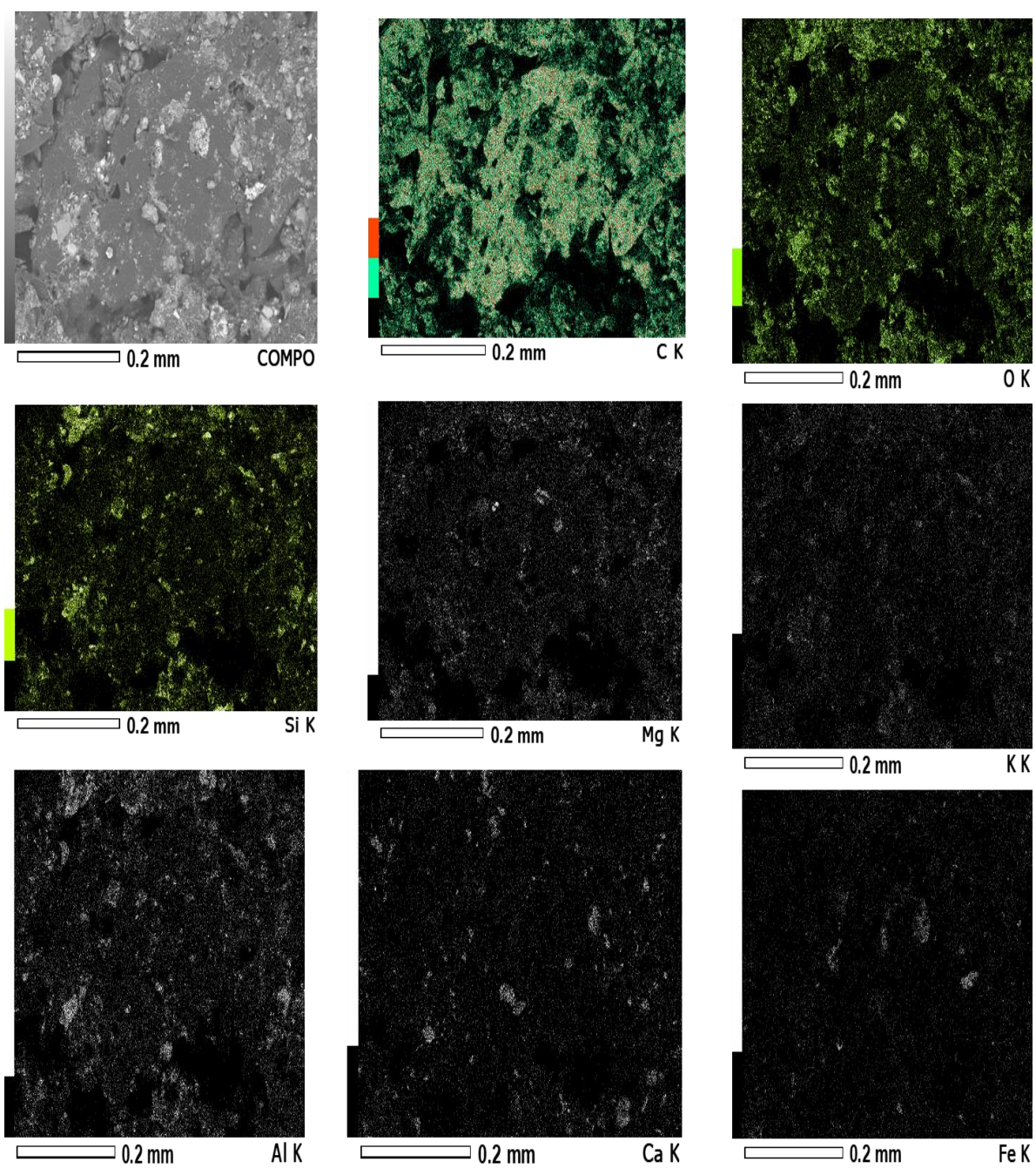


Figure 4.76: Elemental mapping of HFB (97:3HR) produced from 8% pitch-7% molasses cured at 200°C for 60 min.

