

ACTIVATED CEMENT CLINKER CATALYST DEVEPOMENT FOR BIODIESEL PRODUCITON

SHAHID ALI

A thesis submitted in fulfilment of the requirements for the award of the degree of Master of Engineering (Chemical Engineering)

Faculty of Chemical and Natural Resources Engineering UNIVERSITI MALAYSIA PAHANG

June 2013

ABSTRACT

World oil and gas output is expected to pass its peak in the next few years, while demand will go on rising. Renewable sources of energy (e.g. Algae biomass and agricultural crops) can make an important contribution to secure sustainable and diverse energy supplies and are therefore an essential element of a cost-effective climate change program. For now, renewable energy from biodiesel has been touted as one of the most promising substitutions for petroleum-derived diesel. Production of biodiesel is also a proven technology with established commercialization activities. Combustion of biodiesel as fuel is more environment-friendly while retaining most of the positive engine properties of petroleumderived diesel. Currently, the commercially used catalysts like Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH) etc, has given birth to problems like expensive availability, non-recyclability, complex recovery system and saponification problems. Secondly, biodiesel production from edible has being directly contributing to the high costs of vegetable oils. Based on high composition of CaO in the calcinated product of limestone it is selected as the potential candidate for biodiesel production in this research. This research model helps to create a better understanding and awareness towards the value and the importance of using an insoluble heterogeneous Activated Cement Clinker Catalyst (ACCC), with a simple activation process that avoids the saponification problem, easily recoverable from a reaction mixture without washing or neutralization and the catalytic activity is not negatively affected by the free fatty acids and the catalyst material is easily recycled for use in subsequent catalytic reactions. The catalyst after dispersing in methanol and thermal activation shows immense increase in the surface area. The research was being carried out to analyze the effect of ACCC on conventional and microwave assisted biodiesel production. The ideal reaction conditions to get 96.80% of conversion were methanol to oil, molar ratio, 5:1; catalyst concentration used, 6 wt %; reaction temperature of 55°C and retention time of 50 mins for microwave assisted transesterification (MAT), while, at temperature of 60°C and a retention time of 80 min for conventional method from rubber seed oil (RSO). Catalyst analyzed for surface area by Surface Analyzer shows a decline in its surface area as the catalyst proceeds through recycling and reusing process, with surface area of 59.5 m²/gm at the first cycle and 13.54 m²/gm at the fifth cycle. The biodiesel produced is within the limits being described by ASTM D 6571.

ABSTRAK

Sumber minyak dan gas dunia dijangka akan melepasi tahap pengeluarannya dalam beberapa tahun mendatang, namun permintaan sumber itu semakin meningkat. Sumber tenaga yang boleh diperbaharui (contohnya biomas Alga dan tanaman pertanian) akan memberikan sumbangan yang penting bagi menjamin bekalan pelbagai tenaga yang berterusan seterusnya menjadi elemen penting yang menjimatkan kos dalam program perubahan tersebut. Sehingga kini, tenaga yang boleh diperbaharui daripada biodiesel berjaya menggantikan diesel daripada sumber petroleum. Penghasilan biodiesel juga membuktikan kejayaan dan pengiktirafan teknologi yang ada dengan penghasilannya yang telah dikomersialkan. Penggunaan biodiesel sebagai sumber bahan api adalah lebih mesra alam sekitar disamping mengekalkan sifat-sifat yang sama seperti petrodiesel. Pada masa ini, pemangkin yang digunakan secara komersial seperti Natrium Hidroksida (NaOH), Kalium Hidroksida (KOH) dan sebagainya mempunyai masalah seperti harga pemangkin yang mahal, tidak dapat dikitar semula, sistem pengasingan pemangkin yang kompleks dan penghasilan sabun semasa tindakbalas. Tambahan lagi, penghasilan biodiesel daripada sumber makanan telah menyebabkan kenaikan harga pada minyak sayuran. Berdasarkan kepada komposisi Kalsium Oksida (CaO) yang tinggi dalam batu kapur yang dibakar membuktikan ianya berpotensi menjadi pemangkin proses penghasilan biodiesel dalam kajian ini. Model kajian ini akan memberi pemahaman dan kesedaran yang lebih baik tentang potensi dan kepentingan menggunakan pemangkin tidak larut Klinker Simen yang Diaktifkan (ACCC), dengan proses pengaktifan yang mengelakkan penghasilan sabun, memudahkan pengasingan pemangkin daripada campuran tindakbalas tanpa memerlukan proses pembersihan atau peneutralan dan aktiviti pemangkin tidak direncatkan oleh kandungan asid lemak bebas dan sisa pemangkin boleh diguna semula untuk tindakbalas seterusnya. Pemangkin yang telah diaktifkan dengan metanol dan pengaktifan haba menunjukkan peningkatan yang lebih baik dari segi luas permukaan. Kajian ini telah dijalankan untuk mengenalpasti kesan ACCC terhadap penghasilan biodiesel melalui proses konvensional dan micro. Keadaan tindak balas yang ideal untuk mendapatkan 96.80% biodiesel adalah menggunakan nisbah metanol dan minyak, 5:1; kepekatan pemangkin, 6% mengikut berat; suhu tindakbalas pada 55°C dan masa tindakbalas pada 50 minit untuk proses penghasilan ester dengan tenaga mikro (MAT), manakala, pada suhu 60°C dan masa tindakbalas 80 minit bagi kaedah konvensional daripada minyak biji getah (RSO). Pemangkin yang dianalisis bagi menentukan luas permukaan menggunakan Surface Analyzer menunjukkan penurunan di kawasan permukaan selepas dikitarsemula dan diguna semula dengan luas permukaan sebanyak 59.5 m²/gram pada kitaran pertama dan 13.54 m²/gram pada kitaran kelima. Biodiesel yang dihasilkan dalam kajian ini telah memenuhi spesifikasi penghasilan biodiesel ASTM D 6571.

