APPLICATION OF RESPONSE SURFACE METHODOLOGY (RSM) FOR THE OPTIMIZATION PARAMETERS OF HYDROCHAR PRODUCTION FROM COCONUT HUSK USING HYDROTHERMAL CARBONIZATION

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by

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LIST OF SYMBOLS

B_o	Constant term
B_i	Coefficient of linear parameters
B_{ij}	Coefficient of interaction parameters
B_{ii}	Coefficient of quadratic parameters
k	Number of variables
Y	Response

LIST OF ABBREVIATIONS

AAD	Absolute average deviation
BBD	Box-Behnken Design
CCD	Central Composite Design
HHV	Higher heating value
HTC	Hydrothermal carbonization
LTP	Low temperature pyrolysis
RSM	Response surface methodology

ABSTRAK

Suatu keadaan yang ideal dan optimum untuk penghasilan maksimum arang hidro kelapa sabut melalui penghidratan hidrotermal (HTC) telah dikaji. Pengoptimuman dan analisis keadaan operasi yang jelas iaitu suhu reaksi dan masa dilakukan berdasarkan eksperimen yang dilakukan dalam kajian sebelumnya pada julat 180 to 240°C dan 48 to 96 jam. Simulasi dilakukan untuk mengkaji pengaruh keadaan operasi (suhu tindak balas, masa dan nisbah biojisim-air) terhadap hidrokar melalui karbonisasi hidrotermal kelapa sabut dengan julat yang diambil dari kajian sebelumnya pada suhu 180-260 ° C, 0.5-2 jam dan 1:5 1:15. Data simulasi dioptimumkan dan dianalisis dengan menggunakan metodologi tindak balas permukaan dalam pakar reka bentuk untuk merancang eksperimen. Berdasarkan reka bentuk komposit pusat terpilih (CCD), model kuadratik dikembangkan untuk menghubung-kaitkan keadaan operasi dan hasil hidrochar. Hasil hidrchar dioptimumkan dari eksperimen yang dilakukan dalam kajian sebelumnya diperoleh pada 60.669% pada 194.121 ° C dan 48 jam. Dari data simulasi, hasil hidrokchar diperoleh pada 70.909% pada 180 ° C, 0.5 jam dan 1:15 wt%.

APPLICATION OF RESPONSE SURFACE METHODOLOGY (RSM) FOR THE OPTIMIZATION PARAMETERS OF HYDROCHAR PRODUCTION FROM COCONUT HUSK USING HYDROTHERMAL CARBONIZATION

ABSTRACT

An ideal and optimum conditions for maximum production of hydrochar yield of coconut husk via hydrothermal carbonization (HTC) were investigated using optimization method. The optimization and analysis of significant operating conditions which were reaction temperature and residence time was done based on the experiment conducted in the previous study at hydrothermal carbonization temperature range from 180 to 240°C and 48 to 96 h. The simulation was carried out to study the effect of operating conditions (reaction temperature, residence time and biomass-water ratio) on hydrochar through hydrothermal carbonization of coconut husk with the range taken from previous studies at 180-260°C, 0.5-2 h and 1:5-1:15 wt% respectively. Simulation data was optimized and analysed by using response surface methodology (RSM) in Design Expert to design the experiments. Based on chosen Central Composite Design (CCD) method, a quadratic model was developed to correlate the operating conditions and hydrochar yield. The optimized hydrochar yield from the experiment conducted in previous study was obtained at 60.669% at 194.121°C and 48 h. From the simulation data, hydrochar yield was obtained at 70.909% at 180°C, 0.5 h and 1:15 wt%.

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Biomass is a sustainable energy source that has gained recognition due to its potential to transform into different form of energy. Coconut husk is a potential biomass introduced for the alternative to the charcoal due to its continuous supply, higher energy efficiency and lower ash content. Hydrothermal carbonization technique is used to convert biomasses to hydrochar. Based on the previous studies, reaction temperature and residence time was identified as the main parameters affecting the hydrochar yield. Chapter 1 includes the overview of this research and optimization of the hydrochar production from coconut husk. In general, this chapter summarizes the research background of hydrothermal carbonization process and the application of response surface methodology (RSM), problem statement and the objectives of this final year project.

1.2 BACKGROUND

Biomass become one of the most important sources of energy due to its sustainability, and available abundantly. Due to the increase in production cost, limitation of non-renewable resource and environmental concern, biomass became as one of the most effective and alternative approach for potential sustainable energy production. The current energy production by burning the fossil fuels gives dangerous threat due to the emission of greenhouse gases such as carbon dioxide (McKendry, 2002). (McKendry, 2002) stated in their study, burning biomass for energy production reduces the effect of global warming and green house effects due to carbon dioxide that release during the process basically absorbed by the replanting harvested biomass.

