CATALYTIC CRACKING OF BIO-OIL TO ORGANIC LIQUID PRODUCT: DETERMINATION OF OPTIMUM CONDITION

by

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11125

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ABBREVIATIONS AND NOMENCLATURES

ANOVA	Analysis of Variance
DOF	Degree of Freedom
FTIR	Fourier Transform Infrared
GCMS	Gas Chromatogram Mass Spectrometer
HDO	Hydrodeoxygenation
IR	Infrared
MTEC	National Metal and Materials Technology Center
OLP	Organic Liquid Product
PC	Percent Contribution
PPE	Personal Protective Equipment
S/N	Signal to Noise Ratio
SS	Sum of Square
V	Variance

CHAPTER 1 INTRODUCTION

1.1 Background Study

An importance of renewable energy sources have rapidly increased due to a high price of crude oil and environmental concerns caused by the use of fossil fuel. Currently, the energy for transportation alone consumes an approximately 38% of petroleum, followed by the industrial sector, which consumes about 14% of petroleum. The other sectors which consume a lot of energy are the aviation, power generation, and marine (Absi, H.M., 1997). Figure 1 indicates the distribution of crude petroleum oil consumed by various sectors (Siregar, T.B., 2005).

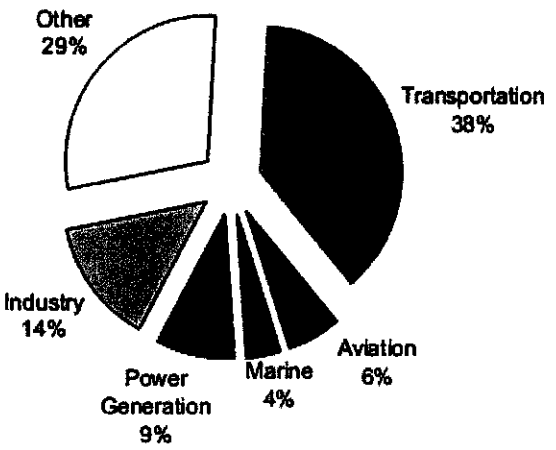

Figure 1: Distribution of crude petroleum oil consumption by various global sectors [12]

The mounting demand for gasoline, kerosene and diesel will raise global big problems as petroleum is not a renewable source. As petroleum reserves are depleting year by year, thus a continuous effort and supply of petroleum is required in searching for new alternative sources. Natural gas seems like the best alternative, but the problem of transportation and safe handling makes it difficult to be distributed to the rural areas. On the other hand, coal can be converted to gasoline; however, that involves a high production cost and unfortunately this product has poor quality (Siregar,T.B., 2005).

Bio-fuel appears as a promising alternative for energy source. This resource is renewable and also environmental friendly due to none of sulfur and nitrogen content. Furthermore it is easy to be handled and transported, as it appears in liquid form. Of various energy resources, bio-oil has attracted global attention as a promising renewable energy resource. Bio-oil is liquid fuel produced by fast pyrolysis typically, of biomass.

Bio-oil generally contains a mixture of highly oxygenated compounds, a wide variety of acids, and trace water, and as a result, bio-oil exhibits some undesired properties, such as thermal instability and acidity. The high water and oxygen content present in the bio-oil affects the homogeneity, polarity, heating value, viscosity and acidity of the oil (Zhang, Q., et al, 2006). Thus, various compounds of the bio-oil react through many chemical reactions (e.g. polymerization) resulting in dramatic changes in the bio-oil's properties (Park, H.J., 2011). Consequently, bio-oil needs to be upgraded to remove the unfavourable characteristics. In particular, a high content of oxygen in bio-oil results in a lower heating value if compared to conventional fuels. As a result, the bio-oil needs to be upgraded to reduce the content of oxygenates so that it can be used as a substitute for the conventional fuels in the future.

Catalytic cracking which is the breaking up of large hydrocarbon molecules into smaller, more useful pieces is a suitable technology to eliminate the oxygen content from the bio-oil. The suitable method to crack the bio-oil is vital and the yield of organic liquid product (OLP) will be also observed. The challenge still lies in the development of catalyst and cracking process. A stable, shape selective and high acidic catalyst is needed in order to achieve high conversion and gasoline selectivity in this process. Therefore, this research is to identify the best catalyst and the bio-oil to catalyst ratio to yield the highest OLP especially gasoline.

1.2 Problem Statement

As the oil reserves are depleting and the escalating crude oil prices, the need of an alternative fuel source is becoming increasingly vital. Considering the fact that the energy consumption is increasing and limited fossil fuels are nearly exhausted, with increasing populations and economic developments, renewable energy should be widely explored in order to renovate the energy sources structure and keep sustainable development safe. One prospective method is the conversion of biomass into bio-oil and then upgrading the bio-oil over catalysts. Furthermore, since biomass is carbon neutral and hardly contains sulphur, nitrogen and ash components, its harmful effects on the environment would be minimized, compared to conventional fossil fuels (Park, H.J., 2011).

Bio-oil itself contains a lot of oxygenated compounds and other complex compositions. Bio-oil is inherently unstable. The various compounds in the bio-oil will react through many chemical reactions, such as polymerizations, during the storage of bio-oil, resulting in adverse changes in the bio-oil's properties, especially increasing viscosity over time. Methods such as catalytic cracking with different catalyst have been developed to encounter the unstable characteristics of bio-oil. By using the catalytic cracking, the oxygen in the oxygenated compounds of bio-oil is being converted to other elements. Unfortunately, the yield of hydrocarbons is generally low because of the high yields of char, coke and tar. These undesired products, which are deposited on the catalyst and cause its deactivation, make a periodical or continual regeneration necessary (Vitolo, S., et al, 1999).

In order to increase the yield of oil and to decrease the yield of solids, different kinds of catalysts, amount of catalyst, reaction for temperature and the flow rate of nitrogen is investigated. Organic liquid product (OLP) is a product that is obtained after the catalytic cracking process. OLP can be comprised of gasoline, kerosene, diesel and gas (Tamunaidu, P. and Bhatia, S., 2007).

1.3 Objectives

The objective of this research is to

i) To understand the theory and mechanism of catalytic cracking

ii) To stabilize the bio-oil and study the yield of organic liquid product using catalytic cracking

iii) To maximize the yield of organic liquid product with four variables which are the type of catalysts; catalyst to bio-oil ratio; temperature and nitrogen flow rate

iv) To study the relationships between the variables and catalytic cracking

v) To determine the optimum condition for the catalytic cracking

1.4 Scope of Study

The experiment was designed to study the different variables for bio-oil cracking to OLP, which are the types of catalysts, catalyst to bio-oil ratio, temperature and nitrogen flow rate. This research focuses on several aspects such as follows: the setting up of an experiment using the semi-batch reactor, the applied catalysts, the temperature, the catalyst to bio-oil ratio, the flow rate of nitrogen and the products obtained.

First, the semi-batch reactor will be set up before the sub sequential study is being carried out. Second, the reaction time for each reaction will be carried out. Third, the experimental runs are arrayed in the Taguchi software. Fourth, the experiments are conducted to identify the best combination which produces the highest yield. Fifth, the statistical analysis is done based on the results obtained. Sixth, the interactions between the factors are investigated and discussed. Lastly, the properties of products obtained will be further investigated and compared with bio-oil.

CHAPTER 2 LITERATURE REVIEW

2.1 Bio-oil

Bio-oil is a dark brown, free flowing liquid organic liquids. Bio-oil is formed in a process called pyrolysis wherein plant material, such as sawdust or bagasse from sugar cane, is exposed to very high temperature in an oxygen free environment. Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen and it typically occurs under pressure and at operating temperatures above 430 °C. (Mohan, D., 2006).

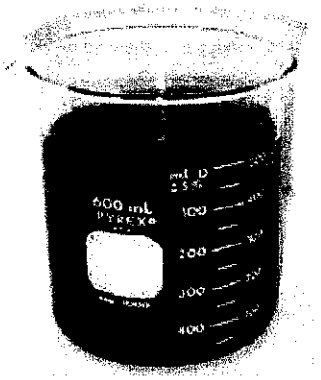

Figure 2: Bio-oil

The presence of oxygen is the primary reason for the difference in the properties and behaviour between hydrocarbon fuels and biomass pyrolysis oils. Although the pyrolysis liquid is called "bio-oil", it actually is immiscible with liquid hydrocarbons, because of its high polarity and hydrophilic nature. Different feedstock yields different composition of bio-oil.

Bio-oil contains a group of compounds, including aldehydes, ketones, carboxylic acid, alcohol, phenolics, carbohydrates, degraded lignin and water. Moreover, oligomeric species derived from lignin and cellulose is also contained in bio-oil (Udomsap, P., et al, 2011). Table 1 describes the physical property between the general bio-oil and the heavy fuel oil (Mortensen, P.M., et al, 2011).

Table 1: Comparison between bio-oil and the heavy fuel oil [4]

Physical Property	Value	
	Bio-oil	Heavy fuel oil
Water (wt%)	15 - 30	0.1
pH	2.5 - 3.8	
Specific Gravity	1.2	0.94
Elemental Composition (wt%)		
C	55.0 – 65.0	83.0 – 86.0
H	5 .0- 7.0	11.0 – 14.0
O	28.0 – 40.0	< 1.0
N	< 0.4	< 1.0
S	< 0.05	< 4.0
Ash	< 0.2	< 0.1
HHV (MJ/kg)	16-19	44
Viscosity, at 500° C (cP)	40-100	180

2.2 Catalytic Cracking

Catalytic cracking can become routes for production of second generation bio-fuels in the future, but its route is still far from industrial application (Mortensen, P.M., et al, 2011). The oxygen containing bio-oils are catalytically decomposed to hydrocarbons with the removal of oxygen as water, carbon dioxide or carbon monoxide (Zhang, Q., 2006). Zeolite catalysts are usually used in the catalytic cracking reaction. High temperatures ranging from 300°C to 600°C are needed to decrease the oxygen content (Mortensen, P.M., et al, 2011).

Although catalytic cracking is regarded as a cheaper way to convert the oxygenated feedstocks to lighter fractions, the results seem not promising due to high coking and poor quality of the fuels obtained (Zhang, Q., et al, 2006). Catalytic cracking is preferred than hydrodeoxygenation (HDO) because no hydrogen is required and the processing under ambient pressure reduces the operating cost (Park, H.J., 2011).

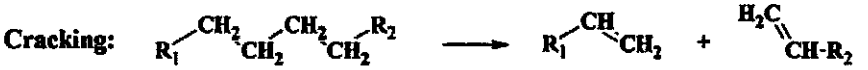

Figure 3: Examples of reactions associated with and catalytic cracking [4]

There are two types of catalytic cracking, namely homogenous and heterogenous catalytic cracking. Homogenous catalytic cracking occurs when the catalyst and the reactants are both in the same phase, either gas or liquid. Nevertheless not much work has been done on homogenous catalytic cracking. Heterogenous catalytic cracking occurs when the reactants and the catalyst are in different phases.

Almost all the reactions involving heterogenous catalytic reaction occur at the interface between the solid catalyst and the fluid or gas phase. The reactions are catalyzed in seven stages, as illustrated in Figure 3 (Siregar, T.B., 2005):

i. Diffusion of the reactants to the external surface of the catalyst.

ii. Diffusion of the reactants from pore mouth to the internal catalytic surface.

iii. Adsorption of the reactants on the catalyst surface.

iv. Reaction of the adsorbed reactants in which it is converted to a product molecule.

v. Desorption of the products from the catalyst surface.

vi. Diffusion of the products from the interior of the catalyst to the external surface.

vii. Mass transfer of the products from the external surface into the process stream.

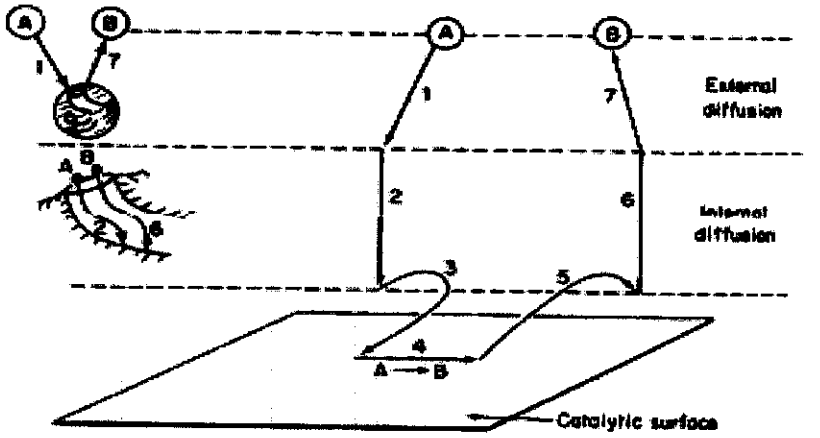

Figure 4: The reaction occurring in heterogeneous cracking [12]

Table 2 illustrates what can be expected for the compositions and the characteristics between raw pyrolysis oil, HDO oil, zeolite cracking oil and crude oil (as a benchmark).

Table 2: Comparison between characteristics of bio-oil, catalytically upgraded bio-oil, and crude oil [4]

	Bio-oil[a]	HDO[b]	Zeolite cracking[c]	Crude oil[d]
Upgraded bio-oil				
Y_{Oil} [wt%]	100	21–65	12–28	–
$Y_{Waterphase}$ [wt%]	–	13–49	24–28	–
Y_{Gas} [wt%]	–	3–15	6–13	–
Y_{Carbon} [wt%]	–	4–26	26–39	–
Oil characteristics				
Water [wt%]	15–30	1.5	–	0.1
pH	2.8–3.8	5.8	–	–
ρ [kg/l]	1.05–1.25	1.2	–	0.86
$\mu_{50°C}$ [cP]	40–100	1–5	–	180
HHV [MJ/kg]	16–19	42–45	21–36[e]	44
C [wt%]	55–65	85–89	61–79	83–86
O [wt%]	28–40	<5	13–24	<1
H [wt%]	5–7	10–14	2–8	11–14
S [wt%]	<0.05	<0.005	–	<4
N [wt%]	<0.4	–	–	<1
Ash [wt%]	<0.2	–	–	0.1
H/C	0.9–1.5	1.3–2.0	0.3–1.8	1.5–2.0
O/C	0.3–0.5	<0.1	0.1–0.3	≈0

Oxygen containing bio-oils are catalytically decomposed to hydrocarbons with the removal of oxygen as water, carbon dioxide or carbon monoxide (Zhang, Q., et al, 2006). The yield of the OLP can be calculated using the formula below.

