FINAL YEAR PROJECT 2: DISSERTATION

OPTIMIZATION AND ESTERIFICATION OF KAPOK SEED OIL VIA ULTRASONICATION ASSISTED TECHNOLOGY

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Abstract

Energy and vegetable oil prices have caused many biodiesel producers to turn to seed oil as feedstock. These oils contain high levels of free fatty acids (FFA) which make them difficult or impossible to convert to biodiesel by conventional production methods. Esterification is required for high FFA feedstock such as Kapok seed oil. FFA value must be low in order to produce biodiesel. High FFA value will result in soap production. In addition, ultrasonication technique has the potential to reduce the amount of catalyst used, reaction temperature, reaction time and oil to alcohol ratio relative to conventional method. The study determined that ultrasonication assisted technique can save a lot of time and energy for the esterification process in order to reduce the free fatty acid content of the Kapok seed oil. The objective of this project is to reduce the FFA content of the feedstock and to optimize using RSM. The experiment will be using Kapok seed oil, methanol (CH_3OH), and sulphuric acid (H_2SO_4). The free fatty acid content of the Kapok seed oil will be first determined. The Kapok seed oil will then be reacted with methanol as an alcohol and sulphuric acid to reduce the free fatty acid of the oil. The catalyst for the reaction will be sulphuric acid (H_2SO_4). The reaction between Kapok seed oil and methanol will be conducted using ultrasonication method. After determining the FFA% of the Kapok seed oil which is 6 wt. %, the oil will undergo esterification process via ultrasonication to reduce the FFA content. This process results in significant FFA reduction and based on the optimized condition, the FFA content is (0.44%). The optimization is done using Response Surface Methodology (RSM). The optimized parameters are (19.22:1) for alcohol to oil ratio, 6.83 wt. % for catalyst amount, 22.76 minutes for reaction time and at a frequency of 39.61 kHz. Therefore, this project shows that Kapok Seed Oil has to potential to be a feedstock to produce biodiesel.

Acknowledgement

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Abbreviation and Nomenclatures

FFA: Free Fatty Acid
FAME: Fatty Acid Methyl Ester
FAAE: Fatty Acid Alkyl Ester
KSO: Kapok Seed Oil
RSM: Response Surface Methodology
ANOVA: Analysis of Variance
R: Regression

CHAPTER 1

INTRODUCTION

1.1 Background

This project is related to the esterification process of non-edible oil to produce bio-diesel via ultra-sonication. In this case, the non- edible oil that will be used will be Kapok seed oil. Kapok is also known as *Ceiba Pentendra* There is two main ways to produce bio-diesel from non- edible oil which is transesterification process and esterification process. In this project, esterification process will be conducted to produce bio-diesel. Biodiesel is commonly made by reacting lipids with alcohol delivering unsaturated fat esters. The reaction between fatty acid and alcohol is named esterification. Biodiesel is one of the new conceivable substitutes of normal fuel for motors and is delivered from distinctive vegetable oils or animal fats. [1] Ultrasonic is an exceptionally alluring apparatus for creating biodiesel from vegetable oil and animal fats, on the grounds that it brings down the expense of handling, accelerates esterification, does not oblige higher temperatures, and produces a higher quality of biodiesel. The longitudinal vibrations of the ultrasonic test are transmitted into the fluid as ultrasonic waves comprising of interchange developments and clamping. [2]

1.2 Problem Statement

Determination of FFA content inside the oil is one of the most important things in transesterification of biodiesel. For feedstock which contains less than 3% of FFA content, pre-treatment of the feedstock is not required and one step of process which is direct transesterification reaction is sufficient. If the free fatty acid of the oil is more than 3 wt. %, esterification process is required to reduce the free fatty acid content of the oil. The principle issues are: long transforming times (up to 8 h for every cluster), constrained feedstock and transfer of the homogeneous (base) catalyst. Esterification is favoured over transesterification system this is on the grounds that transesterification technique will create soap if the free fatty acid is high. As of late, numerous analysts have utilized ultrasound (US)-helped procedures to advance and lessen response times of both the transesterification and esterification responses. Acoustic cavitation-based advances have been viewed as an intent to minimize mass-exchange constraints. Cavitation is a phenomenon of nucleation, development, and consequent breakdown (semi adiabatic) of micro bubbles in a fluid medium. The breakdown of air pockets form hot spots portrayed by high temperatures (in the scope of 1000–15000 K) and pressures (in the scope of 500–5000 bar) generally however millions in the reactor. Notwithstanding the era of hotspots, cavitation might likewise create profoundly sensitive free radicals and turbulence. At the point when a cavitation air pocket crumples close to a robust surface, fluid planes are delivered and fast flies of fluid are crashed into the surface of a molecule (because of the unbalanced breakdown of air pockets), bringing about improved transport of the species towards the strong surf. [4]

1.3 Objective

The objectives of the project are:-

1. To characterize the Kapok seed oil.
2. To reduce the free fatty acid of Kapok seed oil by esterification process and its optimization using Response Surface Methodology (RSM).
3. To study the parametric effect on esterification process using ultrasonication assisted technique such as ultrasonic frequency, reaction time, catalyst required and oil to alcohol ratio.

1.4 Scope of Study

The experiment will be using Kapok seed oil, methanol (CH_3OH), and sulphuric acid (H_2SO_4). The free fatty acid content of the Kapok seed oil will be first determined. The Kapok seed oil will then be reacted with methanol as an alcohol and sulphuric acid to reduce the free fatty acid of the oil. [10] The catalyst for the reaction will be sulphuric acid (H_2SO_4). The reaction between Kapok seed oil and methanol will be conducted using ultrasonication method.

1.5 Relevancy and Feasibility of the Project

This project emphases on optimization and esterification of Kapok seed oil via Ultrasonication assisted technique. Ultrasonication is an advanced technique relative to the conventional method. Ultrasonication technique requires less reaction time, lower temperature, lower amount of catalyst relative to conventional method and low oil to alcohol ratio. It is important to determine the reaction time, frequency, catalyst required and oil to alcohol ratio via ultrasonication technique.

This project is within capability of a final year student to be executed with help and guidance from the supervisor and the coordinator. The time frame is also feasible and the project can be completed within the time allocated. It is hoped that the acquiring of equipment and materials needed for the experiment runs smoothly for the accomplishment of this project.

CHAPTER 2

LITERATURE REVIEW

2.1 Kapok Seeds/ oil

Malaysian Kapok (Ceiba Pentadra) is commonly found in northern parts of peninsular Malaysia. The fruits of this tree are in the form of capsules containing -a floss in which a number of dark brown seeds are embedded. The floss has been used for centuries to stuff pillows and cushions. The seeds are normally discarded. In rural areas, however, the seeds are roasted and consumed after removing the husk. Sometimes they are germinated prior to use. The oil content of Kapok seeds, from different parts of Malaysia is in the range of 20 to 25 per cent. The characteristics of the oil were found to be close enough to that of cotton-seed oil; and consequently can be commercially utilized as edible oil. The seeds of other kapok species have also been examined for their oil content and fatty acid composition. The oil is reported to be rich in unsaturated fatty acids and contains a variable proportion of cyclopropenoid fatty acids, mainly malvalic and sterculic. The cyclopropenoid fatty acids (CPFA) have been shown to produce numerous physio-logical disorders in farm and laboratory animals. [3]

Figure 1: Kapok Seed Oil

2.2 Biodiesel

Over the past decade, interest in biodiesel use has grown due to the increasing price of petroleum and the effect of carbon emissions on climate change. Biodiesel is a non-toxic and biodegradable alternative fuel, which can be used in conjunction with or as a substitute for petroleum diesel fuel. The first account for the production of biodiesel was in 1937 by the Belgian professor G.Chavanne of the University of Brussels, who applied for a Patent (Belgian Patent 422,877) for the "Procedure for the transformation of vegetable oils for their uses as fuels". The chemical structure of biodiesel is that of a fatty acid alkyl ester, which is clean burning. Biodiesel contains no polycyclic aromatic hydrocarbons, and emits very little sulphur dioxide, carbon monoxide, carbon dioxide, and particulates, which greatly reduces health risks when compared to petroleum diesel.

The use of vegetable oils directly in diesel engine had been commemorated early since 1900, when Rudolf diesel tested peanut oil in a diesel engine and. Though the cost of vegetable oil is higher compared to diesel, it was used at times when there arose an imminent threat of petroleum based fuel deprivation. In the years gone by, the usage of vegetable oils directly in diesel engine is hindered by their own setbacks such as high viscosity, poor volatility and poor cold flow properties Biodiesel, mono alkyl ester of long chain fatty acid, derived from vegetable oil or animal fat and, can be used in diesel engine without any modifications because of its potential benefits. Its prevalence together with its renewability and bio degradability is accompanied by other advantages such as decreased HC (hydrocarbon), CO (carbon monoxide), and particulate matter emissions.

However, in the pursuit of using biodiesel in diesel engine, it suffers a setback of slightly higher NO_2 (nitrogen oxide) emission owing to the presence of surplus oxygen. In the process of selecting suitable oil for biodiesel production, there are several considerations such as availability, cost, stability and manufacturing method. In recent times, the demand for edible vegetable oil has increased and there are concerns such as high cost and negative impact on food chain. Therefore, non-edible oils such as Jatropha (*Jatropha carcus*), Karanja (*Pongamia pinnata*), Nagchampa (*Callophyllum inophyllum*), rubber seed (*Hevca brasiliensis*), Neem (*Azadirachta indica*), Mahua (*Madhucha indica*), Jojoba (*Simmondsia chinensis*), and microalgae are being used as prominent source for biodiesel production as they are readily and abundantly available. Moreover, non-edible plants can be grown in waste lands, which further benefits as green cover to waste land. In the current generation, researchers have forfeited using edible vegetable oil as source for biodiesel production and rather they have set their sight on non-edible oils for the reasons explained above. In the wake of all contemporary issues pertaining to the choice of suitable feedstock for biodiesel production, various studies on the characterization of biodiesel form non-edible oils as substitute for diesel have been investigated by many researchers. In this regard, the non-edible kapok oil (*Ceiba pentandra*) could be a potential alternative source for biodiesel production. Kapok tree is grown in India, Malaysia and other parts of Asia, while it also has great economic importance for domestic and industrial use in Nigeria. The pods of the tree contain seeds surrounded by a fluffy, yellowish fibre, that is a mix of lignin and cellulose, and notably, about 120 ‑ 175 seeds could be found inside each pod. The oil extracted from the seed is being considered as an indispensable source for synthesizing biodiesel and researchers are deliberating to harness it. [5]

2.3 Influence of Free Fatty Acid on Biodiesel Production

Feedstock quality in large part dictates what type of catalyst or process is needed to produce fatty acid alkyl esters (FAAE) that satisfies relevant biodiesel fuel standards such as ASTM D6751. If the feedstock contains a significant percentage of free fatty acid (FFA) (<3 wt. %), typical homogenous alkaline base catalyst potassium hydroxide will not be effective as a result of an unwanted side reaction in which the catalyst reacts with FFA to form soap and water. In fact, base – catalysed trans esterification will not occur if the FFA content of the feed stock is 3 wt. % or greater.

In a typical mineral acid pretreatment procedure, FFA is esterified to the corresponding fatty acid methyl esters (FAME) in the presence of heat, excess methanol, and sulphuric acid catalyst. [6]

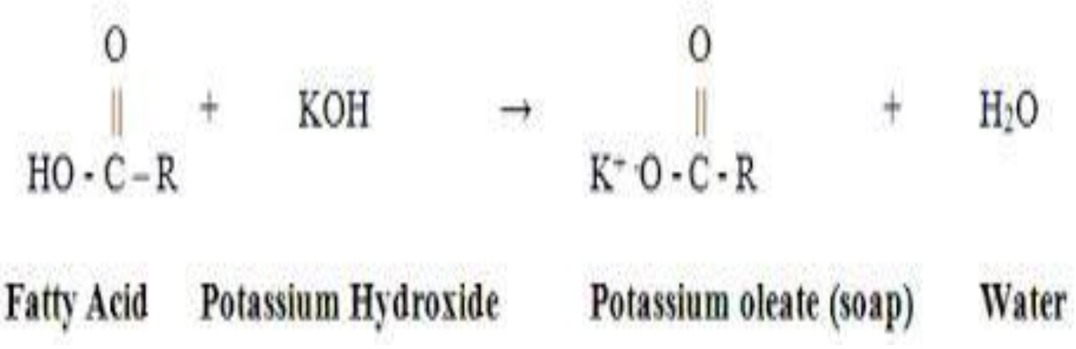


Figure 2: Saponification Process

2.4 Ultrasonication Technology

Ultrasonic is a very desirable tool for producing biodiesel from vegetable oil and animal fats, because it lowers the cost of processing, speeds up transesterification, does not require elevated temperatures, and produces a higher grade of biodiesel. The longitudinal vibrations of the ultrasonic probe are transmitted into the liquid as ultrasonic waves consisting of alternate expansions and compressions. The pressure fluctuations give birth to microscopic bubbles (cavities) which expand during the negative pressure excursions, and implode violently during the positive excursions. As the bubbles collapse, millions of shock waves eddy, and extremes in pressure and temperature are generated at the implosion sites. Although this phenomenon, known as cavitation, lasts but a few microseconds, and the amount of energy released by each bubble is minimal, the cumulative amount of energy generated is extremely high. [7]

- With ultrasonic, the amount of catalyst required for the transesterification of oil to biodiesel is substantially reduced.

