SYNTHESIS OF BIODIESEL FROM PALM OIL AND SEA MANGO OIL USING SULFATED ZIRCONIA CATALYST

JIBRAIL B KANSEDO

UNIVERSITI SAINS MALAYSIA

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SYNTHESIS OF BIODIESEL FROM PALM OIL AND SEA MANGO OIL USING SULFATED ZIRCONIA CATALYST

by

JIBRAIL B KANSEDO

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TABLE OF CONTENTS

Page

ACKNOWLEDGEMENT ii

LIST OF TABLES ix

LIST OF FIGURES xi

LIST OF PLATES xv

NOMENCLATURE AND ABBREVIATION xvi

ABSTRAK xviii

ABSTRACT xx

CHAPTER 1 INTRODUCTION 1

- 1.1 Heterogeneous Transesterification 3
- 1.2 Feedstock for Biodiesel Production 5
- 1.3 Problem Statement 8
- 1.4 Project Objectives 9
- 1.5 Organization of Thesis 10

CHAPTER 2 LITERATURE REVIEW 12

- 2.1 Biodiesel 12
  - 2.1.1 Definition of Biodiesel 12
  - 2.1.2 Advantages and Disadvantages of Biodiesel 13
  - 2.1.3 Transesterification Process 14
  - 2.1.4 Methods and Catalysts in Transesterification Process 16
  - 2.1.5 Feedstock for Biodiesel Production 17
    - 2.1.5 (a) Vegetable Oils and Animal Fats 17
    - 2.1.5 (b) Alcohol 19
  - 2.1.6 Variables Affecting the Transesterification Process 20
    - 2.1.6 (a) Moisture and Free Fatty Acids Contents 20
    - 2.1.6 (b) Molar Ratio of Alcohol to Oil and Type of Alcohol 21
    - 2.1.6 (c) Type and Amount of Catalyst 22
    - 2.1.6 (d) Reaction Time and Temperature 23

2.1.6 (e) Mixing Intensity 24
2.1.6 (f) Co-Solvent 24
2.2 Characterization of Fatty Acid Methyl Esters Produced from the Transesterification Process 25
2.2.1 Quantitative and Qualitative Analysis 25
2.2.2 Fuel Properties and Characterization of FAME 25
2.3 Development of Solid Catalyst for Heterogeneous Transesterification Process 29
2.4 Supported Sulfated Zirconia 36
2.4.1 Synthesis of Supported Sulfated Zirconia 36
2.4.2 Effect of Various Preparation Parameters 40
2.4.2 (a) Effect of Precursor and Sulfating Agent 40
2.4.2 (b) Effect of Calcination Temperature 41
2.4.3 Characterization of Supported Sulfated Zirconia 41
2.4.4 Supported Sulfated Zirconia in Transesterification and Esterification Process 42

CHAPTER 3 MATERIALS AND METHODOLOGY 45
3.1 Materials and Chemicals 45
3.2 Equipment and Facilities 46
3.3 Synthesis, Optimization and Characterization of Sulfated Zirconia Catalyst 48
3.3.1 Synthesis of Sulfated Zirconia Catalyst 48
3.3.1 (a) Effect of Calcination Temperature 49
3.3.1 (b) Effect of Calcination Period 50
3.3.1 (c) Catalytic Performance of Synthesized Sulfated Zirconia Catalyst 50
3.3.2 Optimization of Sulfated Zirconia Catalyst 50
3.3.3 Characterization of Sulfated Zirconia Catalyst 51
3.3.3 (a) Fourier Transform Infra Red Spectroscopy (FTIR) with Pyridine as Probe Molecule 51
3.3.3 (b) Scanning Electron Microscopy (SEM) 52
3.3.3 (c) X-Ray Diffraction (XRD) 52

3.3.3 (d) Thermogravimetric Analysis (TGA) 52
3.3.3 (e) Brunauer-Emmett-Teller Method (BET) 53
3.4 Extraction and Characterization of Sea Mango (*Cerbera odollam*) oil 54
3.4.1 Extraction of Sea Mango Oil 54
3.4.2 Characterization of Sea Mango Oil 56
3.5 Transesterification Process Study 56
3.5.1 Development of Design of Experiment (DOE) 57
3.5.2 Transesterification Process using Optimized Sulfated Zirconia Catalyst 58
3.5.3 Transesterification Process using Montmorillonite KSF Catalyst 58
3.5.4 Experimental Set-Up for the Transesterification Process Study 60
3.5.5 Transesterification of Sea Mango Oil Using Various Methods 61
3.6 Analysis 64
3.6.1 Gas Chromatography 64
3.6.2 Calculation of FAME Yield 64
3.7 Durability and Reusability Study for Sulfated Zirconia Catalyst 67
3.8 Characterization of Fatty Acid Methyl Esters (FAME) 67
3.9 Kinetic Study – Determination of Reaction Rate and Kinetic Parameters for Transesterification Process 68

CHAPTER 4 RESULTS AND DISCUSSION 70
4.1 Synthesis, Optimization and Characterization of Sulfated Zirconia Catalyst 70
4.1.1 Synthesis of Sulfated Zirconia Catalyst 71
4.1.1 (a) Effect of Calcination Temperature 71
4.1.1 (b) Effect of Calcination Period 72
4.1.1 (c) Supported vs. Unsupported Sulfated Zirconia Catalyst and Effect of Catalyst/Support Ratio 74
4.1.2 Optimization of Sulfated Zirconia Catalyst 76

4.1.3 Characterization of Sulfated Zirconia Catalyst 76
  4.1.3 (a) Scanning Electron Microscope (SEM) 77
  4.1.3 (b) Fourier Transform Infra Red Spectroscopy (FTIR) with Pyridine as a Probe Molecule 79
  4.1.3 (c) X-Ray Diffraction (XRD) 80
  4.1.3 (d) Thermogravimetric Analysis (TGA) 82
  4.1.3 (e) Brunaeur-Emmett Teller Method (BET) 83
4.1.4 Summary 84
4.2 Extraction and Characterization of Sea Mango (*Cerbera Odollam*) Oil 84
4.3 Transesterification Process Study 87
4.3.1 Transesterification Process using Optimized Sulfated Zirconia Catalyst 87
  4.3.1 (a) Development of Design of Experiment (DOE) 87
  4.3.1 (b) Development of Regression Model Equation 89
  4.3.1 (c) Model Adequacy Check 89
  4.3.1 (d) Effect of Transesterification Process Variables 92
  4.3.1 (e) Optimization of Transesterification Process Variables 103
4.3.2 Transesterification Process using Montmorillonite KSF Catalyst 104
  4.3.2 (a) Development of Design of Experiment 104
  4.3.2 (b) Development of Regression Model Equation 106
  4.3.2 (c) Model Adequacy Check 106
  4.3.2 (d) Effect of Transesterification Process Variables 108
4.3.3 Comparison of Transesterification Processes Using Optimized Sulfated Zirconia Catalyst and Montmorillonite KSF Catalyst 114
4.3.4 Transesterification of Sea Mango (*Cerbera Odollam*) Oil using Various Methods 115
4.3.5 Comparison Between Palm Oil and Sea Mango Oil as Oil Feedstock in the Transesterification Process 116

4.4 Reusability and Regenerability Study of Sulfated Zirconia Catalyst 117
4.5 Characterization of Palm Fatty Acid Methyl Esters (Palm FAME) 118
4.6 Kinetic Study – Determination of Reaction Rate and Rate Parameters for Transesterification Process 119

CHAPTER 5 CONCLUSIONS AND RECOMMENDATION 126
5.1 Conclusions 126
5.2 Recommendations 128

