

**BIODIESEL PRODUCTION VIA HETEROGENEOUS
TRANSESTERIFICATION OF PALM OLEIN AND WASTE OILS**

by

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS.....	ii
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	xii
ABSTRAK.....	xiii
ABSTRACT.....	xv
CHAPTER 1 : INTRODUCTION.....	1
1.1 History of biodiesel.....	1
1.2 Biodiesel	2
1.3 Global biodiesel production	7
1.4 Benefits of biodiesel	8
1.5 Economic aspects of biodiesel	11
1.6 Biodiesel in Malaysia.....	12
1.7 Transesterification.....	15
1.7.1 Mechanisms of transesterification	17
1.7.2 Factors affecting transesterification	19
1.8 Catalysts in transesterification	21
1.8.1 Homogeneous catalysts in transesterification	21
1.8.2 Heterogeneous catalysts in transesterification	22
1.8.3 Enzymatic catalysts in transesterification	24
1.8.4 Non-catalytic transesterification reaction	25
1.9 Calcium oxide as a heterogeneous catalyst in transesterification	27

1.9.1 Neat CaO as a catalyst in transesterification.....	29
1.9.2 Loaded CaO as a catalyst in transesterification	33
1.9.3 Supported CaO as a catalyst in transesterification.....	34
1.9.4 Mixed CaO as a catalyst in transesterification.....	36
1.9.5 CaO from wastes as a catalyst in transesterification.....	37
1.10 Mechanism of CaO-catalyzed transesterification	38
1.11 Feedstocks for transesterification.....	39
1.11.1 Neat palm olein as feedstock in transesterification.....	39
1.11.2 Residual oil from spent bleaching clay as feedstock in transesterification	40
1.11.3 Chicken oil as feedstock in transesterification.....	41
1.11.4 Algae as lipid source in transesterification	41
1.12 The effect of free fatty acid and moisture in transesterification	42
1.13 Problem statements	44
1.14 Research objectives.....	45
CHAPTER 2 : MATERIALS AND METHODS	46
2.1 Materials	46
2.2 Preparation of oil samples for transesterification	46
2.3 Characterization of Oil.....	47
2.3.1 Determination of acidity	47
2.3.2 Determination of iodine value	48
2.3.3 Determination of volatile matter	49
2.3.4 Determination of water content.....	50
2.4 Catalysts preparation for transesterification	50

2.4.1 Neat calcium oxide as a catalyst in transesterification	50
2.4.2 Crab shell as a catalyst in transesterification	50
2.4.3 Cockle shell as a catalyst in transesterification.....	51
2.5 Catalyst characterizations	52
2.5.1 TGA and TGA-FTIR analyses of the catalysts.....	52
2.5.2 Surface analysis (BET method) of the catalysts	52
2.5.3 TEM analysis of the catalysts	52
2.5.4 SEM-EDX analysis of the catalysts.....	52
2.5.5 XRD analysis of the catalysts	53
2.5.6 XRF analysis of the catalysts.....	53
2.5.7 Basicity analysis of the catalysts.....	53
2.6 Transesterification reaction.....	54
2.7 Analysis of methyl esters	56
2.7.1 Qualitative analysis of methyl esters	56
2.7.2 Quantitative analysis of methyl esters	56
2.8 Statistical analysis in optimization of parameters.....	57
2.9 Catalyst leachability test	58
CHAPTER 3 : RESULTS AND DISCUSSION	59
3.1 Oil characterization.....	59
3.1.1 Characteristics of oils.....	59
3.1.2 Characteristics of SBC oil.....	61
3.1.3 Characteristics of chicken oil.....	62
3.2 Catalyst characterization	63
3.2.1 TGA and TGA-FTIR analyses of the catalysts.....	63

3.2.2 Surface analysis (BET method) of the catalysts	67
3.2.3 TEM analysis of the catalysts	72
3.2.4 SEM-EDX analysis of the catalysts	73
3.2.5 XRD analysis of the catalysts	75
3.2.6 XRF analysis of the catalysts	77
3.2.7 Basicity analysis of the catalysts.....	78
3.3 Transesterification of RBD-PO.....	80
3.3.1 Influence of calcination temperature in transesterification.....	80
3.3.2 Influence of catalyst amount in transesterification	82
3.3.3 Influence of methanol to oil mass ratio in transesterification	85
3.3.4 Determination of methyl esters yield	88
3.3.5 Statistical analysis in optimization of parameters.....	89
3.4 Transesterification using mixed-catalyst at different catalysts combinations	96
3.5 Transesterification of waste oils	97
3.5.1 Transesterification using residual oil from SBC.....	97
3.5.2 Transesterification using chicken oil	102
3.6 Reusability of mixed-catalyst in transesterification.....	103
3.6.1 Basicity pattern of reused mixed-catalyst	103
3.6.2 XRD pattern of reused mixed-catalyst.....	106
3.6.3 Surface properties of reused mixed-catalyst	108
3.6.4 Catalyst recovery	111
3.7 Catalyst leachability of mixed-catalyst	112
3.8 Tolerance of mixed-catalyst towards FFA.....	114
3.9 Tolerance of mixed-catalyst towards moisture	120
3.10 Properties of the prepared biodiesel using RBD-palm olein.....	125

CHAPTER 4 : CONCLUSIONS	128
REFERENCES.....	130
LIST OF PUBLICATIONS	

LIST OF TABLES

Table 1.1	Various oil/fat sources in biodiesel preparation.....	6
Table 1.2	Bonuses and penalties for new vehicles in France for their corresponding CO ₂ emissions	11
Table 1.3	Properties of calcium oxide.....	28
Table 3.1	Properties of oils	59
Table 3.2	Fatty acid composition of RBD-PO	61
Table 3.3	Fatty acid composition of SBC oil.....	62
Table 3.4	Fatty acid composition of chicken fat	63
Table 3.5	TEM particle size of calcined (900 °C, 2 h) catalyst	72
Table 3.6	XRF results of calcined (900 °C, 2 h) catalyst from different sources .	77
Table 3.7	Basicity of uncalcined catalysts towards Hammett indicators.....	78
Table 3.8	Basicity of calcined catalysts towards Hammett indicators.....	79
Table 3.9	Basicity of fresh catalysts before and after calcination at 900 °C	79
Table 3.10	Yield of methyl esters for different catalysts	89
Table 3.11	Factorial design, star points, and centre points with their corresponding responses using Lab-CaO-900 catalyst	90
Table 3.12	Factorial design, star points, and centre points with their corresponding responses using MC-CaO-900 catalyst	90
Table 3.13	Factorial design, star points, and centre points with their corresponding responses using C-CaO-900 catalyst.....	91
Table 3.14	Optimized conditions of reactions with different catalysts.....	95
Table 3.15	Methyl esters produced using mixed-catalyst.....	96
Table 3.16	First and second oil extractions with different solvent combinations.	100
Table 3.17	Surface properties of fresh and spent mixed-catalyst	110
Table 3.18	Properties of the prepared biodiesel with different catalysts	126

LIST OF FIGURES

Figure 1.1	World oil consumption	3
Figure 1.2	EU and member states' biodiesel production from 1998 to 2008	8
Figure 1.3	USA and EU-15 carbon dioxide emission profile	10
Figure 1.4	General equation of transesterification	15
Figure 1.5	Step-wise transesterification reaction of triglycerides	17
Figure 1.6	Mechanism of the base-catalyzed transesterification.....	18
Figure 1.7	Mechanism of the acid-catalyzed transesterification	19
Figure 1.8	Dissociation pressure of CO ₂ versus temperature for transformation of calcium carbonate to calcium oxide.....	29
Figure 1.9	Possible mechanism of CaO-catalyzed transesterification	39
Figure 1.10	Saponification reaction of fatty acid	43
Figure 1.11	Hydrolysis reaction of ester	43
Figure 2.1	Photograph of mud crab (<i>Scylla serrata</i>).....	51
Figure 2.2	Photograph of cockle shells (<i>Anadara granosa</i>)	51
Figure 2.3	Experimental set-up for transesterification reaction	55
Figure 2.4	TLC plate showing spots of triglycerides and methyl esters	56
Figure 3.1	Typical chromatogram of RBD-PO methyl esters.....	60
Figure 3.2	TGA thermogram of (A) Lab-CaO, (B) MC-CaO and (C) C-CaO	65
Figure 3.3	Decomposition of calcium carbonate.....	65
Figure 3.4	TGA-FTIR Vapor Phase library match for decomposition of (A) Lab-CaO, (B) MC-CaO and (C) C-CaO	67
Figure 3.5	BET adsorption-desorption isotherm of Lab-CaO (A) uncalcined and (B) calcined at 900 °C, 2 h.....	69
Figure 3.6	BET adsorption-desorption isotherm of MC-CaO (A) uncalcined and (B) calcined at 900 °C, 2 h.....	70