4.6 Comparison between the properties of Hybrid Fuel Briquette produced and some proposed benchmarks

There are no international standards such as British standards, American standards and so on, available to measure the compliance of properties of coal – biomass briquettes that could be used as fuel for energy and metallurgical applications. However, there are few works that proposed some benchmark properties that could be used to determine the suitability and quality of briquettes to be used for domestic and industrial applications (Richard, 1990; Speight, 2012; Thoms *et al.*, 1999; Yip *et al.*, 2007)

The hybrid fuel briquettes produced in this study was benchmarked against the proposed properties of briquettes required for thermal plants and rotary kiln DRI operations as shown in Table 4.17 based on the result of Richard (1990), Speight (2012), Thoms *et al.* (1999) and Yip *et al.* (2007). It was observed that the hybrid fuel briquettes produced in this study are of higher qualities in terms of physical, mechanical and combustion properties. Therefore, the properties of the hybrid fuel briquettes produced in the present study are recommended to be adopted as standard benchmarks to determine the suitability of fuel briquettes to be used as feedstock in power plant and rotary kiln for energy generation and DRI making process, respectively.

Table 4.17: Briquette properties compared with some proposed benchmarks required for feedstock of thermal plants/ direct reduced iron (DRI) making process

	Benchmarks	Present work
Ash content	$\leq 20\%^*$	< 20 %
AFT	>1200°C *	1230-1350°C (DT-FT)
VM	< 25% *	<20%
Fixed carbon	> 45% *	>60%
Sulphur	$\leq 1\%^*$	0.7-0.9%
IRI	>50 (Richard, 1990,Thoms <i>et al.</i> , 1999)	>7000
CCS	80% CCS of coal /CCS of oven coke 6.9 -30Mpa (Yip <i>et al.</i> , 2007)	7 -11.5 MPa
Moisture	<8%*	1-3%
Reactivity	Good reactivity	54%
Lumps/fines	5-20 mm	Briquette H = 20 mm, D = 25 mm
WRI	>95% (Thoms <i>et al.</i> , 1999)	99%
Drop to fracture	NA	>200 (times/2m)
HHV	NA	>24 MJ/kg
Bulk density	1.19-1.40g/cm ³ *	1.1-1.35g/cm ³
TSI (room temp.)	95% (Thoms <i>et al.</i> , 1999)	>97%

*Speight (2012), NA - Not available.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions were drawn from this study;

- i. The preliminary characterisation shows that the woody biomass (Teak and Melina) had fixed carbon (FC), volatile matter (VM), ash, higher heating value (HHV) in the range of 8.92 - 11.73 %, 79.26 - 81.42%, 1.73 - 2.15%, 18.39 - 18.72 MJ/kg, respectively, while coal had 66.92% FC, 13.77% VM, 17.94 ash and HHV of 23.13 MJ/kg.
- ii. The thermal decomposition study of woody biomass showed that 80% weight loss occurred at temperature lower than 400°C. However, sufficient decomposition of hemicellulose and cellulose to obtain carbon-rich solid residue needed for briquetting was obtained within the torrefaction temperature range (200 - 300°C). This consequently led to the optimisation of torrefaction conditions in order to obtain maximum mass yield, HHV and energy yield for the woody biomass during torrefaction.
- iii. The optimised torrefaction conditions for the woody biomass were: particle size, 2 mm; temperature, 260°C; and residence time, 60 min. This resulted in higher FC (41 - 42%), lower VM (54.09 - 54.20%) and greater HHV (23.46 - 23.63 MJ/kg).
- iv. The best formulation ratio for the HFB (coal and torrefied biomass) production was 97:3 using blend of 8% pitch and 7% molasses as binder under 28 MPa.
- v. The mechanical strength such as drop to fracture (200 times/2m) and cold crushing strength (11 MPa) as well as energy content (24 MJ/kg) of the HFB were higher compared with proposed benchmarks obtained from literatures. The ultimate and proximate analyses of the HFB showed a minor improvement compared with that of

raw coal. The ash fusion temperature of the HFB progressed from 1240 to 1350°C for the initial deformation to final fusion.

- vi. The HFB produced has sufficient mechanical strength with desirable combustion properties and thus can be used for energy generation and as feedstock for the production of iron and steel through direct reduction route. Therefore, this HFB is recommended for domestic and industrial applications.