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

Table 3 summarizes operating parameters, product yield, degree of deoxygenation, and other results of the work conducted in the bio-oil upgrading. Various catalysts have been tested. Hydrodeoxygenation and catalytic cracking with zeolite catalysts are observed.

Table 3: Overview of catalysts investigated for catalytic upgrading of bio-oil [1]

Catalyst	Setup	Feed	Time [h]	P [bar]	T [°C]	DOD [%]	O/C	H/C	Y_{oil} [wt%]
Hydrodeoxygenation									
Co-MoS_2/Al_2O_3	Batch	Bio-oil	4	200	350	81	0.8	1.3	26
Co-MoS_2/Al_2O_3	Continuous	Bio-oil	4[a]	300	370	100	0.0	1.8	33
Ni-MoS_2/Al_2O_3	Batch	Bio-oil	4	200	350	74	0.1	1.5	28
Ni-MoS_2/Al_2O_3	Continuous	Bio-oil	0.5[a]	85	400	28	-	-	84
Pd/C	Batch	Bio-oil	4	200	350	85	0.7	1.6	65
Pd/C	Continuous	Bio-oil	4[b]	140	340	64	0.1	1.5	48
Pd/ZrO_2	Batch	Guaiacol	3	80	300	-	0.1	1.3	-
$Pt/Al_2O_3/SiO_2$	Continuous	Bio-oil	0.5[a]	85	400	45	-	-	81
Pt/ZrO_2	Batch	Guaiacol	3	80	300	-	0.2	1.5	-
Rh/ZrO_2	Batch	Guaiacol	3	80	300	-	0.0	1.2	-
Ru/Al_2O_3	Batch	Bio-oil	4	200	350	78	0.4	1.2	36
Ru/C	Continuous	Bio-oil	0.2[a]	230	350–400	73	0.1	1.5	38
Ru/C	Batch	Bio-oil	4	200	350	86	0.8	1.5	53
Ru/TiO_2	Batch	Bio-oil	4	200	350	77	1.0	1.7	67
Zeolite cracking									
GaHZSM-5	Continuous	Bio-oil	0.32[a]	1	380	-	-	-	18
H-mordenite	Continuous	Bio-oil	0.56[a]	1	330	-	-	-	17
H-Y	Continuous	Bio-oil	0.28[a]	1	330	-	-	-	28
HZSM-5	Continuous	Bio-oil	0.32[a]	1	380	50	0.2	1.2	24
HZSM-5	Continuous	Bio-oil	0.91[a]	1	500	53	0.2	1.2	12
MgAPO-36	Continuous	Bio-oil	0.28[a]	1	370	-	-	-	16
SAPO-11	Continuous	Bio-oil	0.28[a]	1	370	-	-	-	20
SAPO-5	Continuous	Bio-oil	0.28[a]	1	370	-	-	-	22
ZnHZSM-5	Continuous	Bio-oil	0.32[a]	1	380	-	-	-	19

[a] Calculated as the inverse of the WHSV.
[b] Calculated as the inverse of the LHSV.

It can be observed that most of the reactions happen in continuous reactor. The difference between HDO and catalytic cracking is the difference between the operating pressure. However, the results of HDO are more promising if compared with the zeolite cracking but the zeolite cracking are more economically affordable. Much more work is needed on the stabilization and upgrading of bio-oils with some modifications to equipment configuration before adopting them in our daily life (Zhang, Q., et al, 2006).

2.3 Organic Liquid Product (OLP)

OLP are products that are obtained after the catalytic cracking process. OLP can be comprised of gasoline, kerosene, diesel and gas (Hew, K.L, et al, 2010). The composition of OLP was defined according to the boiling range of petroleum products in three fractions, for example gasoline fraction (60°C to 120°C), kerosene fraction (120°C to 180°C) and diesel fraction (180°C to 200°C) (Tamunaidu, P. and Bhatia, S., 2007).

In the literature review (Hew, K.L., et al, 2010), there are equations to calculate the yield of OLP and the yield of gasoline. After the product has cooled down, there are two layers of the liquid product, namely the organic and the aqueous fractions. The aqueous phase is separated from condensed liquid products using a syringe. The OLP produced from the catalytic cracking is weighed to determine the yield of OLP. Some amount of OLP is weighed and distilled using a micro lab scale distillation unit at atmospheric pressures with boiling range of 60°C to 120°C for an hour.

As for the aqueous fraction, it is expected to contain mainly water and some organic components that are soluble in water such as alcohol and carboxylic chains (Hew, K.L., et al, 2010). The boiling range for each fraction was identified by injecting commercial samples of gasoline, kerosene and diesel in the gas chromatograph (Tamunaidu, P. and Bhatia, S., 2007). Increasing weight hourly space velocity (WHSV) will result in increasing OLP yield due to more bio-oil will diffuse to catalyst internal interior (Siswanto, D.Y., et al, 2008).

2.4 Catalysts

The catalysts control the type of fuel and its yield in the organic liquid product (Tamunaidu, P. and Bhatia, S., 2007). It also reduces the oxygen content of the oil and increase the aromatic content through the selectivity of the pore size and activity of the catalyst (Paul, T.W. and Nugranad, N., 1999). There are three types of catalysts used in the catalytic cracking which are the zeolite-based catalysts, mesoporous catalysts and the metal catalysts (Park, H.J., 2011).

Zeolites have been the most widely used catalysts in petrochemical industries over the past decades. Attempts to use the bio-oil as a fuel for petrochemical processes, zeolites have been applied to the stabilization process of bio-oil, for instance, upgrading via deoxygenation (Park, H.J., 2011). Properties of catalysts are governed by acidity, pore shape and size (Tamunaidu, P. and Bhatia, S., 2007). Several literature reviews about the conditions, reactors and catalysts are reviewed and the important results are shown.

HZSM-5 zeolite catalyst produces a highly deoxygenated oil with a very high heating value and good combustibility (Vitolo, S., et al., 1999). There are several literature reviews compare the types of catalysts used, which are the HY zeolite, Al-MCM-41, transition metal catalysts and other catalysts. As a result, HZSM-5 afforded the best performance in terms of conversion, gasoline yield, selectivity to aromatics and coke formation. Other than that, there are a few literature reviews which review the optimum condition for the catalytic cracking. Factors such as, types and the acidity of catalysts, the porosity and surface area of catalysts as well as catalyst-to-feed ratio will affect the yield of the organic liquid product.

As mentioned earlier, various feedstocks will have different of composition of bio-oil. Thus the conversion of different phenols, aromatics, oxygen contents are depending on the feedstocks. An increased temperature will result in a decrease in the oil yield and an increase in the gas yield. The benefits of catalytic cracking using zeolites does not require co-feeding of hydrogen and therefore be operated at atmospheric pressure.

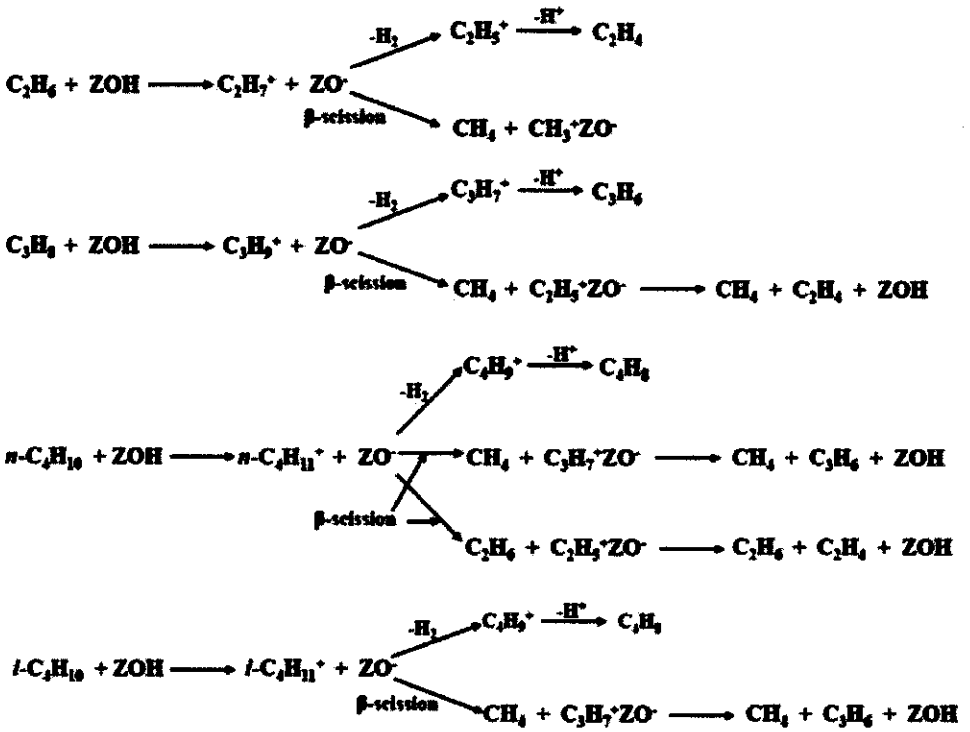

Figure 5: The reaction routes for activation of C2 to C4 alkanes on HZSM-5 catalyst [1]

Yield of the organic phase from the thermal cracking is an important benchmark to evaluate the employed catalysts, and closely related to the acid intensity of catalyst, total amount of acid, ratio of Si/Al, and the micro-structure of the solid (Guo, X.Y., et al, 2004). Guo mentions that the catalyst will affect the distribution of activity sites. In general, the higher the ratio of Si/Al is, the greater the activity and stability of the catalyst are; the stronger the acidity, the greater the activity and selectivity (Guo, X.Y., et al, 2004)

Most of the experiments are done in the online catalytic cracking with continuous reactor. Online catalytic cracking is feeding the pyrolysis vapour into the reactor. High concentration of active acid sites, their high thermal stability, and high size selectivity make zeolites the catalyst of choice in refining operations.Currently, articles about online catalytic cracking in the semi-batch reactor are rarely seen nor found.

2.5 Comparative Study Between Fossil-fuel Based Cracking and Catalytic Cracking of Bio-oil

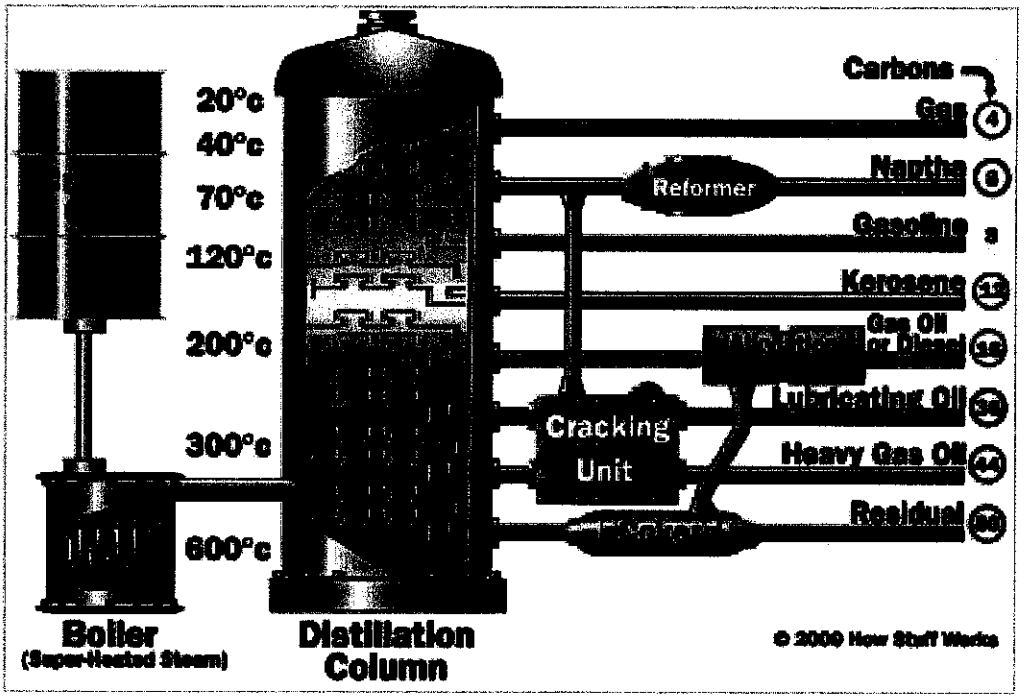

Figure 6: An oil refinery with a cracking unit [11]

Crude oil is a fossil fuel, meaning it was made naturally from decaying plants and animals living in millions of years. Crude oils vary in colour, from clear to tar-black, and in viscosity, from water to almost solid (Freudenrich, C, n.d.). The problem with crude oil is that it contains hundreds of different types of hydrocarbons all mixed together. Oil refining is the process to separate the crude oil into useful parts. Different hydrocarbon chain lengths all have progressively higher boiling points, so they can all be separated by distillation. The most widely used conversion method is called cracking as it uses heat and pressure to crack heavy hydrocarbon molecules into lighter ones.

Catalytic cracking process in the oil refining uses a catalyst to speed up the cracking reaction. Catalysts include zeolite, aluminum hydrosilicate, bauxite and silica-alumina. fluid catalytic cracking - a hot, fluid catalyst (538°C) cracks heavy gas oil into diesel oils and gasoline. Hydrocracking - similar to fluid catalytic cracking, but uses a different

catalyst, lower temperatures, higher pressure, and hydrogen gas. It takes heavy oil and cracks it into gasoline and kerosene (jet fuel) (Freudenrich, C., n.d.).