REFERENCES 129
APPENDIX A 141
LIST OF PUBLICATIONS 143

LIST OF TABLES

		Page
Table 1.1	Different types of vegetable oils: oil content, oil yield and producing areas	6
Table 2.1	Fatty acid composition of vegetable oil samples	19
Table 2.2	Standard specifications for biodiesel fuel (B100) blend stock for distillate fuels (ASTM D6751)	26
Table 2.3	European standard for biodiesel (EN 14214)	27
Table 2.4	Fuel properties of processed liquid palm oil (PLPO/Malaysian Petroleum diesel (PD) blends	28
Table 2.5	Comparison of different technologies to produce biodiesel	30
Table 2.6	Differences between homogenous, heterogeneous and non-catalytic transesterification process	30
Table 2.7	Typical solid catalysts in the transesterification process	32
Table 2.8	Preparation procedure for sulfated zirconia	39
Table 2.9	Techniques used for characterization of sulfated zirconia	42
Table 3.1	List of materials and chemicals	45
Table 3.2	List of equipment and facilities	47
Table 3.3	Range and levels of the transesterification process variables for the transesterification of palm oil using optimized sulfated zirconia catalyst	58
Table 3.4	Range and levels of the transesterification process variables for the transesterification of palm oil using montmorillonite KSF catalyst	59
Table 3.5	Reaction conditions for the transesterification of sea mango oil using various catalysts	63
Table 3.6	Area of the FAME peaks from a default report of GC-FID (Standard)	65
Table 3.7	The value of R_{SD} for each ester	66
Table 3.8	List of testing methods	67
Table 4.1	Optimum values for supported and unsupported sulfated zirconia catalysts	76
Table 4.2	Summary report of BET for supported sulfated zirconia catalysts prepared at different calcination temperatures	83
Table 4.3	Vegetable oils: Oil content and yield	85
Table 4.4	Properties of sea mango oil compared to palm oil	86

Table 4.5 Fatty acid content of sea mango oil compared to palm oil 86
Table 4.6 Experimental design matrix and results for the transesterification process using optimized sulfated zirconia catalyst 88
Table 4.7 Analysis of variance (ANOVA) for the regression model equation and coefficients after eliminating insignificant terms 90
Table 4.8 Experimental design matrix and results for the transesterification process using montmorillonite KSF catalyst 105
Table 4.9 Analysis of variance (ANOVA) for the regression model equation and coefficients after eliminating insignificant terms 107
Table 4.10 Comparison between supported sulfated zirconia and montmorillonite KSF in the transesterification of palm oil 114
Table 4.11 Transesterification of *Cerbera odollam* oil and palm oil using different catalysts 115
Table 4.12 Summary of palm FAME characterization compared to American (ASTM D 6751) and European (EN 14214) biodiesel standard 118
Table 4.13 Global reaction rate constant and correlation coefficient extracted from the $[1-(1-X)^{1-2.9}]/1-2.9$ vs. t plot 123
Table A.1 Percentage of fatty acids in palm oil and sea mango oil 141

LIST OF FIGURES

		Page
Figure 1.1	Process flow diagram of a typical biodiesel production	2
Figure 1.2	Malaysia production of palm oil from year 1964 to 2006	7
Figure 2.1	Division of methods in the transesterification process	17
Figure 2.2	Acid strength of sulfated zirconia (SO_4^{2-}/ZrO_2) compared to other liquid and solid superacids as determined by Hammett-indicator method	37
Figure 2.3	Schematic illustration of the two-step method for the preparation of sulfated zirconia	38
Figure 3.1	Summary of the synthesis of sulfated zirconia catalyst	49
Figure 3.2	Schematic diagram of the batch reactor	61
Figure 3.3	Peaks of FAME from a GC-FID	65
Figure 4.1	Yield of palm FAME using supported and unsupported sulfated zirconia catalysts at varied calcination temperature (calcination period = 2.5 hr, reaction temperature = 150 ^oC, reaction period = 2.5 hr, ratio of oil to methanol = 1:8, amount of catalyst = 8 wt%, ratio of catalyst/support = 2 g/g)	71
Figure 4.2	Yield of palm FAME using supported and unsupported sulfated zirconia catalysts at varied calcination period (calcination temperature = 400 ^oC, reaction temperature = 150 ^oC, reaction period = 2.5 hr, ratio of oil to methanol = 1:8, amount of catalyst = 8 wt%, ratio of catalyst/support = 2 g/g)	73
Figure 4.3	Yield of palm FAME using supported and unsupported sulfated zirconia catalysts at varied calcination period (calcination temperature = 600 ^oC, reaction temperature = 150 ^oC, reaction period = 2.5 hr, ratio of oil to methanol = 1:8, amount of catalyst = 8 wt%, ratio of catalyst/support = 2 g/g)	74
Figure 4.4	Yield of palm FAME using supported zirconia catalyst at varied ratio of catalyst/support (calcination temperature = 400 ^oC and calcination period = 2.5 hr, reaction temperature = 150 ^oC, reaction period = 2.5 hr, ratio of oil to methanol = 1:8, amount of catalyst = 8 wt%)	75
Figure 4.5	Scanning-electron micrograph of the sulfated zirconia catalyst calcined at 400 ^oC	78

Figure 4.6 Scanning-electron micrograph of the sulfated zirconia catalyst calcined at 600 ^{o}C 78

Figure 4.7 Scanning-electron micrograph of the sulfated zirconia catalyst calcined at 800 ^{o}C 79

Figure 4.8 Fourier transform infrared spectroscopy for the sulfated zirconia catalysts after pyridine adsorption 80

Figure 4.9 XRD patterns of the sulfated zirconia catalysts prepared at various calcination temperature 81

Figure 4.10 Thermogravimetric analyses (TGA) diagram of the sulfated zirconia catalyst 82

Figure 4.11 Predicted versus experimental yield of palm FAME using sulfated zirconia catalyst 91

Figure 4.12 Response surface plot of the effect of reaction period (2 hr and 4 hr) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying reaction temperature (ratio of oil to methanol = 1:8, amount of catalyst = 6 wt%) 94

Figure 4.13 Two dimensional drawing of the effect of reaction period (2 hr and 4 hr) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying reaction temperature (ratio of oil to methanol = 1:8, amount of catalyst = 6 wt%) 94

Figure 4.14 Response surface plot of the effect of ratio of oil to methanol (1:6 and 1:10) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying reaction temperature (reaction period = 3 hr, amount of catalyst = 6 wt%) 96

Figure 4.15 Two dimensional drawing of the effect of ratio of oil to methanol (1:6 and 1:10) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying reaction temperature (reaction period = 3 hr, amount of catalyst = 6 wt%) 96

Figure 4.16 Response surface plot of the effect of amount of catalyst (4 wt% and 8 wt%) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying reaction temperature (reaction period = 3 hr, ratio of oil to methanol = 1:8) 97

Figure 4.17 Two dimensional drawing of the effect of amount of catalyst (4 wt% and 8 wt%) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying reaction temperature (reaction period = 3 hr, ratio of oil to methanol = 1:8) 97

Figure 4.18 Response surface plot of the effect of ratio of oil to methanol (1:6 and 1:10) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying reaction period (reaction temperature = 120 ^{o}C, amount of catalyst = 6 wt%) 99

Figure 4.19 Two dimensional drawing of the effect of ratio of oil to methanol (1:6 and 1:10) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying reaction period (reaction temperature = 120 ^{o}C, amount of catalyst = 6 wt%) 99

Figure 4.20 Response surface plot of the effect of amount of catalyst (4 wt% and 8 wt%) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying reaction period (reaction temperature = 120 ^{o}C, ratio of oil to methanol = 1:8) 101

Figure 4.21 Two dimensional drawing of the effect of amount of catalyst (4 wt% and 8 wt%) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying reaction period (reaction temperature = 120 ^{o}C, ratio of oil to methanol = 1:8) 102

Figure 4.22 Response surface plot of the effect of amount of catalyst (4 wt% and 8 wt%) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying ratio of oil to methanol (reaction temperature = 120 ^{o}C, reaction period = 3 hr) 102

Figure 4.23 Two dimensional drawing of the effect of amount of catalyst (4 wt% and 8 wt%) on the inverse yield of palm FAME using sulfated zirconia catalyst at varying ratio of oil to methanol (reaction temperature = 120 ^{o}C, reaction period = 3 hr) 103

Figure 4.24 Predicted versus experimental yield of palm FAME using montmorillonite KSF catalyst 108

Figure 4.25 Response surface plot of the effect of reaction temperature and amount of catalyst on the yield of palm FAME 111

Figure 4.26 Two dimensional drawing of the effect of reaction temperature and amount of catalyst on the yield of palm FAME 111

Figure 4.27 Response surface plot of the effect of reaction period and amount of catalyst on the yield of palm FAME 113

Figure 4.28 Two dimensional drawing of the effect of reaction period and amount of catalyst on the yield of palm FAME 113

Figure 4.29 Catalytic performance of the used sulfated zirconia and regenerated sulfated zirconia after few runs 117

Figure 4.30 Profile of the transesterification process using sulfated zirconia catalyst at isothermal conditions at 60 to 180 ^{o}C 120