5.2 Recommendations

It is recommended that the production of HFB should be encouraged by the Federal Government of Nigeria as it will alleviate the present burden on oil and gas as the major source of energy generation in the country. The use of HFB should also be encouraged as feedstock (reductant) in the production of direct reduced iron (DRI) through rotary kiln, which can serve as alternative route to iron and steel production. This can be used along with blast furnace at the Ajaokuta Steel Complex, Kogi state, as well as Delta Steel company, Warri, Delta state, if resuscitated.

Suggestions for future work

The production of HFB from other types of coal slack and lignocellulosic (woody and non-woody) should further be explored to determine their mechanical strength and combustion properties.

Lignocellulosic woody biomass contain high amount of lignin that can act as binder. Hence, briquetting of coal slack and torrefied lignocellulosic woody biomass without other binder should also be carried out.

Production of DRI through rotary kiln route using HFB as one of its feedstock should be carried explored.

Production of DRI in a Tunnel kiln is a viable option for the utilization of biochar produced from woody biomass using torrefaction process. Therefore, the feasibility of partial

or total replacement of coal fines with biochar as reductant in the process should be investigated.

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APPENDICES

**Table A1: Analysis of variance (ANOVA) of the adjusted model for MY of Melina wood
during torrefaction**

MY	Degree of freedom	Sequential Sum of square	Adj. Sum of square	F-Value	P-Value
Model	7	4554.70	650.67	28.93	0.000
Linear	3	4350.99	1450.33	64.49	0.000
TT	1	4326.02	4326.02	192.35	0.000
RT	1	1.18	1.18	0.05	0.824
PS	1	23.79	23.79	1.06	0.334
2-Way	3	140.86	46.95	2.09	0.180
Interactions					
TT*RT	1	26.24	26.24	1.17	0.312
TT*PS	1	111.36	111.36	4.95	0.057
RT*PS	1	3.27	3.27	0.15	0.713
3-Way	1	62.85	62.85	2.79	0.133
Interactions					
TT*RT*PS	1	62.85	62.85	2.79	0.133
Error	8	179.92	22.49		
Total	15	4734.63			
$R^2 = 0.9620$, Adj. $R^2 = 0.9287$					

Table A2: Analysis of variance (ANOVA) of the adjusted model for HHV of Melina wood during torrefaction

HHV	Degree of freedom	Sequential Sum of square	Adj. Sum of square	F-Value	P-Value
Model	7	136.871	19.553	12.95	0.001
Linear	3	122.247	40.749	26.99	0.000
TT	1	116.316	116.316	77.05	0.000
RT	1	1.266	1.266	0.84	0.387
PS	1	4.666	4.666	3.09	0.117
2-Way	3	9.516	3.172	2.10	0.178
Interactions					
TT*RT	1	1.904	1.904	1.26	0.294
TT*PS	1	6.477	6.477	4.29	0.072
RT*PS	1	1.134	1.134	0.75	0.411
3-Way	1	5.108	5.108	3.38	0.103
Interactions					
TT*RT*PS	1	5.108	5.108	3.38	0.103
Error	8	12.076	1.510		
Total	15	148.947			
$R^2 = 0.9196$, Adj. $R^2 = 0.8492$					

**Table A3: Analysis of variance (ANOVA) of the adjusted model for EY of Melina wood
during torrefaction**

EY	Degree of freedom	Sequential Sum of square	Adj. Sum of square	F-Value	P-Value
Model	7	2640.50	377.21	29.54	0.000
Linear	3	2559.43	853.14	66.81	0.000
TT	1	2556.57	2556.57	200.21	0.000
RT	1	0.35	0.35	0.03	0.873
PS	1	2.52	2.52	0.20	0.669
2-Way	3	75.77	25.26	1.98	0.196
Interactions					
TT*RT	1	11.21	11.21	0.88	0.376
TT*PS	1	46.82	46.82	3.67	0.092
RT*PS	1	17.75	17.75	1.39	0.272
3-Way	1	5.30	5.30	0.42	0.537
Interactions					
TT*RT*PS	1	5.30	5.30	0.42	0.537
Error	8	102.15	12.77		
Total	15	2742.66			
$R^2 = 0.9677$, Adj. $R^2 = 0.9395$					

