

PRODUCTION OF BIODIESEL
FROM RUBBER SEED

KARTHIK A/L VASUTHEAVAN

BACHELOR OF CHEMICAL ENGINEERING
UNIVERSITI MALAYSIA PAHANG

UNIVERSITI MALAYSIA PAHANG
BORANG PENGESAHAN STATUS TESIS

JUDUL : PRODUCTION OF BIODIESEL FROM RUBBER SEED

SESI PENGAJIAN : 2011/2012

Saya _____ **KARTHIK A/L VASUTHEAVAN**

(HURUF BESAR)

mengaku membenarkan tesis (PSM/Sarjana/Doktor Falsafah)* ini disimpan di Perpustakaan Universiti Malaysia Pahang dengan syarat-syarat kegunaan seperti berikut :

1. Tesis adalah hakmilik Universiti Malaysia Pahang
2. Perpustakaan Universiti Malaysia Pahang dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. **Sila tandakan (✓)

SULIT (Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)

TERHAD (Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)

TIDAK TERHAD

Disahkan oleh

(TANDATANGAN PENULIS)

(TANDATANGAN PENYELIA)

Alamat Tetap:

ASSOCIATE PROFESSOR
DR. MD. MAKSUDUR R. KHAN
Nama Penyelia

Tarikh: January 2012

Tarikh: January 2012

CATATAN:

- * Potong yang tidak berkenaan.
- ** Jika tesis ini **SULIT** atau **TERHAD**, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai **SULIT** atau **TERHAD**.
- ◆ Tesis dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana secara penyelidikan, atau disertasi bagi pengajian secara kerja kursus dan penyelidikan, atau Laporan Projek Sarjana Muda (PSM).

UNIVERSITI MALAYSIA PAHANG
CENTER FOR GRADUATE STUDIES

We certify that the thesis entitled “Production of Biodiesel from Rubber Seed” is written by Karthik a/l Vasutheavan. We have examined the final copy of this thesis and in our opinion; it is fully adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering. We herewith recommend that it be accepted in partial fulfillment of the requirements for the degree of Bachelor of Chemical Engineering.

Name of External Examiner

Signature

Institution:

Name of Internal Examiner

Signature

Institution:

PRODUCTION OF BIODIESEL FROM RUBBER SEED

KARTHIK A/L VASUTHEAVAN

Thesis submitted in partial fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature :

Name of Supervisor : ASSOC. PROF. DR. MD. MAKSUDUR R. KHAN

Position :

Date :

STUDENT'S DECLARATION

I hereby declare that the work in this thesis entitled "Production of Biodiesel from Rubber Seed" is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :

Name : KARTHIK A/L VASUTHEAVAN

ID Number : KA08081

Date :

To my beloved parents and siblings

.

ACKNOWLEDGEMENTS

Firstly, I want to express gratitude to my father Mr. Vasutheavan for the moral support he gave me. He was like a shadow in my working by helping me in every angle.

I would like to thank my supervisor, Mr. Dr. Maksudur R Khan for his invaluable advice and contributions to this work. His insights and high standards have definitely helped to shape this work. It is a pleasure to have an advisor being so joyful in his work.

My thank goes to the Undergraduate Research Project Coordinator and other lecturers from Faculty of Chemical and Natural Resources Engineering for giving me guidance in completing this thesis. Special thank goes to FKKSA laboratory owner, Mr. Zainal, Miss Hafiza and also our research officer for their special heart to help me.

Thanks to former and present colleagues especially Santini, Kritiga Shankar and Safwan for helping me thorough out my PSM work. I appreciate a lot the way you helped me. Thank you again.

ABSTRACT

The objective of this research is to produce biodiesel from rubber seed oil. Rubber seed oil (RSO) was obtained from rubber seed by soxhlet and microwave assisted extraction methods. Hexane was used as a solvent in the soxhlet extraction process. The yield of oil from rubber seed by soxhlet extraction method was found to be higher (34 – 40%) than by the microwave extraction method (30 – 32%). The physic-chemical properties of the RSO was measured and it was found that the RSO contained 22 wt.% of free fatty acids (FFA). The viscosity of the oil was found as 33.2 cm²/s at 40°C. Biodiesel was prepared by two-step method, where in the first step, the FFA was converted to fatty acid ethyl ester (FAEE) by acid catalyzed esterification, and in the second step the triglycerides (TG) was converted to FAEE by base catalyzed transesterification. Effect of different parameters, such as ethanol/oil molar ratio, temperature, catalyst concentration had been studied for both steps. In the first step, which is acid catalyzed esterification, the optimum parameters were found as 1:6 molar ratio of oil to ethanol, 0.5% of catalyst (H₂SO₄) and at 50°C. The product from the first step was separated in a separating funnel to draw off the excess alcohol, catalyst and water. The optimum parameters for the second step were as follows: 1:6 molar ratio of oil to ethanol, 0.5wt.% of catalyst (NaOH) and temperature of 50°C. After gravity separation of biodiesel from the glycerene layer, it was washed with hot water until a translucent product was obtained. The biodiesel was dried in the rotary vacuum evaporator at 100C for 1 h and the product was characterized. The viscosity of the final biodiesel was found as 5.92 cm²/s and FFA content was undetectable. The gas chromatography analysis shows that the amount of methyl ester found in the sample is quite high.

ABSTRAK

Objektif kajian ini adalah untuk menghasilkan biodiesel dari minyak biji getah. Minyak biji getah (RSO) telah diperolehi daripada benih getah oleh kaedah gelombang mikro soxhlet and pengekstrakan dibantu. Heksana telah digunakan sebagai asolvent dalam proses soxhlet extraction. Hasil minyak dari biji getah melalui kaedah pengekstrakan soxhlet adalah didapati lebih tinggi (34 - 40%) berbanding dengan kaedah pengekstrakan gelombang mikro (30 - 32%). Ciri-ciri kimia obat urus-RSO itu adalah diukur dan didapati bahawa RSO mengandungi 22 berat.% Daripada asid lemak bebas (FFA). Kelikatan minyak yang ditemui sebagai $33.2 \text{ cm}^2 / \text{s}$ pada 40°C . Biodiesel telah disediakan oleh kaedah dua langkah, di mana dalam langkah pertama, FFA telah ditukar kepada asid lemak etil ester (FAEE) oleh esterification catalyzed asid, dan dalam Langkah kedua trigliserida (TG) telah ditukar kepada FAEE oleh transesterification catalyzed asas. Kesan parameter yang berbeza, seperti etanol / nisbah minyak molar, suhu, kepekatan pemangkin telah dikaji bagi kedua-dua langkah-langkah. Dalam langkah pertama, yang esterification catalyzed asid, parameter optimum telah didapati sebagai 1:06 nisbah molar minyak etanol, 0.5% daripada pemangkin (H_2SO_4) dan pada 50°C . Produk dari langkah yang pertama telah dipisahkan dalam saluran memisahkan menarik alkohol yang berlebihan, pemangkin dan air. Parameter optimum untuk langkah kedua adalah seperti berikut: 1:06 molar nisbah minyak etanol, 0.5wt% pemangkin (NaOH) dan suhu 50°C . Selepas pemisahan graviti biodiesel dari lapisan glycerene, ia telah dibasuh dengan air panas sehingga produk lut telah diperolehi. Biodiesel ini dikeringkan di dalam penyejat vakum putar pada 100°C selama 1 h dan produk dicirikan. Kelikatan biodiesel akhir ditemui sebagai $5,92 \text{ cm}^2 / \text{s}$ dan kandungan FFA tidak dapat dikesan. Analisis gas kromatografi menunjukkan bahawa jumlah methyl ester yang terdapat di dalam sampel adalah agak tinggi.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	TITLE PAGE	iii
	DECLARATION	iv-v
	ACKNOWLEDGEMENTS	vii
	ABSTRACT	viii
	ABSTRAK	ix
	TABLE OF CONTENTS	x
	LIST OF TABLES	xiv
	LIST OF FIGURES	xv
	LIST OF SYMBOLS	xvi
	LIST OF APPENDICES	xvii
1	INTRODUCTION	
	1.1 Overview of Research	1
	1.2 Research Objectives	8
	1.3 Scopes of Study	8
	1.4 Problem Statement	9
2	LITERATURE REVIEW	
	2.1 Introduction	10
	2.2 Feedstocks	13
	2.2.1 Free fatty acids	15
	2.3 Overview of Rubber seed Oil(RSO)	17
	2.4 Overview of the Process	18

2.4.1	Pyrolysis	18
2.4.2	Micro emulsion	18
2.4.3	Transesterification	19
	2.4.3.1 Homogeneous base-catalyzed transesterification	20
	2.4.3.2 Homogeneous acid-catalyzed transesterification	21
	2.4.3.3 Two-Step Method Esterification	26
2.5	The Advantage of Biodiesel	37

3 RESEARCH METHODOLOGY

3.1	Introduction	30
3.2	Design experiments	30
	3.2.1 Raw materials	30
	3.2.2 Equipments	31
	3.2.3 Procedures	31
	3.2.3.1 Rubber seed oil preparation	31
	3.2.3.2 Preparation of biodiesel from rubber seed oil	34
	3.2.3.2.1 Acid value analysis	34
	3.2.3.2.2 Two step method	35
	3.2.3.2.2.1 Acid catalyzed Esterification	35
	3.2.3.2.1.2 Base catalyzed Transesterification	35
	3.2.3.2.3 Viscosity analysis	35
	3.2.3.2.4 Pycnometer analysis	35
	3.2.3.2.5 GC-MS analysis	36

4	RESULT AND DISCUSSION	
4.1	Oil content in rubber seed	37
4.1.1	Soxhlet extraction	37
4.1.2	Microwave extraction	37
4.1.3	Comparison with soxhlet and microwave extraction	38
4.2	Acid value of RSO	38
4.3	The properties of raw rubber seed oil	39
4.4	Acid Esterification	39
4.4.1	Effect of alcohol to oil molar ratio	40
4.4.2	Effect of acid catalyst amount	41
4.4.3	Effect of reaction temperature	42
4.4.4	Comparison between parameters result	42
4.5	Base catalyzed transesterification	43
4.5.1	Effect of ethanol to oil molar ratio	44
4.5.2	Effect of base catalyst amount	45
4.5.3	Effect of reaction temperature	46
4.5.4	Comparison between the parameters result	47
4.6	Physical-chemical properties of biodiesel	47
4.6.1	Gas Chromatography Analysis (GC-MS)	48
5	CONCLUSION AND RECOMMENDATION	
5.1	Conclusion	50
5.2	Recommendation	50
	REFERENCES	51
	APPENDICE A	54
	APPENDICE B	55
	APPENDICE C-1	56
	APPENDICE C-2	57
	APPENDICE C-3	58
	APPENDICE D-1	59

APPENDICE D-2	60
APPENDICE D-3	61
APPENDICE E	62
APPENDICE F	63
APPENDICE G	64

LIST OF TABLES

TABLE	TITLE	PAGE
2.1	Fatty acid percentage in rubber seed oil	19
3.1	Soxhlet extraction conditions	38
3.2	Microwave extraction conditions	39
3.3	Conditions of the GC-MS	42
4.1	Comparison with soxhlet and microwave extraction	44
4.2	Acid value of RSO	45
4.3	Properties of raw rubber seed oil	46
4.4	Properties of biodiesel	54
4.5	GC analysis peak and its substance	58

LIST OF FIGURES

FIGURE	TITLE	PAGE
2.1	Esterification of TG	11
2.2	Transesterification process route	11
2.3	Transesterification process	12
2.4	Acid esterification catalysed reaction	12
2.5	Composition of various biodiesel feedstocks	13
2.6	Transesterification of vegetable oil	21
2.7	The reaction mechanism by using strong base catalyst	23
3.1	Rubber seed	30
3.2	Rubber seed kernel	30
3.3	Soxhlet extraction apparatus	31
3.4	Microwave extractor apparatus	32
3.5	Rotary evaporator	32
3.6	Process Flow Diagram for the Preparation of Biodiesel.	34
4.1	Graph of molar ratio vs conversion efficiency (Temperature=50°C and amount of catalyst= 0.5%)	40
4.2	Graph of amount of catalyst vs conversion efficiency (Temperature=50°C and Oil/Ethanol=1:6)	41
4.3	Graph of Temperature vs conversion efficiency (Oil/Ethanol=1:6 and amount of catalyst= 0.5%)	42
4.4	Graph of molar ratio vs conversion efficiency (Temperature=50°C and amount of catalyst= 0.5%)	44
4.5	Graph of amount of catalyst vs conversion efficiency (Temperature=50°C and Oil/Ethanol=1:6)	45
4.6	Graph of Temperature vs conversion efficiency (Oil/Ethanol=1:6 and amount of catalyst= 0.5%)	46
4.7	GC-MS	48

LIST OF SYMBOLS

P	-	Pressure
m	-	Mass
°C	-	Degree Celsius
kg	-	Kilogram
K	-	Degree Kelvin
mL	-	Mililiter

LIST OF APPENDICE

APPENDICE	TITLE	PAGE
A	GC analysis for 1:6 RSO to etanol molar ratio, 0.5% amount of catalyst and 50°C	63
B	Composition from GC Anlysis	64
C-1	Effect of oil to ethanol molar ratio (Temperature= 50°C and amount of catalyst = 0.5% was held constant)	65
C-2	Effect of amount of catalyst over conversion (Temperature= 50°C and oil:ethanol=1:6 was held constant)	66
C-3	Effect of reaction temperature (Oil:ethanol=1:6 and amount of catalyst = 0.5% was held constant)	67
D-1	Effect of oil to ethanol molar ratio (Temperature= 50°C and amount of catalyst = 0.5% was held constant)	68
D-2	Effect of amount of catalyst over conversion (Temperature= 50°C and oil:ethanol=1:6 was held constant)	69
D-3	Effect of reaction temperature (Oil:ethanol=1:6 and amount of catalyst = 0.5% was held constant)	70
E	Density readings	71
F	Viscosity readings	71
G	MSDS of Ethanol	71

CHAPTER 1

INTRODUCTION

1.1 Overview of research

Many years before the first diesel engine become functional, scientists E.Duffy and J.Patrick has conducted the transesterification of a vegetable oil as early as 1853. After that, on 10 August of 1893, Rudolf Diesel's prime model that is an engine ran on its own power by only using peanut oil as the fuel. That is the day that called "International Biodiesel Day". In 1912, Rudolf Diesel had said that the use of vegetable oils for engine fuels may seem insignificant during his time but it may become as important as petroleum and the coal-tar products in future. Just like he said, now the non edible oil from vegetable oils is more attractive then edible oils in this present time. The non edible oil from vegetable oils and animal fats is used in many applications. One of the applications is production of biodiesel.