- Ultrasonic processing is fast, usually minutes, compared to one hour or more using conventional batch reactor systems.

- Biodiesel yield is typically around 95%.

- Ultrasonic processors generate non-inertial cavitation and have only one moving part.

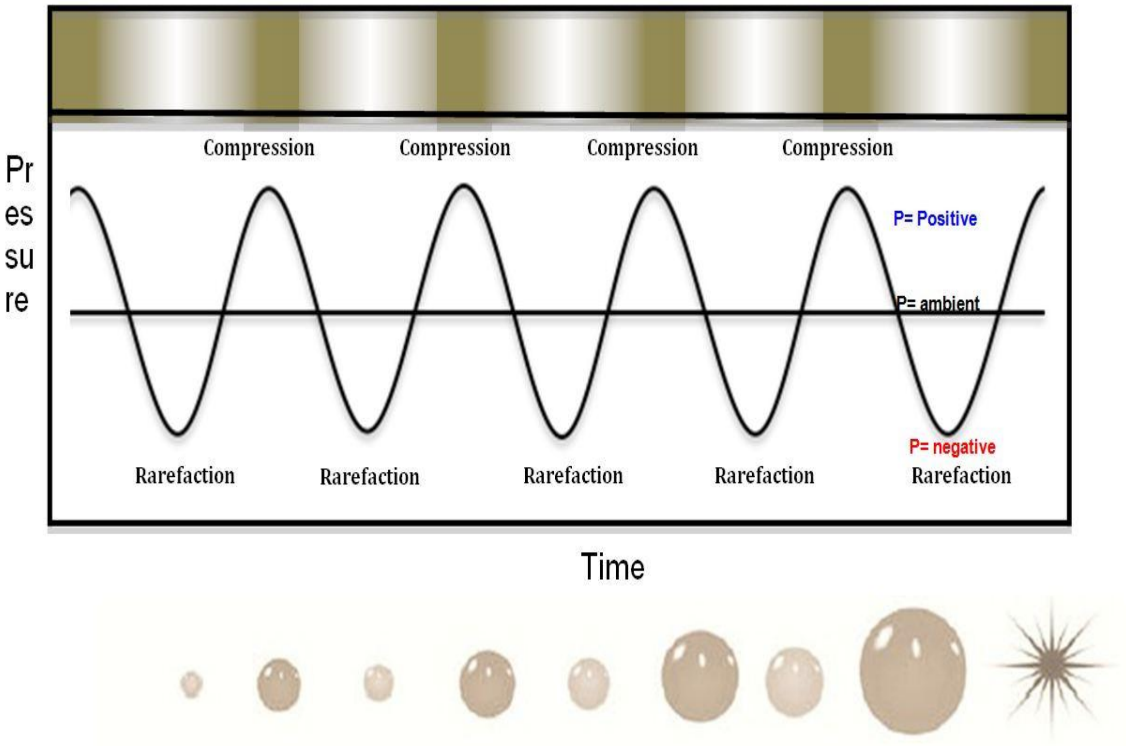
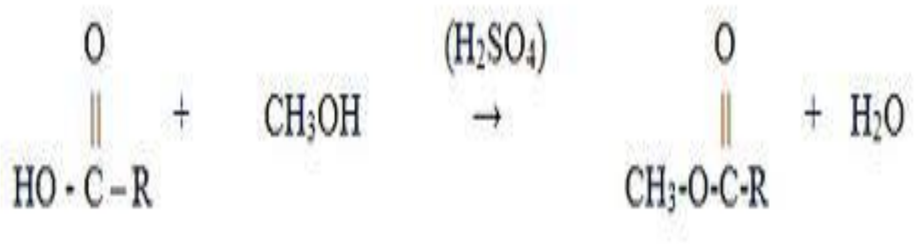


Figure 3: Ultrasonication Mechanism

2.5 Esterification

Esterification, as it applies to biodiesel production, is the chemical reaction by which a fatty acid, typically a free fatty acid in degraded or second-use oil, reacts with an alcohol to produce an alkyl ester and water. The process differs from the transesterification reaction in that the reaction is occurring directly between the alcohol and the fatty acid molecule. The intermediate steps of cleaving the fatty acid chains from the glycerin backbone are not present. For this reason, no glycerin is produced during the esterification reaction. [8]



$$\mathrm{HO{-}\overset{\overset{O}{\|}}{C}{-}R} + \mathrm{CH_3OH} \xrightarrow{(\mathrm{H_2SO_4})} \mathrm{CH_3{-}O{-}\overset{\overset{O}{\|}}{C}{-}R} + \mathrm{H_2O}$$

Figure 4: Esterification Process

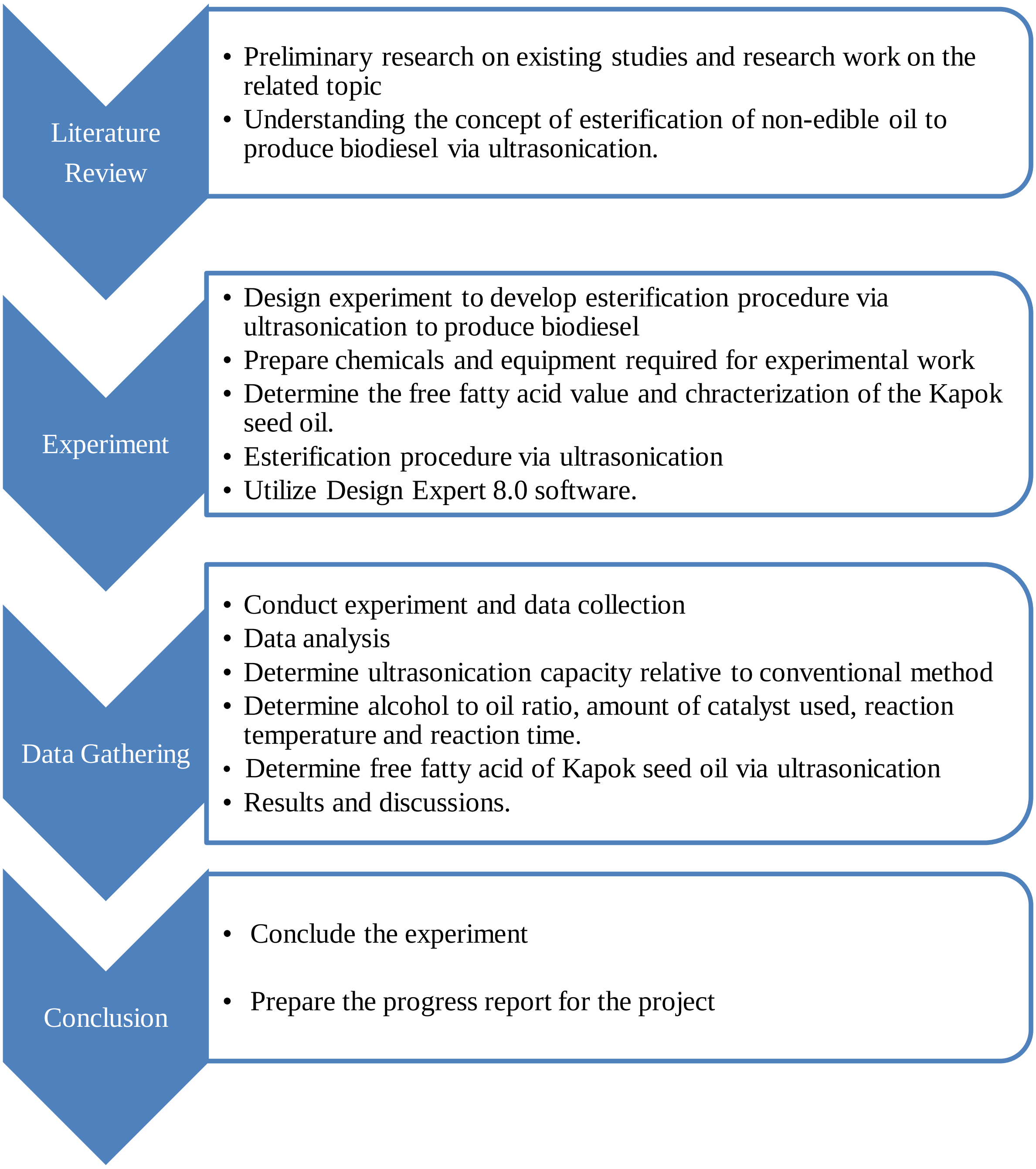
2.6 Response Surface Methodology

Response surface methodology (RSM) is a collection of mathematical and statistical techniques for empirical model building. By careful design of experiments, the objective is to optimize a response (output variable) which is influenced by several independent variables (input variables). An experiment is a series of tests, called runs, in which changes are made in the input variables in order to identify the reasons for changes in the output response. Originally, RSM was developed to model experimental responses (Box and Draper, 1987), and then migrated into the modelling of numerical experiments. The difference is in the type of error generated by the response. In physical experiments, inaccuracy can be due, for example, to measurement errors while, in computer experiments, numerical noise is a result of incomplete convergence of iterative processes, round-off errors or the discrete representation of continuous physical phenomena (Giunta et al., 1996; van Campen et al., 1990, Toropov et al., 1996). In RSM, the errors are assumed to be random. The application of RSM to design optimization is aimed at reducing the cost of expensive analysis methods (e.g. finite element method or CFD analysis) and their associated numerical noise. The problem can be approximated with smooth functions that improve the convergence of the optimization process because they reduce the effects of noise and they allow for the use of derivative-based algorithms.

CHAPTER 3

METHODOLOGY

3.1 Key Milestone



Literature Review

- Preliminary research on existing studies and research work on the related topic
- Understanding the concept of esterification of non-edible oil to produce biodiesel via ultrasonication.

Experiment

- Design experiment to develop esterification procedure via ultrasonication to produce biodiesel
- Prepare chemicals and equipment required for experimental work
- Determine the free fatty acid value and chracterization of the Kapok seed oil.
- Esterification procedure via ultrasonication
- Utilize Design Expert 8.0 software.

Data Gathering

- Conduct experiment and data collection
- Data analysis
- Determine ultrasonication capacity relative to conventional method
- Determine alcohol to oil ratio, amount of catalyst used, reaction temperature and reaction time.
- Determine free fatty acid of Kapok seed oil via ultrasonication
- Results and discussions.

Conclusion

- Conclude the experiment
- Prepare the progress report for the project

3.2 Esterification Process and Acid Value Calculation

Experiments were run on a laboratory scale using standard laboratory glassware and equipment. The basics steps for the experiments are listed below: [9]

1. Oil and methanol are measured up in weight and volume respectively and order specified by the experimental design and placed into the beaker.

2. The reaction vessel is weighed and the weight recorded. This step is to monitor methanol loss during the reaction. Laboratory film is used to seal the beaker to prevent methanol lose.

3. Sulphuric acid is added in to beaker based on the catalyst weight percentage.

4. The sample in the beaker then undergone ultrasonication process.

5. The probe temperature is set at 60^0C for all **21** runs. The temperature of the reaction remain constant for all the run.

6. Once the sample has undergone ultrasonic treatment, the sample is collected and it will stored for approximately two days so that the sample can settle down.

7. The coarse looking layer of the sample will be the esterified product meanwhile the clear liquid will be the residue such as catalyst.

8. To determine the FFA value, the coarse looking liquid will be tested.

Titration for Acid Value

Adaptation of AOCS Method Cd 3d-63 (To read low valued 1-4 of acid value)

Reagents:

Titrant	KOH (85% assay)	0.66 g/500 ml isopropanol = 0.02M
Solvent	Isopropanol: Toluene	(1:1)
Indicator	Phenolphthalein	1 g/ 100 ml isopropanol = 1 %

Equipment: Burette, 50 ml beaker, stir plate and magnetic bar.