TABLES OF CONTENTS

Page

SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
DEDICATION	iv
ACKNOWLEDGEMENTS	v
ÀBSTRACT	vi
ABSTRAK	vii
TABLE OF CONTENTS	viii
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF SYMBOLS/ABBREVIATIONS	xiv

CHAPTER 1 INTRODUCTION

1.1	Overview	1
1.2	History of biodiesel	1
1.3	Background	3
1.4	Hypothesis of Research	5
1.5	Problem statement	5
1.6	Research objectives	5
1.7	Scope of research	5
1.8	Organization of thesis	6

CHAPTER 2 LITERATURE REVIEW

2.1	Introduction	8
	2.1.1 The origin of biodiesel	13
	2.1.2 Biodiesel development in Malayisa	16
	2.1.3 Trends towards commercial scale production	20
2.2	Constraints and concerns related to biodiesel industry	22
2.3	Biodiesel feedstock options	23
2.4	Rubber plantation and rubber seed oil in Malaysia	26
	2.4.1 Abundance of raw material	29

	2.4.2 2.4.3 2.4.4		30 32 34
2.5	Cataly	est for biodiesel production	36
	2.5.1 2.5.2	Homogeneous catalyst for biodiesel production Heterogeneous catalyst	37 37
2.6	Micro	wave Technology	41
	2.6.1	Microwave Assisted Extraction	42
	2.6.2	Microwave Assisted Biodiesel Production	42
2.7	Future	e Opportunities	43
2.8	Challe	enges To Be Faced In The Rubber Biodiesel Industry	44
	2.8.1	Supply Chain	45
	2.8,2	Preferred Technology	45
	2.8.3	Research and Development	46
	2.8.4	Government Support	47
	2.8.5	Public Support	48
2.9	Recor	nmendations	49
2.10			52

ix

CHAPTER 3 MATERIALS AND METHODS

3.1	Introduction	53	
3.2	Research Methodology Layout		
3.3	Plant Material	54	
3.4	Soxhlet Extraction Process	54	
3.5	Microwave Assisted Extraction (MAE)	56	
3.6	Solvent Seperation	57	
3.7	Characterization of RSO	58	
	3.7.1 Determination of Acid Value	58	
	3.7.3 Determination of Kinematic Viscosity	59	
	3.7.4 Functional Group Analysis	60	
	3.7.5 Tri-glycerides (TAG) analysis of RSO	60	
3.8	Lime Stone based Catalyst	61	
	3.8.1 Catalyst Activation	61	
	3.8.2 Surface Area Analysis of Clinker Catalyst	64	
3.9	Transesterification Process	64	
	3.9.1 Microwave Assisted Transesterification (MAT) Reaction	64	
	using RSO		

3.10	FAME Analysis of RSO Biodiesel	65
3.11	Properties of RSO and WCO Biodiesel	66

CHAPTER 4 RESULTS AND DISCUSSTION

	4.1	Characteristics of Rubber Seeds	67
		4.1.1 Physical Properties	67
		4.1.2 Moisture content and Oil content Analysis	68
	4.2	Comparison of Microwave assisted and Soxhlet Extraction processes	70
	4.3	Characterization of Rubber Seed Oil	71
		4.3.1 Functional Groups Rubber Seed Oil	71
		4.3.2 MRSO Composition Analysis	72
	4.4	Cement Clinker Catalyst Characterization and Activation	73
		4.4.1 Clinker Characterization	73
		4.4.2 Catalyst Screening and Activation	74
÷	4.5	Microwave Assisted Transesterification reaction using RSO	75
	4.6	Effect of Reaction Conditions on Biodiesel Production	76
		4.6.1 Effect of Methanol to Oil ratio on Percent Conversion	76
		4.6.2 Effect of Catalyst Concentration on Percent Conversion	77
		4.6.3 Effect of Temperature on Percent Conversion	78
		4.6.4 Effect of Reaction time on Percent Conversion	80
		4.6.5 Reaction Efficiency of Microwave irradiation and conventional Bath	81
		4.6.6 Recyclability of Clinker Catalyst and its effect on Percent Conversion	82
	4.7	Leaching effect of Cement Clinker catalyst	84
	4.8	FAME composition Analysis of Rubber Seed Oil Biodiesel	85
	4.9	Biodiesel Purification and Cleaning	86
	4.10	Properties of RSO and WCO Biodiesel	87
	4.11	Advantages of Cement Clinker Catalyzed Transesterification Reaction	