Biodiesel is a renewable source. Biodiesel refers to a vegetable oil or animal fats based diesel fuel consisting of long chain alkyl esters such as methyl, propyl or ethyl. Biodiesel is produced by chemically reacting vegetable oil such as rubber seed oil (RSO) with an alcohol such as methanol. At the present time, biodiesel is being preferred more than the petroleum fuel because of the high oil prices and to limit greenhouse gas

emissions. Biodiesel is also safe, non-toxic and biodegradable in water, contains less sulfur and has a high flash point (>130c). Biodiesel is also less polluting than petroleum diesel because combustion of biodiesel produces less carbon monoxide, unburned hydrocarbons and sulfur dioxide. The lubricating effects of the biodiesel also may extend the lifetime of engines.

Vegetable oils have high viscosity and hence four methods used to reduce the high viscosity of the oil. The four methods are dilution, micro emulsion, pyrolysis and transesterification. But, in the present time biodiesel is mainly produced by the transesterification process of vegetable oils or animal fats and also by the extraction from algae. Transesterification is the reaction of a animal fat or vegetable oil with an alcohol to form esters and glycerol. Glycerol is used in many common products such as soap; hence there is a little waste that should be cleared in that product.

Rubber seeds or also known as *Heveabrasiliensis*, are an abundant source of non edible oil that is available in Malaysia. The seeds also remain underutilized although the oil produced can be used in many applications. Mechanical extraction process used to extract the oil from rubber seeds. Rubber seed oil (RSO) contains high in free fatty acids (FFA) that makes the oil feasible to use in the production of biodiesel. According to its free fatty acid composition, rubber seed oil is rich in unsaturated fatty acid such as oleic acid linoleic acid and linolenic acid. Hence, rubber seed oil is a good source for the production of biodiesel.

There are many type of transesterification process. Example of it is;

1. Homogeneous alkali (base) catalyzed transesterification
2. Homogeneous acid-catalyzed transesterification
3. Two step method esterification.

The Transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined

by the nature of the fatty acids attached to the glycerine. The nature of the fatty acids can in turn affect the characteristics of the biodiesel. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalysed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production, either base can be used for the methyl ester. A common product of the transesterification process is Rape Methyl Ester (RME) produced from raw rapeseed oil reacted with methanol.

Successful transesterification reaction is signified by the separation of the ester and glycerol layers after the reaction time. The heavier, co-product, glycerol settles out and may be sold as it is or it may be purified for use in other industries, e.g. the pharmaceutical, cosmetics etc.

Straight vegetable oil (SVO) can be used directly as a fossil diesel substitute however using this fuel can lead to some fairly serious engine problems. Due to its relatively high viscosity SVO leads to poor atomisation of the fuel, incomplete combustion, coking of the fuel injectors, ring carbonisation, and accumulation of fuel in the lubricating oil. The best method for solving these problems is the transesterification of the oil.

The engine combustion benefits of the transesterification of the oil are:

- Lowered viscosity
- Complete removal of the glycerides
- Lowered boiling point
- Lowered flash point
- Lowered pour point

Biodiesel is a clean burning alternative fuel, produced from domestically grown, renewable resources. Biodiesel contains no petroleum products, but can be blended at any concentration with diesel from fossil sources to create a biodiesel blend. It can be used in compression-ignition (diesel) engines with little or no modification. Biodiesel is simple to use, biodegradable, non-toxic, and basically free of sulphur compounds and aromatics.

When Rudolf Diesel designed his prototype diesel engine a century ago, he ran it on peanut oil. He planned that diesel engines would operate on a variety of vegetable oils. But when petroleum diesel fuel arrived on the marketplace, it was cheap, reasonably efficient, and readily available, and therefore quickly became the diesel fuel of choice.

Biodiesel is made in a chemical process called transesterification, where organically derived oils (vegetable oils, animal fats and recycled restaurant greases) are combined with alcohol (usually methanol) and chemically altered to form fatty esters such as methyl ester. The biomass-derived esters can be blended with conventional diesel fuel or used as a neat fuel (100% biodiesel). The process results in two products -- methyl esters (the chemical name for biodiesel) and glycerine (a valuable by-product usually sold for use in the production of soap).

Biodiesel should not be confused with straight vegetable oil! Fuel-grade biodiesel is produced to strict industry specifications (ASTM D6751 in the US) in order to ensure proper combustion and engine performance. Biodiesel is the only alternative fuel for motor vehicles up to now (2004) to have fully completed the health effects testing requirements of the 1990 Clean Air Act Amendments. Biodiesel that meets ASTM D6751 and is registered with the Environmental Protection Agency is a legal motor fuel for sale and distribution as such. Raw vegetable oil cannot meet biodiesel fuel specifications, it is not registered with the EPA, and it is not a legal motor fuel, despite widespread use in many areas. To express it more exactly: Biodiesel is defined as mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, conforming to ASTM D6751 specifications for use in diesel engines. Biodiesel refers to the pure fuel before blending with diesel fuel.

Biodiesel is less damaging to the environment because it is made from renewable resources and has lower emissions compared to fossil diesel. The toxic effects are even less than from table salt and it biodegrades as fast as sugar when spilled. Since it is made from renewable resources such as rape seeds or similar oil plants, its use decreases dependence on imported oil, whilst contributing to the local rural economy.

With agricultural commodity prices approaching record lows, and petroleum prices reaching ever new record highs, it is clear that more can be done to utilize domestic surpluses of vegetable oils while enhancing energy security. Oil plants will grow in many areas where other agriculture is possible. Because biodiesel can be manufactured using existing industrial production capacity, and is used with conventional equipment, it provides a very good way of securing energy supplies in the short term.

Increased utilization of renewable biofuels can result in measurable micro-economic benefits for both the industrial and agricultural sectors as well as positively affecting the balance of trade. A study completed in 2001 by the U.S. Department of Agriculture states that an annual increase by the equivalent of 760 million litres of soy-based biodiesel demand would boost the total cash receipts from crops by USD5.2 billion cumulatively by 2010, leading to an average farm income increase of USD300 million per year net over this period. In addition to being a domestically produced, renewable alternative fuel for diesel engines, biodiesel has positive performance attributes such as increased cetane number, high fuel lubricating value and high oxygen content.

Biodiesel is one of the most rigorously tested alternative fuels on the market. A number of independent studies have been completed with the results showing biodiesel performs as well as fossil diesel whilst causing much less damage to the environment and human health compared to diesel. That research includes studies performed by the U.S. Department of Agriculture, U.S. Department of Energy, Stanadyne Automotive Corp., Lovelace Respiratory Research Institute, and Southwest Research Institute. Biodiesel is the first and, up to now, the only alternative fuel to have completed the rigorous Health Effects testing requirements of the Clean Air Act. Biodiesel has been shown to perform similarly to diesel in more than 80 million successful road kilometres, using virtually all types of diesel engines, a great deal of off-road distance and countless marine hours. There are now more than 300 major fleets use the fuel in the US alone.

Pure biodiesel (B100) has a solvent effect, which may well release deposits accumulated on tank walls and in pipes from operation. It will also attack paint and similar surfaces, given the chance. Using high blends of biodiesel, the release of deposits may clog filters initially and care should be taken to replace fuel filters until the build-up of deposits is eliminated. This issue is less of a problem with B20 blends, and there is no evidence that lower-blend levels such as B2 have caused filters to become blocked.

B20 and B2 refer to the American system of designating the percentage of biodiesel in a blend. B20 contains 20 % biodiesel and B2 contains 2 % biodiesel by volume. The rest will consist of standard fossil diesel fuel.

The recent switch to low-sulphur diesel fuel has caused most OEMs to switch to components that are also suitable for use with biodiesel. In general, biodiesel used in pure form can soften and degrade certain types of elastomers and natural rubber compounds relatively quickly. These were commonly used in engines up to a few years ago, so there may be a compatibility issue with older vehicles. Using high percentage blends can impact fuel system components (primarily fuel hoses and fuel pump seals) that contain elastomer compounds incompatible with biodiesel, although the effect is lessened as the biodiesel blend level is decreased. Experience has shown that no changes to gaskets or hoses are necessary when using B20, even in older engines.

The final issue to be covered is that of shelf life. Most fuel today is used up long before six months, and many petroleum companies do not recommend storing hydrocarbon diesel for more than six months. The current industry recommendation is that biodiesel be used within six months, or reanalysed after six months to ensure the fuel meets ASTM specifications (D-6751).

On the negative side, biodiesel does not supply the same energy yield per area that energy plants for use in a biodigester would. The methane produced there would give about twice the energy that the same area devoted to oil plants for biodiesel production would recover. Biodiesel has the great advantage of being useable in existing engines with very little being needed in the way of adaptation. In cold climates it will probably prove impossible to use pure biodiesel (B100), but mixtures up to 20 % biodiesel (B20) should cope with most climates. Preheating of the fuel is also a

possibility, which is unavoidable in many areas, even using standard diesel from fossil sources. This advantage means that the technology can be applied generally without any preparation stage. Converting fleets of vehicles to gas propulsion is a very costly and time-consuming business, to say nothing of the down-time caused.

Biodiesel, generally in the form of B20, is used in federal, state, and transit fleets, private truck companies, ferries, tourist boats and launches, locomotives, power generators, home heating furnaces, and other equipment, especially in the agricultural sector. Regulated fleets are being rewarded for implementing biodiesel use into their heavy-duty vehicles. For every 1700 litres of biodiesel used in any blend level per year, a provision under the Energy Policy Act of 1992, as amended in 1998, credits these fleets with one required alternative-fuel light-duty vehicle. Furthermore, there is growing interest in using biodiesel where workers and school children are exposed to toxic diesel exhaust, in aircraft to control local pollution near airports, and in locomotives and power generators that face restricted use unless emissions can be reduced. One example is Eastman Chemical Co. of Kingsport, Tennessee, who have switched all 200 delivery vehicles over to biodiesel B20 use.

1.2 Research Objectives

The main objective for this research is to produce biodiesel from rubber seed oil by two step method and to study the properties of biodiesel produced.

1.3 Scope of Study

In order to achieve the objective, there are several scope was have been identified

1. Extraction of RSO by two different methods, such as Soxhlet and microwave extraction.
2. Characterization of the RSO

3. Synthesis of biodiesel from the oil by two-step method.

1.4 Problem Statement

Rubber seed oil is one of the non edible oil but still the use of rubber seed oil in industry is not so efficient compared to other feedstocks. Rubber seed oil contains a high significant percentage of free fatty acid.

An experiment should be conducted to see whether rubber seed oil can be used as an oil to produce biodiesel or not. The viscosity of rubber seed oil is high. Hence, a comparison should be made to see whether the biodiesel produced from rubber seed oil still contains high viscosity or not.

Different origin has different value of oil content in rubber seed. Hence, we do not know which origin has the optimum oil content. The source of rubber seed from Malaysia has taken to analysis the oil content.

Direct transesterification is not feasible in rubber seed oil because rubber seed oil contains high percentage of FFA. High percentage of FFA leads to the formation of soap in the oil. Hence, a best method should be studied for producing biodiesel from rubber seed oil.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Biodiesel is produced from the vegetable oil or animal fats. It is either produced from edible oil or non edible oil. But in the present time, production of biodiesel from non edible oil is feasible because it's safe and less pollute to the environment.

Biodiesel is environmentally friendly compared to petrol diesel. It reduces the emission of carbon monoxide and carbon dioxide. Biodiesel also contains high cetane rating compared to petrol diesel[1]. Hence, it can improve the performance of the engine.

Biodiesel is produced by using vegetable oils and animal fats. The main components of vegetable oils and animal fats are triglycerides or also known as esters of fatty acids attached to a glycerol. The triglycerides contain several different fatty acids. These fatty acids differ from each other by their physical and chemical composition. Hence, these fatty acids will be the parameter in influencing the property of the vegetable oil and animal fat. This oil contains high viscosity and that is the main

obstacle to use it as a fuel. Chemical reactions are used to lower the viscosity of these oils.

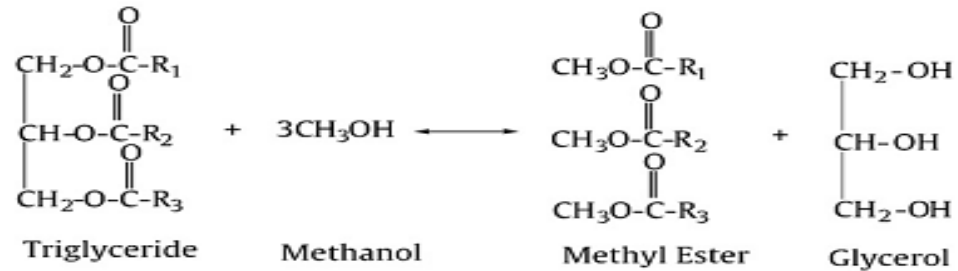


Figure 2.1: Esterification of TG

In that reaction, triglycerides are converted into fatty acid methylester (FAME), in the presence of short chain alcohol, such as methanol or ethanol, and a catalyst, such as alkali or acid, with glycerol as a by-product.

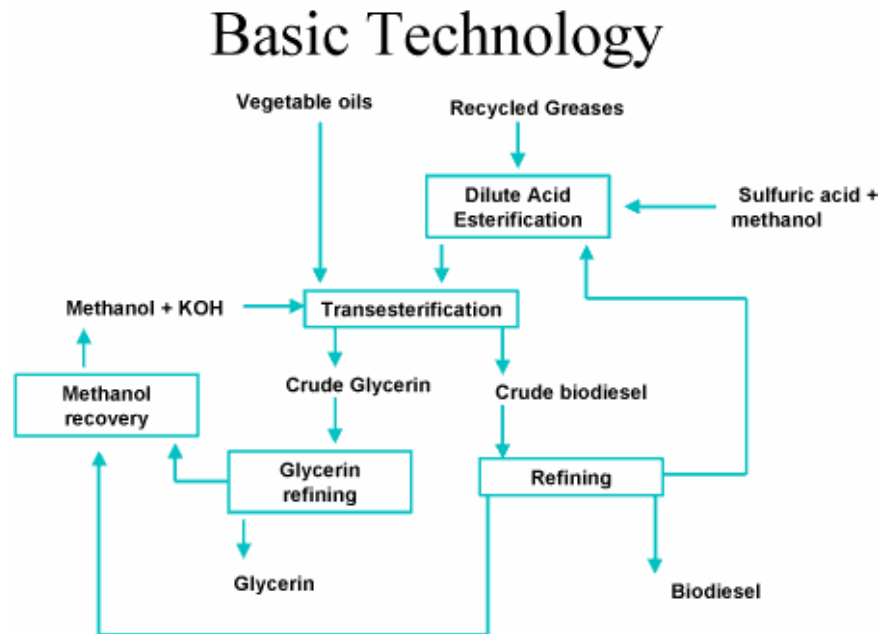


Figure 2.2: Transesterification process route

The transesterification process reacts an alcohol (like methanol) with the triglyceride oils contained in vegetable oils, animal fats forming fatty acid alkyl esters

(biodiesel) and glycerin. The reaction requires heat and a strong base catalyst, such as sodium hydroxide or potassium hydroxide. The simplified transesterification reaction is shown below.