Figure 3.7	BET adsorption-desorption isotherm of C-CaO (A) uncalcined and (B) calcined at 900 °C, 2 h.....	71
Figure 3.8	TEM micrographs of calcined (900 °C, 2 h) catalysts (A) Lab-CaO, (B) MC-CaO and (C) C-CaO.....	73
Figure 3.9	SEM images of Lab-CaO (A) uncalcined and (B) calcined at 900 °C, 2 h	74
Figure 3.10	SEM images of MC-CaO (A) uncalcined and (B) calcined at 900 °C, 2 h	74
Figure 3.11	SEM images of C-CaO (A) uncalcined and (B) calcined at 900 °C, 2 h	74
Figure 3.12	Powder XRD patterns of (A) Lab-CaO, (B) MC-CaO and (C) C-CaO at various calcination temperatures	76
Figure 3.13	The effect of calcination temperature on methyl esters content	81
Figure 3.14	Influence of catalyst amount on the methyl esters content using (A) Lab-CaO-900, (B) MC-CaO-900 and (C) C-CaO-900	85
Figure 3.15	Influence of methanol/oil mass ratio on the methyl esters content using (A) Lab-CaO-900, (B) MC-CaO-900 and (C) C-CaO-900.....	88
Figure 3.16	Interactive effect between factors for reactions using (A) Lab-CaO-900, (B) MC-CaO-900 and (C) C-CaO-900	95
Figure 3.17	Cumulative oil yield extracted with different solvents	98
Figure 3.18	Methyl esters content of residual oil from SBC using mixed-catalyst under optimal reaction conditions.....	101
Figure 3.19	Methyl esters content of chicken oil using mixed-catalyst under optimal reaction condition	102
Figure 3.20	Basicity of (A) uncalcined and (B) calcined (900 °C, 2 h) fresh and spent mixed-catalyst.....	105
Figure 3.21	Methyl esters content for reuse of mixed-catalyst	106
Figure 3.22	XRD pattern of spent catalysts for ten consecutive reuses	107
Figure 3.23	Reaction between catalyst and water	107
Figure 3.24	Reaction between catalyst and glycerol	108
Figure 3.25	XRD pattern of calcined spent catalysts for ten consecutive reuses	108

Figure 3.26	Methyl esters content of uncalcined and calcined spent mixed-catalyst	111
Figure 3.27	Recovery of catalyst after each reuse.....	112
Figure 3.28	Standard curve for calcium by AAS	113
Figure 3.29	Methyl esters content for various amounts of catalyst.....	114
Figure 3.30	Methyl esters content under optimized conditions for various FFA content.....	115
Figure 3.31	Methyl esters content using different catalyst amount with various FFA content	118
Figure 3.32	Methyl esters content of different MeOH/oil ratio under various FFA content	119
Figure 3.33	XRD pattern of spent catalyst with 4 wt.% FFA (a) uncalcined and (b) calcined.....	120
Figure 3.34	Methyl esters content for different water contents under optimal reaction conditions	121
Figure 3.35	Generation of methoxide ion in the presence of water.....	122
Figure 3.36	Methyl esters content under various water contents for different catalyst amounts	123
Figure 3.37	Methyl esters content for different water contents under various MeOH/oil mass ratios	124
Figure 3.38	XRD pattern of spent catalyst with 3 wt.% water content, (a) uncalcined catalyst and (b) calcined catalyst	125

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
C-CaO	Cockle shell calcium oxide
C-CaO-900	Cockle shell calcium oxide calcined at 900 °C, 2 h
CPO	Crude palm oil
FAME	Fatty acid methyl esters
FFA	Free fatty acids
GHG	Greenhouse gases
Lab-CaO	Laboratory calcium oxide
Lab-CaO-900	Laboratory calcium oxide calcined at 900 °C, 2 h
MC-CaO	Mud crab shell calcium oxide
MC-CaO-900	Mud crab shell calcium oxide calcined at 900 °C, 2 h
ME	Methyl esters
MeOH	Methanol
MW	Molecular weight
RBD-PO	Refined, bleached and deodourized palm olein
SBC	Spent bleaching clay
SEM-EDX	Scanning electron microscopy-electron dispersive X-ray
TEM	Transmittance electron microscopy
TGA	Thermogravimetric analysis
TGA-FTIR	Thermogravimetric analysis-Fourier transform infra red
XRD	X-ray diffraction
XRF	X-ray fluorescence

PENGELUARAN BIODISEL MELALUI PROSES TRANSESTERIFIKASI HETEROGEN MINYAK OLEIN SAWIT DAN MINYAK BUANGAN

ABSTRAK

Dalam kajian ini, kalsium oksida (CaO) telah digunakan sebagai mangkin heterogen dalam transesterifikasi trigliserida dengan metanol untuk menghasilkan metil ester (biodisel) sebagai produk utama. CaO makmal dan juga buangan CaO daripada cengkerang ketam (*Scylla serrata*) dan kerang (*Anadara granosa*) telah digunakan sebagai mangkin heterogen dalam transesterifikasi olein sawit, minyak buangan tanah luntur terpakai dan lemak ayam. Bagi meningkatkan aktiviti bermangkin, mangkin-mangkin tersebut perlu diaktifkan pada suhu 900 °C selama 2 jam. Selepas pengaktifan pada suhu tersebut, mangkin berubah kepada CaO daripada struktur asal CaCO₃. Keadaan tindak balas yang optima bagi kesemua mangkin terlibat adalah 5% (berdasarkan berat minyak) dan nisbah jisim metanol terhadap minyak ialah 0.5:1 dan dengan menggunakan keadaan optima ini, metil ester melebihi 98% dapat diperolehi dalam masa 3 jam, pada suhu refluks metanol. Pengoptimuman keadaan tindak balas secara eksperimen telah disahkan secara statistik dengan menggunakan metodologi permukaan respons. Mangkin campuran cengkerang ketam dan kerang dalam nisbah jisim 1:1 juga mempamerkan aktiviti yang setara dengan mangkin individu. Mangkin campuran ini boleh diguna semula dalam tindak balas ini sebanyak sembilan kali, selepas dibersihkan dengan pelarut (metanol dan *n*-heksana) dan diaktifkan pada suhu 900 °C selama 2 jam. Metil ester yang terhasil dengan kaedah ini menepati piawaian EN 14103 yang menetapkan kandungan metil ester minimum 96.5%. Tambahan pula, mangkin campuran ini mempunyai toleransi terhadap kandungan air sebanyak

3% dan kandungan asid lemak bebas sehingga 4%. Metil ester yang terhasil dengan menggunakan mangkin-mangkin tersebut menepati kesemua spesifikasi utama biodisel.