**Table A4: Analysis of variance (ANOVA) of the adjusted model for MY of Teak wood
during torrefaction**

	Degree of	Sequential	Adj. Sum	F-Value	P-Value
Mass yield	freedom	Sum of square	of square		
Model	7	3908.56	558.37	35.28	0.000
Linear	3	3818.78	1272.93	80.43	0.000
TT	1	3799.80	3799.80	240.10	0.000
RT	1	3.36	3.36	0.21	0.657
PS	1	15.62	15.62	0.99	0.350
2-Way	3	77.73	25.91	1.64	0.256
Interactions					
TT*RT	1	47.51	47.51	3.00	0.121
TT*PS	1	8.48	8.48	0.54	0.485
RT*PS	1	21.74	21.74	1.37	0.275
3-Way	1	12.06	12.06	0.76	0.408
Interactions					
TT*RT*PS	1	12.06	12.06	0.76	0.408
Error	8	126.61	15.83		
Total	15	4035.17			
$R^2 = 0.9790$, Adj. $R^2 = 0.9606$					

**Table A5: Analysis of variance (ANOVA) of the adjusted model for HHV of Teak wood
during torrefaction**

HHV	Degree of freedom	Sequential Sum of square	Adj. Sum of square	F-Value	P-Value
Model	7	92.0623	13.1518	86.34	0.000
Linear	3	91.7316	30.5772	200.73	0.000
TT	1	90.1076	90.1076	591.52	0.000
RT	1	0.4523	0.4523	2.97	0.123
PS	1	1.1718	1.1718	7.69	0.024
2-Way	3	0.2834	0.0945	0.62	0.621
Interactions					
TT*RT	1	0.1314	0.1314	0.86	0.380
TT*PS	1	0.0018	0.0018	0.01	0.916
RT*PS	1	0.1502	0.1502	0.99	0.350
3-Way	1	0.0473	0.0473	0.31	0.593
Interactions					
TT*RT*PS	1	0.0473	0.0473	0.31	0.593
Error	8	1.2186	0.1523		
Total	15	93.2809			
$R^2 = 0.9869$, Adj. $R^2 = 0.9755$					

**Table A6: Analysis of variance (ANOVA) of the adjusted model for EY of Teak wood
during torrefaction**

EY	Degree of freedom	Sequential Sum of square	Adj. Sum of square	F-Value	P-Value
Model	7	2044.23	292.03	8.26	0.004
Linear	3	1889.64	629.88	17.82	0.001
TT	1	1848.36	1848.36	52.30	0.000
RT	1	38.53	38.53	1.09	0.327
PS	1	2.75	2.75	0.08	0.787
2-Way	3	140.74	46.91	1.33	0.332
Interactions					
TT*RT	1	52.38	52.38	1.48	0.258
TT*PS	1	29.03	29.03	0.82	0.391
RT*PS	1	59.33	59.33	1.68	0.231
3-Way	1	13.86	13.86	0.39	0.549
Interactions					
TT*RT*PS	1	13.86	13.86	0.39	0.549
Error	8	282.72	35.34		
Total	15	2326.95			
$R^2 = 0.9186$, Adj.$R^2 = 0.8474$					