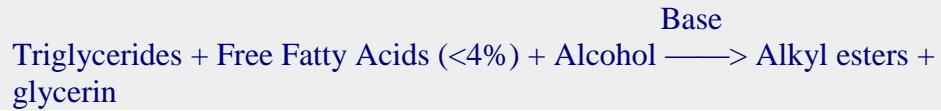


Figure 2.3: Transesterification process

Feedstocks with more than 4% free fatty acids, which include inedible animal fats and recycled greases, must be pretreated in an acid esterification process. In this step, the feedstock is reacted with an alcohol (like methanol) in the presence of a strong acid catalyst, converting the free fatty acids into biodiesel. The remaining triglycerides are converted to biodiesel in the transesterification reaction.

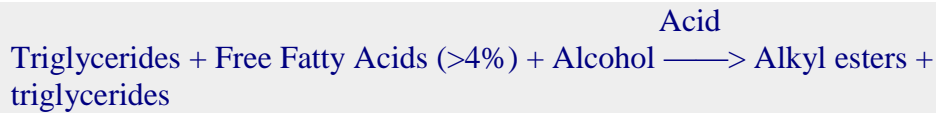


Figure 2.4: Acid esterification catalysed reaction

2.2 Feedstocks

Biodiesel can be made from any plant or animal derived oils. However, some oils are better than others for making biodiesel. We can partly describe oils by the original source, like peanut oil, canola oil, soy oil, beef tallow, and on and on. New oils can also be hydrogenated which alters how they make biodiesel. There are drying oils and non drying oils. Waste oils need more information, like FFA content, and water content.

"Organic oils are three long strings of fatty acids attached to a glycerin molecule. The Fatty Acids can vary in length and in how they are bonded or put together. The way we describe Fatty Acids is by the number of carbon atoms in it and the number of double bonds. We typically see between 12 and 26 carbon molecules in our oils and oils with zero to three double bonds.

Different oils have different blends of fatty acids as you can see from the chart below.

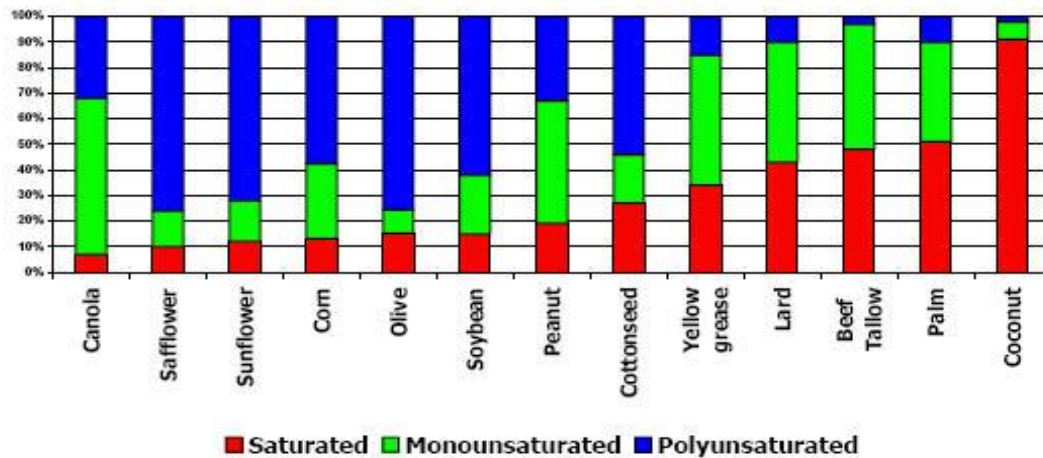


Figure 2. Composition of various biodiesel feedstocks

Figure 2.5: Composition of various biodiesel feedstocks

Fatty acids without double bonds are called saturated fats. The lower the saturated fat content, the lower the gel point of the biodiesel made from it. Fatty acids containing double bonds are called unsaturated. The double bonding site is somewhat unstable and can break off or be chemically altered in the presence of heat and water [7]. Unsaturated fats tend to spoil faster than saturated fats. If oil contains too many double bonded sites the oil becomes a "drying oil".

2.2.1 Free Fatty Acids

A fatty acid is a carboxylic acid with a long unbranched aliphatic tail, which is either saturated or unsaturated. Most naturally occurring fatty acids have a chain of an even number of carbon atoms, from four to 28.^[1] Fatty acids are usually derived from triglycerides or phospholipids. When they are not attached to other molecules, they are known as "free" fatty acids.

Butyric acid, also called butanoic acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$), is a fatty acid occurring in the form of esters in animal fats and plant oils. As a glyceride, it makes up 3–4 percent of butter; the disagreeable odour of rancid butter is that of butyric acid resulting from hydrolysis of the glyceride. The acid is of considerable commercial importance as a raw material in the manufacture of esters of lower alcohols for use as flavouring agents; its anhydride is used to make cellulose acetatebutyrate, a useful plastic.

Butyric acid can be artificially manufactured by aerial oxidation of butyraldehyde. It is a colourless liquid, soluble in water and miscible with common organic solvents; it freezes at $-4.26\text{ }^\circ\text{C}$ ($24.33\text{ }^\circ\text{F}$) and boils at $163.53\text{ }^\circ\text{C}$ ($326.35\text{ }^\circ\text{F}$). An isomer, isobutyric acid ($(\text{CH}_3)_2\text{CHCO}_2\text{H}$), or 2-methylpropanoic acid, is found both in the free state and as its ethyl ester in a few plant oils. It is commercially less important

than butyric acid. It is generally similar to butyric acid; it freezes at $-46.1\text{ }^{\circ}\text{C}$ ($-51\text{ }^{\circ}\text{F}$) and boils at $153.2\text{ }^{\circ}\text{C}$ ($307.8\text{ }^{\circ}\text{F}$).

Linoleic Acid is the principle fatty acid in many vegetable oils, including cottonseed oil, soybean oil, and corn oil. It is also abundant in rapeseed oil (from members of the mustard family, *Brassicaceae*) and is used in the manufacture of margarines, shortening, and salad and cooking oils.

Triglycerides built from linoleic acid are oils because of the double bonds in their chains of carbon atoms. Since margarine and shortening manufacturers want a soft solid, they bubble hydrogen through the oil in the presence of a nickel catalyst. This hydrogenation process brings about several changes, including the partial saturation of the carbon chains as hydrogen atoms attach to carbon atoms that were originally joined by double bonds. The replacement of carbon-carbon double bonds with single bonds allows the carbon chains to become flexible. As a result, the molecules can pack together more closely and the oil is converted to a fat. The hydrogenation process is stopped sooner if the oils are destined to become softer (tub) margarines.

The elimination of the double bonds during the hydrogenation also reduces the likelihood of attack by oxygen, so that the fat remains fresh longer. Nasty-smelling molecules are removed by passing superheated steam through the molten fat. This also removes the molecules responsible for color, so carotenes of various kinds are added to restore a butterlike appearance. The odor of butter is simulated by adding butanedione. The flavor is enhanced and sharpened by emulsifying the fats with skimmed milk that has been cultured with bacteria that produce lactic acid. The nutritional value is improved by the addition of vitamins A and D. And finally, natural surfactant molecules (lecithins, which are triglyceride like substances with one side chain containing a phosphatelike group) are added to ensure that the entire concoction hangs together.

Molecules that contain the carbonyl group ($=C=O$) are called ketones and are responsible for many natural flavors and odors. Methyl ketones exist in their precursor form in fresh butter as alkanolic acids. As such, they may be only marginally important in contributing to the flavor of fresh butter. However, when heated, the precursors are converted to methyl ketones and their total concentration rises above their FTV. Thus they are very important in providing flavors associated with heated or cooked foods containing butter. Methyl ketones are important flavor components, especially of blue cheeses; *Penicillium roqueforti* for instance produces 2-pentanone, 2-heptanone and 2-nonanone.

Diacetyl (2,3-Butanedione) shown at left, is another ketone flavorant and is very important in providing the rich or heated note in butter flavor. Diacetyl is also the primary flavor compound in starter cultures and distillates which are used in producing cultured butter. It is a volatile yellow liquid ketone with a cheese-like smell. It is, in fact, the molecule that gives butter its characteristic flavor and the molecule you should have in mind when you smell it; for when cream is incubated with bacteria, they produce some butanedione. After incubation, the cream is churned. This breaks down the sheaths around the fat droplets, and they coalesce into a soft, solid mass. Sheep's milk and goat's milk are richer in short-chain triglycerides than cow's milk, and cheese made from them (such as Roquefort) is richer in pungent molecules.

Diacetyl and acetoin produced by *lactic streptococci* are flavors characteristic of butter, buttermilk and sour cream. Diacetyl also imparts a yellow colour to dairy products; it is formed from citrate via oxaloacetate and pyruvate which is de-toxified to form diacetyl and acetoin. An essential step is transport of citrate into the cell by an inducible citrate permease. Natural diacetyl can also be obtained from starter distillate, a by-product from the manufacture of dairy starter cultures.

You may be able to smell butanedione by sniffing your armpits or someone's unwashed feet, because it is a contributor to the odor of fermenting perspiration. Fresh sweat is almost odorless, but the action of the bacterium *Streptococcus albus*, which is present on the skin, increases its acidity and makes an inviting feast for other bacteria; they, in turn, excrete pungent compounds including butanedione.

2.3 Overview of rubber seed oil(RSO)

Rubber seed is a waste product from rubber plantations. It contains nutritive values that can be harnessed as food for human, feed for animals or biofuel for energy. Rubber seed can be used to extract its oil. The rubber seed oil that has been extracted contains many free fatty acids. From a recent analysis, the fatty acid contained in rubber seed oil is:

Saturated	18.9 %
palmitic acid	10.2 %
stearic acid	8.7 %
Unsaturated	80.5 %
oleic acid	24.6 %
linoleic acid	39.6 %
linolenic acid	16.3 %

Table 2.1: Fatty acid percentage in rubber seed oil

Because of the high percentage of free fatty acid in rubber seed oil, it has to be acid esterified first to reduce the FFA percentage. Then, the acid esterified oil can be used to produce biodiesel.

2.4 Overview of the process

2.4.1 Pyrolysis

Pyrolysis is formally defined as chemical decomposition induced in organic materials by heat in the absence of oxygen. In practice, it is not possible to achieve a completely oxygen-free atmosphere; actual pyrolytic systems are operated with less than stoichiometric quantities of oxygen. Pyrolysis transforms hazardous organic materials into gaseous components, small quantities of liquid, and a solid residue (coke) containing fixed carbon and ash. Pyrolysis of organic materials produces combustible gases, including carbon monoxide, hydrogen and methane, and other hydrocarbons. Pyrolysis typically occurs under pressure and at operating temperatures above 430 °C (800 °F).

2.4.2 Micro Emulsion

Microemulsions are clear, stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. An emulsification is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1–150 nm range, formed spontaneously from two normally immiscible liquids. Vegetable oils contain high viscosity and hence this method can be used to lower the viscosity of the oils.

The formation of micro-emulsions (co-solvency) is a potential solution for reducing the viscosity of vegetable oil. Micro-emulsions are defined as transparent, thermodynamically stable colloidal dispersions. The droplet in micro-emulsions ranges from 100 to 1000 Å. A micro-emulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, an alcohol and a surfactant and a cetane improver, with or without diesel fuels. Water (from aqueous ethanol) may also be present in order to use lower-proof ethanol, thus increasing water tolerance of the microemulsions. The use of micro emulsions with solvents such as methanol, ethanol,

and 1-butanol has also been studied as a means of solving the problem of high viscosity of vegetable oils. Micro emulsions are isotropic, clear or translucent thermodynamically stable dispersions of oil, water, a surfactant, and often a small amphiphilic molecule, called a co surfactant. Ziejewskiet *al.* (Ziejewski, Kaufman, Schwab,andPryde, 1984) prepared an emulsion of 53.3% (v/v) alkali-refined and winterized sunflower oil, 13.3% (v/v) 190-proof ethanol and 33.4% (v/v) 1-butanol. This non-ionic emulsion had a viscosity of 6.31×10^{-6} m²/s at 40oC, a cetane number of 25, a sulfur content of 0.01 %, free fatty acids of 0.01 %, and an ash content of less than 0.01%. Lower viscosities and better spray patterns were obtained by increasing the amount of 1-butanol. Schwab *et al.* Reported that 2-octanol was an effective amphiphile in the micellarsolubilization of methanol in triolein and soybean oil. However, in a laboratory screening endurance test, irregular injector needle sticking, heavy carbon deposits, in complete combustion and an increase of lubricating oil viscosity were reported (Ziejewski, Kaufman, Schwab,andPryde, 1984).

2.4.3 Transesterification

Transesterification is a process of exchanging the organic group R'' of an ester with the organic group R' of an alcohol.

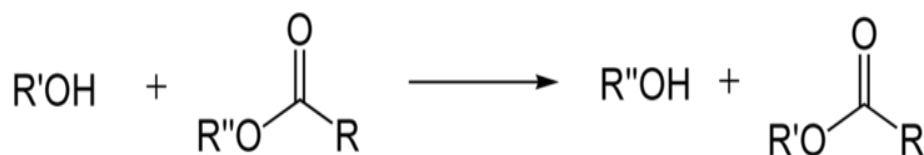


Figure 2.6: Transesterification of vegetable oil

Strong acids catalyze the reaction by donating a proton to the carbonyl group, thus making it a more potent electrophile, whereas bases catalyze the reaction by removing a proton from the alcohol, thus making it more nucleophilic.

2.4.3.1 Homogeneous Alkali (Base) Catalyzed Transesterification

Base catalyzed reaction uses strong base such as NaOH, KOH, Sodium Meth oxide and others. The base is dissolved in the alcohol to disperse solid catalyst into the oil. Any water in the process promotes the saponification reaction and inhibits the transesterification reaction.