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1	Conclusion	90
5.2	Recommendations	91

х

REFERENCES

AFFEND		
A1	Weight percent calculation for effect of methanol to oil ratio by MAT	102
	process	
A2	Weight percent calculation for effect of catalyst concentration by	103
	MAT process	
A3	Weight percent calculation for effect of methanol to oil ratio (WCO)	117
A4	Weight percent calculation of sodium methoxide loaded cement	118
	clinker catalyst	
B1	GC Analysis for percent area conversion of RSO biodiesel by MAT	104
B1 (A)	GC Analysis for percent area conversion of RSO biodiesel by MAT	105
B2	GC- Spectrum of RSO Biodiesel By Conventional Method	108
B 2 (A)	GC- Analysis for percent area conversion of RSO Biodiesel by	109
	Conventional Method	
C1	List of Awards and Publications	112

92

LIST OF TABLES

Table No.	Title	Page
2.1	The Development of Palm Biofuels in Malaysia	16
2.2	National Biofuel Policy: strategic objectives	18
2.3	List of active and under construction biodiesel plants in Malaysia, 2008	20
2.4	List of suspended and closed biodiesel plants in Malaysia	22
2.5	Planted Hectarage of NR on Estates and Smallholdings in Malaysia	27
2.6	Fatty acid composition of MRSO	28
2.7	Physical and Psychochemical Properties of Malaysian Rubber Seed Oil	29
2.8	Estimated Oil production by major vegetable oil crops including Rubber Seed Oil	30
2.9	Fuel properties of rubber seed methyl ester and diesel fuel	31
2.10	Proximate analysis of Malaysian Rubber seed oil	35
2.11	Amino acid profile of rubber seed	35
2.12	Nutrient requirements of Meat-Type Hens for Breeding Purposes as Units per Hen per Day (90 % dry matter)	36
2.13	List of heterogeneous catalysts developed for biodiesel production	40
3.1	GC-MS parameters for oil composition analysis	61
3.2	GC-MS parameters for FAME analysis for RSO and WCO	65
4.1	The physical properties of Jatropha, Karanja, Castor and Rubber seeds	68
4.2	Moisture and oil content analysis of rubber seeds	68
4.3	Comparison between Soxhlet and Microwave extraction	70
4.4	Properties of Malaysian Rubber Seed Oil	71
4.5	FTIR group analysis of RSO	71
4.6	Fatty Acid composition of Rubber Seed Oil	73
4.7	X-ray florescence (with XRD) analysis of CCC	73
4.8	Calcination effect on percent area conversion	74
4.9	FAME composition of microwave assisted biodiesel from rubber seed oil	85
4.11	Biodiesel properties of B100 from RSO	87

LIST OF FIGURES

Figure No.	Title	Page
2.1	Malaysia primary energy supply in 2008	10
2.2	Malaysia total Carbon dioxide emissions from fossil fuels	11
2.3	Reaction scheme for trans-esterification reaction	13
2.4	Biodiesel production from 2005 to 2010	16
2.5	General Cost breakdown for biodiesel production	24
3.1	Reasearch methodology	54
3.2	Rubber Seeds	55
3.3	Soxhlet Extraction Apparatus	55
3.4	Milestone Ethose E Microwave Solvent Extraction Labstation	56
3.5	Milestone's ETHOS E Compact terminal bright screen display	57
3.6	BUCHI Rotavapor R-200	58
3.7	Extracted Rubber Seed Oil	58
3.8	Process flow diagram for clinker preparation and characterization	63
4.1	Extraction process of oil from crushed rubber seeds	69
4.2	IR Spectral Interpretation of RS	72
4.3	SEM pictures of the 3 wt% activated cement clinker	75
4.4	Effect of methanol to oil ratio of 4 wt% clinker catalyst, at 55°C for a period of 45 minutes at 200KW power	77
4.5	Effect of catalyst amount on conversion rate with 5:1; methanol to oil ratio and at 55°C for a period of 45 minutes at 200 W power	78
4.6	Smaller particles of the limestone based catalyst (higher than 6 wt%) adhered together	79
4.7	Effect of temperature on conversion rate at 200 W power, with 5:1 methanol to oil ratio and 6.0 wt. % of catalyst for 45 mins	79
4.8	Effect of time on conversion rate, at a temperature of 60°C, with 5:1 methanol to oil ratio and 6wt. % catalyst	80
4.9	Effect of MAT and conventional bath on conversion rate of MRSO	81
4.10	Effect of catalyst recyclability on conversion rate, at 60°C with methanol to oil ratio of 5:1 and 6 wt. % of catalyst at 200 W	82
4.11	SEM images of Catalyst recycling process	83
4.12	X-Ray Diffraction Compositon Analysis of CCC	84
4.13	G-C analysis of FAME of rubber seed oil	85
4.14	Water washing of clinker catalyzed RSO Biodiesel	86
4.15	Process flow diagram for microwave assisted biodiesel production using cement clinker catalyst	89