Procedure:

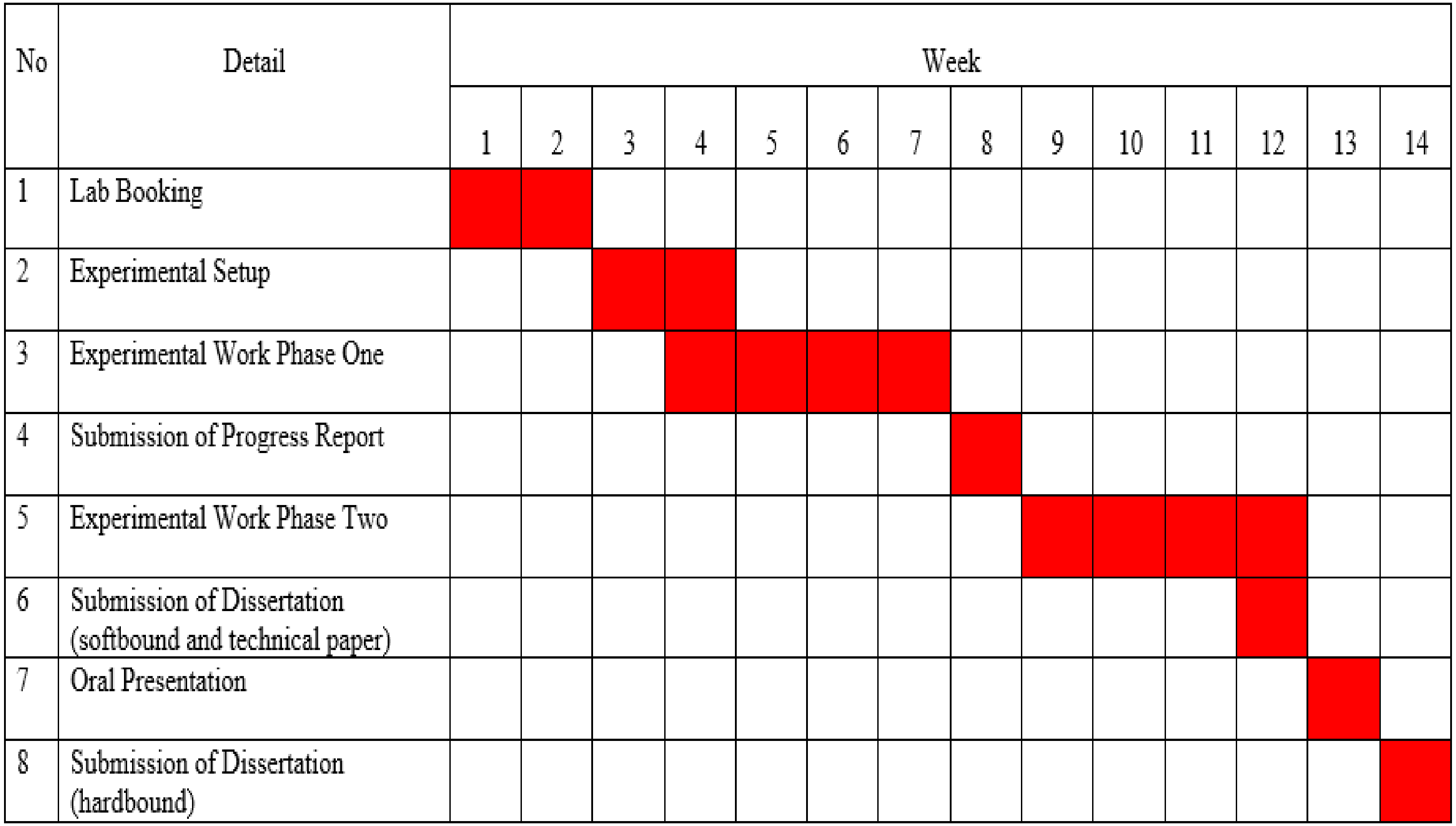
1. Fill burette with KOH titrant
2. Aliquot 25 ml solvent into beaker with stir bar
3. Add 0.4 ml indicator
4. Note volume on burette
5. Add titrant drop-wise with stirring until faint pink colour remains. (5-20 drops, ~ 0.1 ml)
6. Note volume on burette. Record volume used for blank.
7. Add 2 gram of sample. (Note the exact weight) (Should turn clear)
8. Mix until fully dissolved
9. Add titrant drop-wise until faint pink colour remains. (~2-8 ml)
10. Note volume on burette. Record volume used for sample.

Calculations:

Determine acid value by: $[(A-B) \times N \times 56.11]/ W$

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

3.3 Gantt Chart



No	Detail	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Lab Booking	🟥	🟥												
2	Experimental Setup			🟥	🟥										
3	Experimental Work Phase One				🟥	🟥	🟥	🟥							
4	Submission of Progress Report								🟥						
5	Experimental Work Phase Two									🟥	🟥	🟥	🟥		
6	Submission of Dissertation (softbound and technical paper)												🟥		
7	Oral Presentation													🟥	
8	Submission of Dissertation (hardbound)														🟥

CHAPTER 4

Results and Discussion

As shown in the Table 1 below, we can see that various journals have different parameters such as catalyst required, alcohol to oil ratio, reaction frequency and reaction time set for the esterification process

The applications of ultrasound in chemical processing enhance both the mass transfer and chemical reactions, this science called as sonochemistry. It offers the potential for shorter reaction cycles, cheaper reagent and less extreme physical conditions, leading to less expensive and perhaps chemical producing smaller plant. Therefore, this reduces the activation energy for the esterification reaction thus less catalyst is required.

Ultrasonication increases the rate of the esterification reaction of the Kapok seed oil into biodiesel as well as significantly reduces the amount of excess alcohol required for processing. This allows a change from the production from batch processing into continuous flow processing. Biodiesel is normally produced in batch reactors that use heat and mechanical mixing as its energy input.

Ultrasonication does not require elevated temperatures. The longitudinal vibrations of the ultrasonic probe are transmitted into the liquid as ultrasonic waves consisting of alternate expansions and compressions. The pressure fluctuations give birth to microscopic bubbles (cavities) which expand during the negative pressure excursions, and implode violently during the positive excursions. As the bubbles collapse, millions of shock waves eddy, and extremes in pressure and temperature are generated at the implosion sites. Although this phenomenon, known as cavitation, lasts but a few microseconds, and the amount of energy released by each bubble is minimal, the cumulative amount of energy generated is high. [7]

Reaction Temperature	45^0C	30^0C	70^0C	30^0C
Catalyst Used	NaOH/KOH	H_2SO_4	H_2SO_4	H_2SO_4
Frequency	21.5 kHz	40 kHz	21 kHz	40 kHz
Reaction Time	35 minutes	90 minutes	20 minutes	30 minutes
Author	Alternative method for Fatty Acid Alkyl- Ester Production: Paula Mazo, Gloria Restrepo, Luis Ruiz, Universidad de Antioquia. Grupo Procesos Fisicoquimicos Aplicados Colombia.	Ultrasonic FFA esterification in Nila Tilapia Oil. Santos et Al.	Acid catalysed biodiesel synthesis from Jatropha Oil: Mechanistic aspects of Ultrasonic infestation. Hanif Ahmed Choudhury, Ritesh S.Malani, Vijayanand S.Malalkar	Optimization of continuous acid catalysed esterification for FFA reduction in mixed crude palm oil using static mixer coupled with high intensity ultrasonication Krite Somnuk, Pruttikarn Smithmaitne, GompunPratrepchaikul

Table 1: Four study papers stating the parameters values for the process.

Using Design Expert 8.0, the parameters of the experiment is set.

RUN	Alcohol to oil ratio	Catalyst Amount (wt. %)	Reaction time (min)	Frequency (Hz)	Acid Value (ml KOH/g oil)	FFA (%)
1	15.00	7.50	14.89	30.00	1.39	0.695
2	10.00	10.00	20.00	40.00	2.07	1.035
3	15.00	7.50	27.50	46.82	0.98	0.49
4	15.00	7.50	27.50	30.00	1.29	0.645
5	20.00	5.00	35.00	40.00	1.17	0.585
6	20.00	10.00	20.00	20.00	1.40	0.7
7	15.00	7.50	27.50	13.18	1.74	0.87
8	23.41	7.50	27.50	30.00	1.45	0.725
9	15.00	3.30	27.50	30.00	1.40	0.7
10	15.00	7.50	27.50	30.00	1.29	0.645
11	10.00	5.00	20.00	20.00	1.45	0.725
12	.15.00	.750	27.50	30.00	1.34	0.67
13	15.00	7.50	40.11	30.00	1.34	0.67
14	15.00	7.50	27.50	30.00	1.40	0.7
15	10.00	10.00	35.00	40.00	3.52	1.76
16	10.00	5.00	35.00	20.00	1.04	0.52
17	20.00	10.00	35.00	20.00	1.34	0.67
18	15.00	7.50	27.50	30.00	1.34	0.67
19	15.00	11.70	27.50	30.00	1.23	0.615
20	6.59	7.50	27.50	30.00	1.17	0.585
21	20.00	5.00	20.00	40.00	1.34	0.67

Table 2: Process Parameters

4.1 Acid value of Kapok seed oil before undergoing ultrasonication.

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(21.5-0.1) x 0.02 x 56.11] / 2 = **12 ml KOH/ g oil**

<u>Run 1</u>: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15
0.037 x 15= 0.5576 mole Methanol

Methanol mass:
0.5576 x 32.08= 17.88 gram

Volume Methanol:
17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.3 ml   A= 2.9 ml   W= 2.1 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(2.9-0.3) x 0.02 x 56.11] / 2.1 = **1.39 ml KOH/ g oil**

FFA % = 1.39 ml KOH/g oil / 2 = 0.695%

Figure5: Sample 1

Run 2: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

$Mole_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 10

0.037 x 10= 0.37 mole Methanol

Methanol mass:

0.37 x 32.08= 11.86 gram

Volume Methanol:

11.86 g/0.7918 g/ml = 15 ml Methanol

Catalyst = 10 wt. %

30 g oil x 10/100 = 3 g Catalyst.

Acid value calculation

B= 0.5 ml A= 4.2 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(4.2-0.5) x 0.02 x 56.11] / 2 = **2.07 ml KOH/ g oil**

FFA % = 2.07 ml KOH/g oil / 2 = 1.035%

Figure 6: Sample 2

Run 3: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15
0.037 x 15= 0.5576 mole Methanol

Methanol mass:
0.5576 x 32.08= 17.88 gram

Volume Methanol:
17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.1 ml   A= 2.2 ml   W= 2.4 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(2.2-0.1) x 0.02 x 56.11] / 2.4 = **0.98 ml KOH/ g oil**

FFA % = 0.98 ml KOH/g oil / 2 = 0.49%

Figure 7: Sample 3

Run 4: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15
0.037 x 15= 0.5576 mole Methanol

Methanol mass:
0.5576 x 32.08= 17.88 gram

Volume Methanol:
17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.5 ml   A= 2.8 ml   W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(2.8-0.5) x 0.02 x 56.11] / 2 = **1.29 ml KOH/ g oil**

FFA % = 1.29 ml KOH/g oil / 2 = 0.645%

Figure 8: Sample 4

Run 5: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 20

0.037 x 20= 0.74 mole Methanol

Methanol mass:

0.74 x 32.08= 23.73 gram

Volume Methanol:

23.73 g/0.7918 g/ml = 29.98 ml Methanol

Catalyst = 5 wt. %

30 g oil x 5/100 = 1.5 g Catalyst.

Acid value calculation

B= 1.4 ml   A= 3.5 ml   W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(3.5-1.4) x 0.02 x 56.11] / 2 = **1.17 ml KOH/ g oil**

FFA % = 1.17 ml KOH/g oil / 2 = 0.585%

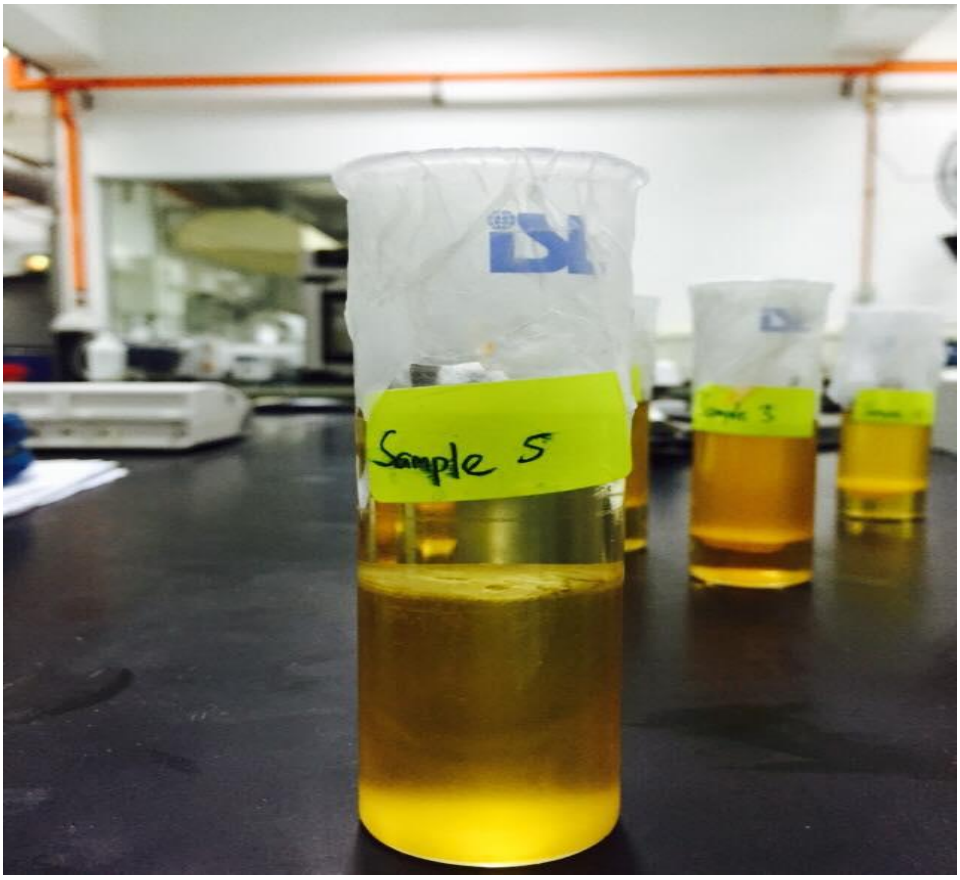


Figure 9: Sample 5

<u>Run 6</u>: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 20
0.037 x 20= 0.74 mole Methanol

Methanol mass:
0.74 x 32.08= 23.73 gram

Volume Methanol:
23.73 g/0.7918 g/ml = 29.98 ml Methanol

Catalyst = 10 wt. %

30 g oil x 10/100 = 3 g Catalyst.