They can also be converted into any form of fuel such as solid, liquid and gas (Özbay *et al.*, 2001).

In Malaysia, about 168 million tonnes of biomass waste is generated every year. Palm oil waste accounts approximately about 94% of biomass feedstock while agricultural, rice and sugarcane waste contribute about 4%, 1% and 1% respectively. In 2010, palm oil industry generated about 80 million dry tonnes of biomass It is expected that 100 million dry tonnes of solid biomass generated by 2020. This include empty fruit bunches (EFB), mesocarp fibres (MF) and palm kernel shells (PKS) and trunks. National Biomass Strategy 2020 focuses on oil palm biomass as a starting point and later be extended to include biomass from another sources.

However, although the processing mills from the palm oil waste is considerably high, there are some competitive applications of these residues such as paper production, construction of board fillers and bio composites (Abdullah and Sulaim, 2013). Due to environmental concern and cost-effective benefits, many companies have recycled the biomass waste to generate heat and energy for their own production instead of spending more on biofuel.

Coconuts are one of agricultural industries that produce huge amount of agricultural waste in tropical countries worldwide. Mostly in developing countries, coconut wastes are subjected to open burning that leads to the release of CO_2 emissions.

Table 1.1 Highest coconut production in the world (Burton, 2018)

Rank	Country	Coconut Production (tons)
1	Indonesia	18,300,000
2	Philippines	15,353,200
3	India	11,930,000
4	Brazil	2,890,000
5	Sri Lanka	2,513,000
6	Vietnam	1,303,000
7	Papua New Guinea	1,200,000
8	Mexico	1,064,000
9	Thailand	1,010,000
10	Malaysia	646,932
11	United Republic of Tanzania	530,000
12	Myanmar	425,000
13	Solomon Islands	410,000
14	Vanuatu	410,000
15	Ghana	366,183

Coconut husk can be potentially used as alternative for biomass production producing bio-char, bio-oil and gas (Suman and Gautam, 2017). They are more preferred because of the common crop that continuously available for the constant supply. Coconut fruit produces approximately 35-40 % coconut husk that consists of 30% fibre (Ibrahim Yerima, 2018). Based on (Yong *et al.*, 2009) coconut husk has higher heating value, HHV at 3500-4000 kcal/kg, ash content at 4-5% and moisture content of 15%. These is due to high level of lignin and cellulose content.

Thermochemical processes to convert biomass to energy offer several advantages, including fast reaction time and high energy yield. (Kambo and Dutta, 2015). Typically, thermal conversion processes such as pyrolysis, gasification, and hydrothermal carbonization are used to generate common energy from biomass. Even though the yield generated may vary for the same operating parameters, such as temperature, it is essential to keep the operating parameters the same. The process of pyrolysis is a simple one, which uses oxygen-free atmosphere to increase the temperature. The process of pyrolysis is straightforward, and the technology is well develop. High ash content produced during the pyrolysis since the volatile release increases the cost of cleaning, which in turn causes higher ash content. (Wang *et al.*, 2019). Tars are created as a result of the gasification process, and this has an effect on the maintenance cost. This shows that the HTC is the best pretreatment procedure for biomass conversion, as HTC yields the most hydrothermal carbon (HTC).

Hydrothermal carbonization, HTC is the pre-treatment process for the conversion of biomass to renewable solid fuel called hydrochar. The process technique is carried out in a closed system under pressure with water as the reaction medium at 180-250˚C producing hydrochar, water and soluble organics (Elaigwu and Greenway, 2019; Rodriguez Correa *et al.*, 2019). HTC comes as an alternative to reduce the energy consumption in torrefaction process due pre-dying of wet biomass before the decomposition reaction can be executed (Wang *et al.*, 2019).

Different stable carbon-rich solid, char is generated via different type of thermochemical pre-treatment. Slurry hydrochar and biochar are produced from the HTC and pyrolysis respectively. Physical and chemical properties of char is significantly different based on the type of process used (Kambo and Dutta, 2015). Kambo and Dutta (2015) in their study, HTC is a best process option due to the production of hydrochar. Hydrochar contains higher heating value with lower alkali and alkaline earth metallic content.

