

MULTISTAGE METHANOLYSIS
OF CRUDE PALM OIL
FOR BIODIESEL PRODUCTION
IN A PILOT PLANT

WINARDI SANI

A Thesis submitted in
fulfillment of the requirement for the award of the Doctor of Philosophy

Faculty of Mechanical and Manufacturing Engineering

Universiti Tun Hussein Onn Malaysia

MAY 2014

This work is dedicated especially to my beloved family lena,
hanan, ilma, and adelia



ACKNOWLEDGMENT

The author would like to express his sincere appreciation to his supervisor, Assoc. Prof. Dr. Khalid bin Hasnan for his necessary support and conscientious supervision through out the duration of his research. The same appreciation goes also to Prof. Ir. Mohammad Zainal bin Md Yusof for the thorough advices.

The cooperation given by the esteem Department of Plant and Automotive Engineering, Faculty of Mechanical and Manufacturing Engineering is as well highly appreciated. Special thanks are dedicated to the Higher Education Ministry of Malaysia for the partial funding of the research under Fundamental Research Grant Scheme. Honour goes also to everyone involved directly or indirectly towards the completeness of this thesis.



PTTA
PERPUSTAKAAN TUNKU TUN AMINAH

ABSTRACT

Crude palm oil (CPO), which is available in abundant in Malaysia, is used as the feedstock in this research work. The work starts with the analysis of the physical and chemical properties of the feedstock and the associated product to obtain the major fatty acid compositions of triglyceride applicable in the crude palm oil. The kinetic models describing the change in the concentrations of the triglycerides, intermediates, alcohol, and the products during the reaction course are formulated through the corresponding kinetic mechanism. By looking at the kinetic mechanisms of the reaction, the chemical reaction is better understood.

The ultimately proposed kinetic models of the biodiesel production from crude palm oil and methanol under the presence of a base catalyst follow the second order differential equations without a shunt reaction. The emphasis of this research work is on the study of the methanolysis of the crude palm oil under a base catalyst (transesterification) to produce biodiesel at high quality and maximum yield. The concentration profiles of the reactants and the products employed in the transesterification are obtained by solving numerically the associated differential equations with introducing the published reaction rate constants applied in a laboratory scale. The effect of the reversible transesterification reaction shows that each concentration profile of the reactants and the products tends to achieve an equilibrium after certain reaction time.

The simulation results of the kinetic models are implemented in the pilot plant to produce biodiesel from CPO. Due to impurities such as unwanted gums and pigment, the feedstock must first undergo a physical treatment including degumming and bleaching processes. The high content of water and free fatty acid containing in CPO requires an esterification process. The main objective of this process is to lower that value to a minimum level to avoid the undesired effects such as saponification and inefficiency of the catalyst. Methanolysis of triglyceride under an alkaline catalyst, transesterification, can be subsequently carried out. Production of biodiesel in a larger scale needs a particular material handling compared to that in laboratory scale. Uncertainty of isothermal state during the reaction

course, uniform mixing in the catalyst preparation, and the effect of the inert gas as the process safety agent will affect adversely the conversion and also the yield. Consequently, the transesterification process must be carried out in stages to achieve a high conversion of palm oil to biodiesel. To attain this objective, the molar ratio of palm oil to methanol for each stage can be adjusted to minimize the methanol usage and the steam consumption. In a batch-mode operated plant, the conversion can vary from a batch to a another batch process. With this approach, it is expected that the high conversion above 96.5 % by weight, as requested by EN 14214 standard, as well as a high yield of biodiesel can be achieved.

Gas chromatography (GC) analysis method was used to determine the methyl ester contents during the reaction progress. Based on these accurate experiment data along with the simulation results, a validation was done. Technical improvements in the plant operation can therefore be deduced towards the best plant performance and a high quality of biodiesel product.



PTTA UTHM
PERPUSTAKAAN TUNKU TUN AMINAH

ABSTRAK

Di dalam kajian penyelidikan ini, minyak sawit mentah (CPO) yang tersedia banyak di Malaysia digunakan sebagai bahan suapan. Penyelidikan ini diawali dengan menganalisa sifat-sifat fizikal dan kimia bahan suapan dan produk berkaitan bagi mendapatkan kandungan asid lemak pada triglyceride di dalam minyak sawit mentah. Model kinetik yang menggambarkan perubahan kepekatan daripada triglyceride, produk antara, alkohol, dan produk utama selama berlangsungnya tindakbalas, dirumuskan berdasarkan pada mekanisma kinetik yang sesuai. Melalui pengamatan mekanisma kinetik, tindakbalas kimia lebih mudah difahami.

Model kinetik untuk menghasilkan biodiesel daripada minyak sawit mentah dicadangkan mengikut persamaan separa dua tanpa reaksi *shunt*. Tumpuan kerja penyelidikan ini adalah kepada kajian metanolisis minyak sawit mentah dengan katalis alkali (transesterifikasi) bagi menghasilkan biodiesel berkualiti tinggi dan keluaran maksima. Profil kepekatan daripada reaktan dan produk di dalam proses transesterifikasi ini diperolehi dengan menyelesaikan persamaan separa tersebut secara numerik. Pekali kadar tindakbalas yang berlaku untuk skala makmal dan telah tersiar diterapkan bagi tujuan tersebut. Pengaruh boleh balik proses transesterifikasi dapat dilihat pada kecenderungan profil kepekatan menuju kepada keadaan seimbang selepas masa tertentu.

Hasil simulasi daripada model kinetik digunakan di dalam ujikaji skala pilot. Kerana bendasing seperti gam dan pigmen yang tidak dikehendaki wujud di dalam minyak sawit mentah, ianya perlu dipisahkan melalui proses penyahangam dan pelunturan. Tingginya kandungan air dan asid lemak bebas (FFA) di dalam CPO, ia memerlukan proses esterifikasi. Tujuan utama proses ini adalah mengurangkan kadar kandungan kedua-dua parameter tersebut bagi mengelak kesan negatif seperti saponifikasi dan ketidakberkesanan katalis. Proses selanjutnya iaitu metanolisis dengan katalis alkali, atau transesterifikasi. Memproses biodiesel dalam skala lebih besar daripada skala makmal memerlukan penanganan berbeza. Meskipun gas unggul diperlukan untuk keselamatan proses, tindakbalas kimia di

dalam skala pilot memerlukan keadaan operasi pada suhu malar dan campuran sekata katalis di dalam metanol. Untuk mencapai objektif yang ditetapkan, nisbah molar minyak sawit terhadap metanol untuk setiap peringkat dapat disesuaikan. Ini penting bagi menjamin penggunaan metanol dan stim kepada paras terendah.

Kaedah analisis gas chromatography (GC) digunakan untuk menentukan kandungan methyl ester selama proses tindakbalas kimia berlangsung. Berdasarkan kepada data ujikaji yang tepat dan hasil simulasi, validasi dapat dilakukan. Penambahbaikan di dalam pengoperasian loji dapat dicadang bagi menghasilkan prestasi terbaik loji dan hasil keluaran biodiesel berkualiti tinggi. Dapat disimpulkan, objektif reaktor di dalam usaha untuk mencapai kadar hasil maksima dan kualiti tinggi produk biodiesel dapat dicapai dengan cara pengoperasian secara berperingkat.



PTTA UTHM
PERPUSTAKAAN TUNKU TUN AMINAH

CONTENTS

| | | |
|----------|--|----------|
| 1 | INTRODUCTION | 1 |
| 1.1 | Research background | 1 |
| 1.2 | Problem Statement | 3 |
| 1.3 | Research Objectives | 5 |
| 1.4 | Scope of the Research Study | 6 |
| 1.5 | New Scientific Contribution | 6 |
| 2 | LITERATURE REVIEW | 8 |
| 2.1 | Feedstock Properties | 8 |
| 2.2 | Fatty Acids Profiles in Crude Palm Oil | 11 |
| 2.3 | Physical Properties of the Feedstock and Product | 14 |
| 2.4 | Biodiesel Properties | 16 |
| 2.5 | Chemical Reaction Principles | 21 |
| 2.6 | Catalysis | 22 |
| 2.6.1 | Homogeneous Catalysis | 23 |
| 2.6.1.1 | Acid Catalysis | 24 |
| 2.6.1.2 | Para Toluene Sulfonate Acid, PTSA | 24 |
| 2.6.1.3 | Base Catalysis | 25 |
| 2.6.1.4 | Sodium Metoxide | 25 |
| 2.6.2 | Heterogeneous Catalysis | 25 |
| 2.7 | Rate of reaction | 27 |
| 2.7.1 | Conversion and Yield | 30 |
| 2.8 | Chemical Reactions for Biodiesel Production | 31 |
| 2.8.1 | Esterification | 31 |
| 2.8.1.1 | Kinetics of Esterification of FFA | 33 |
| 2.8.2 | Transesterification | 34 |
| 2.8.2.1 | Kinetics of the Palm Oil Methanolysis | 36 |
| 2.8.3 | Catalyst | 37 |
| 2.8.4 | Variables Affecting the Transesterification Reaction | 38 |
| 2.8.4.1 | Free Fatty Acid and Moisture | 38 |
| 2.8.4.2 | Catalyst Type and Reactants Concentration | 40 |

| | | |
|----------|---|-----------|
| 2.8.4.3 | Mixing Intensity | 41 |
| 2.8.4.4 | Alcohol Type and Molar Ratio of Alcohol to Oil | 41 |
| 2.8.4.5 | Reaction Time and Temperature | 42 |
| 2.8.5 | Simulation of the kinetics of the methanolysis of triglycerides | 43 |
| 2.9 | Reaction Mechanism in Biodiesel Production | 44 |
| 2.9.1 | Reaction Mechanism of Esterification | 45 |
| 2.9.2 | Mechanism of Acid-Catalyzed Transesterification | 46 |
| 2.9.3 | Mechanism of Base-Catalyzed Transesterification | 47 |
| 2.9.4 | Soap Formation | 49 |
| 2.10 | Kinetic Models of Transesterification | 49 |
| 2.11 | Phase Separation and Purification | 54 |
| 2.12 | Summary | 55 |
| 3 | RESEARCH METHODOLOGY | 56 |
| 3.1 | Framework of Research Methodology | 56 |
| 3.2 | Biodiesel Production | 57 |
| 3.2.1 | Pretreatment of Crude Palm Oil | 59 |
| 3.3 | Phase Regions and Reaction Progress | 60 |
| 3.4 | Experimental Procedures | 62 |
| 3.4.1 | Degumming and Bleaching of CPO | 62 |
| 3.4.2 | Esterification Procedures | 65 |
| 3.4.3 | Procedure for the Multistage Methanolysis | 67 |
| 3.4.3.1 | First Stage Methanolysis | 67 |
| 3.4.3.2 | Second Stage Methanolysis | 68 |
| 3.4.4 | Purification | 69 |
| 3.5 | Gas Chromatography Analysis Methods | 70 |
| 3.5.1 | GC Measurement Parameters Setting | 72 |
| 3.5.1.1 | Procedures for Ester Content Analysis | 72 |
| 3.5.1.2 | Procedures for Glycerol Analysis | 72 |
| 3.5.2 | Expression of the Analytical Results | 74 |
| 3.5.2.1 | Determination of Ester Content | 75 |
| 3.5.2.2 | Determination of Glycerol Content | 75 |
| 3.5.3 | Fatty Acid Methyl Ester (FAME) Content | 77 |
| 3.6 | Summary | 77 |
| 4 | RESULTS AND ANALYSIS | 79 |
| 4.1 | Solution of the Kinetic Model | 79 |
| 4.1.1 | Runge-Kutta Method Fourth Order | 82 |
| 4.1.2 | Simulation of the Kinetics Model | 82 |

