# SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS BASE CATALYST FOR TRANSESTERIFICATION OF PALM OIL

**by**

**NORAINI BINTI RAZALI**

**Thesis submitted in fulfillment of the**
**requirements for the degree of**
**Master of Science**

**SEPTEMBER 2009**

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**UNIVERSITI SAINS MALAYSIA**
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Noraini Razali, September 2009.

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# LIST OF SYMBOLS

| Symbols | Descriptions | Unit |
|---|---|---|
| $A$ | Arrhenius factor (pre-exponential factor) | Dimensionless |
| $C_{TG}$ | Concentration of triglyceride | (mol/dm$^3$) |
| $C_{TG,0}$ | Concentration of initial triglyceride | (mol/dm$^3$) |
| $C_{FAME}$ | Concentration of FAME | (mol/dm$^3$) |
| $C_{TG}$ calc | Simulated data of concentration of triglyceride | (mol/dm$^3$) |
| $C_{TG}$ exp | Experimental data of concentration of triglyceride | (mol/dm$^3$) |
| $C_{MeOH}$ | Concentration of methanol | (mol/dm$^3$) |
| $-dC_{TG}/dt$ | Differential of $C_{TG}$ polynomial with respect to time (t) | (mol/dm$^3$.h) |
| $dX/dt$ | Differential of conversion of triglyceride with respect to time | (mol/h) |
| Df | Dilution factor | Dimensionless |
| $Ea$ | Activation energy | (kJ/mol) |
| $k$ | Reaction rate constant | (dm$^3$/mol.h) |
| $[\text{ME pure}]_{SD}$ | Concentration of ester in the standard references | (g/l) |
| m | Order of reaction | Dimensionless |
| n | Order of reaction | Dimensionless |
| $N_A$ | Initial numbers of moles | (mol) |
| $R$ | Gas constant | (J/mol.K) |
| $R_{SD}$ | Ratio of peak area of ester to peak area of internal standard references | Dimensionless |
| $R_{SP}$ | Ratio of peak area to peak area of internal standard in the sample | Dimensionless |
| $-r_A$ | Rate of reaction | (mol/dm$^3$.h) |
| $-r_{TG}$ | Rate of reaction of triglyceride | (mol/dm$^3$.h) |
| $T$ | Reaction temperature | (K) |
| $t$ | Reaction time | (h) |
| X | Conversion of triglyceride | Dimensionless |
| $V$ | Total volume | (dm$^3$) |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| a. u | Arbitrary unit |
| AMS | Anionic surfactant templated mesoporous silica |
| ANOVA | Analysis of variance |
| ASTM | American Society for Testing and Materials |
| BET | Brunauer-Emmett-Teller |
| BJH | Barrett-Joyner-Halenda |
| CCD | Central composite design |
| CCO | Coconut oil |
| $CO_2$ | Carbon dioxide |
| CCRD | Central composite rotatable design |
| CMK | Ordered mesoporous carbon |
| DF | Degree of freedom |
| DOE | Design of experiment |
| EDX | Energy dispersive X-ray spectroscopy |
| FAME | Fatty acid methyl ester |
| FID | Flame ionization detector |
| FFAs | Free fatty acids |
| FSM | Folded sheet mesoporous materials |
| HMS | Hexagonal mesoporous silica |
| $H_2O$ | Water |
| HCl | Hydrochloric acid |
| IEA | International energy association |
| ISO | International standard organization |
| IUPAC | International Union of Pure and Applied Chemistry |

| | |
|---|---|
| KI | Potassium iodide |
| $KNO_3$ | Potassium nitrate |
| KOH | Potassium hydroxide |
| MCM | Mobil composition of matter |
| MeOH | Methanol |
| MPOB | Malaysian Palm Oil Board |
| MPOC | Malaysian Palm Oil Council |
| MS | Mean square |
| MSU | Michigan State University material |
| NaOH | Sodium hydroxide |
| $NO_X$ | Nitrogen dioxide |
| P104 | Pluronic 104 |
| P123 | Pluronic 123 |
| P(EO)n- | Poly(ethylene oxide)n |
| P(PO)m- | Poly(propylene oxide)m |
| PILC | Pillared interlayered clays |
| PKO | Palm kernel oil |
| RPO | Refine palm oil |
| RSM | Response Surface Methodology |
| SAXS | Small angle X-ray scattering |
| SBA | Santa-Barbara amorphous |
| SEM | Scanning electron microscope |
| $SO_2$ | Sulphur dioxide |
| SS | Sum of square |
| TEM | Transmission electron microscope |

| | |
|---|---|
| TEOS | Tetraethylorthosilicate |
| TCP | Tri-block copolymer |
| TG | Triglyceride |
| TLCT | True liquid crystal templating |
| TMOS | Tetramethylorthosilicate |
| TMS | Transition metal oxide mesoporous molecular sieve |
| WCOs | Waste cooking oils |
| XRD | X-ray diffraction |

