Bio-oil Production from Pyrolysis of Rice Husk

by

Mu'ez bin Razami

Dissertation submitted in partial fulfilment of

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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(Dr. Suzana Yusup)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

December 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources of persons.

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(MU'EZ BIN RAZAMI)

ABSTRACT

The process of pyrolysis of biomass has been very useful to convert organic materials into a useful source of renewable energy which is bio-oil. However, the properties of bio-oil produced such as oxygenated compound, carboxylic acids, as well as the water content will depend on the type of plants or organic material it was derived. Therefore, the focus here is to study the properties of bio-oil derived from different sources of organic materials, in this case is risk husk.

We are now facing a big world crisis which is the depleting of fossil fuels energy resources. Furthermore, the combustion of fuels has led to the environmental pollution because of the carbon emission. The discovery of new sources of energy like bio-oil that have the potential to replace the current fuel and give no harm to the environment will bring a new hope to the world.

However, the properties of bio-oil are not stable because of the various compounds in the bio-oil which can react through many chemical reactions. During storage for example, the polymerizations reaction will occur resulting in adverse changes in the bio-oil's properties, especially increasing viscosity over time. Basically, the scope of study will cover the reaction condition such as particle size, temperature, heating rate, and nitrogen gas flow rate in the reactor. The responding aspects that need to be analyzed are organic liquid product yield, chemical and physical properties of the bio-oil produced as well the chemical composition of the bio-oil produced.

The signal to noise ratio and ANOVA table is constructed to identify the credibility of the results. Taguchi method will be used in the experiment to array the variables and to know the credibility of the result. From the analysis, the optimum operating condition for the pyrolysis process is using 0.355-0.5mm particle size, at 450 ˚C with 10˚C/min heating rate and 100ml/min of nitrogen flow rate which has the highest yield of 31.82 weight %.

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ABBREVIATION AND NOMENCLATURE

ANOVA	Analysis of Variance
DOF	Degree of Freedom
GCMS	Gas Chromatogram Mass Spectrometer
MTEC	National Metal and Materials Technology Center
PC	Percent Contribution
S/N	Signal to Noise Ratio
SS	Sum of Square
V	Variance

CHAPTER 1 INTRODUCTION

1.1 Background Study

None has had a more significant influence on society other than fossil fuels. Oil, in all its forms can be say as "transportation fuel" that enables most of the modern types of transportation possible to run and transports both people and goods around the globe. As for today, the world consumption on oil is mostly on automobiles which is 44.2%, next to heating oil and diesel fuels 27.8%, closely followed by petrochemicals products 22.2%, while 9.6% on jet fuel and the other 2.7% on asphalt. Figure 1 shows the world consumption of oils based on difference sectors mentioned. ("Fossil Fuels", n. d.)

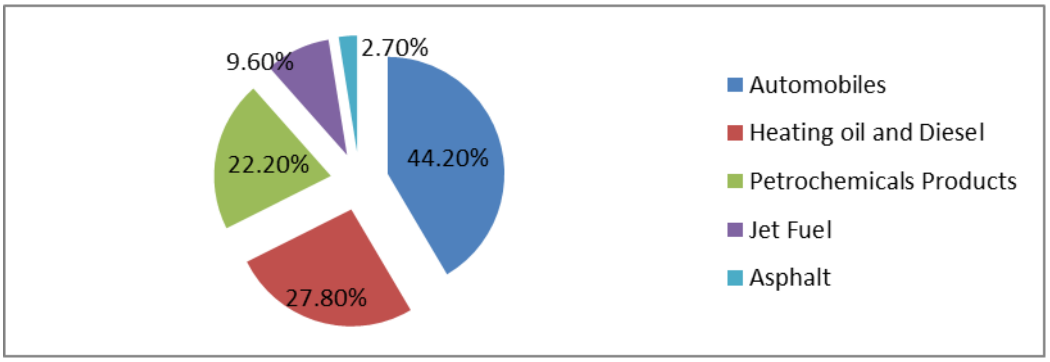

Figure 1.1: Distribution of World's Consumption by Various Sectors

However, the Energy Information Administration (EIA) of the United States predicted that less than half the total conventional oil reserves of the world will have been depleted and exhausted by 2025 regardless of the rapid growth of world demand for petroleum products which include existing oil reserves and foreseen reserves of oil reservoir. This will raise global big problem since fossil fuels is non-renewable source of energy. The alternative energy such as solar energy seems like to be a solution for this problem. Nevertheless, since it totally depends on the sun, it is less efficient to use this technology in areas with low sunlight intensity. The other alternative energy such as gasoline can be produced from coal. Unfortunately, the production cost is high and the quality of the product is very low (Siregar, 2005).

In fact, bio-fuels are one of the favourable alternative energy sources. Furthermore, it is a renewable energy and harmless to the environment due to none of sulphur and nitrogen content. In the room temperature, it will appear to be in the liquid form making it easier for transportation and handling purpose. For that reason, it turns out to be an attention to the world as a promising renewable energy resource. Bio-oil is a liquid fuel usually produced from biomass by fast pyrolysis process.

Generally bio-oil contains a wide variety of acids, a mixture of highly oxygenated compounds, and trace water making bio-oil exhibits some undesired properties such as high acidity and thermal instability. The properties such as homogeneity, polarity, heating value, viscosity and acidity will also being affected by the present of water and oxygen content present in the bio-oil (Zhang, 2006). Thus, unlike to the other conventional fuels, the properties of bio-oil are not stable. During storage, various compounds in the bio-oil can react through many chemical reactions (e.g. polymerizations) resulting in adverse changes in the bio-oil's properties, especially increasing viscosity over time (Hyun, 2011). In particular, a high content of oxygen in bio-oil results in a lower heating value if compared to conventional fuels. Consequently, bio-oil needs to be upgraded to remove the unfavourable characteristics so that it can be used as a substitute for the conventional fuels.

Pyrolysis is a process when the organic materials (feedstock) is heated in the absence of oxygen, vaporises and condenses to form a dark brown mobile liquid (bio-oil). It is a complex process and subjected to the influence of many factors such as texture structures of biomass, water content, inherent minerals, heating rates, reactor patterns or configurations, operating conditions of the reactors, presence of additives such as catalysts, as highlighted by Jun et al. (2006).Various kinds of plants and organics materials can be used as the raw material for the pyrolysis process. Difference raw of material will have different properties, chemical composition and the reactivity towards the process of pyrolysis. Even if the bio-oil is produced from the same type of plant but grew up in different places will not have the same quality.

1.2 Problem Statement

As the main source of energy for all sectors is gradually depleting and nearly exhausted, as well the increasing population and developing economy demands lots of energy causing the need for more alternative fuel sources. Scientists struggling to find the alternative fuels that can compensate the needs of human kind while causing less or no harm to the environment. The promising alternative fuel that has been found is bio-oil which is produced from the process of pyrolysis of bio-mass. Its effect to the environment is far less than the conventional fossil fuels since bio-oil is a carbon neutral compound and hardly contains sulphur, nitrogen and ash components (Hyun, 2011).

Bio-oil can be produced from different kinds of raw materials especially organic compounds and plants. The bio-oil produced is highly dependent on the raw material it was derived. For this project, the raw material being under study is rice husk. Rice husks are an agricultural residue obtained as a by-product of the rice milling industry. The world-wide production of rice husks is approximately 100 million tonnes yearly. In Malaysia, it is estimated over 9 million tonnes of rice waste are generated (Fairous Salleh, et al., 2011). The disposal problem caused by the unused agricultural residue can be solved by utilisation of this source of biomass through energy recovery processes. This would also help to generate useful energy (Paul, 1999).

There are several factors that will affect the pyrolysis process and hence affect the quality and quantity of the bio-oil produced. In this project, rice husks will be subjected to pyrolysis reaction under four considered factors. The reaction will be varied between 4 factors and the results will be analysed as its effect on the bio-oil yield, properties and composition. By using Taguchi software, the best 9 out of 81 runs can be calculated.

1.3 Objectives

The objective of this research is to

i. To produce bio-oil from pyrolysis reaction using rice husk as a feedstock.
ii. To discover the optimum operating parameters for the semi-batch reactor in UTP to produce bio-oil (reaction temperature, nitrogen gas flow rate, heating rate and particle size).
iii. To discover how different operating parameters of the reactor affect the bio-oil produced (yield, properties and chemical composition).

1.4 Scope of Study

The experiment was designed to investigate:

i. Particle size of rice husks.
ii. Heating rate.
iii. Reaction temperature.
iv. Nitrogen gas flow rate in the reactor.

The aspects that being analysed to study the difference of bio-oil produced from Thai rice husk and Malaysian rice husk:

i. The liquid bio-oil yield.
ii. The chemical and physical properties of the bio-oil produced.
iii. The chemical composition of the bio-oil produced.

Firstly, the semi batch reactor will be set up before the sub sequential study is being carried out. Secondly, the reaction condition such as temperature, nitrogen gas flow rate, particle size and heating rate tests are conducted in order to determine the best conditions which has the highest yield of organic liquid product (bio-oil). Lastly, the products obtained will be further investigated to study difference between Thai and Malaysian rice husk.