| | | |
|----------|---|------------|
| 4.2 | Feedstock and Process Parameters | 86 |
| 4.2.1 | Composition of Feedstock and Biodiesel | 86 |
| 4.2.2 | Process Parameters | 88 |
| 4.3 | Material Balance | 90 |
| 4.3.1 | Conversion FFA to Biodiesel | 92 |
| 4.3.2 | Methanol Consumption and Water Generation | 92 |
| 4.3.3 | Triglyceride Consumption and Its Products | 93 |
| 4.4 | Base-Catalyst Methanolysis | 94 |
| 4.4.1 | First Stage Methanolysis | 94 |
| 4.4.1.1 | Neutralization | 94 |
| 4.4.1.2 | Soap Formation From FFA | 95 |
| 4.4.1.3 | Second Biodiesel and Methanol Consumption | 96 |
| 4.4.2 | Second Stage Methanolysis | 97 |
| 4.4.3 | Effect of Molar Ratio | 98 |
| 4.5 | Energy Consumption and Operating Cost | 102 |
| 4.6 | Data Analysis | 103 |
| 4.6.1 | Determination of Ester Content | 104 |
| 4.6.2 | Methyl Esters Profile | 105 |
| 4.6.3 | Analysis of the Methyl Ester Profiles | 107 |
| 4.6.4 | Determination of Glycerol and Intermediates Content | 109 |
| 4.6.5 | Calibrations by Standard Solutions | 109 |
| 4.6.6 | Percentage of the Residues | 111 |
| 4.7 | Summary | 113 |
| 5 | CONCLUSION AND RECOMMENDATION | 114 |
| 5.1 | Conclusions | 114 |
| 5.2 | Future Work and Recommendation | 118 |
| 5.3 | List of Related Publications | 119 |
| | REFERENCES | 121 |
| A | Material Balance | 129 |
| A.1 | Material Balance for Case Study #1 | 129 |
| A.2 | Material Balance for Case Study #2 | 135 |
| A.3 | Material and Product Specifications | 139 |
| A.3.1 | Cost of Feedstock and Chemical | 140 |
| B | Mechanical Stirrer and Reactor Geometry | 141 |
| B.1 | Reactor Geometry | 142 |
| B.2 | SCADA System | 143 |

| | |
|---|------------|
| C GC and Analytical Methods | 145 |
| C.1 GC Components | 145 |
| C.1.1 Carrier Gas | 145 |
| C.1.2 Injector and Detector | 145 |
| C.2 Samples Preparation | 146 |
| C.2.1 Reagents and Sampling for Methyl Ester Determination . . | 146 |
| C.2.2 Reagents and Sampling for Glycerol Determination | 146 |
| C.2.2.1 Calibration solutions | 147 |
| C.2.3 Reagents and Sampling for Determination of Methanol Con- tent | 148 |
| C.3 Calibrations for Glycerol Contents | 149 |
| C.4 Experimental Report Data | 150 |
| C.4.1 GC Data Analysis for Esterification | 151 |
| C.4.2 GC Data Analysis for the First Stage Base-Catalyzed Methanol- ysis | 152 |
| C.4.3 GC Data Analysis for the Second Stage Base-Catalyzed Methanolysis | 154 |
| C.5 TLC Analysis Method | 155 |
| C.6 FFA Analysis Method | 157 |
| D RUNGE KUTTA COMPUTER CODES | 159 |



LIST OF FIGURES

| | | |
|------|---|----|
| 2.1 | Formation of triglycerides, Smith (2012) | 11 |
| 2.2 | Skeletal structures of stearic acid and oleic acid, Man, Haryatia, Ghazalib, and Asbia (1999) | 12 |
| 2.3 | Triolein, Diglyceride and Monoglyceride | 13 |
| 2.4 | Cetane structure, $C_{16}H_{34}$ | 19 |
| 2.5 | Oleic Acid Methyl Ester, $C_{19}H_{36}O_2$ | 19 |
| 2.6 | Influence of Catalyst on Activation Energy during the Reaction Course, D K Chakrabarty (2009) | 23 |
| 2.7 | Steps involved in a reaction on a solid catalyst, Froment and Bischoff (1979) | 26 |
| 2.8 | Esterification of FFA | 32 |
| 2.9 | Transesterification of a Simplified Palm Oil with Methanol | 35 |
| 2.10 | Hydrolysis of Triglyceride to form FFA | 38 |
| 2.11 | Formation of Soap | 39 |
| 2.12 | Concentration Profiles for TG, DG, MG, Methyl Ester, and Methanol | 43 |
| 2.13 | Conversion of TG to Methyl Ester at different times | 44 |
| 2.14 | Reaction Mechanism of Esterification, McMurry (2008) | 45 |
| 2.15 | Transesterification reaction | 46 |
| 2.16 | Reaction Mechanism of Acid Transesterification | 47 |
| 2.17 | Reaction Mechanism of Base Transesterification, B.S. Bahl (1999) | 48 |
| 2.18 | Soap Formation in a Base Transesterification | 49 |
| 2.19 | Transesterification of triglyceride with Methanol to Methyl Ester | 50 |
| | (a) Converting TG to DG and Methyl Ester | 50 |
| | (b) Converting DG to MG and Methyl Ester | 50 |
| | (c) Converting MG to G and Methyl Ester | 50 |
| 3.1 | Methodology of the Research Study With the Outcomes | 57 |
| 3.2 | Block flow diagram for the biodiesel production, Sani, Hasnan, and Yusof (2012) | 58 |
| 3.3 | Phase regions and the concentration profiles | 61 |
| 3.4 | Process Flow Diagram for the Pretreatment of CPO | 63 |

| | | |
|------|---|-----|
| 3.5 | Process Flow Diagram for the Esterification and Transesterification | 64 |
| 3.6 | Summary the Multistage Methanolysis Processes | 66 |
| 3.7 | Pictures of the Reactor and its dual impellers | 68 |
| | (a) Reacting Vessel | 68 |
| | (b) Dual Impeller | 68 |
| 3.8 | Schematic Diagram of GC Instrument | 70 |
| 4.1 | Concentration Profiles for TG, DG, MG, Methyl Ester, and Methanol | 83 |
| 4.2 | Concentration Profiles for DG and MG | 84 |
| 4.3 | Conversion of TG to Methyl Ester at different times | 85 |
| 4.4 | Material Streams for Esterification | 92 |
| 4.5 | Transesterification of Tripalmitin with Methanol | 94 |
| 4.6 | Conversion Profiles for the various molar ratio | 101 |
| 4.7 | Separation of Biodiesel Mixtures on a TLC Plate | 103 |
| 4.8 | Typical chromatogram for the Ester Content | 105 |
| 4.9 | Ester content distribution for sample #1 | 106 |
| 4.10 | ME Profiles for two Different Samples | 107 |
| 4.11 | Chromatogram for the glycerol standard solutions | 111 |
| A.1 | Material Streams for Esterification | 129 |
| B.1 | Geometrical Features of a Stirrer | 141 |
| B.2 | Geometry of the tranesterification reactor, VE 202 | 143 |
| B.3 | Geometry of the esterification reactor, VE 201 | 143 |
| B.4 | SCADA System for the Plant Operation | 144 |
| C.1 | Developing Chamber and TLC plate | 156 |
| C.2 | FFA Test Titration Apparatus | 157 |



LIST OF TABLES

| | | |
|------|---|----|
| 2.1 | General Components of Crude Palm Oil | 9 |
| 2.2 | Typical Compositions of Crude Palm Oil | 10 |
| 2.3 | Common fatty acid profiles of palm oil, Edem (2002) | 13 |
| 2.4 | Fuel Properties of CPO, M.Snäre and P.Maki-Arvela (2009) | 14 |
| 2.5 | Physical Properties of Feedstock and Product | 15 |
| 2.6 | Biodiesel Fuel Standard, EN 14214,Knothe (2006) | 17 |
| 2.7 | Viscosity of Fatty Acids and Methyl Esters [mm ² /s] | 18 |
| 2.8 | Comparison of Homogeneous and Heterogeneous Catalysts. | 27 |
| 2.9 | FFA Levels Recommended for Transesterification | 40 |
| 2.10 | Homogeneous Catalyzed Transesterification [1em] | 43 |
| 3.1 | Parameters for the pretreatment of CPO | 63 |
| 3.2 | Process Variables for Esterification of CPO | 66 |
| 3.3 | Process Variables for the First Transesterification | 68 |
| 3.4 | Stepwise Flashing Conditions | 70 |
| 3.6 | GC Instrument Parameter for EN 14105 | 72 |
| 3.5 | GC Instrument Parameter for EN 14103 | 74 |
| 4.1 | Reaction Rate Constants, k_i at 65 °C, Narváez, Rincón, and Sánchez (2007) | 81 |
| 4.2 | Typical material properties of the Feedstock | 87 |
| 4.3 | Molar Mass and Density of CPO | 87 |
| 4.4 | Fatty Acid to Methyl Ester | 88 |
| 4.5 | Typical Analysis of BPO | 89 |
| 4.6 | Reaction Specification per Batch | 90 |
| 4.7 | Feedstock Composition | 90 |
| 4.8 | Material balance | 91 |
| 4.9 | Summary of the Material Balance after Second Stage | 97 |
| 4.10 | Reaction Specification #2 per Batch | 99 |

| | | |
|------|---|-----|
| 4.11 | Material Consumption #2 | 99 |
| 4.12 | Summary of the Material Balance for Sample #2 | 100 |
| 4.13 | Esterification at $t = 15$ minutes [1em] | 104 |
| 4.14 | Summary of the Methyl Ester Contents | 105 |
| 4.15 | Summary of the Ester Contents in the Biodiesel Production | 108 |
| 4.16 | Data of the Calibration Solution for Glycerol Analysis | 109 |
| 4.17 | Coefficients of the Calibration Functions | 110 |
| 4.18 | Percentage of the Residue | 112 |
| | | |
| A.1 | Feedstock Composition and Specification | 130 |
| A.2 | Molecular Weight, M , of the Compounds in [kg/kmol] | 130 |
| A.3 | Reaction Specifications for Case Study #1 | 131 |
| A.4 | Material Balance for Case Study #1 | 131 |
| A.5 | Material Balance for Case Study #2 | 135 |
| A.6 | Material and Product Specifications | 139 |
| A.7 | Cost of Feedstock | 140 |
| | | |
| C.1 | Preparation of Calibration Solutions | 148 |
| C.2 | GC Instrument Parameter for EN 14110 | 149 |
| C.3 | Calibration of Glycerol | 150 |
| C.4 | Calibration of Mono Glycerol | 150 |
| C.5 | Calibration of Diglycerol | 150 |
| C.6 | Calibration of Triglycerol | 150 |
| C.7 | Esterification at $t = 15$ minutes | 151 |
| C.8 | Esterification at $t = 30$ minutes | 151 |
| C.9 | Esterification at $t = 45$ minutes | 152 |
| C.10 | Esterification at $t = 60$ minutes | 152 |
| C.11 | First Stage Methanolysis at $t = 15$ minutes | 152 |
| C.12 | First Stage Methanolysis at $t = 30$ minutes | 153 |
| C.13 | First Stage Methanolysis at $t = 45$ minutes | 153 |
| C.14 | First Stage Methanolysis at $t = 60$ minutes | 153 |
| C.15 | Second Stage Methanolysis at $t = 15$ minutes | 154 |
| C.16 | Second Stage Methanolysis at $t = 30$ minutes | 154 |
| C.17 | Second Stage Methanolysis at $t = 45$ minutes | 154 |
| C.18 | Second Stage Methanolysis at $t = 60$ minutes | 155 |
| C.19 | Summary of the Biodiesel Production | 155 |