**BIODIESEL PRODUCTION VIA HETEROGENEOUS
TRANSESTERIFICATION OF PALM OLEIN AND WASTE OILS**

ABSTRACT

In the present work, attempts have been made to use calcium oxide (CaO) as a heterogeneous catalyst in the transesterification of triglycerides with methanol to produce methyl esters (biodiesel) as the main product. Laboratory CaO as well as waste CaO from the shells of crabs (*Scylla serrata*) and cockles (*Anadara granosa*) have been successfully utilized as catalysts to transesterify palm olein as well as waste adsorbed oil from SBC and chicken oil. In order to enhance the catalytic activity, the catalysts have to be calcined at 900 °C for 2 h. Upon calcination the catalysts transformed to CaO from the initial CaCO₃ structure. The optimal reaction conditions were found to be: 5 wt.% catalyst amount (based on oil weight) and 0.5:1 methanol to oil mass ratio for all the catalysts and under these reaction conditions, over 98% methyl esters content was achieved in a 3 h reaction period at the reflux temperature of methanol. This experimental optimization was well validated statistically using response surface methodology. Furthermore, the mixed-catalyst of crab and cockle shells at a 1:1 weight ratio showed similar activity as the individual catalysts. The mixed-catalyst could be reused up to nine times, after simple solvent (methanol and *n*-hexane) washing and calcination steps to meet the minimal methyl esters content of 96.5%, as required by the EN 14103 standard. In addition, the mixed-catalyst exhibits good tolerance towards the presence of 3% water and up to 4% free fatty acid. The methyl esters produced using the catalysts were found to conform to all the key specifications of biodiesel.

CHAPTER 1

INTRODUCTION

1.1 History of biodiesel

Producing biodiesel is not a new idea as the concept dates back to the 1800s when the French government, at the Paris Exhibition, demonstrated the use of arachide oil (peanut oil) as a fuel. Although the engine was made to use mineral oils, it was tested and worked with vegetable oils without any modification being made. They found that the oil was almost as effective as the natural mineral oils. In addition, the oils have also been used for lubricating the engine. The use of the same oils as fuel and as lubricant of the engine has proved a success. As an improvement, transesterification of vegetable oils was carried out successfully by Duffy and Patrick in 1853.

Forty years later, in 1893, Rudolph Diesel successfully inked an important research article on biodiesel, entitled '*The theory and construction of a rational heat engine*'. He had intensively researched the potential of vegetable oils as replacement for conventional diesel, which marked the invention of the diesel engine (from whence the engine obtained the name). Diesel's engine model was a single cylinder, and exhibited its maiden performance in Germany on the 10th of August 1893. To commemorate the great historical achievement, the 10th of August has been declared International Biodiesel Day (Bajpai and Tyagi, 2006). It is worth noting here that Nicklaus Otto had already invented a similar internal combustion engine much earlier (1876), however, it was less efficient than that of Diesel's (Knothe, 2005a; Demirbas, 2007a).

Although in the late 1800s, research on fuel from vegetable sources was intense and receiving much attention, it was only during the early 1900s that engine manufacturers started to modify their diesel engines to cater for petro-based diesel. The main reason for the delayed implementation was the availability of the fossil diesel at an affordable price compared to the cost of biodiesel production. Much later, in the 1990s, France recommenced the effort to produce a green fuel, biodiesel. This time, rapeseed oil was used to produce biodiesel, which was blended into regular diesel fuel at 5% (B5) and at a much higher ratio of 30% (B30) for public transportation. The current rebirth of biodiesel can be seen as realizing the speech by Diesel in 1912, in which Diesel noted that *'the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time'* (Bajpai and Tyagi, 2006).

1.2 Biodiesel

Fatty acid alkyl esters, also known as biodiesel, are regarded as the best substitute for conventional petro-based diesel fuel. The current oil consumption of about 86 million barrels per day (US Energy Information Administration, 2010) and the limited oil reserves have positioned biodiesel as a future fuel for diesel engines. It is evident from Figure 1.1 that the demand for fuel is increasing from year to year. The statistic translates to an increase in energy demand of about four thousand barrels per day.

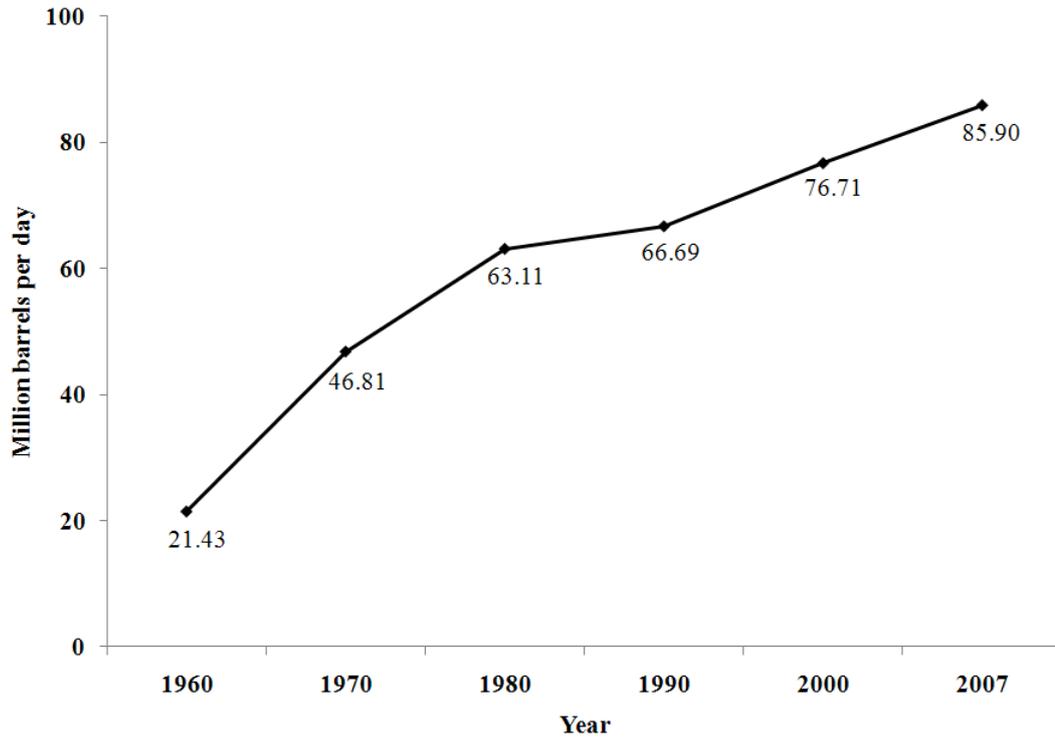


Figure 1.1 World oil consumption (US Energy Information Administration, 2010)

The global environmental quality is very much affected by the emissions from transportation and industry. In the period of 1970 to 2004, the global emissions of greenhouse gases (GHG) increased as high as 70%, from 28.7 to 49.0 gigatonnes of carbon dioxide-equivalent (World Energy Council, 2009). Consequently, the use of less-polluted energy sources has been of interest to scientists for many years.

The use of energy from renewable sources is not a dream. Recently, The Energy Report (2011) by the World Wide Fund for Nature (WWF) predicted that by the middle of this century (year 2050), the world would obtain all the energy needs from renewable sources. The report made ten recommendations for a 100% renewable energy future. The recommendations are:

- (1) Clean energy:- To promote and develop renewable energy for all by 2050.
- (2) Grids:- To share and exchange clean energy via grids and trade.

- (3) Access:- To provide clean energy to everyone on this earth.
- (4) Money:- To invest in renewable energy and energy-efficient materials and buildings.
- (5) Food:- To stop food waste and make land available for nature, forestry and biofuel production.
- (6) Materials:- To develop durable materials, reduce, reuse and recycle materials.
- (7) Transportation:- To promoting public transport. Promote electrification, support hydrogen-fuelled and research into other alternative fuels.
- (8) Technology:- To develop national, bilateral and multilateral plans to promote research and development of efficient and renewable energy.
- (9) Sustainability:- To develop and enforce strict sustainability criteria so that the renewable energy is compatible with the environment.
- (10) Agreements:- To support climate and energy agreements to provide global guidance and cooperation on renewable energy.

The hope of achieving renewable energy by 2050 comes with challenges; however, the ten recommendations will inspire governments as well as the corporate sector to work towards realizing a green future. The report also warned that although nuclear power is another alternative energy, radioactive wastes are highly dangerous with radiation around for many years.

Biodiesel being a less-polluted energy source could be the best substitute or blending portion to the relatively more polluted conventional diesel fuel. Biodiesel is prepared via a catalytic reaction of triglycerides and alcohol (usually methanol). In the case of methanol, the biodiesel produced is also known as fatty acid methyl esters (FAME).