Figure 4.31 $[1-(1-X)^{1-2.9}]/1-2.9$ vs. t plot at different reaction T 122

Figure 4.32 Arrhenius plot of rate constant vs. reciprocal of reaction T 124

Figure 4.33 Comparison between experimental and simulated conversion vs. time curve at reaction temperature of 150 ^{o}C 125

LIST OF PLATES

Page

Plate 3.1 Fruit and kernel of sea mango 55

Plate 3.2 Soxhlet apparatus 55

Plate 3.3 Batch reactor with a temperature controller for the transesterification study 60

Plate 3.4 Electrothermal heating mantle with a reflux system, using one-neck round bottom flask 63

NOMENCLATURE AND ABBREVIATIONS

α	Alpha (Axial distance from center point which makes the design rotatable
x_i	Variables studied
x_j	Variables studied
b_o	Offset term
b_j	Linear effect
b_{ij}	First order interaction effect
b_{jj}	Squared effect
k	Global reaction rate constant
ANOVA	Analysis of Variance
AOCS	American Oil Chemists’ Society
BET	Brunaeur-Emmett-Teller
CCD	Central Composite Design
CPO	Crude Palm Oil
DF	Dilution factor
DG	Diglycerides
DOE	Design of Experiment
F-value	Fischer test value (Measurement of distance between individual distributions)
FAME	Fatty Acid Methyl Esters
FTIR	Fourier Transform Infra Red Spectroscopy
GC-FID	Gas Chromatography with Flame Ionization Detector
GC-MS	Gas Chromatography Mass Spectrometer
GL	Glycerol
H NMR	Hydrogen Nuclear Magnetic Resonance
HPLC	High Performance Liquid Chromatography
IS	Internal Standard (Methyl Heptadecanoate)
ME	Methyl Esters
MG	Monoglycerides
ML	Methyl Linoleate
MM	Methyl Myristate
MO	Methyl Oleate
MP	Methyl Palmitate

MPOB	Malaysian Palm Oil Board
MS	Methyl Stearate
NIR	Near Infra Red
PLPO	Processed Liquid Palm Oil
PO	Palm oil
PD	Petroleum Diesel
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
SMO	Sea mango oil
SZ	Sulfated Zirconia
TG	Triglycerides
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction

SINTESIS BIODIESEL DARIPADA MINYAK KELAPA SAWIT DAN MINYAK MANGGA LAUT MENGGUNAKAN MANGKIN ZIRCONIA TERSULFAT

ABSTRAK

Penghasilan biodiesel daripada minyak kelapa sawit dan minyak mangga laut telah dikaji. Dua jenis mangkin heterogen telah digunakan dalam kajian ini; (a) mangkin zirconia tersulfat yang disintesis dalam makmal dan (b) mangkin komersial montmorillonite KSF. Bahagian awal dalam kajian ini adalah untuk mensintesis, mengoptimasi dan mencirikan mangkin zirconia tersulfat. Mangkin zirconia tersulfat yang dihasilkan ini kemudiannya digunakan dalam penghasilan biodiesel (proses transesterifikasi). Mangkin kedua, montmorillonite KSF (sebagai perbandingan) digunakan secara terus dalam proses transesterifikasi. Minyak kelapa sawit bertapis digunakan sebagai bahan pemula utama manakala minyak mangga laut digunakan sebagai bahan pemula sampingan. Minyak mangga laut ini diperolehi melalui pengekstrakan minyak daripada biji buah mangga laut. Pensintesisan mangkin zirconia tersulfat telah dijalankan menggunakan dan tanpa menggunakan penyokong. Aluminium oksida (Al_2O_3) digunakan sebagai penyokong. Mangkin zirconia tersulfat tersokong didapati mempunyai aktiviti pemangkinan yang tertinggi. Dengan menggunakan 6% berat mangkin zirconia tersulfat tersokong, sebanyak 82.8% hasilan metil ester asid lemak kelapa sawit (*palm FAME*) telah dihasilkan pada suhu tindakbalas 180 ^{o}C, masa tindakbalas 180 minit dan nisbah minyak kepada metanol pada 1:8. Menggunakan kuantiti mangkin yang sama, sebanyak 83.4% hasilan metil ester asid lemak mangga laut (sea mango FAME) telah dihasilkan pada keadaan tindakbalas yang sama. Apabila mangkin komersial montmorillonite KSF digunakan, hasilan ester yang lebih rendah telah didapati. Hasilan ester kelapa sawit paling tinggi oleh mangkin montmorillonite KSF adalah sebanyak 79.6% (suhu tindakbalas 190 ^{o}C, masa tindakbalas 180 minit, nisbah minyak kepada metanol pada 1:8 dan amaun mangkin 3 wt%) manakala hasilan paling tinggi ester mangga laut oleh montmorillonite KSF adalah sebanyak 48.3% pada keadaan tindakbalas yang sama. Dalam kajian ini, minyak mangga laut didapati mempunyai potensi yang amat baik untuk digunakan sebagai bahan pemula dalam penghasilan biodiesel oleh kerana hasilan minyaknya yang tinggi sebanyak 54%. Pencirian mangkin zirconia tersulfat tersokong telah dijalankan menggunakan FTIR, XRD, BET, TGA dan SEM. Didapati bahawa mangkin zirconia tersulfat tersokong ini mempunyai sifat asid lampau serta luas permukaan dan keliangan yang rendah. Pencirian ester (*palm FAME*) menunjukkan bahawa mangkin zirconia tersulfat dan montmorillonite KSF merupakan mangkin yang baik dalam penghasilan biodiesel yang menepati piawaian biodiesel antarabangsa dan Malaysia. Kinetik tindakbalas transesterifikasi menggunakan mangkin zirconia tersulfat turut dikaji dan kadar pembolehubahnya juga telah dipelajari. Tenaga pengaktifan sebanyak 50.05 kJ/mol dan faktor frekuensi 1.4×10^{5} min^{-1} telah diperolehi bagi tindakbalas transesterifikasi ini.

SYNTHESIS OF BIODIESEL FROM PALM OIL AND SEA MANGO OIL USING SULFATED ZIRCONIA CATALYST

ABSTRACT

The production of biodiesel from palm oil and sea mango oil (*Cerbera odollam* oil) using heterogeneous catalysts was studied. Two types of heterogeneous catalysts (a) sulfated zirconia which was synthesized in the laboratory and (b) a commercial montmorillonite KSF were used. The initial part of this research project was to synthesize, optimize and characterize sulfated zirconia catalyst. Then, the synthesized sulfated zirconia catalyst was used in the production of biodiesel (transesterification process). The second heterogeneous catalyst (for comparison purpose) a commercial montmorillonite KSF was used directly in the transesterification process. Refined palm oil was used as feedstock whereas sea mango oil was used as an alternative feedstock. Sea mango oil was extracted from the seeds of sea mango fruits. The synthesis of sulfated zirconia was carried out with and without a support. Aluminium oxide (Al_2O_3) was used as support. Supported sulfated zirconia gave the highest catalytic activity. With a catalyst loading of 6 wt%, palm fatty acid methyl esters (palm FAME) yield of 82.8% was obtained at the following reaction conditions; reaction temperature of 180 ^oC, reaction period of 180 minutes and ratio of oil to methanol at 1:8. Using the same catalyst loading, sea mango fatty acid methyl esters (sea mango FAME) with a yield of 83.4% were obtained at the same reaction conditions. On the other hand, when commercial montmorillonite KSF catalyst was used, a lower yield was obtained. The highest yield of palm FAME produced using montmorillonite KSF was 79.6% (reaction temperature of 190 ^{o}C, reaction period of 180 minutes, ratio of oil to methanol at 1:8 and amount of catalyst 3%) and only 48.3% yield of sea mango FAME was produced at the same reaction condition. Nevertheless, sea mango oil was found to be a potential feedstock for biodiesel production due to its high oil content of 54%. The characterization of the supported sulfated zirconia was carried out using FTIR, XRD, BET, TGA and SEM. It was found that the supported sulfated zirconia has properties of solid superacid with low surface area and low porosity. The characterization of palm FAME indicated that the supported sulfated zirconia and montmorillonite KSF are reliable catalysts for the production of biodiesel that meets the international and Malaysian standard of biodiesel. The kinetic of the transesterification reaction using sulfated zirconia catalyst was also studied and the rate parameters were determined. An activation energy value of 50.05 kJ/mol and frequency factor of 1.4×10^{5} min^{-1} were obtained for the transesterification reaction.