PTM UTHM
PUSAT TEKNOLOGI MAKANAN TUNKU TUN AMINAH

LIST OF SYMBOLS AND ABBREVIATIONS

| Symbols | Abbreviation | Unit |
|-----------|----------------------------------|---------------------------------------|
| p | Pressure | bar |
| T | Temperature | K |
| t | Time | s or min. |
| C | Concentration | mol/m ³ |
| R | Universal Gas Constant | 8.314 $\frac{\text{J}}{\text{mol s}}$ |
| X | Conversion | % |
| Y | Yield | |
| r_n | Molar Ratio | |
| M | Molecular Weight | g/mol |
| m | Mass | kg |
| n | Number of Moles | mol |
| ppm | Part Per Million | |
| pK_a | Acid Dissociation Constant | |
| E_a | Activation Energy | kJ/mol |
| r | Reaction Rate | mol/min |
| V | Volume | m ³ |
| ν | Stoichiometric Coefficient | |
| A | Area | m ² |
| IV | Iodine Value | |
| Re | Reynold Number | - |
| rpm | Rotation Per Minute | $\frac{1}{\text{min}}$ |
| E or ME | Methyl Ester | |
| O or MeOH | Methanol | |
| G or GL | Glycerol | |
| TG | Triglyceride | |
| DG | Diglyceride | |
| MG | Monoglyceride | |
| FFA | Free Fatty Acid | |
| FA | Fatty Acid | |
| DOBI | Deterioration of Bleaching Index | |

| Symbols | Abbreviation | Unit |
|----------------|--|-------------|
| PTSA | Para Toluene Sulfonate Acid | |
| GC | Gas Chromatography | |
| TLC | Thin Layer Chromatography | |
| FAME | Fatty Acid Methyl Ester or Biodiesel | |
| FID | Flame Ionization Detector | |
| EN | European Norm | |
| ASTM | American Society for Testing and Materials | |
| CPO | Crude Palm Oil | |
| BPO | Bleached Palm Oil | |



CHAPTER 1

INTRODUCTION

This chapter deals with the research background, the problem statement, and the associated objectives necessary for the research work. The subsequent section sets the scope of works and the intended objectives for completing the tasks. At the end of the chapter, the expected new scientific contribution to the body of knowledge is given.

1.1 Research background

The scarcity of fossil fuels and increasing emissions of combustion-generated pollutants as well as their fluctuate costs will make biomass resources more attractive Gerpen and Knothe (2005). Many experts suggest that the current oil and gas reserves would suffice to last only a few more decades. To fulfill the rising energy demand and replace reducing petroleum reserves, fuels such as biodiesel and bioethanol are in the forefront of alternative technologies. Accordingly, the viable alternative for compression-ignition engines is the biodiesel, Demirbas (2008). Palm oil is widely grown in southeast Asia; 90% of the palm oil produced is used for food and the remaining 10% for non-food consumption, such as the production of oleo-chemicals Leng (1999).

A fact is that we are in the early phases of truly historic transition – from an economy based largely on petroleum to a more diversified economy in which renewable plant biomass will become a significant feedstock as an alternative energy resource, (Dale and Kim (2006)). The development of the petroleum refining industry over the past century provides many instructive lessons for the future biobased economy. Malaysia is fortunate to have a plentiful supply of the bioenergy resource. The golden crop of Malaysia, oil palm, is regarded as the

most-effective oil crop with an average annual yield of 3.5 – 5.0 tons of palm oil per hectare, Choo Yuen May (2005). It offers a potential environment-friendly alternative energy.

With oil palm as the bio-based feedstock available in abundant, the suitable process routes must be selected for production of biodiesel as an alternative energy for fuel. Selection of the right process routes include physical, chemical and thermal treatment of the feedstock for biodiesel production. The ultimate selection determines the utility requirement and process equipment or unit operations to be used. This kind of tasks is carried out at the beginning stage of process plant design and supported by means of a Computer-Aided Process Engineering (CAPE) software (Peter-Helmus, 2008).

In many countries including Malaysia the development of biodiesel production is driven by the need to increase security of energy supply for the transportation sector by having a renewable source at hand, have an environmentally friendly fuel available for the diesel combustion engine, reduce health and security risks, and provide the customer with a reliable fuel at a reasonable cost-benefit ratio (Reaney, Hertz, and McCalley (2005); MPICM (2006)). Commercial fuels are predominantly derived from fatty acids and their derivatives that are used as biodiesel fuel and fuel components. Methyl esters of fatty acids or blends of fatty acid methyl esters with conventional diesel fuels from fossil sources have been used in the market. Although other esters have been studied as fuels, the relative cost benefits and ease of preparing, methyl esters have allowed these sources to dominate the current commercial production.

Universiti Tun Hussein Onn Malaysia (UTHM) has embarked a biodiesel production pilot plant with a capacity of 1 metric ton (MT) per batch of production. Crude palm oil is used as the feedstock and biodiesel with fuel grade quality is the main product. The plant is designed to produce biodiesel from any vegetable oil regardless of the oil sources. Fortunately, in Johor especially Batu Pahat, the oil source is mainly originated from palm-based oil and additionally, the state of Johor is the biggest producer of palm oil in the peninsular of Malaysia. Therefore, using palm-based feedstock for biodiesel production is the practical choice towards a sustainable green energy development.

This research study will elaborate on the performance of the reacting unit operations for the methanolysis of crude palm oil to produce biodiesel. These reacting vessels represent the heart of the biodiesel plant, in which a high-value product is

produced through chemical transformation. The chemical reactor therefore is a crucial component of the entire plant, and its high performance must be ensured. Plant engineers are concerned with each reactor's specific yield, selectivity, safety, environment, quality and purity as well as the degree to which reactors support overall plant economic viability and optimal operational conditions.

For the methanolysis of crude palm oil, the performance of the reactor is measured on the basis of the conversion/consumption of the feedstock and the yield or product. Reaction kinetics is a useful tool to describe the chemical reactions of the reactants and the corresponding products inside a reactor during the course of the overall reaction. Many active research studies have been done in biodiesel production during the last two decades using a variety of feedstock. Darnoko and Cheryan (2000a) has experimentally developed the reaction kinetic models of the palm oil transesterification in the laboratory scale. Devender S. Negi (2007) and Nouredini and Medikonduru (1997) investigated the empirical kinetic behavior of biodiesel production using palm oil and soy oil at the same scale. However, published research data on the kinetic model of the methanolysis of crude palm oil especially in a medium scale such as the UTHM pilot plant, are still not available. The kinetics of a reaction is determined by measuring concentrations of the reactants and products as a function of time.

Following the stoichiometry, methyl ester or biodiesel is formed through a simple catalyzed reaction of one mole of oil with three moles of methanol. Problems will be encountered if the oil contains impurities and the product purity is of high importance. In the pilot scale where its nature differs from the laboratory one, suitable efforts must be done to prepare the oil free from impurities and useful purification methods must be carried out to obtain the specified product quality.

1.2 Problem Statement

1. Kinetic Model of Biodiesel Production in a Pilot Scale is not available.

Driven by the lack of published literatures on the kinetic models deduced from the reaction mechanism describing the methanolysis of crude palm oil and triglyceride under presence of certain catalysts, it has led to an indispensable need to get a suitable and practical tool for operating the plant reactors towards a high performance. The expected tool should be able to

help explain how the transformation of the reactants to both the products and the byproducts as well the role of the associated catalyst.

The reacting system occurs in a reactor. A batch-mode operating plant consists of a sequence of reactors that work independently. A typical feature of a process plant operating in a batch mode is the inconsistent reactor performance from batch to batch due to non-uniformities, time variants conditions, unsteady-state production, and downtime for filling and discharging. A chemical reactor performance is measured on the conversion of the feedstock to the desired product and the selective yield regardless of what various conditions. Any failure in the reactor performance will make it difficult to take an appropriate action if the process engineering tool in form of the applicable kinetic models for the biodiesel production is not at hand.

Additionally, operating a reactor under non-isothermal conditions for a batch-mode operating plant is not advisable due to high energy consumption and uncontrolled conditions that could lead to an unstable situation as suggested in Korovski and Linniger (2005) However, the reaction rate constants of the kinetics equations investigated in a laboratory scale can be utilized to estimate the actual the concentration profiles of the reacting compounds during the reaction course. Owing to the difference in the inherent nature of the two scales such as dimension, heat supply, mixing intensity, and an uncertainty in the reaction condition, it will cause the reaction behavior in the laboratory scale to be different than that in the pilot scale. Additionally, a batch-mode processing plant enables a wide range of products or product grades in the same equipment compared to the continuous process, Ray Sinnot (2009).

2. Process Variables Settings for the Plant Operation with a capacity of 1 MT are not defined.

Consequently, in the actual batch-mode plant operation, the right composition of the reacting components being processed must be set correctly from a batch to another batch, or from a stage to another stage. The utmost attention must be given to the molar ratio of methanol to triglyceride as well as the catalyst usage during the transesterification process. To much use of methanol will cause a high energy consumption in the methanol recovery, otherwise, the reaction will be incomplete. Furthermore, a pilot plant at a

scale of 1 MT is used for the research study.

3. Process Route in the Pretreatment of CPO needs to be selected.

Another technical issue in the production of biodiesel from crude palm oil is the impurities contained in CPO must be first separated in the pretreatment plant. In palm oil industries, CPO undergoes not only degumming, bleaching, and neutralization process, but also a deodorizing treatment for removal the naturally unpleasant odor due to odiferous matter. Therefore, preparing CPO suitable for the esterification process must be also analyzed and a proper synthesis route in the pretreatment plant shall be selected.

1.3 Research Objectives

The objectives of the research study will achieve the following targets:

1. Process routes for biodiesel production commencing from the pretreatment of crude palm oil and the subsequent steps up to purification of the product are properly selected. The function of the unit operation and the desired product specifications are also included.
2. Formulate the kinetic models of the methanolysis of the triglyceride deduced from the reaction mechanism.
3. Solve the kinetic models of the methanolysis of triglyceride under an alkaline catalyst numerically and simulate them to evaluate the methyl ester's profile during the reaction progress.
4. Examine experimentally the reactor performance in term of the conversion of the palm oil by operating the pilot plant to transform the crude palm oil to biodiesel under specific conditions.
5. Propose the useful process variables derived through both the simulation results and the experimental validation in order to achieve the best performance of the biodiesel production pilot plant.

