CHARACTERISTICS OF TORREFIED EMPTY FRUIT BUNCHES USING MICROWAVE HEATING

by

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A thesis submitted in fulfillment of the requirements for the degree of Bachelor of Applied Science (Material Technology) with honors

FACULTY OF EARTH SCIENCE
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2017

DECLARATION

I declare that this thesis entitled "Characteristics of torrefied empty fruit bunches using microwave heating" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : .....

Name : _____

Date : _____

ACKNOWLEDGEMENT

Alhamdulilah, first of all I would like to thank God, without his bless I will not completed this thesis**.** I also would like to express my gratitude to the personnel my main supervisor Encik Muhammad Iqbal Bin Ahmad for his encouragement, guidance and motivation. Not forgotten my co-supervisor also Encik Mat Sukhairi Bin Mat Rasat for his critics, trust, encouragement and attention in improving my research methodology.

I also would like to express my gratitude to the personnel of Faculty of Earth Science (FSB) and Laboratory staffs for their help, support, advices and knowledge. My special thanks also dedicated to Knowledge Management Centre, Universiti Malaysia Kelantan in helping supply the relevant literatures. I am also obliged to express my appreciation towards my beloved father, mother and sister for their enduring patience, moral and financial supports. Lastly, to all my friends, who endure together with me, a heartfelt gratitude to you. Thank you for everything. May God bless all of you.

ABSTRACT

In this study, response surface methodology (RSM) based on central composite rotatable design (CCRD) was applied to determine the optimum condition for torrefaction of empty fruit bunch (EFB) using microwave heating process. Three operating variables, namely sample mass (g), sample size (micron) and nitrogen gas flow rate (ml/min). RSM based upon CCRD can be applied to correlate the experimental microwave heating result. The predicted optimum conditions for the torrefaction process was at 15 g for sample mass, 500 micron for sample size and 30 ml/min for nitrogen gas flow rate, resulting in colours of sample, volatile matter content, density, fixed carbon content and moisture content of respectively. Physically, the colours of sample change to the dark brown and blacks after torrefaction process. Based on density values, raw EFB density is 0.265 g/cm^3 and torrefied EFB is 0.259 g cm^3.Torrefaction process can change the density value of EFB due the mass loss during the process. The moisture content result shows the decreasing values of sample with based on initial mass and final mass. Thus, for maximum production of torrefied can be obtain, with colour changing, low volatile matter content, moisture content and density via microwave heating system can be optimized using RSM.

ABSTRAK

Kaedah gerak balas permukaan atau reka bentuk eksperiment (RSM) berdasarkan pusat reka bentuk berputar komposit (CCRD) digunakan untuk mengetahui keadaan optimum bagi bahan bakar tandan buah kosong menggunakan process pembakaran torrefaksi microwave. Tiga pemboleh ubah digunakan dalam proses ini iaitu berat sampel (g), saiz sampel (micron) dan aliran gas nitrogen (ml/min). CCRD dalam RSM boleh digunakan untuk dikaitkan dengan keputusan pembakaran torrefaksi menggunakan mikrowave. Anggaran keadaan optimum bagi proses pembakaran ialah pada berat sampel 15 g, 500 micron saiz sampel dan 30ml/min untuk aliran gas nitrogen. Proses ini akan menghasilkan berbeza berdasarkan warna sampel, kandungan bendasing, ketumpatan, kandugan karbon dan kandungan kelembapan secara tidak langsung. Secara fizikalnya, warna sampel akan bertukar dari keperangan kepada hitam selepas pembakaran. Berdasarkan keputusan nilai ketumpatan, ketumpatan EFB asal ialah 0.265g /cm^3 dan EFB yang telah dibakar ialah 0.259 g/cm^3. Proses pembakaran ini boleh mengubah nilai ketumpatan sampel disebabkan mengurangan berat sampel selepas proses. Nilai kandungan kelembapan menunjukkan penurunan juga berdasarkan berat awal dan akhir sampel. Dengan itu, bagi memperoleh penghasilan maksimum bahan bakar berdasarkan perubahan warna, pengurangan penghasilan bendasing, kandungan kelempaban dan ketumpatan melalui pembakaran menggunakan mikrowave berdasarkan keputusan RSM.

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LIST OF ABBREVATIONS

Sin	Sine
d	Distance
hkl	Miller Indices
MC	Moisture Content
EFB_R	Empty Fruit Bunch Raw
Wt %	Weight Percentage
g	Gram
m	Meter
QC	Quality Check
XRD	X-Ray Diffraction
EFB	Empty Fruit Bunch
PKC	Palm Kernel Cake
PKS	Palm Kernel Shell
H/C	Hydrogen Per Carbon
O/C	Oxygen Per Carbon
VOCs	Volatile Organic Compounds
NO	Nitrogen Oxides
W	Watt
CAC	Cocoanut active charcoal
PCS	Pyrolysed corn starch
ANOVA	Analysis of variance
cm	Centimeter

LIST OF SYMBOLS

Λ	Wavelength
Θ	Theta
/	Divide
X	Multiplication
%	Percentage
=	Equal to
M	Micron
>	More than
<	Less than

CHAPTER 1

INTRODUCTION

1.1 Background Of Study

Biomass is a renewable, potentially sustainable and environmentally benign source of energy. According to Tye *et al*., (2011), biomass contribute about 12% of today's world primary energy supply, while in many developing countries, its contribution range from 40% to 50%. World production of biomass is estimated at 146 billion metric tons a year (Balat *et al*., 2005). Some farm crops and trees can produce up to 20 metric tons per acre of biomass a year. Biomass in definition is any organic matter such as wood, crops, seaweed, animal wastes that can be used as an energy source (Noor Azlina, 2013). Biomass is becoming an attractive energy resource as it offers benefits in terms of its potential sustainability and carbon neutrality (Smith *et al.*, 2016).

In the world, biomass commonly takes from waste product such as from animal or plant. The demands palm oil as biomass increase in various products such as biofuel and energy. Since 1961, Malaysian palm oil produces around 40% of the world's palm oil. By the richest flora and fauna in Malaysia, the palm oil gained many environmental issues from the production. The production of biochar using microwave were problem because the non-uniform bulk heating of dielectrics, by microwave irradiation (Arshanitsa *et al*., 2016).

Carbon, hydrogen, nitrogen, oxygen, and some other elements like sulphur and phosphorus together form most life on earth. Carbon forms a very large number of organic compounds because it can form strong bonds with itself and with other

elements. Because of the amounts of carbon living things have, all organic things are considered “carbon-based”. Also, each carbon atom can form 4 single covalent bonds. Carbon is the only element that can form long chain-shaped molecules. When iron is heated up with carbon, hard steel is formed. Carbon materials with a wide range of structural and morphological features, including carbon black (Sumita *et al*., 1991), carbon fibers (Vivekanandhan *et al*., 2012), carbon nanotubes (CNTs) (Andrews *et al*., 2004) and graphene (Du *et al*., 2012), have been extensively investigated as reinforcing materials in various types of polymer. Carbon materials are fabricated from various carbon-rich precursors, including graphite, coal, pitch, benzene, toluene and other gaseous hydrocarbons, which are derived from petroleum resources (Anstey *et al*., 2016).

Recently, carbon-based materials have attracted interest in oil spillage due to its low density, high porosity and large specific surface area. Expanded graphite is expected to intercalate a variety of organic and inorganic substances, which could make these substances stable in its interlayer. However, the removal of oil, special lubricating oil, by expanded graphite is not available in recent years (Yao *et al.*, 2016). Carbon accounting methods that include import and export of forest products were proposed early 1990s. This approach was suggested in the IPCC guidelines for National Greenhouse Gas Inventory (Houghton *et al.*,1997) to estimate carbon flow because of wood use in countries other than its origin. Winjum et al. (1998) suggested accounting carbon flow into the atmosphere because of combustion, use, and decaying in the consuming country.

1.2 Problem Statement

Torrefaction is a one process involve in biomass to produce biochar, bio coke and charcoal. Nowadays, the researches of biomass energy are growing to improve the productivity and reduce the releasing carbon dioxide gas into atmosphere for sustain the environment. The biomass research more focus on organics acid, hydrocarbon and syngas in pyrolysis. The structure and composition of biomass will change at torrefaction process (Ren *et al.*,2014). The lack of studies of the basics of heating of torrefaction by microwaves results in lack of clarity about the related physical phenomena and available options for controlling the characteristics of microwave-assisted processes involving carbon and its derivatives (Moon *et al.*, 2015).

1.3 Objective

The objectives of this research as follows:

1. To produce the torrefied material using microwave heating.

2. To determine the correlation of response surface methodology (RSM) with microwave heating process and analyse the element and phase of raw and torrefied materials x-ray diffraction (XRD).

1.4 Research Scope

The synthesis of element involve in the torrefied material from the empty fruit bunch (EFB) by using torrefaction process. The heating process using microwave heating to be analyse the torrefied material using Response Surface Methodology (RSM) and the selection of torrefied samples based on size and mass with analyse the EFB using XRD. The changing of torrefied and raw composition in the can be examine with XRD. The element and their phase on amorphouse or crystallinity in

raw and torrefied material by comparing based on XRD graph. The outcome of chemical composition that exhibit from raw and torrefied can be estimate with their crystallinity index by crystallographic analysis.

CHAPTER 2

LITERATURE REVIEW

2.1 Renewable Energy

Renewable energy is the energy used source from the nature that continuously replenished. The sources in the renewable energy such as from the Sun, wind, Earth's heat and plants. From the development of renewable energy had optimized the structure of power source and laws of power regulatory (He *et al*., 2016). The research of scientists in renewable energy have been looked to alternate from depends on fossil fuels and reduce greenhouse gas emissions into atmosphere (Bader *et al*., 2016).

To reduce the impact to the environmental, the used of biomass for energy purpose are growing well to provide energy using renewable resources (Nunes *et al*., 2016).

2.2 Biomass

Malaysia also has one of the world's richest flora and fauna. The palm oil industry has gained much negative attention in recent years because of the many environmental problems associated with oil palm expansion and palm oil production. This thesis aims at identifying and describing the multiple environmental consequences of palm oil production in Malaysia with particular focus placed on land use change over the last few decades. Drawn conclusions are that the growth of the palm oil industry is driven by various synergistic factors such as population growth, governmental policies and changed consumption patterns; and that the main environmental issue related to the palm oil industry is the land use conversion from forest to oil palm. Because of this conversion the palm oil industry contributes to biodiversity loss, soil degradation, water pollution and GHG emissions. Most

emissions to the air are related to forest fires that emerge during the clearing of land before establishing a plantation. Measures have been taken to prevent further loss of forests and to reduce pollution. These measures are, however, insufficient. Disagreement concerning what is to be considered areas of high (ecological) conservation value and what is to be classified as forest and non-forest aggravates a sustainable palm oil development. There seems to be an urgent need for comprehensive land use cover maps that detect areas of ecological importance. The importance of biomass is to reduce the waste in industries which can convert to the useful product such as fuel.

2.2.1 Functional of Biomass

From the biomass, it can be converted to solid, liquid or gaseous fuels. Other than that biomass usually used as energy or fuels that can be used to generate electricity from heating such as charcoal. In the same way, biomass can be used in variety field as means a basic life functions, direct combustion, liquids of fuels or gaseous fuel production.

2.3 Microwave Background

Torrefied biomass pyrolysis was performed in the batch microwave oven which was the same apparatus used for the biomass torrefaction process (Ren *et al*., 2013). The appearance of standing waves, the position of the maximum intensity in which it is not changed in time, the different polarity of biomass constituents and admixtures, and the restricted depth of microwave penetration lead to the non-uniform distribution of energy inside the biomass and therefore the appearance of the high temperature gradient. The microwave heating of wood and straw pellets in an immovable reactor using a microwave device has proven the above mentioned remarks. The one batch pellets differed strongly by their colour and physical

properties. The carbonized black colour pellets, together with the pellets in which moisture was not removed completely, were presented (Arshanitsa *et al.*, 2016).

The configuration of a microwave field in the used devices in terms of the standing wave ratio (SWR) has not been studied. SWR is an important parameter of an electromagnetic field, which shows how efficiently power is transmitted from the power source, through the transmission line (resonator) into the substrate (biomass) (Arshanitsa *et al*., 2016). Microwave radiation heat the absorber first, then the biomass samples were then be heated indirectly by conduction, results in the decomposition of the sample (Azim *et al.*, 2013).

There are two main contributions using the microwave field as a source of energy for heating and promoting the chemical reactions, namely, thermal and non-thermal effects. Based on Table 2.1, the thermal effects reveal themselves as the volumetric heating of the material because of the responses of polar molecules and ions to the changes in the direction of the electric field generated by the electromagnetic field at the microwave frequency. The non-thermal effect is classified as the chemical process acceleration that cannot be achieved by conventional heating methods at a given temperature. According to the literature, the non-thermal effect is connected with the decreasing of the apparent activation energy caused by electrostatic energy stabilization. Like thermal effects, the origin of non-thermal effects can be also explained by the response of polar molecules and ions to the electromagnetic field.

It is well known that, in a given temperature range, the extent of thermodegradation of the substrate is higher at a lower heating rate

Table 2.1 : The characteristics of biomass pellets are after microwave and convective heating (Arshanitsa *et al.*, 2016).

Parameters	Microwave heating			Convective heating		
	230°C	280°C	300° C	230° C	280°C	300°C
Wheat pellets						
Average heating rate (°C min^{-1})	22.3	22.6	22.8	10.3	8.6	8.4
Mass loss (%)	11.7	37.4	43.3	7.8	29.2	49.3
O/C (molar ratio)	0.60	0.42	0.36	0.62	0.48	0.31
Char yield at 600°C (%)	24.7	37.9	42.2	24.1	33.9	56.1
HHV (Mj kg^{-1})	20.5	23.7	24.9	19.6	22.2	25.6
Softwood pellets						
Average heating rate (°C min^{-1})	19.8	20.7	20.8	11.6	9.3	8.8
Mass loss (%)	9.1	22.3	30.0	7.7	18.4	38.6
O/C (molar ratio)	0.61	0.51	0.48	0.69	0.55	0.42
Char yield at 600°C (%)	23.7	29.8	33.2	18.7	27.3	40.6
HHV (Mj kg^{-1})	20.5	22.1	23.0	19.3	21.3	23.8

2.3.1 Torrefied

Torrefaction is also known as mild pyrolysis that occurs at relatively low temperatures (200-300°C) over moderate residence times (1-3 hours). Importantly, the torrefaction process begins with stages of initial heating, pre-drying, post-drying and intermediate heating designed to facilitate evaporation of water and attain a target torrefaction temperature. These stages may involve the consumption of external energy or auto-consumption of gaseous products to generate heat. Although torrefaction plants are generally located close to a source of waste or superfluous heat, added expense or diminished efficiency may result when this kind of heat is not available. This torrefied fuel is a solid, which has properties intermediate between biomass and biochar (Saddawi *et al*., 2012).

The yield of mass and energy from the original biomass to the torrefied biomass is strongly dependent on torrefaction temperature, reaction time, and biomass type (Bergman *et al*., 2009). Main products of torrefaction are fairly high levels of char (70%) and torrefaction gas (30%) (Van der Stelt *et al*., 2011).