Based on the numerous studies, the temperature, biomass to water ratio and residence time were stated as factors that give great influence on the performance of the hydrochar produced during the hydrothermal carbonization process. From the previous study, temperature and residence time are stated as the most important factors for the production and properties of hydrochar. These operating conditions proven to be the key parameters affecting the percentage yield and physiochemical properties of hydrochar. Studies have been reported by Zhou *et al.* (2019), increasing the temperature condition will decrease the functional group and yield of biochar. Increase residence time will affect composition, surface area and pore characteristics of biochar.

However, the previous study was mainly highlighted the respective effects of the factors to the properties and yield of hydrochar without focusing on the interactive effects among the factors towards the hydrochar and the optimization of these factors. The optimization is necessary to improve the performance and efficiency of the product formed. Moreover, optimization of the influence parameters will provide a maximum benefit of the production process. However, multi-factor optimization is used recently rather than one-factor optimization due to complete effects of the factors to the response, shorter time consumption and lower expanses (Bezerra *et al.*, 2008).

Response surface methodology (RSM) is the most common method used for the optimizing and improving the product in the production process. RSM consists of the collection of statistical and mathematical techniques that are depended on fit empirical model to data obtained under the chosen experimental design. RSM can reduce the number of experimental runs by simultaneously optimize the several variables that influenced the response of interest. Central Composite design (CCD), Box-Behnken design and Doehlert Matrix are the three-level factorial design known for the optimization process.

1.3 PROBLEM STATEMENT

Coconut husk is a potential agricultural crop resource with the ability to provide better alternative of biomass fuel and a good source of charcoal. Current technologies of biomass energy conversion process possessed several drawbacks. Pyrolysis and gasification are not suitable as they operate at higher temperature, higher maintenance cost and higher energy consumption. Hydrothermal carbonization is proposed currently due to low operating cost, higher energy yield, lower operating temperature and more effective as compared to other technologies. Based on the previous study, HTC of coconut husk has been conducted to determine the effect of reaction conditions on hydrochar. However, the optimization of the reaction conditions for the hydrochar production using response surface methodology has not been done in the previous study. Therefore, focus of this work is to determine the reaction temperature, residence time and biomass-water ratio as these parameters known to affect greatly the properties of hydrochar. In addition to that, design of the experiment and analysis of the result are conducted to obtain higher yield and quality and determine the optimum conditions of the hydrochar.

1.4 OBJECTIVES

I. To optimize the reaction conditions (reaction temperature, residence time and biomass-water ratio) by using Response Surface Technology (RSM) for maximum hydrochar yield.

II. To determine the effect of operating conditions (reaction temperature, residence time and biomass-water ratio) on hydrochar properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass

Biomass is a lignocellulosic material taken from the living organisms that its resource is able to convert fuel to solid, liquid and gas (Kambo and Dutta, 2015). Biomass sample with higher amount of lignin content leads to a higher yield. However, the concentration of cellulose, hemicellulose and lignin are different with type of biomass used (Rodriguez Correa et al., 2019).

The coconut fruit is one of the agricultural crop resources that can potentially process into energy sources such as charcoal. They are one of the effective biomass fuel and sources of charcoal due to high lignin content and continuous supply (Ibrahim Yerima, 2018). In a study conducted by Yong et al. (2009), the coconut husk contains high lignin and cellulose content at 45.84% and 43.44% respectively. The calorific value recorded high at 14.644-16.736 MJ/Kg, low moisture content at 15% and low ash content at 5%.

Study conducted by Nakason et al. (2018), coconut husk and rice husk were used to compare their ability and potential as renewable fuel resource. With the same process parameters at 140˚C to 200˚C and 1 h to 4 h, coconut husk clearly shown a better solid fuel than rice husk. The HHV recorded high at the 20.7 MJ/Kg to 23.9 MJ/Kg and highest yield at 77.1%.

2.2 Hydrochar

Hydrochar is a high carbon-rich solid by product that is produced from HTC pre-treatment process whether using dry or wet biomass (Kambo and Dutta, 2015). Different type of pre-treatment process used are the factors that differentiate the type of char generated. According to several studies, hydrochar has potential as an alternative as energy source, reducing the reliance on conventional energy sources. Oumabady et al. (2020) stated that hydrochar is a compound with aromaticity and similar thermal behaviour to current conventional energy sources, making it possible to replace sources such as coal.

2.3 Hydrothermal Carbonization

Thermochemical processes are conversion methods mostly used to transform biomass into energy, fuel and char. Some processes require specific feedstock conditions before feed into the process such as moisture content and carbon density (Román et al., 2018). Sustainability, compatibility with existing facilities, conversion yield and cost are considered for choosing the suitable conversion process. Hydrothermal carbonization (HTC) is a promising conversion technique over pyrolysis and gasification due to its low cost, simple process and unrequired pre-drying process (Elaigwu and Greenway, 2019).