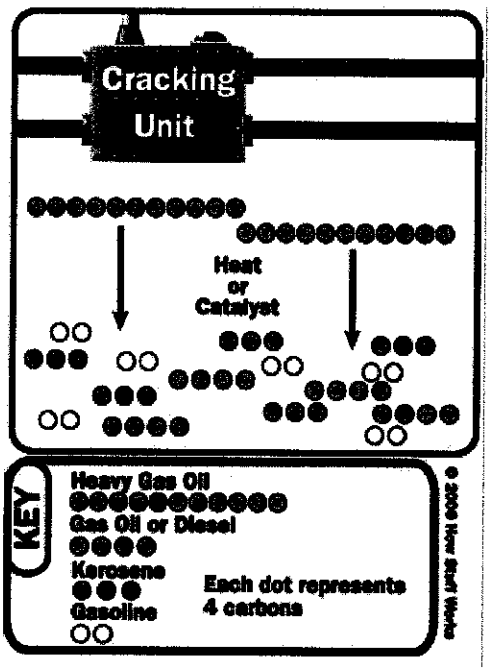

Figure 7: Cracking of the heavy hydrocarbons to small parts [11]

The catalysts used for the catalytic cracking of bio-oil are almost the same as the catalysts used for the oil and gas industry. Using intense heat (about 600°C), low pressure and a powdered catalyst, the catalytic cracking equipment can convert most of the heavy fractions into smaller more useful molecules. The only difference is the efficiency between the two fields. Cracking in the oil and gas industry are stabile and well known while the catalytic cracking for the bio-oil is still new.

The prospect of catalytic bio-oil upgrading should be seen not only in a laboratory perspective, but also in an industrial one. Zeolite cracking is the most attractive path due to more attractive process conditions, in terms of the low pressure operation and independence of hydrogen feed and this could make it easy to implement in industrial scale (Mortensen, P.M., et al, 2011).

The following table shows the development in the oil composition through the different process steps. From bio-oil to HDO oil, it is seen that the reaction of larger oxygen containing molecules decreases and the fraction of smaller molecules increases. Through the hydrocracking the smaller oxygen containing molecules is converted, in the end giving a pure hydrocarbon product (Mortensen, P.M., et al, 2011). Table 4 illustrates the oil composition on a water-free basis (in mol%) through the bio-oil upgrading process

Table 4: Oil composition on a water-free basis (in mol%) through the bio-oil upgrading process [4]

	Bio-oil	HDO oil	Hydrocracked oil
Ketones/aldehydes	13.77	25.08	0
Alkanes	0	4.45	82.85
Guaiacols etc.	34.17	10.27	0
Phenolics	10.27	18.55	0
Alcohols	3.5	5.29	0
Aromatics	0	0.87	11.53
Acids/esters	19.78	25.21	0
Furans etc.	11.68	6.84	0
Unknown	6.83	3.44	5.62

2.6 Taguchi Orthogonal Array

Essentially, traditional experimental design procedures are too complicated to use. A vast number of experimental works have to be carried out when 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, R.S. and Padmanabhan, G., 2012).

Taguchi Orthogonal Array is used to minimize the number of experimental runs needed for the experiment. Application of Orthogonal Array is a part of Taguchi Method (Taguchi, G. and Jugulum, R., 2002). Signal to noise ratios are used as a measure of the functionality of the system. Taguchi method is employed to obtain the optimal operation conditions. Taguchi's Orthogonal arrays are highly fractional orthogonal designs. The designs can be used to estimate main effects using only a few experimental runs.

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

There are three quality characteristics considered in the signal to noise ratio, which are the smaller, nominal or larger. The fact of quality "for bigger is better" is defined as the determining factor is the highest of yield of product that we want, which will be applied in our experiment. The greater the value, the smaller the product variance to the target value (Ranjit, R., 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 detecting any differences in the average performance of groups of items tested. ANOVA helps in testing the significance of all the main factors (Rama, R.S. and Padmanabhan, G., 2012). To construct the ANOVA table, we need to have the degree of freedom (DOF), 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.

2.7 Summary of Important Literature Reviews

Below is the table of the findings from important literature reviews in assisting in this final year project. By reading more journals and literature reviews, more knowledge and practical skills have been learnt. So, some relevant literature reviews had been summarized. The methods or variables might be different, but the result shows significant findings that can help in the topic. The literature reviews are discussed.

Table 5: Summary of Significant Literature Reviews

[illegible]	[illegible]	[illegible]	[illegible]
Objective	To identify the optimum operating condition for catalytic cracking		
Reaction	Continuous	Batch	Continuous
Bio-oil Source	Canadian oak, Swedish pine and pine	Empty fruit bunch (EFB)	Palm
Catalysts	1. HZSM-5 with silica-alumina ratio of 50 2. HZSM-5 with silica-alumina ratio of 80 3. H-Y with silica alumina ratio of 80	ZSM-5	1. HZSM-5 2. Zeolite β 3. USY zeolite 4. HZSM-5 with zeolite β 5.HZSM-5 with USY zeolite
Catalyst Weight	2g	10 – 30g	10, 20 and 30% HZSM-5 (for hybrid catalysts)
Temperature	410 - 490°C	450 - 500°C	350 - 450°C
Testing Parameters	Overall product distribution	- Yield of OLP - Yield of gasoline	Yield of OLP
Findings	The highest yield of oil obtained at 450°C with HZSM-5/50.	The optimum condition is 400°C, reaction time of 15min and catalyst weight of 30g with 91.67% of gasoline yield.	HZSM-5 gives the best performance at 350°C with 53 wt% while for hybrid catalyst, USY HZSM-5(30%) gives highest yield of OLP (46.8 wt%)

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. By literature reviewing, the possible methods of catalytic cracking, the reactors, the processes are identified. Comparable studies between types and characteristics of the catalysts, catalyst to bio-oil ratio (weight basis), nitrogen flow rate and temperature are conducted. Besides, characterization of the bio-oil is analyzed.

2nd Stage: Determination of Variables and Levels

The variables and levels for the experiment are planned. The variables and levels are important to determine the optimum condition. Similar journals or papers are reviewed as well.

3rd Stage: Screening

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.

4th Stage: Experiment Design

The experiment is planned and conducted based on the procedure. The precautions and the MSDS for each chemical are studied properly. The appropriate PPE (Personal Protective Equipment) are worn during the whole experiment.

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 Experiment Research Methodology

3.2.1 Raw Material

Bio-oil is obtained from National Metal and Materials Technology Center (MTEC), Thailand. The source of bio-oil is from wood chip and with slow pyrolysis. The bio-oil is characterized by viscosity, water content, pH, density, ash content, CHNS analysis, pH, calorific value, infrared spectroscopy and GC-MS.

3.2.2 Experimental Procedure for Determination of Reaction Time

1. Condition for the determination of reaction time is selected, which is the HZSM-5 zeolite catalyst, temperature of 450°C, catalyst to bio-oil ratio of 3:30 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 mixture of catalysts and bio-oil are mixed thoroughly.
3. The borosilicate tube's weight is recorded and the mixture is poured into the tube.
4. The sample bottle is also weighed.
5. The experiment is set up and nitrogen gas is purged for 5 minutes at 500ml/min before the experiment.
6. The temperature of the heater and thermocouple is recorded every minute.
7. The time of the first droplet of OLP is recorded and the experiment is stopped when there are three constant readings of thermocouple readings or there are no more reactions.
8. Once the reaction time for the first reaction is determined, the same procedure is run with the same set up but with the time interval of 5 minutes, ± 5 minutes.

3.2.3 Experimental Procedure for Catalytic Cracking of Bio-oil to Organic Liquid Product (OLP)

1. The factors and the levels are keyed in the Design Expert software and the runs for each experiment is conducted based on the array.
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 yield of OLP.
5. The runs are conducted based on the array by using the Design Expert software.
6. The results are recorded in the Design Expert software and the optimum condition is determined.

Table 6: Taguchi L9 Array with 4 Factors and 3 Levels

Run	Factor 1 A – Catalyst	Factor 2 B – Temperature (°C)	Factor 3 C – Bio-oil to Catalyst Ratio – (Weight Basis) (g/ml)	Factor 4 D – Nitrogen Flow Rate (ml/min)
1	H-Y	450	2:30	100
2	H-Y	400	1:30	500
3	H-Y	350	3:30	300
4	H-β	400	3:30	100
5	HZSM-5	400	2:30	300
6	HZSM-5	350	1:30	100
7	H-β	350	2:30	500
8	H-β	450	1:30	300
9	HZSM-5	450	3:30	500

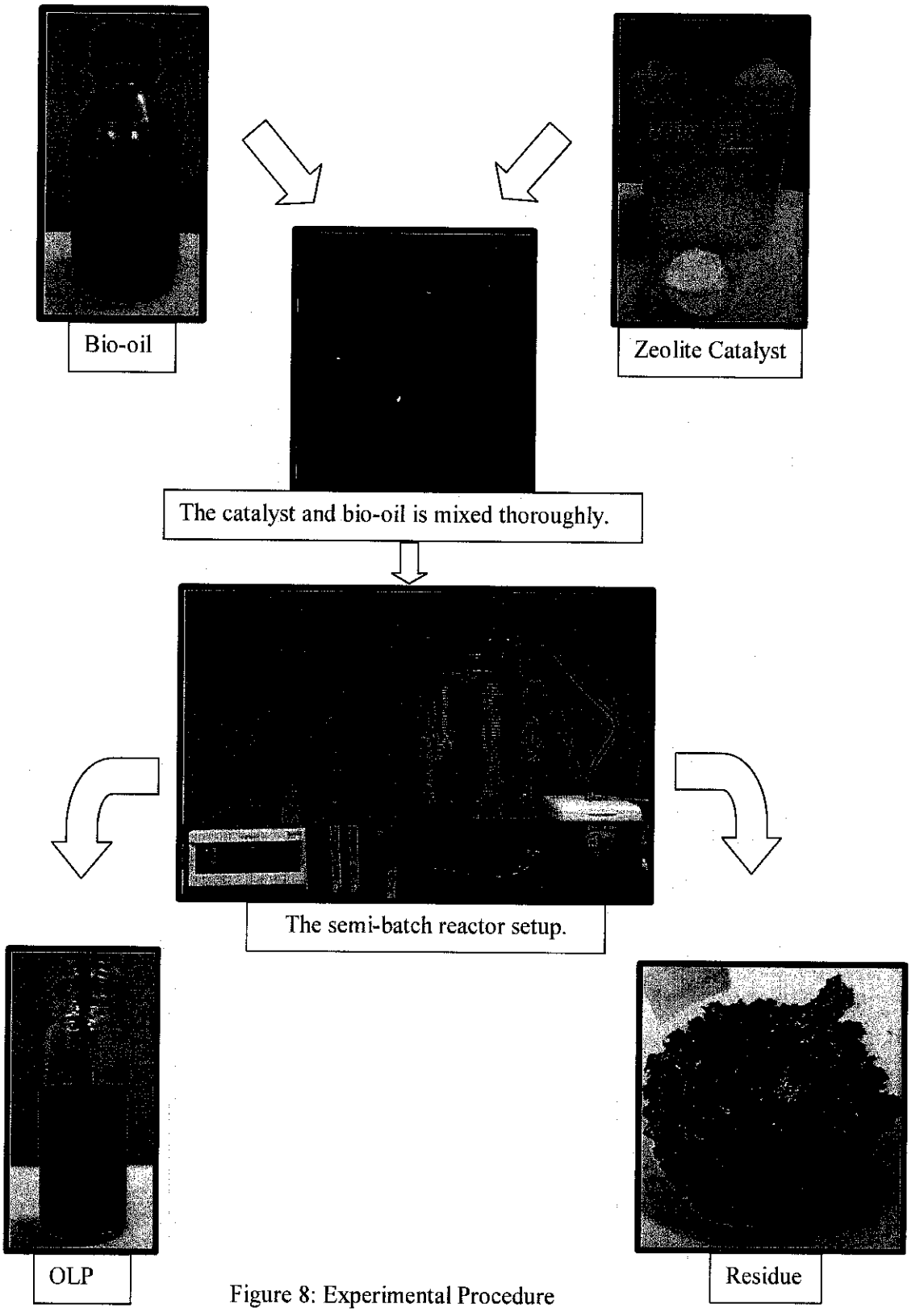

Figure 8: Experimental Procedure

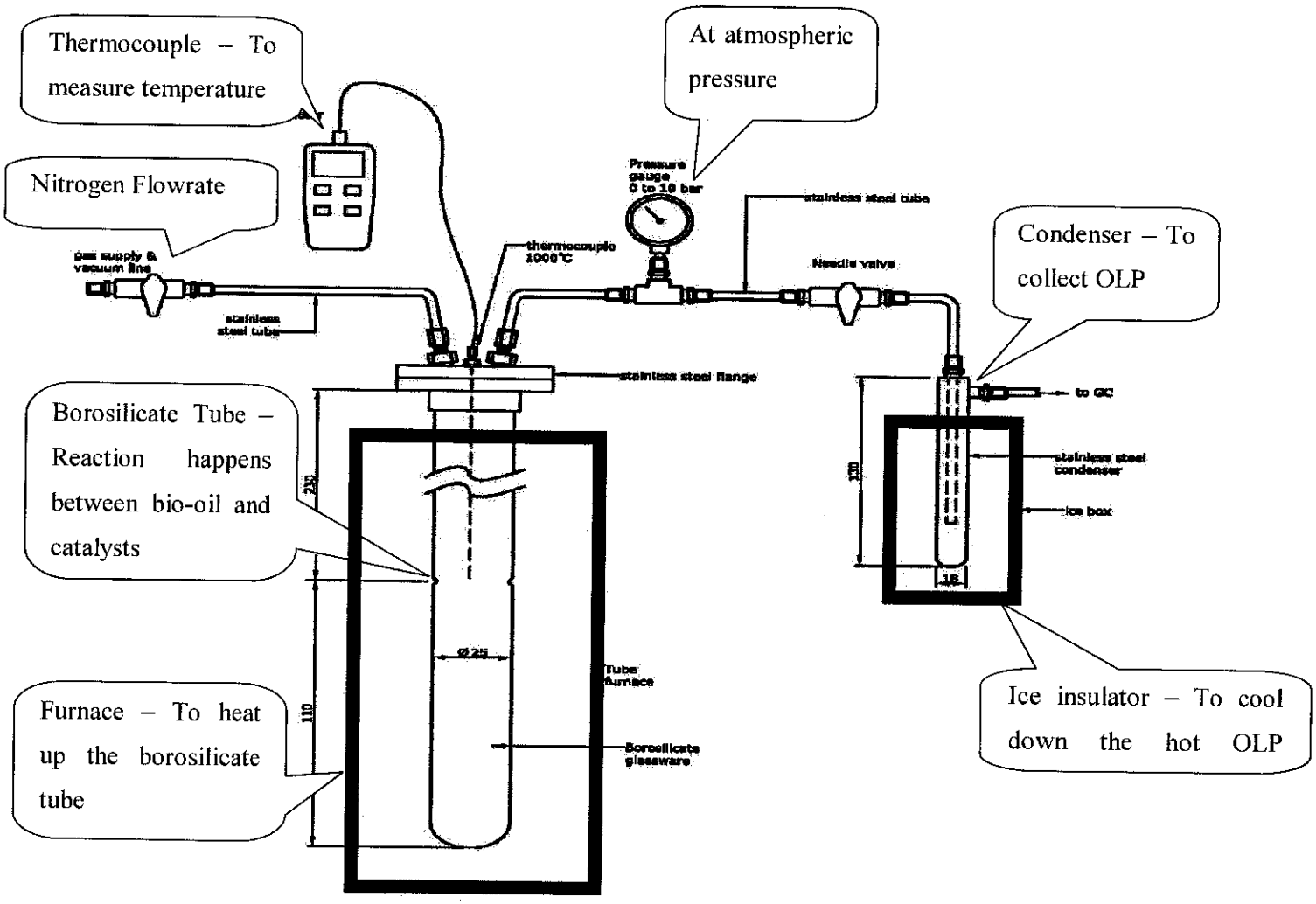

Figure 9: Schematic Diagram of Semi-Batch Reactor

3.3 Experiment Apparatus and Instruments

3.3.1 Equipments

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 10: Semi-Batch Reactor with Numberings from 1 to 4