1.4 Scope of the Research Study

To achieve the mentioned research objectives, the scope of the research study along with the related assumptions and limitations are listed as follows:

1. Assumptions and limitations:
 - a) The physical properties data of the feedstock and product are obtained from the published data.
 - b) The fatty acids composition comprising the palm oil is limited to five major components, myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid. The other minor components are relative to their mass percentage negligible.
 - c) The reaction rate coefficients necessary for solving the partial differential equations numerically are obtained from the experimentally published data.
 - d) Transport effects on the rates of concentration change are excluded, since these may complicate, or even obscure, the principal objectives of the work. The concentration gradient within the reactor is therefore spatially negligible.
 - e) The reactors in the UTHM pilot plant operates at an isothermal condition and 1 metric ton (1 MT) of capacity.
2. Scope of works:
 - a) Only the methyl ester contents during the reaction progress are investigated by using GC analyze method. This component contributes above 95% of biodiesel.
 - b) Purification of crude biodiesel to biodiesel for fuel uses a hot water washing method to minimize the material cost.

1.5 New Scientific Contribution

The main expected scientific contribution of the research is the application of the multistage methanolysis of crude palm oil in the reacting vessels. This method enables the batch-mode operating pilot plant to deliver a high conversion of the feedstock and a high yield of biodiesel under specific process variables. Having

the right process variables in the hand, a process engineer can operate the plant more convenient regardless of the various conditions encountered from a batch to another batch, or from a stage to another stage of the transesterification process. Moreover, the underlying knowledge lies in the kinetic models deduced from the reaction mechanism that is better understood. This mechanism is a useful tool to describe how the reacting compounds react with other under a particular condition. The multistage methanolysis could be extended to a continuous biodiesel production if a demand in a larger quantity would be in place.



CHAPTER 2

LITERATURE REVIEW

The possibility of using vegetable oils as fuel has been recognized since the beginning of diesel engines. Vegetable oil has too high a viscosity for use in most existing diesel engines as a straight replacement of fuel oil. Transesterification (esters exchange) is the most common method to solve the problem. It is a chemical reaction of a fat or oil (triglyceride) with an alcohol to form esters and glycerol. This chapter will elaborate the state of the art in the biodiesel production from an initial feedstock to the final product through the literatures reviews. Moreover, theoretical fundamentals in organic chemistry relevant to biodiesel production are included.

2.1 Feedstock Properties

Biodiesel can be made from any plant oils with over 350 oil-bearing crops being identified for the production of biodiesel, Ng, Ng, and Gan (2009). The selection of feedstock for biodiesel production depends primarily on region, price and chemical properties. The dominant feedstock varies among countries, since the suitability of vegetation is very much dependent on local climates. The predominant raw material in European countries is rape seed, while in the United States (US) soybean is the most widely used feedstock. For a tropical climate like Malaysia palm oil is the common feedstock for biodiesel production.

Determining the chemical and physical properties of crude palm oil as the feedstock for biodiesel production is of importance for proper selection of the process routes. A (2000) as cited in Morad, Aziz, and Zin (2006) has classified crude palm oil into five physical and chemical groups as shown in Table 2.1. The main component of crude palm oil is triglyceride which composes 90 – 98% of the to-

Table 2.1: General Components of Crude Palm Oil

| Group | Components |
|-------------------------|---|
| Oil | Triglyceride, Diglyceride, Monoglyceride Free Fatty Acid |
| Oxidized Products | Peroxide |
| Non-oil but oil soluble | Carotene, Tocopherol, Phospholipids |
| Impurities | Metal particles |
| Water solubles | Water (Moisture) Glycerol, Chlorophyl pigments |

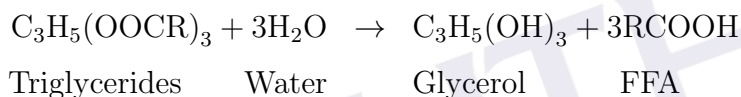
tal mass, Canakci and Sanli (2008). Some of the groups and components must be removed partially or completely through refining process to meet the desired feedstock specification. Free fatty acid (FFA) is the fatty acid that is not bound on the glycerol backbone of triglycerides. FFA originates from the breakdown of triglycerides into its component fatty acid and glycerol units, and results from the exposure of triglycerides to moisture or from enzymatic processes. Copeland and Belcher (2002) reveals that a high FFA in a vegetable oil generally indicates that the oil was poorly processed or that there has been some triglyceride breakdown after refining. FFA also indicates the degree of purity of oil. A purer oil possesses a lower value of this number. Kima, Kim, Lee, and Tak (2002) recommends that phospholipid commonly referred to as gums must be removed because of their strong emulsifying action. This component causes an undesirable flavor and a coloring pigment. The emulsifying action is therefore the main suspect causing the oxidative instability of the crude palm oil. Moreover, phospholipids contain phosphorus, nitrogen bases and sugars are the main suspect that needs to be removed totally in the degumming by coagulating the phosphatides contents with phosphoric acid as reported in Morad et al. (2006) and Akoh and Min (2008).

Peroxide is an oxidation product that causes rancidity when the oil reacts with oxygen. The tocopherol and carotene content in oil acts naturally as an antioxidant and makes the oil a reddish brown color. Wei, Maya, Ngan, and Hock (2004) has investigated that trace metals such as iron (Fe) and copper (Cu) are undesirable and usually resulted from the mechanical wear at the mills and refineries. These metals are pro-oxidant and hence reduce the oil quality. The presence of moisture in oil can hydrolyze the triglycerides into free fatty acids and glycerol

Table 2.2: Typical Compositions of Crude Palm Oil

| Composition | Unit | Value |
|-------------------------|-----------------------|---------------|
| Triglyceride | % | ≥ 95 |
| FFA | % | 3.5 |
| Diglycerides | % | 2 – 6 |
| Colour | - | reddish brown |
| Moisture and Impurities | % | 0.25 |
| Peroxide | meq/kg O ₂ | 1.0 |
| DOBI | - | 2 - 3.5 |
| Phosphorus | ppm | 15 |
| Iron | ppm | 5 |

leading to an adverse effect in the oil quality as shown in the following reaction:



Where, R is the long chain fatty acid consisting of the carbon-hydrogen bonds. Understanding the crude palm oil components as aforementioned is essential in process engineering. The typical compositions of Malaysian crude palm oil is summarized in Table 2.2 as reported in Basiron and May (2005). These compositions certainly will determine the suitability of the crude oil for applications. As shown in Table 2.2, triglycerides are the major component of a palm oil. As evaluated in Basiron (2005), monoglycerides and diglycerides are also present in a small amount as an artifact of the refining process. The fatty acid chains in triglyceride can vary in number of carbons and in structure (single or double bonds). These two factors affect greatly in the chemical and physical characteristics of the palm oil. Knowledge about the detailed structures of the triglycerides present in palm oil is necessary because they define some of the physical characteristics of the oil. The melting points of triglycerides are dependent on the structures and position of the component acids present. They also affect the emulsifying behavior of the oil. The semi solid nature of palm oil at room temperature has been attributed to the presence of the unsaturated fraction.

The partial glycerides are formed in the extraction process. Oil obtained from unbruised sterilized fruits shows trace levels of partial glycerides. Random analyses of samples of refined palm oil, palm olein, and palm stearin have shown the presence of about 6% diglycerides with trace amounts of monoglycerides, (Basiron

(2005)). These partial glycerides are important as they are known to affect the crystallization behavior of the oil. Furthermore, the semi solid present in the oil at a normal condition is due to the process of solidification occurring in the oil as a consequence of its chemical properties. The various structures in the molecular triglyceride (saturated and unsaturated) with the associated chemical characteristics reveal obviously the physical states at that temperatures, hence affecting the melting behavior of the oil. A classical method to measure the degree of the unsaturation in fats and oils is called an iodine value (IV) measurement. Hereby, an iodine-bromide (Hanus reagent) or iodine monochloride (Wijs reagent) reagent is reacted with the double bond and an excess reagent (as iodine) is then titrated with sodium thiosulphate solution to obtain its level of unsaturation.

2.2 Fatty Acids Profiles in Crude Palm Oil

Triglycerides or triacylglycerol making off the major component of the vegetable oils and animal fats are chemically a compound of triesters formed from three molecules of fatty acids with a glycerol molecule as the backbone, as shown in Figure 2.1, Smith (2012). Fatty acids consist of the elements carbon (C), hydrogen (H) and oxygen (O) arranged as a carbon chain skeleton with a carboxyl group (-COOH) at one end.

The functional groups, represented by R_1, R_2, R_3 , are fatty acids consisting of the long-chains of carbon-hydrogen bonds. The identity of the three fatty acids in

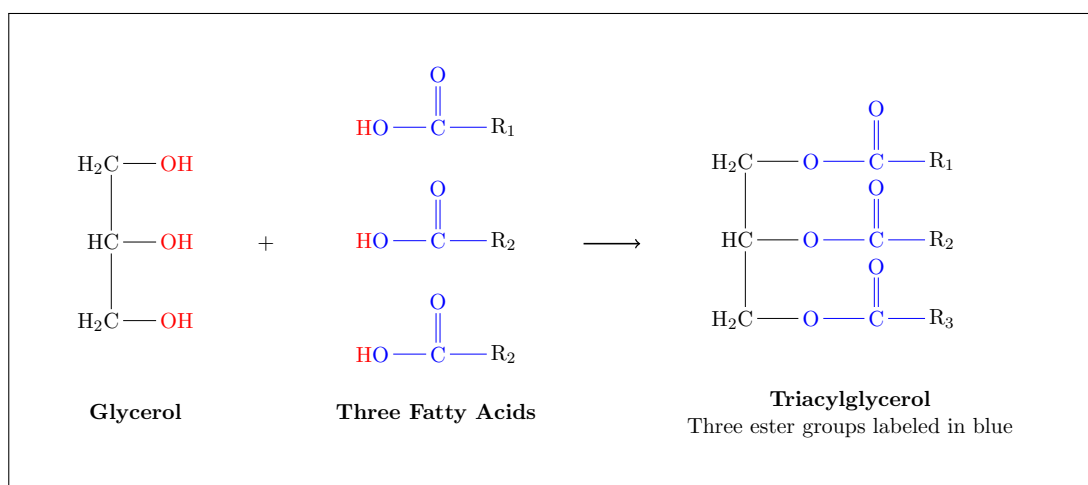


Figure 2.1: Formation of triglycerides, Smith (2012)

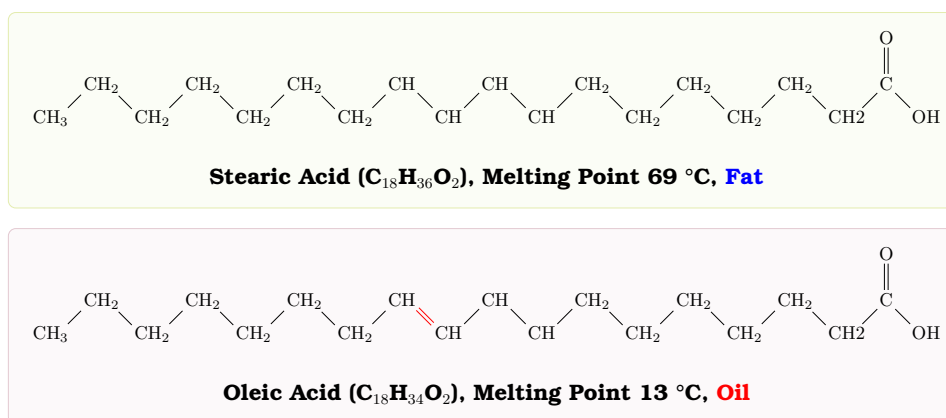


Figure 2.2: Skeletal structures of stearic acid and oleic acid, Man et al. (1999)

the triacylglycerol determines whether it is oil or fat. Increasing the number of the double bonds in the fatty acid chain decrease the melting point of the triacylglycerides. Fats have higher melting points, hence they are solid at room temperature. Oil, in contrast, is liquid at room temperature due to its lower melting points. This different physical phase is affiliated to the double bond of the carbon chain. A large number of double bonds induce a liquid form, whereas fats derived from a few number of double bonds or single carbon-carbon bonds are solid. Fatty acids are called saturated, if they have all the hydrogens that the carbon atoms can hold or do not have any double bond between the carbons.