Acid value calculation

B= 1.2 ml   A= 3.7 ml   W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(3.7-1.2) x 0.02 x 56.11] / 2 = **1.40 ml KOH/ g oil**

FFA % = 1.40 ml KOH/g oil / 2 = 0.7%

Figure 10: Sample 6

Run 7: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15
0.037 x 15= 0.5576 mole Methanol

Methanol mass:
0.5576 x 32.08= 17.88 gram

Volume Methanol:
17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.5 ml   A= 3.6 ml   W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(3.6-0.5) x 0.02 x 56.11] / 2 = **1.74 ml KOH/ g oil**

FFA % = 1.74 ml KOH/g oil / 2 = 0.87%

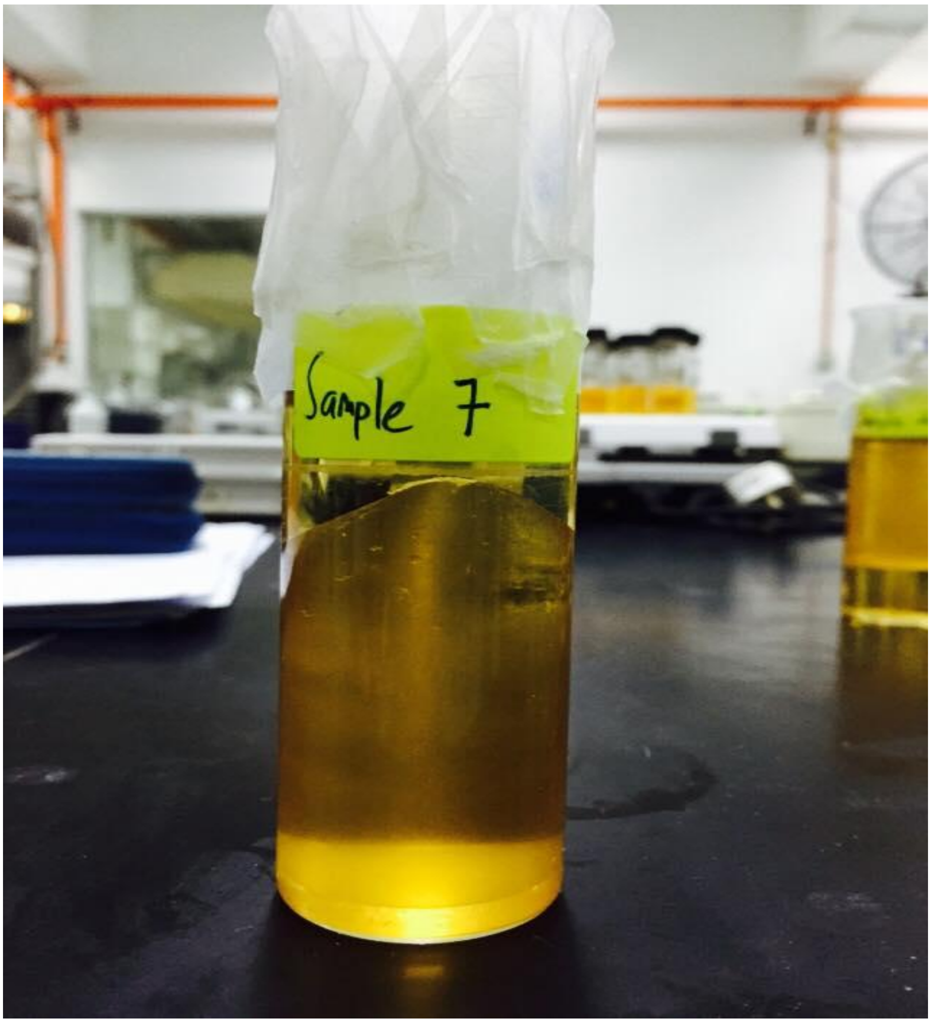


Figure 11: Sample 7

Run 8: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 23.41
0.037 x 23.41= 0.87 mole Methanol

Methanol mass:
0.87 x 32.08= 27.78 gram

Volume Methanol:
27.78 g/0.7918 g/ml = 35.1 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.6 ml A= 3.2 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(3.2-0.6) x 0.02 x 56.11] / 2 = **1.45 ml KOH/ g oil**

FFA % = 1.45 ml KOH/g oil / 2 = 0.77%

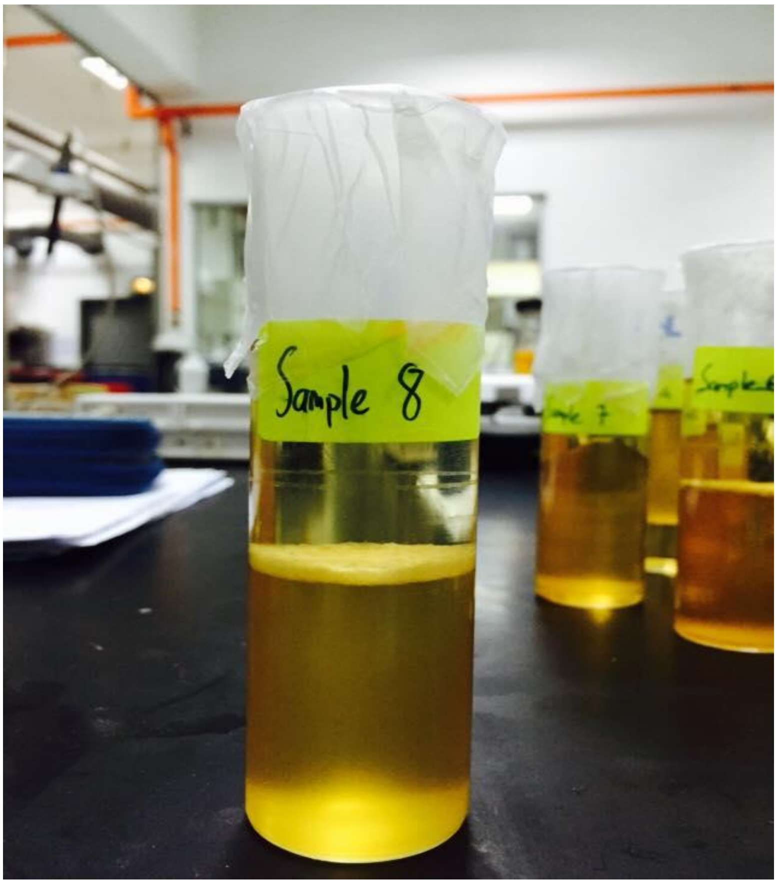


Figure 12: Sample 8

Run 9: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15

0.037 x 15= 0.5576 mole Methanol

Methanol mass:

0.5576 x 32.08= 17.88 gram

Volume Methanol:

17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 3.3 wt. %

30 g oil x 3.3/100 = 0.99 g Catalyst.

Acid value calculation

B= 0.6 ml   A= 3.1 ml   W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(3.1-0.6) x 0.02 x 56.11] / 2 = **1.40 ml KOH/ g oil**

FFA % = 1.40 ml KOH/g oil / 2 = 0.7%

Figure 13: Sample 9

Run 10: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15
0.037 x 15= 0.5576 mole Methanol

Methanol mass:
0.5576 x 32.08= 17.88 gram

Volume Methanol:
17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.3 ml   A= 2.6 ml   W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(2.6-0.3) x 0.02 x 56.11] / 2 = **1.29 ml KOH/ g oil**

FFA % = 1.29 ml KOH/g oil / 2 = 0.645%

Figure 14: Sample 10

Run 11: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 10
0.037 x 10= 0.37 mole Methanol

Methanol mass:
0.37 x 32.08= 11.86 gram

Volume Methanol:
11.86 g/0.7918 g/ml = 15 ml Methanol

Catalyst = 5 wt. %

30 g oil x 5/100 = 1.5 g Catalyst.

Acid value calculation

B= 0.6 ml A= 3.2 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(3.2-0.6) x 0.02 x 56.11] / 2 = **1.45 ml KOH/ g oil**

FFA % = 1.45 ml KOH/g oil / 2 = 0.725%

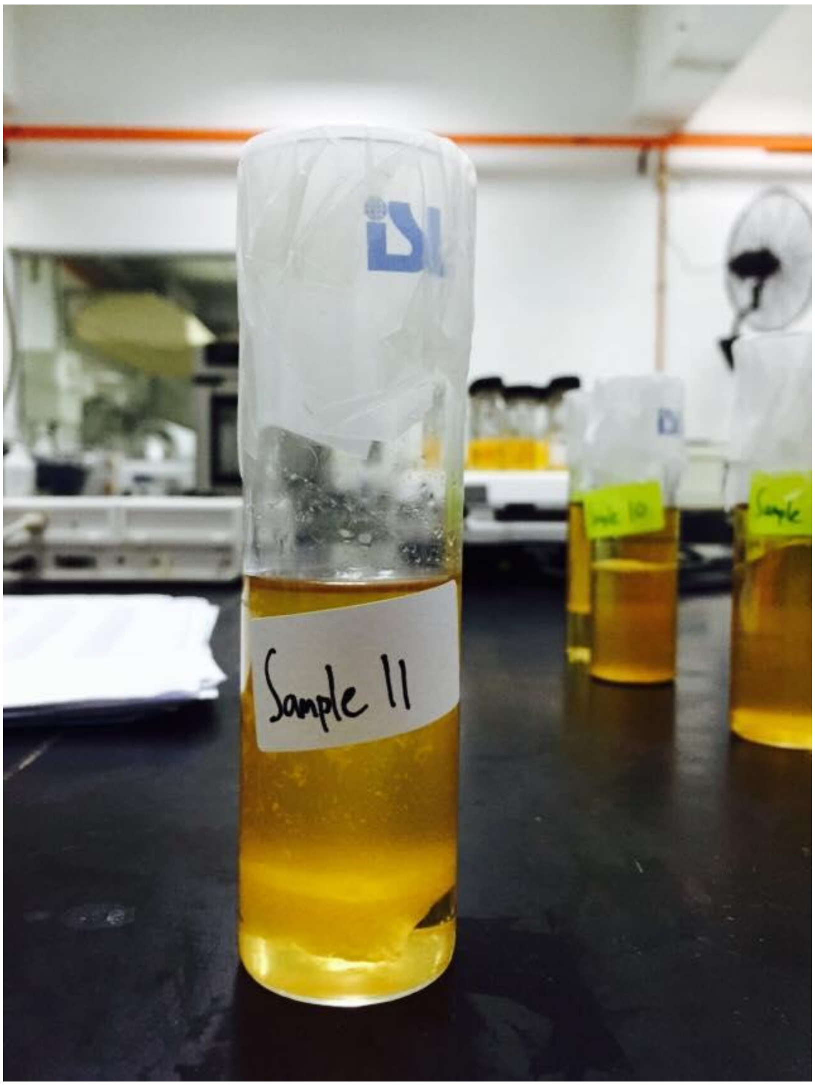


Figure 15: Sample 11

<u>Run 12</u>: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15
0.037 x 15= 0.5576 mole Methanol

Methanol mass:
0.5576 x 32.08= 17.88 gram

Volume Methanol:
17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.4 ml A= 2.8 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(2.8-0.4) x 0.02 x 56.11] / 2 = **1.34 ml KOH/ g oil**

FFA % = 1.34 ml KOH/g oil / 2 = 0.67%

Figure 16: Sample 12

Run 13: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15
0.037 x 15= 0.5576 mole Methanol

Methanol mass:
0.5576 x 32.08= 17.88 gram

Volume Methanol:
17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.8 ml A= 3.2 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(3.2-0.8) x 0.02 x 56.11] / 2 = **1.34 ml KOH/ g oil**

FFA % = 1.34 ml KOH/g oil / 2 = 0.67%

Figure 17: Sample 13

<u>Run 14</u>: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15

0.037 x 15= 0.5576 mole Methanol

Methanol mass:

0.5576 x 32.08= 17.88 gram

Volume Methanol:

17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.4 ml A= 2.9 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(2.9-0.4) x 0.02 x 56.11] / 2 = **1.40 ml KOH/ g oil**