Once the alcohol mixture is made, it is added to the triglyceride. The reaction that follows replaces the alkyl group on the triglyceride in a series of reactions. The carbon on the ester of the triglyceride has a slight positive charge, and the oxygen have a slight negative charge, most of which is located on the oxygen in the double bond. This charge is what attracts the RO⁻ to the reaction site.

This yields a transition state that has a pair of electrons from the C=O bond now located on the oxygen that was in the C=O bond. These electrons then fall back to the carbon and push off the glycol forming the ester. Then two more RO groups react via this mechanism at the other two C=O groups. This type of reaction has several limiting factors. RO⁻ has to fit in the space where there is a slight positive charge on the C=O. So MeO⁻ works well because it is small.

As the R on RO⁻ gets bigger, reaction rates decrease. This effect is called steric hindrance. That is why methanol and ethanol are typically used. There are several competing reactions, so care must be taken to ensure the desired reaction pathway occurs. Most methods do this by using an excess of RO⁻. The acid catalyzed method is a slight variant that is also affected by steric hindrance.

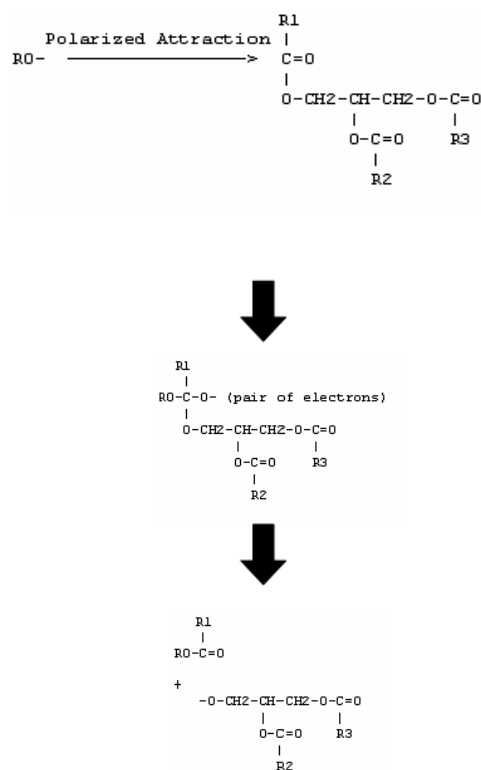


Figure 2.3: The reaction mechanism by using strong base catalyst

Figure 2.7: The reaction mechanism by using strong base catalyst

2.4.3.2 Homogeneous acid-catalyzed transesterification

This method is not popular compared to the base catalyzed method because this method is slower. But this method also does have advantages. Acid catalyst can simultaneously catalyze both esterification and transesterification[13]. They also can produce biodiesel from low cost lipid feedstocks such as cooking oil and grease. However, acid-catalyzed system is not a popular choice for commercial applications due to slower reaction rate, requirement of high reaction temperature, high molar ratio of alcohol to oil, separation of the catalyst, serious environmental and corrosion related problem.

Biodiesel is currently produced via transesterification of triglycerides with an alcohol such as methanol. The transesterification of triglycerides comprises of three sequential, reversible reactions wherein triglycerides react to form diglycerides, monoglycerides and glycerol[3]. On a side note, it is important for one to know the triglyceride content of the oil when purchasing.

Traditional biodiesel processing is comprised of two broad categories: esterification (or a variation of it such as glycerolysis, enzymatic or temporary solid catalysis) and transesterification. The traditional esterification process uses methanol with a homogenous acid catalyst such as sulfuric acid to convert free fatty acids (FFAs) into esters. Traditional transesterification uses a homogenous base catalyst such as sodium methylate or potassium methylate along with methanol to convert the triglycerides into biodiesel and glycerin.

The point of discussion for this article is traditional homogenous catalyst such as sulfuric acid, and sodium or potassium methylate, and their drawbacks as applicable to variable FFA material in a multifeedstock environment[17].

In a very low FFA (less than 1 percent) feedstock environment, catalysts such as sodium or potassium methylate make good sense, but in a high FFA environment, one starts to encounter various issues with these catalysts.

A catalyst is a chemical that helps speed up the chemical process without actually participating in it. How a homogenous catalyst such as sulfuric acid or sodium methylate differs in this is also an important part of the discussion.

There are two kinds of catalysts typical to any biodiesel process: homogeneous and heterogeneous. Homogeneous catalysts function in the same phase (liquid, gaseous, etc.) as the reactants. Typically, homogeneous catalysts are dissolved in a solvent with the substrates. Heterogeneous catalysis is the opposite of homogeneous catalysis, meaning it occurs in a different phase than the reactants[6]. Most heterogeneous

catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place. The total surface area of solid has an important affect on the reaction rate; the smaller the catalyst particle size, the larger the surface area for a given mass of particles.

Homogeneous catalysts for biodiesel production have been around for quite some time, but heterogeneous catalyst is a fairly newer development in the realm of biodiesel production. Typically sulfuric acid is used as the homogeneous acid catalyst for the esterification of FFAs. Sometimes though, hydrochloric acid is also used.

An ester can react with another alcohol. In that case, the new alcohol is derived from the original ester formed, and the new ester is derived from the original alcohol. Thus, an ethyl ester can react with methanol to form a methyl ester and ethanol. This process is called transesterification.

Transesterification is extremely important for biodiesel. Biodiesel as it is defined today is obtained by transesterifying the triglycerides with methanol. Methanol is the preferred alcohol for obtaining biodiesel because it is the cheapest, and most available, alcohol. For the reaction to occur in a reasonable time, however, a catalyst must be added to the mixture of the oil and methanol. Often present in small amounts, catalysts accelerate the speed of a reaction and, in many cases, virtually no reaction would occur without one.

The catalyst used for carrying out transesterification is usually sodium hydroxide (NaOH) or potassium hydroxide (KOH) or sodium methylate (SMO). These compounds belong to a class of materials known as bases and also are inorganic compounds, often used in organic chemistry for carrying out or catalyzing reactions. Other bases are also suitable for the transesterification reaction. The counterparts of bases are known as acids. Many acids can also be used as catalysts for transesterification[10]. However, the base-catalyzed reaction has advantages such as a higher reaction rate.

A fatty acid and base react to form a new compound, called soap and water. Compounds such as soap, in which the hydrogen (proton) of an acid has been replaced with a metal ion, are often called salts.

The reason that such compounds exist is that materials such as NaOH or KOH can split apart, or dissociate, in a fashion that gives Na^+ and OH^- (or K^+ and OH^-) in which the protons and electrons are not evenly distributed, leading to charged particles. Thus, having the same charge, Na^+ or K^+ can replace H^+ here.

The most common homogenous catalysts used in the biodiesel production is sulfuric acid during esterification and sodium methyllate during transesterification. Typical biodiesel processing that involves high FFA oil is comprised of two steps, esterification and transesterification. During esterification, a predetermined quantity of sulfuric acid based on the FFA content of the oil being processed, is added to oil with high FFA and methanol. There are various ways of processing esterification, at atmospheric pressure and 65 degrees Celsius to 70, or under high pressure and high temperatures, etc.. The important byproduct of esterification process is water, which dilutes the catalyst thereby hindering in the esterification process.

One of the points to note here is transesterification also occurs in the presence of sulfuric acid apart from esterification. Repeated experiments by various researchers show a majority of transesterification would have occurred by the time esterification has reached its equilibrium.

After reducing the FFA of the oils through the esterification process to less than 1 percent, the oil goes into the transesterification phase. Another point of interest here is that some technologies do recommend going straight into transesterification if the feedstock FFA content is less than 4 percent. The downside to this, however, is that there would be a lot more usage of catalyst. It also results in substantial product loss due to the formation of soap. Higher process costs are also possible, due to acid number issues that need to be fixed so the fuel can meet the ASTM D6751 specification.

During transesterification, once the calculated amount of catalyst (SMO) and required amount of methanol is dosed into the reactor, the process would not change whether using batch or continuous, the temperature is maintained around 65 degrees Centigrade. The reaction kick starts.

At the same time when the triglycerides are converted to diglycerides and monoglycerides, the FFAs are converted to soaps. The higher the FFA content is when starting, the greater production of soap there will be. Almost 90 percent of the soap goes into the glycerin phase in the settling process or centrifuging. Contrary to some of the claims out there, to completely eliminate soaps before water washing or dry-wash step is nearly impossible.

There is also some residual homogenous catalyst left over from the biodiesel process, which has to be removed in the washing stage as well.

Potential issues with high FFA feedstock processing using the traditional homogenous catalyst include higher acid number, yield losses, higher post-cleaning processes, quality of glycerin, product consistency, and process consistency due to changing starting FFAs. If proper care is taken and quality is monitored, these issues can be addressed sulfuric acid or SMO in the variable FFA materials, especially those with high FFA content and multi-feedstock product. Due to the general availability of the products, the price is fairly competitive and there are little issues with product supply.

Another advantage of the homogenous catalyst is its usability. Since the operations occur in the same phase as your reactants, the handling becomes that much easier. Handling all liquids is easier than handling one liquid and one solid or a combination of them.

Some of the drawbacks of using the homogenous catalyst for biodiesel production are water formation during acid esterification hinders the process. Care should be taken to get rid of water via drying, and this adds to the cost. Reusability—

though there are claims of reusing the catalyst, it's rarely seen if ever done on a production scale, due to the costs involved. Corrosive nature of the catalysts involved. The popular acid (H_2SO_4) and base (SMO) catalysts currently used in the biodiesel production process are fairly corrosive in nature and need to be handled extremely carefully. The SMO tends to absorb water and needs to be under a nitrogen blanket. For shorter storage durations or when the liquid has short turnaround, blanketing can be avoided[14]. As always, plan for the worst in a production environment so you are not caught flatfooted. SMO tends to settle and potentially lose its original power over a period of time if unused and sitting. The related troubleshooting and fixing is extremely time-consuming and expensive. Multiple stages of processes (multi-stage esterification, and multi-stage transesterification). With multiple stages involved, there is loss of heat, transfer time, wear and tear and employee training time to address all processes.

The heterogeneous, enzymatic and other kinds of catalysts are picking up in the market with some of the major developments coming in the past year. With continued developments and improvements, the cost and operational advantages a recyclable heterogeneous catalyst would provide will outweigh the homogenous catalyst.

2.4.3.3 Two-step method esterification

Homogeneous catalysts showed greater performance toward transesterification to obtain bio-diesel. The problems associated with the homogeneous catalysts are the high consumption of energy, form unwanted soap byproduct by reaction of the FFA, expensive separation of the homogeneous catalyst from the reaction mixture and generation large amount of wastewater during separation and cleaning of the catalyst and the products. The use of heterogeneous catalysts could be an attractive solution.

Heterogeneous catalysts can be separated more easily from reaction products. Undesired saponification reactions can be avoided by using heterogeneous acid catalysts. They enable the transesterification of vegetable oils or animal fats with high contents of FFAs, such as deep-frying oils from restaurants and food processing. Bio-

diesel synthesis using solid catalysts could potentially lead to cheaper production costs because of reuse of the catalyst and the possibility for carrying out both transesterification and esterification simultaneously.

Satoshi et al. carried out the transesterification of soybean oil with methanol to fatty acid ester over the solid super acid catalysts of WZA (tungstated zirconia–alumina), SZA (sulfated zirconia–alumina), and STO (sulfated tin oxide) at 200–300 °C in fixed bed reactor under atmospheric pressure and reported WZA as a promising solid acid catalyst for the production of bio-diesel from soybean oil (coner hand, high conversion over 90%).

In other hand, the high FFA contained oil is undergoes acid catalyzed esterification in order to reduce its FFA percentage. Two layers will be formed through this process. Top layer which contains alcohol and other impurities is filtered off. The bottom layer undergoes base catalyzed esterification to produce biodiesel and glycerol. Glycerol is filtered off and the biodiesel is washed to obtain pure biodiesel.

2.5 The advantage of biodiesel

Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning every day because of the increase in the petroleum price and the environmental advantages.

Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are at least five reasons that justify its development, such as provides a market for excess production of vegetable oils and animal fats, decreases the country's dependence on imported petroleum although will not eliminate. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that overall CO₂ emissions were reduced by 78% compared with petroleum-based diesel fuel (Sheehan, Camobreco, Duffield, Graboski, and Shapouri, 1998). The exhaust emissions of carbon monoxide, unburned hydrocarbons, and

particulate emissions from biodiesel are lower than with regular diesel fuel. Unfortunately, most emissions tests have shown a slight increase in oxides of nitrogen (NO₂). When added to regular diesel fuel in an amount equal to 1–2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel (Canakci, Van Gerpen, 2001).

Biodiesel is produced from a variety of vegetable oils, including but not limited to palm, rape, canola, soy, linseed, coconut, mustard and cotton oils. It can also be manufactured from tallow oil and yellow grease (used cooking oils). Several different kinds of fuels are called biodiesel: usually biodiesel refers to an ester, or an oxygenate, made from the oil and methanol, but alkane (non-oxygenate) biodiesel, that is, biomass to liquid biomass-to-liquid (BTL) fuel is also available. Sometimes even straight vegetable oil unrefined vegetable oil is called biodiesel. Unrefined vegetable oil requires fuel pre heating and filtration due to issues with coagulation, and also some modification to the fuel system. In contrast, alkane biodiesel is of a similar viscosity to petrochemical diesel, and is usually of a higher quality than petrochemical options available on the U.S. market.

Biodiesel reduces emissions of carbon monoxide (CO) by approximately 50 % and carbon dioxide by 78 % on a net lifecycle basis because the carbon in biodiesel emissions is recycled from carbon that was already in the atmosphere, rather than being new carbon from petroleum that was sequestered in the earth's crust. (Sheehan, 1998)

Biodiesel contains fewer aromatic hydrocarbons" aromatic hydrocarbons: benzofluoranthene: 56 % reduction; Benzopyrenes: 71 % reduction. It also eliminates emissions of sulphur (SO₂), because biodiesel does not contain sulphur.

Biodiesel reduces the emission of Particulate, by as much as 65 % of small particles of solid combustion products. This reduces cancer risks by up to 94 % according to testing sponsored by the US Department of Energy.

Biodiesel has a flash point of 160 °C, and is classified as a non-flammable liquid by the US Occupational Safety and Health Administration. This property makes biodiesel relatively safe to produce, resulting in higher safety margins for storage and transfer. Also vehicles fuelled by pure biodiesel are far safer in Car accidents than ones powered by petroleum diesel or the explosively combustible gasoline.

Biodiesel is biodegradable and non-toxic, in fact an average 60 kg person would need to consume more than 3 litres of Biodiesel to cause death 50% of the time, making biodiesel ten times less toxic than Sodium chloride table salt. In addition it is as biodegradable as sugar, and has significantly fewer emissions than petroleum-based diesel (petro-diesel) when burned. Biodiesel functions in current diesel engines, and is the strongest candidate to replace fossil fuels as the world's primary transport energy source.