Study conducted by (Wang et al., 2019), HTC and low temperature pyrolysis (LTP) was compared and evaluated for the production of solid carbon char. Reaction temperature recorded for HTC was lower that LTP at 200˚C and 300˚C respectively for same char yield at approximately 67%. Leaching of inorganic elements into the liquid phase in HTC process reduced the ash content in sample and recorded lower than in LTP at 0.13%-0.61% under the same reaction temperature (Wang et al., 2019).

Table 2.1 Summary of previous studies published on the production of hydrochar via hydrothermal carbonization

No	Biomass	Specific parameters	Result	Relevant studies
1.	Corn Stover	Temperature: 305˚C Residence time: 60 min Biomass to water ratio: 0.114	Solid yield: 29.91% HHV: 25.42 MJ/Kg	(Mohammed *et al.*, 2020)
2.	Spent coffee ground	Temperature: 216˚C Residence time: 60 min	Solid yield: 64% Calorific value: 31.6 MJ/Kg	(Afolabi, Sohail and Cheng, 2020a)
3.	Anaerobic digestate	Temperature: 230˚C pH: 3	Carbon recovery rate: 0.36 Dry mass recovery : 0.25	(Stutzenstein *et al.*, 2018)
4.	Rice straw	Temperature: 180 Reaction temperature: 20 min Water to biomass ratio: 15	Solid yield: 57.9% HHV: 17.8 MJ/Kg	(Nizamuddin *et al.*, 2019)
5.	Canola stalk	Optimum condition: Temperature: 207˚C Reaction time: 82 min	Solid yield: 53.38% Carbon recovery rate: 52.66 O/C ratio: 0.69	(Salimi *et al.*, 2017)
6.	Macadamia shells	Temperature: 220 ˚C Reaction time: 60 min Water to biomass ratio: 11	Solid yield: 57.58% HHV: 22.69 MJ/Kg	(Fan *et al.*, 2018)

2.4 Optimization Using Response Surface Methodology

Response surface methodology (RSM) is one of the most effective methods for process optimization with the combination of design and analysis of experiments, modelling technique and optimization method (de Oliveira et al., 2019). Conventional technique for optimization of multivariable system is considered unsuitable and contains several drawbacks such as time consuming and requires more experimental data (Behera et al., 2018). Behera et al. (2018) stated in their studies, conventional technique is unreliable due to not representing the combined effect of the influence parameters.

RSM consists of mathematical and statistical techniques that depended on the fit of the polynomial equation to the experimental data obtained from the chosen experimental design (Bezerra et al., 2008). It can effectively be applied to the dependent variables (responses) that are influenced by several independent variables (factors). For RSM method, experimental data is collected and control parameters influencing the process need to be identified. The relationship between dependant and independent variable is studied mathematically. Maximization and minimization functions are conducted in optimization methods to improve the process parameters (de Oliveira et al., 2019). Bezerra et al. (2008) and Aydar, (2018) stated that the RSM consist of some stages:

1) Selection of independent variable
2) The choice of experimental design
3) The mathematical- statistical treatment of data
4) Evaluation of fitted model
5) Determination of optimum values for the variables

2.4.1(a) Screening Variables

It can be said that there are variety of factors that affect the hydrochar process significant and non-significantly. The evaluation of individual effect of each factor is unfeasible due to high expense and number of experimental runs required (Yolmeh and Jafari, 2017). Moreover, it also leads to increase in time consumption. Practically, it is impossible to control each and every factor that affect the response(s) in the process. Hence, it is important to select and control those with major effects to the process response(s). Screening design is used to acknowledge those factors that contribute largely on the response(s). Full and fractional factorial designs (2-4 factors) are commonly used for this step considering its efficiency and economic advantages (Bezerra et al., 2008). In these designs, only the main effects are estimate and the insignificant interactions between independent variables are neglected.