CHAPTER 1

INTRODUCTION

Petroleum-based fuel plays an important role in the energy sector mainly as fuel for power plants, running vehicles and motor engines in the transportation sector. However, petroleum-based fuel is not sustainable and the prices are also not stable. Due to these factors, new alternative energy especially renewable energy has been widely studied to fulfill the world's insatiable demand for energy. Examples of the new alternative energy are solar, wind, geothermal and biomass (Omer, 2008). Nevertheless, most of these alternative energy are only capable of generating thermal and electrical energy, whereas more than 40% of the world energy demand is in liquid form. Therefore, the use of biomass as a new source of alternative liquid fuel has attracted a lot of attention lately.

One of the options of utilizing biomass as liquid fuel is the use of vegetable oil in diesel engines. However, vegetable oils cannot be directly used in diesel engines due to its high viscosity. In order to utilize vegetable oils successfully in unmodified diesel engines, the viscosity of the vegetable oil must be lowered. Several methods have been developed to reduce the viscosity of the vegetable oil. These methods include blending with diesel, pyrolysis, microemulsification (co-solvent blending), and transesterification (Ma & Hanna, 1999).

Currently, blending and transesterification are the most common ways to lower the viscosity of vegetable oil. Blending is easier because it does not involve any chemical modification of the vegetable oil. However, blending is less attractive because it requires purification of the vegetable oil prior to the blending process. Transesterification, on the other hand does not require purification of the vegetable oil. However, transesterification process involves chemical reactions to convert vegetable oil into biodiesel, which recently has become well known. Compared to blending, transesterification process is superior due to its ability to reduce effectively the viscosity of the vegetable oil and produces fuel which has similar properties with diesel. **Figure 1.1** shows the schematic of a typical process flow diagram for biodiesel production.

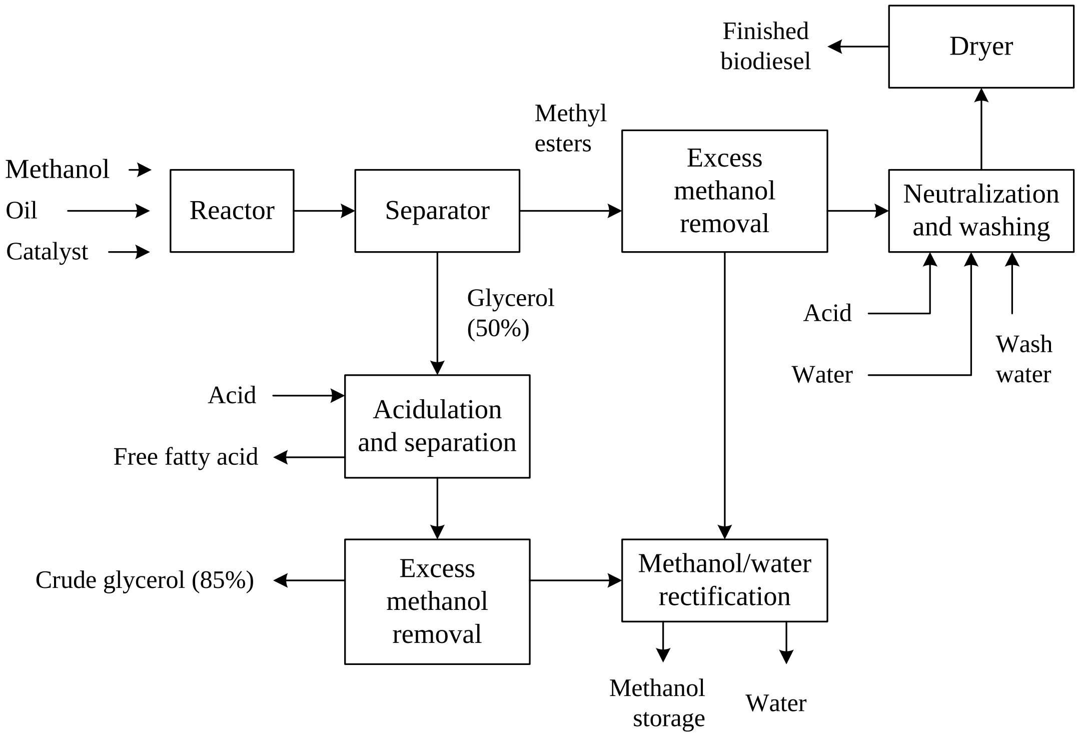


Figure 1.1 Typical process flow diagram for biodiesel production (Gerpen, 2005)

There are two ways to carry out the transesterification process; catalytic and non-catalytic process. Under catalytic process, there are two methods namely homogenous and heterogeneous. Homogeneous transesterification method has been long regarded as the easiest method to produce biodiesel. Unfortunately, homogeneous transesterification has many problems including complexity of the product separation and purification processes due to homogeneous nature of its mixture (reactants, catalyst and product). Homogenous transesterification process also tends to produce soap which leads to usage of a lot wash water and also formation of emulsion in the mixture. The formation of emulsion in the mixture could worsen the complexity of the separation and purification process. Furthermore, it could contribute to the loss of triglycerides. All these downsides eventually lead to a very high production cost. Due to these disadvantages, other alternatives have been considered; heterogeneous and non-catalytic transesterification process.

Non-catalytic transesterification process requires no catalyst. However, it is also less favorable due to its high energy demand as non-catalytic process usually operates at supercritical temperature and pressure of the alcohol (Fukuda *et al.*, 2001; Ma & Hanna, 1999; Madras *et al.*, 2004; Marchetti *et al.*, 2007b). Furthermore, at supercritical conditions, non-catalytic transesterification process tends to become very difficult to handle. Due to these factors, other alternative method, which has a lower operational cost and simpler operational process, has to be considered. Thus, heterogeneous transesterification provides a better solution.

1.1 Heterogeneous Transesterification

The benefits of heterogeneous transesterification process include easier and simpler separation process (as the catalyst is in different phase from the product/reactants) and elimination of soap formation. Heterogeneous transesterification is a relatively cheaper alternative to the current homogenous transesterification for biodiesel production. Heterogeneous transesterification process is also easier to perform due to moderate temperature and pressure required in the process compared to that of non-catalytic supercritical transesterification technology.

There are three types of heterogeneous transesterification process; basic (alkali), acidic and enzymatic. Up until today, there are many catalysts developed and used in the heterogeneous transesterification process. Examples of the heterogeneous catalysts are metal oxides (Liu *et al.*, 2008; Zhu *et al.*, 2006), zeolites (Suppes *et al.*, 2004; Xie *et al.*, 2007) and active metals loaded on supports (Albuquerque *et al.*, 2008; Jitputti *et al.*, 2006; Park *et al.*, 2008). Each type of heterogeneous transesterification process has their own challenges. Enzymatic transesterification process for instance, requires activity of a living organism or cells (enzyme) to convert vegetable oil to biodiesel. This makes the enzymatic process very sensitive to disturbances. The enzyme could be easily inhibited when the conditions are unsuitable (Ranganathan *et al.*, 2008). The enzymatic reactions are also very specific due to its specific active sites. Moreover, enzymes are costlier compared to basic and acidic solid catalysts. Due to these reasons, heterogeneous transesterification processes using basic and acidic solid catalysts seem to be more attractive. However, the heterogeneous transesterification itself has other challenges. The solid catalysts for the heterogeneous transesterification process must possess good catalytic properties to produce the desirable product. This actually has become the main hurdle in the development of heterogeneous catalysts that is to synthesize a very reactive catalyst that can catalyze the heterogeneous transesterification process.

1.2 Feedstock for Biodiesel Production

One of the starting materials required for the production of biodiesel via transesterification process is oil feedstock. Since vegetable oil is oil feedstock that is readily available in large quantities, it has been widely used for the conversion to biodiesel. **Table 1.1** shows the common vegetable oil available in the world with its oil content, oil yield and major producing area. Majority of these vegetable oil have been utilized for the production of biodiesel via transesterification process such as soybean oil (Antunes *et al.*, 2008; Ferreira *et al.*, 2007; Liu *et al.*, 2008; Yin *et al.*, 2008), rapeseed oil (Li *et al.*, 2006a ; Morin *et al.*, 2007 ; Saka & Kusdiana, 2001), canola oil (Dube *et al.*, 2007; Kulkarni *et al.*, 2007), palm oil (Crabbe *et al.*, 2001; Jitputti *et al.*, 2006; Joelianingsih *et al.*, 2008; Sarin *et al.*, 2007; Trakarnpruk & Porntangjitlikit, 2008) and sunflower oil (Granados *et al.*, 2007; Stamenkovic *et al.*, 2008).