Figure 2.2 illustrates the difference between two fatty acids in the skeletal structure, Smith (2012). Stearic acid consists only a single carbon-carbon bond, called a saturated fatty acid, and oleic acid has one double carbon-carbon bond. It is an unsaturated fatty acid. Hence, oleic acid is oil in room temperature, while stearic acid is fat or solid. Furthermore, fatty acids are frequently represented by a notation such as C18:1 for oleic acid. This notation indicates that the fatty acid consists of an 18-carbon chain and 1 double bond or unsaturated. Stearic acid has a notation C18:0 because it has 18 carbon chain and no double bond or saturated.

The composition of fatty acids in triglycerides may vary depending upon the oil sources. Triolein (C₅₇H₁₀₄O₆) and tristearin (C₅₇H₁₁₀O₆) are examples of simple triglycerides derived from oleic acid and stearic acid, respectively. Man et al. (1999) has observed that triglycerides of palm oil comprise naturally of various fatty acids. It makes the triglycerides being a complex chemical compound. Moreover, fatty acids may combine with any of the three hydroxyl (-OH) groups of the glycerol to create a wide diversity of compounds.

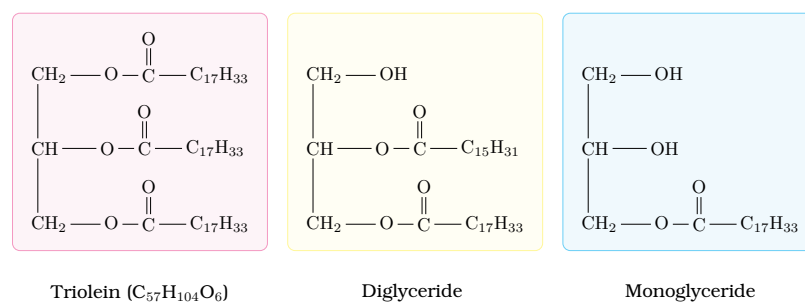


Figure 2.3: Triolein, Diglyceride and Monoglyceride

Figure 2.3 shows that diglyceride or diacylglycerol (DG), each of which has two fatty acid, oleic acid or palmitic acid, respectively. A monoglyceride or monoacylglycerol (MG) has only one fatty acid bond to the glycerol molecule. Therefore, replacing a functional group R_1 with an hydroxyl group in a triglyceride yields a MG, whereas a MG is formed by replacing the second functional group (R_2) with another hydroxyl group. Referring to Figure 2.3, the functional group bonded to the glycerol, R_2 , comes from oleic fatty acid. The structure of DG is illustrated in the middle of the figure. Crude palm oil may contain up to 6% of this compound.

According to M.Snäre and P.Maki-Arvela (2009) and Edem (2002) the fatty acid or composition of palm oil are shown in Table 2.3. The major constituents of palm oil are formed by palmitic and oleic acids, 45% and 39% by weight, respectively. The greater the carbon number of the fatty acid, the higher is the melting point (MP). Moreover, the saturated fatty acids have higher melting points than the unsaturated counterparts. In other words, the unsaturated content causes the

Table 2.3: Common fatty acid profiles of palm oil, Edem (2002)

| Fatty acid | Chemical structure | % | MP [°C] | BP [°C] |
|-----------------|---|----|---------|---------|
| Myristic (14:0) | $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$ | 1 | 54 | 163.5 |
| Palmitic (16:0) | $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ | 45 | 62 | 309.0 |
| Stearic (18:0) | $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ | 4 | 69 | 332.6 |
| Oleic (18:1) | $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ | 39 | 13 | 334.7 |
| Linoleic (18:2) | $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ | 11 | -9 | 230.0 |

fatty acids to have characteristics of a liquid. With the 50 – 50 % composition of the saturated and the unsaturated components in the crude palm oil, it causes the semi solid phase of the oil at the normal condition. Linoleic acid content contributes to the low melting point of the crude palm oil. With this component distribution, CPO is suitable in a tropical country.

Table 2.4: Fuel Properties of CPO, M.Snäre and P.Maki-Arvela (2009)

| Properties | Testing Method | Unit | Mean Value |
|--------------------------|----------------|-------|------------|
| Viscosity at 50 °C | D 445 | cSt | 25.6 |
| Flash Point | D 93 | °C | 268 |
| Density at 50°C | D 1298 | kg/L | 0.889 |
| Gross Heat of Combustion | D 240 | kJ/kg | 39,690 |
| Sulphur Content | D 4294 | wt. % | 0.03 |

Table 2.4 lists the fuel properties of crude palm oil along with the associated testing method, M.Snäre and P.Maki-Arvela (2009) and Edem (2002). The high kinematic viscosity of CPO compared to the viscosity of biodiesel specification (1.9–6.0 cSt) is the main reason of the transesterification which its function is to lower its value to meet the specification for fuel. Flash point of CPO is also too high compared to the fuel specification (130 °C minimum).

2.3 Physical Properties of the Feedstock and Product

The typical properties of the crude palm oil with the corresponding methyl esters as the products of the transesterification reaction, are tabulated in Table 2.5, WebBookNIST (2013). Referring to this table, the viscosity of the product (methyl ester) reduces significantly after transesterification reaction compared to the corresponding feedstock. The average viscosity of methyl esters owing to the various composition of the components in biodiesel is listed in Table 2.4. Its value is ideally at around 4.4 mPa·s that matches the EN specification (3.5 - 5.0), Gerhard Knothe (2005).

Table 2.5: Physical Properties of Feedstock and Product

| Feedstock | | | | | | |
|------------------|--|-----------|----------------------|---------------|------|-----------------|
| Fatty Acid | Chemical Structure | M | Density | Viscosity | MP | BP |
| | | [kg/kmol] | [kg/m ³] | [mPa·s] | [°C] | [°C] |
| Myristic | C ₁₄ H ₂₈ O ₂ | 228.37 | 862.2 | 5.83 (70 °C) | 58 | 250.5 |
| Palmitic | C ₁₆ H ₃₂ O ₂ | 256.42 | 849.0 | 7.80 (70°C) | 64 | 271.5 |
| Stearic | C ₁₈ H ₃₆ O ₂ | 284.48 | 847.0 | 7.79 (80 °C) | 70 | 291 |
| Oleic | C ₁₈ H ₃₄ O ₂ | 282.46 | 854 | 19.91 (40 °C) | 14 | 285 |
| Linoleic | C ₁₈ H ₃₂ O ₂ | 280.45 | 903 | 13.46 (40 °C) | -9.5 | 229 |
| Product | | | | | | |
| Methyl Ester | Chemical Structure | M | Density | Viscosity | MP | BP |
| | | [kg/kmol] | [kg/m ³] | [mPa·s] | [°C] | [°C] |
| Methyl Myristate | C ₁₅ H ₃₀ O ₂ | 242.40 | 855 | 3.3 | 18 | 323 |
| Methyl Palmitate | C ₁₇ H ₃₄ O ₂ | 270.45 | 852 | 4.38 | 28 | 211.5 (30 mmHg) |
| Methyl Stearate | C ₁₉ H ₃₈ O ₂ | 298.50 | 840 | 5.85 | 39 | 215 (15 mmHg) |
| Methyl Oleate | C ₁₉ H ₃₆ O ₂ | 296.49 | 870 | 4.51 | -5 | 219 (15.2 mmHg) |
| Methyl Linoleate | C ₁₉ H ₃₄ O ₂ | 294.47 | 889 | 3.65 | -35 | 192 (4 mmHg) |

The melting point of each product decreases relative to the initial source. This is advantageous for fuel injection. Only the biodiesel component of methyl stearate has a high melting point which in turn is disadvantage compared to diesel fuel. This adversely affect is fortunately compensated by the very low melting point of methyl oleate and methyl linoleate. Finally, the biodiesel has a low melting point, approximately 8.54 °C on average. Furthermore, each methyl ester contains oxygen atom implying lower air consumption for fuel combustion in an engine, and hence lower pressure is required for ignition. Fatty acids have a higher melting point than ester due to their stronger intermolecular forces caused by the hydrogen bonding when comparing them with compounds of the similar size, Smith (2012).

2.4 Biodiesel Properties

Triglyceride means tri-esters of glycerol. Therefore, palm oil contains three ester functional groups (RCOOR_1), where R and R_1 represent the alkyl groups. Breaking these tri-esters from the glycerol backbone yields biodiesel. The chemical structure of biodiesel is similar to fossil diesel containing a long chain of carbon and hydrogen. Biodiesel however, contains a few oxygen atoms. As biodiesel is made up from various fatty acids components, petrodiesel or diesel fuel comes naturally in a mixture of different petroleum-derived components, consisting of paraffins, isoparaffins, naphthenes, olefins and aromatic hydrocarbons, each with their own physical and chemical properties. Petroleum diesel fuels with 9 to 20 carbon atoms have a boiling range between 170 °C and 350 °C, Knothe (2006), whereas biodiesel's boiling points are in the range of 190 °C to 323 °C, as listed in Table 2.5 .

Diesel fuel must satisfy a wide range of engine types, differing operating conditions and duty cycles, as well as variations in fuel system technology, engine temperatures and fuel system pressures. It must also be applicable for a variety of climates. The properties of each grade of diesel fuel must furthermore be balanced to provide satisfactory performance over an extremely wide range of circumstances. In some respects, the substantial quality standards represent certain compromises so that all the performance requirements can be satisfied. By controlling specifications and properties, it is possible to satisfy the requirements of compression ignition engines with a single grade of diesel fuel. The most commonly used guidelines for diesel fuel quality are established by ASTM International in the United States and EN (European Committee for Standardization, CEN) in the European Union. The difference of these two standards are subtle. EN standards are selected for this research purpose because they specify the minimum methyl ester content of biodiesel in the test method. Selected parameters of biodiesel specifications following EN 14214 are listed in Table 2.6 .