# SINTESIS DAN PENCIRIAN MANGKIN BES BERLIANG MESO UNTUK TRANSESTERIFIKASI MINYAK KELAPA SAWIT

## ABSTRAK

Disebabkan keprihatinan terhadap persekitaran dan ekonomi, haluan penyelidikan dalam pemangkinan pada masa kini telah diubah daripada homogen kepada sistem heterogen yang pusat aktifnya disokong oleh pepejal. Kegiatan mangkin bes pepejal baru-baru ini telah tertumpu kepada substrat silika berliang meso disebabkan oleh luas permukaan tinggi, saiz liang sekata dan kestabilan hidroterma yang menjanjikan peluang yang sangat baik untuk diaplikasikan sebagai mangkin dan penyokong mangkin. Dalam kajian ini, SBA-15 (bahan berliang meso) telah dikaji sebagai penyokong mangkin. Sintesis sokongan SBA-15 telah dikaji dengan mengubah parameter proses yang berbeza iaitu kesan suhu tindakbalas, nisbah tetraetilortosilikat/triblok kopolimer (TEOS/TCP), pH larutan sol-gel dan masa rawatan hidroterma. Bahan SBA-15 tertakluk kepada penganalisis permukaan, XRD, TEM dan SEM untuk mengkaji luas permukaan BET, kehabluran dan morfologi sokongan masing-masing. Keadaan optimum untuk SBA-15 telah dipilih berdasarkan kepada keputusan pencirian. Keadaan optimum telah diperoleh pada suhu sintesis 60 $^{o}$C, nisbah TEOS/TCP 1.52, pH 1.7 dan masa rawatan hidroterma 36 jam. Mangkin bes berliang meso telah dibangunkan dengan perkongsian tiga sebatian potassium yang berbeza (KI, $KNO_3$, KOH) dibebankan pada SBA-15 melalui kaedah persenyawaan dengan suhu pemanasan pada 350 $^{o}$C selama 3 jam. Ketiga-tiga jenis mangkin ini telah digunakan di dalam proses transesterifikasi dan hasil FAME telah diselidik. Hasil yang paling tinggi diperoleh dengan menggunakan mangkin KOH/SBA-15 dan bebanan yang paling tinggi didapati pada 20 wt. % KOH pada sokongan SBA-15. Selain daripada itu, sokongan yang berbeza juga telah dikaji iaitu HZSM-5 dan $Al_2O_3$. Kajian pengoptimuman proses transesterifikasi merangkumi kesan suhu (50-90 $^oC$), nisbah metanol kepada minyak (6:1-14:1), berat mangkin (1-5 wt. %) dan masa tindakbalas (2-6 jam). Kaedah sambutan permukaan (RSM) telah digunakan untuk proses pengoptimuman bagi mencapai hasil FAME yang paling tinggi dan pada masa yang sama untuk menilai keadaan diantara parameter-parameter yang saling bertindak balas. Keadaan optimum diperoleh dengan aktiviti yang memberikan hasil FAME yang paling tinggi iaitu sebanyak 84.3 % pada suhu tindakbalas pada 70 $^oC$ dengan nisbah metanol kepada minyak 11.6 , berat mangkin 3.91 wt. % dan masa tindakbalas 4.54 jam. Disamping menunjukkan aktiviti bermangkin tinggi, KOH/SBA-15 boleh juga diguna semula untuk sekali lagi kitaran dengan penurunan aktiviti hanyalah sebanyak 15.6 %. Disamping itu, mangkin tersebut juga boleh digunakan di dalam proses transesterifikasi minyak terpakai dengan penghasilan FAME sebanyak 77 %. Tambahan lagi, tenaga pengaktifan yang rendah telah diperoleh di dalam proses transesterifikasi ini iaitu sebanyak 46.37 kJ/mol. Daripada kajian ini, didapati bahawa KOH/SBA-15 merupakan sejenis mangkin yang berkesan untuk proses transesterifikasi minyak sawit.

# SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS BASE CATALYST FOR TRANSESTERIFICATION OF PALM OIL

## ABSTRACT

Due to environmental and economic concerns, current research trend in catalysis has been shifting from homogeneous into heterogeneous systems in which the active centers are supported on a solid. The pursuit of solid base catalyst has been recently focused on mesoporous silica substrates due to very high surface area, uniformity in pore size and hydrothermal stability which promising great opportunity for application as catalysts and catalytic supports. In the present study, SBA-15 (mesoporous material) was studied as a catalyst support. The synthesis of SBA-15 support was studied by varying different process parameters i.e. effects of reaction temperature, tetraethylorthosilicate/triblock copolymer (TEOS/TCP) ratio, pH of sol-gel solution and hydrothermal treatment time. The SBA-15 materials were subjected to surface analyzer, XRD, TEM and SEM in order to study BET surface area, crystallinity and morphology of the support, respectively. The optimum conditions for the SBA-15 were chosen based on the characterization results. The optimum conditions were obtained at 60 $^{o}$C synthesis temperature, 1.52 TEOS/TCP ratio, pH 1.7 and 36 h of hydrothermal treatment time. Mesoporous base catalysts were developed by incorporating three different potassium compounds (KI, $KNO_3$, KOH) loaded on SBA-15 by impregnation method with heating at a temperature of 350 $^{o}$C for 3 h. All of these three types of catalyst were used in the transesterification process and the yield of FAME was investigated. The highest yield was obtained using KOH/SBA-15 catalyst and the optimum KOH loading was found to be at 20 wt. %. Otherwise, the different supports were also studied i.e. HZSM-5 and $Al_2O_3$.