This project is feasible within the scope and the time allocated. The first half of this project will be focusing on the through literature review of the related researches to obtain the basic understanding and knowledge about the project and to see the areas of improvement. The second half of the project mainly focuses on conducting experiments and collected results and data. These results collected will then be analysed and investigated critically. This project is also feasible to be carried out using the facilities available in UTP. The semi batch reactor (tube furnace reactor) is a suitable reactor that can be used for slow pyrolysis process. For the feedstock, Malaysian rice husks will be obtained from the regular supplier. As for the Thai rice husks, it will be easily obtained since UTP has been already have the connection with the Thailand research centre (National Metals and Materials (NSTDA).

CHAPTER 2 LITERATURE REVIEW

2.1 Bio-oil

Bio-oil is a dark brown, free flowing organic liquids produced from pyrolysis process. Bio-oil contains highly oxygenated compound, carboxylic acids, aldehydes, phenolics, carbohydrates, ketones, degraded lignin and water depend on the type of plants or organic material it was derived. Usually, bio-oil is derived from biomass wastes such as corn straws, empty fruit branches and rice husk.

Figure 2.1: Bio-oil

However, unlike to the other conventional fuels, the properties of bio-oil are not stable. The primary reason for the difference in the properties and behaviour between hydrocarbon fuels and biomass pyrolysis oils is the presence of oxygen. During storage, various compounds in the bio-oil can react through many chemical reactions (e.g. polymerization) resulting in adverse changes in the bio-oil's properties, especially increasing viscosity over time. As a result of the instability, the bio-oil aging is occurring. This instability can actually be minimized or decreased either through the stabilization process after pyrolysis through upgrading, or modification to the pyrolysis process to reduce the amount of oxygenated compound formed.

Table 1 describes the difference in the physical properties between the bio-oil and the fuel oil (Mortensen, 2011).

Table 2.1: Comparison between bio-oil and the heavy fuel oil [11]

Physical Property	Value	
	Bio-oil	**Fuel oil**
Moisture content (wt%)	15 – 30	0.1
pH	2.5 – 3.8	
Specific Gravity	1.2	0.94
Elemental Composition (wt%) C H O N S Ash	54.0 – 65.0 5.5 - 7.0 28.0 – 40.0 < 0.4 < 0.05 < 0.2	83.0 – 86.0 11.0 – 14.0 < 1.0 < 1.0 <4.0 < 0.1
HHV (MJ/kg)	16-19	44
Viscosity, at 500 °C (cP)	40-100	180

The high water and oxygen content present in the bio-oil are the primary reason for the difference in the properties and behaviour between hydrocarbon fuels and biomass pyrolysis oils as it affects the homogeneity, polarity, heating value, viscosity and acidity of the oil (Zhang, 2006).

2.2 Pyrolysis

Pyrolysis is a process of degradation and decomposition of biomass in high temperature with the absence of oxygen that will produce mainly on organic liquid oils as well as gases, char and other products (Abdullah, 2008). Pyrolysis can be classified into two categories which are fast pyrolysis and slow pyrolysis. Fast pyrolysis process is when the feedstock is rapidly heated in high temperature. The heating rates can reach to 1000K/min. The heating rates for slow pyrolysis can be slow as 100K/min and below. Usually, the reaction temperature for both cases is in the range of 300°C to 500°C. The difference in heating rate results in significant dissimilarity in quality of bio-oil produced.

In slow pyrolysis process, the vapour residence time is longer than fast pyrolysis process causes secondary cracking reaction to happen which mainly contributing in producing gas. Meanwhile in fast pyrolysis, the short vapor residence time and the rapid quenching of those vapors will produce high yields of liquid. Table 2.2 summarizes the difference between fast and slow pyrolysis.

Fast Pyrolysis	Slow Pyrolysis
Very short residence time (a few seconds)	Long vapour residence time (up to a few minutes or hours)
High heating rates (exceeding 1000K/min)	Low heating rates (below 100K/min)
High reaction temperature (500 °C or higher)	Low reaction temperature (about 300 °C)
Generates primarily organic liquid product (bio-oil)	Generates primarily gas

The liquid yield or bio-oil is the desired product from the pyrolysis process and the conversion of the biomass to liquid yield can be calculated using the formula below:

$$\text{Yield}_{\text{bio-oil}} = \left(\frac{m_{bio-oil}}{m_{biomass}}\right) \times 100$$

Meanwhile, the overall conversion of biomass into gas and oil products can be determined by using the formula:

$$\text{Conversion}_{\%} = \left(\frac{m_{biomass} - m_{residue}}{m_{biomass}}\right) \times 100$$

2.3 Summary of Important Literature Reviews

Below is the table of the findings from important literature reviews in assisting in this final year project. The methods or variables might be different, but some of the result shows significant findings that can help in the topic. The literature reviews are discussed. From these literature findings, the factors of pyrolysis process under study such as reaction temperature, nitrogen gas flow rate, particle size, and heating rate can be determined considering the facilities, type and size of reactor available in UTP as well.

Year	Author	Paper Title	Factors				Yield
			Particle Sizes	Reaction Temperature	Heating Rate	Nitrogen Gas flow rate	
2009	Natrajan. E, and Ganapathy Sundaram. E	Pyrolysis of Rice Husk in a Fixed Bed Reactor	1.18 -1.80 mm (the liquid and solid yield increase but the gas yield decrease)	400^oC - 600^oC	20^oC/min 40^oC/min 60^oC/min	-	34.17- 42.52% at 500^oC temperature, heating rate 60^oC/min and particle size 1.18 -1.80 mm
2007	Z. Ji-lu	Bio-oil from Fast Pyrolysis of Rice Husk	-	420,480,540^oC	600^oC/s = 3600^oC/min	0.4 m3/h = 6 666.67 cm3/min	56% at 465^oC reaction temperature.
2000	Paul T. Williams	Comparison of Products from the pyrolysis and catalytic pyrolysis of rice husks	0.25-1.0mm	400^oC - 600^oC (the liquid yield decrease but the gas yield increase)	-	-	At 400^oC (46.5% oil and 6.5% gas)
2007	W. T. Tsai, M. K. Lee	Fast Pyrolysis of Rice Husk: Product Yields and Compositions	0.420-0.50mm 0.25-0.42mm 0.177-0.25mm 0.125-0.177mm **<0.5mm** The char yield will decrease with the particle size	400-800^oC (highest yield at 800^oC), optimum **500^oC**	100-500^oC (highest yields at **200^oC** and 500^oC/min)	500-1500cm^3/min there is no obvious influence on the yield at the higher nitrogen flow rates (1000 cm3/min)	Maximum yield could be obtained with high heating rates(>200^oC) at reaction temperature around >500^oC is >40%

2010	Hyeon Su Heo et al.	Fast Pyrolysis of Rice Husk under different reaction conditions	0.04mm	400-550^oC Maximize at tem between 400-450^oC		5000cm^3/min	50% at temperature 450^oC, flow rate 5000cm^3/min and feeding rate 2.5g/min
2010	Khairuddin Md Isa et al.	Thermogravimetric analysis and the optimisation of bio-oil yield from fixed-bed pyrolysis of rice husk using response surface methodology (RSM)	0.6mm	400^oC - 500^oC	100^oC/min	100cm^3/min	Highest yield of 48% at 473.37^oC reaction temperature, 100^oC/min heating rate, using 0.6mm particle size and 100cm^3/min nitrogen flowrate.
2011	Tianju Chen et al.	Effect of hot vapor filtration on the characterization of bio-oil from rice husks with fast pyrolysis in a fluidized-bed reactor	0.2-0.6mm	500^oC	-	60liter/min = 60 000cm^3/min	42% at 500^oC reaction temperature and 0.2-0.6mm particle size.

Table 2.3: Summary of the Significant Literature Reviews

2.4 Taguchi Orthogonal Array

For all intents and purposes, common experimental design procedures are too complex to use. A lot of experimental works have to be done as the number of process parameters increases. In order to solve this problem, the Taguchi method uses a special design of orthogonal arrays to study the entire parameter space with only a small number of experiments (Rama, 2012).

Taguchi Orthogonal Array is used to minimize the number of experimental runs needed for the experiment. Orthogonal Array is a part of Taguchi Method application (Genichi, 2002). Signal to noise ratios are used to measure the functionality of the system. In other words, Taguchi method is used to obtain the optimal operation conditions. Taguchi's Orthogonal arrays are highly fractional orthogonal designs which can be used to evaluate main effects using only a few experimental runs.

Taguchi method is employed to determine the affect of different parameters on the mean and variance of a process performance characteristic. The greatest advantages of this method are saving effort in conducting experiments, saving experimental time, reducing the cost, and discovering significant factors quickly. Also, statistical analysis of variance (ANOVA) can be employed to indicate the impact and importance of each factor instead of signal to noise ratio (S/N) analysis.

In the signal to noise ratio, there are three quality characteristics being considered which are the smaller, nominal or larger. The definition of quality "for bigger is better" is the determining factors that producing the highest of yield of desired product, which will be applied in the experiment. The greater the value, the smaller the product variance to the target value (Ranjit, 1990). The equation used to calculate the S/N is:

$$\frac{S}{N} = -10log_{10}\left(\frac{1}{n} \times \sum \frac{1}{y^2}\right)$$

where n is the runs and y is the result.