Official methods of physical analysis used to characterize conventional diesel are applicable and meaningful when applied to biodiesel and provide useful information. Biodiesel chemistry leads to a number of physical characteristics that are unique when compared with diesel fuels. Most biodiesel preparations have higher viscosity, density, initial boiling point, final boiling point, cold-filter plugging point, and flash point than conventional diesel fuels. Virtually all of these characteristics are due to the high average molecular weight of the component esters of biodiesel. Boiling point and flash point, for example, are related to vapor

Table 2.6: Biodiesel Fuel Standard, EN 14214, Knothe (2006)

| Property | Testing Method | Value | Unit |
|--|-------------------|------------|-------------------------|
| Ester content | EN 14103 | 96.5 min. | (% w/w) |
| Kinematic viscosity, 40°C | EN ISO 3104 | 3.5 – 5.0 | mm ² /s |
| Density, 15°C | EN ISO 3675 | 860 – 900 | kg/m ³ |
| Flash point | EN ISO 3679 | 120 min. | °C |
| Sulfur content | EN ISO 20846 | 10 max. | mg/kg |
| Cetane number | EN ISO 5165 | 51 min. | - |
| Water content | EN ISO 12937 | 500 max. | mg/kg |
| Oxidation stability, 110°C | EN I4112 | 6 min. | h |
| Acid value | EN 14104 | 0.50 max. | mg KOH/g |
| Iodine value | EN 14111 | 120 max. | g I ₂ /100 g |
| Linolenic acid content | EN 14103 | 12.0 max. | % (w/w) |
| Polyunsaturated (≥ 4 double bonds) | | | |
| Methyl Ester | EN 14103 | 1 max. | % (w/w) |
| Methanol content | EN I4110 | 0.20 max. | %(w/w) |
| MG content | EN 14105 | 0.80 max. | %(w/w) |
| DG content | EN 14105 | 0.20 max. | %(w/w) |
| TG content | EN 14105 | 0.20 max. | %(w/w) |
| Free glycerol | EN 14105 EN 14106 | 0.020 max. | %(w/w) |
| Total glycerol | EN I4105 | 0.25 max. | %(w/w) |
| Phosphorus content | EN I4107 | 10.0 max. | mg/kg |

pressure.

The technical definition of biodiesel is a fuel suitable for use in compression ignition (diesel) engines that is made of fatty acid monoalkyl esters derived from vegetable oils or animal fats. When methanol is used as the alcohol, the biodiesel is produced from these types of oil are called fatty acid methyl esters (FAME). Biodiesel standards are in place in a number of countries in an effort to ensure that only high-quality biodiesel reaches the marketplace. Moser (2009) lists the EN 14214 (European Committee for Standardization, CEN) in the European Union, and summarized in Tables 2.6.

Kinematic viscosity is the primary reason why biodiesel is used as an alternative fuel instead of neat vegetable oils or animal fats. In general, viscosity is defined as the resistance by one portion of a material moving over another portion of

the same material. Dynamic viscosity (η) is defined as the ratio of shear stress existing between layers of moving fluid and the rate of shear between the layers. The resistance to flow of a liquid under gravity (kinematic viscosity, ν) is the ratio of (η) to the density (ρ) of the fluid, as formulated in Equation 2.4.1.

$$\nu = \frac{\eta}{\rho} \quad (2.4.1)$$

The high kinematic viscosities of vegetable oils and animal fats ultimately lead to operational problems such as engine deposits when used directly as fuels. The kinematic viscosity of biodiesel is approximately an order of magnitude less than typical vegetable oils and is slightly higher than petrodiesel, Moser (2009); Gerpen and Knothe (2005). If fuel viscosity is low, the leakage will correspond to a power loss for the engine. If fuel viscosity is high, the injection pump will be unable to supply sufficient fuel to fill the pumping chamber. Again, the effect will be a loss in power. However, Crabbe, Nolasco-Hipolito, Kobayashi, Sonomoto, and Ishizaki (2001) reported that the viscosity of crude oil is about 10 times or higher that of No.2 diesel fuel. This is associated with large triglyceride molecule and its higher molecular mass. After transesterification, biodiesel derived from palm has a viscosity value of 5.0 cSt at 40°C, Demirbas (2006) with the density of 880 kg/m³ at 15.5°C. Gerhard Knothe (2005) investigated the kinematic viscosities of the biodiesel fuel components related to the fatty acid parents. Table 2.7 shows the data for the common fatty acids and the corresponding methyl esters measured at 40 °C.

Table 2.7: Viscosity of Fatty Acids and Methyl Esters [mm²/s]

| Fatty acid/Ester | Fatty Acid Structure | | | | |
|------------------|----------------------|-------------------|-------------------|-------------------|-------------------|
| | C _{14:0} | C _{16:0} | C _{18:0} | C _{18:1} | C _{18:2} |
| Triglycerides | nd | nd | nd | 32.94 | 24.91 |
| Acid | nd | nd | nd | 19.91 | 13.46 |
| Methyl | 3.30 | 4.38 | 5.85 | 4.51 | 3.65 |

The viscosity of the lower fatty components is not detected (nd) at 40°C due to their high melting point, see Table 2.3. The kinematic viscosity of each methyl ester component is in the range of 3 – 5 mm²/s that are applicable for diesel engines.

Ester content indicates the completeness of the transesterification. Even after a fully complete transesterification reaction, small amounts of tri-, di-, and monoacylglycerols will remain in the biodiesel product. The glycerol portion of the acylglycerols is summarily referred to as bound glycerol. When the bound glycerol is added to the free glycerol remaining in the product, the sum is known as the total glycerol. Limits for bound and total glycerol are also included in biodiesel standards. EN 14214 requires not more than 0.25% of total glycerol in the final biodiesel product that can be measured using a gas chromatographic (GC) method.

Cetane number or ignitibility is one of the most important properties of a diesel fuel imparting its readiness to auto ignite at the temperatures and pressures present in the cylinder when the fuel is injected. It represents the ignition quality of a diesel fuel. It measures also an ignition delay of a fuel. Ignition delay is a time period between the start of injection and start of combustion of the fuel. Fuels with a higher cetane number have shorter ignition delays, providing more time for the fuel combustion process to be completed. The cetane number scale clarifies an important aspect of the composition of the molecular structure of the compounds comprising diesel fuel. Long chain, unbranched, saturated hydrocarbons (alkanes) have high cetane number and good ignition quality while branched hydrocarbons (and other materials such as aromatics) have low cetane number and poor ignition quality. The term *cetane number* is derived from a straight chain alkane with 16 carbons ($C_{16}H_{34}$), or hexadecane, also called cetane, as shown in Figure 2.4.

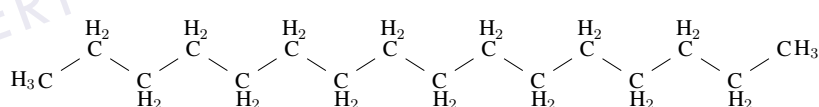


Figure 2.4: Cetane structure, $C_{16}H_{34}$

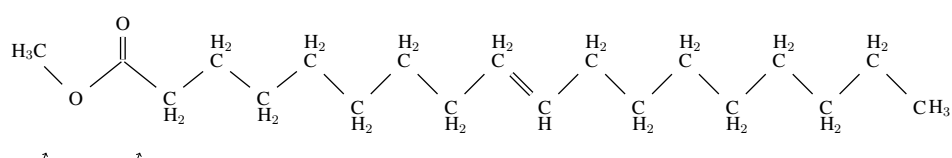


Figure 2.5: Oleic Acid Methyl Ester, $C_{19}H_{36}O_2$

The long unbranched hexadecane is the high quality standard on the cetane scale and has been assigned as having a cetane number of 100. On the other hand,

highly branched alkanes are low quality compounds on the cetane scale and have low cetane numbers. Biodiesel's long chain fatty acids methyl ester are similar to long chain alkanes with number of carbons ranging from 14 to 22, for example the oleic acid methyl ester as shown in Figure 2.5. The cetane scale clarifies why triacylglycerols as found in vegetable oils and derivatives thereof are suitable as alternative diesel fuel. The key is the long, unbranched chains of fatty acids, which are similar to those of the n-alkanes of good conventional diesel fuel, Gerpen and Knothe (2005). Demirbas (2006) reported the Cetane Number of palm-based biodiesel at a value of 62 whereas the standard value is 51 minimum.

Water content affects both the oxidative and hydrolytic stability of biodiesel during the storage. Water can be present in a fuel as dissolved water and free water. Petroleum-based diesel fuel can absorb only ≈ 50 ppm of dissolved water, whereas biodiesel can absorb as much as 1500 ppm. Although this dissolved water can affect the stability of the fuel, free water is more strongly associated with corrosion concerns. The EN standard limits the amount of water content to 500 ppm. However, biodiesel must be kept dry. Furthermore, water can also contribute to microbial growth in the fuel. This problem can result in acidic fuel and sludge that will plug fuel filters. Higher acid value is caused by the oxidation of biodiesel with air. This change is accompanied by a darkening of the biodiesel color from yellow to brown and the development of a *paint* smell. In the presence of water, more over the esters can hydrolyze to a long-chain FFA, which also cause the acid value to increase. The reason for auto oxidation is the presence of the double bonds in the chains of many fatty acid compounds. The auto oxidation of unsaturated fatty compounds proceed at different rates depending on the number and position of the double bonds. The species formed during the oxidation process cause the fuel to eventually deteriorate. Excess water in the fuel can lead to not only corrosion but it can also foster the growth of microorganisms.

Flash point for pure biodiesel (120 °C) is much higher than for petroleum diesel (70 °C). Minimum flash points of both biodiesel and petrodiesel are required to meet fire safety specifications. Minimum flash point is set to assure that excess methanol was removed during the manufacturing process, since methanol reduces the flash point. In addition, presence of methanol in biodiesel can also affect fuel pumps, seals and elastomers, and can result in poor combustion properties.

Sulfur content is limited in order to reduce sulfate and sulfuric acid pollutant emissions and to protect exhaust catalyst systems.

Acid number is primarily an indicator of free fatty acids in biodiesel and increases if a fuel is not properly manufactured or has undergone oxidative degradation. Fuel system deposits and reduced life of fuel pumps and filters contribute to an acid number higher than 0.80 that exceeds the maximum value of 0.50.

Free and total glycerin numbers are a measure of the unconverted (triglyceride) or partially converted triglycerides (monoglycerides and diglycerides) as well as by-product triglycerols present in the fuel. High amounts of free and total glycerin can cause fouling in storage tanks, fuel systems, and engines, along with plugging filters and producing other problems.

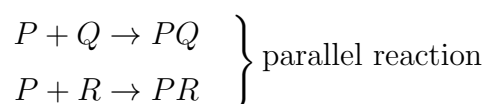
Phosphorous content in biodiesel, even in a small amount, can damage catalytic converters. Phosphorous levels above 10 ppm are present in some vegetable oils, and this requirement ensures that a phosphorous level reduction process is conducted.

Carbon residue measures the tendency of a fuel to form carbon deposits in an engine.

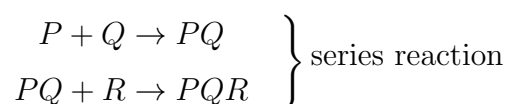
Thus, biodiesel esters are characterized by their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pour point, gross heat of combustion, and volatility. Biodiesel fuels produce slightly lower power and torque and consume more fuel than No. 2 diesel (D2) fuel. Biodiesel is however better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability, Ng et al. (2009).

2.5 Chemical Reaction Principles

A chemical reaction is represented by a chemical equation using one or two arrows sign between the reactants and the products. For a simple reaction, the reaction takes place in only one direction or called irreversible, and a unidirectional arrow represents the reaction. Many chemical reactions in a batch reactor, however, occur in a complex manner such as reversible, parallel and series reactions of the contributing substances. An example for a parallel reaction is:



and a series reaction of the reactants and an intermediate products:



If the reaction take place in one phase alone, the system is called a homogeneous. A reaction is heterogeneous if it requires the presence of at least two phases in the course of reaction. A reaction with a supply of heat to the system is called endothermic, otherwise an exothermic reaction that releases heat to the surrounding. Hydrocarbon cracking reaction is an example of an endothermic reaction.