The optimization study of the transesterification process encompassed the effect of temperature (50-90 °C), methanol to oil ratio (6:1-14:1), weight of catalyst (1-5 wt. %) and reaction time (2-6 h). Response surface methodology (RSM) was employed for the optimization process to achieve the highest FAME yield and to evaluate the interaction between the parameters at the same time. The optimum conditions were found to give the best activity of 84.3 % of FAME yield at 70 °C of reaction temperature with a methanol to oil ratio of 11.6, 3.91 wt. % of catalyst and 4.54 h of reaction time. Besides showing high catalytic activity, KOH/SBA-15 could be reused for one more run with an activity drop of merely 15.6 %. Beside that, the catalyst also can be used in the transesterification process of waste cooking oil with 77 % of FAME yield. Furthermore, low activation energy of 46.37 kJ/mol was obtained for the transesterification process. From this study, it was demonstrated that the KOH/SBA-15 was an effective catalyst for the transesterification process of palm oil.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Energy crisis

Demand for energy and its resources is increasing every day due to the rapid outgrowth of population and urbanization. The major energy demand is fulfilled from the conventional energy resources like coal, petroleum and natural gas. These sources are in the verge of getting exhausted. It was estimated that the oil sources might be depleted by 2050 (Goyal *et al*., 2008). Moreover, the process of obtaining energy from these sources causes atmospheric pollution, resulting in problems like global warming and acid rain. This has triggered recent interest in alternative sources to petroleum-based fuels. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available (Meher *et al*., 2004).

Biofuels i.e. fuels made from biological ingredients instead of fossil fuels have potential for the widest reach, and are more economical than other alternatives. Between 1980 and 2005, worldwide production of biofuels increased by an order of magnitude – from 4.4 to 50.1 billion litres (Murray, 2005) as shown in Figure 1.1. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector (Demirbas, 2008). Bioethanol and biodiesel are the two most common biofuels used worldwide. Biodiesel is defined by the European Parliament in Directive 2003/30/EC as a ‘methyl-ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel’ (Mcleod *et al*., 2007).

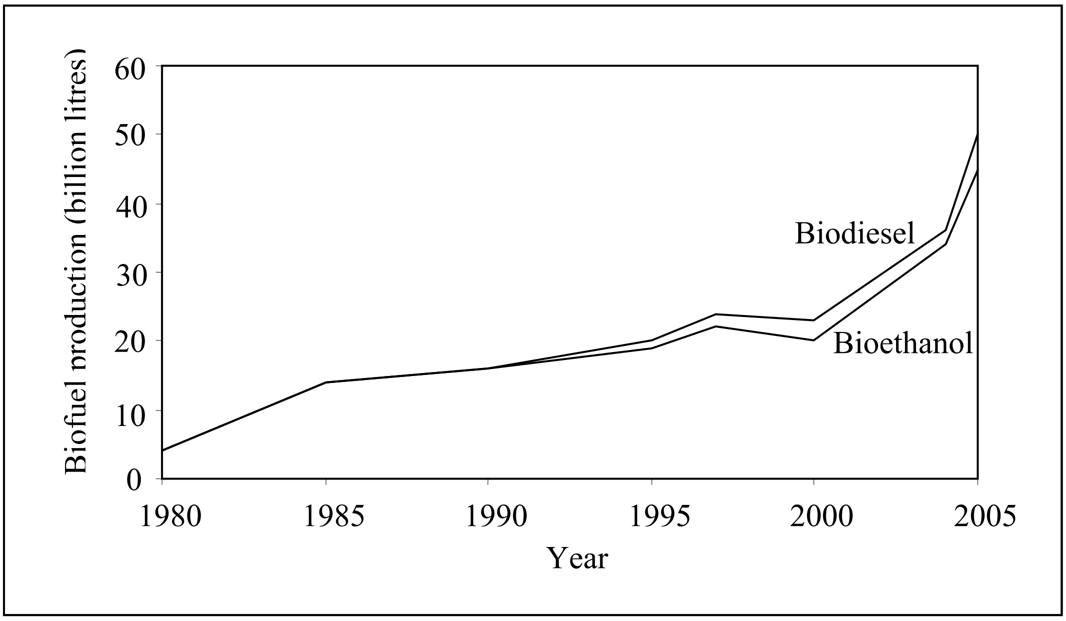

Figure 1.1: Global production of bioethanol and biodiesel between 1980 and 2005 (Murray, 2005).