xiii

LIST OF SYMBOLS/ABBREVIATIONS

Wt%	Weight percent
Min	Minutes
G	Gram
°C	Degree Centigrade
ml	Milliliter
ASTM	American Society for Testing and Materials
КОН	Potassium Hydroxide
RSO	Rubber Seed Oil
WCO	Waste cooking oil
FTIR	Fourier Transform Infrared Radiation
MRSO	Malaysian Rubber Seed Oil
F.A	Fatty Acid
Mol. Wt.	Molecular Weight
% A.C	Percent area compostion
XRD	X-ray Diffraction
CaO	Calcium oxide
SiO ₂	Silicon Dioxide
Al ₂ O ₃	Aluminum Oxide
CO ₂	Carbon dioxide
FAME	Fatty Acid Methyl Ester
CCC	Cement clinker catalyst

MAE	Microwave assisted extraction		
C.M	Conventional method		
TAG	Tri-acylglycerides		
W	Watt		
М	Mole		
HCL	Hydrochoric Acid		
N-Hexane	Normal Hexane		
GC-MS	Gas chromatography mass spectroscopy		
SEM	Scanning Electron Microscopy		
μm	Micro meter		
S.V	Saponification Value		

CHAPTER 1

1.1. OVERVIEW

This chapter describes the background of biodiesel, rubber seed oil, heterogeneous catalyst CaO and microwave assisted biodiesel production. The first part of chapter explains about history of biodiesel. Meanwhile the second part explains a brief background of CaO as a catalyst for production of biodiesel from different type of oils. A thorough introduction about microwave assisted biodiesel production is also explained in this section. Finally for the last part of this chapter, problem statement, objectives and the scope of study are described.

1.2. HISTORY OF BIODIESEL

It is generally recognized that the first era of the 21st century will witness a significant change in focus of the energy supply industry in the world. World oil and gas output is expected to pass its peak in the next few years, while demand will go on rising. Renewable sources of energy (e.g. Algae biomass and agricultural crops) can make an important contribution to securing sustainable and diverse energy supplies and are therefore an essential element of a cost-effective climate change program.

Extensive studies have been conducted for the use oilseeds as a potential source of biofuel. For production of biofuel, mass cultivation of seeds is carried out in various regions of the world. The important fuels synthesized from seeds are vegetable oils.Many countries have implemented high sophisticated techniques for enhancing the production of biodiesel. The idea to use biodiesel or vegetable oils as a fuel for diesel engines is more than a hundred years old and was first proposed by Dr. Rudolf Diesel himself in the early 1900's. One prototype of his new engine presented at the World's Exhibition in Paris in 1900 ran on a fuel derived from peanut oil. However due to the discovery of cheaper mineral oils interest in the use of fuels derived from plant oils diminished. Except for some attempts at utilizing renewable sources during the Second World War it was only in the 1970's that the worldwide oil crises and a growing ecological awareness led to the rediscovery of plant oils and animal fats as possible alternatives to hydrocarbon based fuels.

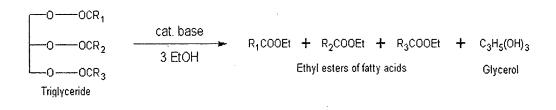
Bio-diesel is a clean burning alternative to mineral diesel fuel that is produced from renewable resources such as animal fats and vegetable oils including but not limited to soy bean oil, palm oil, tallow (animal fat), and used waste cooking oil (WCO) all of which may be referred to generally as fat.

Biodiesel production is the process in which a sample of the cleaned feedstock oil is titrated with a standardized base solution in order to determine the concentration of free fatty acids (carboxylic acid) present in the waste vegetable oil sample. These acids are then either esterified into biodiesel and into bound glycerides, or removed, typically through neutralization.