2.4.1(b) Selection of Experimental Design

The selection of experimental design is based on the condition of data set. The simple model can be used based on a linear function. First order model is proposed when the data set does not represent curvature. However, it is important that the response(s) well fitted into the equation:

$$y = \beta_o \sum_{i=1}^{k} \beta_i x_i + \varepsilon \quad \ldots (2.1)$$

Where,

y= responses

k= number of variables

β_o= constant term

β_i = coefficient of linear parameters

x_i= Variables

ε= residual

For a response function to the experimental data that cannot be expressed by linear function (curvature), the second-order model must be used. A model equation for second-order interaction is shown as below:

$$y = \beta_o \sum_{i=1}^{k} \beta_i x_i + \sum_{1 \le i \le j}^{k} \beta_{ij} x_i x_j + \varepsilon \quad \ldots (2.2)$$

Where,

B_{ij} = coefficient of interaction parameters

It is important for the polynomial function to contain quadratic terms, in order to determine a critical point (maximum, minimum or saddle). The equation is shown as below:

$$y = \beta_o \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} {x_i}^2 + \sum_{1 \le i \le j}^{k} \beta_{ij} x_i x_j + \varepsilon \quad \ldots (2.3)$$

Where,

B_{ii} = coefficient of quadratic parameters

2.4.1(c) Evaluation of the Fitted Model

The estimated response(s) can possibly calculate via model equation and regression coefficient (Yolmeh and Jafari, 2017). However, the mathematical model that fitted the function to the experimental data can sometimes not appropriate and not satisfactory. The analysis of variance (ANOVA) is applied to evaluate suitability of model fitted. ANOVA is carried out to analyse the experimental data from several runs using RSM (Oumabady et al., 2020).

The Fischer test value (F-value) and probability (p-value) are used to determine regression model of the response(s). A model is said to be well fitted into the experimental data if it shows the significant regression. Sasikumar and Viruthagiri (2008), stated that the model is significant due to higher F-value and very low p-value. From the result regression analysis corresponding to equation model, response(s) that well fitted into model equation is shown by the high R^2 value.

However, Yolmeh and Jafari (2017) explained that the accuracy of the model cannot simply indicate by the R^2 index. This is because the R^2 index only measure the number of the decreasing changeability of response from the repressor variable in the model. In their research, absolute average deviation (AAD) was proposed that provide better accuracy measurement. AAD is an average of absolute deviation from central point and it is calculated using formula as below:

$$\mathrm{AAD} = \left\{\left[\sum_{i=1}^{p}\left(\frac{|\mathrm{yi\ exp} - \mathrm{yi\ calc}|}{\mathrm{yi\ exp}}\right)\right]/\mathrm{p}\right\} \times 100 \quad \text{... (2.4)}$$

Where,

P= number of experiments

Yi exp = experimental response

Yi calc= calculated response

Both R^2 index and AAD must be determine to identify the accuracy or the model. R^2 index must be close to 1 and the AAD between estimated and observed data should be as low as possible.

Based on Bezerra et al. (2008), the significant of regression can be evaluated by the ratio between media of square of regression (MS_{reg}) and media of square of residual (MS_{res}). This ratio is then being compared to Fisher distribution (F test). Significant value of this ratio must be higher that the F value for the mathematical model to be well fitted to the experimental data.

$$\frac{MS_{reg}}{MS_{res}} \approx F_{vreg,vres} \quad \ldots (2.5)$$

Lack of fit test is the other options to evaluate the model. F test is used to determine the statistical significance of the model equation. A ratio between media of square of lack of fit (MS_{lof}) and media of square of pure error (MS_{pe}) is then compared to the F test, based on respective degree of freedom related to lack of fit (v_{lof}) and pure error (v_{pe}) variances. The model labelled as satisfactory when the ratio is lower than the tabulated value,F.

$$\frac{MS_{lof}}{MS_{pe}} \approx F_{vlof,vpe} \quad \ldots (2.6)$$

Table 2.2 The summary of previous optimization studies via RSM

Optimization	Independent variables	Dependent variable(s)	Design Method	Model	References
Hydrochar production from Paper Board Mill Sludge	Reaction temperature, Residence time	BET surface area, pore volume, hydrogen to carbon (H/C) ratio, oxygen to carbon ratio (O/C) ratio	Integrated optimal (I-optimal)	Quadratic polynomial (BET surface area, pore volume, H/C ratio) 2 factor interaction (O/C ratio)	(Oumabady *et al.*, 2020)
Hydrothermal carbonization of Rice straw	Reaction temperature, reaction time, particle size, biomass to water ratio	Hydrochar yield	Central Composite Design (CCD)	Quadratic polynomial	(Nizamuddin *et al.*, 2019)
Hydrochar production from spent Coffee Grounds	Reaction temperature, Residence time	Hydrochar yield, calorific value	Central Composite Design (CCD)	Quadratic polynomial (Hydrochar yield), linear (calorific value)	(Afolabi, Sohail and Cheng, 2020b)
Nutrient and Carbon Recovery from Anaerobic Digestate	Carbonization time, temperature, pH	Dry mass recovery, Carbon recovery, Nitrogen recovery, Phosphorus recovery, oxygen to carbon ratio (O/C) ratio	Central Composite Design (CCD)	Second degree polynomial	(Stutzenstein *et al.*, 2018)