FFA % = 1.40 ml KOH/g oil / 2 = 0.7%

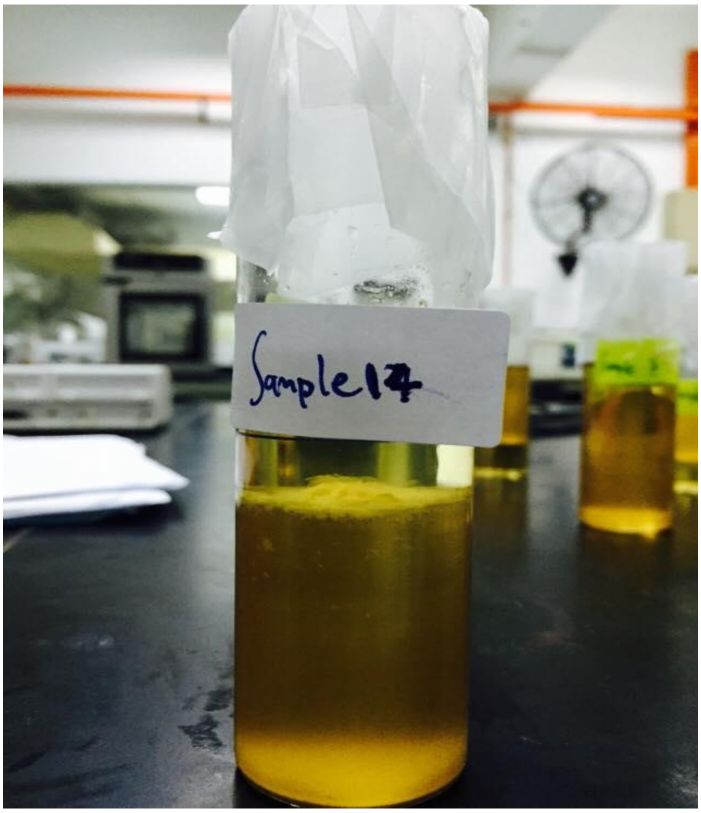


Figure 18: Sample 14

Run 15: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 10
0.037 x 10= 0.37 mole Methanol

Methanol mass:
0.37 x 32.08= 11.86 gram

Volume Methanol:
11.86 g/0.7918 g/ml = 15 ml Methanol

Catalyst = 10 wt. %

30 g oil x 10/100 = 3 g Catalyst.

Acid value calculation

B= 0.3 ml   A= 6.9 ml   W= 2.1 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(6.9-0.3) x 0.02 x 56.11] / 2.1 = **3.52 ml KOH/ g oil**

FFA % = 3.52 ml KOH/g oil / 2 = 1.76%

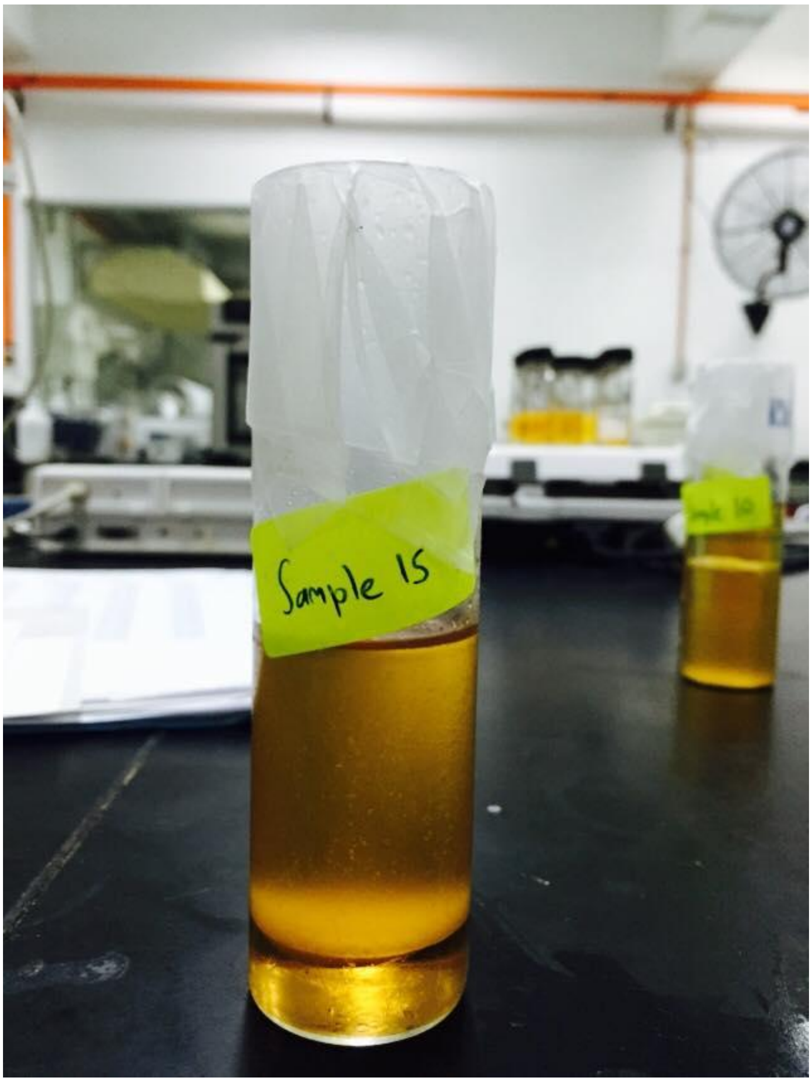


Figure 19: Sample 15

Run 16: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

$Mole_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 10

0.037 x 10= 0.37 mole Methanol

Methanol mass:

0.37 x 32.08= 11.86 gram

Volume Methanol:

11.86 g/0.7918 g/ml = 15 ml Methanol

Catalyst = 5 wt. %

30 g oil x 5/100 = 1.5 g Catalyst.

Acid value calculation

B= 0.3 ml   A= 2.8 ml   W= 2.77 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(2.8-0.3) x 0.02 x 56.11] / 2.77 = **1.04 ml KOH/ g oil**

FFA % = 1.04 ml KOH/g oil / 2 = 0.52%

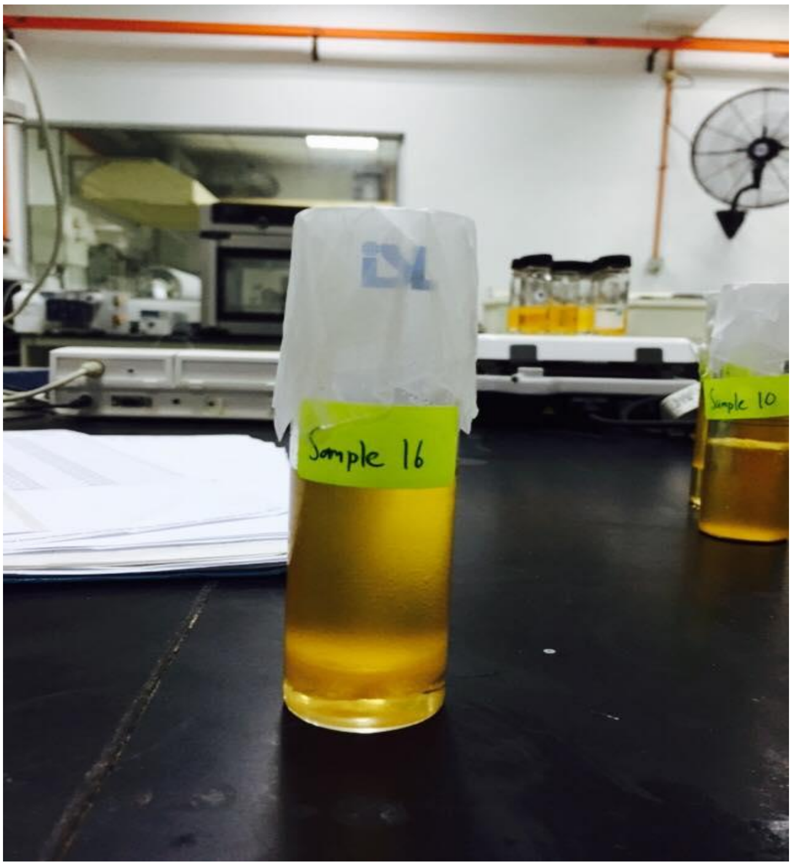


Figure 20: Sample 16

Run 17: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 20
0.037 x 20= 0.74 mole Methanol

Methanol mass:
0.74 x 32.08= 23.73 gram

Volume Methanol:
23.73 g/0.7918 g/ml = 29.98 ml Methanol

Catalyst = 10 wt. %

30 g oil x 10/100 = 3 g Catalyst.

Acid value calculation

B= 1.1 ml A= 3.5 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(3.5-1.1) x 0.02 x 56.11] / 2 = **1.34 ml KOH/ g oil**

FFA % = 1.34 ml KOH/g oil / 2 = 0.67%

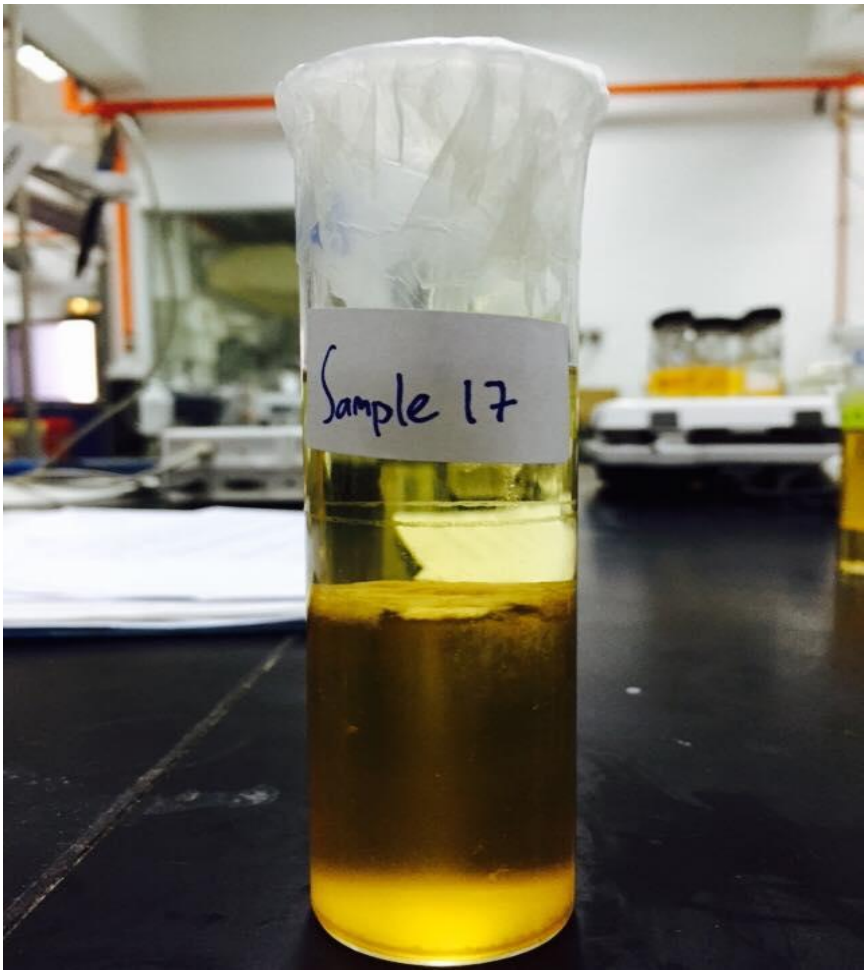


Figure 21: Sample 17

<u>Run 18</u>: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15
0.037 x 15= 0.5576 mole Methanol

Methanol mass:
0.5576 x 32.08= 17.88 gram

Volume Methanol:
17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.4 ml A= 2.8 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(2.8-0.4) x 0.02 x 56.11] / 2 = **1.34 ml KOH/ g oil**

FFA % = 1.34 ml KOH/g oil / 2 = 0.67%

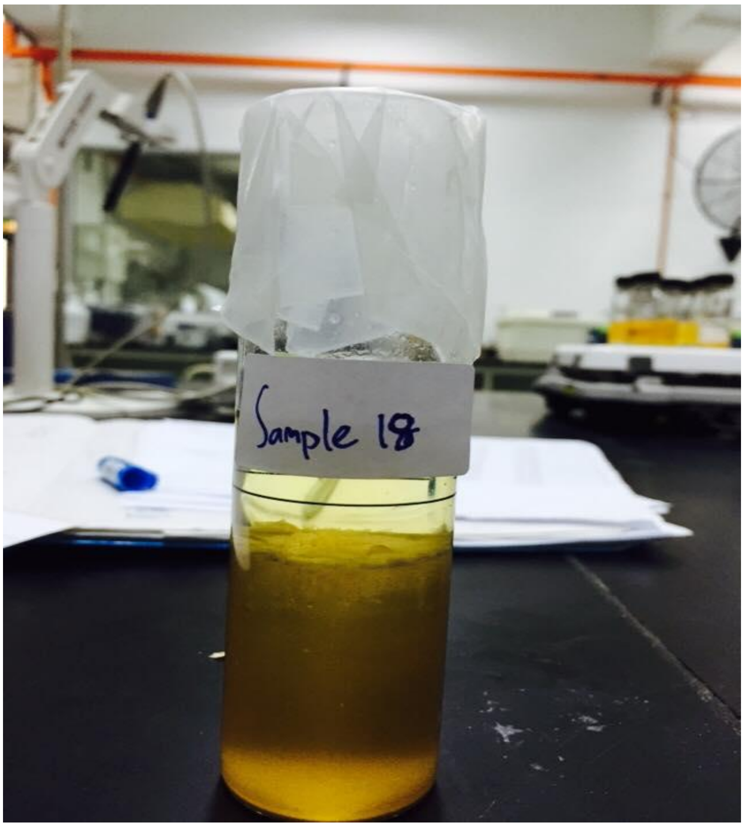


Figure 22: Sample 18

Run 19: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 15

0.037 x 15= 0.5576 mole Methanol

Methanol mass:

0.5576 x 32.08= 17.88 gram

Volume Methanol:

17.88 g/0.7918 g/ml = 22.6 ml Methanol

Catalyst = 11.70 wt. %

30 g oil x 11.70/100 = 3.51 g Catalyst.