In the transesterification reaction the base was added in excess to ensure completetransesterification. The calculated quantity of base (usually NaOH) is added slowly to the alcohol and it is stirred until it dissolves. Sufficient alcohol is added to make up three full equivalents of the triglyceride, and an excess of usually six parts alcohol to one part triglyceride is added to drive the reaction to completion.

Triglyceride + MeOH	\rightarrow	Diglyceride	FAME (1)
Diglyceride + MeOH	\rightarrow	Monoglyceride	FAME (2)
Monoglyceride + MeOH	\rightarrow	Glycerol	FAME (3)

A reaction scheme for transesterification is as follow,



Products of the reaction include not only biodiesel, but also byproducts, soap, glycerin, excess alcohol, and trace amounts of water. All of these byproducts must be removed, though the order of removal is process-dependent. The density of glycerin is greater than that of biodiesel, and this property difference is exploited to separate the bulk of the glycerin byproduct by mean of settling or centrifugation. Residual methanol is typically removed through distillation and reused, though it can be washed out (with water) as a waste as well.

1.3. BACKGROUND

The main role in the process of producing Biodiesel from the transesterification reaction of triglycerides with alcohols is played by the catalyst. Several kinds of catalysts have been used for the production of biodiesel. For the production of biodiesel from rubber seed oil with high free fatty acid content, the use of alkaline catalysts such as sodium hydroxide is undesirable because of the formation of relatively large amounts of soaps, leading to product loss and difficulty in the separation and purification of the biodiesel produced (Kouzu et al., 2008).

Using heterogeneous base catalysts rather than homogeneous base catalysts for biodiesel production has some advantages. Heterogeneous base catalysts are reusable, noncorrosive, show greater tolerance to water and free fatty acids (FFAs) in feedstock, improve biodiesel yield and purity, have a simpler purification process for glycerol and are easy to separate from the biodiesel product (Freedman et al., 1986; Schwab et al., 1988; Ma and Hanna, 1999; Hanh et al., 2009; Kildiran et al., 1996). Many heterogeneous catalysts has been developed to cope with the problem (Kawashima et al., 2008; Kouzo et al., 2008; Xie et al., 2006). Calcium oxide (CaO) is one of the most

common used heterogeneous base catalysts for the transesterification of vegetable oil. Producing biodiesel using CaO as a solid base catalyst has many advantages, such as higher activity, mild reaction conditions, reusable, low cost and so on (Koopmans et al., 2006; Mazzocchia et al., 2004).

Liu et al. (2008) examined the transesterification of soybean oil to biodiesel using powder CaO as a solid base catalyst. The results showed a 12:1 molar ratio of methanol to oil, addition of 8 wt.% catalyst, 333 K reaction temperature and 2.03% water content in methanol gave the best results, and the biodiesel conversion rate exceeded 95% at 3 h. Reddy et al. (2006) produced biodiesel using nanopowder calcium oxide (nanoCaO) under room-temperature. However, the reaction rate was low and it required 6–24 h to obtain high conversion after eight cycles with soybean oil and three cycles with poultry fat. Ming et al. carried out the microwave assisted biodiesel conversion rate. Nano powder for 60 minutes at 65°C and obtained 96.6% of conversion rate al., (2009). His work showed that 96.6% of conversion rate can be achieved in 60 mins by using considerably high 7:1 methanol/oil ratio, catalyst 3% wt., at a reaction temperature of 65°C.

Generally biodiesel production uses heating coils to heat up the feedstocks consuming a large amount of energy. Microwave irradiation has been an alternative heating system in transesterification over the past few years. As a result, drastic reductions in the quantity of by-products and a short separation time have been obtained (Hernando et al., 2007). Microwave irradiation also provides a comfortable, safe and clean way of working with chemical reactions (Koopmans et al., 2006). Today, microwave irradiation is widely used in many areas including assisting transesterification of vegetable oils to produce biodiesel (Meng et al., 2009, Azcanand Danisman, 2007; Hsiao et al., 2010). The use of microwave for preperativechemsitry, it is often possible to accelerate reactions and improve selectivity (Mazzocchia et al., 2004; Azcan and Danisman, 2008; Tatlier et al., 2007)

The aim of the present study is to examine the effect of activated cement clinker catalyst on the transesterification of high FFA oil. According to previous studies (Meng

et al., 2009, Colucci et al., 2005; Barnard et al., 2007; Hanh et al., 2008; Tan and Lee, 2008; Koc, 2009), the methanol/ oil molar ratio (Meng et al., 2009; Barnard et al., 2007; Hanh et al., 2008; Tan and Lee, 2008; Koc, 2009) amount of catalyst used (Meng et al., 2009, Colucci et al., 2005; Hanh et al., 2008; Koc, 2009], reaction temperature (Meng et al., 2009; Colucci et al., 2005; Barnard et al., 2007; Hanh et al., 2008) and reaction time were also important factors influencing the transesterification of soybean oil.