## 1.2 Biodiesel production worldwide

The global biodiesel industry has grown significantly over the past decade, captivating the interest of various industry groups. However, currently only a small fraction of world biodiesel production exchanged internationally. As shown in Table 1.1, the year 2002 saw the biodiesel production was highest in Europe with a capacity of 1353 million litres. The European Union account for 90 % of all biodiesel production worldwide. In Europe, the principal biodiesel-producing countries are France, Germany, and Italy. All other countries accounted for only 10 % of combined world biodiesel capacity (Fulton *et al.*, 2004). The fuel is used mainly as a diesel blend, typically 5 % or 20 %. However, in Germany, biodiesel is commonly sold in its 100 % “neat” form, and dispensed in some 700 filling stations. Some European vehicle manufacturers have approved the use of 100 % biodiesel in certain engines (e.g. VW, BMW), while others have been concerned about vehicle/fuel compatibility issues and potential NOx emission increases from pure biodiesel, and have limited their warranties to cover only lower-level blends (Fulton *et al.*, 2004).

Table 1.1: World biodiesel capacity in 2002 (Fulton *et al.*, 2004).

| **Country** | **Biodiesel production capacity (million liters)** | **Typical use** |
|---|---|---|
| United states | 70 | blends<25 % |
| **IEA North America (total)** | **70** | |
| Austria | 32 | blends<25 % |
| Belgium | 36 | |
| Denmark | 3 | |
| France | 386 | mainly 5 % blends |
| Germany | 625 | 100 % biodiesel, some blends |
| Italy | 239 | blends<25 % |
| Spain | 9 | |
| Sweden | 17 | blends<25 % |
| UK | 6 | |
| **EU (total)** | **1353** | |
| Poland | 80 | |
| **IEA Europe (total)** | **80** | |
| **World** | **1503** | |

In Asia-Pacific, a number of biodiesel initiatives are being developed to capitalize on the region's immense palm oil production capacity. Indonesia, the world's second largest producer of palm oils recently announced plans to invest US$1.1 billion to develop 8 to 11 additional palm oil-based biodiesel plants by 2010 (Armbruster and Coyle, 2006). The governments of Thailand, the Philippines, Singapore, Japan, Korea, China and Australia are also actively pursuing energy policies aimed at increasing the production or use of biodiesel (Fulton *et al.*, 2004).

## 1.3 Malaysian biodiesel status

Malaysia currently accounts for 51 % of world palm oil production and 62 % of world exports, and therefore also for 8 % and 22 % of the world's total production and exports of oils and fats. As the biggest producer and exporter of palm oil and palm oil products, Malaysia has an important role to play in fulfilling the growing global need for oils and fats in general (MPOC, 2008). Malaysia is now looked upon as the pioneer palm biofuel producer. Malaysia has embarked on a comprehensive palm biofuel programme since 1982 and has successfully established the use of palm methyl esters and the blend of processed palm oil (5%) with petroleum diesel (95%) as a suitable fuel for the transport and industrial sectors. Malaysian government formulated the National Biofuel Policy in August 2005 to spurs the Malaysian biodiesel industry (MPOC, 2006). The National Biofuel Policy envisions:

1. Use of environmentally friendly, sustainable and viable sources of energy to reduce the dependency on depleting fossil fuels
2. Enhanced prosperity and well-being of all the stakeholders in the agriculture and commodity based industries through stable and remunerative prices.

With the current trend towards renewable fuels, Malaysia has the edge over other nations as the pioneering palm biodiesel producer. Until now, the Malaysian government has approved 91 licences with a total approved capacity of 10.2 million tonnes of biodiesel. As at the end of October 2008, a total of 14 plants are in operation with a total production capacity of 1.68 million tonnes (D-8 Secretariat, 2008). Therefore, palm biodiesel is considered the most possible substitute for conventional diesel fuel in Malaysia.

## 1.4 Biodiesel

### 1.4.1 Source of vegetable oils

Raw materials contribute to a major portion in the production of biodiesel. The choice of raw materials depends mainly on its availability (Rashid *et al.*, 2008), cost and climate (Barnwal and Sharma, 2005; Sharma and Singh, 2008) in each countries. Depending upon those factors, different countries are looking for different types of vegetable oils as substitutes for diesel fuels. Generally, the most abundant vegetable oil in a particular region is the most common feedstock. Thus, rapeseed and sunflower oils are predominantly used in Europe, soybeans are commonly used in the United States for food products which has led to soybean biodiesel becoming the primary source for biodiesel in this country. In India, jatropha oil is used as a significant fuel source, palm oil in the South-East Asia (mainly Malaysia and Indonesia) and coconut oil are being considered in the Philippines (Barnwal and Sharma, 2005; Demirbas, 2007). World vegetable oil consumption between 1980 and 2003 is tabulated in Table 1.2. The worldwide consumption of soybean oil is the highest in 2003 (27.9 million metric tones) followed by palm oil with 27.8 million metric tones of worldwide consumption.