5. Borosilicate Tube
6. Brookfield Viscometer DV-I+
7. Metrohm 870 Karl Fischer Titrino Plus
8. Anton Paar Density Meter DMA 4500 M
9. WiseTherm Programmable Digital PID Control Muffle Furnace
10. Schott Instruments pH Meter
11. LECO CHNS Analyser 932
12. IKA C5000 Bomb Calorimeter
13. Perkin Elmer Spectrum One Spectrometer
14. Agilent Gas Chromatography Mass Spectrometry GCMS-5975C

3.3.2 Materials

1. Bio-oil
2. Zeolite Catalysts: HZSM-5, H-Y and H-β
3. Methanol (for washing)

* Pictures are available in the Appendix.

3.4 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 7: Testing Parameters

No.	Testing Parameters	Instruments	Methods	Sample Size	Venue
1	Viscosity	Brookfield Viscometer DV–I+	ASTM D445	13mL	Block P
2	Water Content	Metrohm 870 Karl Fischer Titrino Plus	ASTM D1744	A few drops	Block P
3	Density	Density Meter DMA 4500 M	ASTM D4052	2mL	Block P
4	Ash content	WiseTherm Programmable Digital PID Control Muffle Furnace	ASTM D482	3g	Block P
5	Elemental Analysis (CHNS)	LECO CHNS Analyser 932	ASTM D5291	1g	Block 4
6	pH	Schott Instruments pH Meter	-	-	Block P
7	Calorific Value	IKA C5000 Bomb Calorimeter	-	0.5 - 1.0g	Block 4
8	Functional Group Infrared Spectroscopy	Perkin Elmer Spectrum One FTIR Spectroscopy	-	A few drops	Block 4
9	Component Analysis GCMS	Agilent Technology GC/MS 5975C	-	1.5 mL Vial Tube	Block 4

3.4.1 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.

3.4.2 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.

3.4.3 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 can be obtained through the density meter. The samples are measured at 15°C.

3.4.4 Ash Content

Ash content is measured by combusting the product in the muffle furnace. After the combustion reaction at 600°C with the ramping rate of 10°C per minute and holding time of 3 hours, the weight difference is calculated to know the ash content.

3.4.5 Elemental Analysis

LECO CHNS Analyser 932 is an elemental analyzer used to determine the amount of Carbon, Hydrogen, Nitrogen and Sulphur contained in the organic or inorganic solvent. The oxygen content is calculated by using the formula:

Oxygen Content=100-C-H-N-S-Water Content-Ash Content

3.4.6 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.

3.4.7 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.

3.4.8 Functional Group Infrared Spectroscopy

The Perkin Elmer Spectrum One FTIR Spectrometer is used to identify functional groups that exist in the samples. The readings and functional groups will be identified with the help of the infrared spectroscopy correlation table.

3.4.9 Component Analysis GC-MS

GCMS 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 Gantt Chart for FYP II

NO	DETAIL / WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Research and literature review	■	■														
2	Experiment procedure drafting and testing -Determination of reaction time		■	■	■	■											
3	Real experiment testing						■	■		■	■						
4	Characterization of OLP									■	■	■					
5	Progress report submission									■							
6	Pre SEDEX												■				
7	First draft report submission													■			
8	Soft copy dissertation submission													■			
9	Technical paper submission														■		
10	Oral presentation																■
11	Project dissertation submission (Hard Bound)														■	■	■

● Suggested milestone

■ Process

3.6 Key Milestone

No.	Activities	Week	Specific Date	Remarks
1	Regular meeting with supervisor to update and discuss about the project	Once in two weeks	Every Friday	Still ongoing
2	FYP II briefing	1	24th May	Done
3	Progress report	8	14th July	Done
4	Pre-SEDEX	11	30th July	Done
5	First draft submission	12	6th August	Done
6	SEDEX	12	8th -9th August	Done
7	Submission of soft copy dissertation	12	10th August	Done
8	Submission of technical paper	13	15th August	Done
9	Oral presentation	15	27th, 28th, 29th August	
10	Hardbound dissertation	17	14th September	

CHAPTER 4 RESULT AND DISCUSSION

4.1 Determination of Reaction Time

The yield of OLP is calculated and the graph of OLP yield vs time is plotted.

Table 8: Yield of OLP and the Reaction Time

Alternative Run	Reaction Time (Minutes)	Yield of OLP (wt %)
1	5	48.89
2	10	68.90
3	15	63.81

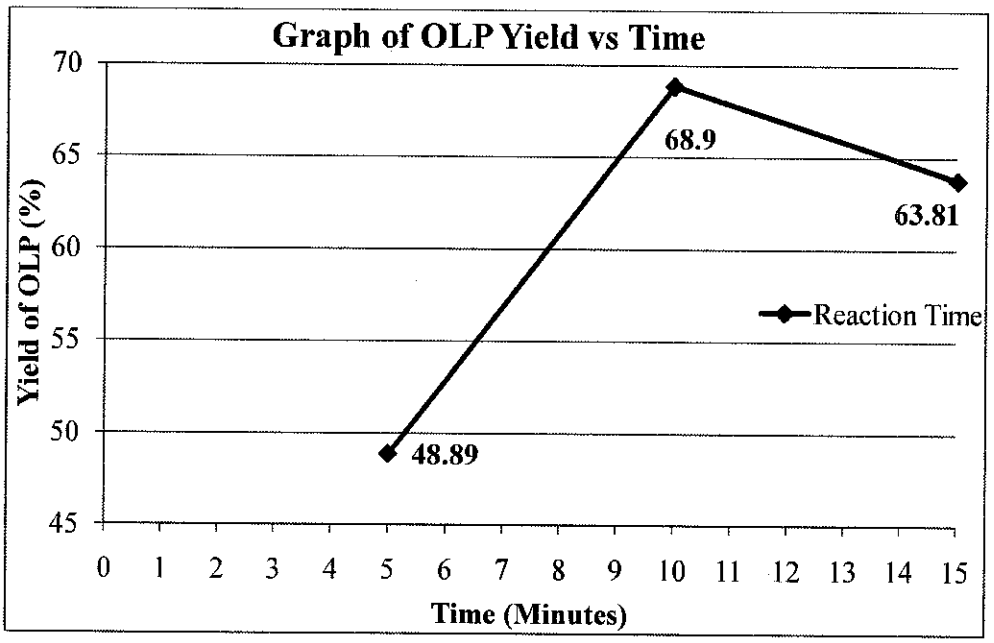

Figure 11: Graph of OLP Yield vs Time

The reaction time is 10 minutes as it has the highest yield of OLP. In 5 minutes, the yield of OLP is 48.89 wt% as some of the bio-oil has not being reacted. In 15 minutes, the yield of OLP has been decreased to 63.81 wt %. The yield has decreased because the conversion of liquid to gas occurs due to secondary cracking process (Hew, K.L., et al, 2010). More gas instead of OLP has been produced in secondary cracking process.

4.2 Experimental Results

There are two types of experimental analysis in this report, namely the statistical analysis and the properties characterization. The statistical analysis is the result of the data, the ANOVA table and relationship graphs which relate the parameters while the properties characterization is the comparison of analysis between the bio-oil and the OLP.

4.2.1 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.

Table 9: Taguchi Experiment Design L9 with Results

Run	Factor A: Catalyst	Factor B: Temperature (°C)	Factor C: Catalyst to Bio-oil Weight Ratio (wt%)	Factor D: Nitrogen Flow Rate (ml/min)	Yield of OLP (weight percent)	Signal to Noise Ratio (S/N)
1	H-Y	450	2:30	100	76.26	37.65
2	H-Y	400	1:30	500	72.23	37.17
3	H-Y	350	3:30	300	71.66	37.11
4	H-β	400	3:30	100	74.77	37.47
5	HZSM-5	400	2:30	300	74.13	37.40
6	HZSM-5	350	1:30	100	72.29	37.18
7	H-β	350	2:30	500	68.69	36.74
8	H-β	450	1:30	300	75.83	37.60
9	HZSM-5	450	3:30	500	73.38	37.31
Meanwhile, the software proposes another optimum condition.						
10	**H-Y**	**450**	**1:30**	**100**	**78.25**	**37.87**

4.2.2 Process Optimization

The conversion of bio-oil into OLP involves complex reaction whereby hundreds of new substances formed during the reaction. The highest yield is found in the Run 1 with the yield of 76.26 wt% while the lowest yield is found in the Run 7 with 68.69 wt% of OLP. In the Taguchi L9 array, by using H-Y catalyst, at the temperature of 450°C, nitrogen flow rate at 100 ml/min and 2 grams of catalyst produce the highest yield of OLP.

However, the software proposes another combination which will yield higher OLP (76.62 wt%) than Run 1 (76.26 wt%). This is possible because in Taguchi L9 Orthogonal Array, there are some combinations that are not arrayed by the software. Instead of running 81 runs, Taguchi reduces the number of runs to only 9 runs. The optimal condition predicted by the software is by using H-Y catalyst at the temperature of 450°C with the catalyst to bio-oil ratio of 1:30 and nitrogen flow rate of 100ml/min.

The experimental confirmation test (Run 10) based on Taguchi's design approach is verified. The confirmation experiment is vital and highly recommended by Taguchi to verify the experimental results (Ross, P.J. 1996). The prediction for the optimum condition by the Taguchi software has been proven to produce the highest yield of OLP.

When these conditions were tested experimentally for two trials, 78.65 and 77.86 wt% are obtained respectively with the average of 78.25 wt% and standard deviation of 0.56. The signal to noise ratio (S/N) of the optimum run is 37.87. The difference between the predicted and the real values are 0.02%.

$$\text{Percentage of error (\%)} = \left|\frac{Predicted - Experimental}{Predicted}\right| \times 100\%$$

$$= \left|\frac{76.62 - 78.25}{76.62}\right| \times 100\%$$

$$= 2.13$$

Taguchi L9 Orthogonal Array has identified the combination which produces the highest yield of OLP.

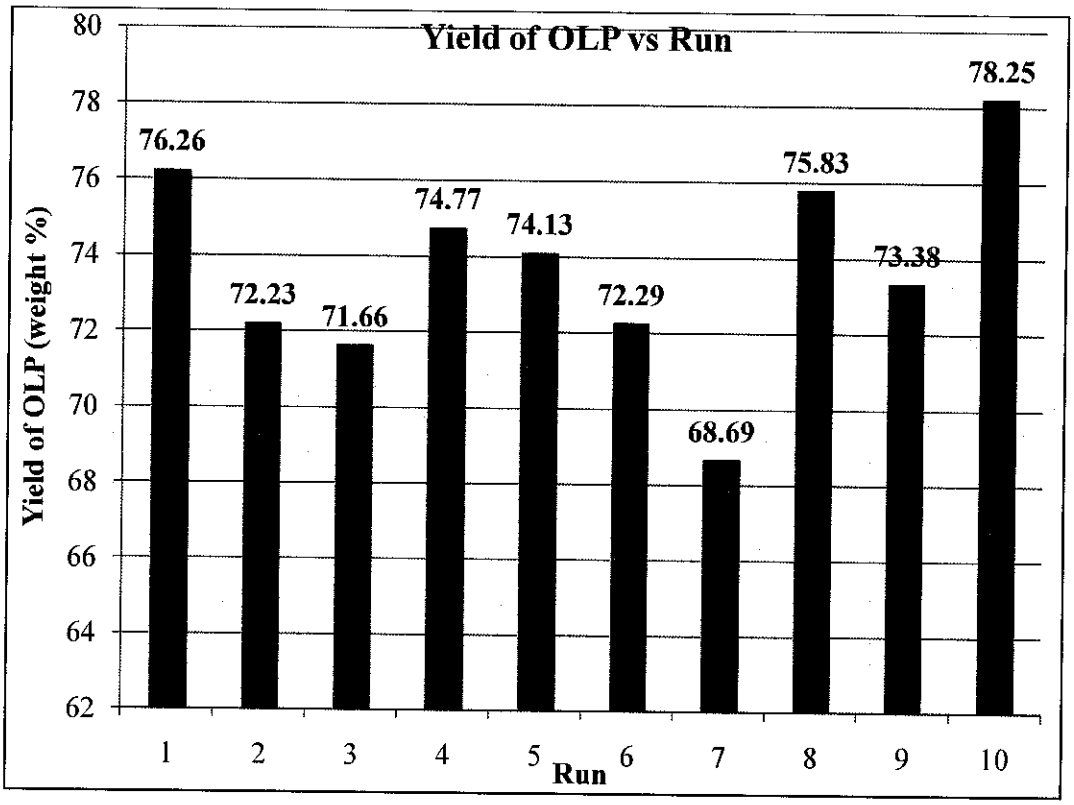

Figure 12: Yield of OLP vs Run

4.2.3 Signal to Noise Ratio (S/N)

Signal to Noise Ratio (S/N) is a variance index 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 OLP. More OLP obtained meaning more chances of getting the composition of gasoline, diesel, kerosene and gas as well as the probability of better catalytic cracking process.