Stoichiometrically, a mole of triglyceride needs three moles of methanol to produce a mole of glycerol and three moles of methyl esters. Glycerol is the by-product of the reaction. The reaction involves the breakdown of the glycerol structure and exchanges of alkyl groups between the alcohol and ester part of the triglyceride molecule; as such, the reaction is known as transesterification.

Interestingly, a recent US patent revealed that methanol, one of the reactants in this reaction, can be produced from glycerol itself, thus opening up an avenue to produce raw materials from the by-product of the same reaction (Goetsch et al., 2008). Among the three major routes, transesterification seems to be the best, compared to heating and microemulsions, for reducing the viscosity as well as minimizing engine complications (Pryde, 1984). The main purpose of transesterifying vegetable oils is to lower the viscosity while at the same time raising the volatility. Although vegetable oils have a similar caloric value as diesel fuel, their direct use as engine fuel poses several engine complications such as coking and trumpet development on injectors, carbon deposits, sticking of oil ring, and thickening and gelling of the engine lubricating oil (Ryan et al., 1984; Ma and Hanna, 1999).

Triglycerides for biodiesel production comes from various sources, as listed in Table 1.1. Edible as well as inedible oils and waste oils are being utilized as feedstocks in producing biodiesel. Most recently, algae (seaweed) has been found to be one of the potential lipid sources for the preparation of biodiesel.

Table 1.1 Various oil/fat sources in biodiesel preparation

Source	Reference(s)
Edible oil	
Palm oil	Boey et al., 2009a; Salamatinia et al., 2010
Palm kernel oil	Alamu et al., 2008; Ngamcharussrivichai et al., 2010
Soybean oil	Rashtizadeh et al., 2010; Silva et al., 2010a
Rapeseed oil	Kawashima et al., 2009; Yoo et al., 2010
Coconut oil	Kumar et al., 2010; Nakpong et al., 2010
Sunflower oil	Veljkovic et al., 2009; Sun et al., 2010
Peanut oil	Nguyen et al., 2010; Perez et al., 2010
Corn oil	Bi et al., 2010; Dantas et al., 2011
Cotton oil	Nabi et al., 2009a; Papadopoulos et al., 2010
Inedible oil	
Jatropha oil	Zanette et al., 2011; Deng et al., 2010
Karanja oil	Nabi et al., 2009b; Kamath et al., 2011
Castor oil	Cesar and Batalha, 2010; Santana et al., 2010
Neem oil	Martin et al., 2010; SathyaSelvabala et al., 2010
Rubber seed oil	Yusup and Khan, 2010; Yang et al., 2011
Mahua oil	Godiganur et al., 2009; Jena et al., 2010
Jojoba oil	Al-Widyan and Al-Muhtaseb, 2010; Shehata and Razek, 2011
Waste oil/fat	
Used cooking oil	Chakraborty and Banerjee, 2010; Tan et al., 2011
Spent bleaching clay oil	Lim et al., 2009; Huang and Chang, 2010
Chicken fat	Guru et al., 2010 ; Hoque et al., 2011
Duck fat	Chung et al., 2009
Mutton tallow	Haas and Foglia, 2005; Bhatti et al., 2008
Beef tallow	Teixeira et al., 2009; Liu et al., 2011
Fish oil	El-Mashad et al., 2008; Lin and Li, 2009
Grease	Wang et al., 2008
Algae	
<i>Neochloris oleoabundans</i>	Levine et al., 2011
<i>Schizochytrium limacinum</i>	Johnson and Wen, 2009
<i>Dunaliella tertioleeta</i>	Krohn et al., 2011
<i>Spirulina</i>	Xu and Mi, 2011

Apart from the triglyceride sources listed, there are many other sources that have been used in producing biodiesel. Among them are okra seeds (Anwar et al., 2010),

coffee beans (Franca et al., 2008; Oliveira et al., 2008), papaya, rambutan, black and white sesame seeds (Winayanuwattikun et al., 2008), mustard seeds (Jham et al., 2009), coriander seeds (Moser and Vaughn, 2010), apricot seeds (Gumus and Kasifoglu, 2010), rice bran (Lei et al., 2010; Lin et al., 2009), moringa (Kafuku et al., 2010; Silva et al., 2010b), tobacco (Veljkovic et al., 2006; Usta et al., 2011) and many others.

Biodiesel can be used in its neat form (B100), however, older vehicles may need minor modifications to the fuel lines and related rubber components to use it in its pure form (Vasudevan and Briggs, 2008). Neat biodiesel (B100) requires biodiesel-compatible engine components. However, currently B20 (20% biodiesel and 80% petroleum diesel, by volume) is the preferred choice, as at this ratio no cold-weather complications are noted and no engine modification is required. In the UK and the US, B20 is the blending choice; however, France increases the bio portion (50%, known as B50) in the vehicle fuel (World Energy Council, 2009). There is considerable evidence of the need of biodiesel in the near future as more and more countries are conscious of the tail-pipe exhaust profile and its significant effects on the deterioration of the environment globally. Again, the ability of direct blending of biodiesel into petro-diesel fuel is another added merit to the many advantages of biodiesel.

1.3 Global biodiesel production

The production of biodiesel grew steadily in the early 1990s and more rapidly in recent years, and is expected to grow more swiftly in the coming years. The EU, especially Germany, France and Italy, account for 60% of the global biodiesel

production (Figure 1.2) (European Biodiesel Board, 2010; Oosterveer and Mol, 2010).

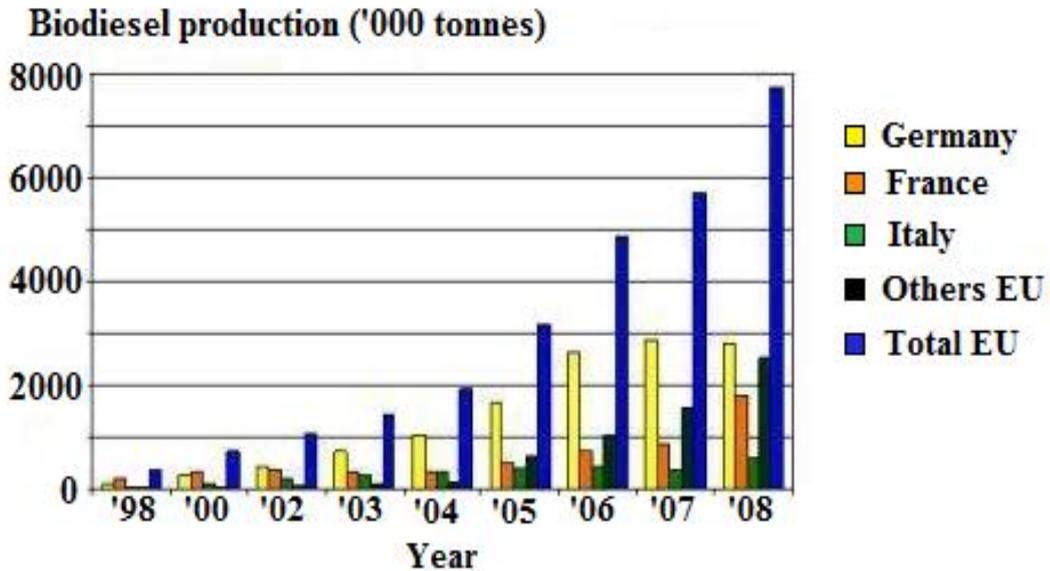


Figure 1.2 EU and member states' biodiesel production from 1998 to 2008 (European Biodiesel Board, 2010)

1.4 Benefits of biodiesel

Biodiesel is a renewable fuel since it is produced from infinite sources of plant oils and animal fats. This makes biodiesel readily obtainable as long as the supplies of vegetable oils or animal fats are available. Unlike petro-based fuels, searching for oil wells is not required for this green fuel. From the environmental viewpoint, biodiesel is a clean burning fuel (for its oxygen content) with low exhaust emissions, free from sulphur and carcinogen content, decreasing emissions of polycyclic aromatic hydrocarbon (PAH), soot, carbon monoxide, hydrocarbon and aromatics, thus biodiesel is regarded as a non-toxic and biodegradable fuel. Vehicles with biocomponent fuel are needed for cleaner air, especially in the busy cities where the air pollution is intense.