1.4. HYPOTHESIS OF RESEARCH

Limestone with highest composition of $CaCO_3$, known as a raw meal undergoes calcination process where the decarbonation occurs at 850°C becomes free CaO. The calcinated product after clinkering contains high composition of CaO and hence, can be a potential catalyst candidate for the production of biodiesel.

1.5. PROBLEM STATEMENT

Currently, the problems related to catalysts in producing biodiesel on commercial scale are; the formation of relatively large amounts of soaps , leading to product loss and difficulty in the separation and purification of the biodiesel and conversion at the cost of high reactants inputs, high retention time, and are non-recyclable.

1.6. RESEARCH OBJECTIVES

The main objective of the research is

• To develop a heterogeneous catalyst for biodiesel production that is efficient (high conversion), recyclable and easy to separate from the product.

1.7. SCOPE OF RESEARCH

The most important parameters regulating the production of biodiesel are the feedstock, type of catalyst used, conversion, and production yield. This study offers the prospect of achieving the goal of high utilization and conversion of the Malaysian Rubber Seed Oil (MRSO) and waste cooking oil to biodiesel by utilizing several complementary

techniques. At first the crude oil from rubber seeds was extracted using a conventional Soxhlet extraction and microwave extraction techniques. The crude oil undergoes various processes of refinement and reduction of free fatty acid to minimize the saponification process. At first the catalyst was synthesized from a calcinated finely ground limestone by chemically activating them with methanol at temperature ranging from 50 to 100°C. Once activated the catalyst were characterized for their porosity, surface area, morphology, size distribution, as well as their chemical properties using equipment such as X-Ray Diffraction, Brunauer-Emmett-Teller (BET), Fourier transform infrared spectroscopy (FTIR), and Scanning Electron Microscopy (SEM). A comprehensive kinetics study regarding the catalyst loading, effect of temperature, residence time and its recyclability were performed using the newly synthesized catalyst. Microwave assisted transesterification are also studied as they can provide faster transesterification process and higher conversion than the conventional process.

Further purification of the methyl esters via degumming, filtration, washing with fuller earth and centrifugation to remove the trace catalyst were carried out once the reaction competed. Both the crude oil and the biodiesel were tested for its soap content, fatty acid content, viscosity, flash point, refractive index, calorific value, iodine value, cetane number, density (Ramadhas et al., 2005; ASTM D6751) as well as full examination of its composition using the gas chromatography mass spectrometry. Compliance tests to the internationally recognized biodiesel standard such as ASTM D6751 are also performed on the biodiesel.

1.8 ORGANIZATION OF THESIS

This thesis has been prepared to give details on the facts, observations, arguments, and procedures in order to meet its objectives. Chapter one generally gives the brief background of a biodiesel production process, the problem statement, objectives and scope of the research. Chapter two presents the literature review of biodiesel production using different types of catalysts, methods and different feedstock options for biodiesel production, constraints and concerns in biodiesel industry, and future opportunities are being discussed. Chapter three carries out the presentation of detailed work done during this research i.e. oil extraction using microwave assisted and soxhlet extraction process,

catalyst activation process, production of biodiesel by microwave technology, conventional method using cement clinker catalyst from rubber seed and waste cooking oil. Chapter four addresses the oil yields based on extraction methods, effect of reaction conditions on biodiesel production, biodiesel properties, advantages of cement clinker catalyst. The most representative optimized methods for biodiesel production are discussed. The conclusions of the present research are summarized and presented in Chapter five. Suggestions and recommendations for the future work are also presented in this chapter.

CHAPTER 2

LITERATURE REVIEW

The development and prospects of biodiesel in Malaysia are discussed in this chapter. Then, the major components making up of biodiesel in Malaysia such as the feedstock, production technology and products are discussed in detail. Furthermore, the key components i.e. catalyst, biodiesel production process, and Malaysia's feedstock options are being discussed. The current constraints and concerns about problems faced by the biodiesel industry are also being highlighted. Potential of Malaysian Rubber Seed Oil (MRSO) as an alternative biodiesel source is discussed in detail. Advantages of RSO biodiesel are discussed together with the challenges that are going to be faced in utilizing this new biodiesel feedstock and a need for change of pace of the current conventional methods with Microwave assisted transesterification. Lastly, several recommendations are presented from the author's point of view regarding the prospects of Malaysian Rubber Seed oil becoming one of the contributing feedstock for biodiesel production.