4.2.4 ANOVA Table

ANOVA table is created for statistical analysis of the data. The results are further justified 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. In other words, it is a significant factor.

By comparing the percentage of contribution of the factors, the temperature (B) is found to have the biggest effect on the yield of OLP with 64.38%. This is in agreement with the previous study, Hew in reference 2. Next the highest effect on yield of OLP belongs to the nitrogen flow rate (D) with a percentage contribution of 34.73%, followed by the catalyst to bio-oil ratio (C) and type of catalyst (A) with percent contribution of 0.61% and 0.28% respectively, showing less significance on the outcome of the experiment.

Table 10: ANOVA Table

Source of Variance	Degree of Freedom	Sum of Square	Variance	Percent Contribution	Remarks
Type of Catalyst (A)	2	0.12	0.06	0.28	-
Temperature (B)	2	28.39	14.20	64.38	Significant
Catalyst to Bio-oil Ratio (C)	2	0.27	0.14	0.61	-
Nitrogen Flow Rate (D)	2	15.31	7.66	34.73	Significant
Total	8	44.10	-	100.00	-

4.2.5 Effect of Nitrogen Flow Rate and Temperature Towards Yield of OLP

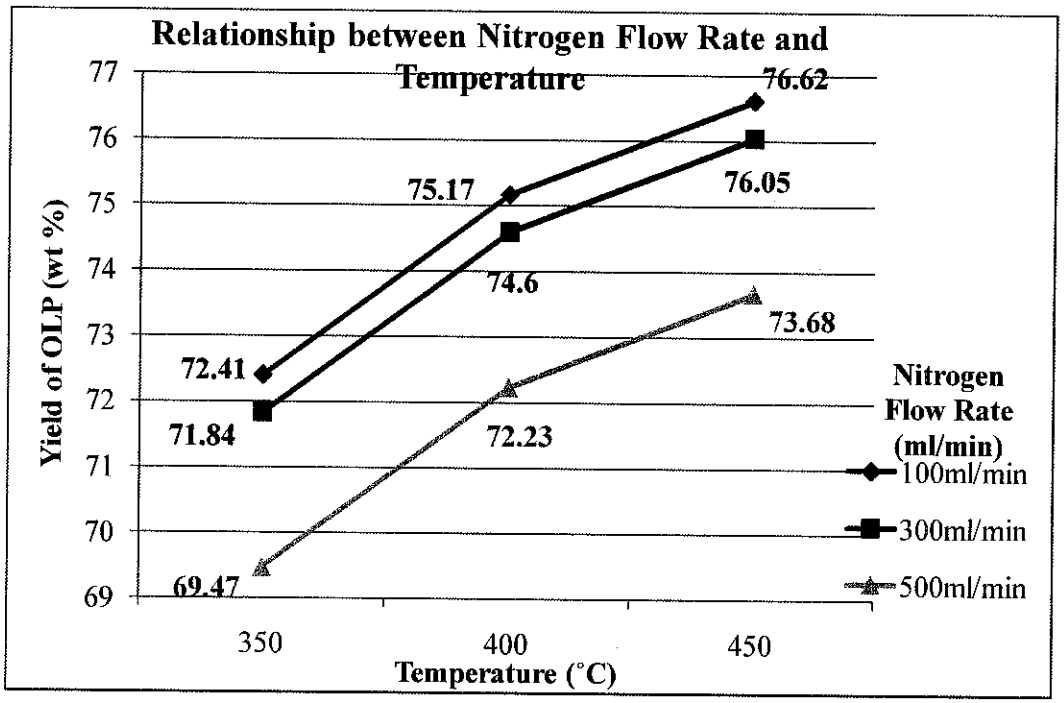

Figure 13: Relationship between Nitrogen Flow Rate and Temperature

As we observe from the graph, when the temperature is increased from 350°C to 450°C, the yield of OLP is increased also. Temperature has strong influence on the yield of OLP. An increase in temperature will induce vapourization of liquid product to gas which results in decrease yield of OLP (Hew, K.L., et al, 2010). Therefore, 450°C is the optimum temperature for this catalytic cracking process. The yield increases as catalytic cracking is an endothermic reaction, whereby it requires heat for the reaction.

As for the nitrogen flow rate, 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 reaction between the catalyst and the bio-oil from happening. In contrast, slower flow rate will increase the reaction rate between the catalyst and the bio-oil, thus producing more OLP. So, 100ml/min is the optimum flow rate.

4.2.6 Effect of Catalyst to Bio-oil Ratio and Type of Catalyst Towards Yield of OLP

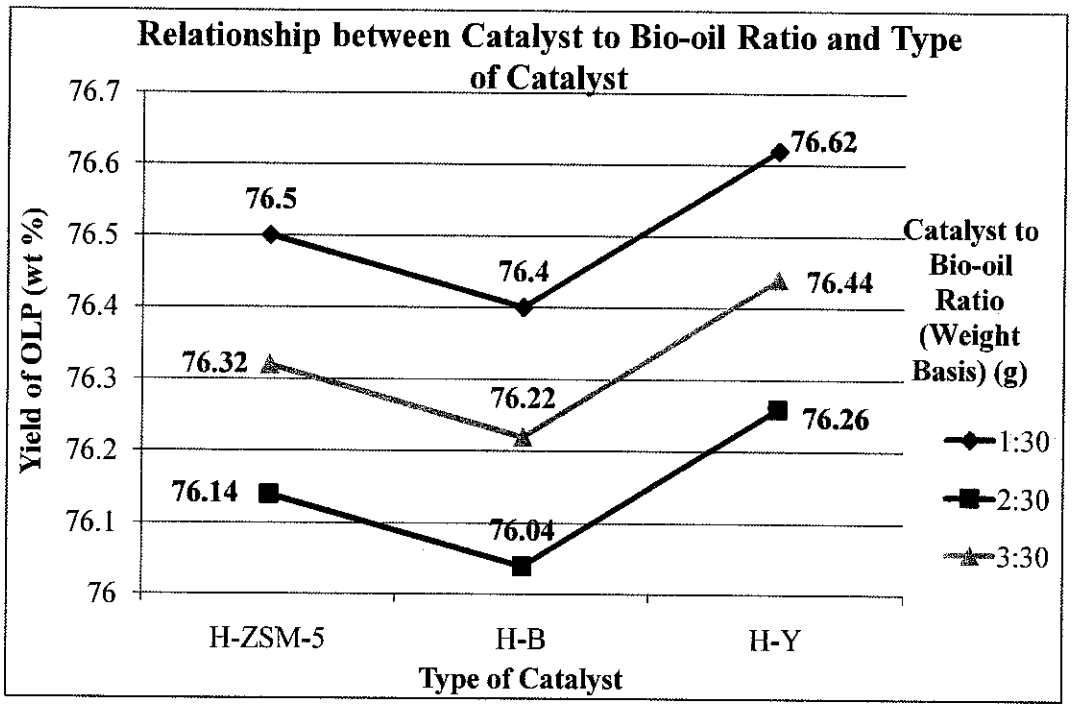

Figure 14: Relationship between Catalyst to Bio-oil Ratio and Type of Catalyst

From Figure 15, the ideal catalyst to bio-oil ratio is 1:30. The catalyst used is 1 gram. The yield of OLP is found to be lower for both 2g and 3 g of catalyst compared to 1g of catalyst used. The yield of OLP approaches constant values when the amount of the catalyst is increased from 2g to 3g.

As the amount of catalyst increases, the yield of OLP decreases. When the volatile intermediates formed during the catalytic cracking process pass over the catalyst surface into the pores of the catalyst, the acidity of catalyst might induce the secondary cracking (Pan, P., et.al., 2010). As a result, the OLP reduces and cokes are remained on the catalyst surface and in its pores forming residues. The catalyst itself has certain number of active sites in its interior of the pore. It can just accommodate a certain amount of reactant, in this case, it is bio-oil. The presence of coke in the internal structure of the catalyst reduces the formation of OLP (Siswanto, D.Y., et al, 2008).

Among the three zeolite catalysts, H-Y is ranked number 1 followed by HZSM-5 and H-B. The three zeolite catalysts show good signs of catalytic cracking in which the catalysts have cracked the bio-oil to OLP. Below is a table of the characterisation of the catalysts from the Zeolyst website.

Table 11: Characterisation of the Zeolite Catalysts[19]

Catalysts	SiO_2/Al_2O_3 Mole Ratio	Surface Area m^2/g
HZSM-5	30.6	357
H-β	75	565
H-Y	5.2	531

Different SiO_2/Al_2O_3 mol ratio of the zeolite yield different acidities. The acidity of the zeolite increases as the Si/Al ratio decreases. (Wang, Q.Y. and Lin, W.M., 2004). The stronger the acidity, the greater the activity of the catalyst, thus, producing more yield (Guo, X.Y., et al, 2004). The best catalyst is the H-Y catalyst as it has lesser Si/Al ratio.