In Malaysia, the most abundantly available vegetable oil is palm oil. Malaysia is currently the world second largest producer of palm oil after Indonesia. The production of palm oil in Malaysia from year 1964 to year 2006 is given in **Figure 1.2**. Based on **Figure 1.2**, it can be seen that the production of crude palm oil has been increasing from year 1964 to year 2006. This indicates that palm oil can be used as a stable supply of oil feedstock not only as food (edible oil), but also for the production of biodiesel (transesterification process). This therefore makes palm oil a viable feedstock for the production of palm biodiesel.

Table 1.1 Different types of vegetable oils: Oil content, oil yield and producing areas (O'Brien, 2004)

Oil	**Oil content (%)**	**Oil yield (Pounds/Acre)**	**Major producing area**
Oilseeds:			
Canola	40 – 45	525 – 590	Canada, China, India, France, Austria, U.K., Germany, Poland, Denmark, Czechoslovakia, U.S.
Corn	3.1 – 5.7	215 -390	U.S. Mexico, Canada, Japan, China, Brazil, South Africa, Argentina, Russia, Commonwealth of Independent States (CIS), Belgium, France, Italy, Germany, Spain, U.K.
Cottonseed	18 – 20	185 – 210	China, Russia, U.S. India, Pakistan, CIS, Brazil, Egypt, Turkey, Australia
Peanut	45 – 50	1120 – 1245	China, India, Nigeria, U.S., Senegal, South Africa, Argentina
Safflower	30 – 35	545 – 635	China, U.S., Spain, Portugal
Soybean	18 – 20	400 – 590	U.S., Brazil, Argentina, China, India, Paraguay, Bolivia
Sunflower	35 – 45	460 – 590	Russia, Argentina, CIS, Austria, France, Italy, Germany, Spain, U.S., U.K.
Tree fruits and kernels:			
Coconut	65 – 68	650 – 870	Philippines, Indonesia, India, Mexico, Sri Lanka, Thailand, Malaysia, Vietnam, Mozambique, New Guinea, Ivory Coast
Olive	15 – 35	90 – 260	Spain, Italy, Greece, Tunisia, Turkey, Morocco, Portugal, Syria, Algiers, Yugoslavia, Cyprus, Egypt, Israel, Libya, Jordan, Lebanon, Argentina, Chile, Mexico, Peru, U.S., Australia
Palm	45 – 50	2670 – 4450	Malaysia, Indonesia, China, Philippines, Pakistan, Mexico, Bangladesh, Colombia, Ecuador, Nigeria, Ivory Coast
Palm Kernel	44 – 53	267 – 445	Malaysia, Indonesia, China, Philippines, Pakistan, Mexico, Bangladesh, Colombia, Ecuador, Nigeria, Ivory Cost

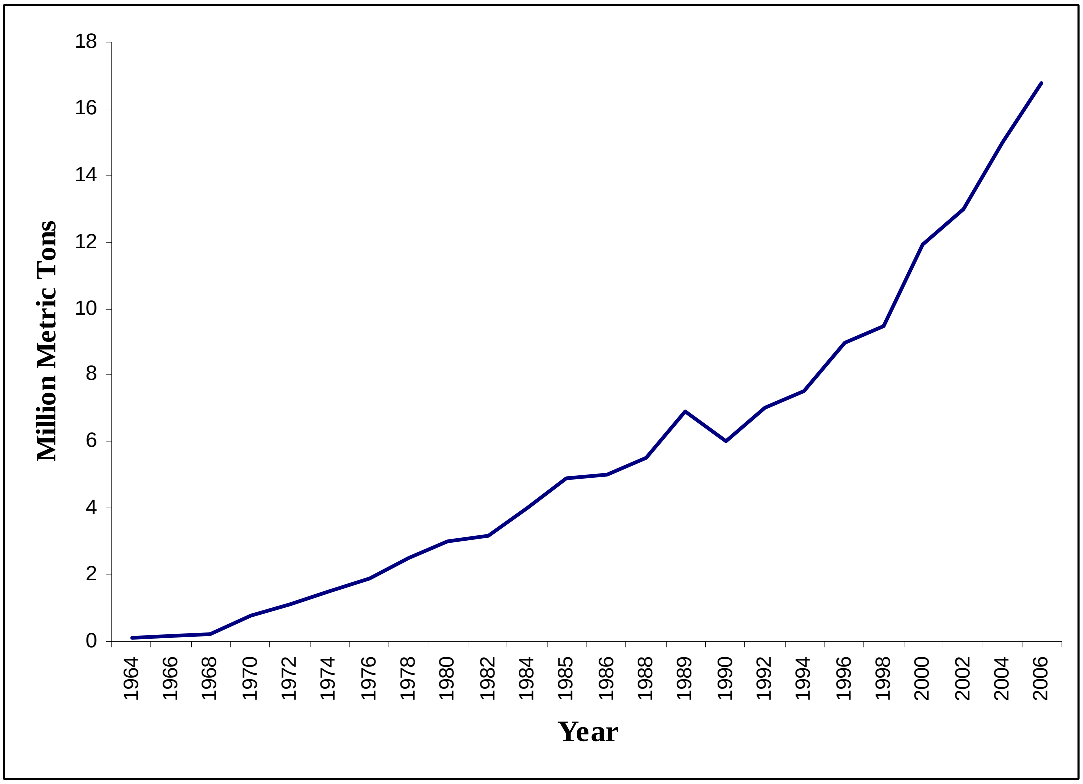


Figure 1.2 Malaysia production of palm oil from year 1964 to 2006 (MPOB, 2008)

Nevertheless, the conversion of edible oil to biodiesel gives another problem. Conversion of edible oil to fuel (biodiesel) led to controversies as famine and hunger still exist around the globe. Channeling edible oil into fuel industries makes biodiesel to actually compete limited land availability with the food industry for the same oil crop. Thus, instead of utilizing arable land to grow food, it is now being used to grow fuel. This subsequently raises the price of edible oil and therefore makes the biodiesel produced economically unfeasible compared to petroleum derived diesel. In order to overcome this issue, other alternative oil feedstock must be used to replace the edible oils in the biodiesel production. Few sources have been identified such as waste cooking oil and oil from non-edible producing plants such as jatropha oil (*Jatropha curcas* oil) (Berchmans & Hirata, 2008; Kumar Tiwari *et al.*, 2007; Shah & Gupta, 2007; Tamalampudi *et al.*, 2008), algae oil (Chisti, 2007, 2008), and waste oil (Issariyakul *et al.*, 2007; Lapuerta *et al.*, 2008a; Tsai *et al.*, 2007; Yagiz *et al.*, 2007).

As for non-edible sources in Malaysia, there are few choices; jatropha, rubber seeds and sea mango (*Cerbera odollam*). The former has a brighter commercial prospect, judged from the opening of new jatropha plantations around the country. Rubber seeds are readily available since there are already a lot of mature rubber plantations around the country. In contrast to the previous two, sea mango generally is unknown in the biodiesel production. Sea mango trees however are widely planted locally as ornamental plant by roadsides. Up until today, sea mango (*Cerbera odollam*) has never been used in the transesterification research.

1.3 Problem Statement

Biodiesel has been accepted worldwide as the immediate solution to the heavily reliance on petroleum-derived diesel oil. However, current commercial production technology of biodiesel via homogenous transesterification has a lot limitation, making the cost of biodiesel production economically unfeasible. On the other hand, heterogeneous transesterification process provides a cheaper, less problematic and easier operation compared to homogenous and non-catalytic transesterification processes. However, reactivity of the heterogeneous (solid) catalysts has always become a problem. Not many solid catalysts could produce high yield of fatty acid methyl esters (FAME) in the transesterification process. Hence, it becomes a challenge to create a practical, durable and highly reactive solid catalyst which can be used in the transesterification process.

The controversies of edible oils being converted to fuel bring new dimension to the transesterification process. Prolonged dependence and increasing demand on edible oil as feedstock created a siphon which draws bigger portion of edible oils into the fuel industry. This consequently threatens the supply of edible oil to food industry. Due to these factors, it is crucial to find other alternative oil feedstock to substitute edible oil in the production of biodiesel (transesterification process).