The factors that make it one of the main candidates to replace fossil fuels as the world's primary transport energy source are: it is a renewable, clean-burning fuel that can deliver benefits both to the environment and to vehicle engines. Biodiesel can be distributed using today's infrastructure, and its use and production is increasing rapidly (especially in Europe, the United States, and Asia). Fuel stations are making biodiesel available to consumers and in Germany for example there are 1600 stations nationwide, and a growing number of transport fleets use it as an additive in their fuel.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

The purpose of this chapter is to describe the process flow of the project and how it will be conducted. All the parameters that affect the results of the process are considered in this chapter. Methodology can properly refer to the theoretical analysis of the methods appropriate to a field of study or to the body of methods and principles particular to a branch of knowledge.

3.2 Design Experiment

3.2.1 Raw materials

Rubber seed was collected from local market. Ethanol (99.8%), Hexane (99-100%), Sodium hydroxide pellets (96%), Phenolphthalein (pH 8.2-9.8), Isopropanol, Acetone (99%) and Sulphuric acid (98%) were purchased from Fisher Chemicals. All the chemicals used are analytical reagent grade.

3.2.2 Equipments

Soxhlet extractor is used to extract oil from rubber seed. Microwave extractor (Ethos E- Milestone) is also used to extract oil from rubber seed. Rotary evaporator is used to separate hexane and oil after the extracting process. Viscometer is used to analyze biodiesel viscosity at 40°C. Pycnometer is used to analyze biodiesel density. For analyze biodiesels composition character, GC-MS is used.

3.2.3 Procedures

3.2.3.1 Rubber seed oil preparation

Five kg of rubber seed is collected and clean it with distillate water if it is covered with mud and impurities. The seed kernel was separated and weighted to measure the seed to kernel ratio. Rubber seed, a brown colored seed weighted from 2.68 to 5.04 g bears a kernel varies from 1.53 g to 3.00 g of weight which was 53.74–68.35% of the seed. However average wt. % of the kernel is 58.83%.



Figure 3.1 Rubber seed



Figure 3.2: Rubber seed kernel

Rubber seed is left to dry because usually it contains a high moisture content. The rubber seed is crushed in a blender to reduce its size. The blended rubber seed is

placed in soxhlet extractor to extract rubber seed oil with hexane as the organic solvent in 1: 3 rubber seed to hexane ratio. The extracted oil is collected and rotary evaporator is used to separate the oil and hexane. The rubber seed oil is used in the next step which is acid esterification. Microwave extractor is also used to extract the oil from rubber seed. 100g of rubber seed sample were weighted and loaded into the extraction vessel. 100 mL of hexane is added to the sample which act as solvent. Circulating cold water was cooled for 30 minutes in prior before starting the experiment. After adding the sample, the sample vessel and the condenser was connected. The extractions were performed at 1000W of power, 45 minutes of extraction time, at a temperature of 60-70°C and at a pressure of 1.1 bar. After extraction, the vessel is cooled to room temperature before removing the reflux condenser. After the extraction was complete, the sample is filtered. Finally the weight of the sample is taken.

Table 3.1: Soxhlet extraction conditions

Method	Soxhlet extraction
Time for one batch	6 hrs
Initial amount	80% of timble
Solvent	Hexane
Raw material	Raw, blended rubber seed



Figure 3.3: Soxhlet extraction apparatus

Table 3.2: Microwave extraction conditions

Temperature	60 °C
Extraction Time	30 min
Cooling	To room temperature
Filtering/Rinsing	With same solvent system



Figure 3.4: Microwave extractor apparatus



Figure 3.5: Rotary evaporator

3.2.3.2 Preparation of biodiesel from rubber seed oil

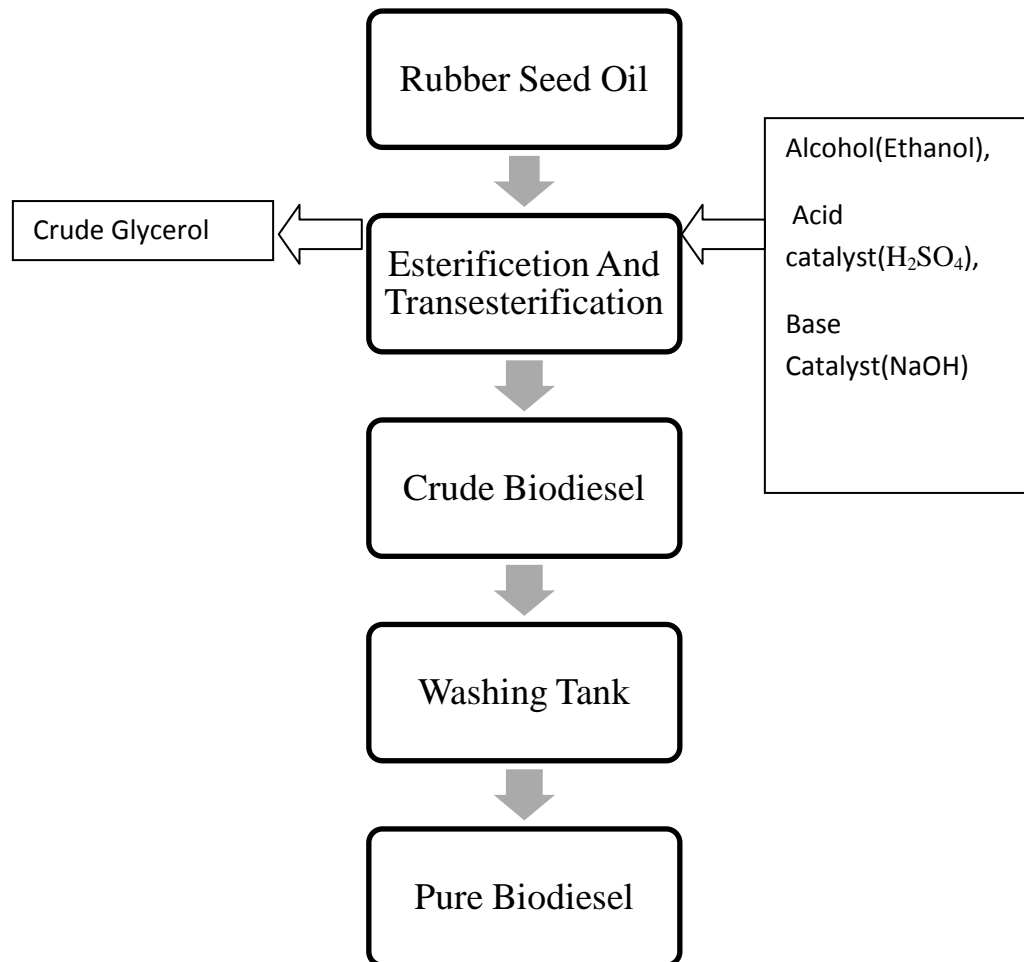


Figure 3.6: Process Flow Diagram for the Preparation of Biodiesel.

3.2.3.2.1 Acid value analysis

One mL of CRSO is mixed with 10 mL of isopropanol. The mixture is stirred well for awhile. Two or three drop of phenolphthalein indicator is dropped into the mixture and titrated with NaOH to find the percentage of FFA in the oil.

3.2.3.2.2 Two step method

A two-step acid-catalyzed ethanolysis of higher FFA containing oil (rubber seed oil) was adopted for the complete conversion of FFA and TG to fatty acid ethyl esters.

3.2.3.2.2.1 Acid catalyzed esterification(First Step)

The first step was carried out at 30 °C and atmospheric pressure. The molar ratio of ethanol/FFA was 3/1. Typically, 45 g rubber seed oil was put into a 250ml beaker. The beaker was placed in an electric heater with a temperature controller and magnetic stirrer. Preheated the oil to the temperature of 40 °C. Sulfuric acid (0.1 wt% of oil) was mixed with required amount of ethanol and transferred into the reaction medium. After 2 h the contents were cooled to room temperature, and reaction product was washed with hot water until clear water found. The organic phase was collected and dried.

3.2.3.2.1.2 Base catalyzed transesterification(Second Step)

The dried sample (38g) from the first step was put into a 250ml beaker, mixed with 0.1 wt% sodium hydroxide and three times the stoichiometric amount of methanol required for the total conversion of TG. The beaker was closed securely. The beaker was placed in an electric heater with a temperature controller and magnetic stirrer. The transesterification was performed under vigorous stirring at 30°C. After 2 h the contents were cooled to room temperature, and reaction product was washed with hot water until clear water found. Two layers will be formed which are crude biodiesel and glycerol. Top layer which is biodiesel is collected and washed with acetone to purify.

3.2.3.2.3 Viscosity analysis

Biodiesel is analyzed using viscometer at 40°C to obtain the viscosity.

3.2.3.2.4 Pycnometer analysis

Pycnometer is used to get the density of the biodiesel.

3.2.3.2.5 GC-MS analysis

A GC-MS instrument equipped with a mass selective detector operating in the electron impact mode is used to study the compositions of the extracted essential oils. The GC part is equipped with a capillary column. Temperature-programming of the oven included an initial hold at 40 °C for 5 minutes and a rise to 240 °C at 3 °C per minutes followed by additional rise to 300 °C at 5 °C per minutes. The extracts obtained were submitted to GC analysis in a HP 7890A gas chromatography equipped with a GCT Premier mass spectrometer and a capillary column of DB-5MS (J & W Scientific) with dimension of 30.0m×0.25mm i.d×0.25_μm film thickness.

The injector is set at 290 °C. The samples are diluted with *n*-hexane (1/10, v/v) and a volume of 1.0 μl is injected to the GC with the injector in the split mode (split ratio: 1/10). Carrier gas, He, is adjusted to a linear velocity of 0.8 ml min⁻¹. The compounds of the extracted essential oils are identified by comparing their mass spectral fragmentation patterns with those of similar compounds from a database. For each compound on the chromatogram, the percentage of peak area relative to the total peak areas from all compounds is determined and reported as relative amount of that compound.

Analysis of the essential oil samples were carried out using a gas chromatography. The samples were injected to the sample port. Table 3.3 shows the conditions of the GC.

Table 3.3: Conditions of the Gas Chromatography

Detector	Flame Ionization Detector (FID)
Carrier Gas	Helium Gas
Carrier Gas flow rate	30 cm/sec
Inlet pressure	2.92 psi
Temperature	40 °C to 290 °C
Oil samples injected	1 μL

CHAPTER 4

RESULT & DISCUSSION

4.1 Oil content in rubber seed

The oil was extracted from the seed by two methods such as soxhlet extraction and microwave extraction method. After extraction of oil the volume of oil was measured. The yield by weight of the mass of seed was calculated and compared.

4.1.1 Soxhlet extraction

The oil content obtained by using soxhlet extractor is 34-40%.

4.1.2 Microwave extraction

The oil content obtained by using microwave extractor is 32-36%.

4.1.3 Comparison with soxhlet and microwave extraction

Table 4.1 Comparison with soxhlet and microwave extraction

Soxhlet extractor	Microwave extractor
Oil content (vol/wt)	Oil content (vol/wt)
34-40%	32-36%

The oil content in soxhlet was 34-40% and in microwave extractor was 32-36%. It obviously seen that using soxhlet the yield will be high but soxhlet extractor is very time consuming. The extracting time for soxhlet is 6 hours and for microwave extractor is 1 hour. Microwave extractor was so demanding among PSM students by that time. So, soxhlet has chosen as the extracting equipment.

4.2 Acid value of RSO

RSO contains high percentage of FFA and the percentage is found by the equation shown below.

$$\% FFA = \left[X \text{ mL NaOH} \cdot \frac{1 \text{ L NaOH}}{1000 \text{ mL NaOH}} \cdot \frac{0.1 \text{ mol NaOH}}{1 \text{ L NaOH}} \cdot \frac{1 \text{ mole FFA}}{1 \text{ mole NaOH}} \cdot \frac{278 \text{ g FFA}}{1 \text{ mole FFA}} \right] \times 100\%$$

The FFA percentage in RSO is found to be 22.04%.

4.3 The properties of raw rubber seed oil

The physical-chemical properties of raw rubber seed oil are studied and the results are shown in table 4.2.

Table 4.2: Properties of raw rubber seed oil

Properties	Experimental value
Physical state	Liquid
Color	Brown
Specific gravity at 25 ⁰ C	0.926
Viscosity, mm ² /s at 40 ⁰ C	33.43
FFA wt. %	22.04
Average molecular weight of FFA (gm/mol) ^a	275.5
Molecular weight of oil (gm/mol) ^a	878
Saponification value (mg of KOH/gm of oil) ^a	192
Iodine value, g I ₂ /100 g oil ^a	132.6

^aCalculated from the oil composition reported byMaksudur R Khan[5]

The result of the physical-chemical properties of raw rubber seed oil is very significant with the results from A.Ramadhas and Maksudur R Khan, (Fuel, 2007 and 2011 respectively).

4.4 Acid Esterification

1 litre of CRSO requires 220 ml of ethanol for the acid esterification. The RSO is poured into a flask and heated about 50⁰C. The ethanol is added with the preheated RSO and stirred for a few minutes. 0.5% of sulphuric acid is also added with the mixture.

Heating and stirring is continued for 2 hours at atmospheric pressure. On completion of this reaction, the product is poured into a separating funnel for separating the excess alcohol. The excess alcohol, with sulphuric acid and impurities moves to the top surface and is removed. The lower layer is separated for further reaction (Base esterification).

4.4.1 Effect of alcohol to oil molar ratio

The alcohol used in this reaction was ethanol. For study the effect of ethanol to CRSO molar ratio, temperature and amount of catalyst is held constant as you can see in figure 4.6. Graph of molar ratio to the conversion efficiency is plotted.