4.2.7 Effect of Temperature, Type of Catalyst, Nitrogen Flow Rate and Catalyst to Bio-oil Ratio Towards Yield of OLP

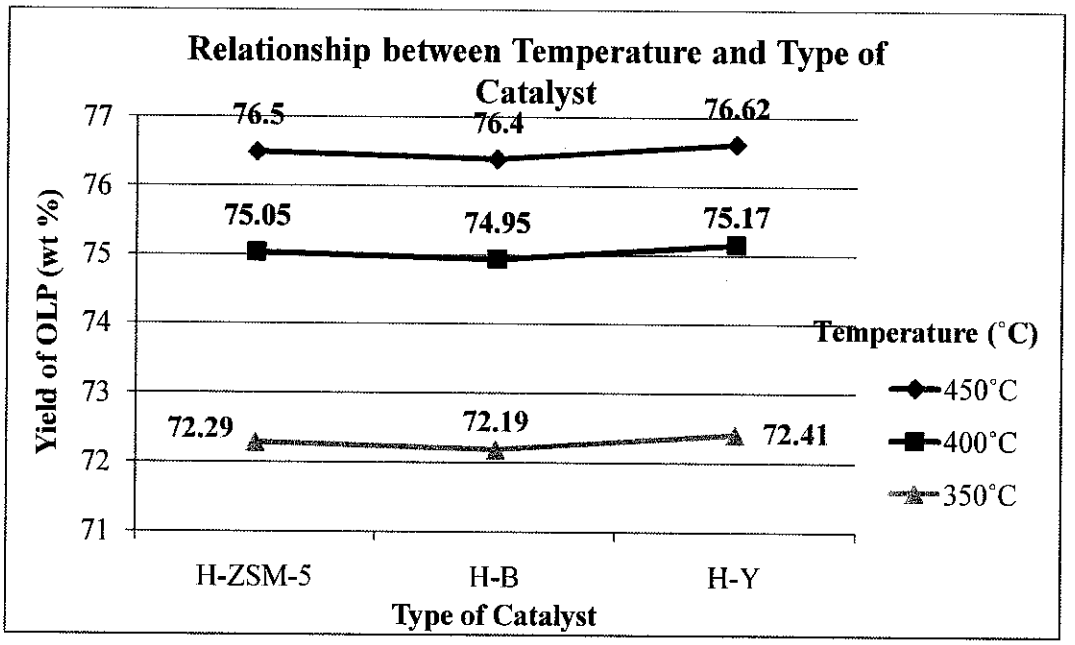

Figure 15: Relationship between Temperature and Type of Catalyst

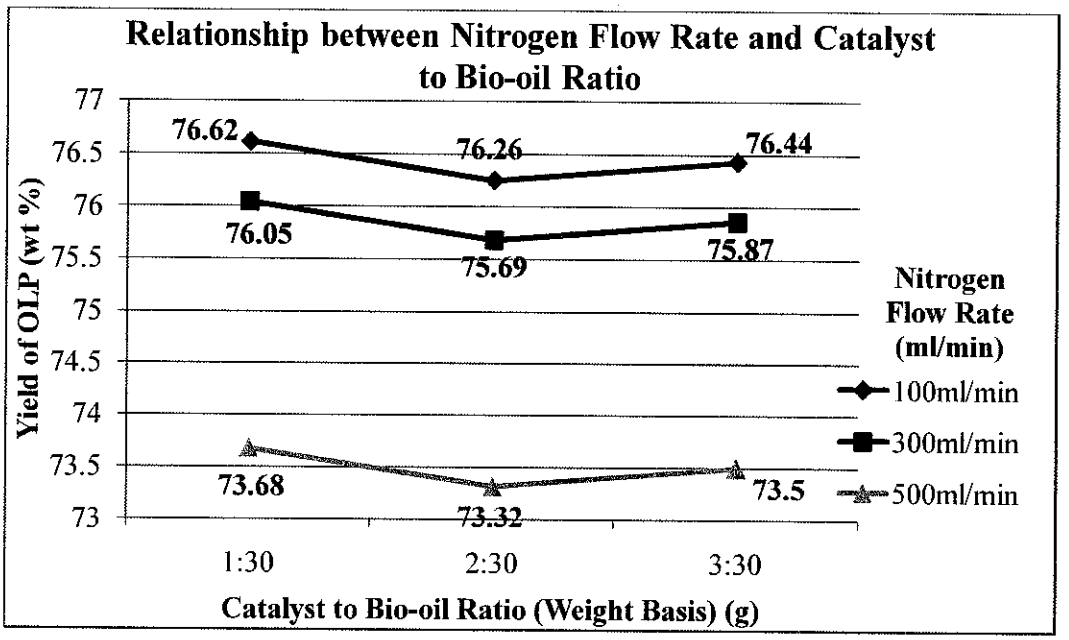

Figure 16: Relationship between Nitrogen Flow Rate and Catalyst to Bio-oil Ratio

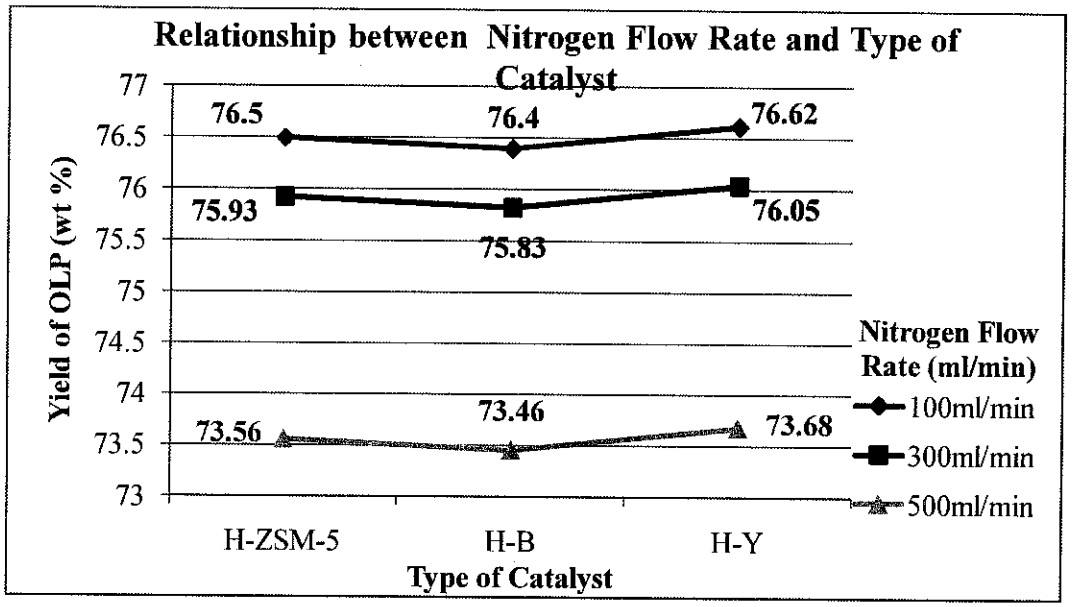

Figure 17: Relationship between Nitrogen Flow Rate and Type of Catalyst

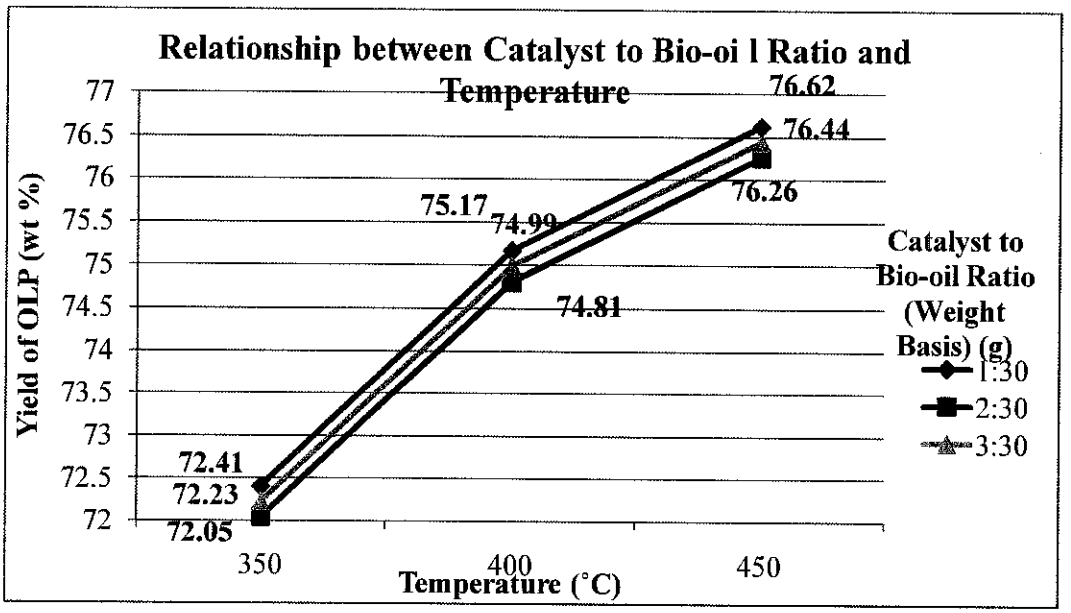

Figure 18: Relationship between Catalyst to Bio-oil Ratio and Temperature

The possible relationships between the four parameters are shown in Figure 15 till Figure 18 with all the information indicating that the optimum condition is using H-Y zeolite catalyst with the ratio of catalyst to bio-oil in 1:30 at the temperature of 450°C and nitrogen flow rate of 100 ml/min.

4.2.8 3D Surface

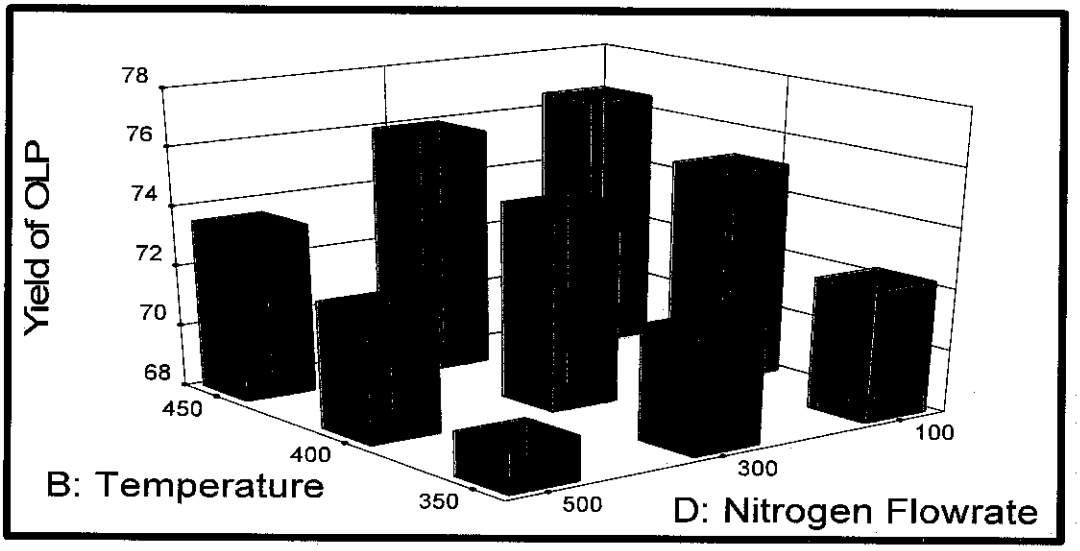

Figure 19: 3D Surface for Temperature and Nitrogen Flow Rate

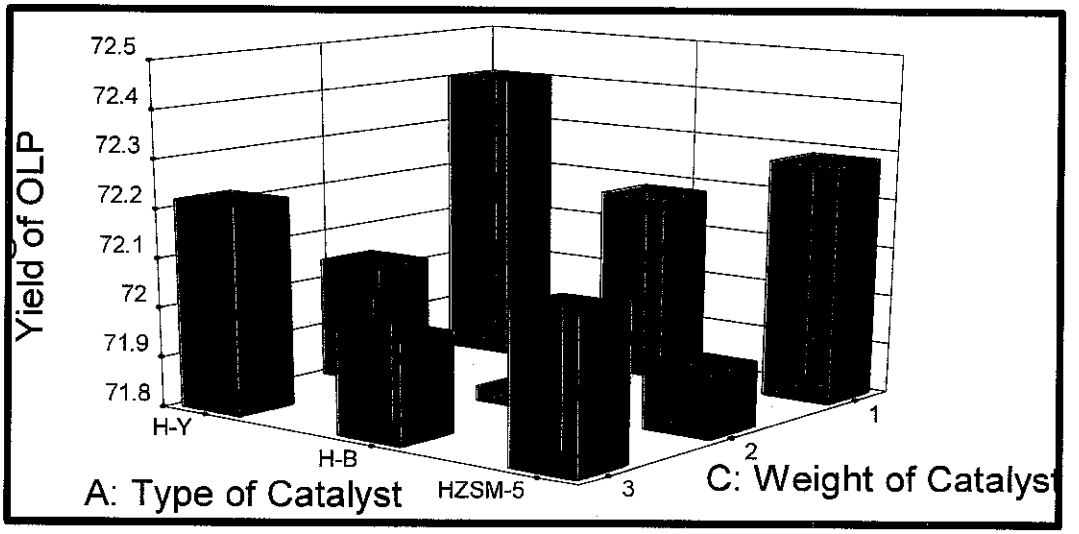

Figure 20: 3D Surface for Type of Catalyst and Weight of Catalyst

From the 3D surface, it clearly states that the optimum temperature is at 450°C with 100ml/min of nitrogen flow, using H-Y zeolite catalyst with the catalyst to bio-oil ratio of 1:30. The highest yield we obtain is 78.25 wt% of OLP.

4.3 Comparison of Properties Analysis

4.3.1 Viscosity Analysis

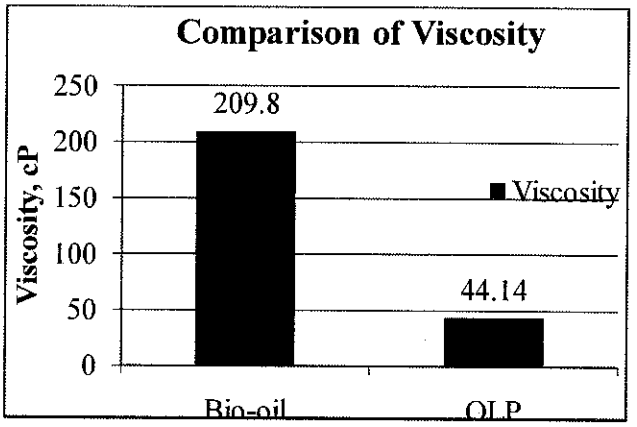

Figure 21: Comparison of Viscosity between Bio-oil and OLP

After catalytic cracking, the viscosity has decreased dramatically from 209.8 cP to 44.14 cP. High viscosity states that polymerization has happened and big molecules are formed within the bio-oil and affects stability. Therefore, lower viscosity is preferred.

4.3.2 Water Content

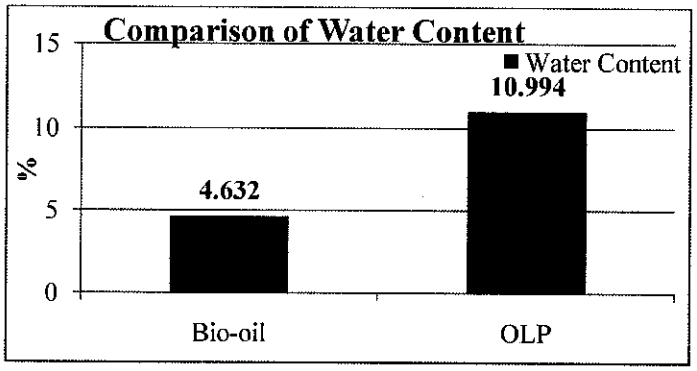

Figure 22: Comparison of Water Content between Bio-oil and OLP

The water content increases in OLP. It is because the water is generated during the catalytic cracking process. A centrifuge should be used to separate the water.

4.3.3 Density Analysis

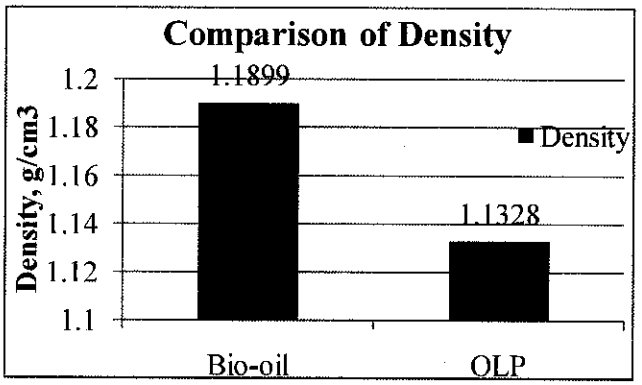

Figure 23: Comparison of Density between Bio-oil and OLP

The density of OLP decreases if compared to bio-oil. The density of bio-oil is 1.1899g/cm^3 while the density for OLP is 1.1328 g/cm^3, measured at 15°C.

4.3.4 Ash Content

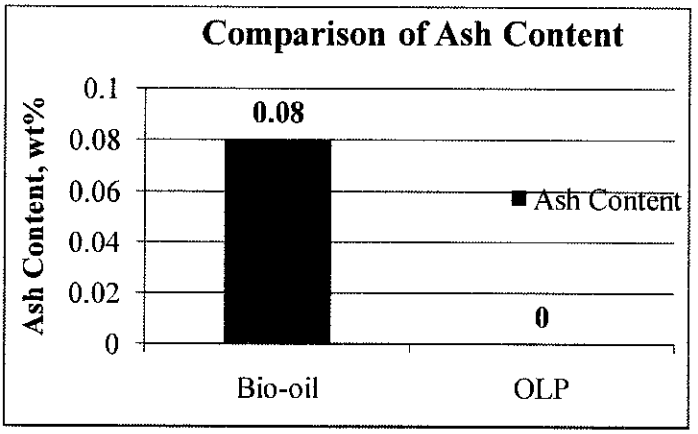

Figure 24: Comparison of Ash Content between Bio-oil and OLP

OLP does not contain any ash content while bio-oil contains 0.08 weight percent of ash content. This signifies that OLP is a clean and green fuel. The ash content in the bio-oil is 0.08 wt%.

4.3.5 Elemental Analysis

Table 12: Comparison of Elemental Analysis between Bio-oil and OLP

Component (%)	Bio-oil	OLP
Carbon	60.350	56.255
Hydrogen	6.101	6.836
Nitrogen	0.504	0.321
Sulphur	0.002	0
Oxygen*	28.331	25.594

* Oxygen Content is calculated by subtraction. 100-CHNS-Ash Content-Water Content

The oxygen content has decreased. Biomass materials of high ash content are not a good source of burning material because ash plays catalytic role in cracking of the liquid products to form gases (Okoroigwe, E., et al., 2012). The low nitrogen and sulphur are low, stating that OLP is an environmentally friendly source of bio-fuel.