In process engineering the chemical reactions take place with or without a catalyst. The reaction is carried out in either a batch, semi batch, or continuous process. The task of a process engineer is among other things is to select the suitable reactor for a particular process. Transesterification process in this research work is a reversible, homogeneous reaction under presence of a catalyst that is carried out in a batch reactor of a biodiesel production plant.

2.6 Catalysis

Reactions occurring very slow under normal conditions can be accelerated using a catalyst. A catalyst is a substance that increases the reaction rate without itself being consumed or changed at the end of the reaction. Hence, the catalyst can be recovered and removed in the subsequent purification process. The phenomenon of catalyst in accelerating a chemical reaction is called catalysis.

If the property of catalyst changes during the reaction, its activity or function will reduce the effectiveness or even become inactive. Practically, a substance that speeds up the rate of a reaction can be considered as a catalyst with or without being chemically changed during the reaction course. The chemical equilibrium is achieved faster with a catalyst, but the position of the equilibrium is unchanged. The presence of a catalyst reduces the activation energy by introducing a new route as depicted in Figure 2.6. Reducing the energy barrier or the activation energy, the reaction may be faster. The presence of a catalyst, X, in the reaction (2.6.1):



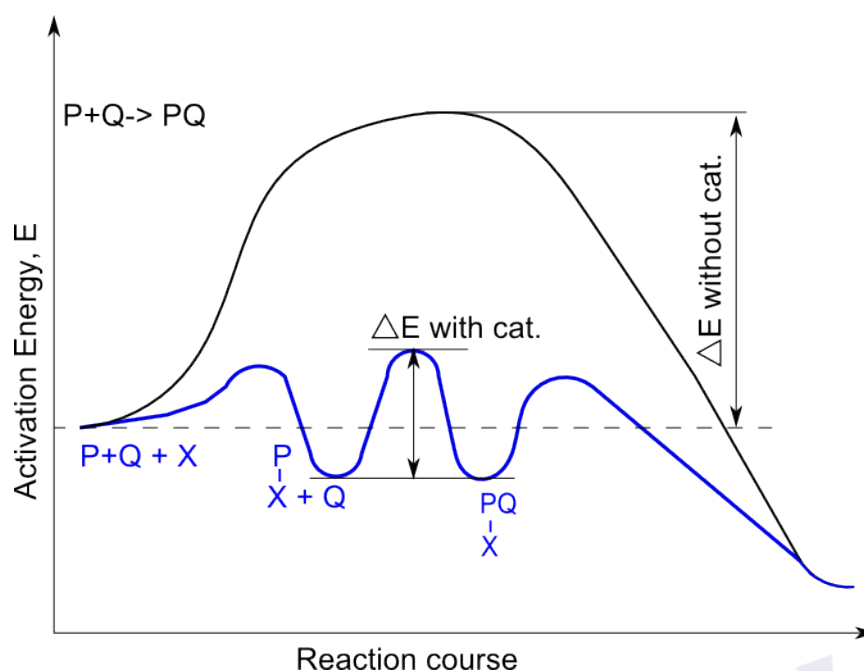


Figure 2.6: Influence of Catalyst on Activation Energy during the Reaction Course, D K Chakrabarty (2009)

taking place very slow, it can be described through the following reaction steps:



The advantage of a catalyst in the reaction is obviously the reduction in the energy consumption and it leads to better selectivity and less waste compared to the reaction without catalyst.

2.6.1 Homogeneous Catalysis

Catalysts can be divided into two main types – homogeneous and heterogeneous. In a heterogeneous reaction, the catalyst is in a different phase from the reactants. In a homogeneous reaction, the catalyst is in the same phase as the reactants. Hence, an extra treatment is required for the removal of a homogeneous catalyst from the product after completing the reaction.

2.6.1.1 Acid Catalysis

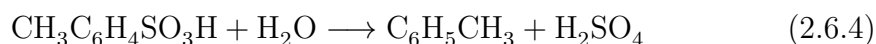
An acid catalysis reaction can be described as follows:



In the reversible Equation (2.6.3a) a proton transfer from the acid catalyst HA which acts as the catalyst, to the reactant or substrate P. The transfer of a proton, leading to the formation of a new reactive intermediate bonding complex, HP^+ . The intermediate bonding reacts then with the reactant Q by releasing the proton to generate the product S. At the end of the reaction, the acid catalyst is regenerate as shown in the Equation (2.6.3c). The concentration of the catalyst additionally shall remain constant that is required in a catalytic reaction.

2.6.1.2 Para Toluene Sulfonate Acid, PTSA

PTSA ($CH_3C_6H_4SO_3H$) is a sulfonic acid of an organic compound and a derivate of a tosyl group (TsOH). Sulfonic acid is acidic due to the hydrogen atom, and is stronger ($pK_a = -2.8$) than a carboxylic acid and is soluble in alcohol and water. PTSA can be used as the homogeneous catalyst in the esterification reaction. The tosylate ion ($CH_3C_6H_4SO_3^-$) is the leaving group in the reaction. If water is present, a toluene and sulfuric acid will be generated according to the following hydrolysis:



In the hydrolysis process, the sulfuric acid formed can be utilized as the acid catalyzed. The strong acidity of the sulfuric acid ($pK_a = -3$) keeps the catalyst effectiveness active and the esterification is always catalyzed along the course of reaction without worrying about the decreasing of the catalysis effectiveness due to water.

REFERENCES

- A. Hayyan, M. Z. Alam, M.E.S Mirghani, N. A. Kabbashi, N. I. N. Hakimi, Y. M. Siran, and S. Tahiruddin. Production of biodiesel from sludge palm oil by esterification process. *Journal of Energy and Power Engineering, ISSN 1934-8975, USA*, 4(1):11 – 17, January 2010.
- A. Sivasamy, Cheah .K, P. Fornasiero, F. Kemausuor, S. Zinoviev, and S. Mier-tus. Catalytic applications in the production of biodiesel from vegetable oils. *Journal of ChemSusChem – Energy and Material*, 2:278–300, 2009.
- A. Singh, B. He, J. Thomson, and J. Van Gerpen. Process optimization of biodiesel production using alkaline catalysts. *Journal of American Society of Agricultural and Biological Engineers*, 12:597–600, 2006. ISSN 0883–8542.
- A. Pérez J.E. Andrade, P.J. Sebastian, and D. Eapen. A review of bio-diesel production processes. *Biomass and Bioenergy, Elsevier*, 35:1008–1020, January 2011.
- Abdul Aziz A. The effect of CPO quality parameters (FFA, M & I, IV, PV, AV , DOBI and colour) on the refinery production efficiency. In *Proceedings of the 2000 National Seminar on Palm Oil Milling, Refining Technology, Quality and Environment*, pages 79 – 88, Genting Hotel, Genting Highlands, Malaysia, July 2000.
- Ainie Kuntom, Siew Wai Lin, Tan Yew Ai, Nor Aini Idris, Mohtar Yusof, and Nuzul Amri Ibrahim Tang Thin Sue. *MPOB Test Methods*, 2005.
- Ayhan Demirbas. Biodiesel production via non-catalytic scf method and biodiesel fuel characteristics. *Energy Conversion and Management, Elsevier*, 65:1–12, 2006.
- Ayhan Demirbas. *Biodiesel: a realistic fuel alternative for diesel engines*. Springer-Verlag London Limited, British Library Cataloguing in Publication Data, 2008.
- B Viswanathan D K Chakrabarty. *Heterogeneous Catalysis*. New Age Science Limited, 2009. ISBN 978 1 906574 09 3.

- B. S Bahl, Arun Bahl *Advanced Organic Chemistry*. S. Chand & Company Ltd., 1999. ISBN 81-219-0061-1.
- Behzadi Sam and Mohammed. M. Farid. Production of biodiesel using a continuous gas-liquid reactor. Technical report, Department of Chemical & Materials Engineering, University of Auckland, Private Bag 92019, Auckland, New Zealand, 2007.
- Bernard Freedman, Royden O. Butterfield, and Everett H. Pryde. Variables affecting the yields of fatty esters from transesterified vegetable oils. *JAOCS*, 61:1638–1643, 1984.
- Bernard Freedman, Royden O. Butterfield, and Everett H. Pryde. Transesterification kinetics of soybean oil. *JAOCS*, 63(10):1375–1380, October 1986.
- Bhaduri Sumit and Doble Mukesh. *Homogeneous Catalysis: Mechanism and Industrial Applications*. John Wiley & Sons, Inc., 2000. ISBN 0-47-471-37221-8.
- Boocock David G. B., Vinnie Mao Samir K., Konar, and Hanif Sidi. Fast one-phase oil-rich processes for the preparation of vegetable oil methyl esters. *Biomass and Bioenergy Journal, Elsevier Science Ltd*, 11(1):43–50, 1996.
- Bryan R. Moser. Biodiesel production, properties, and feedstocks. *The Society for In Vitro Biology, Springer*, 2009.
- Bruce E. Dale and Seungdo Kim. *Biomass Refining Global Impact – The Biobased Economy of the 21st Century*, volume 1 of *Biorefineries – Industrial Processes and Products*, pages 41–65. Wiley-VCH, Weinheim, 2006.
- Casimir C. Akoh and David B. Min. *Food Lipids*. CRC Press, third edition, 2008. ISBN 978–1–4200–4663–2.
- Cattareya Yotkamchornkun Suthat Turapan and Kamchai Nuithitikul. Esterification of free fatty acids in crude palm oil with sulfated zirconia: Effect of calcination temperature. *World Academy of Science, Engineering and Technology*, 65:521–524, 2010.
- Cheah Kien Yoo Choo Yuen May, Ma Ah Ngan. Palm diesel: Green and renewable fuel from palm oil. *Malaysian Palm Oil Board*, pages 3 – 7, 2005.
- Cheng Sit Foon and Choo Yuen May. Kinetics study on transesterification of palm oil. *Journal of Oil Palm Research, MPOB*, 2004.

- Cheng Sit Foon, Choo Yuen May, Ma Ah Ngan, and Chuah Cheng Hock. Kinetics study on transesterification of palm oil. *Journal of Oil Palm Research*, 2004.
- Clarus 500 GC. *Gas Chromatography Hardware Guide*. Perkin Elmer Instruments LLC, 2002.
- D. Darnoko and Munir Cheryan. Kinetics of palm oil transesterification in a batch reactor. *Journal of American Oil Chem Society*, 77(12):1263–1267, 2000a.
- D. Darnoko and Munir Cheryan. Continuous production of palm methyl esters. *Journal of American Oil Chem Society*, 77(12):1269–1272, 2000b.
- D. J. Cole-Hamilton and R. P. Tooze. *Catalyst Separation, Recovery and Recycling*. Number 30 in *Catalysis by Metal Complexes*. Springer Netherlands, 2006. ISBN 978-1-4020-4087-0.
- D.O. Edem. Palm oil: Biochemical, physiological, nutritional, hematological, and toxicological aspects: A reviews. *Journal Plant Foods for Human Nutrition*, 57:319–341, 2002.
- D. R. Palleros. *Experimental Organic Chemistry*. John Wiley & Sons, Inc, 2000. ISBN 0-471-28250-2.
- D. Vidya Sagar L.C. Meher and S.N. Naik. Technical aspects of biodiesel production by transesterification - a review. *Renewable and Sustainable Energy Reviews, Elsevier*, 10(5):246–268, September 2004.
- Dick Copeland and W.Maurice Belcher. Methods for recovering fatty acids. *United States Patent*, (US 6,423,851 B1), July 2002.
- Don Green R. Perry. *Perry's Chemical Engineer's Handbook*. McGraw-Hill Professional, 1997. ISBN 0-07-142294-3.
- Dora E. Lopez Kaewta Suwannakarn David A. Bruce Edgar Lotero, Yijun Liu and Jr James G. Goodwin. Synthesis of biodiesel via acid catalysis. *American Chemical Society*, pages A – K, 2004.
- E. Korovski and Andreas A. Linniger. *Batch Processes*. Taylor & Francais, 2005. ISBN 0–8247–2522–0.
- Edward Crabbe, Cirilo Nolasco-Hipolito, Genta Kobayashi, Kenji Sonomoto, and Ayaaki Ishizaki. Biodiesel production from crude palm oil and evaluation of butanol extraction and fuel properties. *Process Chemistry, Elsevier*, 37:65–71, March 2001.