Acid value calculation

B= 0.5 ml A= 2.7 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(2.7-0.5) x 0.02 x 56.11] / 2 = **1.23 ml KOH/ g oil**

FFA % = 1.23 ml KOH/g oil / 2 = 0.615%

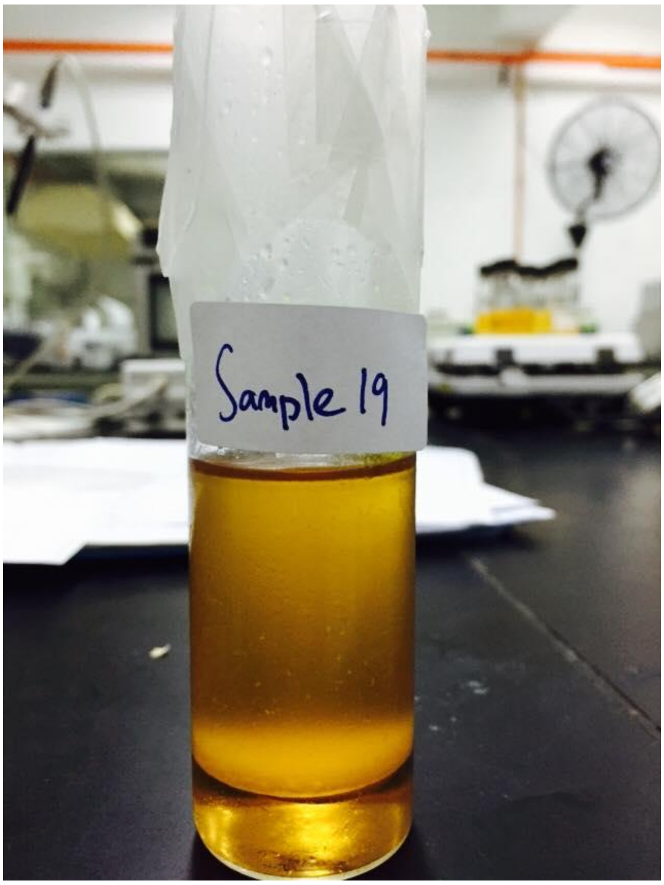


Figure 23: Sample 19

Run 20: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 6.59
0.037 x 6.59= 0.245 mole Methanol

Methanol mass:
0.245 x 32.08= 7.86 gram

Volume Methanol:
7.86 g/0.7918 g/ml = 9.93 ml Methanol

Catalyst = 7.5 wt. %

30 g oil x 7.5/100 = 2.25 g Catalyst.

Acid value calculation

B= 0.4 ml A= 2.5 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(2.5-0.4) x 0.02 x 56.11] / 2 = **1.17 ml KOH/ g oil**

FFA % = 1.17 ml KOH/g oil / 2 = 0.585%

Figure 24: Sample 20

Run 21: 30 gram oil M_{oil} = 807 g/mole $M_{methanol}$ = 32.08 g/mole

Mole $_{oil}$ = 30/807 = 0.037 mole.

Alcohol to Oil ratio: 20
0.037 x 20= 0.74 mole Methanol

Methanol mass:
0.74 x 32.08= 23.73 gram

Volume Methanol:
23.73 g/0.7918 g/ml = 29.98 ml Methanol

Catalyst = 5 wt. %

30 g oil x 5/100 = 1.5 g Catalyst.

Acid value calculation

B= 1.4 ml A= 3.8 ml W= 2 g

[(A-B) x N x 56.11]/ W

A= volume of titrant used for sample
B= volume titrant used for blank
N= Normality of KOH= 0.02 (constant)
W= Weight of sample ~2

[(3.8-1.4) x 0.02 x 56.11] / 2 = **1.34 ml KOH/ g oil**

FFA % = 1.34 ml KOH/g oil / 2 = 0.67%

Figure 25: Sample 21

4.2 Optimization Study of Acid Esterification via Ultrasonication

Response surface methodology (RSM) was utilized to assess the parametric effect of four independent variable which is reaction time, ultrasonic frequency, alcohol to oil ratio and amount of catalyst used. The FFA is considered as an output response at a given set of variables. Design Expert 8.0 software was used to design 21 experiments using central composite. All the experiments were performed according to the designed runs and each run was operated by the following the set process conditions. At each designed run, FFA was calculated as the response variable. Table 2 above shows the detailed experimental designed run along with its output response variable for Kapok Seed Oil (KSO). The FFA content was reduced between the minimum and maximum ranges of 0.49-1.76 wt. % for KSO. The minimum FFA content was obtained at alcohol to oil ratio of 15, catalyst loading of 7.5 wt. %, reaction time of 27.50 minutes and ultrasonic frequency of 46.82 kHz. The maximum FFA content was obtained at alcohol to oil ratio of 10, catalyst loading of 10 wt. %, reaction time of 35 minutes and ultrasonic frequency of 40 kHz.

4.2.1 ANOVA Analysis of Acid Esterification via Ultrasonication

ANOVA (Analysis of Variance) was employed to statistically analyse the output response (FFA %). The ANOVA results for the KSO are given in Table 3 below. The model p-value determined the percentage of error in the model along with individual and combined effects of the input variables. The model p-values obtained were 0.0122 which is less than 0.05, which implies that the model is significant for KSO designed variables with respect to the response. The F-value describes the reliability of the fitted model with the output response. The highest F-value for ultrasonic frequency indicate the highest influence on the output response relative to the catalyst loading, reaction time and alcohol to oil ratio which has low significance on the output response. All of the combined manipulative variables shows significant behaviour based on their p-values (< 0.05). The output response (FFA %) was fitted to the input process variables through regression analysis (R^2). The regression analysis produced response surface equation for the output response model in terms of actual and coded terms. These equation represent a second order polynomial regression model. The regression model equation for the KSO is given below:

$$\begin{aligned} \text{FFA \%} = {} & +0.63 + 0.042A - 0.025B + 0.027C - 0.11D - 0.29AB - 0.079AC \\ & - 0.23AD + 0.12BC + 0.22BD + 0.11CD + 0.033A^2 + 0.034B^2 \\ & + 0.042C^2 + 0.042D^2 \end{aligned} \qquad \text{Eq.(1)}$$

A = Alcohol to oil ratio
B = Catalyst amount (wt. %)
C = Reaction time (minutes)
D = Ultrasonic frequency (kHz)

The fitting of the model was assessed by the regression coefficient (R^2) for the KSO which showed that with a reasonable precision, the models can be used for predicting the output response. The value of the evaluated adjusted R^2 is in a good agreement with R^2 . A sufficient precision determines the signal to noise ratio; and a ratio greater than 4 is desirable. Ratio greater than 4 were obtained for the KSO, indicating sufficient signal.

Source	Sum of Square	Degree of Freedom	Mean Square	F- Value	P-Value Prob>F
Model	1.288575855	14	0.092041133	7.04950038	0.0122
A-Alcohol to Oil Ratio	0.0098	1	0.0098	0.750589457	0.4196
B-Catalyst Amount	0.0036125	1	0.0036125	0.276684124	0.6177
C-Reaction Time	0.009646179	1	0.009646179	0.738808198	0.4231
D-Frequency Factor	0.0722	1	0.0722	5.529852942	0.0569
AB	0.283217142	1	0.283217142	21.69181639	0.0035
AC	0.050403125	1	0.050403125	3.860413699	0.0970
AD	0.180509399	1	0.180509399	13.82535225	0.0099
BC	0.121278125	1	0.121278125	9.288783882	0.0226
BD	0.158199916	1	0.158199916	12.11665195	0.0131
CD	0.095703125	1	0.095703125	7.32997517	0.0352
A^2	0.015995957	1	0.015995957	1.225142534	0.3107
B^2	0.016871933	1	0.016871933	1.292234164	0.2990
C^2	0.026915945	1	0.026915945	2.061512682	0.2011
D^2	0.025806468	1	0.025806468	1.976537013	0.2094

R^2 = 0.9427, Adjusted R^2 = 0.8090, Adequate Precision = 12.840

Table 3: ANOVA analysis of KSO for acid esterification

4.2.2 Predicted versus Actual Plot for KSO Acid Esterification via Ultrasonication

The plotted graph for the predicted values of FFA content versus the actual experimental FFA values were shown below in Figure 26. The graph indicates that all the experimental values are well fitted with the predicted value. The points are also close towards the centre linear line. Only few experimental points are deviated and not close to the centre line. Most of the points lie between the ranges of 0.50 %-0.75% of FFA.

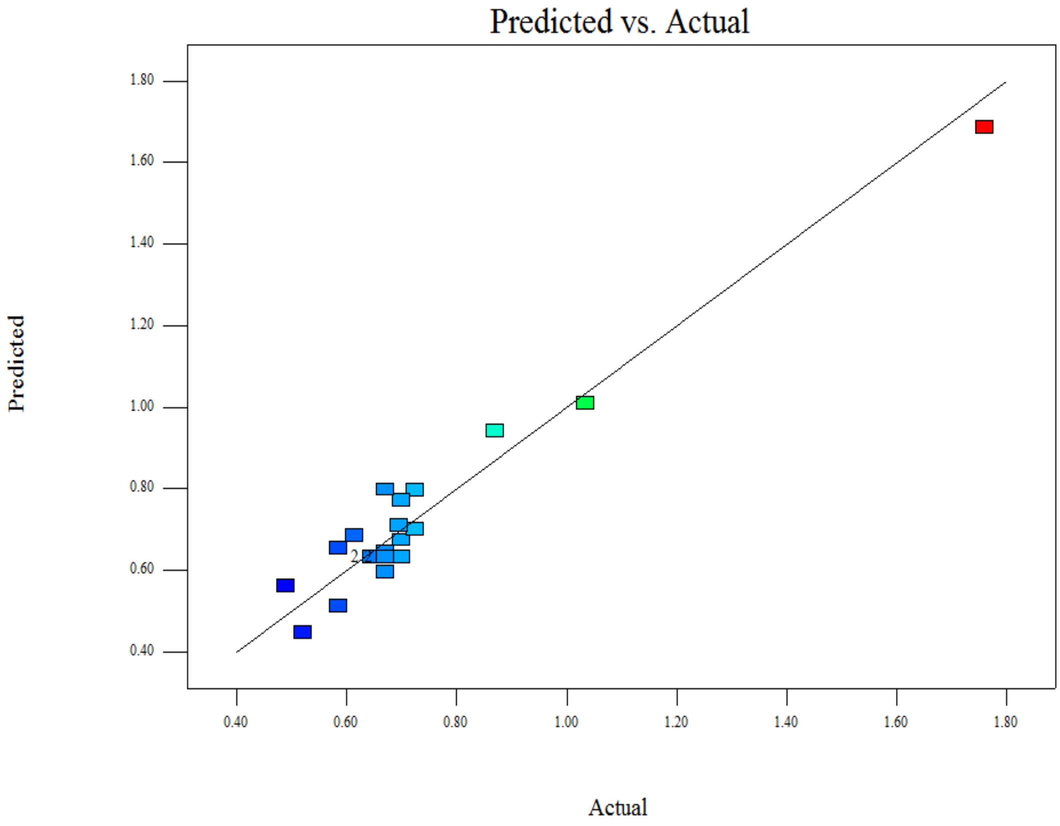


Figure 26: Actual vs. predicted plot for KSO

4.2.3 Perturbation plot for KSO Acid Esterification process via Ultrasonication

The perturbation plot for the acid esterification process via ultrasonication of KSO are shown in Figure 27 below. Perturbation provides the outline variables views on the output response. Based on the figure below, we can deduce that Frequency factor (D) produces the highest effect on the response followed by alcohol to oil ratio (A), reaction time (C) and catalyst amount (B). This is determined by the steepness of the slope shown on the graph below. Frequency factor (D) has the highest slope meanwhile catalyst amount (B) has the lowest slope.