Torrefaction gas contains large yields of products that can be condensed into liquids. These gaseous or liquid products are often used to provide heat for the torrefaction process, but can also be cleaned (as they will contain tars), collected and used elsewhere (Van der Stelt *et al*., 2011). Figure 2.1 shows the various degrees in charring of the bio-coals produced. The products at 143 and 190^{o}C resembled the original biomass (only a slight change in colour) and the product colour darkened only starting at 238 °C, resembling the regular appearance of char and thus indicating a change in composition (Cruz, 2012).

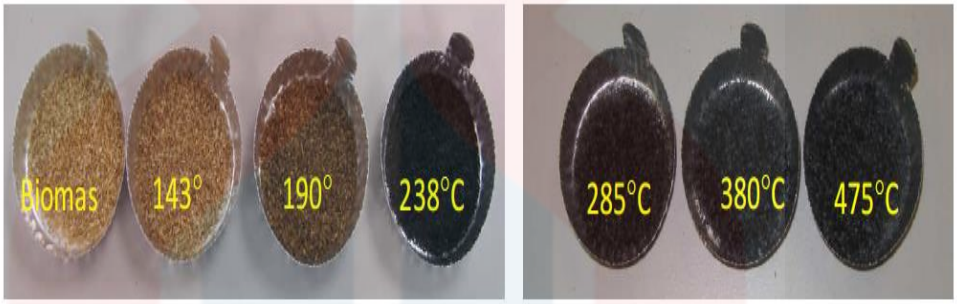


Figure 2.1: Torrefied products at the various temperatures (Cruz, 2012).

Solid products of torrefaction are currently being used as combustion, gasification and fast pyrolysis fuels, often as a replacement for coal or in co-firing (ibid.). In general, torrefaction can yield char that has an improved mass and energy balance over the original feedstock, resulting in improved heating values. In addition, torrefaction char has improved grindability, resulting in less energy use for size reduction before firing. The torrefaction char has lower equilibrium moisture content and, therefore, higher density.

2.4 Effect of Temperature and Time to Torrefied Materials

The torrefaction parameter was known from atmosphere, temperature and time which the torrefaction behaviour can investigate (Uemura *et al*., 2011.). At 200^{o}C the mass loss are 100% from normalized compare with mass variations after

drying. Below 200^{o}C some extraction compounds can be expected to happen and the mass losses below 200^{o}C have maximum 6% weight from the raw biomass. Temperature from 200 – 250^{o}C the acceleration increases of reaction rate with mass loss. In the range of temperatures, the mass loss will take 3%wt for all biomasses. From 250 – 300^{o}C the strong increase of mass loss of biomass have different mass losses (Rodriguez *et al*., 2016). The strong torrefaction with a serious weight loss occurred in the temperature regime above 275^{o}C. Therefore, torrefied biomass contains less moisture. Torrefaction conditions such as reaction temperature and time significantly affected the degree of biomass component decomposition (Ren *et al*., 2013).

The non-uniform bulk heating of dielectrics, including biomass, by microwave irradiation is a common problem. The appearance of standing waves, the position of the maximum intensity in which it is not changed in time, the different polarity of biomass constituents and admixtures, and the restricted depth of microwave penetration lead to the non-uniform distribution of energy inside the biomass and therefore the appearance of the high temperature gradient. The microwave heating of wood and straw pellets in an immovable reactor using a microwave device has proven the above mentioned remarks. The one batch pellets differed strongly by their colour and physical properties. The carbonized black colour pellets, together with the pellets in which moisture was not removed completely, were presented. The low thermal conductivity of pellets of 0.15-0.20 Wm^{-1} K^{-1} does not favour the rapid temperature annealing due to the conductive/convective heat transfer inside the pellets' bulk. The use of reactors rotating around their axial axis allows a considerable decrease in the non-uniformity of microwave heating. In all experiments, the pellets in each batch were of nearly the

same colour. Therefore, the temperature measured by the thermocouple inside the pellets' bulk mixed constantly by rotation was defined as the average temperature of the whole pellets' batch.

It was shown that oven dried wood and straw pellets effectively converted the microwave energy into heat due to the presence of polar groups with different polarity (hydroxyl, phenolic, carboxyl, carbonyl, ester and ether groups) attributed to the major constituents of lignocellulosic carbohydrates and lignin. The presence of water with high dielectric properties increases the heating rate only in the initial step of heating, strongly decreasing it as water evaporation begins. As a result, an oven dried wood and straw pellets were heated up to 300^{o}C faster than wet pellets. In the investigated upper temperatures range (120-320^{o}C), the microwave assisted average heating rates of straw pellets were somewhat higher in comparison with those of wood pellets (Arshanitsa *et al.*, 2016).

2.5 Mass loss

Power level in the microwave effect the mass loss of materials because the Thus, at microwave power of 100W with low temperature of 342^{o}C, insufficient energy to break the weak bonds caused incomplete release of volatile matter which results in higher volatile matter content of the char. However, at 300-1000 W, the maximum temperature achieved range, supplying enough energy to break the bond thus reduced the volatile matter during the pyrolysis process. From Figure 2.2, the volatile matter content remains almost similar for each power used may be due to the small maximum temperature difference between the three powers used. Comparing the trend of volatile matter content of the bio-char to the fixed carbon content, it was observed that increasing microwave power results in increasing fixed carbon content and calorific value of the char from 100 W to 300 W (Azim *et al*.,2013). The release

of volatile matters over the range of microwave power used results in the concentration of fixed carbon content in the bio-char, thus increases the calorific value. There are small gradual decreases of the ash content of the bio-char as the microwave power increase. The more volatile matter released the less ash content of the sample. Based on the quantitative and qualitative analyses of the biochar produced, 300 W was selected as the optimum power to be used for statistical study of the pyrolysis process using RSM. Biochar produced at 300 W was the highest in term of yield percentage that reached almost 40% from the initial sample mass, with almost comparable fixed carbon content, volatile matter content, calorific value and ash content in comparable to those at 600Wand 1000W. Production of highest quantity of bio-char, with highest calorific value and fixed carbon content and lowest in volatile matters content ensures the efficiency of the pyrolysis process in term of energy and cost saving (Azim *et al*., 2013).

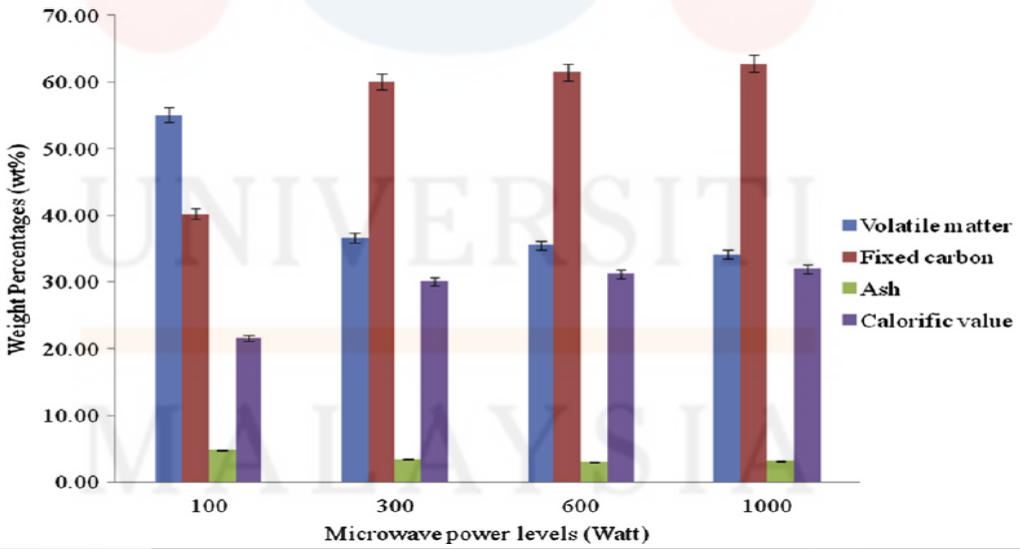


Figure 2.2: Microwave power level effect the mass production of biochar (Azim *et al*., 2013)

2.6 Moisture Content and Density

Table 2.2 shows the cotton stalks were dried, chopped, screened to particle sizes of 1, 5, and 10 mm and stored in air-tight containers for its use in study of the

effect of particle size on lignocellulosic activities. The cellulose, hemicellulose and lignin content of cotton stalks were found to be 37.68, 12.45, and 30.16% (w/w), respectively (Meehnian *et al.*, 2016).

Table 2.2: Effect of particle size and moisture content of cotton stalks (20 days) (Meehnian *et al.*, 2016).

Particle size (mm)	Moisture content (%)	Degradation (%)				Selectivity value
		Dry mass	Cellulose	Hemicellulose	Lignin	
1	45	5.47± 1.01	6.25± 0.75	5.68 ± 1.67	3.33 ± 1.53	0.53
	65	14.13± 2.53	12.66± 1.79	25.21 ± 3.41	24.78± 0.91	1.95
	75	15.13± 3.28	14.13± 2.74	32.93 ± 2.92	30.47± 3.31	2.15
	85	14.13± 1.10	15.88± 4.00	30.08 ± 1.31	32.43± 3.14	2.04
5	45	5.80 ± 1.05	5.66± 0.49	5.69 ± 0.99	3.43 ± 1.65	0.60
	65	13.53± 2.57	11.59± 2.08	24.69 ± 3.43	25.19± 2.01	2.17
	75	14.60± 1.00	11.70± 1.30	22.92 ± 1.65	29.88 ± 0.97	2.55
	85	15.53± 1.51	12.75± 0.92	24.18 ± 1.79	30.09 ± 1.47	2.36
10	45	4.60 ± 0.72	5.26± 0.59	4.10 ± 1.51	3.75 ± 1.23	0.71
	65	9.20 ± 2.27	9.89± 0.49	20.92 ± 3.20	19.33 ± 2.47	1.95
	75	10.33± 2.57	9.91± 1.09	18.93 ± 1.05	21.16 ± 0.12	2.13
	85	12.86± 1.01	12.19± 0.56	21.67 ± 3.01	24.90 ± 3.33	2.04

Under the investigated conditions, the average microwave assisted heating rate of softwood and wheat straw pellets at temperatures from 65^{o}C up to the maximal temperatures in the range of 120-320^{o}C was 20.0^{o}C min $^{-1}$ and 22.5^{o}C min^{-1}, respectively. Table 2.3 show the lignocellulosic cell wall of wheat straw underwent greater alterations during the microwave assisted heating in the temperature range of 230-320^{o}C than those of softwood in terms of the mass loss and carbonization of the residue (Arshanitsa *et al*., 2016).

Table 2.3: Effects of microwave assisted temperatures to the density (Arshanitsa *et al.*, 2016)

Treatment temperature (^oC)	Pellets' characteristics			
	Particles density (kg m^{-3})	Bulk density (kg m^{-3})	HHV (Mj kg^{-1})	Energy density (Gj m^{-3})
Non-treated	1150 ± 46	655	17.95	11.8
230	1050 ± 36	611	20.41 (20.50)	12.5
250	1006 ± 38	595	21.09 (21.14)	12.6
280	950 ± 42	529	22.14 (22.18)	11.7
300	860 ± 44	510	22.85 (23.09)	11.7

2.7 Response Surface Methodology (RSM)

RSM has important applications in the design, analysis and optimization of existing products and unit operations, its use decreasing thus the volume of experiments to select good production of product (Ares, 2014). The main idea behind RSM is the use of a sequence of designed experiments to obtain an optimal response and it explores the relationships between several explanatory variables with one or more response variable (Chen *et al*., 2015). RSM is a statistical tool for designing experiments, building empirical models and evaluating the effects of factors (Geun *et al*., 2011). To elaborate an experimental design, it was necessary to determine all the controlled parameters (or the factors), to which a set of distinct states (or levels) can be imposed (Rhazi *et al*., 2015). The response surface methodology have been designed to include factors with more than three levels which is low level (-1), medium level (0) and high level (+1) in which quadratic models can be established (Ahmed *et al*., 2016). In this study, the relationship between three parameters which is mass, nitrogen flow rate and particle size was performed. The objectives of this study include production of torrefied material using microwave then, to determine the correlation of response surface methodology (RSM) with microwave heating process. As the temperature of the material increases with time, all the material properties get updated influencing the power absorbed (Mishra *et al*., 2015).

2.7.1 RSM Model: Central Composite Rotatable Design (CCRD)

Central Composite designs can fit a full quadratic model. They are often used when the design plan calls for sequential experimentation because these designs can include information from a correctly planned factorial experiment. The central composite rotatable design used because the flexibility and efficiency. CCRD more flexible respect to the 2 way interactions because they comprised at the two level factorial (2^k), center points and axial points. By core 2^k factorial, the option to running a full factorial at the center can have. If all variables are assumed to be measurable, the response surface can be expressed as follows:

$$y = f(X_1, X_2, X_3, \ldots X_k) \qquad (2.1)$$

Where y is the answer of the system, and xi the variables of action called factors. The goal is to optimize the response variable (y)(Aslan, 2007). It is assumed that the independent variables are continuous and controllable by experiments with negligible errors and it also required to find a suitable approximation for the true functional relationship between independent variables and the response surface (Aslan, 2007).

The predicted response in CCRD was capable to be estimated with equal variance based on the direction from the center of design space because the axial outside the design space box defined by the factorial part of design which the CCRD can produce rotatable. The relationship between responses (calorific value, fixed carbon content, volatile matters content and yield percentage of biochar) and three independent factors (reaction time, sample mass and nitrogen flow rate) were investigated in this study. Designed variables suggested by the software are shown, while the experimental and predicted results at each point obtained.

2.8 X-Ray Diffraction

X-ray diffraction (XRD) characterization was used for the structural determination of the powder samples and the pattern was analysed and indexed using powder X-ray software (Chauhan *et al*., 2013). From the pattern of XRD, the machine can analyse the mixture involve in the crystalline phases. XRD also can get quantitative phase analysis which we can know each crystalline phases in the mixture.

The diffract light from x-ray makes the wavelength of x-ray are same with the distance between atoms. Then, the scattering of x-rays from the atom will produce diffraction pattern on the graph which contains the information about the atomic arrangement in the sample within the crystal. For the amorphous pattern the XRD not produce diffraction pattern because amorphous materials do not have a periodic array with long-range.

The position of the diffraction peaks are determined by the distance between parallel planes of atoms. Bragg's law calculates the angle where constructive interference from x-rays scattered by parallel planes of atoms will produce a diffraction peak. Miller indices (hkl) are used to identify different planes of atoms. From the observation diffraction peaks, it can be related to planes of atoms to assist in analysing the atomic structure and microstructure of a sample. When analysing XRD data, the results will be inform the trends corresponding to directionality in the crystal structure by analysing the Miller indices of diffraction peaks.

In most diffractometers, the x-ray wavelength l is fixed. Consequently, a family of planes produces a diffraction peak only at a specific angle 2theta.Here the formula to calculate from Bragg's law:

$$\lambda = 2d_{hkl} \sin \theta \qquad (2.2)$$

λ is the wavelength, θ is the theta. Software Diffrac Eva identify phase of X- Ray diffraction pattern will be used to perform qualitative and quantitative analysis of the sample.