Table 1.2: World vegetable oil consumption (million metric ton) (Demirbas, 2005)

| Oil | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 |
|---|---|---|---|---|---|---|
| Soybean | 23.5 | 24.5 | 26 | 26.6 | 27.2 | 27.9 |
| Palm | 18.5 | 21.2 | 23.5 | 24.8 | 26.3 | 27.8 |
| Rapeseed | 12.5 | 13.3 | 13.1 | 12.8 | 12.5 | 12.1 |
| Sunflower seed | 9.2 | 9.5 | 8.6 | 8.4 | 8.2 | 8 |
| Peanut | 4.5 | 4.3 | 4.2 | 4.7 | 5.3 | 5.8 |
| Cottonseed | 3.7 | 3.7 | 3.6 | 4 | 4.4 | 4.9 |
| Coconut | 3.2 | 3.2 | 3.3 | 3.5 | 3.7 | 3.9 |
| Palm kernel | 2.3 | 2.6 | 2.7 | 3.1 | 3.5 | 3.7 |
| Olive | 2.2 | 2.4 | 2.5 | 2.6 | 2.7 | 2.8 |
| Total | 79.5 | 84.5 | 87.2 | 90.5 | 93.8 | 96.9 |

### 1.4.2 Biodiesel characteristics (quality)

The properties of biodiesel depend very much on the nature of its raw material as well as the technology or process used in the production. The biodiesel is characterized by excellent properties as diesel engine fuels (Xie and Li, 2006) according to International Standard Organization (ISO). The properties are density, viscosity, cetane number, flash and combustion points. Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Flash point is the temperature at which the fuel becomes a mixture that will ignite when exposed to a spark or flame, and higher flash point indicates the safer fuel (Fernando *et al.*, 2007). Density is another important property of biodiesel. It is the weight of a unit volume of fluid. Fuel injection equipment operates on a volume metering system, lead a higher density for biodiesel results in the delivery of a slightly greater mass of fuel. Cetane number is a measure of ignition quality of diesel fuel. The higher the cetane number, the easier the fuel ignites when it is injected into the engine to give more efficient combustion (Demirbas, 2005).

As biodiesel is gaining considerable global attention and market, compliance with standards are vital for its commercialization and market introduction. Standardization of biodiesel is important so that engine manufacturers have reference fuels for engine systems development and also standards play a vital role in warranty issues and regulatory compliance. There are two major biodiesel standards that are most referred to, namely, the European Standard for Biodiesel (EN 14214) and The American Standard Specifications for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels (ASTM 6751) (Foon *et al.*, 2005; Fernando *et al.*, 2007). Table 1.3

shows the palm diesel properties produced by MPOB using both EN 14214 and ASTM 6751 standards. The data shows these palm biodiesels meet respective limits in the aforementioned standards.

Table 1.3: Fuel properties of palm diesel (MPOB, 2005)

| Property | Unit | Palm diesel | EN 14214 | ASTM D6751 |
|---|---|---|---|---|
| Ester content | % mass | 98.5 | 96.5 (min.) | - |
| Density at 15$^oC$ | kg litre$^{-1}$ | 0.8783 | 0.86 to 0.90 | - |
| Viscocity at 40$^0C$ | Mm$^2$ s$^{-1}$ | 4.415 | 3.5 to 5.0 | 1.9 to 6.0 |
| Flash point | $^oC$ | 182 | 120 (min.) | 130 (min.) |
| Cloud point | $^oC$ | 15.2 | - | Report |
| Pour point | $^oC$ | 15 | - | - |
| Cold filter plugging point | $^oC$ | 15 | - | - |
| Sulphur content | % mass | <0.001 | 0.001 (max.) | 0.0015 (min.) (Grade S15) |
| Carbon residue (on 10% distillation residue) | % mass | 0.02 | 0.3 (max.)<br>0.5 (max.) | 0.05 (max.) |
| Acid value | Mg KOH g$^{-1}$ | 0.08 | 0.02 (max.) | 0.8 (max.) |
| Sulphated ash content | % mass | <0.01 | 0.05 (max.) | 0.02 (max.) |
| Basic sediment and water | % mass | <0.05 | 51 (min.) | 0.05 (max.) |
| Cetane number | - | 58.3 | 51 (min.) | 47 (min.) |
| Copper strip corrosion (3 h at 50$^oC$) | Rating | 1a | 1<br>1 | 3 (max.) |
| Iodine value | - | 56 to 83 | 120 | - |
| Content of linoleic acid methyl esters | % mass | <0.5 | 12 | - |
| Content of polyunsaturated fatty acid methyl esters (more than 3 double bonds) | % mass | <0.1 | 1 | - |
| Methanol content | % mass | <0.2 | 0.2 | - |
| Monoglycerides content | % mass | <0.4 | 0.8 | - |
| Diglycerides content | % mass | <0.2 | 0.2 | - |
| Triglycerides content | % mass | <0.1 | 0.2 | - |
| Free glycerol content | % mass | <0.01 | 0.02 | 0.02 (max.) |
| Total glycerol content | % mass | <0.01 | 0.25 | 0.24 (max.) |

### 1.4.3 Biodiesel production process

There are four primary ways to make biofuel from edible oils. There are via direct use and blending, microemulsions, thermal cracking (pyrolisis) and transesterification. Direct use of vegetable oils and/or the use of blends of the oils have generally considered being not satisfactory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems. For microemulsion method, the fuel come out with the problem of irregular injector needle sticking, heavy carbon deposits, incomplete combustion and an increase of lubricating oil viscocity. Despite pyrolisis method was simple compared with other cracking processes, but the pyrolytic chemisty is difficult to characterize because of the variety of reaction products that may be obtained from the reactions that occur.