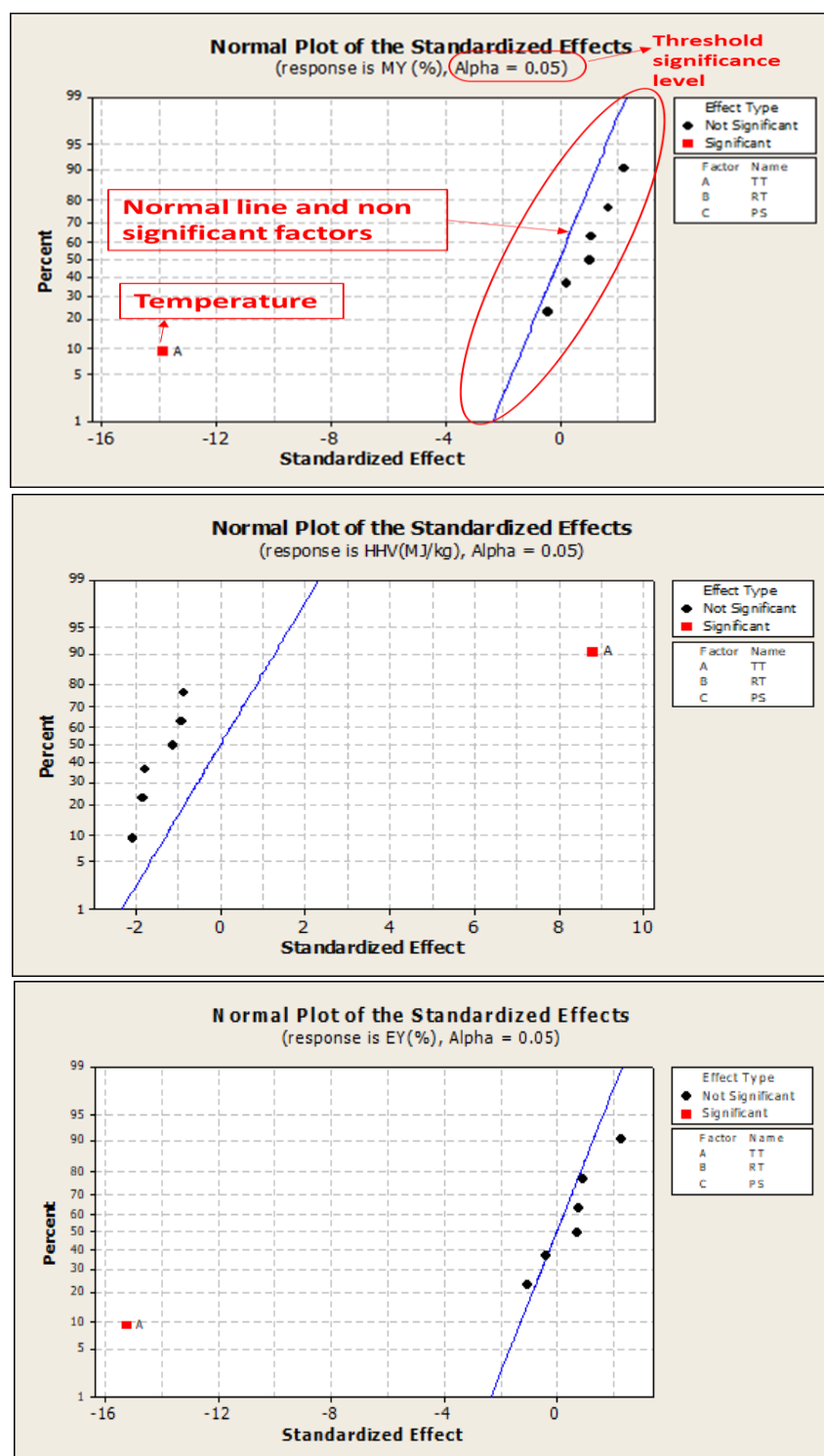


Figure A1: Normal Plot of the standardized effects of parameters on the responses of Melina wood during torrefaction