Based on Figure 2.3, two types of biomass carbon such as CAC and PCS. The CAC was fabricated by pyrolyzing coconut shells, and the PCS was prepared by pyrolyzing fresh corn starch in-house at 500^{o}C in pure N^2 atmosphere for 30 min. Their crystal structure, degree of graphitization and specific surface area and microstructure were examined by X-ray diffraction (XRD) (X'Pert PRO, PANalytical B.V.). CAC and PCS carbon powders were examined by X-ray diffraction, the results are shown in Figure. 2.5. Both CAC and PCS demonstrated characteristics of amorphous structure featured by broadened X-ray diffraction peaks (Figure 2.3) (Duan *et al*., 2016).

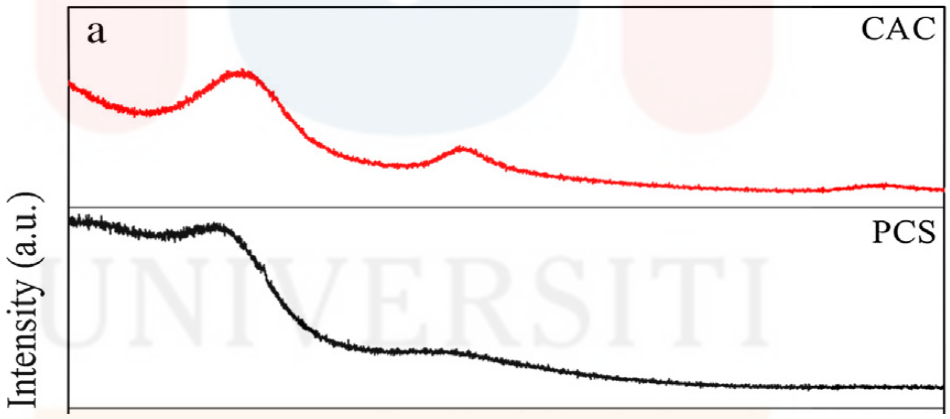


Figure 2.3: XRD patterns of powdery CAC and PCS carbon fuels (Duan *et al*., 2016).

2.8 Summary

The microwave heating process for torrefaction shows the can be effect the production of product and environment. By using microwave the process can be controlled in many variables such as time, mass, temperature and power level. The production with microwave can produce more torrefied material compare others

reactor because the consistency dielectric. The correlation for optimum sample can be done with RSM. The model use was CCRD because it have flexibility and efficient than other model. XRD used for structural analysis which can determine the change of torrefied phase by increasing of time and temperature. It also can determine the carbon element in the torrefied material that exists. We can correlate the torrefaction process input from the output product by optimization RSM and can analyse the phase of torrefaction with different residence time and temperature.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

Torrefaction process was conducted using microwave heating because the less producing the volatile matters and had been used in many sectors of industries as a means of volumetric, instantaneous and selective in heating process (Wang *et al*., 2015). EFB will be used as the material in torrefaction process. The material collected at Kelantan. The equipment for measuring weight is analytical balance. Analytical balance use because the accuracy of measurement are good compare to conversional balance. The sample dried in the oven. After the drying process, the samples were heated in the microwave for torrefaction process. The sample was heated in different temperature but same power level or Watt (W).When the sample are ready for analysis, the technical equipment used are RSM and XRD .

3.2 Materials and Sample Preparations

The raw materials collected from the agriculture waste. The sample will be drying in the oven at 120^{o}C in 2 hours to reduce the moisture content (MC) in the sample. The sample will be grinding by using grinder at the wood laboratory. Reason use grinder to make the form of raw EFB to powder. The grinder located at the workshop. The grinder has the siever size then, the siever sizes that used were 500 micron and 250 micron. The siever was put in the grinder machine grind the sample into small size based on the siever. The zipping plastic bag at the bottom grinder machine and have to tie because the sample flow out from grinder. Grinding the sample took about an hour or half. Almost two bags of raw EFB had been grinded.

After grinding process took place the sample divided into the different size. Collective in different size of sample did to choose did to choose the best size of sample size in produce torrefied materials. The grinding process did at the workshop. Size of sample divided into three sizes in micron such as 250,500 and 750. The material sieved tools using the laboratory grade stainless steel with shaker. The used of sieving to get homogenous size of sample before heating process.

The sieving sample were pack in different zipper bag. Sample placed in locker at the laboratory. Before heating process the sample were weight based on each table. For drying process of raw sample using moisture analyser, the sample put in sterile container before drying.

Then, microwave heating process for the first table parameter used 10g mass of sample and 500 micron for size. Table two use different size and mass in each heating process. Third table had been decided based on table two result which use 15g mass of sample and 500 micron size of sample. The sample put into crucible for heating process in microwave. After took the sample in zipper bag, the sample in the bag was pack back and stored in locker to avoid the absorption of moisture content in the sample.

3.3 Method

In this method before running selected mass and particle size for torrefaction process which is the setup of microwave. After selection of power level, there was statistical analysis of response surface methodology for optimization torrefaction process between mass, nitrogen flow rate and particle size. Analysis by x-ray diffraction was the last stage in this study.

3.3.1 Moisture Test

Moisture test was conducted by moisture test model, Metler Toledo HB43-S Halogen. The moisture analyser usually used in addition to the oven method. In oven heat energy is transferred by the flow of air, which establishes equilibrium between the sample temperature and the surrounding temperature. For calculate the moisture content in the sample, this formula will be use:

$$Moisture\ content\ percentage\ (MC\%) = (\frac{weight\ before - weight\ after}{weight\ \ before})X\ 100 \quad (3.1)$$

Figure 3.1: Moisture analyser

3.3.2 Microwave Set Up

The setup of microwave involves nitrogen tank, temperature controller, crucible, pump and cooling system. Open air was good place for the heating process because the air can flow and not produce unhealthy environment. The use of fan and fume in the laboratory can help the smoke produce from microwave exit while the windows and door keep open during heating process. The use of nitrogen gas to reduce the weight loss compare other gas during torrefaction process based on Eseltine, 2011. Then, the used of alumina crucible for place the sample in the microwave because the resistance of heat properties. Cooling system involve two glass bottles continued the tube with the microwave. The functions of tube attached to transfer the gas or liquid in the microwave during heating process to the bottle.

The amount of liquid and gas released can be calculated based on amount liquid in the bottle after the heating process. The formula used is to calculate the moisture content. Then the sample will be dividing into 4 groups with 2 samples for each group which it will be heating in different temperature from the microwave. The sample will be mark on the beaker with the temperature they will be heated with different power. The power will be used are 150Watt (W) and 300W. Sample A for 200^{o}C, sample B for 250^{o}C and sample C for 300^{o}C**.** Here are microwave will be used in heating process. Figure below are microwave set up which there have nitrogen gas, temperature controller, cooling system and pump. In the microwave, there have chamber which can hold the sample and transfer the heat energy in the microwave. The molecule in the microwave will collide and have kinetic energy then, produce heat energy. Figure 3.2 show the microwave set up system for torrefaction process.

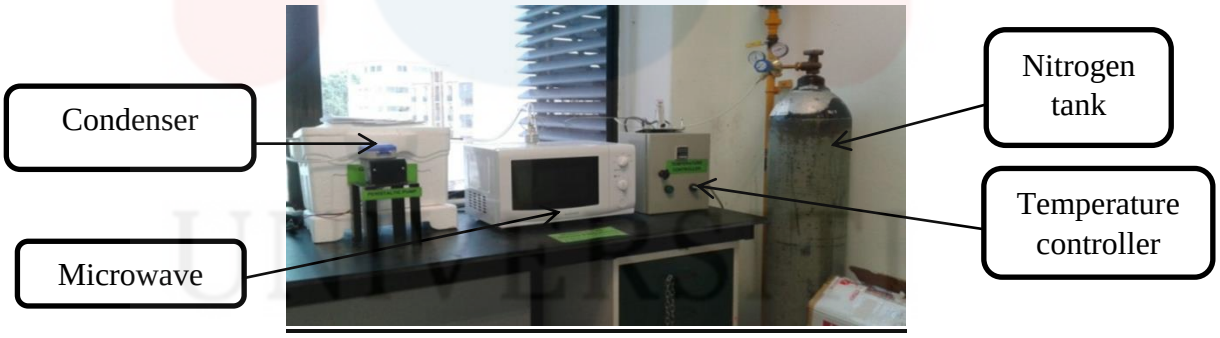


Figure 3.2: Microwave set up

3.4 Response Surface Methodology

RSM was use for the selection of size, mass and nitrogen flow rate. The optimum biochar can be determined from the run of experiment for power level. The data put in the CCRD. The graph and selection of sample can be analysed from the mass, nitrogen flow rate and particle size of sample. Design of experiment (DOE) was design to reduce the number of experiments. It can results the advantages in

reducing used raw materials, gas and time. DOE offers optimization, mixture designs, combined designs and comparative tests (Hossain *et al*., 2016). The used of central composite rotatable design (CCRD) due the information provided as much less number of experiment (Azim *et al*.,2013). The experimental design consist 20 experiments.

Each line of an experimental design represents the experimental conditions of an experiment, and it is represented by a coded variable, of which the values correspond to the levels of the factor which it is associated (Mathieu *et al*.,2000). The lower and higher level for mass is 5 and 15 g, nitrogen flow rate is 5.0 and 45.0 ml/min and particle size is 250 and 750 micron respectively. From Table 4.6, mass represent (A), nitrogen flow rate (B) and particle size (C).

The weight (Y) is selected as response. From the final equation (4.1) shown fitted results into order quadratic model. CCRD consisting of eight factorial points, six axial points and six central that rendered a total of 20 runs of experiment was used to analyse the data acquired from the experimental runs (Azim *et al.*,2013). Design Expert 7.1.6 software was used to determining and optimizing the statistical analysis of the equations.

3.4.1 Optimization Analysis

The condition for three variables, mass in gram (A), nitrogen flow rate in ml / min (B) and particle size in micron (C) where use from statistical analysis. The design of experimental used for available combination of factors that satisfy the requirements (Azim *et al*.,2013).

3.5 Mass Loss

Mass losses were taken after the torrefaction process done. There is formula used to calculate the mass loss.

$$Mass\ loss\ percentage(ML\%) = (\frac{weight\ before - weight\ after}{weight\ of\ before})X\ 100 \quad (3.2)$$

3.6 Density

Density for every sample used same size sterile container. Samples put into the sterile container after cooling process at the microwave. The density was calculated to know the decreasing of sample after torrefaction process. The denser the sample value, increase the moisture content percentage value. There is density formulas used:

$$\text{Density (D)} = (\frac{\text{Mass of sample}}{\text{Volume of sample}}) \quad (3.3)$$

3.7 X-Ray Diffraction Set Up

From X-Ray Diffraction D2 PHASER will be analysis the forms of carbon in samples, crystal plane and size, single phase, composition of element, mixture and of sample can be observe from the XRD diagram of sample. XRD are chosen to analyse sample crystallinity phase and crystalline species in the raw and torrefied material and know the switching of composition in the sample.

The sample will be prepared in the powder form. Figure 3.3 show the XRD machine will be use in analyse the graphite in the sample.

Figure 3.3: XRD D2 Phaser

The sample will be prepared before place in the XRD. For XRD the sample preparation require the a flat plate sample for XRD should have a smooth flat surface if the surface is not smooth and flat, x-ray absorption may reduce the intensity of low angle peaks parallel-beam optics can be used to analyse samples with odd shapes or rough surfaces. Obtain a few tenths of a gram (or more) of the material, as pure as possible. Grind the sample to a fine powder, typically in a fluid to minimize inducing extra strain (surface energy) that can offset peak positions, and to randomize orientation. Powder less than ~10 μm (or 200-mesh) in size is preferred. Then, place into a sample holder or onto the sample surface. Pack the sample powder into a sample holder. Then, smear uniformly onto a glass slide, assuring a flat upper surface. Pack into a sample container. The sample can sprinkle on double sticky tape. Typically if the substrate is amorphous to avoid interference the care will be taken to create a flat upper surface and to achieve a random distribution of lattice orientations unless creating an oriented smear.

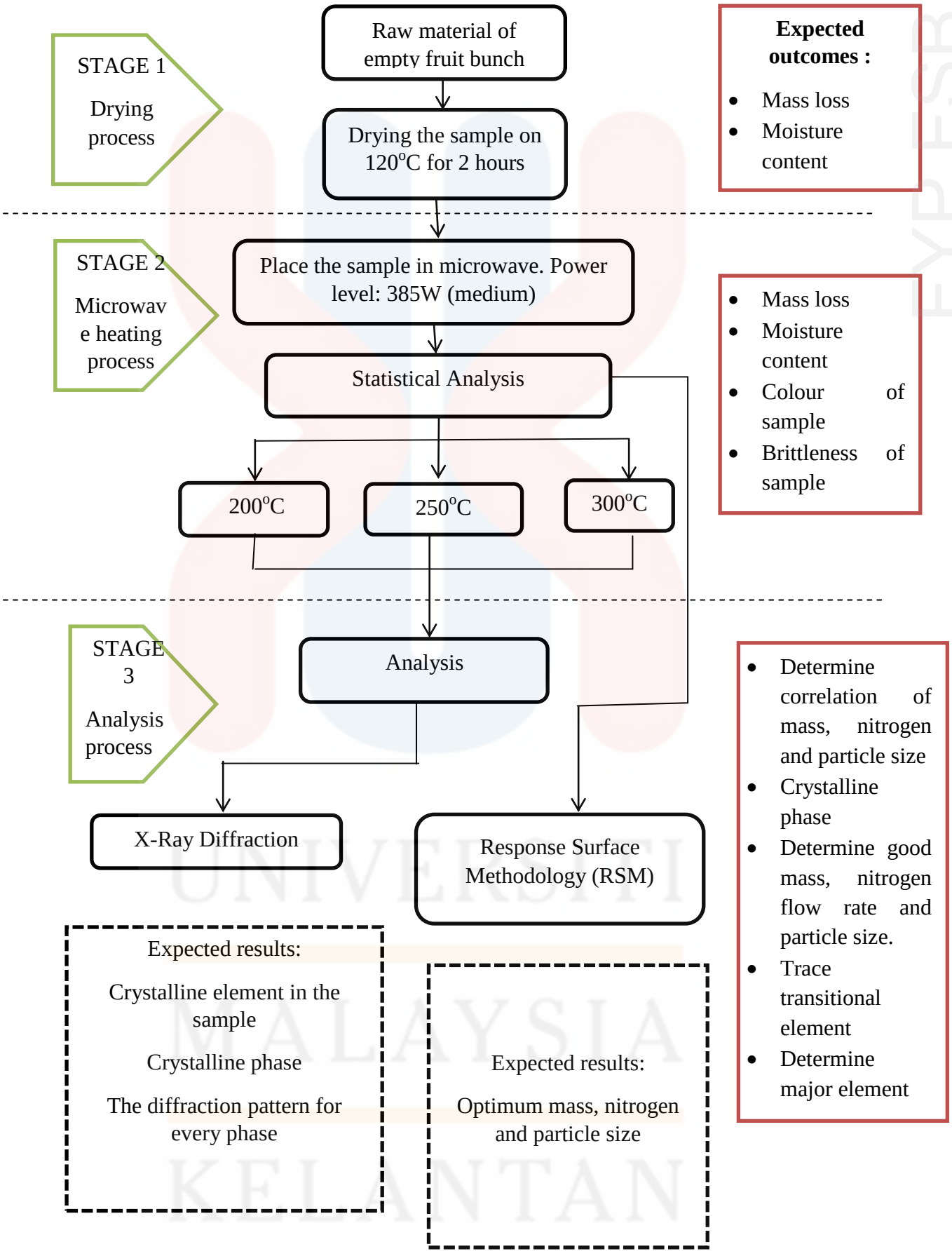
Then, the sample must densely pack and the sample can be randomly oriented grains/crystallites and grain size less than 10 microns. The sample must be homogeneous. The sample should be <10μm in size to get good powder statistics. Then, the samples were ready to analyse into XRD. The radiation must be check before run the sample by using remote. The XRD machine will be switch off the high voltage to open the door. Then, open the instrument door by sliding it up. The sample will be drop down the spherical handle of the sample holder lift. The sample will taking and insert it into the sample position of the sample holder. The sample will lift back into the sample measurement position by pulling up the spherical handle. The instrument door will close by sliding it down and lock by putting the high voltage on.