Therefore, transesterification of vegetables oils to methyl esters appears to be the best method in producing biodiesel due to the simple and effective process (Ma & Hanna, 1999). Batch production is usually carried out to produce biodiesel. This type of reactor can achieve high conversion with long batch time but may require high operating cost per unit production. Therefore, an optimisation of batch operating conditions such as temperature, operating time, etc. is the more efficient approach to obtain a maximum yield in a minimum time or minimum cost, as well as to reach the specific final conditions of the product in terms of quality and quantity. Therefore, operating batch reactors efficiently and economically is very important in industry as far as overall profitability is concerned (Aziz and Mujtaba, 2002).

## 1.5 Heterogeneous catalysts for biodiesel production

Transesterification process is usually prepared in the presence of homogeneous acid or base catalyst. However, as the catalytic activity of a base is higher than that of an acid and acid catalysts are more corrosive, the base catalysis is more preferred and most often used commercially (Xie and Li, 2006). Unfortunately, homogeneous base catalytic systems also have many drawbacks. In the conventional homogeneous method, the removal of the catalyst after reaction is technically difficult and a large amount of wastewater will be produced to separate and clean the catalysts and the products. This will lead to the costly separation and purification process (Kim *et al*., 2004). To overcome these drawbacks, heterogeneous catalyst systems are introduced over homogeneous catalyst system. They are non-corrosive, environmentally benign and present fewer disposal problems. They are also much easier to be separated from the liquid products and can be designed to give higher activity, selectivity and longer catalyst life time (Liu *et al*., 2007b). Furthermore, one of the early pioneering inventions in heterogeneous catalysis was the discovery that increases in the catalyst surface area lead to the significantly improved catalytic efficiency. Solid heterogeneous catalysts are active because much of their surface is exposed to the reacting molecules (Santen and Neurock, 2006).

The design of a catalyst covers all aspects from choice of the active phases to the method of forming particles. A heterogeneous catalyst is a composite material, characterized by: (a) the relative amounts of different components (active species, physical and/or chemical promoters, and supports); (b) shape; (c) size; (d) pore volume and distribution; (e) surface area. Suitable promoters are frequently added to obtain adequate performance. They may either modify the catalyst structure, so improving stability, or enhance the catalytic reactions to give better activity or selectivity. However, the nature of the active species is always the most important factor in heterogeneous catalyst system (Campanati *et al.*, 2003).

## 1.6 Problem statement

Currently, many types of heterogeneous catalysts, such as alkaline earth metal oxides, various alkaline metal compounds supported on alumina, zeolite or metal organic frameworks has been reported that can catalyze transesterification reactions (Liu *et al.*, 2007b). However, zeolites present severe limitations when large reactant molecules are involved, especially in liquid-phase systems as is frequently the case in the synthesis of fine chemicals, due to the fact that mass transfer limitations are very severe for microporous solids. It has a narrow and uniform micropore size distribution due to their crystallographically defined pore system (Taguchi and Schuth, 2005). In order to overcome the existing problem, the pursuit of solid base catalyst has been recently focused on mesoporous silica substrates due to very high surface area, uniformity in pore size and high thermal stability which promise great opportunity for application as catalysts and catalytic supports. However, the frameworks of mesoporous silica materials are neutral and the applicability is limited. Therefore, in this study, KI, KOH and $KNO_3$ have been used as active metal components to improve its catalytic performance. Due to this advantage and limited research dedicated to on heterogeneous transesterification process using mesoporous solid base catalyst, the main goals of this research project are directed towards the synthesis of the high surface area of mesoporous catalyst and the identification of the final metals which meet specific needs for effectively catalyzed transesterification process of palm oil.

In addition, the optimization of the process is different regarding the source of oil, catalyst and operating condition. Hence, in the study, the optimization of the transesterification process has been studied using the Design of Experiment. Otherwise, it has been reported that the heterogeneous catalysts could loose some of activity after their use (Noiroj *et al*., 2008) and will contribute to the homogeneous reaction. Therefore the determination of the leached active species from a solid support is important because the leached active species will give a negative effect on the amount of washing water in industry. Nowadays, many researchers in biodiesel production give their attention in using non-edible oil such as waste cooking oil. Hence, the comparison of the best catalyst performance in the refined palm oil and waste cooking oil will be carried out.

## 1.7 Objectives

1) To identify most suitable conditions for the synthesis of highly ordered mesoporous materials with desired properties and characteristics.
2) To create basic sites in mesoporous materials by different potassium metal sources
3) To characterize the modified and unmodified mesoporous materials in order to establish the understanding on the correlations between the characteristics of modified mesoporous materials with the performance in the transesterification process.
4) To identify and establish a suitable kinetic model for the transesterification process of palm oil with methanol catalyzed by basic modified mesoporous silica catalysts under the optimum conditions.