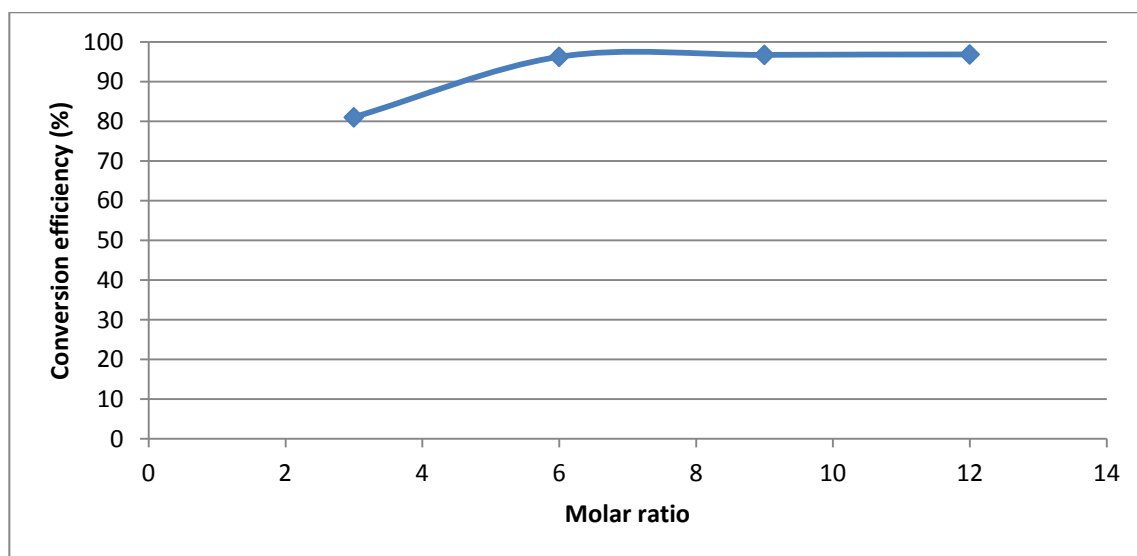


Figure 4.1: Graph of molar ratio vs conversion efficiency (Temperature=50°C and amount of catalyst= 0.5%)

The molar ratio of alcohol to vegetable oil is one of the important factors that affect the conversion efficiency as well as production cost of the biodiesel. The conversion efficiency is defined as the yield of the process represented in terms of percentage. Molar ratio is the ratio of number of moles of alcohol to number of moles of glycerides in the oil. Theoretically, transesterification process requires three moles of alcohol for each mole of oil. However, in practice, the molar ratio should be higher than that of stoichiometric ratio in order to drive the reaction towards completion. As you

can in the graph above, the optimum ethanol to CRSO molar ratio is found to be around 1:6. With further increase in molar ratio there is only little improvement in the conversion efficiency. This first also reduces the viscosity of the oil. High molar ratio has better conversion efficiency but it will make the cost of production high. So, the suitable molar ratio is 1:6 for acid esterification.

4.4.2 Effect of acid catalyst amount

The catalyst used in this reaction is sulphuric acid, H_2SO_4 . The amount of catalyst is increased from 0.1% of the oil to 1.5% of the oil. Temperature and molar ratio is held constant throughout the reaction. Graph of catalyst amount to conversion efficiency is plotted.

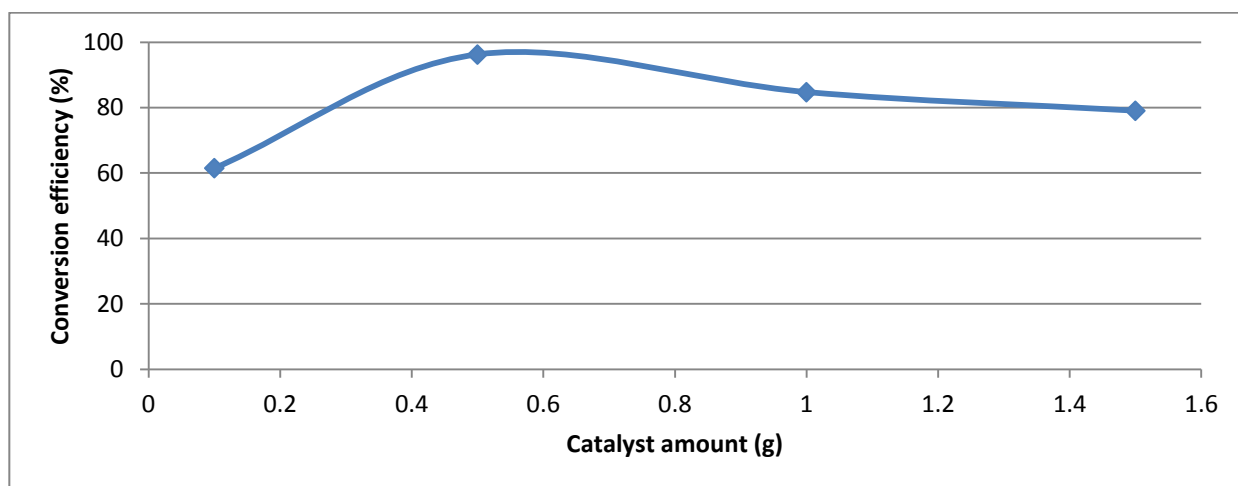


Figure 4.2: Graph of catalyst amount vs conversion efficiency (Temperature=50°C and oil:ethanol=1:6)

The amount of acid catalyst used in the process also affects the conversion efficiency of the process. The catalyst amount is varied from 0.1% to 1.5%. At 0.5% of catalyst amount, the conversion efficiency is at optimum and increasing the amount of catalyst results in decrease of the conversion efficiency. It also noted that excess addition of sulphuric acid, darkens the colour of the product. Lower amount of sulphuric acid addition affect the yield in the second step.

4.4.3 Effect of reaction temperature

Temperature is changed from 30°C to 70°C to study the effect of temperature. Graph of catalyst amount to conversion efficiency is plotted.

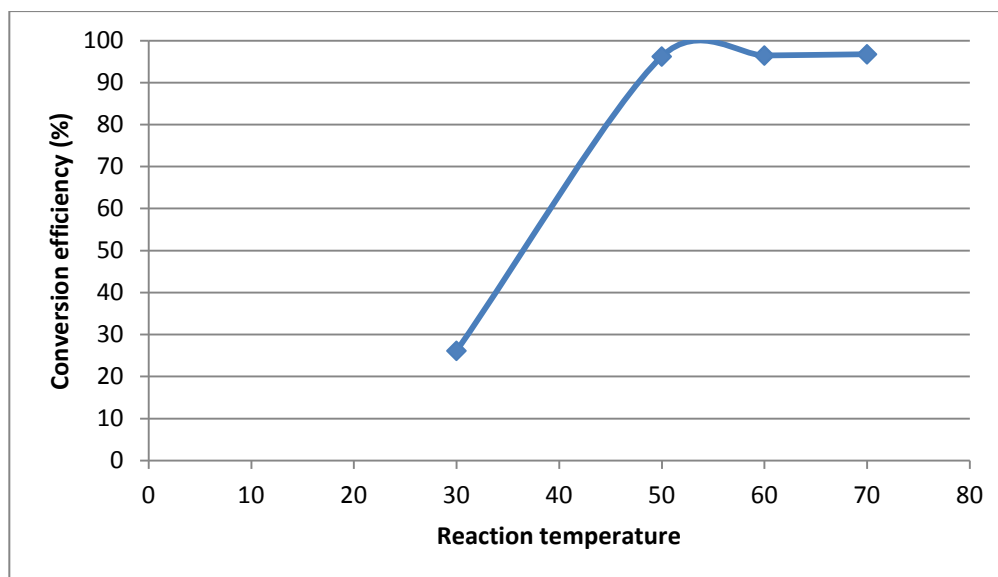


Figure 4.3: Graph of reaction temperature vs conversion efficiency (Oil:ethanol=1:6 and amount of catalyst= 0.5%)

At room temperature the conversion efficiency is so low that is about 26%. Increasing the reaction temperature tends the reaction took place at a faster rate. But the conversion is the same more or less. This is because, at high temperature, there is a chance of loss of ethanol and increase in darkness of the product. High reaction temperature also increases the production cost biodiesel. Hence, the optimum temperature is 50°C.

4.4.4 Comparison between parameters result

The optimum parameter that obtained by altering the oil to ethanol molar ratio is 1:6. Hence by using the same molar ratio for the next parameter which is the amount of catalyst, the optimum amount of catalyst is found to be 0.5% of catalyst by weight percentage of the oil. So, with 1:6 molar ratios and 0.5% catalyst the effect of

temperature is studied and the optimum temperature found out is 50 to 70°C. But, the conversion efficiency through 50 to 70 °C is more or less the same. Hence the optimum parameters for acid esterification are 1:6 oil to ethanol molar ratio, 0.5% amount of catalyst and at 50°C.

4.5 Base catalyzed transesterification

After removing the impurities of the product of the first step, it is transesterified to mono-esters of fatty acids using alkaline catalyst which is NaOH. The parameters affecting the process such as alcohol to oil molar ratio, catalyst amount and reaction temperature are analyzed. This process uses the same experimental setup as the acid esterification.

In this process, the product from acid esterification is preheated to the required temperature of 50°C. Meanwhile, 0.5% of NaOH by the mass of oil is dissolved in ethanol and it is poured into the flask containing preheated oil. The mixture is heated and stirred for 2 hours. The reaction is stopped and the products are allowed to separate into two layers. The lower layer, which contained impurities and glycerol, is drawn off. Methyl esters are washed to remove the entrained impurities and glycerol.

The analysis for the thistransesterification is done with viscosity reduction, theoretical conversion and GC-MS analysis. Theoretical conversion equation is,

$$\textit{Theoretical conversion, } x = \frac{1}{3} X \frac{M_{FAEE}/303}{M_{RSO}/878}$$

4.5.1 Effect of ethanol to oil molar ratio

The alcohol used in this reaction was ethanol. For study the effect of ethanol to oil molar ratio, temperature and amount of catalyst is held constant as you can see in figure 4.4. Graph of molar ratio to the conversion efficiency is plotted.

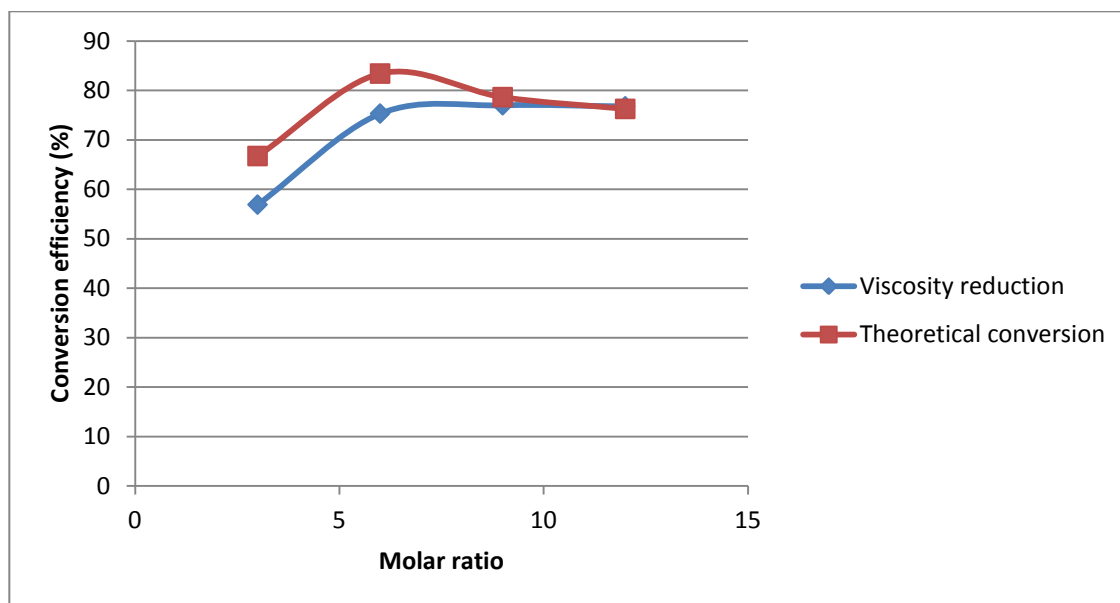


Figure 4.4: Graph of molar ratio vs conversion efficiency (Temperature=50°C and amount of catalyst= 0.5%)

The amount of ethanol required for esterification is analyzed in terms of the molar ratio. Stoichiometrically, the ethanol to triglyceride molar ratio is 3:1. But, in practice this is not sufficient to complete the reaction. Hence, higher molar ratio is used to drive the reaction to completion at a faster rate. The effect of molar ratio on conversion efficiency is shown above.

The pattern showed by viscosity reduction analysis method is increasing at first and more or less constant after the molar ratio of 1:6. The same pattern is observed for the theoretical conversion. Comparing the two methods shows that at molar ratio 1:6, high conversion of oil to biodiesel could achieve. Final product contains two layers which is biodiesel and glycerol. Biodiesel is separated from the mixture by using

separating funnel. The obtained biodiesel still contains excess amount of ethanol. Hence, the excess ethanol moves over the ester layer. The excess ethanol removed by washing with low concentrated HCL acid.

4.5.2 Effect of base catalyst amount

The catalyst used in this reaction is sodium hydroxide, NaOH. The amount of catalyst is increased from 0.1% of the oil to 1.5% of the oil. Temperature and molar ratio is held constant throughout the reaction. The catalyst is diluted with ethanol first before pour into the oil. Graph of catalyst amount to conversion efficiency is plotted.

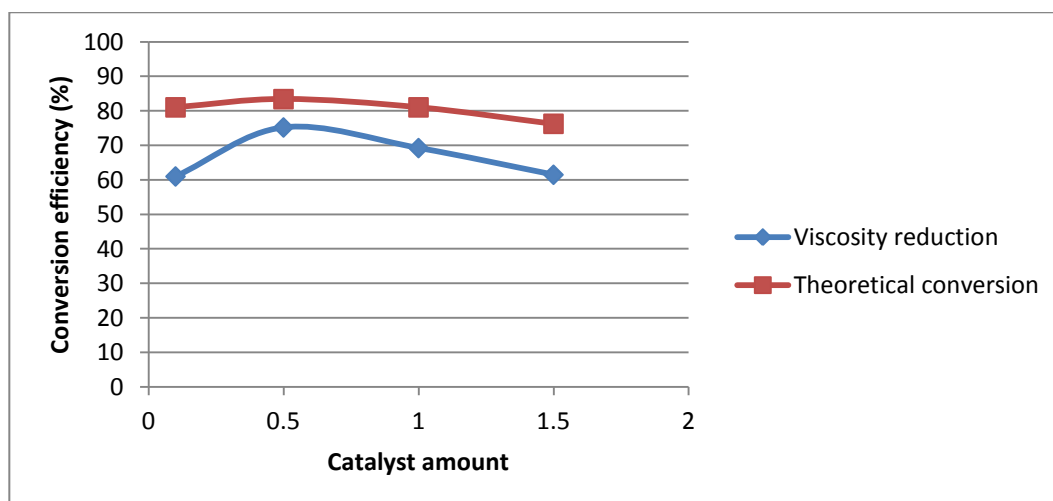


Figure 4.5: Graph of catalyst amount vs conversion efficiency (Temperature=50°C and oil:ethanol=1:6)

From the graph above, it can be concluded that the maximum conversion efficiency is achieved at 0.5%. Addition of excess amount of catalyst, gave rise to the formation of an emulsion, which in increased the viscosity and let to the formation of gels. Esterification does not take place for insufficient amount of NaOH addition.