ANOVA (Analysis of Variance) is a statistically based, objective decision-making tool for identifying any alterations in the average performance of groups of items tested. Besides, ANOVA helps in testing the relevant of all the main factors (Rama, 2012). To construct an ANOVA table, the degree of freedom (DOF) is needed, sum of square (SS), Variance (V) and Percent Contribution (PC). The formula to calculate the sum of square is as follows:

$$SS_A = \left(\sum_{i=1}^{k_A} \frac{A_i^{\,2}}{n_{A_i}}\right) - \frac{T^2}{N}$$

where SS_A is the sum of squares of the factor A, k_A is the number of the levels of factor A, A_i is the sum total of the experimental results at level I of factor A, n_{Ai} is the number of all experimental results at level i of factor A, T is the sum of all experimental results and N is the number of all experiments.

CHAPTER 3 METHODOLOGY

3.1 General Research Methodology

1st Stage: Project Planning Phase

Problem identification and the significance of the project based on the current issue are determined. Since there are four variables for the experiment, which are the reaction temperature, heating rate, particle size and nitrogen flow rate, therefore the possible levels for the variables should be determined.

2nd Stage: Characterization of Bio-oil and Levels of Variables

For the characterization of bio-oil and the levels of the variables, literature review is conducted. Comparable studies between reaction temperature, heating rate, particle size and nitrogen flow rate are conducted. Besides, characterization and component of the bio-oil is analysed.

3rd Stage: Screening and Identification Phase

Basis for the selection criteria are outlined. In the experiment, biomass which is rice husk is provided by National Metal and Materials Technology Center (MTEC), Thailand.

4th Stage: Experiment Design

Decision on the equipments and chemicals involved for the project with clear view of methodology is conducted. Experiment is designed using Expert Design with L9 Taguchi Orthogonal Arrays Design method with 4 factors and 3 levels. Equipments will be identified specifically for analyzing product and chemical purposes.

5th Stage: **Comparative Study**

Statistical analysis and properties testing are conducted. The data is recorded in the Design Expert software. Result is evaluated based on conceptual understanding. The analysis is done on the optimum condition's product and compared with raw bio-oil.

3.2 Research Methodology

This project relies more on the methods of exploration and discovery since there is always space for innovation in this sector. Basically, this project mainly involve in empirical and experimental research, by conducting series of experiment to obtain relevant results which can be a useful data for reference. Using the information gained from the journals reviewed that act as a base for this project; the catalytic pyrolysis process experiments will be conducted by using different configuration and setup of the equipment in order to produce bio-oil from rice husks as raw materials. The results is then can be used as a basis of comparison with the other findings that have been reported on the journals reviewed.

First of all, before starting the experiment, a strong understanding on the concepts and mechanisms of pyrolysis are needed so that the improvement can be made. This can be done by reviewing a lot of journals published in the website which involve from the basic concept of pyrolysis until the very technical data about it. Then, the process is continued with critical thinking to produce an innovation for this pyrolysis process based on the findings from the literature reviews. The facilities available in UTP can be also a factor in this project. Therefore, after all the considered factors have been finalised, a plan can be made in order to complete this project within the time provided.

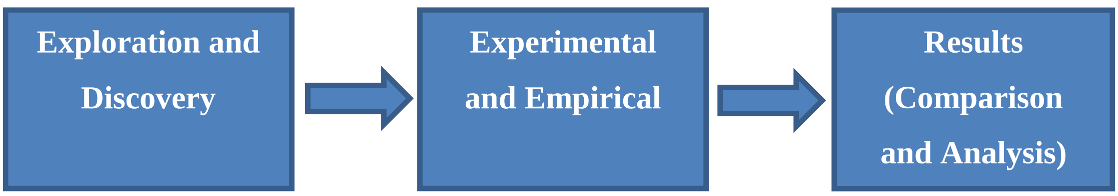

Figure 3.1: The flow of research methodology

3.3 Experimental Procedure

The parameters are selected based on the literature review findings on most of the journals and articles. The particle size is chose to be <0.5mm which is divided into three ranges of sizes: <0.25mm, 0.250 - 0.355mm and 0.355 – 0.50mm. As for the reaction temperature, the optimum condition for pyrolysis process is around 500˚C. This is reported on the majority of the journals reviewed. Therefore, the level of the reaction temperature for this experiment is decided to be 400˚C, 450˚C and 500˚C. The nitrogen gas flow rate is chose to be 100, 300 and 500ml/min suitable to be used in semi-batch reactor available in UTP. The experiment is decided to be run with heating rate of 10, 15 and 20˚C/min as the heater available in the lab can only operate within this range.

3.3.1 Determination of Optimum Parameters of Pyrolysis

1. Condition for the determination of reaction time is selected, which is the temperature of 400˚C, heating rate of 15˚C/min, particle size 0.250-0.355mm and nitrogen flow rate of 500ml/min.
   **Note: The condition is assumed to be the best by referring to the journals and literature reviews. So the condition is chosen for the best condition for the determination of reaction time.*
2. The borosilicate tube's weight is recorded and the rice husk is poured into the tube.
3. The sample bottle is also weighed.
4. The experiment is set up and nitrogen gas is purged for 5 minutes at 500ml/min before the experiment.
5. The temperature of the heater and thermocouple is recorded every minute.
6. The time of the first droplet of liquid yield is recorded and the experiment is stopped when there are three constant readings of thermocouple readings or there are no more reactions.
7. Once the reaction time for the first reaction is determined, the same procedure is run with the same set up.

Table 3.1: Taguchi L9 Array with 4 Factors and 3 Levels

Run	Factor 1 A: Particle Size (mm)	Factor 2 B: Temperature (˚C)	Factor 3 C: Heating Rate (˚C/min)	Factor 4 D: Nitrogen Flow Rate (ml/min)
1	0.250 - 0.355	400	15	500
2	<0.25	500	20	500
3	0.250 - 0.355	500	10	300
4	0.250 - 0.355	450	20	100
5	0.355 – 0.50	500	15	100
6	0.355 – 0.50	450	10	500
7	<0.25	400	10	100
8	<0.25	450	15	300
9	0.355 – 0.50	400	20	300

3.3.2 Pyrolysis of Rice Husk into Bio-oil

1. The level of the factors is based on the optimum condition determined.
2. The experiment is setup based on the picture and nitrogen gas is purged for 5 minutes at 500 ml/min before the experiment.
3. The temperature of the heater and thermocouple is recorded every minute.
4. The time of the first drop is recorded. After 10 minutes, the experiment is stopped and let to cool. The condenser is weighed to calculate the liquid yield.
5. The bio-oil is collected for characterization.
6. Step 1-5 is repeated until enough bio-oil is produced (10 runs).