2.1. INTRODUCTION

It is generally recognized that the first era of the 21st century will witness a significant change in focus of the energy supply industry in the world. World oil and gas output is expected to pass its peak in the next few years, while demand will go on rising. The idea to use biodiesel or vegetable oils as a fuel for diesel engines is more than a hundred years old. Rudolf Diesel patented the first diesel engine in 1892 in Berlin, Germany. He demonstrated a production scale engine nearly 3 m high. Then, in 1900 Rudolf Diesel demonstrated a working diesel engine using peanut oil as fuel at the

World Exhibition in Paris. Before Rudolf passed away he stated "the use of vegetable oil as engine fuels may seem insignificant today but such oils may become, in the course of time, as important as petroleum and the coal tar products of the present time."Initially, Rudolf Diesel was interested in running his engine on either coal or vegetable-based fuels. Petroleum-based fuels became the main source due to lower cost over the past century. However, with the predictions based on Hubbert's curve that "peak" oil may occur within this decade, the price of oil would increase to rise until no longer affordable as world oil reserves approach depletion (IEA, 2008). Renewable sources of energy (e.g. Algae biomass and agricultural crops) can make an important contribution to securing sustainable and diverse energy supplies and are therefore, an essential element of a cost-effective climate change program.

In late 18th and 19th century Industrial revolution made an outset, making energy as a vital factor for human to preserve economic growth and maintain standard of living. The widespread of industrial revolution in Europe had been largely accredited by the high availability of coal as the primary source of energy. Meanwhile, the advent of automobiles, airplanes and electricity had been made possible by the energy usage of petroleum in the twentieth century. Since then, coal and petroleum have become the main sources of energy to human beings. Until today, energy has been continuously derived from conventional sources such as coal, petroleum and natural gas. Fossil fuels still remain as the largest contributor to satisfy the global energy demand despite the discoveries of various alternative energies particularly renewable energy from biofuels and solar.

Today, most of the energy we use comes from fossil fuels: petroleum, coal and natural gas. While fossil fuels are still being created today by underground heat and pressure, they are being consumed more rapidly than they are being created. For that reason, fossil fuels are considered non-renewable; that is, they are not replaced as soon as possible. The renewable energy sources such as biomass, hydro, wind, solar (thermal and photovoltaic), geothermal, marine, and hydrogen will play an important role in the future. By 2040 approximately half of the global energy supply will come from renewable, and electricity generation from renewable will be more than 80% of the total global electricity supply (EWEA, 2005; EREC, 2006).

In Malaysia, the fossil fuels contribution to the total primary energy production stands at 95% in the year 2008, as shown in Figure 2.1 (IEA 2006). Primary energy is essentially raw energy which has not been subjected to any transformation or conversion process and includes natural fossil fuels and renewable energy. This drift is expected to remain the same for the next twenty years to 2030 for Malaysia as it is still a rapidly developing country. Malaysia is promoting the usage of coal as a fuel of choice for power generation before nuclear power becomes viable besides to free up more natural gas for exports and reduce reliance on petroleum.

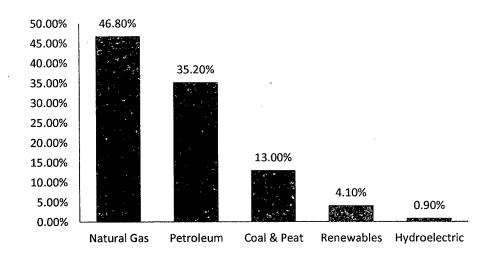


Figure 2.1: Malaysia primary energy supply in 2008(IEA 2006).

The energy embedded inside the fossil fuels has indeed enabled many technological advancements and social economy growth which otherwise may be impossible. However, it has given birth to many environmental issues which can threaten the sustainability of our ecosystem. One of the primary concerns is the greenhouse effect and other types of air pollutants such as sulphur dioxide, hydrocarbons and volatile organic compounds (VOCs). In U.S., of the total amount of greenhouse gases emitted in 2006, about 5.9 billion metric tons were carbon dioxide from energy consumption (the burning of fossil fuels). Another 0.3 billion metric tons CO_2 came from energy-related greenhouse gases other than carbon dioxide for a total of 6.2 out of 7.1 billion metric tons CO_2 or about 87% (EIA 2006). It is predicted that the emissions of greenhouse gases by fossil fuels will increase by 39% in 2030 if no

tremendous effort are thrown in to mitigate it. As shown in Figure 2.2, the total carbon dioxide emissions from fossil fuels in Malaysia has been increasing every year since 1998 except only for the year in 2005 (CDIAC 2010). Immense accumulation of those gases in our atmosphere will ultimately lead to drastic climate changes, acid rain and smog. In addition, the activities of harvesting, processing and distributing those fossil fuels are mostly energy intensive, later which may bring adverse effects to our ecology system.