Therefore, the main aim of this project is to synthesize a solid superacid catalyst (sulfated zirconia) that can be used as catalyst in the heterogeneous transesterification of palm oil to biodiesel. Subsequently, sea mango will be used as oil feedstock to study the feasibility of sea mango oil as a non-edible (alternative) oil for the production of biodiesel.

1.4 Project Objectives

This research project aims to achieve the following specific objectives.

(a) To synthesize, optimize and characterize sulfated zirconia as a solid superacid catalyst for the transesterification of palm oil under a number of catalyst preparation parameters/variables – calcination temperature, calcination period and ratio of catalyst to support

(b) To study and optimize the transesterification of palm oil using optimized sulfated zirconia catalyst under a wide range of operating parameters (reaction temperature, reaction period, ratio of oil/methanol and amount of catalyst) using design of experiment (DOE) and response surface methodology (RSM) and to compare its performance with montmorillonite KSF catalyst

(c) To study the feasibility of a non-edible oil (*Cerbera odollam* oil) as alternative feedstock in the transesterification process

(d) To characterize the product from the transesterification process (palm FAME)

(e) To study the kinetic of the transesterification process

1.5 Organization of Thesis

There are five chapters (including introduction) in this thesis and each chapter gives specific information about this research project.

Chapter 1 gives the introductory of this research project. This chapter starts with the current energy trend that leads to the development of alternative energy particularly biodiesel. This chapter also gives brief overview of the biodiesel production which leads to the development of heterogeneous transesterification process. The problem statement and objectives of this research project are also stated clearly in this chapter.

Chapter 2 gives literature review on this research project background. This chapter begins with information about biodiesel; definitions, common equations and basic principles. Further in this chapter are the reviews of the transesterification processes and methods and the latest research study in the heterogeneous transesterification process. Other topics covered in this chapter are the reviews of catalyst preparation methods for sulfated zirconia catalyst and its latest development in the literature.

Chapter 3 describes the materials and methodology used in this research project. The first part of this chapter gives the list of material and chemicals used in this research project. The subsequent topics describe clearly the methodology of this research project – synthesis, optimization and characterization of the sulfated zirconia catalyst, transesterification process using heterogeneous catalysts (sulfated zirconia catalyst and montmorillonite KSF catalyst), extraction and transesterification process of sea mango oil, characterization of the product of this research project (FAME) and kinetic study.

Chapter 4 presents the results and discussions of this research project. The sequence of topics in this chapter follows the sequence of topics in **Chapter 3**. The first part of this chapter contains the results and discussion obtained from the synthesis, optimization and characterization of sulfated zirconia catalyst followed by the results and discussion obtained from the transesterification process studies. Subsequent topics on this chapter contain the results and discussion for the extraction and transesterification of sea mango oil and characterization of product (biodiesel). The final part of this chapter presents the kinetic study of the transesterification process.

Chapter 5 concludes the research project. Recommendations for future work related to this research project are also given.

CHAPTER 2

LITERATURE REVIEW

This chapter reviews background information on the subject of heterogeneous transesterification process that leads to this research project. It begins with the basic principles of biodiesel, advantages and disadvantages of biodiesel, methods, catalysts and feedstock in transesterification process and variables affecting the transesterification process. Further in this chapter are reviews on the development of heterogeneous catalysts that leads to the development of supported sulfated zirconia catalyst.

2.1 Biodiesel

2.1.1 Definition of Biodiesel

Biodiesel is defined as a domestic and renewable fuel for diesel engines, derived from vegetable oil which meets the specification of ASTM D6751 (Fukuda *et al.*, 2001). Biodiesel consists of alkyl esters, which are produced from the transesterification reaction between triglycerides and alcohol. In experimental studies, the final product is termed as fatty acid alkyl esters or fatty acid methyl esters (FAME) instead of biodiesel unless it meets the specification of ASTM D6751 (Lois, 2007).

2.1.2 Advantages and Disadvantages of Biodiesel

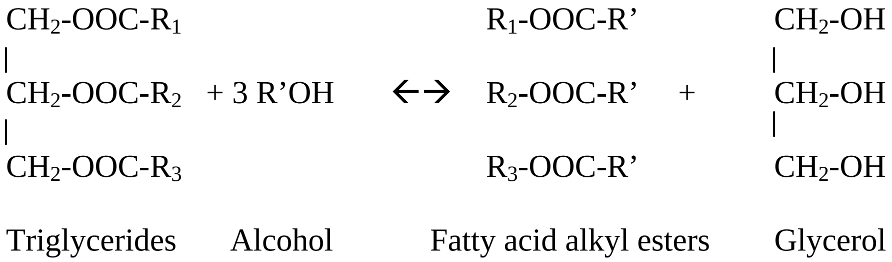
Biodiesel is a sustainable energy (Ma & Hanna, 1999; Omer 2008) that is made from renewable sources such as vegetable oils and animal fats (Barnwal *et al.*, 2005). These sources could always be re-planted or grown to ensure its sustainability. Other than that, biodiesel is a non-toxic and clean energy (Omer, 2008). The emissions from vehicles that are using biodiesel contains lower harmful gases such as carbon monoxide, sulfur dioxide (Demirbas, 2007b; Graham *et al.*, 2008; Roskilly *et al.*, 2008) and aromatic content (Ma & Hanna, 1999) compared to that of using petroleum derived diesel. Biodiesel could also reduce the emission of particulate matters (PM) (Lapuerta *et al.*, 2008b; Ramadhas *et al.*, 2005b).

Biodiesel also acts as a good lubricant to diesel engines (Shahid & Jamal, 2008). This could therefore prolong the self-life of the engines. Biodiesel also has higher flash point which makes it safer to handle compared to diesel (Shahid & Jamal, 2008). Other advantages of biodiesel as diesel fuel are liquid nature portability, readily available, renewability, higher combustion efficiency (Agarwal *et al.*, 2008), higher cetane number (Knothe *et al.*, 2003) and higher biodegradability (DeMello *et al.*, 2007, Lapinskiene *et al.*, 2006).

On the other hand, disadvantages of biodiesel include increased emission of NO_x gas (Agarwal *et al.*, 2006; Ban-Weiss *et al.*, 2007; Lapuerta *et al.*, 2008a), higher cloud and pour points (Ma & Hanna, 1999) and also costlier compared to diesel due to high price of vegetable oils especially those of edible type. However, the cost of biodiesel could vary depending on the source of feedstock (Demirbas, 2008). Biodiesel could also dissolve certain parts of the diesel engines, especially those made of elastomers (Flitney, 2007; Trakarnpruk & Porntangjitkit, 2008). Nevertheless, the advantages of biodiesel superseded the disadvantages generally on the environmental aspects, making it a very popular alternative to petroleum derived-diesel oil.

2.1.3 Transesterification Process

Biodiesel is mainly produced from a chemical process known as transesterification. Transesterification, also known as alcoholysis, is the displacement of alcohol group from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is employed instead of water (Fukuda *et al.*, 2001). The transesterification process consists of three subsequent reversible reactions where the first reaction occurs between triglycerides and alcohol to produce diglycerides and an ester (Sharma *et al.*, 2008). The second reaction continues with diglycerides (from the first reaction) reacting with alcohol to produce monoglycerides and an ester. The third reaction occurs between the monoglycerides (from the second reaction) and alcohol to produce glycerol and an ester. From these reactions, one molecule triglycerides requires three molecules alcohol to form three molecules fatty acid alkyl esters and one molecule glycerol. The general equation of the transesterification process is shown in **Equation 2.1**:



$$\begin{array}{lclclcl} \text{CH}_2\text{-OOC-R}_1 & & & & \text{R}_1\text{-OOC-R'} & & \text{CH}_2\text{-OH} \\ | & & & & & & | \\ \text{CH}_2\text{-OOC-R}_2 & + & 3\ \text{R'OH} & \leftrightarrow & \text{R}_2\text{-OOC-R'} & + & \text{CH}_2\text{-OH} \\ | & & & & & & | \\ \text{CH}_2\text{-OOC-R}_3 & & & & \text{R}_3\text{-OOC-R'} & & \text{CH}_2\text{-OH} \\ \text{Triglycerides} & & \text{Alcohol} & & \text{Fatty acid alkyl esters} & & \text{Glycerol} \end{array} \qquad (\mathbf{2.1})$$

The reaction is endothermic.