In addition, the use of waste oils and fats in biodiesel production also reduces many environment-related complications. As a fuel, biodiesel has a comparable caloric value to petro-diesel, has shown higher combustion efficiency, a higher cetane number and possesses excellent lubricity. The cetane number is used to measure the fuel quality in terms of ignition delay time and the combustion efficiency. As far as safety is concerned, the higher flash point, a measure of the temperature at which the fuel can be ignited, makes biodiesel safer to deal with, transport and stockpile in particular. The option of direct blending with petro-diesel as a fuel in compression-ignition engines at any blending ratio adds merit to biodiesel.

At present, biodiesel is not economically favourable as its cost is more than that of conventional diesel fuel. However, if the various benefits of the fuel are accounted for, including environmental gains, enhancing the rural socio-economic status and reducing foreign exchange, then the economic competitiveness can be truly realized. Politically, producing biodiesel makes a nation totally, or partially independent of other oil producing countries (Ma and Hanna, 1999; Bajpai and Tyagi, 2006; Lapinskiene et al., 2006; Demirbas, 2007a; Knothe, 2009).

One of the main reasons for the conceptualization of biodiesel is the environmental pollution, specifically CO₂ emission. Concerning the CO₂ emission, in 2005 the EU introduced an innovative cost-effective scheme termed the 'Emission Trading Scheme' (ETS), a scheme that Australia, New Zealand and the United States are keen to adopt in their long-term plan for dealing with greenhouse gases. Figure 1.3 provides evidence of the EU's CO₂-reduction pledge, in which it targeted to achieve

a moderate emission of 130 g CO₂ per km in 2012 and an ultimate low emission of 95 g CO₂ per km by 2020 (World Energy Council, 2009).

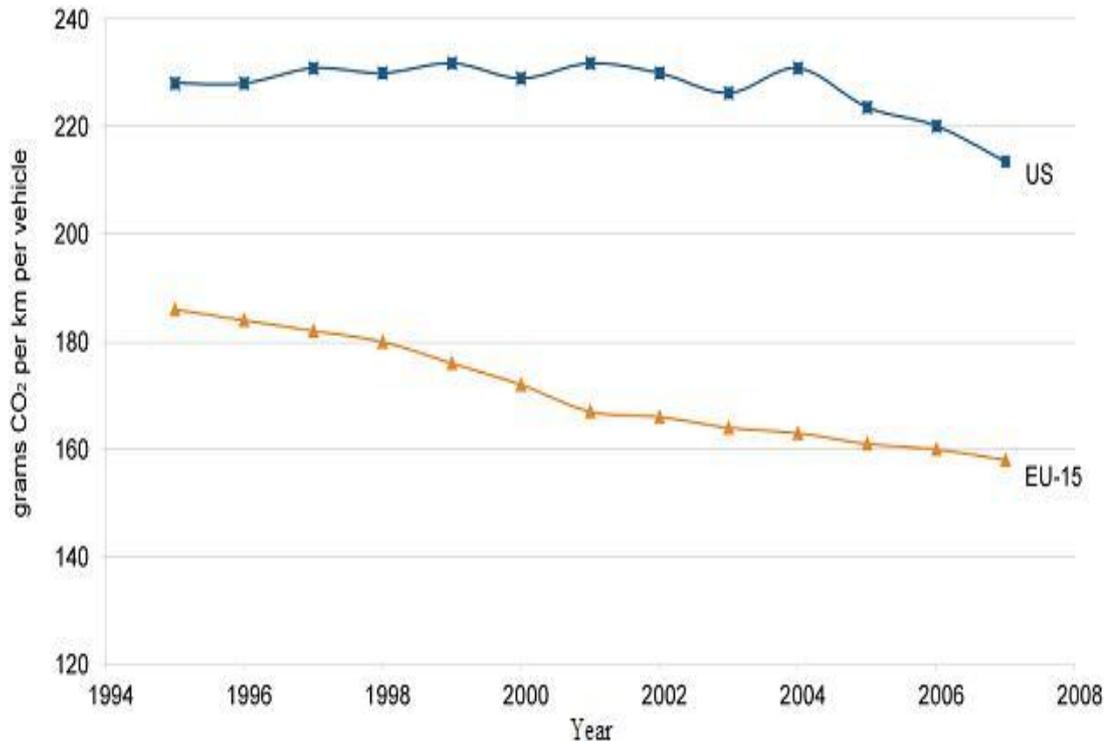


Figure 1.3 USA and EU-15 carbon dioxide emission profile (World Energy Council, 2009)

In addition, the French government has suggested that an incentive be given for lower CO₂ emission vehicles as well as penalties for those that cross the set CO₂ threshold (Table 1.2) (World Energy Council, 2009). Although the cost of biodiesel is still high, the pollution-control pledges and anticipation by the developed continents are confirmation of the demand for biodiesel and its impending usage in both the short and long term. It is the developing nations' responsibility, to a certain extent, to assist the developed nations in realizing their green targets. By looking at these scenarios, research on biodiesel is going to be ever more intense as the related research momentum quickens across the world.

Table 1.2 Bonuses and penalties for new vehicles in France for their corresponding CO₂ emissions (World Energy Council, 2009)

Emission levels (g CO ₂ per km)	< 60	< 100	101 - 120	121 - 130
Bonus in Euro (effective from 5-Dec-2007)	5000	1000	700	200
Emission levels (g CO ₂ per km)	161 - 165	166 - 200	201 - 250	> 250
Penalty in Euro (effective from 1-Jan-2008)	200	750	1600	2600

1.5 Economic aspects of biodiesel

At present, producing biodiesel commercially is not viable as petro-diesel is available at much lower prices than biodiesel. The choices of feedstocks as well as the catalyst systems are the major cost deciding factors in producing biodiesel. Since a large array of feedstocks is available in producing biodiesel, the choice of the right feedstocks is crucial in determining affordable biodiesel (Agarwal, 2007; Lim and Teong, 2010). As such, the utilization of the lower-cost feedstocks such as non-edible oils (which usually can grow on marginal lands), waste/used oils and animal fats are the options. As a note concerning the use of waste/used oils, it is worth recalling the success of Kyoto city, Japan. The city has recorded a remarkable success in utilizing a fraction of biodiesel prepared from used cooking oil to run their 215 municipal trucks as well as 81 municipal buses at B20 composition (20% biodiesel blend). Annually a total of 1.5 million litres of waste oil is collected to produce 1.5 million litres of biodiesel and is blended with petro-diesel to fill the municipal vehicles. As such, the use of oils from waste sources is not an unachievable effort, which not only adds value to the waste materials but also assists

in preserving a relatively greener environment. Furthermore, the utilization of waste oils has a positive impact on the environment. However, the choice of catalysts that are able to resist the presence of FFA and moisture in feedstocks as well as the catalysts' ability to be reused is another consideration to lower the biodiesel production cost. The tolerance of the catalyst towards FFA and moisture is an important aspect to be considered if waste/used oils are to be used as feedstocks. The economic prospect of glycerol (the by-product of the process) could be another way to reduce the biodiesel cost. Glycerol has many uses in the pharmaceutical and cosmetic sectors. As stated earlier, if all the benefits of biodiesel are accounted for, such as the environmental benefit, boost of rural economy, lower foreign exchange and independency on other countries for fuel, then the economic competitiveness of biodiesel can be readily realized.

1.6 Biodiesel in Malaysia

Malaysia is one of the major global producers of palm oil. It produced nearly 17 million tonnes of crude palm oil in year 2010 (Malaysian Palm Oil Board, 2011). As such, Malaysia has very high potential to cater for the global demand of biofuel as it benefits from vast agricultural land and a tropical climate, in which oil palm plantations are very feasible. As the major palm oil producer in the world, biodiesel production will certainly add value to the local palm oil industry. Development in biodiesel will certainly lessen Malaysia's dependency on foreign crude oil imports. Furthermore, it can ease many problems arising from palm oil oversupply by balancing the demand and supply gap. With this in mind, the Ministry of Plantation Industries and Commodities (MPIC) established the National Biofuel Policy (NBP) on 21 March 2006 to encourage the use of biofuels in line with the nation's Five-Fuel

Diversification Policy (Ministry of Plantation Industries and Commodities, 2010).