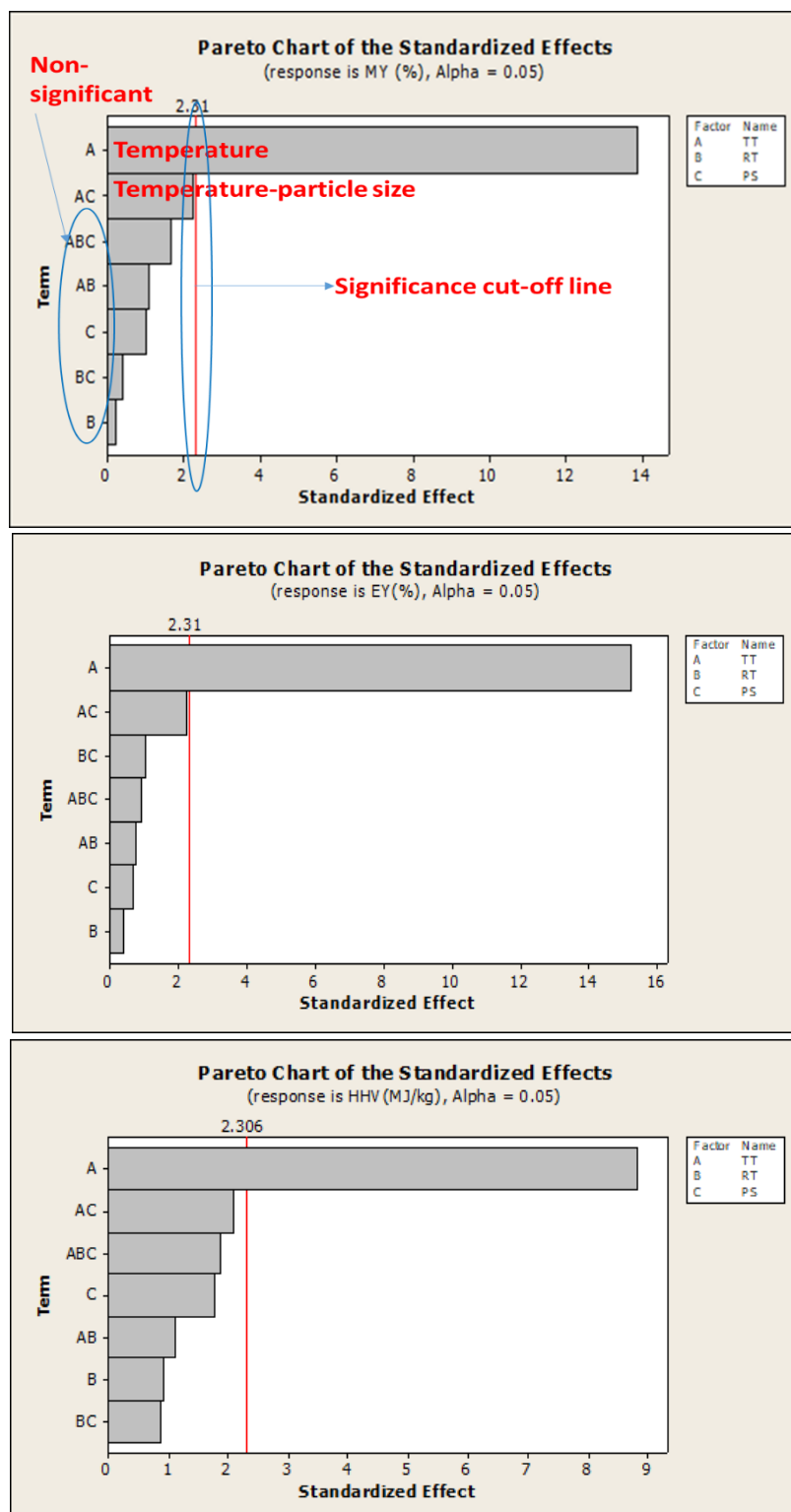


Figure 2A: Pareto plots of the standardized effects of parameters on the responses of Melina wood during torrefaction