The sliding front door of the instrument is routinely opened to insert and change samples. LED light will on the top of screen when the samples are running. It will take 8 minutes per sample to finish the rotating. The software application used to run the analyser that automatically stores data acquired during an analysis in comma-delimited ASCII text format for later computation, display, and printing. Then the sample data will be check. If any errors are found, the sample will be return data to analytical chemist for corrections. The data can print out the data. Shut down the computer.

X-ray "Off" will press button on the screen to discontinue the generation of x-rays. The X-ray indicator on the upper section of the cabinet and on the display panel will turn off. After done run, the XRD must be turn off the circuit-breaker on the back of the rear of the MiniFlex II main body. Then, the computer will turn off. The chiller will leave on. The XRD uses x-ray radiation. Radiation safety training is provided and no one who has not had this training will be given access to the instrument. For the personal protection the safety glasses and protective gloves are recommended whenever reagents or samples are handled. The radiation will be checked of x-ray before run the machine with server meter. XRD was done.

3.8 X-Ray Diffraction Analysis

The sample will be analysing into two part which qualitative and quantitative analysis. The analysis will be use DiffracEva software to interpret the graph of XRD. The qualitative analysis will be analysis based on the powder diffractogram. The peak position, intensities, peak widths and background shape are in the qualitative analysis. Then for the quantitative analysis, the sample will be analyse the intensity of the x-rays diffracted by a certain phase which in the phase mixture.


STAGE 1
Drying process
Raw material of empty fruit bunch
Drying the sample on 120°C for 2 hours
Expected outcomes :
Mass loss
Moisture content
STAGE 2
Microwave heating process
Place the sample in microwave. Power level: 385W (medium)
Statistical Analysis
Mass loss
Moisture content
Colour of sample
Brittleness of sample
200°C
250°C
300°C
STAGE 3
Analysis process
Analysis
Determine correlation of mass, nitrogen and particle size
Crystalline phase
Determine good mass, nitrogen flow rate and particle size.
Trace transitional element
Determine major element
X-Ray Diffraction
Response Surface Methodology (RSM)
Expected results:
Crystalline element in the sample
Crystalline phase
The diffraction pattern for every phase
Expected results:
Optimum mass, nitrogen and particle size

Note :

Stage 1: Sample preparation (process include collecting, drying followed by experimental set up for microwave reactor) and processing oil palm EFB with variable parameter such as torrefaction temperature, residence time and heat input.

Stage 2: Power level selection and statistical analysis using response surface analysis.

Stage 3: Analysis, evaluation and comparison of the obtained experimental data

Figure 3.4: Flow chart torrefied material production analysis in torrefied material

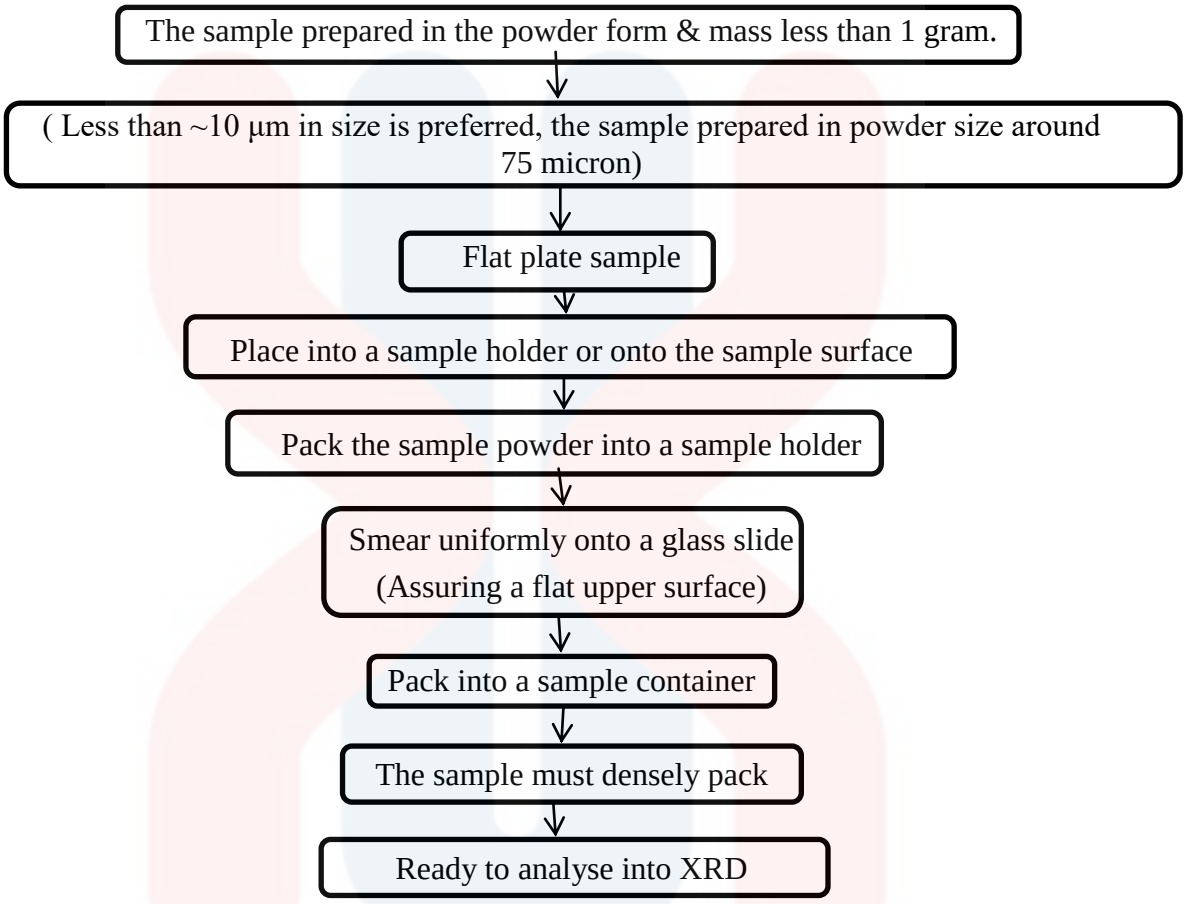


Figure 3.5: Flow chart for sample preparation in XRD.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Overview

The using of empty fruit bunches (EFB) for the sample because the good etiquette in biomass for produce manure, palletization and value added products. The total EFB is more than 10 million tons per year. The rest of EFB are abundant when only 10% was used (Ngadi *et al.*, 2014). Contain of EFB fibres was about 40% to 60% cellulose, 15% to 25% was hemicellulose then 12% to 20% of lignin. The highest composition of cellulose compare to others plant fibres such as bagasse and corn (Ching *et al.*, 2014)

Physical properties were looking at characteristic of EFB that were analysed in mass loss, moisture content and density. The EFB data was collected for comparison between raw and torrefied samples. The data were calculated in Chapter 4 based on the formula provided in Chapter 3. These data also calculated to compare the torrefied samples between three variables in mass (g), time (minutes) and temperature (^{o}C) by using microwave heating process. Microwave heating process was used for the torrefaction process because the microwave can change the parameter in the temperature, power level and time. Selection of parameter based on the correlation of RSM result before the optimum production torrefied sample chosen.

4.1.1 Moisture Content Analysis (MC%)

Moisture content percentage (MC %) for drying raw EFB were high. The moisture content loss during analyse shown 1 day drying low than the 2 days drying. Table 4.1 shows MC% increase with small size (250 micron). The high surface area

in the sample makes the exposed of loss moisture high compared to low surface area. The highest lignolytic enzyme activities, optimal lignin degradation 29.88 ± 0.97% (w/w) with cellulose loss 11.70 ± 1.30% (w/w), were observed in cotton stalks at particle size 5 mm with 75% moisture content after 20 days (Meehnian *et al.*, 2016). The change in biomass size distribution associated with moisture content, possibly due to particle aggregation and the large differences in the biomass size distributions for the 200-400 micron particle size do not have a strong effect on flame length (Pollard, 2015).

Table 4.1: Moisture content percentage (MC%) after using moisture analyser.

Day \ Sample size	250 micron	500 micron	750 micron
Sample (Day 1)			
1	9.58 %	9.46%	9.27%
Sample (Day 2)			
2	11.24%	11.04%	10.78%

From Figure 4.1, the moisture content percentage shows the 1 day drying sample was low moisture loss percentage than 2 day samples. The lowest moisture content percentage was 750 micron size 9.27%. Then, the highest moisture

percentage for 1 day drying was 250 micron size 9.58% because the surface area exposed under thermocouple were large compare to 250 micron. 2 days drying sample for the lowest moisture content percentage was 750 micron (10.78%). The highest loss moisture content percentage is 11.24%. Cellulolytic enzyme activity increased with decrease in particle size and increased moisture content (Meehnian *et al*., 2016).

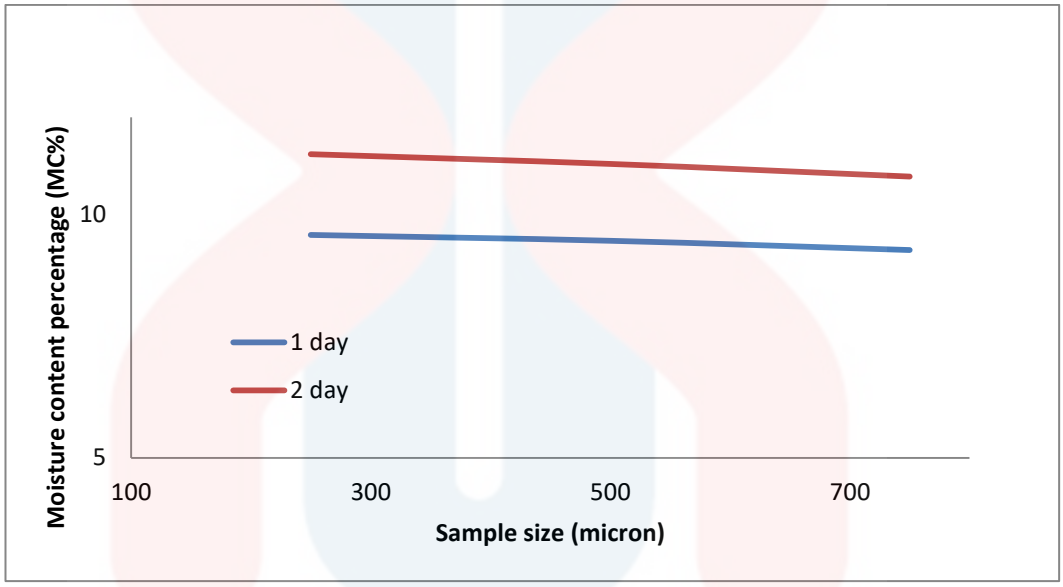


Figure 4.1: Effect of drying sample after heating process using moisture analyser

4.2 Effect of Heating Rate on Different Microwave Power

Figure 4.2 shows the result heating rate against power (Watt). The EFB were handling on the different power level. The size of sample was 500 micron. The ability of the sample to increasing temperature per minutes during conducting heating process can be defines from heating rate. The heating rate increase by increasing of microwave power level was stated from Huang,Chiueh,Kuan & Lo (2016). From the figure shows the lowest of heating rate is 100 W at 2.86^{o}C /min. Then the highest heating rate was is 700 W at the 41.6^{o}C/min.

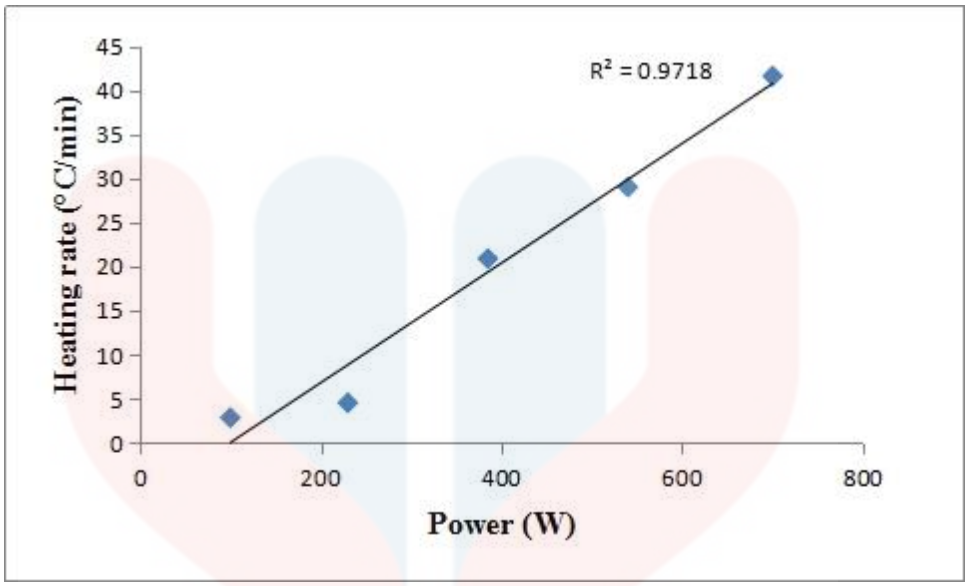


Figure 4.2: Heating rate effect power selection

4.3 Temperature and time

The Figure 4.3 shows the result of temperature profile of torrefaction process. EFB samples with 500 micron size were heated by microwave and different power level. Power level that used in during heating process were 100 W, 230 W, 385 W, 540 W and 700 W. The nitrogen flow rate was 15 ml/min purged into the microwave to maintain inert atmosphere. Heating process was run 40 minutes per power level. Different power level can effect the temperature reading of samples and the selected of best power level from the pattern at Figure 4.4. Liu, Jiaqiang, Deng, Xie & Zhu (2016) stated from 400 to 700 W, there were three stages involved such as slow temperature-rising, a rapid temperature-rising stage and a slow temperature-reduction stage. The higher power such as 385 W,540 W and 700 W, shows the trend of slow temperature rising from minutes 1 to 10,the followed with rapid temperature rising and reduction state or named cooling state.