## 1.8 Scope of study

In this study, the mesoporous material considered is SBA-15. The selection is based on the high surface area and successful application as catalyst support in many reaction systems. The investigation of the suitable synthesis condition consist of main process variables such as the effect of reaction temperature (40-60 $^{o}$C), effect of ratio TEOS/TCP (1.52–3.38), effect of pH (1.7-3.0), effect of hydrothermal treatment time (12-48 h). The resulted SBA-15 catalysts were subjected to comprehensive characterization physical and chemical tests for changes in the characteristics of their structures using surface analyzer, X-ray diffraction (XRD), transmission electron microscope (TEM) and scanning electron microscope (SEM).

The modification of mesoporous silica with metal precursors (KI, KOH and $KNO_3$) was accomplished by impregnation method. The selection of this method was based on the advantages of the method as reported by Huwe and Froba (2007). The impregnation method was used to achieve high quality mesoporous silica as basic material and the possibility of a higher loading of the mesopores with the metals. The parameters studied were the effect of metal loading on mesoporous silica (5-25 wt. %), and different potassium metal sources in obtaining the optimum condition for the best catalyst.

The catalytic behavior of the basic mesoporous catalysts was measured based on response surface methodology model by transesterification of refined palm oil with methanol. The set of operation conditions and optimum condition have been determined using Design of Experiment (DOE) according the suitable ranges regularly reported in literature. The parameter studied were the effect of temperature

(50-90 $^{o}$C), the effect of alcohol to oil molar ratio (6:1-14:1), effect of weight of catalyst (1-5 wt. %), and effect of reaction time (2-6 h). The biodiesel sample was analyzed by gas chromatograph, equipped with a capillary column (nucol, 50 m x 50 um x 53 mm) and a flame ionization detector (FID). Besides that, a kinetic study for the reaction was studied using Arrhenius equation to obtain the activation energy (A), reaction rate ($-r_A$) and order of reaction ($\alpha$).

## 1.9 Thesis organization

This thesis consists of five chapters. Each chapter explains the important information of this research. Chapter One gives an introduction to the world's energy crisis, biodiesel demand, biodiesel production worldwide, Malaysian biodiesel status, sources of vegetable oils, quality and process. The importances of heterogeneous catalyst involved in the biodiesel process are also covered. This chapter also presents the problem statement, objectives of the present studies, research scope and finally the thesis organization.

Chapter Two focuses the literature review of the three main part in this study i.e. FAME, solid base catalyst in transesterification process and catalyst support. The biodiesel section was discussed in term of biodiesel process, palm oil as biodiesel feedstock and operating variables that affect the process. The solid base catalyst part covers the active metals and preparation methods. The next part reviews the mesoporous silica as a support catalyst and operating variables that affect the process. Finally, this chapter covers about the optimization studies in terms of Design of Experiment (DOE) and subsequently kinetic study.

Chapter Three details about the experimental methodology and analysis, the materials and chemical reagents used in the present research work, the experimental setup for transesterification process, experimental method for support and catalyst preparation and modification along with the characterization. Details of the product analysis, optimization studies, performance of catalyst in waste cooking oil, reusability of the catalyst, and kinetic study are also presented.

Chapter Four covers all the results and explanation of the findings in the study. It is divided into seven parts: (a) Characterization of SBA-15 support (b) Characterization of catalyst (c) Effect of operating parameter in catalyst activity (d) Design of experiments (e) Reusability of catalyst (f) Comparison with waste cooking oil (g) Kinetic study and parameter evaluation.

Chapter Five gives the conclusions to the findings made in the present study. It also provides some recommendations for future studies based on the results of the present study.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Biodiesel

Biodiesel refers to fatty acid methyl esters obtained from renewable biomass feedstocks when they are used as fuel in diesel engines and heating systems (Vicente *et al.,* 2004). It consists of mono-alkyl esters usually produced by transesterification with an alcohol (alcoholysis), of the triglycerides found in vegetable oils, animal fats or waste cooking oils (Arzamendi *et al.,* 2007; Marchetti *et al.,* 2007). These esters have significant potential as an alternative diesel fuel both in neat forms or blended with conventional diesel fuels (Xie and Li, 2006). Moreover, biodiesel have a number of advantages to the environment. Diesel engines operated on biodiesel have lower emission of carbon monoxide, unburned hydrocarbons, and air toxics, in particular $SO_2$, thus, avoiding the acid rain formation when petroleum-based diesel fuels are employed. Other advantages of biodiesel are its good lubricant properties that extend the engine life, its high cetane number, its high flash point and its acceptable cold filter plugging point.

### 2.1.1 Transesterification process

The transesterification of vegetable oils is a catalytic reaction involving triglycerides reacting with an alcohol, to produce esters and glycerol as shown in Figure 2.1. In this reaction, R is a mixture of various fatty acid chains. The alcohol commonly used for producing FAME is methanol (where R'corresponds to $CH_3$). The stoichiometry of reaction requires 3 mols of methanol and 1 mol of triglyceride to give 3 mols of fatty acid methyl ester and 1 mol of glycerol. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product (Marchetti *et al.,* 2007). These reactions can be catalyzed either by alkaline or acid catalysts or by lipases (Jackson *et al.,* 2006).