4.3.6 pH

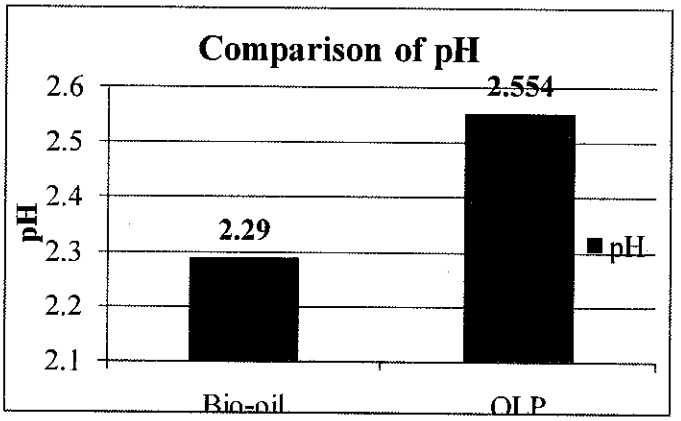

Figure 25: Comparison of pH between Bio-oil and OLP

The pH of OLP increases after the catalytic cracking process, approaching the neutral pH. High acidity is not favoured because it will be difficult during the storage or transportation as it will cause corrosion and cause instability (Udomsap, P., et al., 2011).

4.3.7 Calorific Value

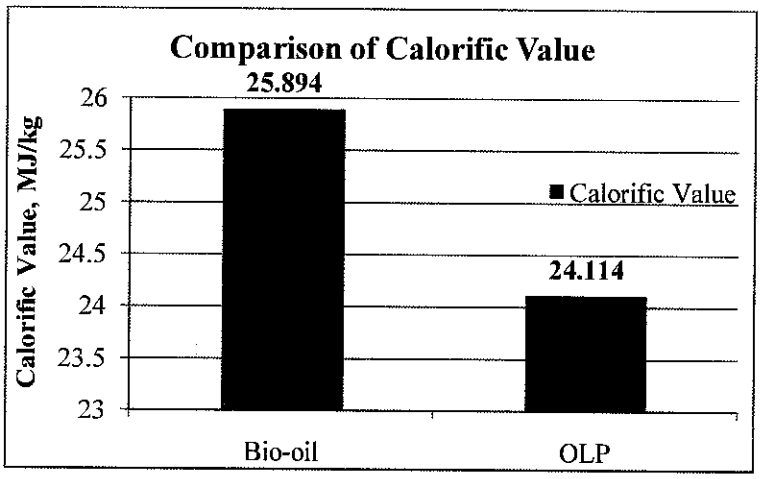

Figure 26: Comparison of Calorific Value between Bio-oil and OLP

The calorific value decreases a little. High calorific value is preferable if it is to be used as a burning fuel. The reason might be because of the water content in the OLP reduces the calorific value. It is recommended to remove the water through boiling process of centrifugation at higher rpm to separate the both miscible layers.

4.3.8 Infrared Spectrometry

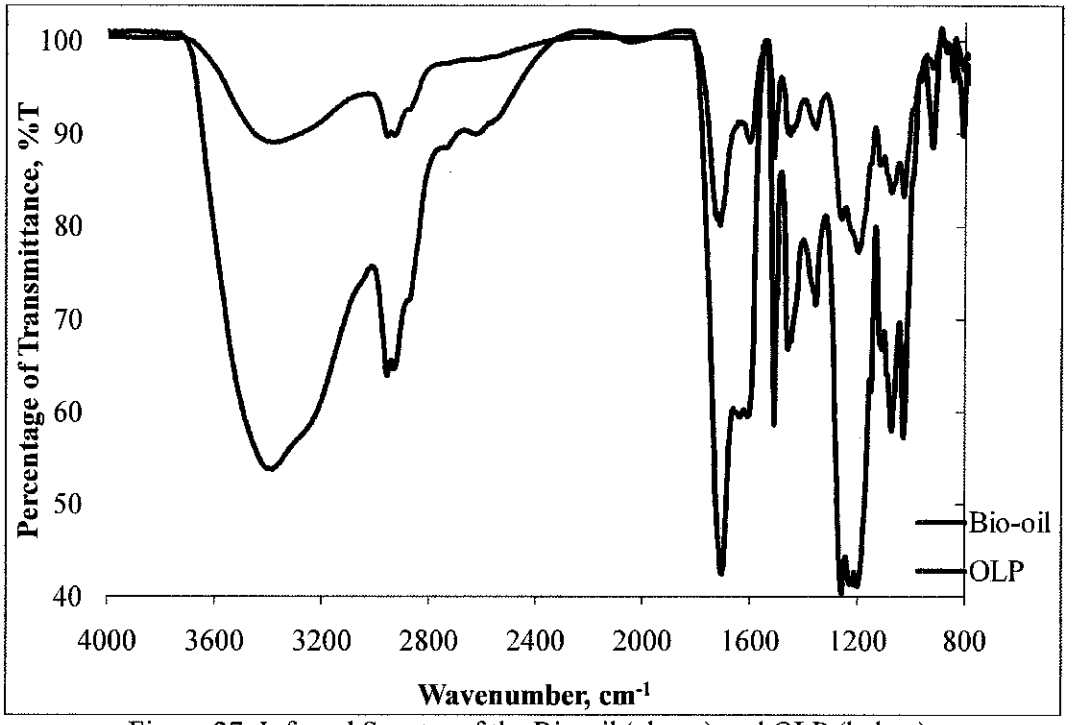

Figure 27: Infrared Spectra of the Bio-oil (above) and OLP (below)

In Figure 24, the IR spectra of bio-oil and OLP are reported and compared among each other. This suggests that bio-oil and OLP have almost the same main structure but with different intensity as we can observe from the y-axis, percentage of transmittance, %T. More components dominate the right side of wavelength 3000cm^{-1}, indicating that more alkyl groups are present in both bio-oil and OLP (Organic Courses Home, n.d.).

The higher the percentage of transmittance, it means that all the frequency passed through the compound without being absorbed. The peaks that are across the graph near the top indicate the weak intensity of the functional groups while strong intensity is defined when we can see a deep valley across the graph (Clark, J., 2007). In Beer Lambert's Law, the percentage of transmittance is inversely proportional to the concentration. (Thermo Spectronic, n.d.). In other words, if the percentage of transmittance is lower, the concentration of the particular functional groups will be higher. The readings are based on the table of characteristic IR absorptions chart.

Aromatisation is detected by the absorption bands in the 3300-3000cm^{-1} region (aromatic C-H stretching vibration). In the region of 1600-1475cm^{-1} (skeletal aromatic C=C stretching vibration) as well as in the region of 650-900cm^{-1} (aromatic C-H stretching vibrations) are evidenced (Vitolo, S., et al., 1999). In the spectrum, the peaks in the region 3500-3200, 1600-1580, 1500-1450cm^{-1} correspond to the bonds in an aromatic ring. The O-H group will be either an alcohol or phenol group. However, in the analysis of GCMS, we have confirmed the band belongs to the phenol group (Organic Courses Home, n.d.).

In the region of 1760-1665cm^{-1}, where the functional groups might be ketones, aldehydes, esters as there are C=O stretches. The C-O stretch band in the 1320-1000cm^{-1} indicates the particular functional group is esters group, which corresponds to the result obtained from the GCMS (Organic Courses Home, n.d.). Therefore, for the phenol group and the esters group, the percent of transmittance of OLP is lower than bio-oil, meaning the intensity of OLP is higher and the concentration of the particular functional group in OLP is higher as well. The gas chromatographic analysis of the OLP is then compared with the bio-oil.

4.3.9 Gas Chromatography Mass Spectrometry

The purpose of the gas chromatography mass spectrometry analysis is to validate the result that is obtained in the FTIR and also pH. The composition of bio-oil and OLP are detected by GC-MS.

Bio-oil itself contains a lot of complex compounds. More than 100 kinds of compounds are detected in the bio-oil and OLPs. Therefore, only the area percentage more than 1% are taken into consideration while the rest of the readings will categorized as the others functional group which includes ethers, furans and others. The area content of the major functional groups, such as, acids, phenols, esters, ketones and aldehydes are compared between the bio-oil and OLP as shown in the Table 12.

Table 13: Chemical Functional Groups in Bio-oil and OLP

Functional Group	Area Content (%)	
	Bio-oil	OLP
Acids	31.32	4.92
Phenols	17.69	67.21
Esters	5.91	7.27
Ketones	7.94	4.21
Aldehydes	2.10	2.44
Others (Ethers, Furans, etc)	35.04	13.95

The change in the phenols is the most obvious, as the functional group increases from 17.69% to 67.21%, correspondence to infrared spectrometry and literature review of (Li, H.Y., 2008). The acids have decreased significantly, correspondence to the pH reading as well as the literature reviews of (University of Limerick, n.d.,), (Guo, Z., 2011), (Li, H.Y., 2008) and (Peng, J., 2008). The esters and aldehydes have also increased while the ketones have decreased. The readings from esters can be verified with the readings from infrared spectrometry. Both FTIR and GC-MS are very useful to verify the results that obtained.