The National Biofuel Policy sets out to attain the following objectives:

- (1) supplementing the depleting supply of fossil fuels with renewable resources
- (2) mobilising local resources for biofuels
- (3) exploiting local technology to generate energy for the transportation and industrial sectors
- (4) paving the way for exports of biofuels and
- (5) benefiting from the spin-off effect of more stable prices for palm oil.

The Policy is driven by five strategic thrusts:

Thrust 1: Biofuel for Transport

Diesel with a blend of 5 % palm biodiesel and 95 % petroleum diesel (B5) will be used for transport and it will be made available throughout the country.

Thrust 2: Biofuel for Industry

B5 diesel will be supplied to the industrial sector including for firing boilers in manufacturing, construction machineries, and generators.

Thrust 3: Biofuel Technologies

The government will fund research, development and commercialization of biofuel technologies.

Thrust 4: Biofuel for Export

The establishment of plants for producing biofuel for export will be encouraged and facilitated.

Thrust 5: Biofuel for Cleaner Environment

The use of biofuel will reduce the use of fossil fuels, minimize the emission of greenhouse gases (carbon dioxide), carbon monoxide, sulphur dioxide and particulates, thus improving the quality of the environment.

Some of the biofuel benefits, as spelt out in the report, are that biodiesel can mitigate the effects of petroleum price escalation, can obviously save in foreign exchange, create new demand for palm oil and stimulate the efficient utilization of raw materials. The government has also introduced several incentives to boost the biofuel industry. Among them are that all biodiesel projects are eligible to be considered for Pioneer Status or Investment Tax Allowance, incentives for strategic or high technology projects and for commercialization of research and development findings. In short, the Biofuel Policy 2006 will help strengthen Malaysia's position as a leading producer and exporter of palm oil as well as in becoming a major biofuel producer. It also increases the gain in revenue from the oil palm sector and directly reduces the subsidy burden of the government for petro-based fuels.

Palm oil-biodiesel has created numerous issues regarding the 'food-for-fuel', and Malaysia is doing its part to make the production as sustainable as possible. The Roundtable on Sustainable Palm Oil (RSPO) has been formed to promote the growth as well as the use of sustainable palm oil. In addition, the Malaysian Palm Oil Wildlife Conservation Fund (MPOWCF) has been set up to conserve the nature and green of the Malaysian forest. These are a few examples of Malaysia's efforts to sustain the production of palm oil. Malaysia has underlined four key steps for global biofuels sustainability – Transparency, Inclusiveness, Proportionality and Sound

science. Malaysia wants a more transparent decision-making process on GHG savings and sustainability criteria. GHG emission savings as high as 62% is obtainable from palm biodiesel (Basiron and Yew, 2009), well above the required minimum GHG emission savings of 35% set by the European Union (EU Renewable Energy Directive 2008, 2011). Malaysia stressed that third world countries should be given a chance to be included in all the leading European Union (EU) discussions. It further highlighted that the creation of new EU sustainable schemes should not compete with or contradicts the currently existing schemes. In addition, the EU should build or add-on to the currently existing schemes on sustainability. Lastly, Malaysia wants the EU to take into consideration all the relevant aspects before announcing any scientific data. Any missed or excluded aspects have a serious implication on the announced data and question the validity of the reported data (Malaysian Palm Oil Board, 2011; Malaysian Palm Oil Council, 2011).

1.7 Transesterification

Transesterification is a catalytic process of alcohol displacement from an ester to another (Figure 1.4).

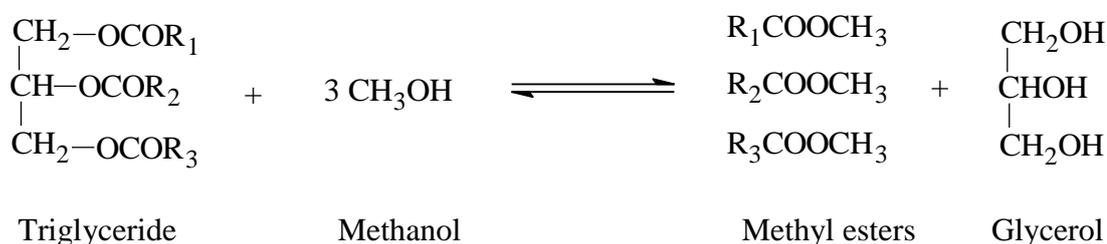


Figure 1.4 General equation of transesterification

Although stoichiometrically, three moles of methanol are required, since transesterification is a reversible process, excess methanol is proposed to shift the

reaction forward. Transesterification between triglycerides and alcohols is commonly known as alcoholysis, and, if methanol is used, then it is called methanolysis. Although other alcohols such as ethanol, propanol, butanol and amyl alcohol can be used, methanol is preferred for its low cost, being the shortest alcohol chain and for its polarity (Demirbas et al., 2009). The methanolysis of oil, together with a suitable catalyst, produces fatty acid methyl esters and glycerol. At the end of the reaction, the latter settles down to form the bottom layer.

It is important to note that the main purpose of transesterification is to lower the viscosity and increase the volatility of the oil. It can be seen from the reaction that the conversion of oil to methyl esters, with suitable catalysts, reduces the molecular weight by up to 66%. The conversion of triglycerides to simple esters reduces the molecular weight of oil to one-third of its original value. In addition, it also reduces the viscosity of oil by a factor of about eight, thus, increasing the volatility (Pryde, 1984). Neat biodiesel has a viscosity of 10 to 20 times higher than that of diesel fuel (Rakopoulos et al. 2006). As mentioned earlier, these two natures of oil, higher viscosity and lower volatility, obstruct the direct use of the oil in diesel engines.

The overall transesterification process is normally a sequence of three consecutive steps, which are reversible reactions, as shown in Figure 1.5. From triglycerides, the first step is the formation of diglycerides, followed by the conversion of diglycerides to monoglycerides and finally from monoglycerides, glycerol is obtained. Since monoglyceride is a more stable intermediate compound than the diglyceride, the third step, which is the ester formation step from the monoglyceride, is believed to be the rate-determining step of the overall reaction (Ma and Hanna, 1999).

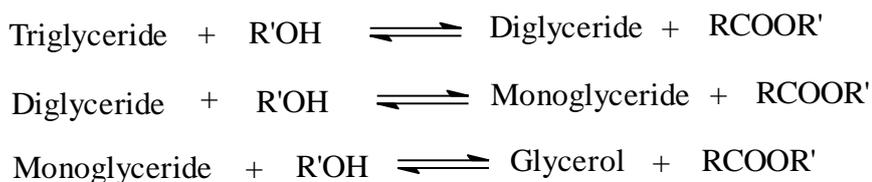


Figure 1.5 Step-wise transesterification reaction of triglycerides (Meher et al. 2006a)

In all three reactions, one methyl ester molecule is produced at each step. Since the reaction is reversible, an excess of alcohol is usually more appropriate to accelerate the forward reaction; the stoichiometric relation between oil and alcohol is 1:3. In the industry, excess alcohol has always been used to accelerate the forward reaction and the alcohol is recovered by stripping at the end of the reaction. Parameters that influence the transesterification reaction are oil to methanol ratio, catalyst amount, reaction temperature, pressure and the quality of oil in terms of FFA and moisture content. Apart from other factors, as noted by Meher et al. (2006a), the oil to methanol ratio is one of the most important variables affecting the methyl esters yield.

1.7.1 Mechanisms of transesterification

(a) Base-catalyzed transesterification

As shown in Figure 1.6, the mechanism of base-catalyzed transesterification can be explained as follows. The first step (1) is the reaction of the base (B) with the alcohol (ROH), producing an alkoxide (methoxide ion in the case of methanol) and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (2) from which the alkyl ester and the corresponding anion of the diglyceride are formed (3). The latter deprotonates the catalyst, thus regenerating the active species (4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle.

Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and a mole of glycerol.

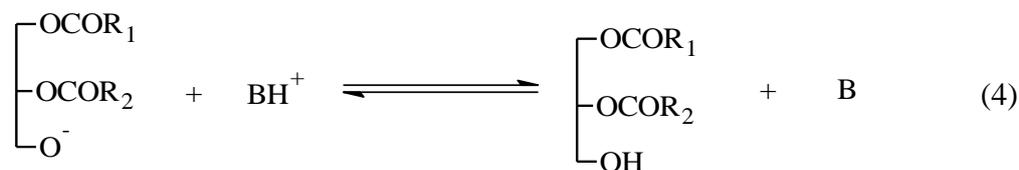
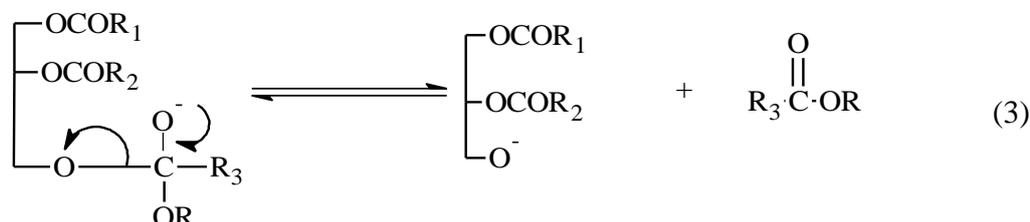
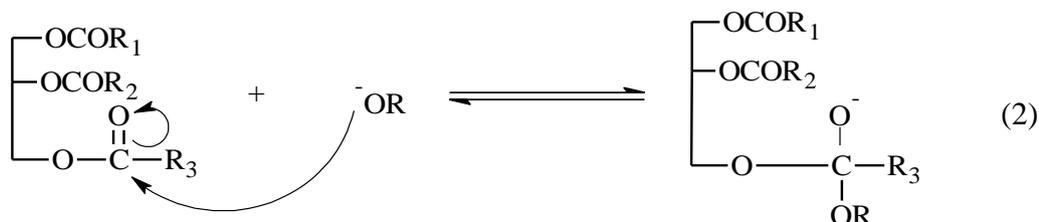
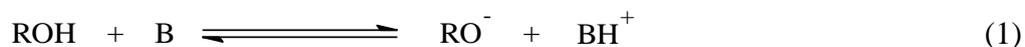


Figure 1.6 Mechanism of the base-catalyzed transesterification (Meher et al. 2006a)

(b) Acid-catalyzed transesterification

Acid-catalyzed transesterification starts with protonation of the carbonyl group, as shown in Figure 1.7. The protonation of the carbonyl group of the ester leads to the carbocation (1), which after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate (2), which eliminates glycerol to form the new ester (3), and to regenerate the catalyst H^+ .

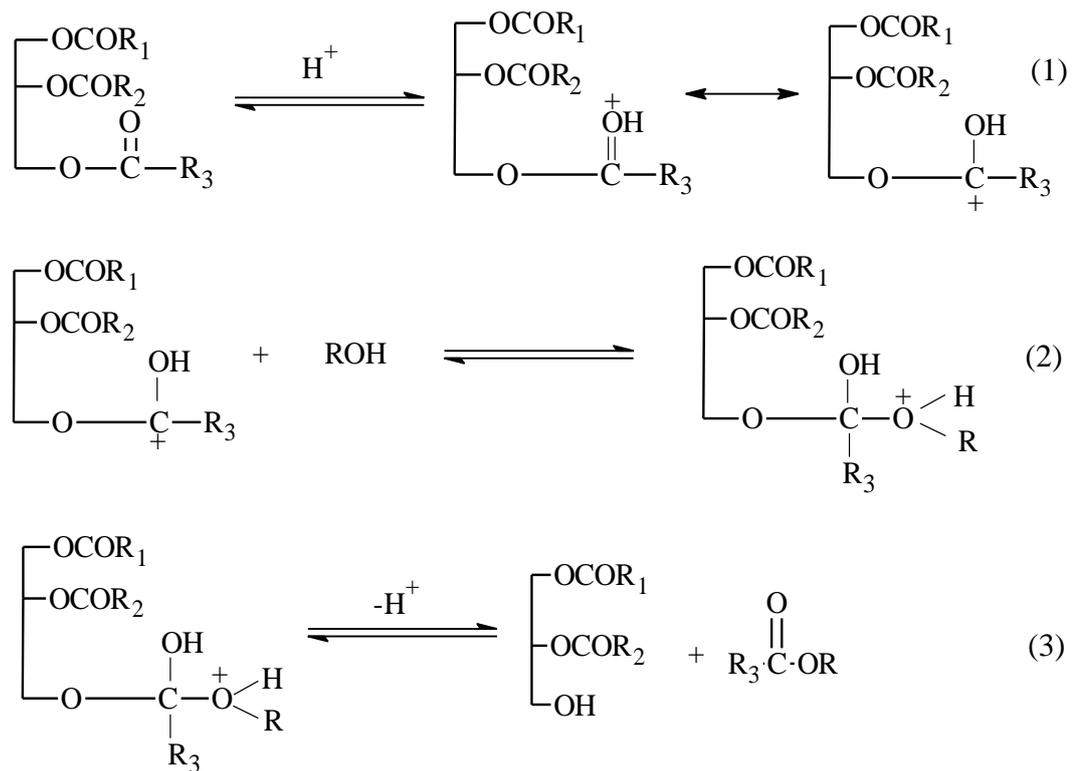


Figure 1.7 Mechanism of the acid-catalyzed transesterification (Meher et al. 2006a)

1.7.2 Factors affecting transesterification

Among the factors affecting transesterification reaction are: (a) catalyst type, (b) catalyst concentration, (c) ratio of alcohol to oil, (d) quality of oil (free fatty acid and moisture content), (e) type of alcohol, (f) reaction temperature, (g) the use of co-solvent, and (h) the effect and type of stirring. Usually, the base catalyst is mostly used in the production of biodiesel. This is because in base-catalyzed transesterification, the kinetic reaction is faster than acid-catalyzed transesterification. The concentration of catalyst, however, varies from 0.4 % to 2 % in alkaline methanolysis as reported by several researchers (Jitputti et al., 2006; Meher et al., 2006a; Xie and Li 2006), although 1 % (wt. %) concentration is very common (Darnoko and Cheryan 2000; Vicente et al., 2007a). As for the quality of oil, it should be free from fatty acids and moisture. If not, base-catalyzed transesterification should be replaced with acid-catalyzed reaction, to avoid any

undesirable side reaction (saponification), which will reduce the yield as well as complicate the separation and purification processes.

As for alcohol type, methanol is always the preferred candidate among all the alcohols for transesterification reaction although some papers describe the use of ethanol (Holser and Harry-O’Kuru 2006; Meher et al., 2006b; Soriano et al., 2006). As for the reaction temperature, most of the researchers recommended 60 to 65 °C as it is very close to the boiling point of methanol (64.5 °C) (Barbosa et al., 2006; Chuang and Brunner 2006) and for co-solvents, hexane, tetrahydrofuran, toluene, benzene and CO₂ (for supercritical methanol) were utilized to enhance the conversion in transesterification as reported by Meher et al. (2006b), Han et al. (2005) and Kim et al. (2004). The use of propane as a co-solvent decreases the severity conditions required for supercritical reaction significantly. Furthermore, the co-solvent can be reused after suitable pretreatment (Cao et al., 2005). Transesterification has also been performed by means of low frequency ultrasound, 28 and 40 kHz, replacing mechanical stirring. By using this method, the reaction time is found to be shortened by 40 minutes and the required catalyst amount is two to three times lower as compared to the reactions without the assistance of ultrasound (Stavarache et al. 2005).