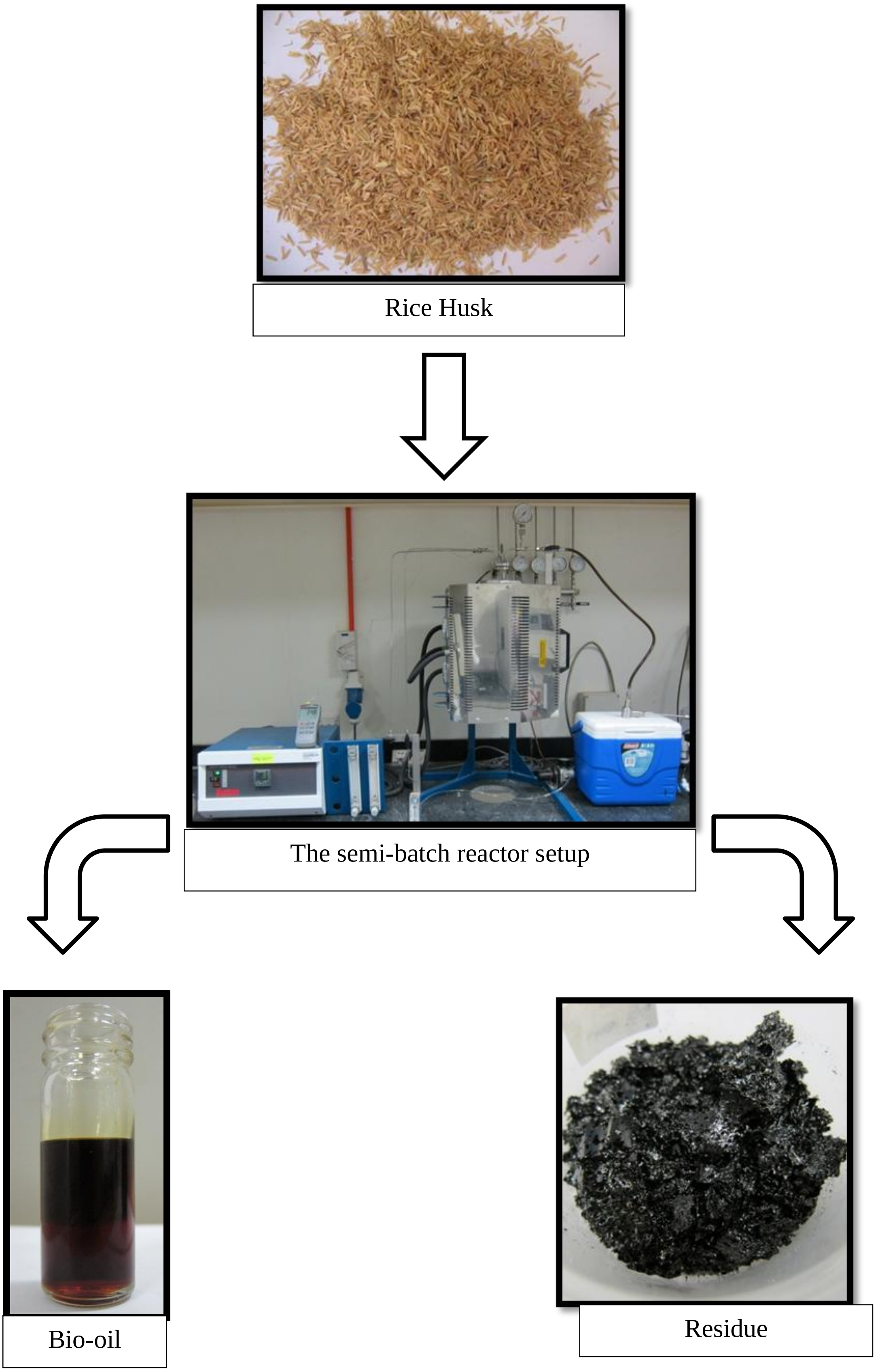

Figure 3.2: Experimental Procedure

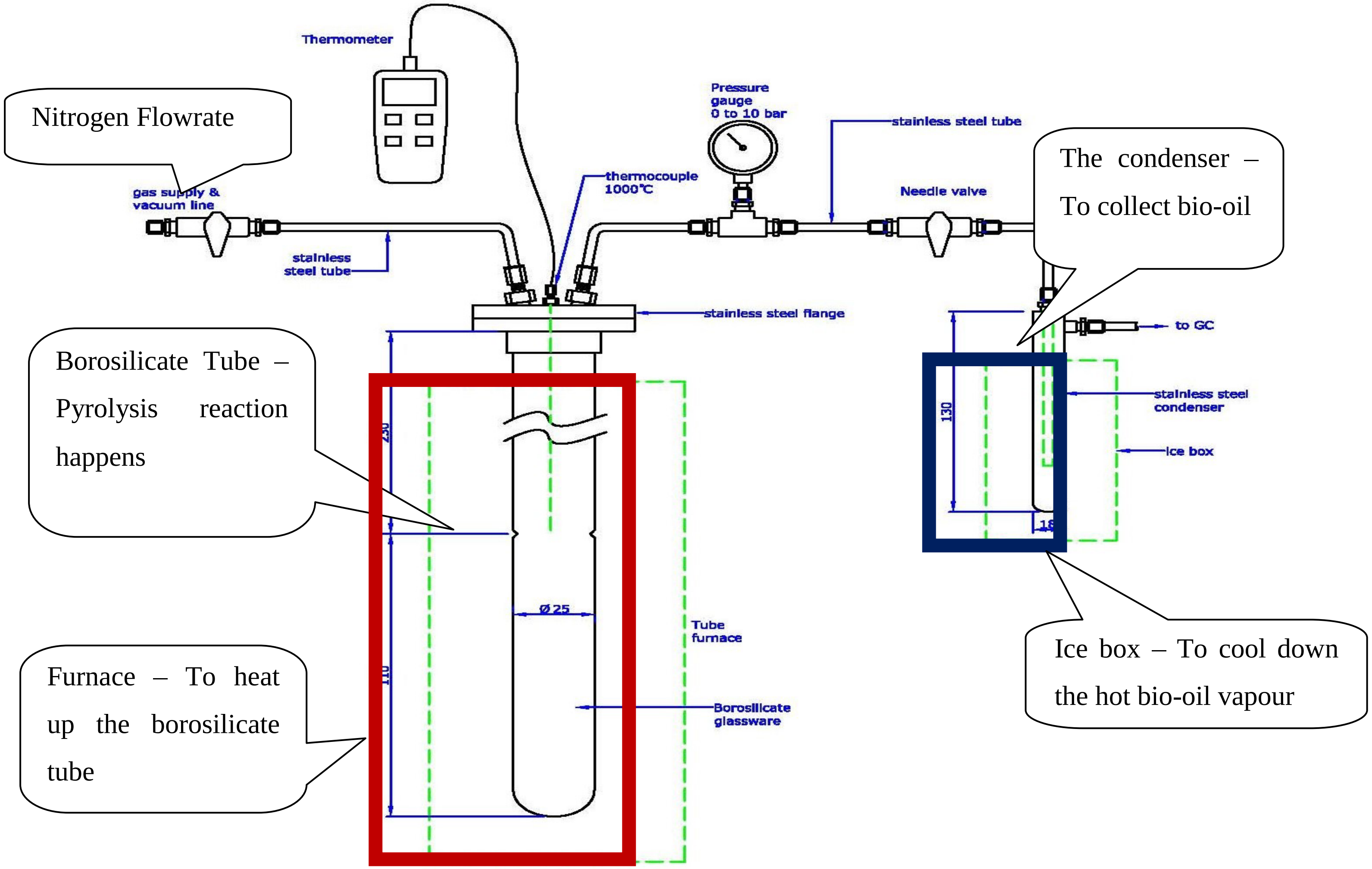

Figure 3.3: Schematic Diagram of Semi-Batch Reactor

3.4 Experiment Apparatus and Instruments

3.4.1 Equipment

1. Semi-batch Reactor (Lenton Thermal Designs with Split Tube Furnace)
2. RS 1319A K-Type Thermocouple
3. KI Key Instruments Nitrogen Flow Controller
4. Coleman Thermozone Insulator

Figure 3.4: Semi-Batch Reactor

5. Borosilicate Tube
6. Gas Chromatography Mass Spectrometry GCMS-QP5050 Shimadzu
7. Schott Instruments pH Meter
8. Brookfield Viscometer
9. Metrohm 870 Karl Fischer Titrino Plus
10. IKA C5000 Bomb Calorimeter
11. LECO (Model 932) CHNS Analyzer
12. Anton Paar Density Meter DMA 4500 M
13. Muffle Furnace

3.4.2 Materials

1. Methanol (for washing)
2. Rice husk

3.5 Characterization and Properties Measurement

An objective of the characterization experiment is to obtain data for the properties of the sample products. Below are the lists of the experiment that will be conducted for sample product characterization.

Table 3.2: Testing Parameters

No	Testing Parameters	Instruments	Methods	Sample Size	Venue
1	Viscosity	Brookfield Viscometer	ASTM D445	13mL	Block P
2	Water Content	Karl Fischer Titrando	ASTM D1744	A few drops	Block P
3	pH	pH Meter	-	-	Block P
4	Calorific Value	Bomb Calorimeter	-	0.4g	Block 4
5	Density	Density Meter	ASTM D4052	2mL	Block P
6	GC-MS	GCMS	-	Vial tube	Block 4
7	CHNS	CHNS Analyzer	ASTM D5291	2mL	Block 4
8	Ash content	Muffle furnace	ASTM D482	3g	Block P

3.5.1 Viscosity

Brookfield Viscometer will be used to measure the viscosity. The viscosity is measured by rotating the spindler at highest torque to get the viscosity in the unit of cPa at 40˚C.

3.5.2 Water Content

Metrohm 870 KF Titrino Plus will be used for measuring water content. This water content experiment can be conducted by measuring sample's weight difference.

3.5.3 pH

The pH of the products is by using Schott Instruments pH meter. The electrode is immersed into the samples and data will be recorded.

3.5.4 Calorific Value

The calorific value or known as heating value is measured by using the IKA C5000 Bomb Calorimeter. The units will be in MJ/kg. The samples are put inside the Bomb Calorimeter and high temperature will be ignited against the sample.

3.5.5 Density

By using the Anton Paar Density Meter DMA 4500 M, the samples are injected to the Density Meter and the readings will be obtained. Besides that, specific gravity will be obtained too.

3.5.6 Gas Chromatography Mass Spectrometry (GCMS)

GCMS-QP5050 Shimadzu is used as a common analytical tool to identify the compounds in the sample. It detects the compounds and determines the mass spectrum to analyse the compound.

3.5.7 CHNS Analyser

LECO CHNS Analyser 932 is an elemental analyer used to determine the amount of Carbon, Hydrogen, Nitrogen and Sulphur contained in organic or inorganic solvent.

3.6 Tools / Software

A computer program called *Design-Expert® Version 8.0.4* produced by Stat-Ease, Inc.is used to assist in determining the optimum number of runs that need to be carried out by varying the 4 factors under study. Taguchi Method which is incorporated in this software is chosen and the L9 method (3^4) is used to determine the optimum number of runs (in this case 9 runs), which includes the variation of 4 factors, each having 3 levels.

The optimum condition is determined by the results obtained from the 9 runs of experiment. Then, 10 series of experiment will be conducted under the optimum condition to produce enough bio-oil for characterization. The characteristics and properties of liquid yield (bio-oil) produced is compared with the standard properties of bio-oil. The result is used to compare with the bio-oil produced from Malaysian rice husk as well.

3.7 Key Milestones

Table 3.3: Key Milestones for Final Year Project (FYP I and II)

NO	DETAIL / WEEK	1,2	3,4	5,6	7,8	9,10	11,12	13,14	15,16	17,18	19,20	21,22	23,24	25,26	27,28
1	Confirmation of FYP topic														
2	Literature Review														
3	Extended Proposal				●										
4	Rough planning of experiments														
5	Secure the source of raw materials and chemicals needed					●									
6	Detailed planning of experiments														
7	Learning Design Expert Software														
8	Obtaining the raw materials and chemicals needed								●						
9	Run experiments and obtaining results														
10	Analyse and interpret the results obtained														
11	Documentation of the whole project and presentation														●

3.8 Gantt Chart

The Gantt chart for FYP II is outlined in Table 3.4.