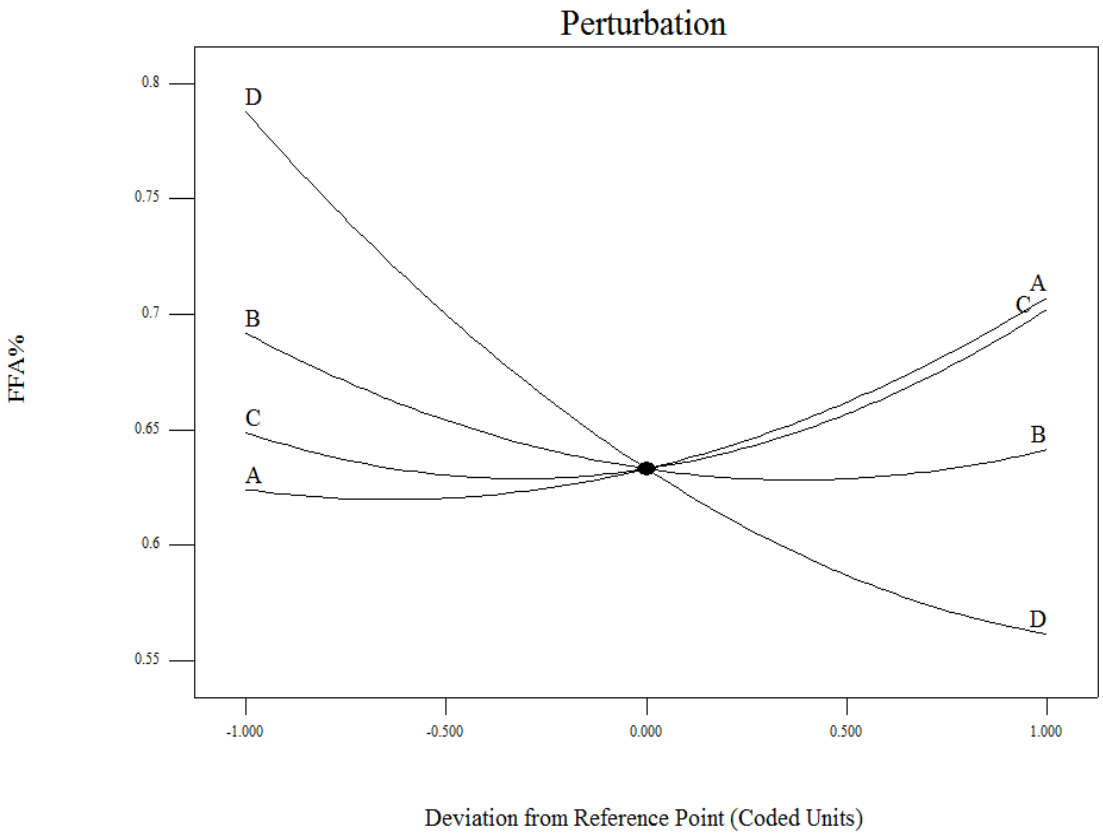


Figure 27: Perturbation plot

4.2.4 Three Dimensional (3-D) Surface Plots.

The 3-D surface plots for KSO acid esterification via ultrasonication process parameters are discussed in this section. The independent and combined effects of four influencing variables on FFA content are discussed.

4.2.4.1 Effect of Alcohol to oil ratio and Catalyst amount on FFA content

The alcohol to oil molar ratio is the second highest process variable that has significance on the FFA content. Figure 28 shows the 3-D effect of alcohol to oil ratio and catalyst loading of FFA content. The figure shows that FFA content decreases by increasing amount alcohol. At a constant catalyst loading, the FFA content reduces by increasing amount of alcohol from 10 to 20. The maximum reduction of FFA content was achieved at a ratio of 20:1. As for catalyst amount, it was identified that FFA content decreases and the amount of catalyst increases. Lowest FFA content was identified at the highest catalyst amount which is 10 wt. %. From this plot, we can deduce that lowest FFA content was obtained at 20:1 alcohol to oil ratio and 10 wt. % of catalyst.

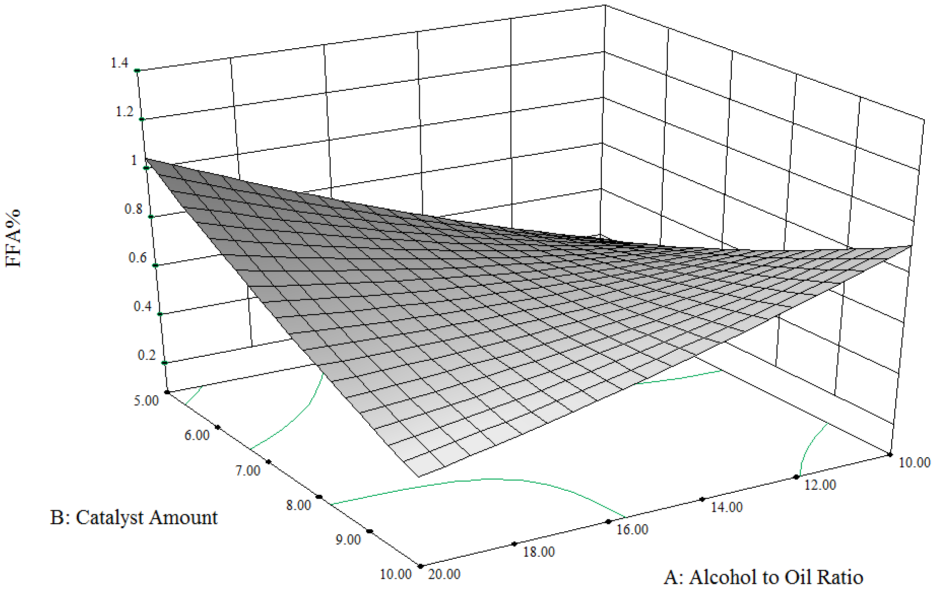


Figure 28: Effect of alcohol to oil ratio and catalyst amount on FFA

4.2.4.2 Effect of Alcohol to oil ratio and Reaction time on FFA content

Figure 29 below shows the combined effect of alcohol to oil ratio and reaction time on FFA content. In this plot, we can see that the FFA content reduces as the alcohol to oil ratio increases. By increasing the reaction time, the FFA content reduces. In this plot, the lowest FFA content can be obtained at the highest reaction time which is 35 minutes and at the highest alcohol to oil ratio which is 20:1.

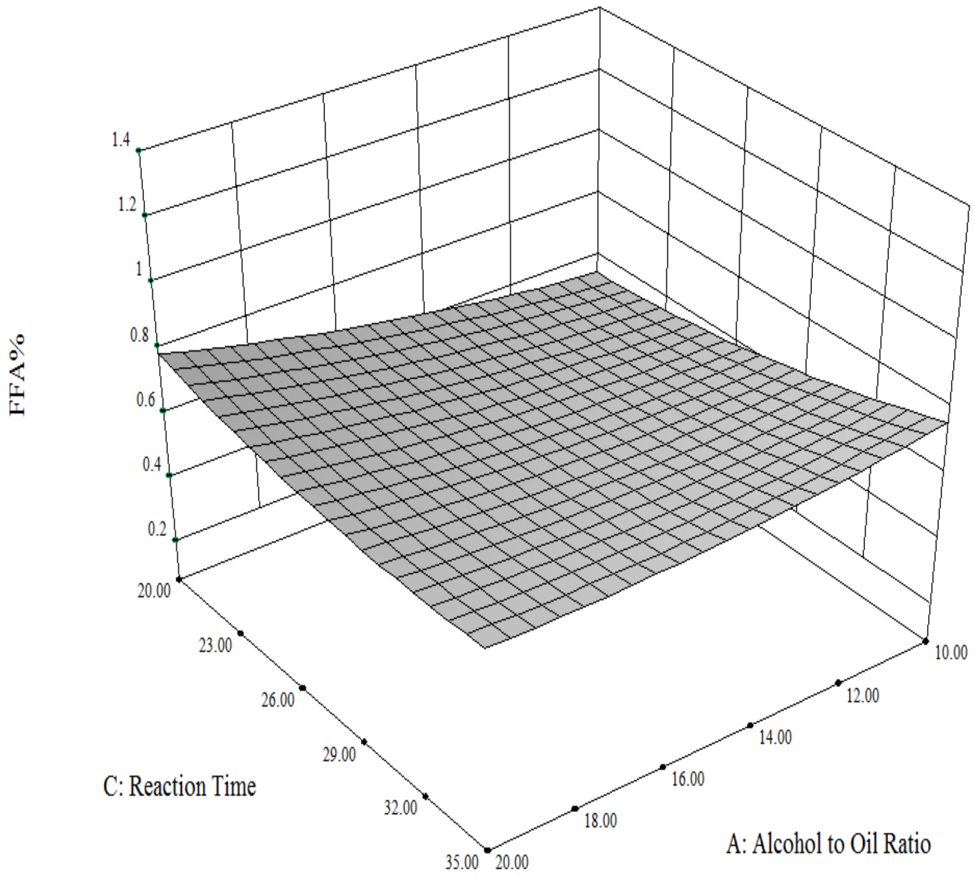


Figure 29: Effect of alcohol to oil ratio and reaction time on FFA

4.2.4.3 Effect of Alcohol to oil ratio and Ultrasonic frequency on FFA content

The ultrasonic frequency is the most significant process variable that contributes to the reduction of FFA content. As we can see from the plot below, the FFA content decreases significantly by increasing the ultrasonic frequency. Higher alcohol to oil ratio does also reduce the FFA content but not as significant as ultrasonic frequency. This is because the longitudinal vibrations of the ultrasonic probe are transmitted into the liquid as ultrasonic waves consisting of alternate expansions and compressions. The pressure fluctuations give birth to microscopic bubbles (cavities) which expand during the negative pressure excursions, and implode violently during the positive excursions. As the bubbles collapse, millions of shock waves eddy, and extremes in pressure and temperature are generated at the implosion sites. Thus higher frequency will increase the mass transfer efficiency between the alcohol and oil.

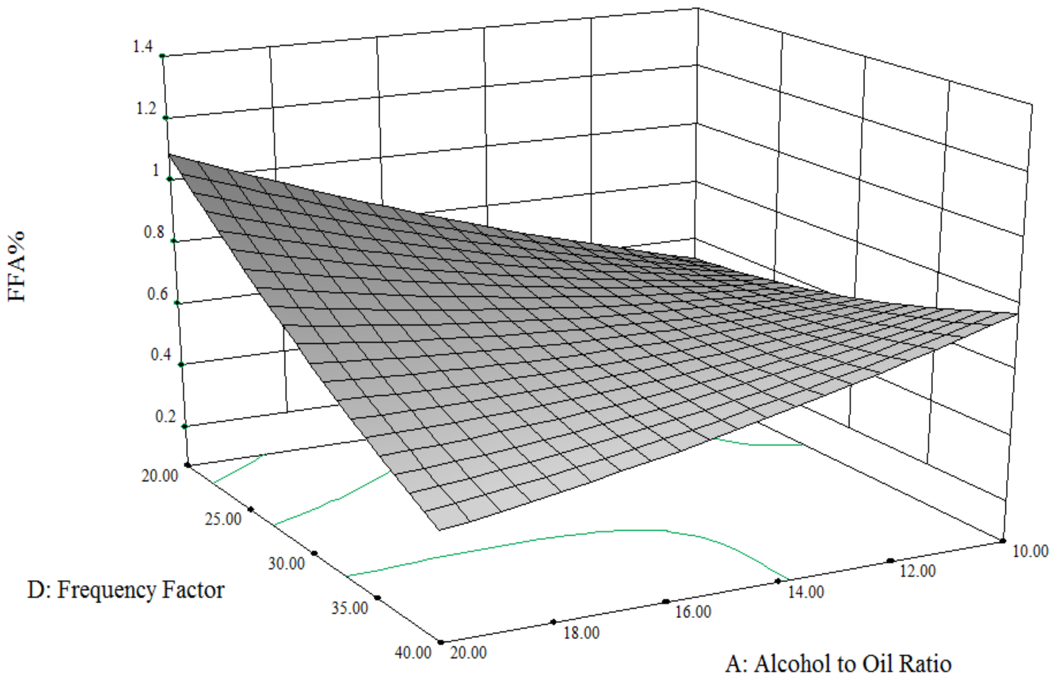


Figure 30: Effect of alcohol to oil ratio and ultrasonic frequency on FFA content

4.2.4.4 Effect of Catalyst amount and Reaction time on FFA content

The plot below shows that the FFA content increases when the amount of catalyst is increasing. The range when the increment of FFA was significant when the amount of catalyst was from 6 wt. % to 10 wt. %. About 0.25% of the FFA was increased when the amount of catalyst was 6 wt. % up to 10 wt. %. From 5 wt. % to 6 wt. % of catalyst, there is still increment in FFA but not so significant. It is better to use lower amount of catalyst based on this plot. The FFA content does decreases as the reaction time increase. 20 minutes to 29 minutes of reaction time reduces the FFA content significantly. After 29 minutes of reaction, the reduction of FFA is not significant as from 20 minutes to 29 minutes of reaction time