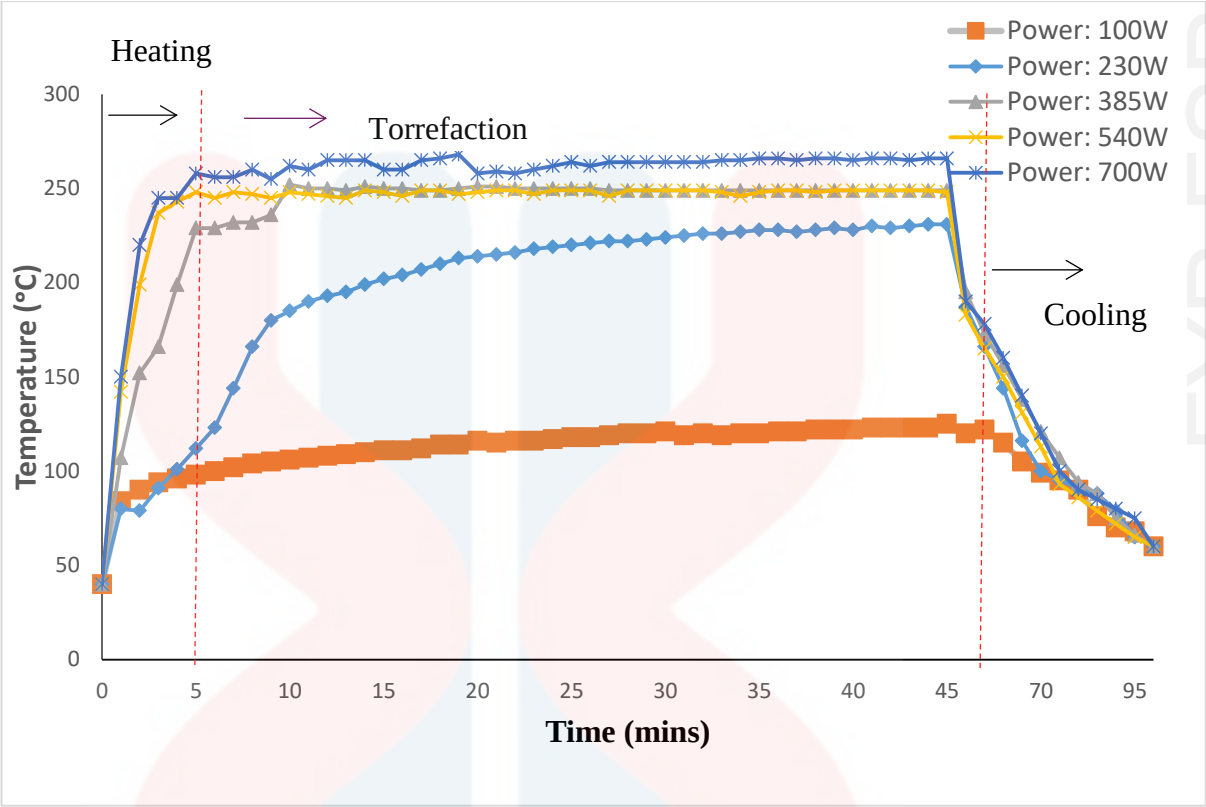


Figure 4.3: Temperature versus time

The power used at low rate such as 100 W and 230 W, the trend of the temperature shows the steps two which the slow temperature rising then temperature reduction state. The insufficient of torrefaction power for heating process was the low power level because the lower of heating value stated by Huang (2016).

Conclusion for selected power level was 385 W for this study because the achievement for all criteria in torrefaction process. 385 W achieve the optimum temperature for three stages in heating rate. The torrefied sample produce after heating process not include ashes phenomena produce after heating process. The ashes occur in white colours as a residue in powder form. Ash occurs because the overload of heating rate during the process.

4.4 Magnetron

Figure 4.4 shows the magnetron movement of electron in the microwave during torrefaction process. The magnetron in the microwave were generate at 2.45 GHz wave discharge operated at power level of 50-1000 (Yeon *et al*.,2017). Frequencies in this study nearly close stated by Yeon (2017). The higher electron produce in the microwave means the higher power level used in the process. The figure shows on/off light at y-axis in the microwave during torrefaction process means a movement of electron inside the microwave. At low power level (100 W), shows the electron move in similar timing during process. The peak 'on' to 'off' was hold for 1 minute. The 100 W cannot be selected because the low heating rate. Then, 200 W shows the peak have many peak and not consistent because the only hold for few seconds. In this process shows the electron movement to low and not suitable for heating process. For 540 and 700 W, the 'on' to 'off' peak hold for long period. 700 W peaks take around 5 minutes in the process. For the higher electron produce during the delay can make thermal shock for the crucible, ashes phenomena and thermal expansion after heating process. The selected power for this study was 385 W because the 'on' peaks take around 1-2 minutes. The production for electron in the microwave high same at 700 W but the problem for thermal shock, thermal expansion and ashes phenomena can be avoided.

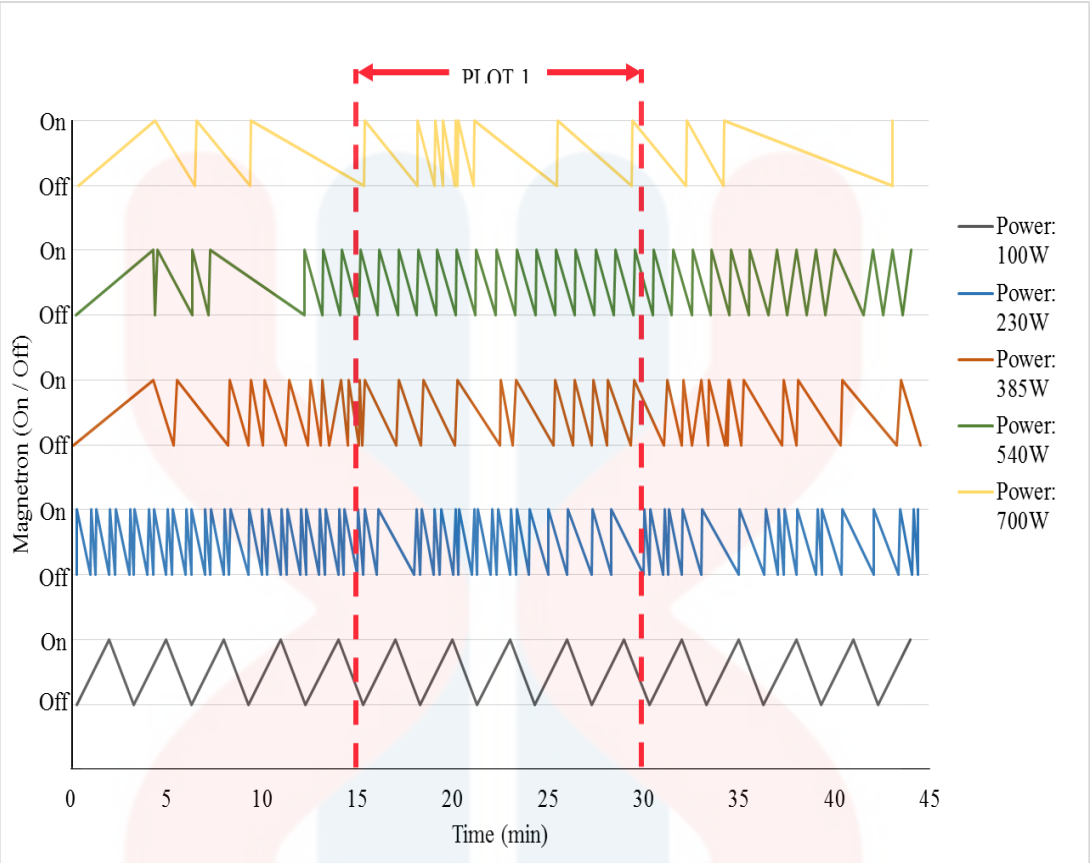


Figure 4.4: Magnetron effect on power selection

4.5 Solid, liquid and gas

Figure 4.5 shows the comparison between yield of solid, liquid and gas after heating process by the microwave. The percentage of solid, liquid and gas were affected by the power level of microwave. The minimum power level was 100 W and the highest power level was 700 W. from the result shows the trend of solid with increasing of power level made the decreasing of solid percentage because the loss of moisture content and decomposition of cellulose, hemicellulose and lignin in the samples stated by W.Chen and Kuo(2011). The highest percentage in remaining solid produce after heating process was 100 W around 78%.The lowest remaining solid was at 700 W with the 22%. The microwave power at 450 W used in 30 minutes formed 23-33% solid yield (Lin,2015). From the figure, the samples at 540 W with

45 minutes remain 20% of solid similar with previous research. The different trend of solid, liquid and gas percentage depends on increase of power level. The percentage of remaining liquid in at the 100 W was 7 %. Then, 700 W of power level shows the remaining liquid was 20%. The liquid (water) were released as major condensable product. The degradation of acetoxy and methoxy-group in xylose unit present hemicellulose fraction shows by releasing of water in the process. The increasing of power and temperature in the process make the increasing of condensable product after heating process. Remaining of gas percentage increase because use of power from 100 W to 700 W. The lowest percentage of gas was 15.4% at 100 W. The highest percentage for remaining gas was at 700 W around 50%. The major gasses formed were carbon monoxide (CO) and carbon dioxide (CO_2). The increasing ratio of CO and CO_2 by the increasing of temperature and power level due the degradation of lignocellulose (Wright *et al*.,2011). Non-condensable product such as hydrogen and methane were also detected. In this study finding result, the trend of gas percentage was increase with the increasing of power level of microwave.

Based on Table 4.2 there are figures show the changing colour of the sample. The sample colour changed after the torrefaction process using microwave heating. Size of the sample used was 500 micron, the holding time was 40minutes, initial mass 10g, nitrogen flow 15ml/min and the temperature was 250^{o}C. By running the Table 4.2, we can know the best power level (Watt) in the microwave to produce the torrefied materials and low volatile. The first sample was by using 100W in Table 4.2.The temperature, time and size of sample are same. The colours shows power level does not lot changing the colour to the dark brown but the weight had loss 2.191g. By using 230 W, the sample changes to black colours at the Table 4.2. More

weight loss in the 5.01g. Third sample at Table 4.2 by using 385 W, the weight loss are 5.78 g. Then for 540 W, the sample colours have black and more brown. The weight loss for the sample was 6.199g. For the sample 700 W, the colour more black and have little ash due to high power level. The weight loss from the sample was 7.659g.

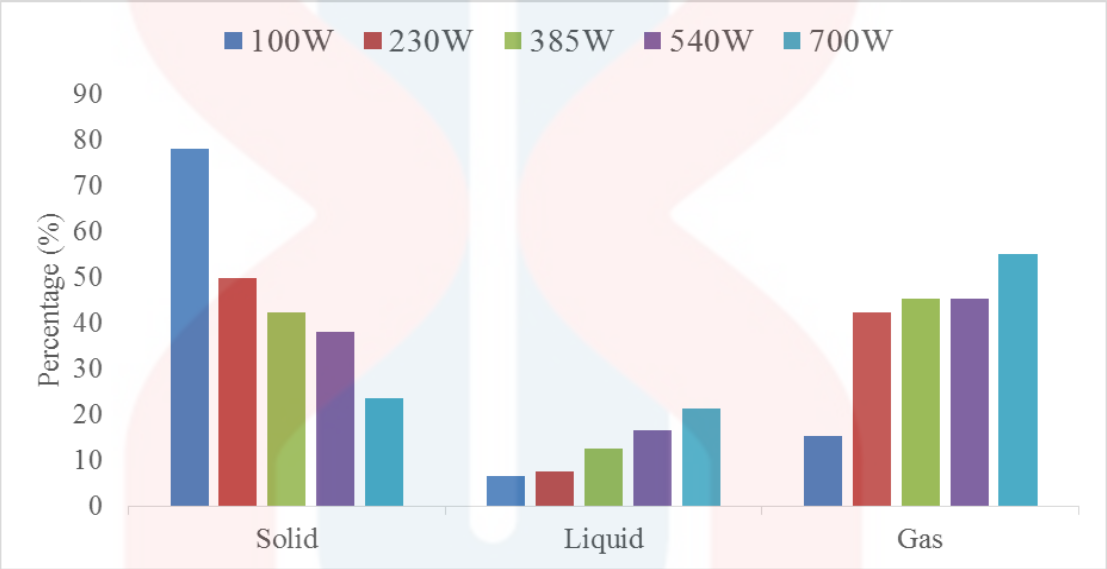


Figure 4.5: Effect power rate on fractional biomass

4.6 Colours

From Table 4.2 the torrefied sample shows the different colours based on torrefaction process. The low power level used to heating process makes the sample not change the colour much. Biomass has very low thermal conductivity and hence to achieve very high rates of heat transfer, the biomass particles are reduced to a very fine size because carbonaceous materials show strong interaction with microwave radiation due to their high electric and thermal conductivity (Salema *et al.*, 2015).

Table 4.2: Empty fruit bunch sample colour change after torrefaction process.

Sample based on power level (Watt)	Observation				
					
	100	230	385	540	700

The colours of sample change from light yellow to the darker in different power level. The darker of the colours in torrefied EFB because the presence of fixed carbon similar with coal colours. Biomass loading height and specific heat capacity affected the temperature and heating behaviour of the sample (Salema *et al*., 2015).

4.7 Response Surface Methodology (RSM)

The combinations of fractionation conditions are shown in Table 4.3. In Table 4.3 where coded levels of independent variables. The independent variables are influence the responses (weight). The relationship between responses (weight) and three independent factors (mass, nitrogen and size) had investigated in this study. The using CCRD designed variables suggested by software to minimize the effects of the uncontrolled factors (Azim *et al*.,2013).

Table 4.3: Independent variable and their levels in design of experimental

Independent variable	Name	Units	Code Levels		
			-1	0	1
A	Mass	gram	5.00	10.0	15.0
B	Nitrogen	ml / min	5.0	25.0	45.0
C	Size	micron	250.0	500.0	750.0

Table 4.4 show the coded and actual level parameter process. The coded values designed from lower to higher level by -1(minimum), 0 (center) and 1 (maximum). In this study, temperature used was 250^{o}C and reaction time was 40 minutes. The power level of microwave used was 385 W. Based on the selected power level, the production of mass and different size of particle makes the biochar after heating process was different. The quantitative and qualitative analyses of the torrefied production the 385 W was selected as the optimum power because the bio-char produced at 385W was the highest in term of yield percentage almost 40% from the initial sample mass, volatile matter content and ash content compare others power level to be used for statistical study of the pyrolysis study using RSM (Azim *et al*.,2013).

Table 4.4: Central composite design of independent variables for process optimization

Std	Coded			Actual		
	A	B	C	A	B	C
1	-1.00	-1.00	-1.00	5.00	5.00	250.00
2	1.00	-1.00	-1.00	15.00	5.00	250.00
3	-1.00	1.00	-1.00	5.00	45.00	250.00
4	1.00	1.00	-1.00	15.00	45.00	250.00
5	-1.00	-1.00	1.00	5.00	5.00	750.00
6	1.00	-1.00	1.00	15.00	5.00	750.00
7	-1.00	1.00	1.00	5.00	45.00	750.00
8	1.00	1.00	1.00	15.00	45.00	750.00
9	-1.68	0.00	0.00	1.59	25.00	500.00
10	1.68	0.00	0.00	18.41	25.00	500.00
11	0.00	-1.68	0.00	10.00	-8.64	500.00
12	0.00	1.68	0.00	10.00	58.64	500.00

13	0.00	0.00	-1.68	10.00	25.00	79.55
14	0.00	0.00	1.68	10.00	25.00	920.45
15	0.00	0.00	0.00	10.00	25.00	500.00
16	0.00	0.00	0.00	10.00	25.00	500.00
17	0.00	0.00	0.00	10.00	25.00	500.00
18	0.00	0.00	0.00	10.00	25.00	500.00
19	0.00	0.00	0.00	10.00	25.00	500.00
20	0.00	0.00	0.00	10.00	25.00	500.00

Table 4.5 shows the experimental and predicted values of weight obtained using model equations (4.1). Predicted values show in Table 4.5 match the experimental values reasonably.