Table 3.4: The Gantt Chart for FYP II

NO	DETAIL / WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■									
2	Submission of Progress Report									●							
3	Project Work Continues									■	■	■	■	■			
4	Pre-SEDEX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

● Suggested milestone

■ Process

CHAPTER 4 RESULT AND DISCUSSION

4.1 Experimental Results

For this report, statistical analysis is used to relate the parameters such as the result of the data, the ANOVA table and relationship graph.

4.2 Statistical Analysis

The experiment is run based on the array from the Taguchi L9 Orthogonal Array. Relationship between the variables is established using the Design Expert software and analysis is conducted for each parameter. Only significant findings are discussed.

\

Table 4.1: Taguchi Experiment Design L9 with Results

Run	**Factor 1 A: Particle Size (mm)**	**Factor 2 B: Temperature (˚C)**	**Factor 3 C: Heating Rate (˚C/min)**	**Factor 4 D: Nitrogen Flow Rate (ml/min)**	**Liquid Yield (Bio-oil)**
1	0.250 - 0.355	400	15	500	24.38
2	<0.25	500	20	500	24.42
3	0.250 - 0.355	500	10	300	22.79
4	0.250 - 0.355	450	20	100	30.94
5	0.355 – 0.50	500	15	100	30.91
6	0.355 – 0.50	450	10	500	23.12
7	<0.25	400	10	100	26.52
8	<0.25	450	15	300	25.89
9	0.355 – 0.50	400	20	300	26.73
Meanwhile, the software proposes another optimum condition.					
10	0.355 – 0.50	450	20	100	31.82

4.2.1 Process Optimization

The conversion of biomass into bio-oil involves a number of complex reactions producing a lot of new substances during the reaction. The highest yield is produced by Run 4 with 30.94 wt% of bio-oil, while run number 3 producing the lowest yield which is 22.79 wt%. In the Taguchi L9 array, the highest yield is obtained by using particle size 0.250-0.355mm of particle size, at the temperature of 450˚C, nitrogen flow rate at 100ml/min and 20˚C/min of heating rate.

However, based on the calculation made by the software, it proposes another combination of parameters which yield higher bio-oil (31.82 wt%) than Run 4 (30.94 wt %). This combination is possible since there are several combinations that are not arrayed by the software before. Taguchi software will calculate and predict the possible optimum condition for the reaction. Instead of running 81 runs of experiment, only 9 runs are conducted. The optimal condition proposed by the software is by using particle size 0.355-0.5mm of rice husk, at the temperature of 450˚C, nitrogen flowrate at 100ml/min with heating rate of 20˚C/min.

Run 10 are then conducted for the experimental confirmation based on Taguchi's design approach. The confirmation is vital and highly recommended to verify the experimental results (Ross, P.J. 1996). The predicted optimum condition has been proven to produce highest yield of bio-oil.

In order to collect enough bio-oil for characterization analysis, Run 10 is conducted for 5 trials and 27.6 gram of bio-oil is produced. For each of the trials, 32.06, 31.87, 32.22, 33.04, and 33.8 wt% of bio-oil are obtained with the average of 32.6 wt% and standard deviation of 0.8. The difference between predicted and the real values are calculated.

$$\text{Percentage of error \%} = \left|\frac{Predicted - Experimented}{Predicted}\right| x\,100$$

$$= \left|\frac{31.82-32.6}{31.8}\right| x\,100$$

$$= 2.45$$

Taguchi L9 Orthogonal Array has identified the combination which produces the highest yield of bio-oil.

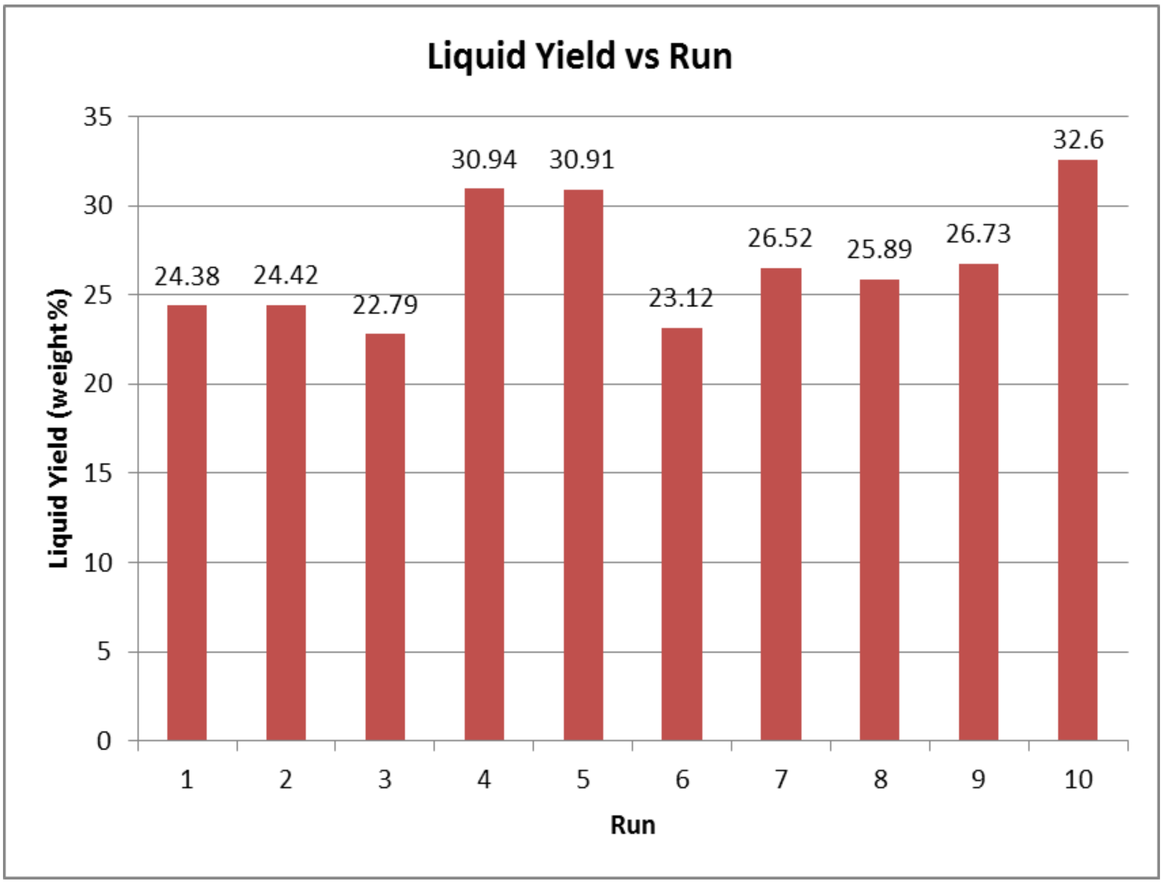

Figure 4.1: Liquid Yield vs Run

4.2.2 Signal to Noise Ratio (S/N)

Variance index Signal to Noise Ratio (S/N) which can used to identify the most optimum condition by selecting the highest S/N value. There are three quality characteristics considered, “the smaller the better”, “the nominal the best” or “the bigger the better”. For this experiment, the fact “the bigger is better” is defined as the determining factor is the percentage yield of bio-oil.

4.2.3 ANOVA Table

ANOVA table is made for statistical analysis of the data. The results are further discussed and summarized in the ANOVA table. In the percent contribution column, the bigger the value, the bigger the factor affects the outcome of the experiment, which means it is a significant factor.

By comparing the percentage of contribution of the factors, the nitrogen flow rate (D) is found to have the biggest effect on the yield of bio-oil with 68.89%. The second highest effect on liquid yield belongs to heating rate (C) with a percentage contribution of 25.06%, followed by particle size (A) and temperature (B) with percent contribution of 3.66% and 1.35% respectively, showing less significance on the outcome of the experiment.

Table 4.2: ANOVA Table

Source of Variance	Degree of Freedom	Sum of Square	Variance	Percent Contribution	Remarks
Particle Size (A)	2	2.66	1.33	3.66	-
Temperature (B)	2	0.99	0.49	1.35	-
Heating Rate (C)	2	19.01	9.50	26.11	Significant
Nitrogen Flow Rate (D)	2	50.13	25.06	68.89	Significant
Total	8	72.79	36.38	100	-