R_1, R_2, R_3 and R' are different type of alkyl group. The elaborate equations of the transesterification process are presented in **Equations 2.2 (a-c)** (Fukuda *et al.*, 2001; Ma & Hanna, 1999):

Triglycerides (TG) + R'OH ←→ Diglycerides (DG) + R'COOR$_1$ (**2.2a**)

Diglycerides (DG) + R'OH ←→ Monoglycerides (MG) + R'COOR$_2$ (**2.2b**)

Monoglycerides (MG) + R'OH ←→ Glycerol (GL) + R'COOR$_3$ (**2.2c**)

Commonly in biodiesel production, side reaction can occur especially in the homogenous transesterification process when catalyst such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) is used. Instead of producing alkyl esters, soap is formed. This side reaction is called saponification. The saponification process is show in the **Equation 2.3** (Demirbas, 2003).

Vegetable oils or fats + NaOH → RCOONa + Glycerin (**2.3**)

2.1.4 Methods and Catalysts in Transesterification Process

Transesterification process can be performed with or without catalyst (Gerpen, 2005; Ma & Hanna, 1999); Marchetti, 2007b; Meher *et al.*, 2006b). Transesterification process using catalyst is called catalytic transesterification process whereas transesterification process without catalyst is called non-catalytic transesterification process. However, conventional transesterification process has been using catalytic process to produce biodiesel due to its simpler operation and shorter reaction period to produce biodiesel (Ma & Hanna, 1999; Marchetti *et al.*, 2007b). Non-catalytic transesterification process usually uses supercritical alcohol such as supercritical methanol (Demirbas, 2005, 2007a; Saka & Kusdiana, 2001; Song *et al.*, 2008; Yin *et al.*, 2008) and supercritical ethanol (Madras *et al.*, 2004) to produce fatty acid alkyl esters (biodiesel).

Catalytic transesterification process is divided into two types; homogenous and heterogeneous process. Homogenous transesterification process usually uses catalysts such as sodium hydroxide (NaOH), potassium hydroxide (KOH) (Dias *et al.*, 2008), sulfuric acid (H_2SO_4) (Marchetti & Errazu, 2008) and hydrochloric acid (HCl) (Al-Widyan & Al-Shyoukh, 2002) to catalyze the transesterification process. Heterogeneous transesterification process on the other hand uses solid catalyst such as metal oxides (Liu *et al.*, 2007; Liu *et al.*, 2008; Marchetti *et al.*, 2007b, Mazzochia *et al.*, 2004), active metals supported on various medium (Park *et al.*, 2008); Xie & Lie, 2006), zeolites (Suppes *et al.*, 2004), resins (Shibasaki-Kitakawa *et al.*, 2007), membranes (Guerreiro *et al.*, 2006) and enzymes (Ranganathan *et al.*, 2008) to catalyze the transesterification process.

The division of methods in the transesterification process is best summarized in **Figure 2.1**:

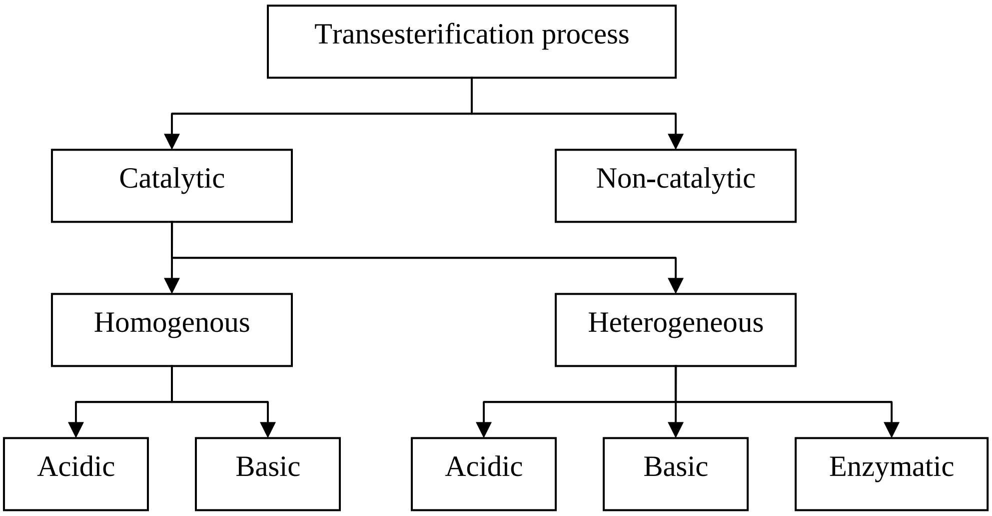


Figure 2.1 Division of methods in the transesterification process

2.1.5 Feedstock for Biodiesel Production

2.1.5 (a) Vegetable Oils and Animal fats

Generally all types of vegetable oil and animal fat could be used as feedstock in the transesterification process. Vegetable oils and animal fats contain triglycerides which are useful in the transesterification process (O'Brien, 2004; Sharma *et al.*, 2008).

Vegetable oils and animal fats for the transesterification process is divided into two types; edible and non-edible type. Vegetable oil of edible type has long been used in the conventional transesterification process (production of biodiesel), largely due to the abundance availability of edible vegetable oil in the global market. Various vegetable oils and animal fats have been used in different countries as feedstock in the transesterification process owing to its availability (Sharma *et al.*, 2008).

Examples of edible oil (vegetable oils and animal fats) that are being studied in the transesterification process are soybean oil (Antunes *et al.*, 2008; Liu *et al.*, 2008; Yin *et al.*, 2008), rapeseed oil (Li *et al.*, 2006a; Morin *et al.*, 2007; Saka &

Kusdiana, 2001), sunflower oil (Arzamendi *et al.*, 2008; Demirbas, 2007a; Granados *et al.*, 2007), palm oil (Crabbe *et al.*, 2001; Jitputti *et al.*, 2006; Kalam & Masjuki, 2002; Song *et al.*, 2008); Trakarnpruk & Porntangjitlikit, 2008), coconut oil (Jitputti *et al.*, 2006) and coffee oil (Oliveira *et al.*, 2008). Examples of non-edible oil in the transesterification process are waste oil (Canakci, 2007; Felizardo *et al.*, 2006; Issariyakul *et al.*, 2007; Ozbay *et al.*, 2008; Wang *et al.*, 2007a; Yagiz *et al.*, 2007; Zheng *et al.*, 2006), jatropha oil (Berchmans & Hirata, 2008; Kumar Tiwari *et al.*, 2007; Sarin *et al.*, 2007; Shah & Gupta, 2007; Talampudi *et al.*, 2008), cottonseed oil (Azcan & Danisman, 2007; Chen *et al.*, 2006; Demirbas 2008b), rubber seed oil (Ramadhas *et al.*, 2005a), algae oil (Christi, 2007, 2008) and tobacco oil (Veljkovic *et al.*, 2006).

Table 2.1 shows the fatty acid composition of some selected vegetable oil samples.

Table 2.1 Fatty acid composition of vegetable oil samples (Demirbas, 2003)

Sample	**16:0**	**16:1**	**18:0**	**18:1**	**18:2**	**18:3**	**Other**
Cottonseed	28.7	0	0.9	13.0	57.4	0	0
Poppyseed	12.6	0.1	4.0	22.3	60.2	0.5	0
Rapeseed	3.5	0	0.9	64.1	22.3	8.2	0
Safflowerseed	7.3	0	1.9	13.6	77.2	0	0
Sunflowerseed	6.4	0.1	2.9	17.7	72.9	0	0
Sesameseed	13.1	0	3.9	52.8	30.2	0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Wheat grain[a]	20.6	1.0	1.1	16.6	56.0	2.9	1.8
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Corn marrow	11.8	0	2.0	24.8	61.3	0	0.3
Castor[b]	1.1	0	3.1	4.9	1.3	0	89.6
Tallow	23.3	0.1	19.3	42.4	2.9	0.9	2.9
Soybean	13.9	0.3	2.1	23.2	56.2	4.3	0
Bay laurel leaf[c]	25.9	0.3	3.1	10.8	11.3	17.6	31.0
Peanut kernel[d]	11.4	0	2.4	48.3	32.0	0.9	4.0
Hazelnut kernel	4.9	0.2	2.6	83.6	8.5	0.2	0
Walnut kernel	7.2	0.2	1.9	18.5	56.0	16.2	0
Almond kernel	6.5	0.5	1.4	70.7	20.0	0	0.9
Olive kernel	5.0	0.3	1.6	74.7	17.6	0	0.8
Coconut	9.7	0.1	3.0	6.9	2.2	0	65.7

[a] Wheat grain oil contains 11.4% of 8:0 and 0.4% of 14: fatty acids.
[b] Castor oil contains 89.6% ricinoloic acid.
[c] Bay laurel oil contains 26.5% of 12:0 and 4.5% of 14:0 fatty acids.
[d] Peanut kernel oil contains about 2.7% of 22:0 and 1.3% of 24:0 fatty acids.