- F. Ma, L. D. Clements, and M. A. Hanna. The effect of catalyst, free fatty acids, and water on transesterification of beef tallow. *American Society of Agricultural Engineers*, 1998.
- Frank Peter-Helmus. *Process Plant Design*. Wiley-VCH, Weinheim, 2008.
- G. Vincent, M. Martinez, and José Aracil. Integrated biodiesel production: A comparison of different homogeneous catalysts systems. *Journal of Bioresource Technology*, Elsevier, pages 297–305, 2004.
- Gavin Towler Ray Sinnott. *Chemical Engineering Design*. Elsevier Ltd, 2009. ISBN 978-0-7506-8551-1.
- Gerhard Knothe. Analyzing biodiesel: Standards and other methods. *Journal of American Oil Chem Society*, 83(10):823–833, 2006.
- Gilbert F. Froment and Kenneth B. Bischoff. *Chemical Reactor Analysis and Design*. John Wiley & Sons. Inc, 1979. ISBN 0-471-02447-3.
- H Nouredini and Medikonduru. Glycerolysis of fats and methyl esters. *Journal of American Oil Chem Society*, 4:419–425, 1997.
- H. Nouredini and D. Zhu. Kinetics of transesterification of soybean oil. *JAACS*, 74(11):1457–1463, 1997.
- In-Chul Kima, Jong-Ho Kim, Kew-Ho Lee, and Tae-Moon Tak. Phospholipids separation (degumming) from crude vegetable oil by polyimide ultrafiltration membrane. *Journal of Membrane Science*, Elsevier, (205):113123, February 2002.
- J. H. Ng, Hoon Kiat Ng, and S. Gan. Recent trends in policies, socioeconomy and future directions of the biodiesel industry. *Clean Techn Environ. Policy*, Springer Verlag, 2009.
- Janice Gorzynski Smith. *Principles of General, Organic, & Biological Chemistry*. Mc Graw Hill, 2012. ISBN 9780073511153.
- Jo Van Gerpen. Biodiesel processing and production title. *Fuel Processing Technology*, Elsevier, 2005.
- Jo Van Gerpen and Gerhard Knothe. *The Biodiesel Handbook*, chapter Fuel Properties. AOCS Press., 2005.
- Jo Van Gerpen M. Canakci. Biodiesel production from oils and fats with high free fatty acid feedstocks. *Journal of Trans ASAE*, 44:1429–1436, 2001.

- John McMurry. *Organic Chemistry*. Thomson Learning, Inc., seventh edition, 2008. ISBN IO:0-495-11628-9.
- José A. Colucci, Ernesto E. Borrero, and Fabio Alape. Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing. *JAACS*, 82 (7), 2005.
- K Komers, F Skopal, R Stloukal, and J Machek. Kinetics and mechanism of the KOH – catalyzed methanolysis of rapeseed oil for biodiesel production. *European Journal of Lipid Science and Technology*, (104):728–737, 2002.
- K. Maeda H. Kuramochi Y. Asakuma, O. Kawanami and K. Fukui. Theoretical study of the transesterification of triglycerides to biodiesel fuel under various conditions. *International Journal of Thermodynamics (IJoT)*, 14(4):193 – 196, 2011.
- Kaewta Suwannakarn. Biodiesel production from high free fatty acid content feedstocks. Master's thesis, the Graduate School of Clemson University, Clemson University, May 2008.
- Kevin R Steidly Gerhard Knothe. Kinematic viscosity of biodiesel fuel components and related components, influence of compound structure and comparison to petrodiesel fuel components. *Journal of the science and technology of Fuel and Energy, Science Direct, Elsevier*, 84(84):1059 – 1065, February 2005. URL www.fuelfirst.com.
- M.A. Marty M. Berrios, J. Siles. A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil. *ScienceDirect, Elsevier, Fuel*(86):2383–2388, March 2007.
- M. J. T. Reaney, P. B. Hertz, and W. W. McCalley. *Bailey's Industrial Oil and Fat Products*, volume 6, chapter 8, pages 223–258. A John Wiley & Sons, Inc., Publication, 6 edition, 2005.
- M. K. Aroua I. M. Atadashi and A. Abdul Aziz. Biodiesel separation and purification: A review. *Renewable Energy, Elsevier*, 2011.
- MPICM. The national biofuel policy, 2006.
- M. Canakci and H. Sanli. Biodiesel production from various feedstocks and their effects on the fuel properties. *Journal of Sociocy for Microbiology*, 35:431–441, 2008.

- M. Canakci and Jo Van Gerpen. A pilot plant to produce biodiesel from high free fatty acid feedstocks. Number 016049. ASAE Annual International Meeting, Sacramento, California, USA, 2001.
- M. Snäre and P.Maki-Arvela. Overview of catalytic methods for production of next generation biodiesel from natural oils and fats. *Russian Journal Physical Chemistry*, 3(7):1035–1043, 2009.
- Michael J. Goff, Nicholas S. Bauer, Shailesh Lopes, William R. Sutterlin, , and Galen J. Suppes. Acid-catalyzed alcoholysis of soybean oil. *JAOCs*, 2004.
- Mohamed A.R. Bhatia S. Leng, T.Y. Variables affecting the yields of fatty esters from transesterified vegetable oils. *Catalytic conversion of palm oil to fuels and chemicals*, 77:156–162, 1999.
- Noor Azian Morad, Mustafa Kamal Abd Aziz, and Rohani Mohd Zin. Process design in degumming and bleaching of palm oil. Research Vote 74198, Centre of Lipids Engineering and Applied Research, Universiti Teknologi Malaysia, UTM, November 2006.
- Octave Levenspiel. *Chemical Reaction Engineering*. John Wiley & Sons, third edition, 1999. ISBN 0-471-25424-X.
- P. C. Narváez, S. M. Rincón, and F. J. Sánchez. Kinetics of palm oil methanolysis. *Journal of American Oil Chemistry Society, Springer*, 11(1):971977, 2007.
- Palligarnai T. Vasudevan and Michael Briggs. Biodiesel production – current state of the art and challenges. *Journal of Ind Microbiol Bioethanol*, 35:421–430, 2008.
- Pogaku Ravindra, Subash Saralan, and Rahmath Abdulla. Lca studies for alkaline and enzyme catalyzed biodiesel production from palm oil. *Advances in Biological Chemistry, Scientific Research*, 12:341–352, Sep 2012.
- Praveen K. S. Yadav, Onkar Singh, and R. P. Singh. Palm fatty acid biodiesel: Process optimization and study of reaction kinetics. *Journal of Oleo Science, Japan of Oil Chemists' Society*, 11:575 – 580, 2010.
- Puah Chiew Wei, Choo Yuen Maya, Ma Aa Ngan, and Chuah Cheng Hock. Degumming and bleaching: Effect on selected constituents of palm oil. *Journal of Oil Palm Research*, 16(2):57–63, December 2004.
- S. M. Sadrameli S. Farajzadeh Bibalan. Kinetic modeling of sunflower oil methanolysis considering effects of interfacial area of reaction system. *Iranian Journal of Chemical Engineering*, 9(1), 2012.

- Satriana and S. Muhammad Dani. Kinetic study of esterification of ffa in low grade CPO using sulfuric acid. *AJChE*, 8(1):1 – 8, 2008.
- Surachai Jansri, Sukritthira B. Ratanawilai, Michael L. Allen, and Gumpon Prateepchaikul. Kinetics of methyl ester production from mixed crude palm oil by using acid–alkali catalyst. *Fuel Processing Technology Journal, Elsevier*, (92): 1543–1548, 2011.
- The European Standard EN14105. Fat and oil derivatives – (fame) – determination of free and total glycerol and mg, dg, tg contents (reference method), 2003.
- Tim Ruppel, Gerald Hall, Timon Huybright, and William Goodman. Free and total glycerol in b100 biodiesel by gas chromatography according to methods en 14104 and astm d6584, 2008.
- Timothy Rupper and Timon Huybright. Fatty acid methyl esters in b100 biodiesel by gas chromatography (modified en 14103), 2008.
- Tobias Kimmel et.al Devender S. Negi, Felix Sobotka. Glycerolysis of fatty acid methyl ester. *Journal of American Oil Chem Society*, pages 83–90, 2007.
- Theerayut Leevijit, Worawut Wisutmethangoon, Gumpon Prateepchaikul, Charktir Tongurai, and Michael Allen. A second order kinetics of palm oil transesterification. In *The Joint International Conference on "Sustainable Energy and Environment (SEE)"*, pages 277 – 281, 2004.
- Triyani Fajriutami, Yong Chan Seo, and Young Hwan Chu. Optimization of two-step catalyzed biodiesel production from soybean waste cooking oil. *Journal of Matter Cycles Waste Management, Springer Japan*, 2012.
- Vinnie Mao D. G. B. Boocock, S. K. Konar and H Sidi. Fast one-phase oil-rich processes for the preparation of vegetable oil methyl esters. *Biomass and Bioenergy, Elsevier Science Ltd*, 11(11):43–50, 1996.
- W. Sani, Khalid Hasnan, and M Zainal Mohd Yusof. Process analysis for esterification and two-step transesterification in the biodiesel production plant. 12 (6):41 – 46, 2012.
- WebBookNIST. National institute of standard and technology, nist, 2013. URL <http://webbook.nist.gov>.
- Weiyang Zhou and D.G.B. Boocock. Phase distributions of alcohol, glycerol, and catalyst in the transesterification of soybean oil. *JAACS*, 83(12):1047–1052, 2006.

- Y.B. Che Man, T. Haryatia, H.M. Ghazalib, and B.A. Asbia. Composition and thermal profile of crude palm oil and its products. *JAACS*, 76(2):237–242, July 1999.
- Y. C. Sharma and B. Singh. Development of biodiesel: Current scenario. *Renewable and Sustainable Energy Reviews, Elsevier*, 2008.
- Y.C Sharma, B. Shingh, and S.N. Upadhyay. Advancements in development and characterization of biodiesel: A review. *Elsevier*, 2008.
- Yusof Basiron *Bailey's Industrial Oil and Fat Products*, volume 6, chapter Palm Oil. John Wiley & Sons Inc., 2005.
- Yusof Basiron and Choo Yuen May. Crude palm oil as a source of biofuel: Its impact on price stabilization and environment. Technical article, Malaysian Palm Oil Board (MPOB), 6 Persiaran Institusi, Bandar Baru Bangi, 43000 Kajang, Selangor, Malaysia, 2005.



PTTA UTHM
PERPUSTAKAAN TUNKU TUN AMINAH