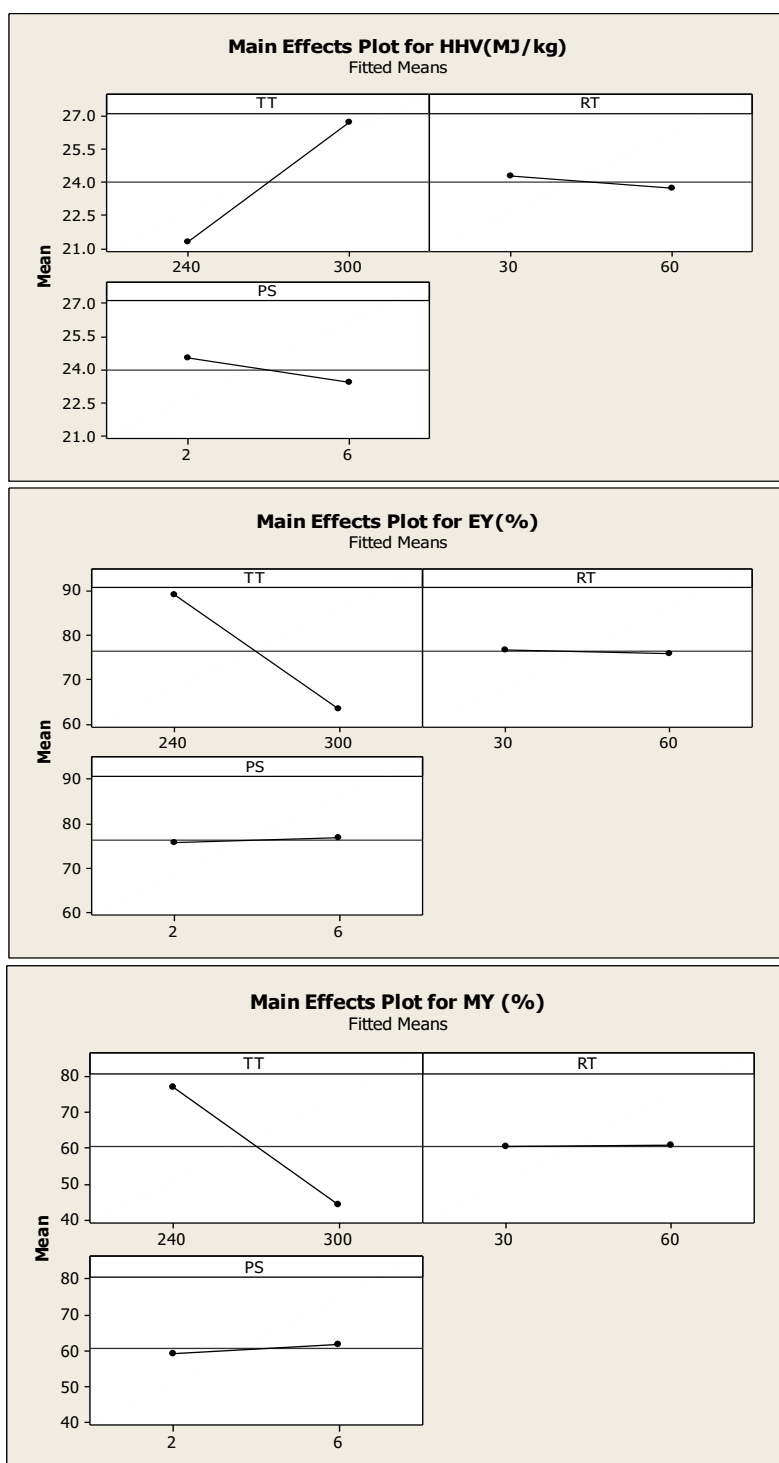


Figure 3A: Main effect plots of parameters on the responses of Melina wood during torrefaction