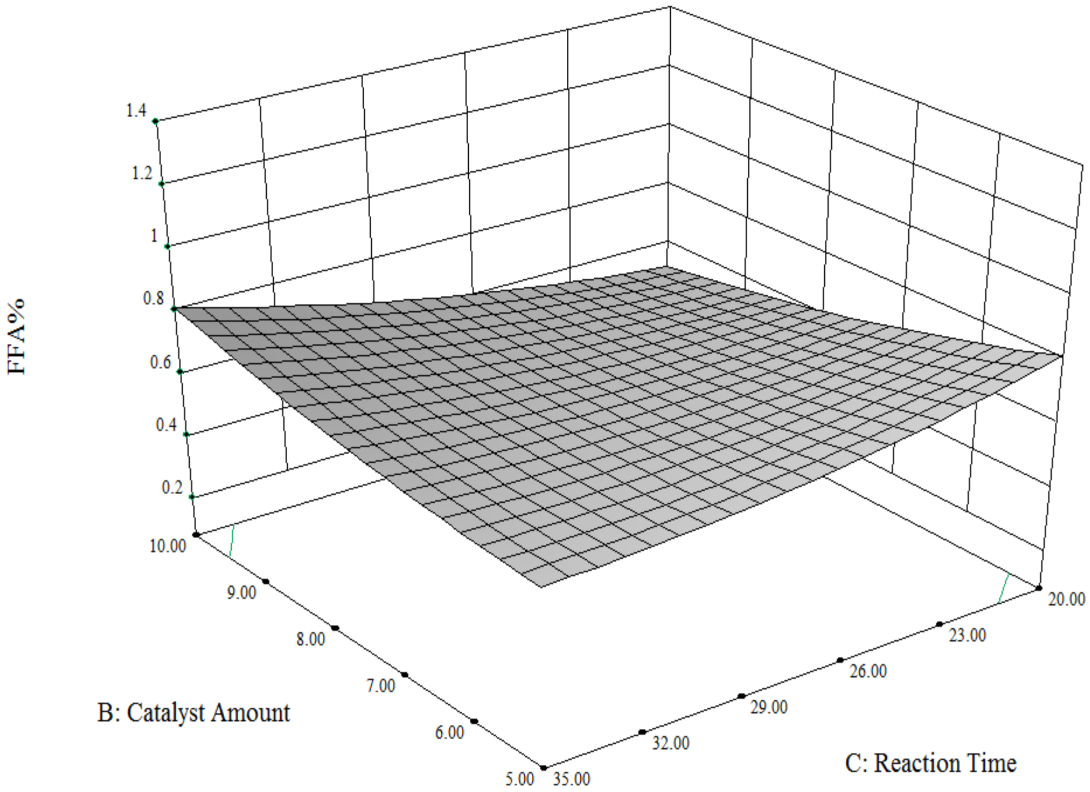


Figure 31: Effect of Catalyst amount and Reaction time on FFA

4.2.4.5 Effect of Catalyst amount and Ultrasonic frequency on FFA content

From Figure 32 below, we can see the effect of catalyst amount and ultrasonic frequency factor on FFA content. The ultrasonic frequency reduces the FFA content significantly. As the frequency increases from 20 kHz to 40 kHz, the FFA content reduces more than 0.4 wt. %. For the catalyst amount, we can see that 5 wt. % to 5.5 wt. % of catalyst reduces the FFA content but not so significant. Catalyst more than 5.5 wt. % increases the FFA content. High frequency and low catalyst amount results in low FFA content.

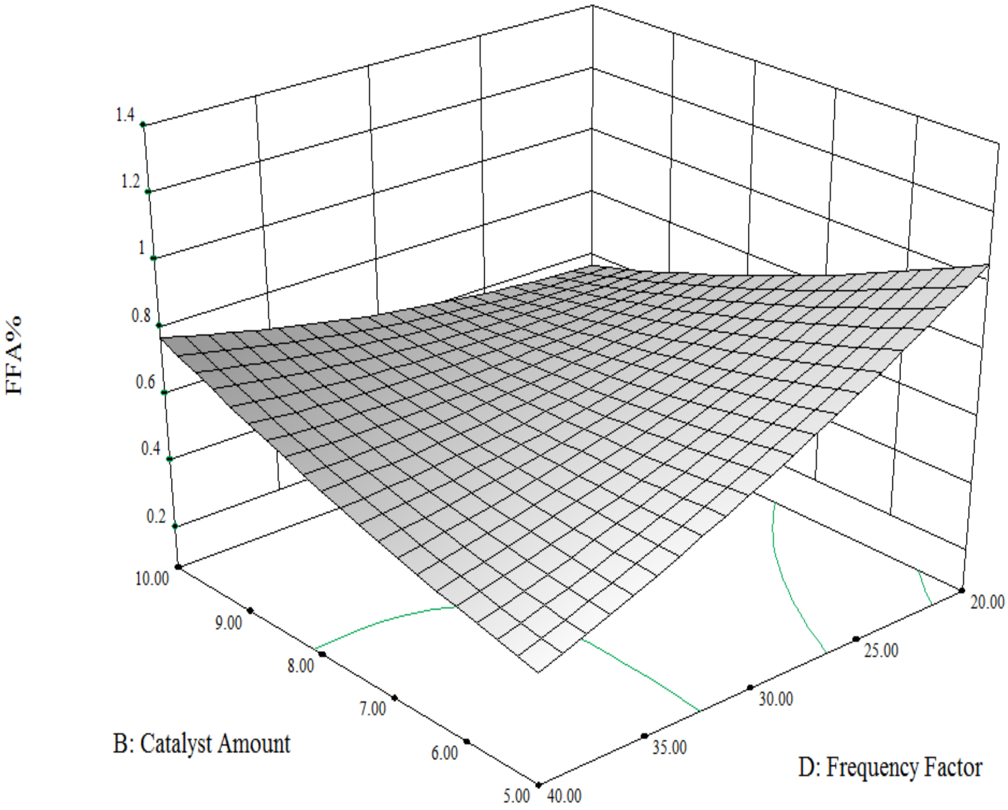


Figure 32: Effect of Catalyst amount and Ultrasonic frequency on FFA content

4.2.4.6 Effect of Reaction time and Ultrasonic frequency on FFA content

Figure 33 below illustrates the effect of reaction time and ultrasonic frequency on FFA content. The ultrasonic frequency has a significant impact on the reduction of FFA content. The FFA content decreases gradually as the ultrasonic frequency is increased from 20 kHz to 40 kHz. Unlike the ultrasonic frequency, as the reaction time increases, the FFA does also increase. From this plot, we can deduce that for this two variable, high frequency and low reaction time results in low FFA content.

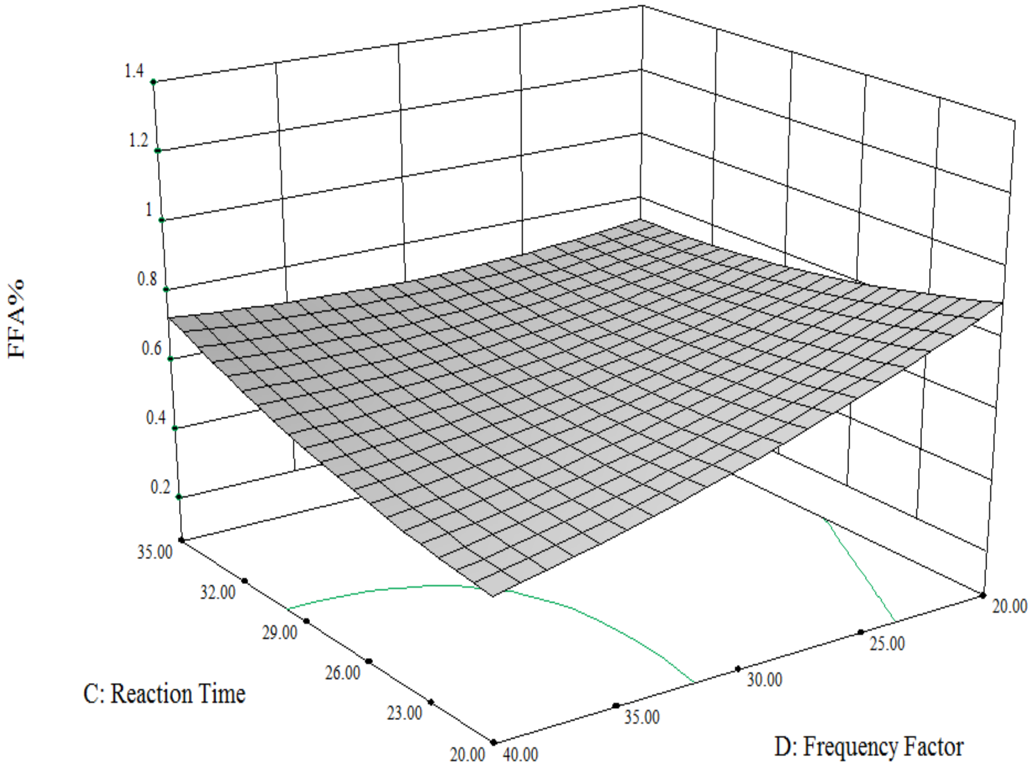


Figure 33: Effect of Reaction time and Ultrasonic frequency on FFA content

4.2.5 Optimization of FFA content for Acid Esterification via Ultrasonication

With the help of Design Expert 8.0 software, the optimized values were obtained using numerical optimization. The optimized value for Kapok Seed Oil (KSO) are shown in Table 4 below. Hanif Ahmed Choudhury, Ritesh S.Malani, Vijayanand S.Malalkar. reported that optimized conditions were alcohol to oil ratio of 20:1, reaction time of 20 minutes, reaction temperature of 70^0C, and ultrasonic frequency of 21 kHz. For this experiment, the optimized ultrasonic frequency is expected to be higher than 21 kHz since the reaction temperature is set constant at 50^0C.

Process Parameters	Units	Optimized
Alcohol to oil ratio	-	19.22
Catalyst amount	Wt. %	6.83
Reaction time	Minutes	22.76
Ultrasonic frequency	kHz	39.61

Table 4: Optimized process parameters for Acid Esterification via Ultrasonication

4.2.6 Reproducibility of Experimental Data at Optimized Condition for Acid Esterification process via Ultrasonication

In Table 5 below, the reproduced experimental data based on the optimized condition is shown. The replicate experiments were performed at optimized condition for FFA content to check the reproducibility and for results verification. The replicate runs were compared with optimized value and predicted value of the model.

Parameters	**Experimental run**			
	First run	**Confirmation runs**		
		1	**2**	**3**
FFA% (KSO)	0.44	0.41	0.45	0.43

Table 5: Confirmation of experimental results at optimized conditions for acid esterification process via ultrasonication

Response	**Experimental**	**Model Predicted**
FFA % (KSO)	0.44±0.01	0.33±0.11

Table 6: Comparison of experimental values with predicted values

4.3 Discussion

The initial Free Fatty Acid (FFA) value of the Kapok seed oil is high which 6%. After the Kapok seed oil undergoes Ultrasonic treatment, the acidity of the seed oil is reduced greatly. The manipulated variables for the **21** runs are Alcohol to oil ratio, Ultrasonic frequency, amount of catalyst and reaction time. The constant variable is the reaction temperature which is set at 50^0C. The optimized condition and parameters is determined using Response Surface Methodology (RSM). We can deduce that Ultrasonic frequency has the highest impact on the response followed by Alcohol to oil ratio, Reaction time and Catalyst amount. This is because the longitudinal vibrations of the ultrasonic probe are transmitted into the liquid as ultrasonic waves consisting of alternate expansions and compressions. The pressure fluctuations give birth to microscopic bubbles (cavities) which expand during the negative pressure excursions, and implode violently during the positive excursions. As the bubbles collapse, millions of shock waves eddy, and extremes in pressure and temperature are generated at the implosion sites. Therefore, elevated temperature is not required and the mass transfer resistance between the alcohol and oil is reduced. The optimized condition is at (**19.22:1**) alcohol to oil ratio, **6.83** wt. % catalyst amount, **22.76** minutes and ultrasonic frequency of **39.61** kHz resulting in **0.44**% of FFA in KSO.

Chapter 5

5.1 CONCLUSION

As a conclusion, this project is important as it deals with free fatty acid reduction using esterification process via ultrasonication. Ultrasonication is believed to be one of the best ways to reduce the content of FFA in a feedstock. Ultrasonic is a very desirable tool for the esterification process because it lowers the cost of processing, speeds up esterification process, does not require elevated temperatures, and requires less amount of catalyst. The optimized condition is at (**19.22:1**) alcohol to oil ratio, **6.83** wt. % catalyst amount, **22.76** minutes and ultrasonic frequency of **39.61** kHz resulting in **0.44**% of FFA in KSO. From this, we can conclude that Kapok Seed Oil (KSO) has a very good potential to become as a feedstock to produce biodiesel. This project is within capability of a final year student to be executed with help and guidance from the supervisor and the coordinator. The time frame is also feasible and the project can be completed within the time allocated.

5.2 Recommendations

- Experiment to be run at higher ultrasonic frequency than current existing frequency. This could reduce the FFA content more than existing results.

- Utilization of different types of alcohol at optimized condition.

- Set the reaction temperature as manipulated variable to study the effect of temperature corresponding to the ultrasonic frequency.

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