2.4.1(d) Determination of Optimal Condition

Critical point can be distinguished as maximum, minimum and saddle. Yolmeh and Jafari (2017) and Bezerra et al. (2008) stated in their studies, optimum point for maximum and minimum can be determined through first derivative of mathematical function which represent the response surface and equates it to zero. The quadratic function is expressed as below:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} {x_1}^2 + \beta_{22} {\beta_2}^2 + \beta_{12} x_1 x_2 \quad \dots (2.7)$$

The optimum point can be obtained by calculating $\frac{\Delta y}{\Delta x_1}$ and $\frac{\Delta y}{\Delta x_2}$ and set to zero:

$$\frac{\Delta y}{\Delta x_1} = \beta_1 + 2\beta_{11} x_1 + \beta_{12} x_2 = 0 \quad \dots (2.8)$$

$$\frac{\Delta y}{\Delta x_1} = \beta_2 + 2\beta_{22} x_2 + \beta_{12} x_1 = 0 \quad \dots (2.9)$$

The above equations are solved to obtain the value of x_1 and x_2.

2.5 Optimization by Response Surface Methodology from Previous Works

In the study conducted by Afolabi, Sohail and Cheng (2020), face-centered Central Composite Design (CCD) was selected for the optimization of operating parameters namely reaction and residence time of spent coffee ground. The design consisted of 13 runs in total and requires three level for each parameter at 180°C, 200°C and 220°C while residence time at 1, 3 and 5 h. The response surface model shows that linear, interaction and quadratic terms were significant for hydrochar yield optimization by referring to F-value and p-value. The model was observed as good fit proven by R^2 of 0.92 and p-value of 0.0002. Maximum hydrochar yield of 64% and calorific value of 31.6 MJ/kg were obtained at optimal parameters of 216°C and 1 h.

However, Zhang *et al.* (2020) conducted an experiment of HTC of wheat straw and further optimized by using Box-Behnken Design method with the operating parameters in the range of 180°C- 260°C and 10-30 min. Three levels of RSM with 29 runs were designed and analysis of variance (ANOVA) was performed. Mass yield recorded maximum of 71.29% at lowest temperature and time of 180°C and 10 min.

Nizamuddin *et al.* (2015) conducted an optimization of process parameters of HTC of rice straw with additional of biomass water ratio as one of the operating parameters. The effect of reaction temperature, residence time and biomass to water ratio on hydrochar yield was optimized by using Central Composite Design (CCD). With the parameters in the range of 180°C-220°C, 20-60 min and 1:5-1:15 w/v respectively, the optimum condition of hydrochar yield was found to be at a 180°C reaction temperature, a 20 min reaction time and a 1:15 w/v biomass to water ratio yielding at 57.9% hydrochar. Nizamuddin *et al.* (2016a) conducted another study on palm shell obtained highest hydrochar yield of 70.6% at optimal conditions of 180°C, 30 min and 1.60 wt% respectively.

2.6 Factor Affecting Hydrochar Properties

Hydrothermal carbonization (HTC) operating conditions play a significant effect for the production yield and properties of the hydrochar as a by-product. The influence of HTC conditions namely reaction temperature, residence time, and biomass-water ratio on hydrochar was investigated in numerous studies throughout the years.

In the research of Afolabi, Sohail and Cheng (2020), hydrochar generation of spent coffee ground shown the highest solid yield at 64% and HHV at 31.6MJ/Kg at optimum conditions of 216˚C and 60 minutes respectively. However, with the increased in temperature from 180˚C to 220˚C and residence time from 1 to 5 h significantly decreased the yield by 13.5% and 8.3 % respectively. This proves the theory that higher reaction temperature and residence time will result in reduction of hydrochar yield. This is due to high thermolytic decomposition of biomass compound influenced by the increase of both operating conditions.

Studies made by J. S. Mohammed et al (2020) supported the previous statement when solid yield recorded low at 29.91% and HHV at 25.42 MJ/Kg when the reaction temperature was set at 305˚C. However, in term of HHV, study conducted by Nizamuddin et al. (2019), explained that higher heating value (HHV) increased from 16.90 MJ/Kg to 21.30 MJ/Kg when increased in temperature. Enhancement of HHV is triggered by the increased in temperature that improving the carbon content and decreasing the oxygen content.