4.2.4 Effect of Particle Size and Temperature towards Liquid Yield

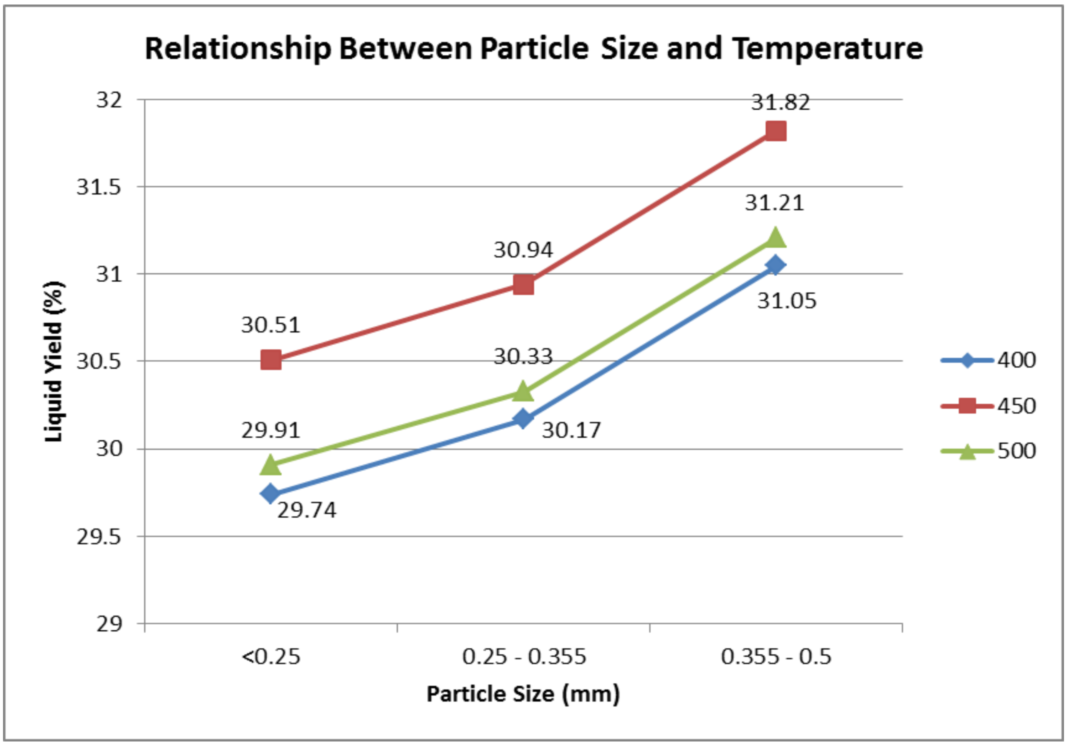

Figure 4.2: Relationship between Particle Size and Temperature towards Liquid Yield

If the particle size decreased, it will lead to decrease of liquid yield because of the residence time of volatiles in the reactor is longer, favoring the cracking of hydrocarbon, when smaller particle are used (Natrajan. E, et.al, 2009). This is mean more residence time of volatiles inside the reactor leads to cracking of heavier molecules (tar) in to lower molecules at lower particle size ranges and it results in increase of gaseous product. [10]

From figure 4.2, the results shows that the liquid yield is slightly increase as the particle size increased from less than 0.25mm to 0.5mm. From the ANOVA table, we know that particle size is not a significant parameter for the experiment and hence have the less effect on the liquid yield production. This result shows that the particle size <0.5mm is suitable to be used for pyrolysis process. This is in agreement with the previous study (W. T. Tsai et al., 2007).

The results shows that the liquid yield increases from 400˚C to 450˚C then decreased when the temperature is further increased to 500˚C. The increase of liquid yield as the temperature increase is due to greater primary decomposition of the sample at higher temperature. The decreased in liquid yield at 500 ˚C may be due to secondary cracking of the pyrolysis liquid in to gaseous product at higher temperature. Thus, the optimum condition is by using particle size 0.355-0.5mm and temperature of 450˚C.

4.2.5 Effect of Heating Rate and Nitrogen Flowrate towards Liquid Yield

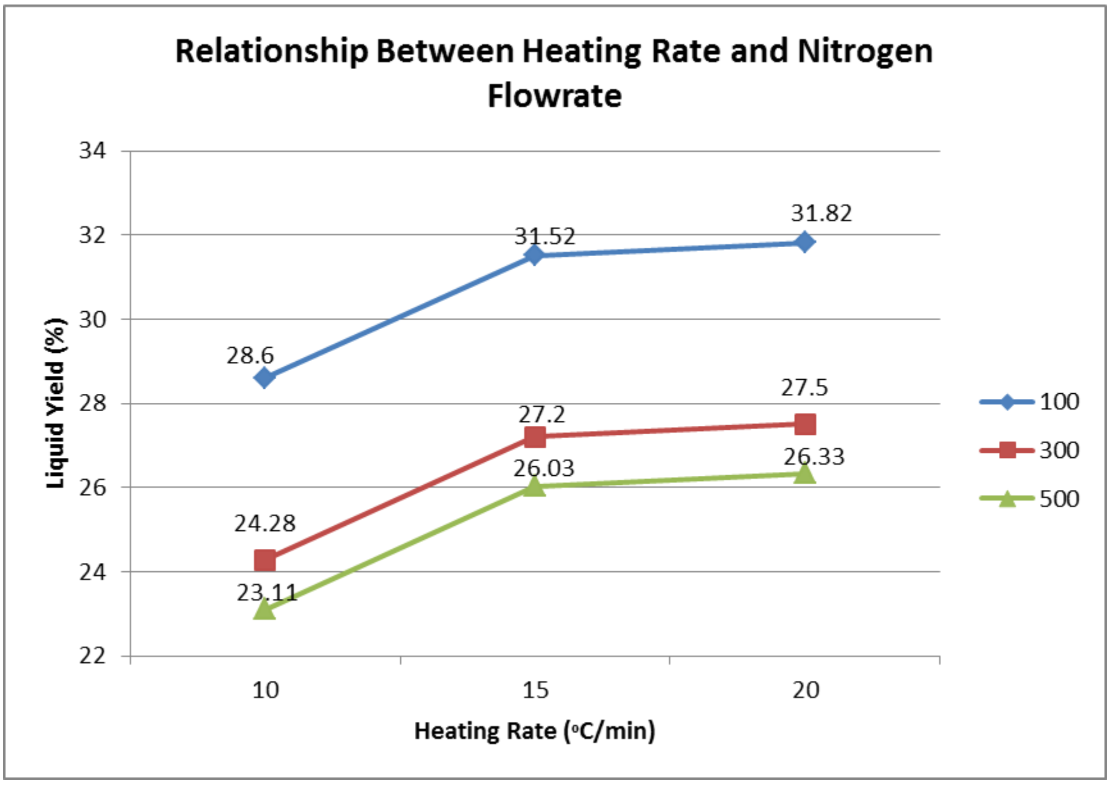

Figure 4.3: Relationship between Heating Rate and Nitrogen Flowrate towards Liquid Yield

Based on the ANOVA table, heating rate is the second largest contribution towards liquid yield. At low heating rates, there may be some resistances to mass or heat transfer inside the particles of the sample, but increasing the heating rate breaks the heat and mass transfer limitation in the pyrolysis and increasing the liquid yield [10]. From the graph above, the highest yield is 31.82 wt% at heating rate 20˚C/min and nitrogen flow rate of 100ml/min.

As for the nitrogen flow rate which is the highest contribution to the liquid yield production, the optimum flow rate is the 100ml/min, followed by 300ml/min and 500ml/min. As the flow of the nitrogen increased, it will enhance the release of the volatile and the rate of bio-char formation will be speeded up (Arash,A.N., et al, 2012). Thus, the quick flow rate will hinder the pyrolysis reaction from happening. Besides, the time for the liquid yield to condense in the condenser aslo decreased thus more liquid will escape to the atmosphere in the form of gases. So, 100ml/min is the optimum flow rate.

4.2.6 Effect of Particle Size and Nitrogen Flowrate towards Liquid Yield

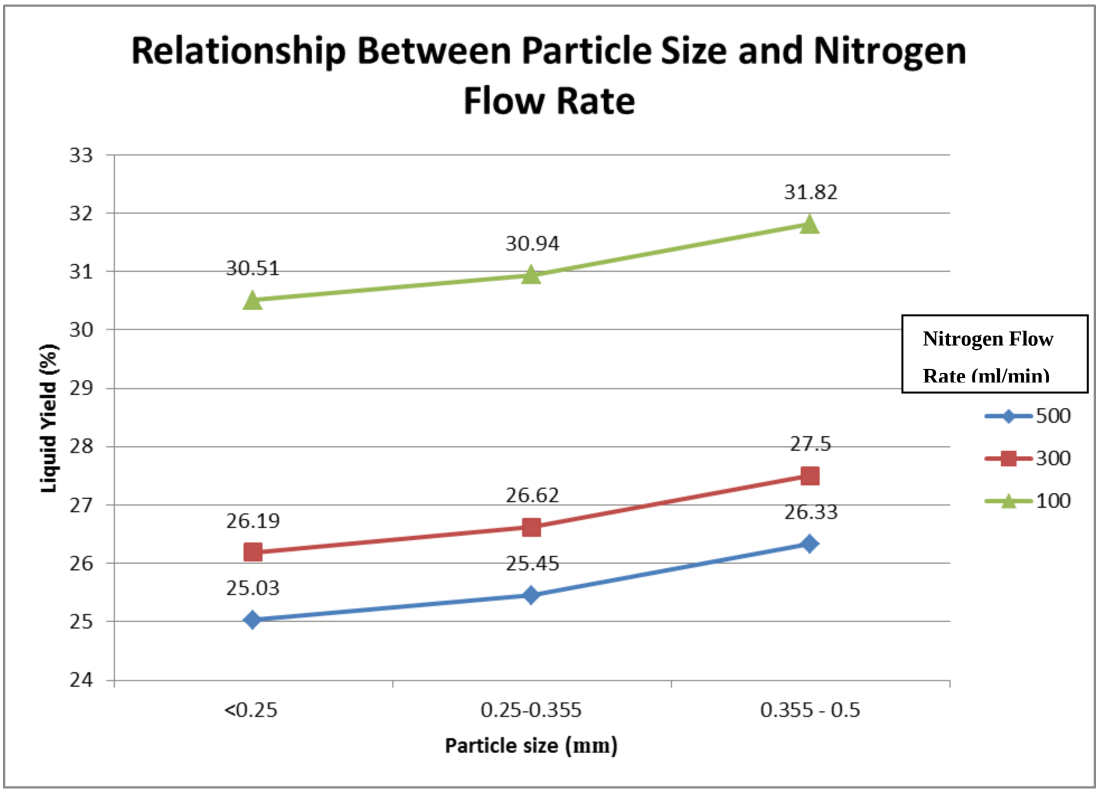

Figure 4.4: Relationship between Particle Size and Nitrogen Flowrate towards Liquid Yield