4.5.3 Effect of reaction temperature

Temperature is changed from 30°C to 70°C to study the effect of temperature. Graph of catalyst amount to conversion efficiency is plotted.

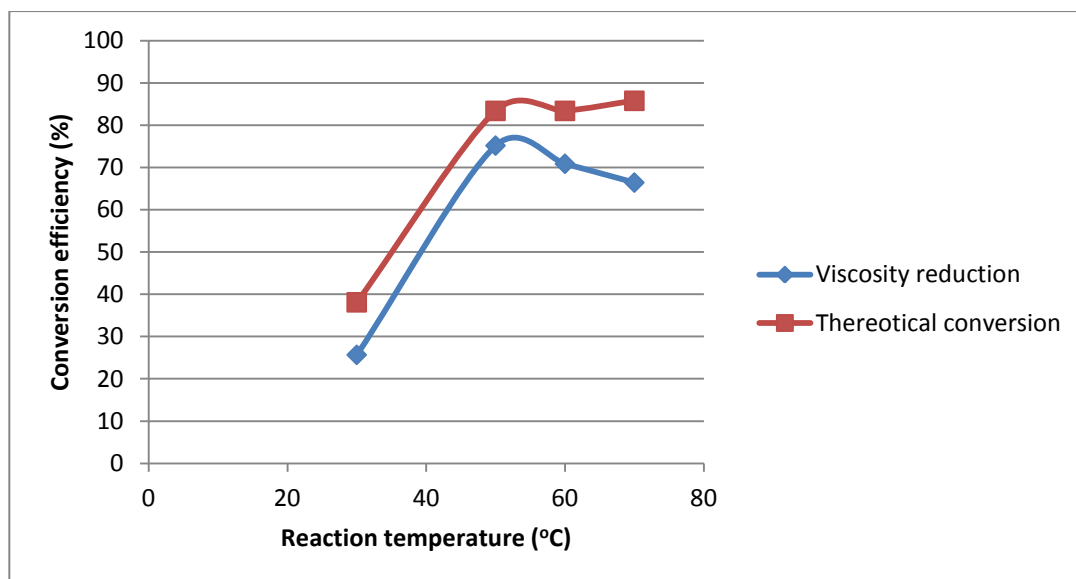


Figure 4.6: Graph of reaction temperature vs conversion efficiency (Oil:ethanol=1:6 and amount of catalyst= 0.5%)

The viscosity reduction method shows a linear increase of conversion by increasing the temperature. The conversion is more or less the same from 50°C to 70°C. The optimum temperature is chosen as 50°C due to the production cost if high temperature involved.

The theoretical conversion at room temperature is much more lower compared to the above method. It can be concluded that there is slow reaction happening at that temperature. At 50°C, the conversion is the high and it decreases slowly as temperature increases. Hence, the optimum temperature is 50°C.

4.5.4 Comparison between the parameters result

The optimum parameter that obtained by altering the oil to ethanol molar ratio is 1:6. Hence by using the same molar ratio for the next parameter which is the amount of catalyst, the optimum amount of catalyst is found to be 0.5% of catalyst by weight percentage of the oil. So, with 1:6 molar ratios and 0.5% catalyst the effect of temperature is studied and the optimum temperature found out is 50 to 70°C. But, the conversion efficiency through 50 to 70 °C is more or less the same. Hence the optimum parameters for base esterification are 1:6 oil to ethanol molar ratio, 0.5% amount of catalyst and at 50°C.

4.6 Physical-Chemical properties of biodiesel

The physical- chemical properties of biodiesel is studied via viscosity, specific gravity, color of the oil and acid value(FFA Weight%). The results are shown in the table 4.3.

Table 4.3: Properties of biodiesel

Properties	Rubber seed oil ethyl ester	Biodiesel Standard(ASTM)	Diesel
Color	Dark brown		
Specific gravity at 25 ⁰ C	0.884	0.88(at15.5°C)	0.85(at15.5°C)
Viscosity mm ² /s at 40 ⁰ C	5.92	1.9 - 6.0	1.3 - 4.1
FFA Weight%	0.45	>0.08	-
Flash point (°C)	120 ^a	100-170	60 – 80
Cloud point (°C)	3 ^a	-3 to 12	-15 to 5
Pour point (°C)	-5 ^a	-15 to 10	-35 to -15

^aCalculated from biodiesel properties reported by MaksudurR Khan et al.[5]

4.6.1 Gas Chromatography Analysis (GC-MS)

(Parameter: 1:6 molar ratio, 0.5% catalyst, 50°C)

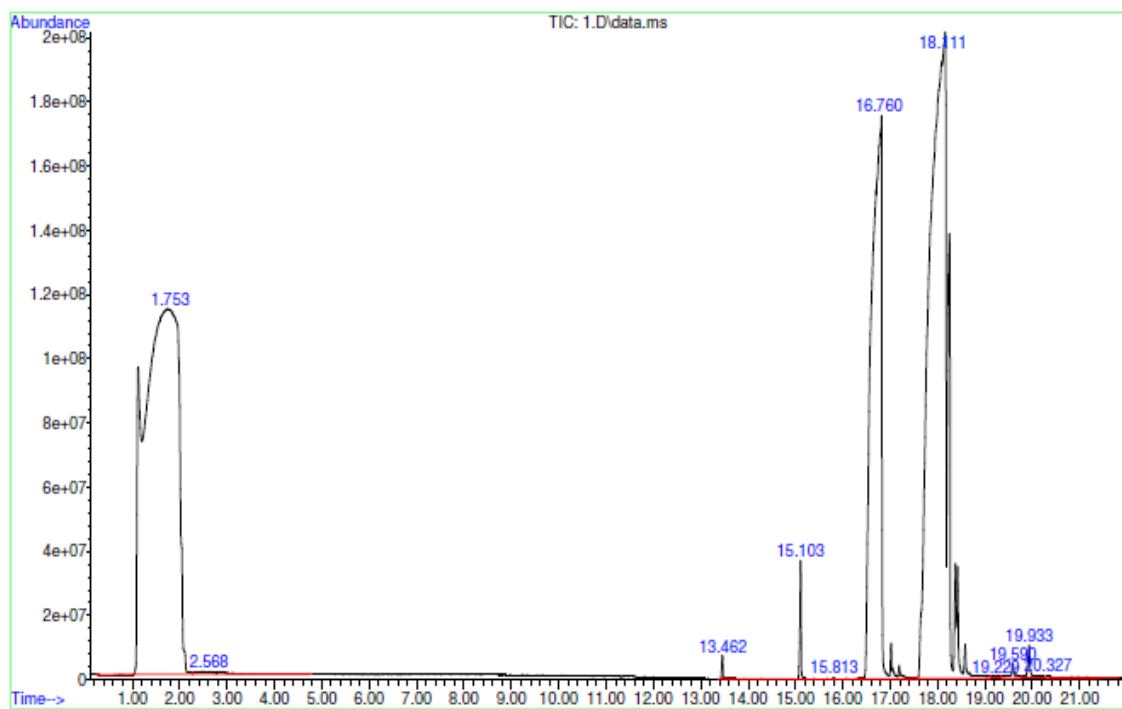


Figure 4.7: GC analysis

Table 4.4: GC analysis peak and its substance

Peak	Retention time	Substance	Composition
1	1.753	Oxirane, 1-propene	0.4119
2	2.568	Propane	0.0032
3	13.462	Dodecanoicacid,Decanoic acid	0.0010
4	15.103	Methyl tetradecanoate, Tridecanoic acid, Methyl tetradecanoate	0.0048
5	15.813	1-Pentanamine, Urea, Acetamide	0.0002
6	16.760	Hexadecanoic acid, Pentadecanoic acid	0.1891
7	18.111	Octadecenoic acid	0.3829
8	19.229	Oleylamine,8-Diaminooctane, Glycyl-dl-alanine	0.0006

9	19.590	Glycine, Cyclopentanemethanamine	0.0020
10	19.933	Eicosanoic acid	0.0031
11	20.327	Cyclopentanemethanamine	0.0013
Total			1.0001

CHAPTER 5

CONCLUSION

5.1 Conclusion

As a conclusion, it can be concluded that the optimum temperature for acid esterification is 1:6 molar ratio, 0.5% amount of catalyst and 50°C. The optimum temperature for base catalyzed transesterification is also 1:6 molar ratio, 0.5% amount of catalyst and 50°C. The analysis of the obtained biodiesel shows a promising comparison with ASTM Standard biodiesel properties. Hence, the rubber seed that obtained from Malaysia is a good source for the production of biodiesel.

5.2 Recommendation

As a recommendation, the different origin has different values of FFA in rubber seed. Hence, comparison should be made to know which origin have the optimum percentage of FFA. Chemicals used in this experiment are hazardous. Hence, proper safety measurement must involve during experiment.

REFERENCES

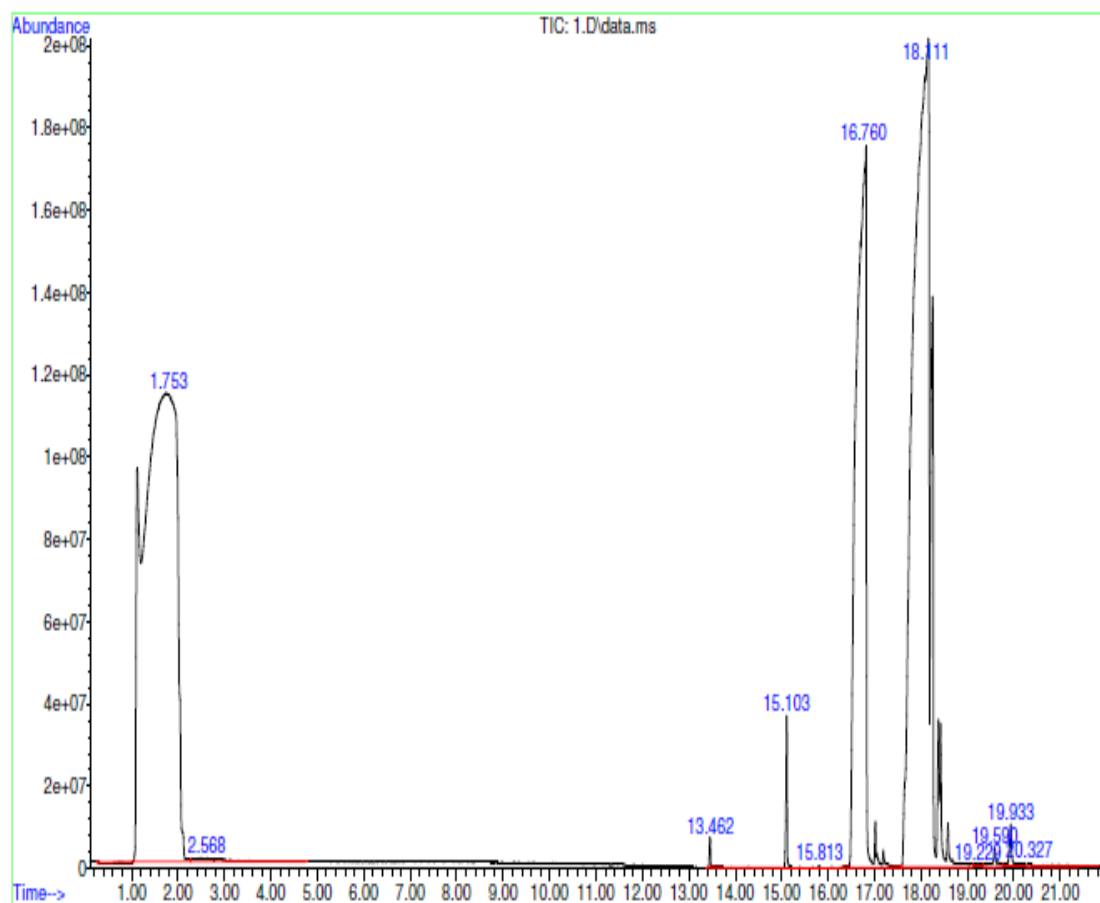
- [1] Amish P. Vyas, Jaswant L. Verma, N. Subrahmanyam, (2009) *A review on FAME production processes*, Fuel, pg 4-10
- [2] Ramadhas AS, Jayaraj S, Muraleedharan C., (2005) *Biodiesel production from high FFA rubber seed oil*, Fuel, pg 22-27
- [3] JoonChing Juan a, Damayani Agung Kartika a, Ta Yeong Wu b, Taufiq-Yap Yun Hin c, (2005) *Biodiesel production from jatropha oil by catalytic and non-catalytic approaches: An overview*, Bioresource Technology, pg 7-11
- [4] Man Kee Lam, Keat Teong Lee, Abdul Rahman Mohamed, (2010) *Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review*; Biotechnology Advances, pg 4-7
- [5] Maksudur R Khan, (2011) *Rubber seed as the a potential source for biodiesel production in Bangladesh*, Fuel, pg 2-6
- [6] Qing Shu, Zeeshan Nawaz, Jixian Gao, Yuhui Liao, Qiang Zhang, Dezheng Wang, Jinfu Wang ; (2010) *Synthesis of biodiesel from a model waste oil feedstock using a carbon-based solid acid catalyst: Reaction and separation*; Bioresource Technology, pg 11-19
- [7] A. F. Iyayi, P. O. Akpaka and U. Ukpeoyibo; (2008) *Rubber seed processing for value-added latex production in Nigeria*; Research Paper, pg 7-18
- [8] I Wayan Susilaa , Orchidea Rachmaniaha, and M. Rachimoellaha, (2010) *Biodiesel from Crude Rubber Seed Oil (CRSO)-Hevea brasiliensis sp. via non-catalytic*

- Process Reaction*, The 1 International Seminar on Fundamental & Application Of Chemical Engineering,pg 6- 15
- [9] Tang, Z., Wang, L., Yang, J.,(2007)*Transesterification of the crude Jatropha curcas L. oil catalyzed by micro-NaOH in supercritical and subcritical methanol*, Eur. J. Lipid Sci. Technol,pg 12- 16
- [10] Jacobson Kathlene, Gopinath Rajesh, MeherLekhaCharan, Dalai Ajay Kumar, Solid acid catalyzed biodiesel production from waste cooking oil. ApplCatalB: Environ (2008) 23- 29
- [11] Wang Z, Zhuge J, Fang H, Prior BA. *Glycerol production by microbialfermentation: a review*. BiotechnolAdv 2001;19:201–23.
- [12] Whittington T. *Biodiesel production and use by farmers: is it worthconsidering?* Western Australia: Department of Agriculture and Food;2006.
- [13] Duncan J.,(2007) *Cost of biodiesel production, energy efficiency, .NBB.Biodiesel production and quality*.Fuel fact sheets. USA: NationalBiodiesel Board.
- [14] Gerpen JV.(2005) *Biodiesel processing and production*, Fuel Process Technology ;pg 86:1097–107.
- [15] Cooke BS, Abrams C, Bertram B.,(2005) *Purification of biodiesel with adsorbentmaterials*,pg 3-8
- [16] Gabelman A, Hwang S.,(1999) *Hollow fiber membrane contactors*,J MembrSci;pg 159:61–106.
- [17] He H, Guo X, Zhu S.,(2006) *Comparison of membrane extraction with traditionalextraction methods for biodiesel production*,J Am Oil ChemSoc;pg 83:457–60.