Nizamuddin *et al.*, (2015) found that higher percentage of hydrochar yield achieved at reaction temperature below than 200 ˚C. This can be proven from previous studies such as Fan *et al.* (2018), Kang *et al.* (2019) and Zhang *et al.* (2020) that recorded higher hydrochar yield at range of 71.22% when the temperature at range of 180 ˚C to 260 ˚C and residence time of 0.5 -2 h were applied.

Another study conducted by (Nizamuddin *et al.*, 2016a) on palm shell proven that higher reaction temperature and residence time will result in lower solid yield of solid products. The study also found that lower percentage of hydrochar yield was obtained when the temperature reached 200°C and above. Reduced amount of hydrochar is due to the release of volatile matters at higher temperatures. Hydrochar yield decreased when increased the residence time from 30 min to 120 min. This is because lighter organic compound and permanent gases formed at higher residence time reducing the solid yield.

CHAPTER 3
METHODOLOGY

This chapter discloses the information on the methods applied in this final year project. It includes the general research flow diagram, simulation of hydrochar yield and process optimization with software Design Expert.

3.1 Overview of Research Methodology

This final year project focused on the simulation and the optimization of hydrochar yield of coconut husk using hydrothermal carbonization (HTC). Response surface methodology (RSM) was applied to obtain ideal and optimum conditions for the highest production of hydrochar yield of coconut husk via hydrothermal carbonization (HTC) and to study the influences of three parameters including reaction temperature, residence time, and biomass water ratio on the hydrochar yield**. Figure 3.1** shows the overview of the activity of this research.