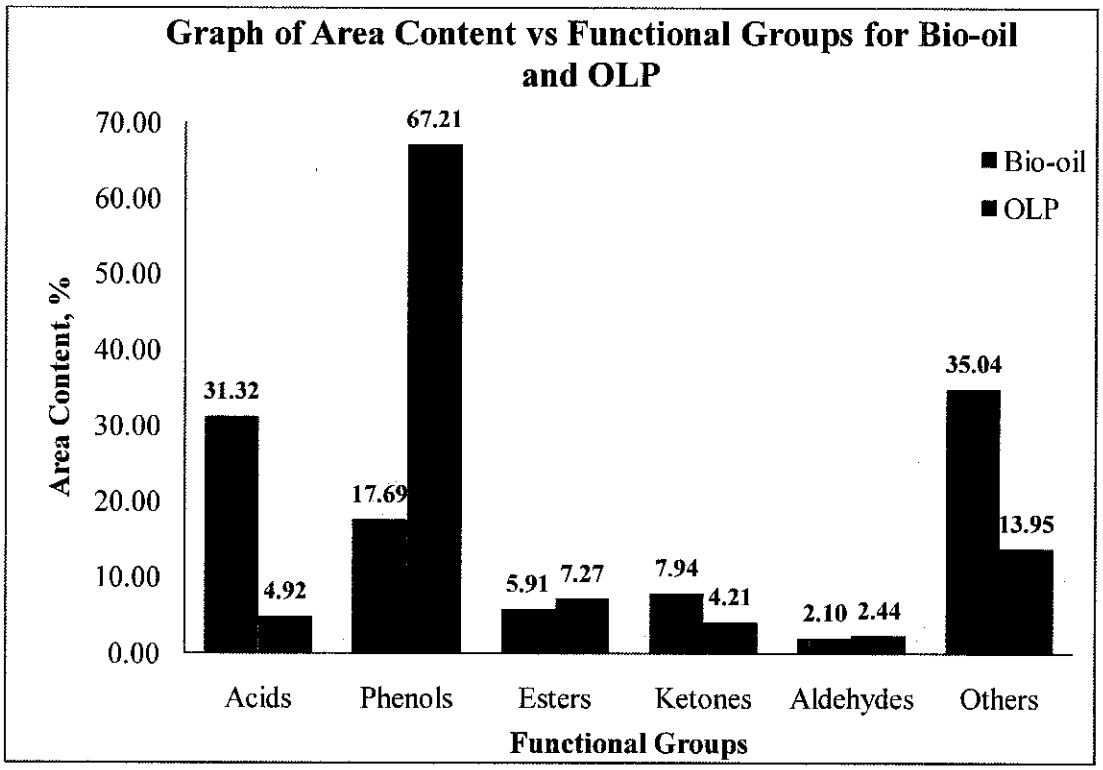

Figure 28: Graph of Area Content and Functional Groups in Bio-oil and OLP

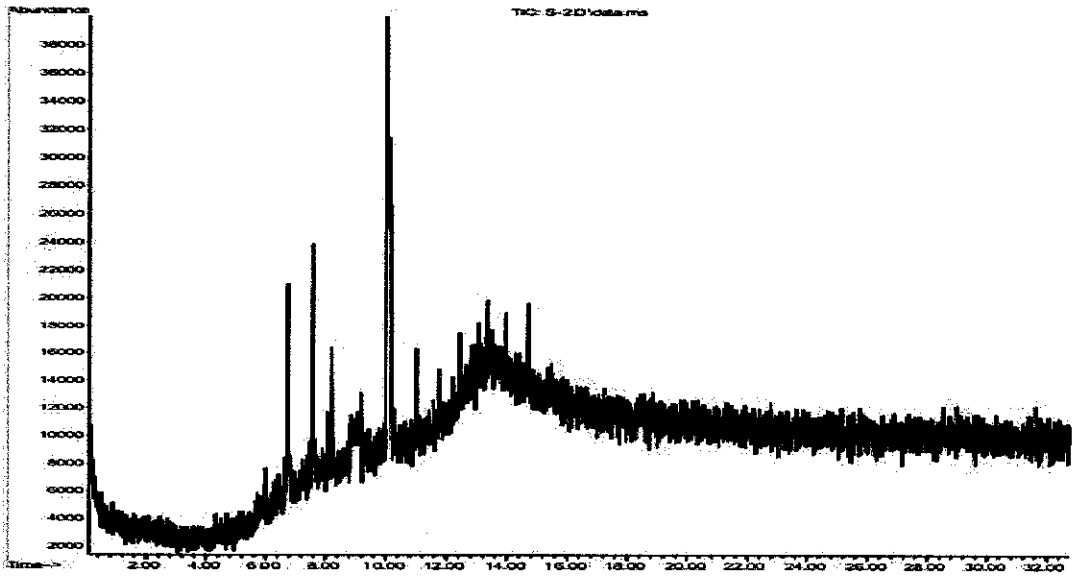

Figure 29: GCMS Chromatogram of Bio-oil

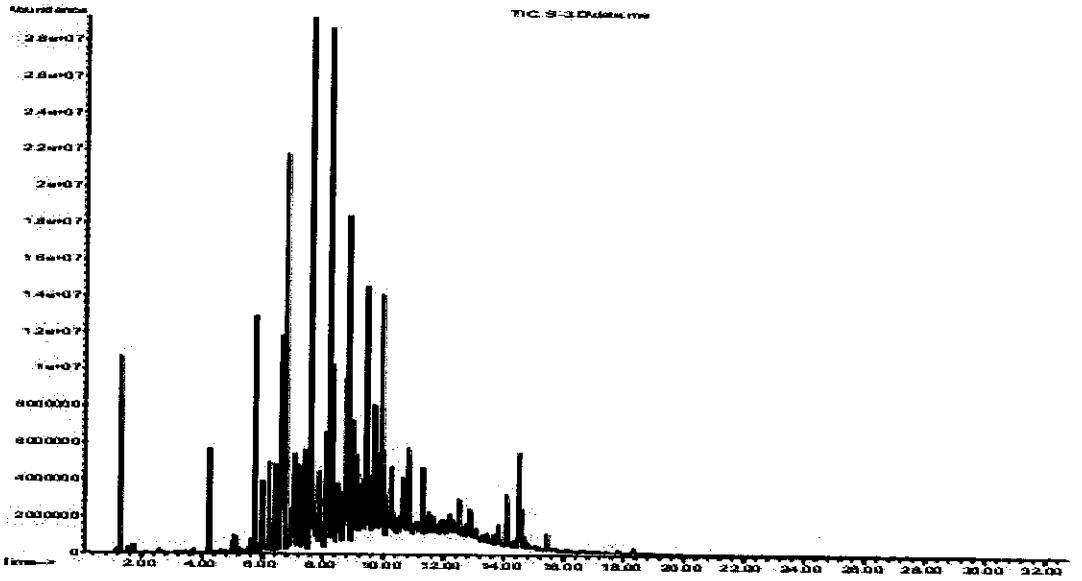

Figure 30: GCMS Chromatogram of OLP

4.4 Overall Discussion

From the analysis that we obtained, the viscosity, density, heating value and the ash content decreases while the pH and water content increase. The decrease in the viscosity is a good sign as it signifies that the chemical composition in the bio-oil has not reacted and forms big molecules which eventually cause instability.

The low ash content, low nitrogen content and no sulphur content during combustion prove that the OLP is an environmentally friendly source of bio-fuel. As time goes by, the internal chemical reactions, such as polymerization, esterification, and transesterification will happen and cause increment in the viscosity and acidity of the bio-oil (Udomsap, P., et al., 2011).

However, the increment in the water content decreases the heating value. If the heating value is low, it is not preferable as it will not provide enough energy for the combustion process. With catalytic cracking process, the bio-oil is cracked into organic liquid products which comprised of gasoline, kerosene, diesel and gas.

Oxygen contents are catalytically decomposed to hydrocarbons with the removal as water, carbon dioxide or carbon monoxide in the OLP (Zhang, Q., et al, 2006). The acidity of the OLP is increased in correspondence to the area content in GC-MS. Higher acidity or known as higher pH appears to be better during storage and transportation. The acidity will cause corrosion if the product is acidic.

In the infrared spectrum analysis, aromatisation is detected with the higher intensity of phenols and esters functional groups in the OLP, and again, in correspondence to the area content in the GC-MS analysis. With the higher yield of OLP, we can get a higher fraction of gasoline, kerosene, diesel and gas, so that is why the objective of the experiment is to identify the optimum condition that will produce highest yield of OLP.

CHAPTER 5 CONCLUSIONS

Due to the increasing demand for fuels, the increased build-up for carbon dioxide in the atmosphere, and the general fact that the oil reserves are depleting, the need of renewable fuels is evident. Biomass derived fuels offers promising route, being the only renewable carbon resource. The complex compounds and the properties such as, high viscosity, high acidity and high oxygen content in the bio-oil are not favoured as it leads to instability. Therefore, in our literature review, catalytic cracking method has been focused to stabilise the bio-oil by converting it to OLP.

In this experiment, there are four variables or also known as factors, which are the type of catalysts, the weight of catalysts, the temperature and the nitrogen flow rate. By using the Taguchi L9 Orthogonal Array, only 9 runs have to be carried out instead of 81. The results are recorded in the Design Expert software. The relationships between the four variables are studied.

By referring to the Taguchi software, the optimum condition is the H-Y catalyst 1 gram, temperature at 450°C and the nitrogen flow rate at 100ml/min. The best condition yields 78.25 weight percentage. 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. After catalytic cracking process, the OLP is obtained and it is comprised of gasoline, kerosene, diesel and gas. With the higher yield of OLP, more valuable components can be extracted.

The combination which produces the highest yield is sent for characterization and compared with the bio-oil. From the analysis, the density, viscosity and ash content decreases and it is favourable to have lower values. The pH increases, approaching the neutral pH, which is favourable. However, the heating value decreases and the water content increases, which are not favourable. The GC-MS and FTIR results can identify the components in the bio-oil and OLP thus comparisons can be made and the effect of catalytic cracking can be studied.

CHAPTER 6 FUTURE WORK AND RECOMMENDATIONS

From the result that we obtained, the heating value seems to be lower than the bio-oil. One of the reason might be because during the catalytic cracking, water, carbon monoxide and carbon dioxide are produced. During the condensation process, the water is being condensed and being collected in the condenser together with the OLP.The water phase can be separated from the OLP by using a centrifuge instrument at 5500 rpm for 15 minutes (Vitolo, S., et al., 1999). The water content will reduce the heating value of the sample. So, in order to get a more accurate result, the water must be separated from the OLP. Besides that, boiling the OLP at the boiling point can evaporate the water content from the OLP as well.

The catalysts should be activated first in the muffle furnace for 24 hours prior to the experiment. This is to make sure that the catalyst is in good condition. Then, after the catalysts have been reacted, studies about regeneration of the catalysts should be experimented as well to study the effect of the used and reused catalysts.

The OLP fractions can be further being separated according to the boiling range to the gasoline fraction and being compared to the conventional gasoline. Properties characterization should be done. Blending of the gasoline from the OLP can be mixed with the conventional gasoline and the effects are studied.

For the cleaning of the borosilicate tube, combustion at the temperature of 550°C for 30 minutes seems to be quite effective in removing the remaining char which sticks to the borosilicate tube. Extra precaution has to be taken when dealing with the borosilicate tube and during the combustions process as it is easily broken and it is costly. Before the reactor is cooled down, the reactor should not be opened as the borosilicate tube might crack. Effective char removal detergent should be purchased to minimize the time of the experiment.

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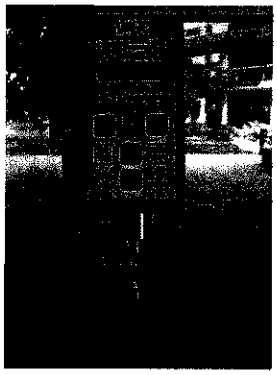
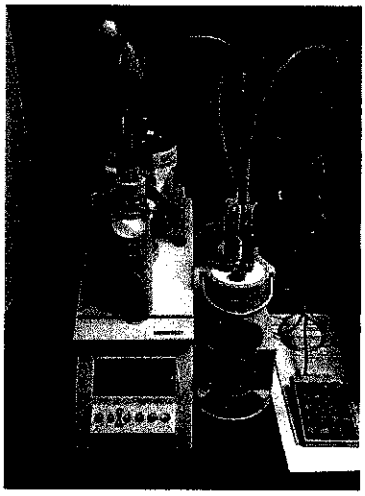
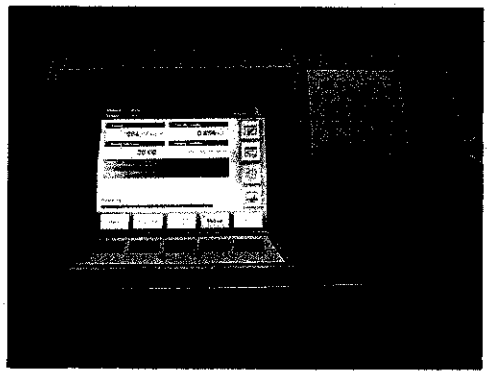
APPENDIX



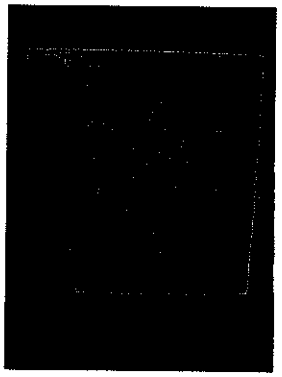
Brookfield Viscometer DV-I+ – used to measure the viscosity in the unit of cP



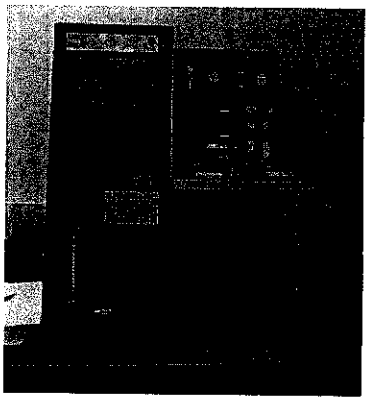
Metrohm 870 KF Titrino Plus – used to measure the water content



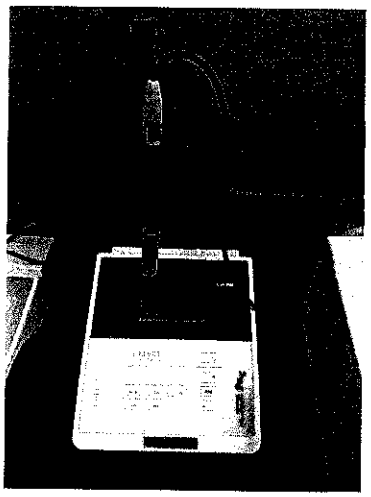
Anton Paar Density Meter DMA 4500 M – used to measure the density and the specific gravity



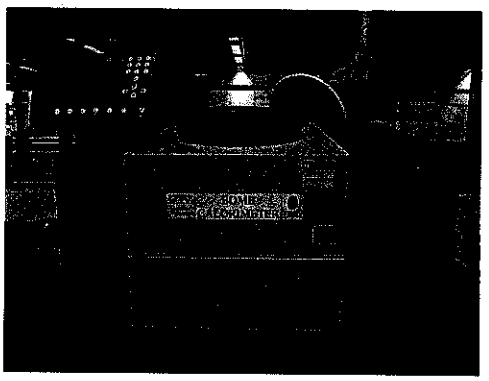
WiseTherm Programmable Digital PID Control Muffle Furnace – used to determine the ash contents in the samples



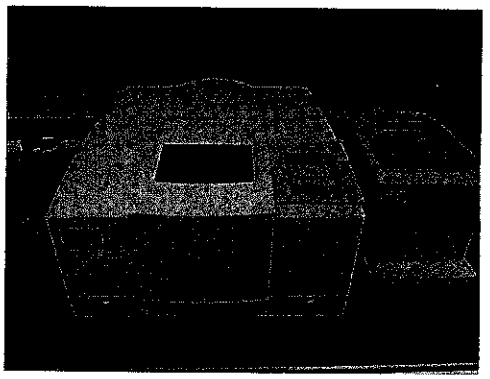
LECO CHNS Analyser 932 – used to determine the content of Carbon, Hydrogen, Nitrogen and Sulphur



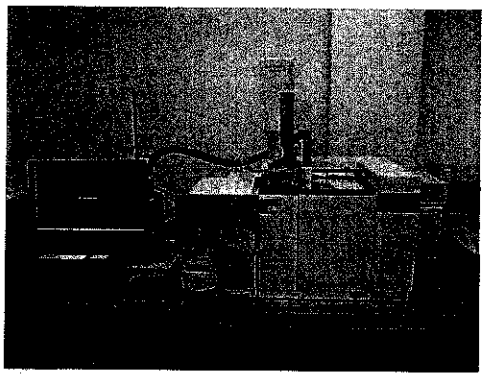
Schott Instruments pH Meter – used to measure the pH of the samples



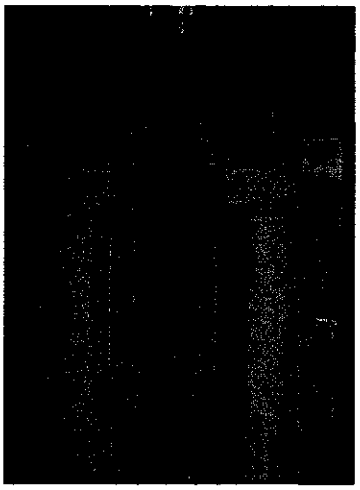
IKA C5000 Bomb Calorimeter – used to measure the calorific value / heating value



Perkin Elmer Spectrum One Spectrometer – used to measure the infrared spectrum

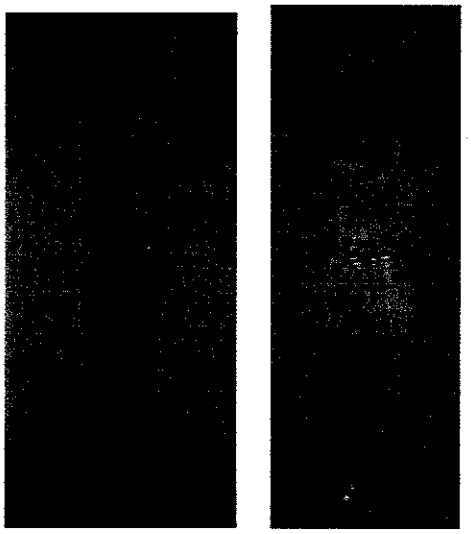


Agilent Gas Chromatography Mass Spectrometry GCMS-5975C – used to identify the components in the sample



The Condition of Borosilicate Tube after Experiment

OLP Flowing Out from the Reactor



The Condition of Borosilicate Tube Before and After Combustion Process