- [18] Predojevic ZJ.,(2008) *The production of biodiesel from waste frying oils: a comparison of different purification steps.* Fuel,pg 87:3522–8.
- [19] Karaosmanoglu F, Cigizoglu KB, Tuter M, Ertekin S.,(1996) *Investigation of therefining step of biodiesel production,*Energy Fuels,pg 10:890–5.
- [20] Canakci M, Van Gerpen J.,(2001) *Biodiesel production from oils and fats with highfree fatty acids,* Trans Am Soc Agric Eng,pg 44:1429–36.
- [21] Berrios M, Skelton RL.,(2008) *Comparison of purification methods for biodiesel,*.ChemEng J,pg 144:459–65.

APPENDIX A

File :D:\Data\psm2011\maksudur 11jan\1.D
Operator : fizalljan
Acquired : 11 Jan 2012 16:01 using AcqMethod RSO.M
Instrument : GCMSD
Sample Name: 1
Misc Info :
Vial Number: 1



Appendix A: GC analysis for 1:6 RSO to ethanol molar ratio, 0.5% amount of catalyst and 50°C

APPENDIX B

Library Search Report

Data Path : D:\Data\psm2011\maksudur 11jan\
 Data File : 1.D
 Acq On : 11 Jan 2012 16:01
 Operator : fizalljan
 Sample : 1
 Misc :
 ALS Vial : 1 Sample Multiplier: 1

Search Libraries: C:\Database\NIST05a.L Minimum Quality: 0

Unknown Spectrum: Apex
 Integration Events: ChemStation Integrator - autoint1.e

Pk#	RT	Area%	Library/ID	Ref#	CAS#	Qual
1	1.754	41.19	C:\Database\NIST05a.L			
			Oxirane, (1-methylbutyl)-	7357	053229-39-3	50
			1-Propene, 2-methyl-	183	000115-11-7	42
			Oxirane, (1-methylbutyl)-	7360	053229-39-3	40
2	2.566	0.32	C:\Database\NIST05a.L			
			Propane	79	000074-98-6	2
			Propane	78	000074-98-6	2
			Propane	77	000074-98-6	2
3	13.461	0.10	C:\Database\NIST05a.L			
			Dodecanoic acid, methyl ester	67169	000111-82-0	81
			Dodecanoic acid, methyl ester	67168	000111-82-0	74
			Decanoic acid, methyl ester	47245	000110-42-9	64
4	15.106	0.48	C:\Database\NIST05a.L			
			Methyl tetradecanoate	86750	000124-10-7	96
			Tridecanoic acid, 12-methyl-, methyl ester	86778	005129-58-8	94
			Methyl tetradecanoate	86753	000124-10-7	93
5	15.811	0.02	C:\Database\NIST05a.L			
			1-Pentanamine	1874	000110-58-7	9
			Urea, methyl-	756	000598-50-5	9
			Acetamide, N-ethyl-	1849	000625-50-3	7
6	16.762	18.91	C:\Database\NIST05a.L			
			Hexadecanoic acid, methyl ester	105639	000112-39-0	87
			Pentadecanoic acid, 14-methyl-, methyl ester	105659	005129-60-2	60
			Pentadecanoic acid, 13-methyl-, methyl ester	105660	005487-50-3	53
7	18.108	38.29	C:\Database\NIST05a.L			
			9-Octadecenoic acid, methyl ester, (E)-	122326	001937-62-8	99
			9-Octadecenoic acid, methyl ester	122299	002462-84-2	99
			8-Octadecenoic acid, methyl ester	122297	002345-29-1	99
8	19.230	0.06	C:\Database\NIST05a.L			
			Oleylamine	103449	000112-90-3	7
			1,8-Diaminooctane	20253	000373-44-4	5
			Glycyl-dl-alanine	20923	000926-77-2	4
9	19.593	0.20	C:\Database\NIST05a.L			
			1-Azacyclononan-2-one	18380	000935-30-8	9
			Glycine, furan-2-yl-methyl ester	26828	1000306-78-7	7
			Cyclopentanemethanamine, 2-amino-	7186	021544-02-5	7
10	19.935	0.31	C:\Database\NIST05a.L			
			Eicosanoic acid, methyl ester	140314	001120-28-1	99
			Eicosanoic acid, methyl ester	140312	001120-28-1	99
			Eicosanoic acid, methyl ester	140313	001120-28-1	99
11	20.330	0.13	C:\Database\NIST05a.L			
			Cyclopentanemethanamine, 2-amino-	7186	021544-02-5	9
			1-Dodecanamine	46744	000124-22-1	9
			1,8-Diaminooctane	20253	000373-44-4	7

Appendix B: Composition from GC Analysis

APPENDIX C-1

Ethanol to CRISO molar ratio	1:3	1:6	1:9	1:12
Temperature (°C)	50	50	50	50
Amount of catalyst (g)	0.5	0.5	0.5	0.5
Initial Concentration of FFA (mol/dm ³)	0.000854	0.000854	0.000854	0.000854
Final Concentration of FFA (mol/dm ³)	0.000162223	3.21536E-05	2.79651E-05	2.70291E-05
Conversion efficiency (%)	80.99579	96.23325	96.72392	96.83358

Appendix C-1: Effect of oil to ethanol molar ratio (Temperature= 50°C and amount of catalyst = 0.5% was held constant)

APPENDIX C-2

Ethanol to CRSO molar ratio	1:6	1:6	1:6	1:6
Temperature (°C)	50	50	50	50
Amount of catalyst (g)	0.1	0.5	1.0	1.5
Initial Concentration of FFA (mol/dm ³)	0.000854	0.000854	0.000854	0.000854
Final Concentration of FFA (mol/dm ³)	0.000328599	3.21536E-05	0.000130358	0.000178891
Conversion efficiency (%)	61.50509	96.23325	84.72876	79.04316

Appendix C-2:Effect of amount of catalyst over conversion(Temperature= 50°C
and oil:ethanol=1:6 was held constant)

APPENDIX C-3

Ethanol to CRSO molar ratio	1:6	1:6	1:6	1:6
Temperature (°C)	30	50	60	70
Amount of catalyst (g)	0.5	0.5	0.5	0.5
Initial Concentration of FFA (mol/dm ³)	0.000854	0.000854	0.000854	0.000854
Final Concentration of FFA (mol/dm ³)	0.000630455	3.21536E-05	3.01609E-05	2.76361E-05
Conversion efficiency (%)	26.14293	96.23325	96.46668	96.76246

Appendix C-3: Effect of reaction temperature (Oil:ethanol=1:6 and amount of catalyst = 0.5% was held constant)

APPENDIX D-1

Oil to ethanol molar ratio	1:3	1:6	1:9	1:12
Temperature (°C)	50	50	50	50
Amount of catalyst (g)	0.5	0.5	0.5	0.5
Analysis method: Viscosity reduction				
Initial viscosity	23.9	23.9	23.9	23.9
Final viscosity	10.3	5.9	5.5	5.55
Viscosity reduction (%)	56.9	75.31	76.99	76.78
Analysis method: Theoretical conversion				
Initial Concentration of TG(mol/dm ³)	0.137	0.137	0.137	0.137
Final Concentration of TG (mol/dm ³)	0.092	0.114	0.108	0.105
Conversion efficiency (%)	66.72	83.40	78.63	76.25

Appendix D-1: Effect of oil to ethanol molar ratio (Temperature= 50°C and amount of catalyst = 0.5% was held constant)

APPENDIX D-2

Oil to ethanol molar ratio	1:6	1:6	1:6	1:6
Temperature (°C)	50	50	50	50
Amount of catalyst (g)	0.1	0.5	1.0	1.5
Analysis method: Viscosity reduction				
Initial viscosity reduction	23.86503	23.86503	23.86503	23.86503
Final viscosity reduction	9.307746	5.920855	7.34562	9.192456
Conversion efficiency (%)	60.99839	75.19025	69.22015	61.48148
Analysis method: Theoretical conversion				
Initial Concentration of TG(mol/dm ³)	0.13714286	0.13714286	0.13714286	0.13714286
Final Concentration of TG (mol/dm ³)	0.11111111	0.11437908	0.11111111	0.10457516
Conversion efficiency (%)	81.01852	83.40142	81.01852	76.25272

Appendix D-2: Effect of amount of catalyst over conversion (Temperature= 50°C and oil:ethanol=1:6 was held constant)

APPENDIX D-3

Oil to ethanol molar ratio	1:6	1:6	1:6	1:6
Temperature (°C)	30	50	60	70
Amount of catalyst (g)	0.5	0.5	0.5	0.5
Analysis method: Viscosity reduction				
Initial viscosity reduction	23.86503	23.86503	23.86503	23.86503
Final viscosity reduction	17.73325	5.920855	6.946058	8.007714
Conversion efficiency (%)	25.69358	75.19025	70.89441	66.44582
Analysis method: Theoretical conversion				
Initial Concentration of TG(mol/dm ³)	0.13714286	0.13714286	0.13714286	0.13714286
Final Concentration of TG (mol/dm ³)	0.10784314	0.11437908	0.11437908	0.11764706
Conversion efficiency (%)	78.63562	83.40142	83.40142	85.78431

Appendix D-3: Effect of reaction temperature (Oil:ethanol=1:6 and amount of catalyst = 0.5% was held constant)

APPENDIX E

	Density, g/ml
CRSO	0.945
Oil from Acid catalyzed transesterification(Optimum parameters)	0.891
Effect of Oil: Ethanol(molar ratio) (Temperature= 50°C and amount of catalyst = 0.5% held constant)	
1:3	0.892
1:6	0.884
1:9	0.924
1:12	0.956
Effect of amount of catalyst (%) (Temperature= 50°C and Oil: Ethanol(molar ratio)=1:6 held constant)	
0.1	0.865
0.5	0.884
1.0	0.892
1.5	0.91
Effect of reaction temperature (Oil: Ethanol(molar ratio)=1:6 and amount of catalyst = 0.5% held constant)	
30	0.873
50	0.884
60	0.891
70	0.935

Appendix E: Density readings

APPENDIX F

	Density, g/ml
CRSO	33.43
Oil from Acid catalyzed transesterification(Optimum parameters)	23.865
Effect of Oil: Ethanol(molar ratio) (Temperature= 50°C and amount of catalyst = 0.5% held constant)	
1:3	10.3
1:6	5.9
1:9	5.0
1:12	5.5
Effect of amount of catalyst (%) (Temperature= 50°C and Oil: Ethanol(molar ratio)=1:6 held constant)	
0.1	9.30775
0.5	5.92086
1.0	7.34562
1.5	9.19246
Effect of reaction temperature (Oil: Ethanol(molar ratio)=1:6 and amount of catalyst = 0.5% held constant)	
30	17.7332
50	5.92086
60	17.7332
70	17.7332

Appendix F: Viscosity readings

APPENDIX G

ETHANOL-MSDS

Identification**Product Name:** Ethanol**Other Names:** Ethanol, Ethyl alcohol**Product Code:** 10476**UN Number:** 1170**Dangerous Goods Class &Subsidiary Risk:** 3**Hazchem Code:** 2SE**Poisons Schedule Number:** None allocated**Use:** General laboratory reagent EEC #: 200-578-6**Packaging Group:** II**Physical Description and Properties****Form:** liquid**Boiling point:** 78 °C**Melting point:** -117 °C**Vapor pressure:** (20 °C) ~ 59 mbar**Flashpoint (Open Cup):** 12 °C**Upper flammability limit:** 15 Vol%**Lower flammability limit:** 3.5 Vol%**Solubility in Water:** water (20 °C) soluble**Ignition temperature:** 425 °C**Colour:** colourless**Odour:** characteristic**Vapor density:** 1.59**Density:** (20 °C) 0.81 g/cm³**Other information:** Highly flammable.**Conditions and substances to be avoided:**

Conditions to be avoided

Strong heating: - (Explosible with air in a vaporous/gaseous state.)

Substances to be avoided

alkali metals, alkaline earth metals, alkali oxides, strong oxidizing agents.

Health Hazard Information:

Toxicological information:

Acute toxicity

LD50 (oral, rat): 7060 mg/kg Sub acute to chronic toxicity

An embryo toxic effect need not be feared when the threshold limit value is observed.

After inhalation of vapors:

Slight mucosal irritations. Risk of absorption.

After eye contact:

Slight irritations.

After ingestion of large amounts: nausea and vomiting. Systemic effect: euphoria. After absorption of large quantities: dizziness, inebriation, narcosis, respiratory paralysis.

After ingestion:

After ingestion: Damage to: mucous membrane. Rapid absorption.

First Aid Information:

Eye contact:

Rinse out with plenty of water with the eyelid held wide open.

Inhalation:

Fresh air. Consult doctor if feeling unwell.

Skin contact:

Wash off with plenty of water. Remove contaminated clothing.

Ingestion:

Drink plenty of water. Induce vomiting. No emetics. No animal charcoal.

Advice to doctors:

Treat symptomatically.

Engineering controls:

Person-related precautionary measures: Do not inhale vapours/aerosols.
Procedures for cleaning / absorption: Take up with liquid-absorbent material. Forward for disposal. Rinse away remainder with water.

Personal protection**Respirator:**

required when vapours/aerosols are generated. Filter A (acc. to DIN 3181) for vapours of organic compounds
Ensure respirator is clean, well-fitting and in good working order. All respirators should comply with Australian Standard AS 1716 and be used in accordance with AS 1715.

Gloves:

required

Eye protection:

Required

Special risks:

Combustible. Vapours heavier than air. Formation of explosible mixtures possible with air. Take measures to prevent electrostatic charging.

Suitable extinguishing media:

Water, CO₂, foam, powder.

Other precautions:

Change contaminated clothing. Wash hands after working with substance.