Table 4.5: Experimental and predicted results for weight, W_1 and W_2 respectively.

Std	Experimental	Predicted
	W_1	W_2
1	2.88	3.85
2	8.59	8.84
3	2.53	2.72
4	7.47	7.64
5	2.96	3.85
6	8.04	8.24
7	3.75	4.28
8	7.92	8.45
9	0.53	0.09
10	8.68	8.72
11	7.53	7.44
12	6.77	7.36
13	6.51	6.59
14	7.53	7.61
15	7.42	7.42
16	6.93	7.25
17	6.59	7.83
18	7.84	8.68
19	6.74	6.94
20	8.69	7.97

The model fitted, the software generated model coefficients, R^2 – values, F-values and significant probabilities and from the values the significance of experimental variable can be justified (Azim *et al.*,2013).

4.7.1 Statistical Analysis

In this study, the response and variables were fitted to each other by regression. Regression analysis is the general approach to fit the empirical model with the collected response data. From Table 4.6 the model F-value of 24.12 shows the model is significant. It also observed that the linear term of mass has does not significant effect on weight due to the high F-value of 173.74. Quadratic term of reaction mass (A^2) has also not significant with weight. Sample nitrogen (B) also does not give significant effect to the weight of bio-char. The interaction between mass (AB) and nitrogen flow rate (BC) do not affect the weight of the bio-char significantly. Among the variables, mass (A) plays major effect to the weight in this study. The increase the mass (A), the weight also increased. The nitrogen flow rate does not really affect the weight due the gas used in this study only to provide an inert condition for the torrefaction process.

Table 4.6: ANOVA for the regression model and respective model term for weight.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	103.33	9	11.48	24.12	<0.0001	significant
A-Mass	82.70	1	82.70	173.74	<0.001	
B-Nitrogen	0.32	1	0.32	0.66	0.4340	
C-Size	0.62	1	0.62	1.31	0.2795	
AB	0.35	1	0.35	0.74	0.4095	
AC	0.24	1	0.24	0.51	0.4895	
BC	0.57	1	0.57	1.20	0.2985	
A^2	18.05	1	18.05	37.92	0.0001	
B^2	0.69	1	0.69	1.46	0.2553	
C^2	1.01	1	1.01	2.13	0.1751	
Residual	4.76	10	0.48			
Lack of Fit	1.60	5	0.32	0.50	0.7649	Not significant
Pure Error	3.16	5	0.63			
Cor Total	108.09	19				

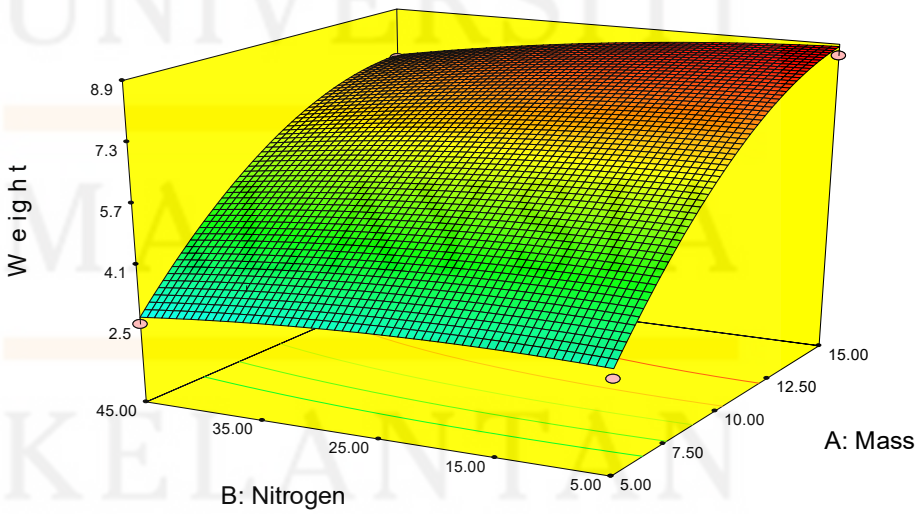
The coefficients of the full regression model equation and their statistical significance were determined and evaluated using design software from State-Ease Inc. The final weight model in terms of coded value is given in Equation (4.1).

$$Y_{Weight} = 7.39 + 2.46A - 0.15\ B + 0.21\ C - 0.21\ AB - 0.17\ AC + 0.27\ BC - 1.12\ A^2 - 0.22\ B^2 - 0.27\ C^2 \quad (4.1)$$

Y is the response, and A, B and C are the coded terms for the three variables selected such as mass (A), nitrogen (B) and size (C). Positive sign in front of each term represent synergistic effect, while antagonistic effect represented by negative sign. ANOVA was used to assess the goodness of fit. The significant quadratic models and the corresponding significant model term for responses table 1 of weight respectively.

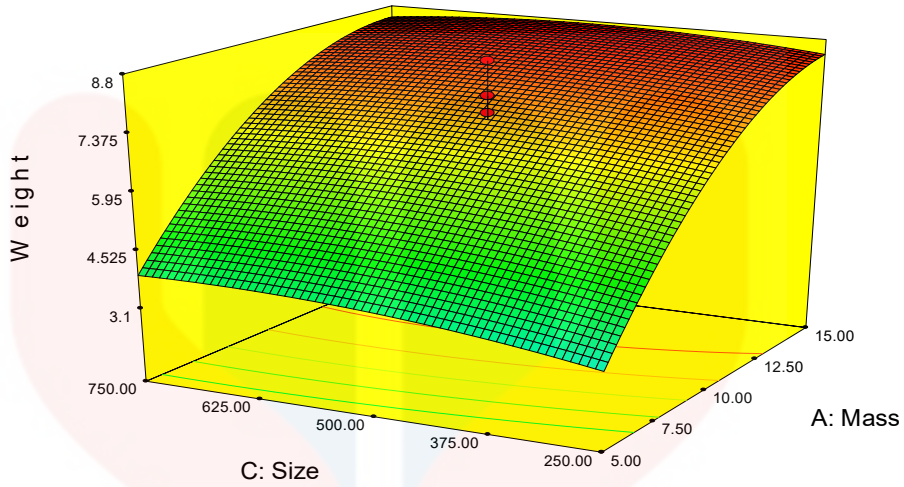
Figure 4.6 shows the effect of mass, nitrogen and size at 250 micron result the responses values. Figure 4.7 shows the effect of mass, nitrogen and size 500 micron result the weight values respectively with the Figure 4.8 which size of sample was 750 micron.

a)



a)

b)



c)

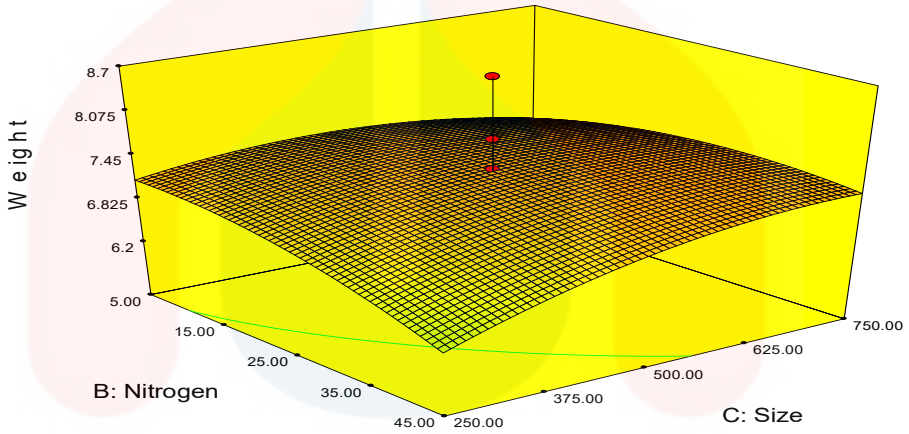
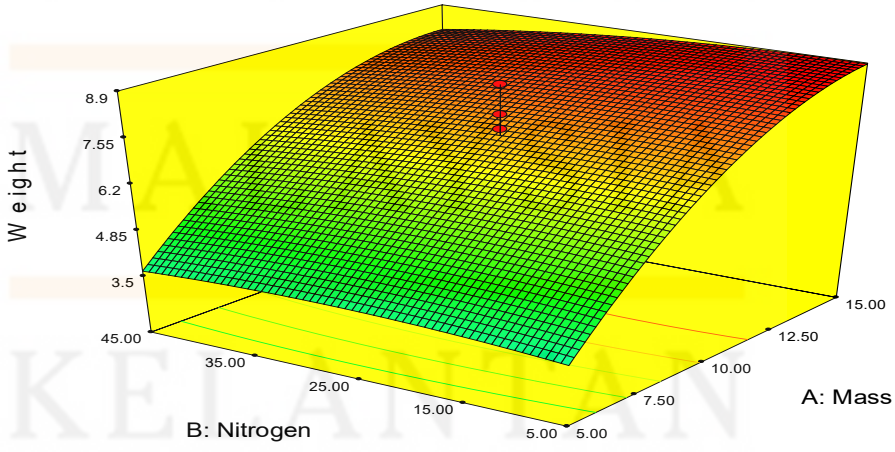
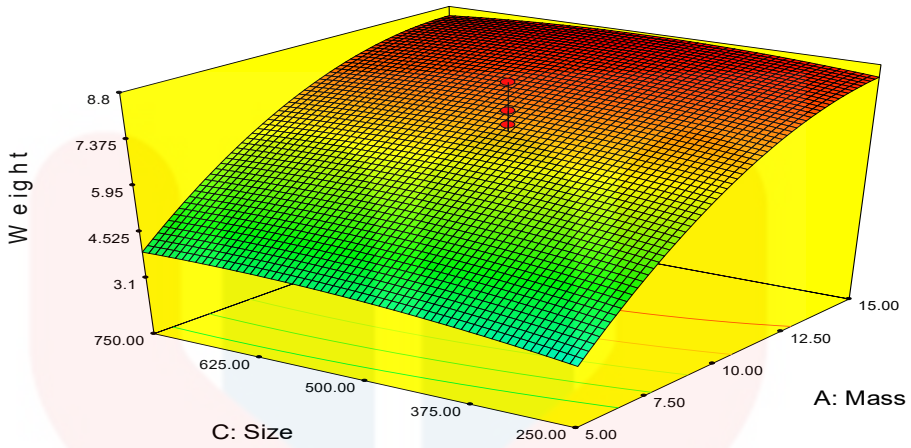


Figure 4.6: Countour plot of weight with size 250 micron: Effect of mass and nitrogen (a), effect of mass and size (b), effect of nitrogen and size (c)

a)



b)



c)

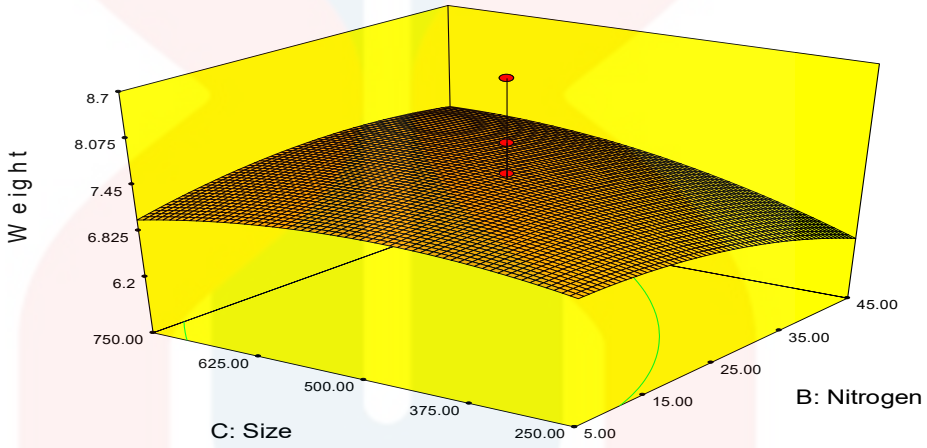
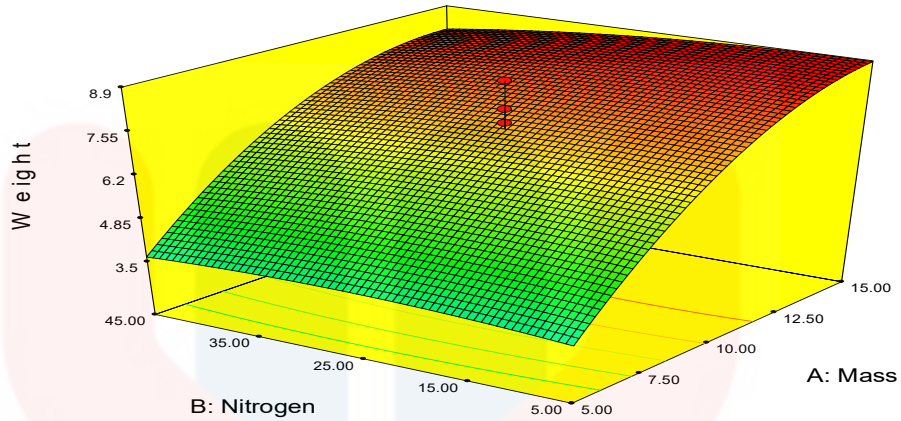


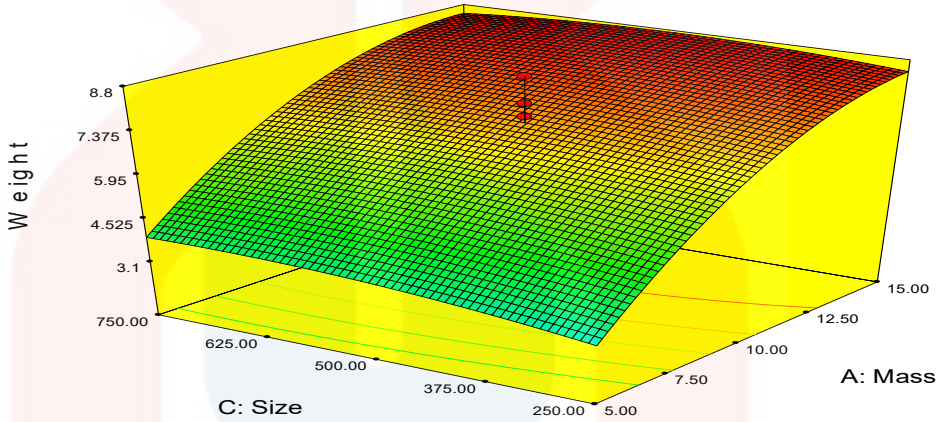
Figure 4.7 : Countour plot of weight with size 500 micron: Effect of mass and nitrogen (a), effect of mass and size (b), effect of nitrogen and size (c).