4.2.7 Effect of Particle Size and Heating Rate towards Liquid Yield

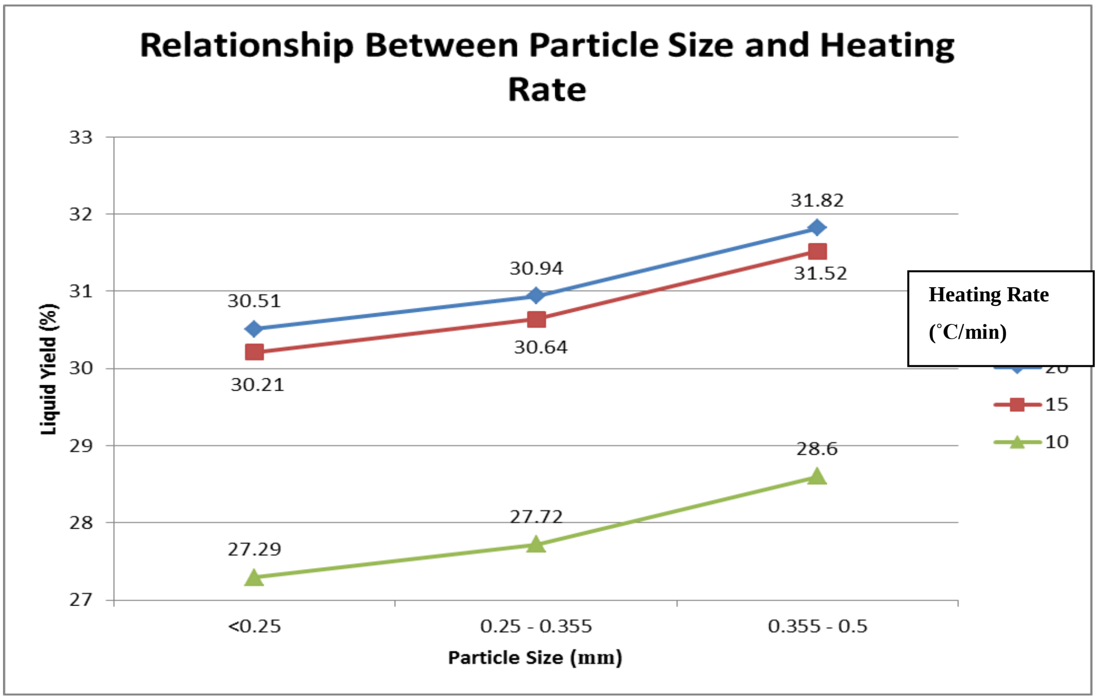

Figure 4.5: Relationship between Particle Size and Heating Rate towards Liquid Yield

4.2.8 Effect of Temperature and Heating Rate towards Liquid Yield

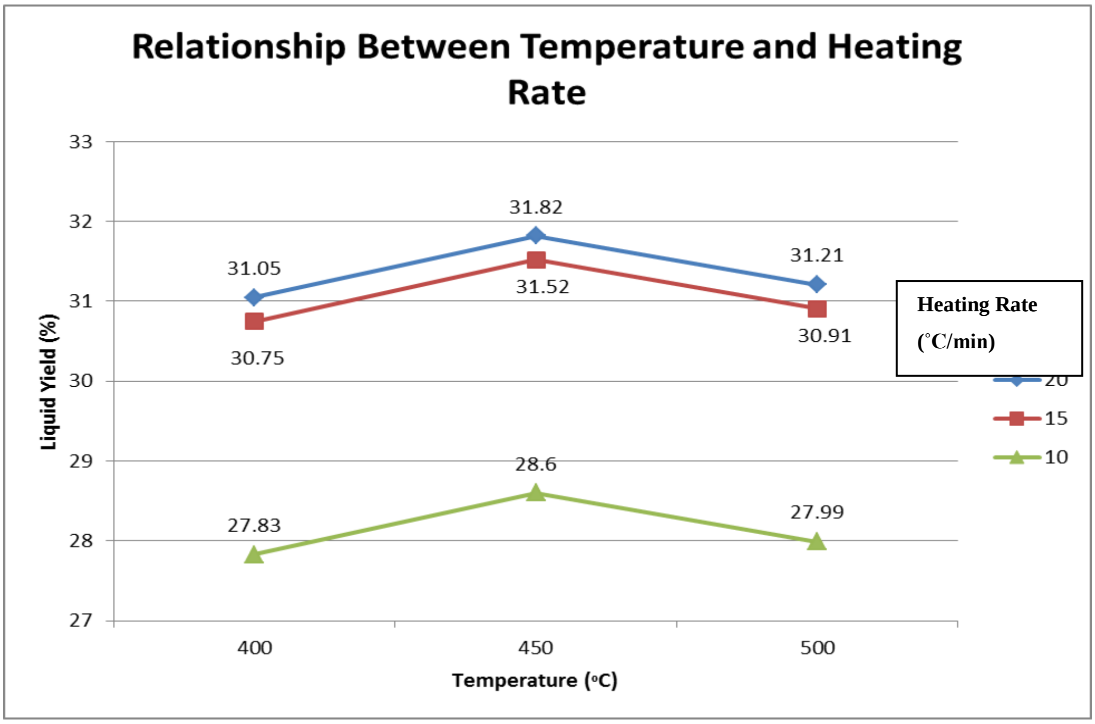

Figure 4.6: Relationship between Temperature and Heating Rate towards Liquid Yield

4.2.9 Effect of Temperature and Nitrogen Flowrate towards Liquid Yield

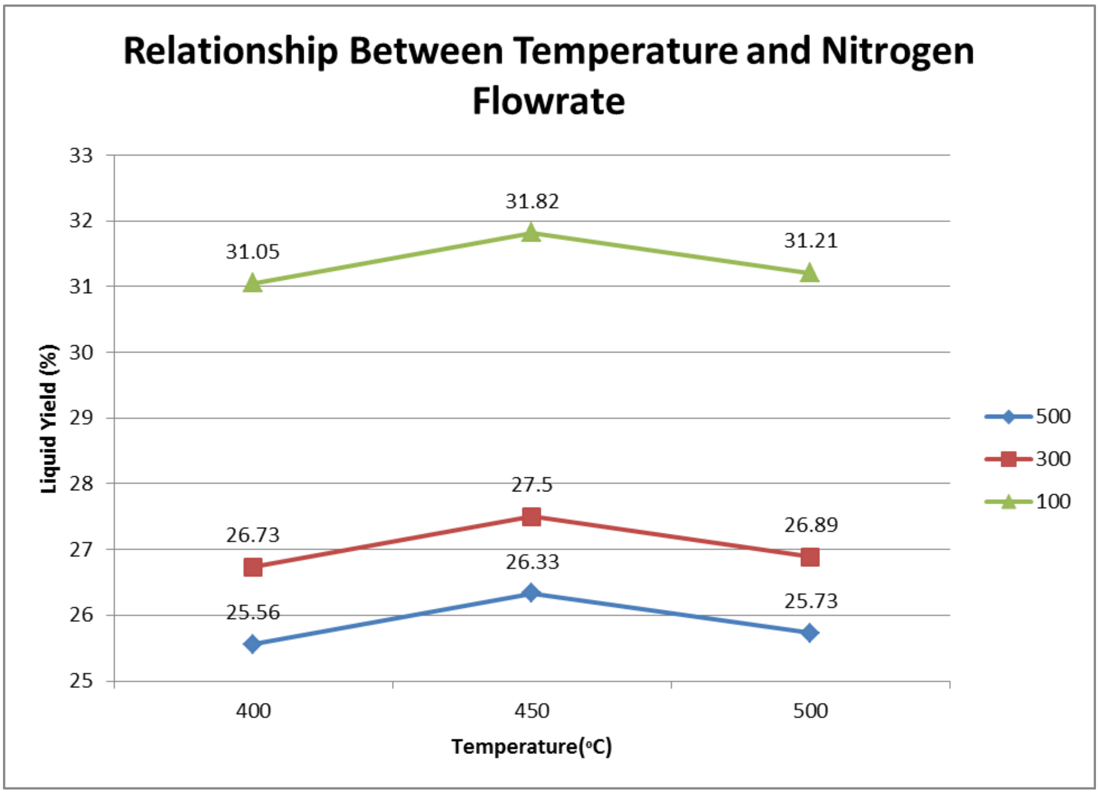

Figure 4.7: Relationship between Temperature and Nitrogen Flowrate towards Liquid Yield

The possible relationships between the four parameters are shown in Figure 4.2 till Figure 4.7 with all the information indicating that the optimum condition is using particle size 0.355-0.5mm at the temperature of 450˚C with heating rate of 20˚C/min and nitrogen gas flow rate of 100 ml/min.