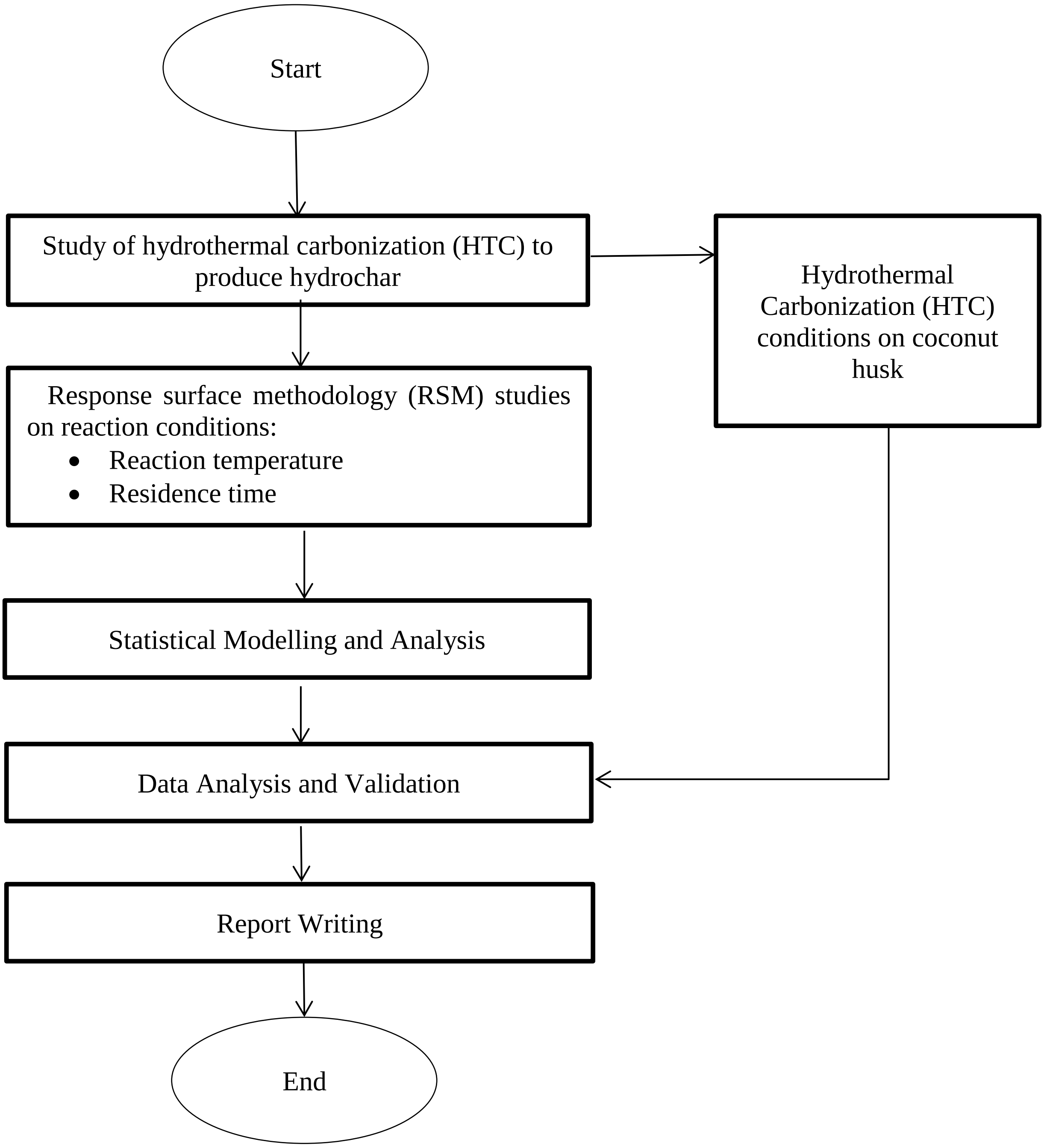

Figure 3.1 Flow diagram of research project

3.2 Design of Experiments

In order to obtain ideal and optimum conditions for the highest production of hydrochar yield of coconut husk via hydrothermal carbonization (HTC), the influences of three parameters including reaction temperature, residence time, and biomass water ratio were studied and optimized. The response surface methodology (RSM) was applied to design the experiments using Design Expert Software (Version 12). The central composite design (CCD) method was chosen among all the available methods to optimize the process parameters influencing the response due its ability and suitability in estimating a quadratic polynomials and effective optimization of involved parameters with lesser number of experiments (Nizamuddin et al., 2016a). Moreover, it also helps to analyse the interaction between parameters and identify main parameter that influenced the response. Sabio et al. (2016) stated that CCD is useful in RSM as it provides an even distribution of experimental points. The CCD consists of a 2^n factorial runs, 2n axial runs and n_c center runs, with n being the number of factors. With n factors, the total number of experiments, N is:

$$\mathrm{N} = 2^{\mathrm{n}} + 2\mathrm{n} + \mathrm{n_c} \quad \dots (3.1)$$

The center points are used to determine the experimental error and reproducibility of the data used (Tan, Ahmad and Hameed, 2008). Experimental design matrix and result are shown in **Table 4.1**, **4.2** and **4.3**. Hydrochar yield (%) is the response used for every set of experiments. These independent variables are coded as -1 and +1 that indicate low and high level. The empirical model was developed that corresponded to hydrochar yield (response) to the independent variables using a second-degree polynomial equation.

Two Independent Variables:

$$Y = A_0 + A_1A + A_2B + A_3AB + A_4A^2 + A_5B^2 \dots (3.2)$$

Three Independent Variables:

$$Y = A_0 + A_1A + A_2B + A_3C + A_4AB + A_5AC + A_6BC + A_7A^2 + A_8B^2 + A_9C^2 \quad ... (3.3)$$

Where

Y= Hydrochar yield (%)

A= Reaction temperature (°C)

B= Residence time (h)

C= Biomass-water ratio (wt%)

3.2.1 Two Independent Variables

Based on previous study, HTC of coconut husk has been conducted to determine the effect of significant parameters including process temperature and residence time. However, the optimization of the significant parameters for the hydrochar production has not been done in the previous study. RSM using CCD is applied for the optimization of these parameters to determine the optimum parameters for highest production of hydrochar. The independent variables studied were reaction temperature; and residence time. Reaction temperature and residence time were taken at the range of 180°C to 240°C and 48h to 96h respectively.

The suggested experimental design consisted of thirteen runs of experiments in total with four factorial points, four axial points and five center points. The number of experiments is calculated as shown in *below*

$$N = 2^2 + 2(2) + 5 = 13 \ldots (3.4)$$

3.2.2 Three Independent Variables

To obtain ideal and optimum conditions for the highest production of hydrochar yield of coconut husk via hydrothermal carbonization, the influences of three parameters including reaction temperature, residence time, and biomass water ratio were studied and optimized with the range taken based on the previous studies. Reaction temperature at the range of 180-260°C was selected based on several studies namely by Afolabi, Sohail and Cheng (2020), Fan et al. (2018), Chen et al. (2017) and Nizamuddin et al. (2016b). Kannan, Gariepy and Raghavan (2017) stated in their studies that HTC is a process that required slow temperature (150-250°C) for the conversion of biomass into carbonaceous material. Residence time was selected at the short time duration at range of 0.5- 2 h by referring to several studies. Biomass water ratio was added as one of parameters to study its influence on the yield and its interaction with other parameters.

Our CCD of three variables consists of 8 factorial points, 6 axial points and 6 center runs, indicates that 20 runs of experiments were required. The total number of experiments, N is shown below.

$$N = 2^3 + 2(3) + 6 = 20 \ldots (3.5)$$