The Figure 4.6, 4.7 and 4.8 resulted that the increasing of nitrogen flow rate, increase the weight of response which means the product of biochar. Based on the Figure 4.7 the actual factor used are size of sample which is 500 micron due design points are above predicted value compared to the other size particles. Then the increase the mass of raw EFB put into crucible can increase the weight of response. The weights of response also include with the presence of ashes phenomena.

a)



b)



c)

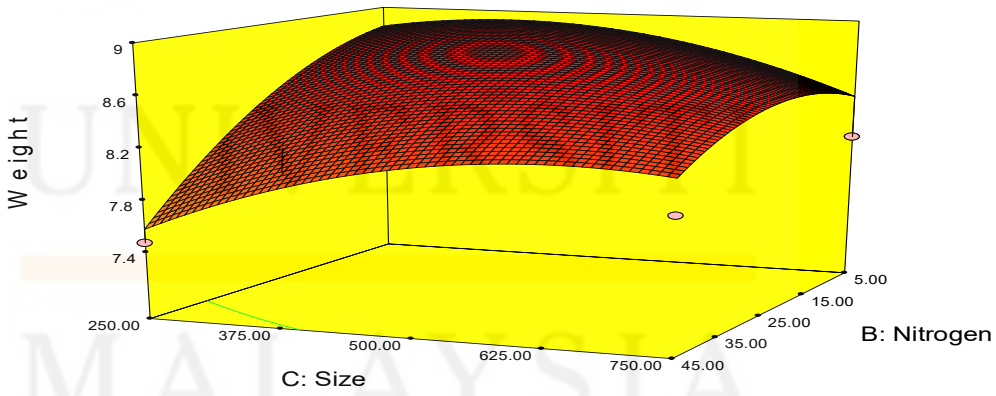


Figure 4.8: Countour plot of weight with size 750 micron: Effect of mass and nitrogen (a), effect of mass and nitrogen (b), effect of nitrogen and size (c).

In order to test the fit of the model, the regression equation and the determination coefficient (R^2) were evaluated. The responses of weight, the values of determination coefficient (R^2 = 0.9560) indicates that the sample variations of

84.88% for weight values is attributed to the independent variables and only 15.12% of the total variation could not be explained by the model. For the value of adjusted determination coefficient (Adj R^2 = 0.9163) is also high to advocate for a high significance of the model. The higher value of the correlation coefficient for response of weight justifies an excellent correlation between the independent variables.

The factors and responses with respectively high and low limit experimental region have to satisfy the creations defined for the optimum working conditions according to Azim et al. (2013). Figure 4.9 show the correlation between actual and predicted value of response. Higher value shown of the correlation coefficient justifies an excellent correlation between the independent variables.

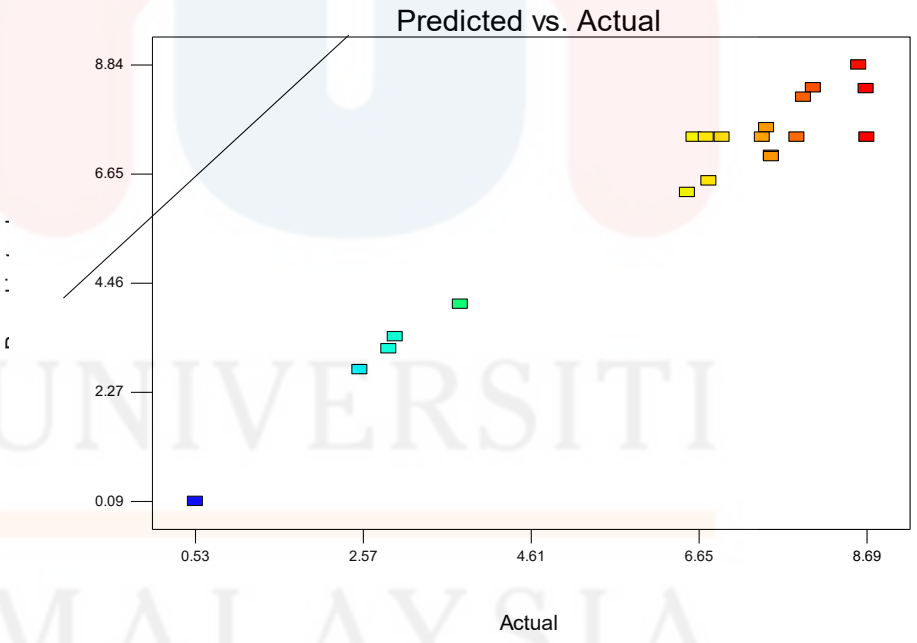


Figure 4.9: Relationship between predicted and actual values of weight

Based on the Figure 4.9 the lower limit is 0.0.53 and upper limit is 8.69. The colours points represent the weight value. All the independent variables and responses from high to low limit the experimental region have to satisfy the creation

defined for the optimum working of experiment conditions as stated in Table 4.5. In Table 4.7 results the pre-set goal of independent variables by the responses value.

Table 4.7: The pre-set goal with the constraints for all the independent factors and response in numerical optimization

Variables	Ultimate goal	Experimental region	
		Lower limit	Upper limit
Mass (g)	Maximize	5.00	15.00
Nitrogen (ml/min)	Is in range	15.00	45.00
Size (micron)	Is target = 500	250	750
Weight	Maximize	0.53	8.96

The goal was set to optimize the weight of the bio-char produced from the experiment with optimum mass, nitrogen and size to achieve as high bio-char production. The optimized condition obtained by DOE was 15g of mass, 30.00 ml/min of nitrogen flow rate and 500 micron of EFB particle size. From the response surface methodology (RSM) based on central composite rotatable design (CCRD) was employed for the optimization of torrefaction in empty fruit bunches (EFB) via microwave heating process. The correlation coefficients obtained for a response justify an excellent correlation between the independent variables.

4.8 Torrefied Material

4.8.1 Colours

The colours of torrefied EFB in Table 4.9 shows the change of colours from light yellow to the black or darker colours. The used of selection power level (385 W), the increasing of temperature and time can change the presence of fixed carbon and ashes phenomena. The highest temperature was 300^{o}C, presence more percentage of darker colours but there are little occurs of ashes phenomena. The product colour darkened only starting at 238 °C, resembling the regular appearance

of char and thus indicating a change in composition (Cruz, 2012). The increasing of residence time also effect the changing of fixed carbon in the torrefaction process due the degraded of lignocellulose bond. The highest holding time shows the colours of sample produce more percentage of black colours compared to 20 minutes and 40 minutes holding time. The black colours sample can highly correlated to the degree thermal treatment (Lam *et al*.,2014).

Table 4.9: Empty fruit bunch colours change after torrefaction process

Sample	Observation		
Raw			
Torrefied sample			
Sample	Observation		
	20 minutes	40 minutes	60 minutes
Temperature : 200°C			
Temperature : 225°C			
Temperature : 250°C			

Temperature : 275°C			
Temperature : 300°C			

4.9 Mass Loss Percentage (ML %)

From Figure 4.10, the lowest mass loss was sample temperature at 200°C, 20 minutes which is 6.2%. The highest mass loss percentage was sample at temperature 300°C, 60 minutes of heating process was about 13.9%. An increase in holding time from 30 to 50 min resulted in a decrease in bio-coal mass yield for a given reaction temperature (Cruz, 2012) .The percent of mass loss increase by increasing time of heating process due the water evaporation in EFB. The mass loss occurs with the higher temperature and holding time which can higher the change of solid to gases form (Harun *et al*.,2010). The effect of temperature rate with power level on solid, liquid and gases yield resulted at Figure 4.5.

There are some conclusion that can made from the study of the effect of heating rate with different of power level, effect of temperature on power selection ,effect of magnetron with different power level and effect temperature to mass loss of sample. The best power selection with the higher mass of torrefaction product was 385 W. The factor of 385 W selection due the ashes phenomena when the highest power level used for heating process which also can make thermal shock to the crucible. The nitrogen flow rate selection was 15 ml/min does not affect the

torrefaction process and biochar sample. The used of nitrogen to keep the inert atmosphere in the microwave during torrefaction process. The mass of sample was 15g due the suitable mass with maximum yield with different mass.

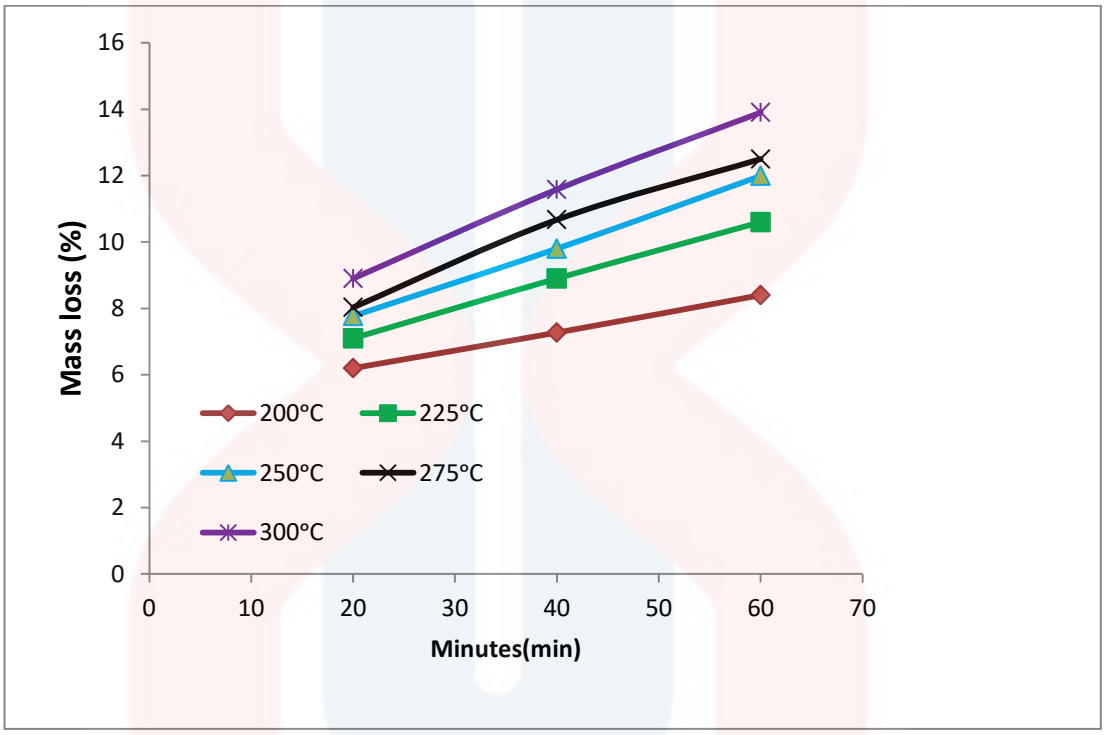


Figure 4.10: Effect of mass loss due the different temperature and residence time

4.10 Density Test

EFB densities were lower based on Rahman (2010). The raw EFB are lower density which is 0.26 g/cm^3. Figure 4.11 show the increasing of temperature and residence time, the sample become denser. The breakdown of bond in the EFB makes the composition of element change.

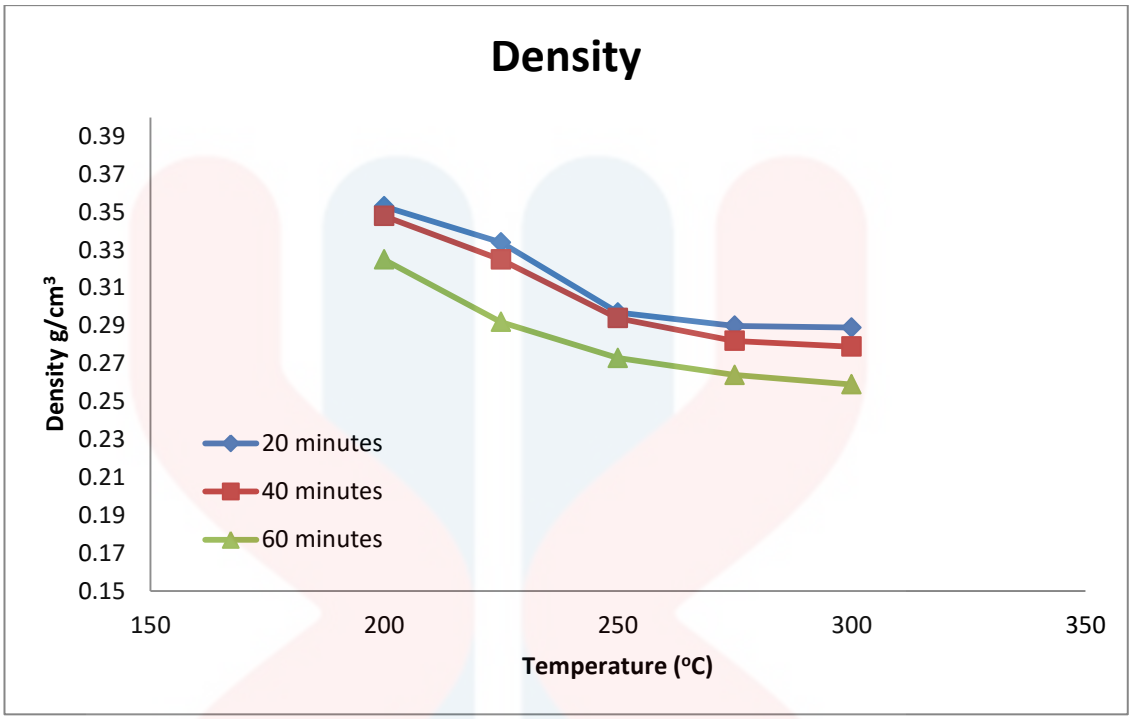


Figure 4.11: Effect temperature and residence time to the density of EFB

The denser sample was temperature 300^{O}C due the depolymerisation of lignocellulose bond with residence time. The lowest density of EFB was sample at temperature 200^{o}C. Residence time of heating also factor of breakdown the lignin, hemicellulose and cellulose sample. Based on Zhang Yu (2015) state the increase of time, affect the carbonization process. The longer time, can complete the char process. According to Thomas D.S (2006) the increasing of temperature can decrease the density. The increasing of temperature can denser torrefied sample due the complete carbonization process and brittleness.