4.2.10 3D Surface

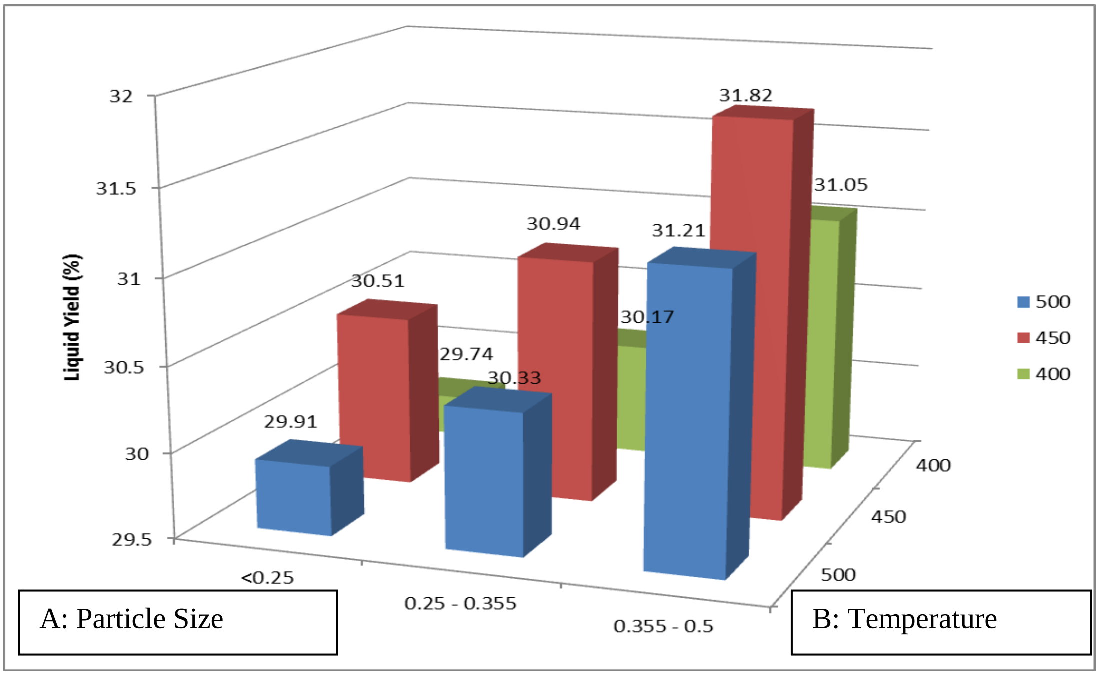

Figure 4.8: 3D Surface for Particle Size and Temperature

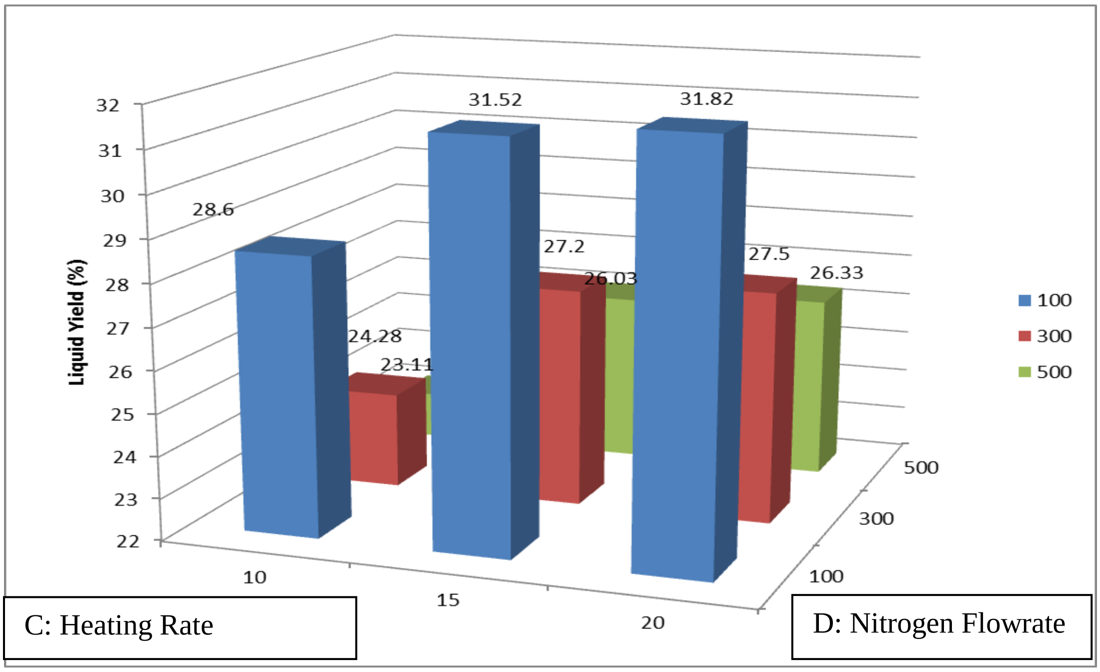

Figure 4.9: 3D Surface for Heating Rate and Nitrogen Flowrate

From the 3D surface, it is clearly seen that the optimum condition is by using 0.355-0.5mm particle size, 450 ˚C temperature, 20 ˚C/min heating rate and 100ml/min nitrogen flowrate.

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

As a result of depleting fossil fuels while the demand still keep on increasing, and the fact that the increased build-up for carbon dioxide in the atmosphere resulting the needs of renewable energy. Fuels derived from biomass is a promising alternative energy as it the only renewable carbon resource. However, the properties of the bio-oil are not stable due to its complex compounds and the properties such as, high viscosity, high acidity and high oxygen content.

Meanwhile, in this experiment, there are four factors selected which are particle size, temperature, heating rate and nitrogen flow rate. Taguchi L9 Orthogoral Array is used to reduce the 81 runs of experiment to only 9 runs. The results of all the nine runs are recorded in the Design Expert software and the predicted optimum condition can be known. The relationships between the four variables are studied.

Based on the predicted optimum condition by the Taguchi software, the optimum condition for pyrolysis reaction is by using the particle size of 0.355-0.5mm, at temperature of 450˚C, heating rate of 20˚C/min and nitrogen flow rate of 100ml/min. The signal to noise ratio and ANOVA table is constructed for the statistical analysis to further strengthen the reliability of the results in terms of the data gathering. The collected bio-oil from the Run 10 is kept in the refrigerator to prevent it from aging before characterization analysis.

5.2 Recommendations

The area of pyrolysis is very huge and there are a lot aspects can be considered to produce a good quality of bio-oil. In producing bio-oil that can be commercialized, a lot of researches need to be done in laboratory scale to find the best possible ways to utilize biomass. The bio-oil produced is then can't be selling directly before being upgraded or stabilized since the properties of the bio-oil is not stable as the conventional fossil fuels. These are some of the recommendations in laboratory scale that can be done in the future:

1. Explore the possibility of producing bio-oil from different source of biomass (for example organic waste, since thousands of pounds of waste are generated every day).
2. Study the effects of using catalysts in pyrolysis process and ways to recover them.
3. Explore the ways to stabilize the properties of the bio-oil produced.

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APPENDIX

Figure 7: Liquid Yield (Bio-oil)

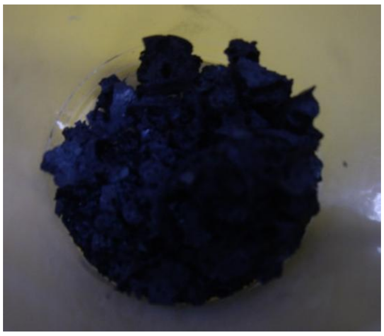

Figure 8: Residue - Contain Char and Ash

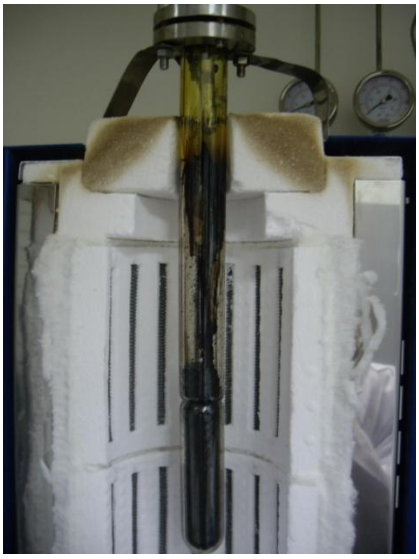

Figure 9: The Condition of Borosilicate Tube after Experiment

Figure 10: Bio-oil Flowing Out from the Reactor

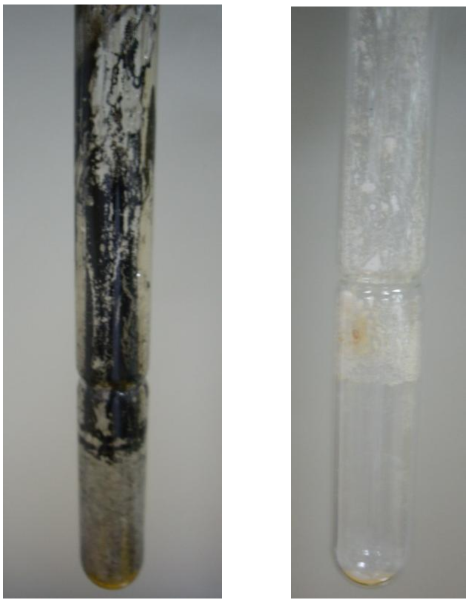

Figure 11: The Condition of Borosilicate Tube Before and After Combustion Process