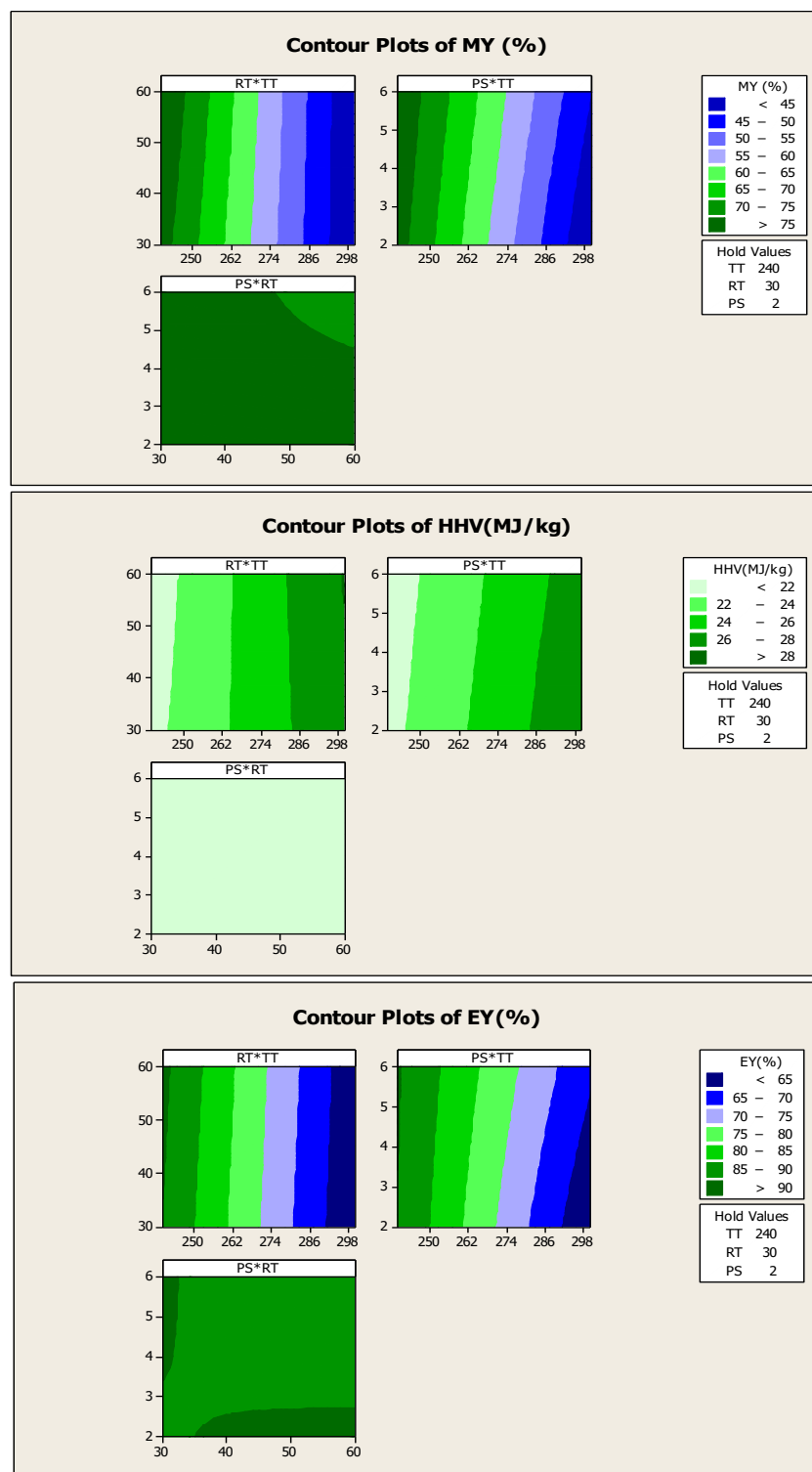


Figure 4A: Contour plots of the interaction effects of parameters on the responses of Melina wood during torrefaction

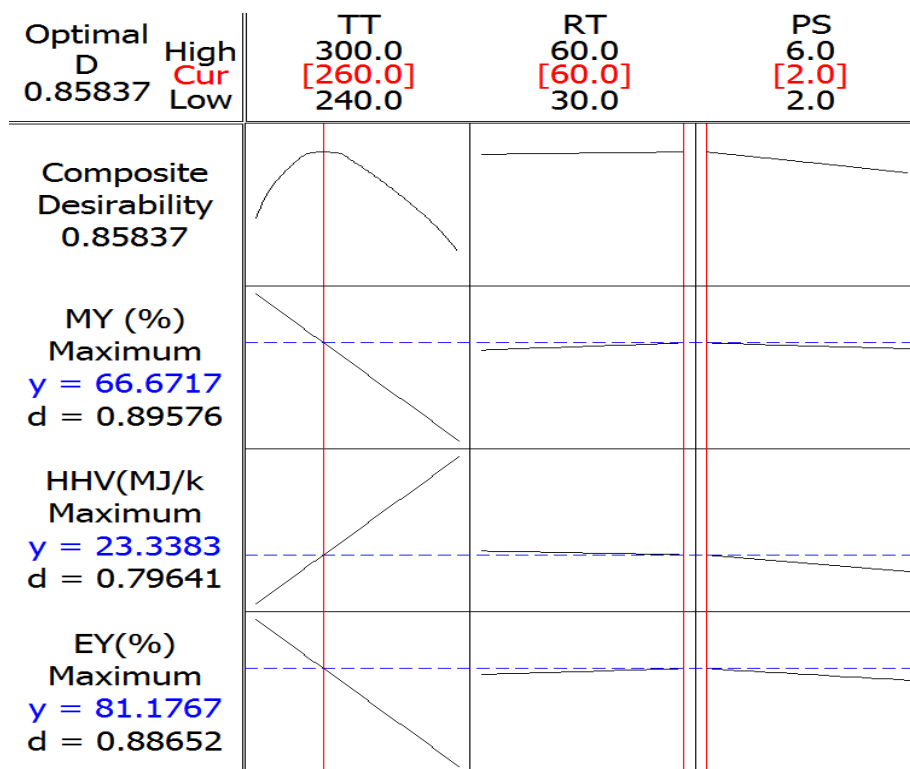


Figure 5A: Response optimization plot of parameters on the responses of Melina wood during torrefaction.