4.11 X-Ray Diffraction Analysis (XRD)

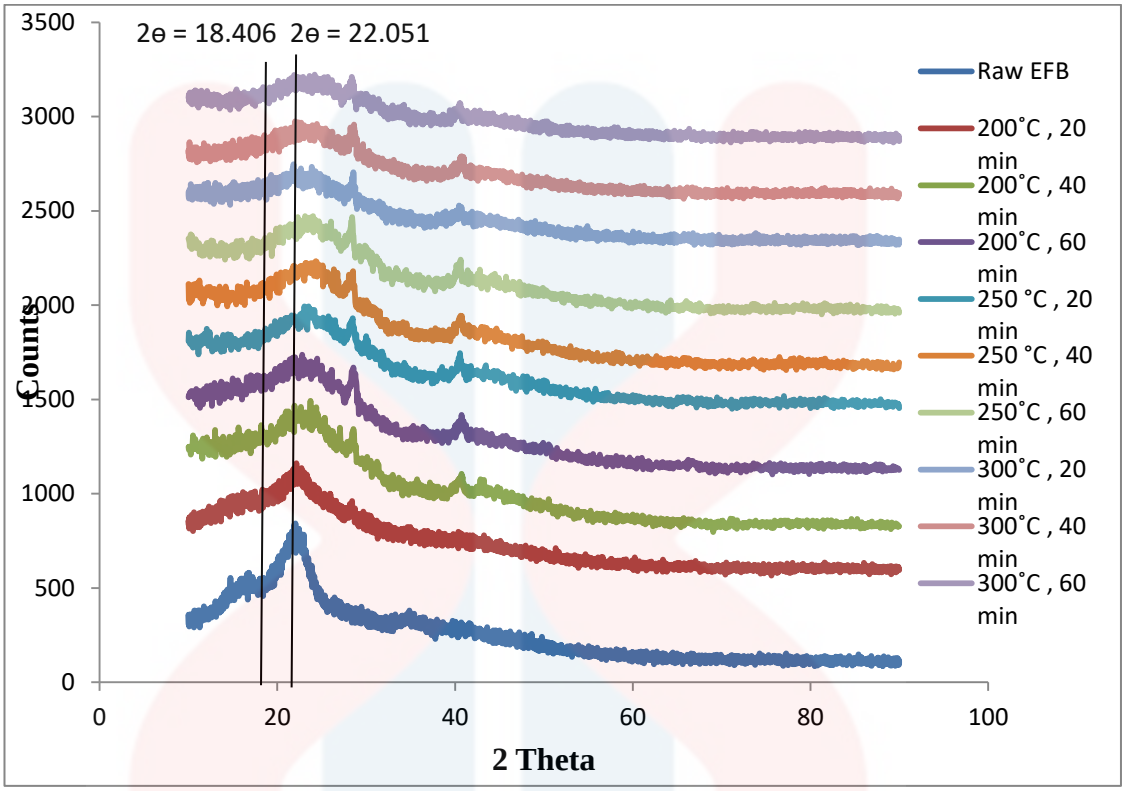


Figure 4.12: Overlay XRD of raw EFB and torrefied EFB

Figure 4.12 show the overlay of x-ray diffractogram of EFB from raw to torrefied temperature at 200, 250 and 300°C. Based on the graph the maximum height at 2Θ = 22.051 were observed to identify the changes of phase from crystalline phase to amorphous phase. The highest peak show that raw EFB have the lignocellulose membrane did not depolymerize. From temperature 200°C to 300°C, the crystalline peak is started to decrease from crystalline phase to amorphous phase. From temperature 200°C to 250°C, the graph still have crystalline peak but from temperature 300°C the graph has changed to amorphous phase because thee lignin, hemicellulose and cellulose degrade or undergo depolymerisation due the heating process.

Based on Figure 4.12, the peak of raw EFB are 843 counts. The peak was highest because the membrane lignocellulose not depolymerization yet. Raw of empty fruit bunch was composed with lignin, cellulose and hemicellulose. The cellulose was tightly bound with lignin and hemicellulose. Crystallinity of cellulose was hard due the presence lignin as a cementing agent. The amount of crystallinity for raw EFB is 99.6% then the amorphouse phase is 0.4%. The content of carbon structure in the raw EFB is hexagonal (COD 9014004) and graphite structure is orthorhombic (COD 9012234).

The peak of torrefied EFB on 200^{o}C and 20 minutes have the highest peak at 662 counts. The crystallinity phase of sample is 99.7% and the amorphouse phase is 0.3%. The figure show that the increasing of crystallinity phase 0.01% due the increasing of temperature. After the heating process began the hemicellulose starts to degrade at range of temperature 150^{o}C to 250^{o}C. The major of fraction in biomass were cellulose, lignin and hemicellulose. Hemicellulose were easiest fractions to be pyrolyzed because the linear polymer structure and short side chains (Osorio *et al*.,2006). The carbon structure in the sample is also hexagonal (COD 9014004) and graphite structure is orthorhombic (COD 9012234). Based on Figure 4.12 the highest peak of torrefied EFB at temperature 250^{o}C 20 minutes is 761 counts. The increasing of peak affects the crystallinity percentage of the biochar. The percentage of crystallinity is 99.8%, and then amorphouse phase percentage is 0.2%. The element in the EFB is converting from amorphouse to crystalline phase. The converting phase occurs due the increasing of temperature. The results show hemicellulose degraded effectively with low temperature. The decomposition of various branches in the hemicellulose with short chain can easily to remove from main bond (Ibrahim *et al*.,2012). The carbon structure in the torrefied EFB is hexagonal (COD 9014004)

and graphite is orthorhombic (COD 9012234). Figure 4.12 show the torrefied EFB at temperature 300^{o}C have 465 counts of the highest peak. The crystallinity percentage of sample is 89.99% and amorphouse phase is 10.01%. The carbon structure in the torrefied EFB is hexagonal and the graphite is orthorhombic structure. The increasing of temperature makes the structure in the sample devolatilization and carbonization of the polymers (Petal *et al*., 2011).

Figure 4.12 Show that the highest peak of sample 200^{o}C 40 minutes is 768 counts. The crystallinity percentage is 99.7% then the amorphouse phase is 0.3%. The increasing of residence time effect the crystalline phase in the sample due the long period of heating process. Hemicellulose starts to remove from the backbone of cellulose. There also have carbon structure and graphite. Figure 4.12 shows the torrefied EFB at 250^{o}C 40 minutes of residence time. The peak shows that the highest peak at 683 counts at 24.327 2 theta. The percentage of crystallinity is 27.3% and amorphouse phase is 72.2%. The sample was amorphouse phase because the decomposition of hemicellulose at 200-250^{o}C and the degradation of lignin and cellulose (Shang *et al.*,2012). Figure 4.12 shows that the highest peak of 300^{o}C 40 minutes EFB is 470 counts at 22.375 2 theta. The crystalline phase percentage is 24.8% and amorphouse phase is 75.2%. The amorphouse percentage rises because the hemicellulose had decomposed due the high temperature of torrefaction. Hemicellulose decomposes directly after water vaporization, at temperatures between 200-380 °C(Cruz, 2012). The carbon structure is hexagonal and graphite is orthorhombic.

Figure 4.12 resulted the highest peak of 200^{o}C 60 minutes EFB is 738 counts at 22.808 2 theta. The percentage of crystalline is 26.2% then amorphouse phase is 73.8%. The carbon structure in the sample is hexagonal and graphite structure is

orthorhombic. As the carbon released from biomass combustion is fixed at relatively small time scales, it can be considered to be near carbon neutral and be used to satisfy the requirements for Renewables Portfolio Standards (RPS) (Pollard, 2015). Figure 4.12 shows that the highest peak in the sample of 250^{o}C, 60 minutes is 622 counts at 23.112 2 theta. The crystalline phase percentage is 24.4%. Then the amorphouse phase percentage is 75.6%. The carbon structure from the figure is hexagonal and the graphite structure is orthorhombic. The conversion rate of biomass into carbon is much faster at higher temperature than at lower temperatures (Salema *et al*., 2015). Figure 4.12 shows the peak of XRD for 300^{o}C 60 minutes. The highest peak for the sample is 411 counts at 22.921 2 theta. The crystalline phase percentage is 26.17% then the amorphouse phase percentage is 75.6%.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Data obtain from this study on characteristic of EFB is useful in future study. The finding in this study determined that correlation of RSM for optimum condition in torrefaction process for production bio-char. Thus, the reducing of volatile matter in torrefaction process can safe the health environment from pollution. The drying process shows the reducing moisture in the EFB are decline based on comparison 1 day and 2 day drying. The mass loss percentage of EFB also shows the effect of volatile after heating are occurs for raw EFB. Then, RSM analysis shows the correlation of mass, size particle and nitrogen flow rate can effect the weight response after heating process and biochar product finally the presence of ashes phenomena. From XRD we can conclude that the presence of carbon and graphite then, reducing of peak with increasing of temperature and time. The change crystallinity phase to amorphouse phase of EFB can factorize with increasing of temperature and residence time during heating due the degradation of hemicellulose, cellulose and lignin in the EFB.

5.1.1 Characteristics of Empty Fruit Bunch

The properties (mass loss, moisture content and density) of EFB were analysed using standard formula or equation. Based on analysis of EFB, it know that mass loss of drying sample that exposed in long period of environment easy to degrade the bond. The mass loss also depends on size of sample because the low surface area resulting the mass loss. From the study, the highest mass loss for drying sample is 250 micron on 2 days drying (9.03%). Moisture content percentage for the

highest is 750 micron 2 days drying (11.24%).Based on selective sample from RSM which is 15g, 500 micron and 30 ml/min resulting in the production of bio-char, mass loss and density of the sample. The denser torrefied sample is 200^{o}C, 60 minutes (0.353g/cm ^{3}). The highest mass loss for torrefied sample at temperature 300^{o}C, 60 minutes (13.90%).

In production biomass industries, the size and mass of sample during heating are main role to produce biochar with the less ash weight and volatile matter via microwave heating process.

5.2 Recommendation

In the future, there are several recommendations that can be considered if this study is to be continued. Characterizations of EFB can be further in in drying sample in long and short period drying and the age EFB pick from the palm oil tree to be compared the breaking of weak bond in EFB. For the further in the optimization, the torrefaction can use block for different part of palm oil tree or other agriculture waste in torrefaction process. The torrefaction process can expand the optimized to increase biomass hydrophobicity and brittleness. Final product of torrefied can be optimization based on correlation between process and feedstock parameters which will favour desired properties such as fixed carbon content, hydrophobicity or microbial degradation resistance.

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APPENDICES

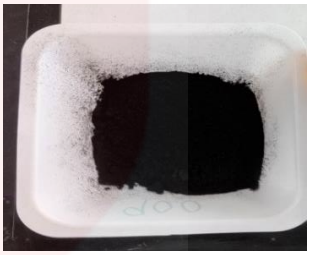
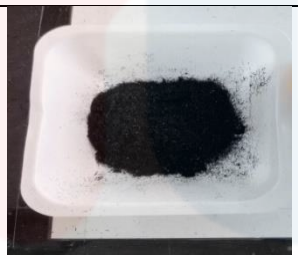
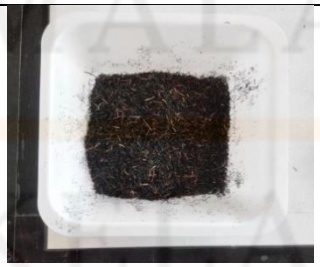
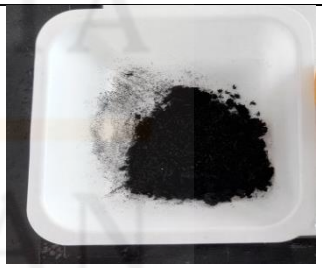
APPENDIX A – RESPONSE SURFACE METHODOLOGY (RSM)

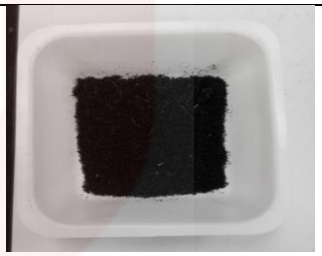
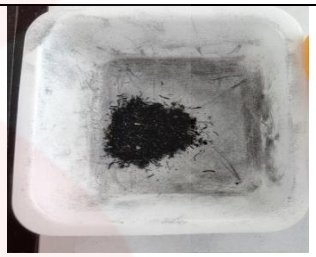
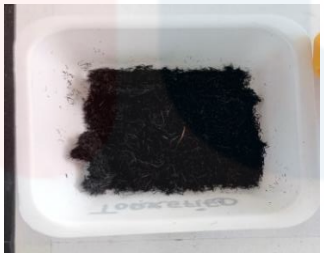
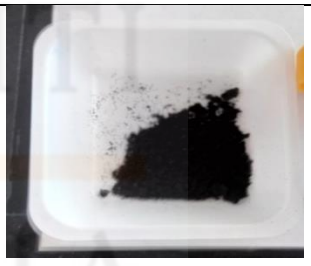
A.1 Raw data for second data for selection of sample size,time of heating and nitrogen flow rate

No	Parameter
Power (Watt)	385
Temperature (^{o}C)	250
Time (minute)	40

Std	Run	Factor 1 A:Mass (gram)	Factor 2 B : Nitrogen (ml / min)	Factor 3 C:Size (micron)	Solid after (gram)
19	1	5.00	5.00	250.00	2.88
15	2	15.00	5.00	250.00	8.59
10	3	5.00	45.00	250.00	2.53
20	4	15.00	45.00	250.00	7.47
4	5	5.00	5.00	750.00	2.96
9	6	15.00	5.00	750.00	8.04
17	7	5.00	45.00	750.00	3.75
14	8	15.00	45.00	750.00	7.92
6	9	1.59	25.00	500.00	0.53
1	10	18.41	25.00	500.00	8.68
2	11	10.00	-8.64	500.00	7.53
13	12	10.00	58.64	500.00	6.77
3	13	10.00	25.00	79.55	6.51
8	14	10.00	25.00	920.45	7.51
18	15	15.00	25.00	250.00	7.42
5	16	10.00	25.00	500.00	6.93
7	17	10.00	25.00	500.00	6.59
12	18	10.00	25.00	500.00	7.84
16	19	10.00	25.00	500.00	6.74
11	20	10.00	25.00	500.00	8.69

A.2 Empty fruit bunch sample colours change after torrefaction process.

Sample run number	Observation	Sample run number	Observation
1		11	
2		12	
3		13	
4		14	
5		15	

6		16	
7		17	
8		18	
9		19	
10		20	

APPENDIX B – TORREFIED EMPTY FRUIT BUNCH

B.1.1 Raw data for first run for selection of heating rate, production of volatile matter (solid, liquid and gas) and power level (Watt)

No	Setting Parameters
1	Temperature : 250 ^{o}C
2	Temperature and magnetron must be log continuously
3	EFB size : 500 micron

No	Time (minute)	N_2 Flow (ml / min)	Temp (^{o} C)	Power level (watt)	Solid before (gram)	Solid after (gram)	Liquid before (gram)	Liquid after (gram)	Gas (gram)
1	40	15	250	100	10	7.809	463.7	0.65	1.541
2	40	15	250	230	10	4.99	463.7	0.768	4.23
3	40	15	250	385	10	4.22	463.7	1.26	4.52
4	40	15	250	540	10	3.80	463.7	1.66	4.54
5	40	15	250	700	10	2.341	463.7	2.14	5.519

B.1.2 Density for raw EFB

Sample	Density
Sample = Raw Mass = 15g Diameter = 4.0 cm Radius = 2.0 cm High = 3.9 cm	Volume = π $(2.0)^2$ (3.9) = 49.0 cm^3 Density = 15g / 49.0 cm^3 = 0.306 g cm^3	Density = 0.306 g cm^3

B.1.3 Mass loss percentage for torrefied EFB

Sample \ Time	20 minute	40 minute	60 minute
Temperature : 200 ^{o}C	6.20%	7.27 %	8.40%
Temperature : 225 ^{o}C	7.10%	8.90 %	10.60%
Temperature : 250 ^{o}C	7.77 %	9.80 %	11.99 %
Temperature : 275 ^{o}C	7.54 %	10.67%	12.04 %
Temperature : 300 ^{o}C	8.90 %	11.58 %	13.90 %

APPENDIX C – GALLERIES

C.1 The process of sieving of EFB particle size and cleaning

- Raw EFB was ready for sieving stage.

- The sieving process of EFB using the vibrator.

- The cleaning of siever after the sieving process using air pressure

- The particle size of 250 micron (above) and 500 micron of EFB (below).

- Alumina crucible used during torrefaction process.