2.1.5 (b) Alcohol

Simpler alcohols (primary alcohol) such as methanol and ethanol are commonly used in the transesterification process due to its better reactivity compared to other higher order alcohols (Solomons & Fryhle, 2000). However, higher order alcohol such as propanol and butanol could also be used in the transesterification process depending on their suitability and compatibility in the transesterification process (Sharma *et al.*, 2008). Recent studies in the literature showed that higher order alcohols could be used in the transesterification process, not only as feedstock but also as solvent which could enhance the transesterification process (Royon *et al.*, 2007).

2.1.6 Variables Affecting the Transesterification Process

There are number of factors which could affect the transesterification process. These factors include moisture content, free fatty acid contents, molar ratio of oil to alcohol, type and amount of catalyst, reaction time, reaction temperature, mixing intensity, and co-solvent (Demirbas, 2007c; Ma & Hanna, 1999; Meher *et al.*, 2006b; Sharma *et al.*, 2008). These factors or variables usually have different effect on the transesterification process depending on the method used for the transesterification process.

2.1.6 (a) Moisture and Free Fatty Acids Contents

Moisture and free fatty acids are two key parameters in determining the viability of the feedstock (vegetable oils) in the transesterification process. Generally, moisture and free fatty acids content of the feedstock must be reduced or lowered (<0.5% for homogenous process) to avoid its undesirable effect on the catalyst and the transesterification reaction (Ma & Hanna, 1999; Sharma *et al.*, 2008). In homogenous transesterification process especially, moisture and free fatty acids in the feedstock could lead to a side saponification reaction, which produces soap and eventually emulsion (Gerpen, 2005; Ma & Hanna, 1999). The formation of soap and emulsion could further complicate the separation and purification process of the final product, which eventually leads to loss of triglyceride and product (biodiesel).

However in other transesterification process, moisture and free fatty acid contents in the feedstock could enhance the yield of fatty acid alkyl esters. For instance, in non-catalytic transesterification process using supercritical fluids for instance, it was found that the moisture and free fatty acid of the feedstock could increase the yield of fatty acid alkyl esters (Kusdiana & Saka, 2004). In enzymatic transesterification process, higher moisture content could enhance the enzymatic activity (Al-Zuhair *et al.*, 2006); Kaieda *et al.*, 2001). Recent development of the transesterification process showed feasible alternative methods for the transesterification process using vegetable oils with high moisture and free fatty acids content; homogenous acidic method using H_2SO_4 as catalyst (Berchmans & Hirata, 2008; Naik *et al.*, 2008), heterogeneous method using resins as catalyst (Marchetti *et al.*, 2007a) and two-step method using acid and base catalysts (Veljkovic *et al.*, 2006).

2.1.6 (b) Molar Ratio of Alcohol to Oil and Type of Alcohol

Based on the stoichiometric of transesterification reaction, every mol of triglyceride requires three moles of alcohol to produce three moles of fatty acid alkyl esters and one mole of glycerol (Ma & Hanna, 1999). In the transesterification process however, alcohol is supplied in excess to induce higher yield of fatty acid alkyl esters. Molar ratio of oil to alcohol at 1:6 is considered as the standard ratio (Fukuda *et al.*, 2001; Gerpen, 2005). However, other researches also shown that molar ratio of oil to alcohol from 1:5 (Alamu *et al.*, 2008) up to 1:8 (Ramadhas *et al.*, 2005a), 1:9 (Sahoo *et al.*, 2007), 1:12 (Meher *et al.*, 2006a), and higher could also be used as the optimum ratio for oil to methanol, depending on the quality of feedstock and method of the transesterification process. However, when the ratio of oil to alcohol is too high, it could give adverse effect on the yield of fatty acid alkyl esters. Some researchers reported that addition of large quantity of methanol, i.e. at ratio of 1:70 and 1:84 could slow down the separation of esters and glycerol phases during the transesterification process, therefore affecting the final yield of fatty acid alkyl esters (Miao & Wu, 2006). It could also promote mass transfer problem between triglycerides, alcohol and catalyst, which eventually could reduce the yield of fatty acid alkyl esters.

Optimization of the ratio of oil to alcohol is usually carried out to determine the optimum ratio of oil to alcohol. Optimization process is usually carried out by varying the ratio of oil to methanol while maintaining the other variables at a certain fixed values and then subsequently comparing the yield or conversion of fatty acid alkyl esters.

2.1.6 (c) Type and Amount of Catalyst

The type and amount of catalyst required in the transesterification process usually depend on the quality of the feedstock and method applied for the transesterification process. For a purified feedstock, any type of catalyst could be used for the transesterification process. However, for feedstock with high moisture and free fatty acids contents, homogenous transesterification process is unsuitable due to high possibility of saponification process instead of transesterification process to occur (Gerpen, 2005).

The yield of fatty acid alkyl esters generally increases with increasing amount of catalyst (Demirbas, 2007b; Fukuda *et al.*, 2001; Ma & Hanna, 1999). This is due to availability of more active sites by additions of larger amount of catalyst in the transesterification process. However, on economic perspective, larger amount of catalyst may not be profitable due to cost of the catalyst itself. Therefore, similar to the ratio of oil to alcohol, optimization process is necessary to determine the optimum amount of catalyst required in the transesterification process.

2.1.6 (d) Reaction Time and Temperature

Current researches have shown that the reaction time for a non-catalytic transesterification process using supercritical alcohol is shorter compared to conventional catalytic transesterification process (Demirbas, 2003, 2005). For a heterogeneous transesterification process, the reaction period varies depending on the reactivity and type of the solid catalyst used.

For a practical and economic feasible transesterification process, it is necessary to limit the reaction time at a certain period. Longer reaction time could also permit reversible transesterification reaction to occur, which eventually could reduce the yield of fatty acid alkyl esters. Thus, optimization of reaction time is also necessary.

The operating temperature for transesterification process depends on the method used. Certain processes, such as homogenous transesterification process and enzymatic transesterification process, generally require moderate temperature to commence the transesterification reaction. However, non-catalytic transesterification process requires high temperature and pressure to yield the desired product (fatty acid alkyl esters). The operating temperature for heterogeneous transesterification process using solid catalyst (except enzymatic process) varies depending on the activation energy and conditions to produce high yield of fatty acid alkyl esters.

2.1.6 (e) Mixing Intensity

Transesterification process is usually associated with mass transfer problem due to opposite polarity of the two feedstock; triglycerides (oil) and alcohol. Triglycerides are hydrophobic whereas alcohol is hydrophilic. Mixing is very important in the transesterification process, as oils or fats are immiscible with alcohol (Meher *et al.*, 2006b). Adequate mixing between these two types of feedstock is necessary to promote contact between these two feedstock, therefore enhance the transesterification reactions to occur. Mechanical mixing is commonly used in the transesterification process. The intensity of the mixing could be varied depending on its necessity in the transesterification process. In general, the mixing intensity must be increased to ensure good and uniform mixing of the feedstock. When vegetable oils with high kinematic viscosity are used as the feedstock, intensive mechanical mixing is required to overcome the negative effect of viscosity to the mass transfer between oil, alcohol and catalyst.

2.1.6 (f) Co-solvent

In the transesterification process, co-solvent is used to enhance the mixing between triglycerides and alcohol. Co-solvent could also function as a reaction medium (Li *et al.*, 2006a), stabilizer (Li *et al.*, 2008) and binder between triglycerides and alcohol to allow contact between the two polar feedstocks. Selection of suitable co-solvent is crucial to enhance the yield of fatty acid alkyl esters. Some co-solvents could also act as an agent to reduce the operating temperature and pressure required for the transesterification process particularly for supercritical transesterification process (Han *et al.*, 2005). Examples of co-solvent include tert-butanol (Royon *et al.*, 2007; Wang *et al.*, 2006), tert-pentanol, isooctane