Transesterification has also been carried out with waste or used oils. Wang et al. (2006) made such an attempt with waste cooking oil from restaurants. They studied two different processes, first, via sulphuric acid catalyzed transesterification, and, second, through the two-step method, ferric sulphate catalyzed reaction followed by KOH catalyzed transesterification at 95 °C. Of the two processes, the second process

gives 97.2 % conversion whereas only 90.0 % conversion is achieved with the first process. Similarly, Felizardo et al. (2006) used waste frying oils to study the best conditions for transesterification. The authors used NaOH as the catalyst and concluded that for oils with an acid value of 0.42 mg KOH/g and with catalyst/oil weight ratio of 0.6 %, conversion above 90 % can be achieved at 60 °C.

1.8 Catalysts in transesterification

Economically, apart from the cost of feedstocks, the catalyst cost accounts for a major part in the biodiesel production. As such, research has to be carried out continuously to devise a stable, cost-effective and, at the same time, sustainable catalyst for a commercially applicable biodiesel process. Consequently, the number of recent research articles on ‘catalysts in transesterification’ has expanded dramatically.

1.8.1 Homogeneous catalysts in transesterification

As far as the catalyst is concerned, a homogeneous catalyst is the preferred choice for producing biodiesel. Hydroxides and methoxides of sodium and potassium are the most common homogeneous catalysts. Freedman et al. (1984) found that 0.5% NaOCH₃ performs much better than 1% NaOH. However, both catalysts are able to transesterify to near completion within one hour of reaction time at 60 °C. A longer reaction time (4 h) is required for similar performance at 32 °C. The authors also noted that the acid-catalyzed transesterification is much slower than the alkali-catalyzed reaction.

Meher et al. (2006a) demonstrated that in the transesterification of Karanja oil, KOH performed excellently with a methyl esters yield above 90% at 1% and 1.25% catalyst dosage, in 1 h reaction at 65 °C with a stirring speed of 600 rpm. Similarly, sodium based homogeneous catalysts (NaOH and NaOCH₃) have shown remarkable performances in the transesterification of rapeseed and soybean oils. Rapeseed methyl esters yield between 93 to 96%. This was achieved in a one hour reaction time with 1-2% NaOH in the following conditions: 7:1 molar ratio, 60 °C, 600 rpm mechanical stirring. Whereas in the transesterification of the soybean oil a yield of more than 80% was obtained with 0.1% NaOCH₃ in 2.5 h reaction time at 65 °C with 10:1 MeOH/oil molar ratio, and 450 rpm shaking speed (Georgogianni et al., 2009; Kim et al., 2010). In transesterification of sunflower oil, Ye et al. (2010) achieved near-completion of acyl conversion in 30 min at 60 °C using 1.2 wt.% NaOH. By using acid catalysts at 5 wt.% concentration, Furukawa and co-researchers (2010) successfully transesterified canola oil in a 2 h reaction at 60 °C; as expected, at a higher MeOH/oil molar ratio of 15:1. Usually, for basic homogeneous transesterifications, a 6 to 9 molar ratio is sufficient.

1.8.2 Heterogeneous catalysts in transesterification

In recent years, researchers have turned their focus to heterogeneous-catalyzed transesterification as the homogeneous-catalyzed transesterification consumes more energy and requires a costly product separation process. Heterogeneous-based transesterification makes the process more cost-effective and, as such, commercialization becomes comparatively easy (Arzamendi et al., 2008; Helwani et al., 2009; Encinar et al., 2010). Sercheli et al. (1999) exhibited the use of alkylguanidines attached to modified polystyrene or siliceous MCM-41 in the

methanolysis of soybean oil and, interestingly, its activity was comparable to that of homogeneous catalysts. Kim and co-workers (2004) described the use of Na/NaOH/ γ -Al₂O₃ in producing near-completion soybean oil methyl esters in 2 h. Tin complex [Sn(3-hydroxy-2-methyl-4-pyrone)₂(H₂O₂)] has been successfully utilized in soybean oil methanolysis, giving a 93% yield in a reaction time of 3 h and with the added advantage of the possibility of recycling the catalyst (Abreu et al., 2005).

Jitputti et al. (2006) demonstrated a series of acidic as well as basic heterogeneous catalysts in the transesterification of palm kernel and crude coconut oils. The catalysts used were ZrO₂, ZnO, SO₄²⁻/SnO₂, SO₄²⁻/ZrO₂, KNO₃/KL zeolite and KNO₃/ZrO₂. The authors found that among the researched catalysts ZnO and SO₄²⁻/ZrO₂ showed the highest activity. In another study, Xie and co-researchers (2006a) proved that potassium loaded on alumina can be a potential solid catalyst in the methanolysis of soybean oil. The calcined (at 500 °C, 5 h) catalyst system at 35 wt.% loading, with a molar ratio of 15:1 (MeOH/oil) and catalyst concentration of 6.5%, converted 87% triglyceride in 7 h. When loaded on a mesoporous MSU-type alumina, KF, LiF and CsF demonstrated to be potential solid catalysts in the transesterification of vegetable oils (Verziu et al., 2009).

Hameed et al. (2009) successfully used a KF/ZnO system in palm oil transesterification with yields exceeding 89% in less than 10 h with a MeOH/oil molar ratio of 11.43: 1 and 5.52 % catalyst amount. As shown by Zhang et al. (2010), heteropolyacid (Cs_{2.5} H_{0.5}PW₁₂O₄₀) is another solid system in the

methanolysis of yellow horn oil. The highest yield of more than 96% was attained in 10 min, at 60 °C, with 12:1 MeOH/oil molar ratio.

1.8.3 Enzymatic catalysts in transesterification

The potential of biocatalysts in biodiesel production is attracting continuous attention and the catalysts perform equally well with their chemical-based counterparts. Shieh et al. (2003) immobilized lipase from *Rhizomucor miehei* (Lipozyme IM-77) to catalyze the methanolysis of soybean oil to achieve more than 92% methyl esters conversion. Dizge and Keskinler (2008) demonstrated the use of 80% immobilized *Thermomyces lanuginosus* lipase in the transesterification of canola oil with a remarkable yield of 90%. A series of lipase (*Pseudomonas fluorescens*, *Burkholderia cepacia* and *Penicillium camembertii*) were utilized in the transesterification of babassu oil by Freitas and co-researchers (2009) to obtain a yield of more than 98% in a reaction time of 48 h.

Xie and Ma (2010) used lipase (*Thermomyces lanuginose*) that was covalently immobilized onto magnetic Fe₃O₄ nano-particles by using an activating agent [1-ethyl-3-(3-dimethylaminopropyl) carbodiimide] in the transesterification of soybean oil. The conversion of over 90% was achieved in the three-step transesterification when 40% immobilized lipase was used. Interestingly, the enzyme catalyst could be used more than three times without a significant loss in the catalytic activity.

There are several advantages of enzymatic reactions, among them are the possibility of regeneration and reuse of the enzyme, relatively larger thermal stability of the enzyme due to the native state, and product separation will be much easier, as the

usual processing step of neutralization can be avoided (Demirbas, 2009; Chattopadhyay et al., 2011). The authors also noted various drawbacks from using this type of catalyst. Among them, the losses of initial activity due to the presence of large oil molecules, lower reaction rate, non-uniformity of number of support enzymes, enzyme deactivation and certainly the cost of this type of catalyst are usually high (Demirbas, 2009; Bajaj et al., 2010). Although this type of reaction is yet to be commercialized, the related articles and patents are evidence of the possibility. Parametric studies under enzymatic transesterification include reaction temperature, pH of the reaction medium, type of microorganisms and the solvent type used in the reaction.

1.8.4 Non-catalytic transesterification reaction

It is worth mentioning here that although transesterification could be carried out without the presence of a catalyst (under the supercritical conditions of methanol) it would result in higher operational cost. For such a catalyst-free reaction, higher temperatures and pressures would be needed to pass the critical temperature of methanol, 240 °C (Minami and Saka, 2006; D'Ippolito et al., 2007), as well as a higher alcohol to oil ratio. Demirbas (2006) investigated the effect of water under these supercritical conditions of methanol and found that unlike conventional catalytic transesterification, the presence of water does not have any negative effect on the yield. The authors concluded that the presence of water, in fact, positively affects the formation of methyl esters under supercritical conditions. The authors reported that utilizing supercritical methanol is also an environmentally accepted process, since no catalyst and product washing and purification is involved. They