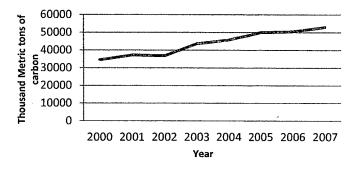


Figure 2.2: Malaysia total Carbon dioxide emissions from fossil fuels (CDIAC, 2010)

Realizing the pros and cons of fossil fuels, many different types of alternative energy have been explored which have the possibility of satisfying the world energy demand while simultaneously ensuring the sustainability of the environment. Recent initiatives to reduce greenhouse gases, particularly carbon dioxide, have led to great interest in vegetable-based fuels because of a plant's inherent ability to capture solar energy through photosynthetic pigments (via light reactions) while efficiently sequestering carbon dioxide (via dark reaction). One such renewable energy in particular will be biodiesel which is mainly derived from vegetable oils or animal fats and has shown great potential to serve as a substitute to petroleum-derived diesel for compression ignition (CI) engine (Agarwal, 2007). Malaysia is one of the countries which actively advocates for the commercial production and usage of biodiesel as fossil fuels replacement due to its rich resources. The current approved installed capacity for biodiesel production is about 10.2 million tonnes in Malaysia (Puah and Choo, 2008).

Most of the currently processed oils in the biodiesel industry come from edible oil sources. These oil sources are of significant importance for human nutrition needs specially with increasing food demand worldwide. Currently, only 10% of the vegetable oils produced are used in the non-food applications and the use of vegetable oils for biodiesel will put pressure on the food use of the commodity (Eevera et al., 2007). The future will be no more far for the world to face the same fuel crisis in the case for biodiesel. Many non-edible oils have been investigated and promising results were obtained. Methyl Esters were produced from Pongamia, cotton seed and beem oils and were verified to be suitable as fuel in climate weather (Ikwuagwu et al., 2000). Rubber Seed oil was among those non-nutritional oils that alkyl esters were synthesized from (Ramdhas et al., 2000). The inspections determined that they can be used in the current diesel machines with no alteration required confirming the adaptability of the produced biodiesel to the current standards (Ramdhas et al., 2008). Using non-edible oils for the production of biodiesel over edible oil sources has many advantages, of which is minimizing the economical and food sacristy impacts resulted from using edible oils, added value to the relevant agricultural industry, contribution to the gross domestic product (GDP) while reducing expenditure over imported fuels, reduction in deforestation rate, diminution in the amount of carbon dioxide and more efficient, productive utilization for the current plantation (Suzana and Mudhar, 2010).

Malaysia is one of the leading producers of natural rubber in the world. The rubber plantation started in Malaysia in 1877. First, the seedlings were brought from the Amazon Basin, and were planted here on experimental basis. Later, when the rubber seedlings were successfully planted, attempts were made to produce it on a commercial scale (Joerg et al., 2000). By 2005, rubber area represented 23.45% (1.250 million ha.) of the plantation industry's total area of 5,305,765 ha, of which the area under oil palm was 4 million hectares (75.50%). The remaining area was shared by cocoa (33,500 ha or 0.63%), pepper (13,745 ha or 0.26%) and tobacco (8,520 ha or 0.16%). Rubber can grow anywhere in Malaysia, because of the suitability of climate and soil; but most of the rubber estates are concentrated in the western coastal plains of Malaysia.

2.1.1. THE ORIGIN OF BIODIESEL

Biodiesel, which can also be known as fatty acid methyl ester (FAME), is produced from trans-esterification of vegetable oils or animal fats with the addition of methanol as shown in Figure 2.3.

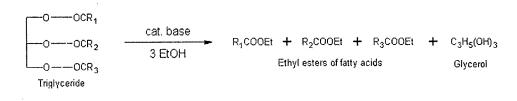


Figure 2.3: Reaction scheme for trans-esterification reaction

It is a process fuel that can be readily used in diesel-engine vehicles, which distinguishes biodiesel from the straight vegetable oils or waste vegetable oils used as fuels in some modified diesel vehicles. Biodiesel is a clear amber-yellow liquid with a viscosity similar to that petro-diesel. Biodiesel is non-flammable and, in contrast to petro-diesel, is non-explosive, with a flash point of 423 K for biodiesel as compared to 337 K for petro-diesel (Demirbas, 2008). Unlike petro-diesel, biodiesel is biodegradable and non-toxic and it significantly reduces toxic and other emissions when burned as a fuel. In general, the liquid has similar composition and characteristics when compare to petroleum-derived diesel such as cetane number, energy content, viscosity and phase changes.

Currently, biodiesel is more expensive to produce than petro-diesel, which appears to be the primary factor in preventing its more widespread use. Current worldwide production of vegetable oil and animal fat is not enough to replace liquid fossil fuel use (maximum replacement percentage: ca. 20 to 25%) (Bala, 2005). Therefore, when blended together with petroleum-derived diesel, it can be used in any CI diesel engine without any modifications (Steven and Lee, 2010). Several of its distinct advantages such as lower greenhouse gases emissions, higher lubricity and cetane ignition rating compare to petroleum derived diesel have enabled biodiesel to become one of the most common biofuels in the world. The advantages of biodiesel as