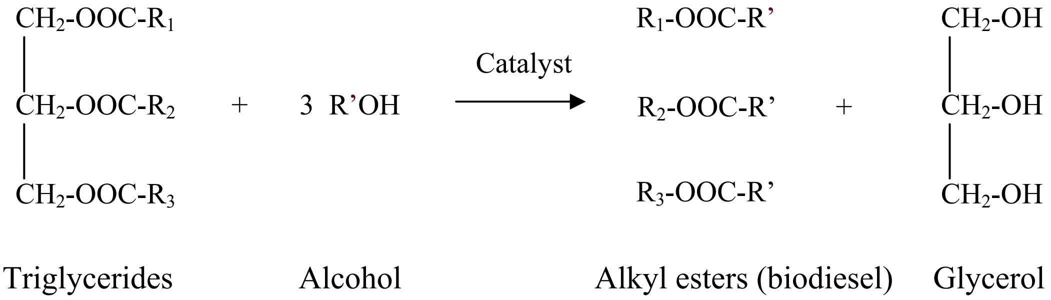

Figure 2.1: Transesterification reaction in the presence of a catalyst

The acid catalyzed process often uses sulfonic acid and hydrochloric acid as catalysts. However the reaction required very long reaction time (48-96 h) and a high molar ratio of methanol to oil even with reflux with ethanol. Besides, acid catalyzed methylation is energy-intensive because it is usually conducted at high temperature (Crabbe *et al.,* 2001). As the catalytic activity of a base is higher than that of an acid and acid catalysts are more corrosive, the base catalysis is preferred to acid catalyzed routes, and is thus most often used commercially (Xie *et al.*, 2007). The most commonly used alkali catalysts are sodium hydroxide (NaOH), potassium hydroxide (KOH) and their carbonates (Vicente *et al.,* 2004).

Enzymatic catalysts like lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems. In particular, the by-products i.e. glycerol can be easily removed without any complex process. In addition, free fatty acids contained in waste oils and fats can be completely converted to alkyl esters. On the other hand, the production cost of a lipase catalyst is significantly greater than that of an alkaline one (Meher *et al.,* 2004).

The transesterification process can be carried out even without catalyst but with considerable increase in temperature. Yield is very low at temperatures below 350 °C and therefore higher temperatures were required. However at temperatures greater than 400 °C thermal degradation of esters occurred. Recently it has been found that alcohols in their supercritical state produce better yield and researches have experimented this process with methanol in its supercritical state (Demirbas, 2006).

Of all the methods mentioned above for production of biodiesel, only alkali process is carried out in an industrial scale. Despite providing much faster reaction rates than heterogeneous catalyst, it is considerably costly to separate homogeneous catalysts from the reaction mixture (Kim *et al.,* 2004; Liu *et al.,* 2007b). Hence, the heterogeneous alkali catalyst will be well focused in this study.

### 2.1.2 Palm oil as biodiesel feedstock

The triglycerides used come from a variety of oils including rapeseed, soybean waste frying oil (Jackson *et al.,* 2006), sunflower, palm and peanut oil, as well as animal fat (Ma and Hanna, 1999). From a chemical point of view, oils from different sources have different fatty acid compositions. Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (Meher *et al.,* 2004). The typical fatty acid compositions and their chemical structure contained in the vegetable oils sources are summarized in Table 2.1 and Table 2.2 respectively. For palm oil, palmitic and oleic acid are the major constituents with amount exceeding 40 % followed by linoleic with 10 %.

Table 2.1: The typical composition of fatty acids in vegetables oil (Jackson *et al.,* 2006).

| Fatty acid | Soybean | Cottonseed | **Palm** | Lard | Tallow | Coconut |
|---|---|---|---|---|---|---|
| Lauric | 0.1 | 0.1 | **0.1** | 0.1 | 0.1 | 46.5 |
| Myristic | 0.1 | 0.7 | **1.0** | 1.4 | 2.8 | 19.2 |
| Palmitic | 10.2 | 20.1 | **42.8** | 23.6 | 23.3 | 9.8 |
| Stearic | 3.7 | 2.6 | **4.5** | 14.2 | 19.4 | 3.0 |
| Oleic | 22.8 | 19.2 | **40.5** | 44.2 | 42.4 | 6.9 |
| Linoleic | 53.7 | 55.2 | **10.1** | 10.7 | 2.9 | 2.2 |
| Linolenic | 8.6 | 0.6 | **0.2** | 0.4 | 0.9 | 0.0 |

Table 2.2: Chemical structure of common fatty acids and their methyl esters contains in all vegetables oil.

| Fatty acid | Structure | Common Acronym | Methyl Esters |
|---|---|---|---|
| Palmitic acid | $R\text{-}(CH_2)_{14}\text{-}CH_3$ | C16:0 | Methyl palmitate |
| Stearic Acid | $R\text{-}(CH_2)_{16}\text{-}CH_3$ | C18:0 | Methyl stearate |
| Oleic Acid | $R\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_3$ | C18:1 | Methyl Oleate |
| Linoleic acid | $R\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH_3$ | C18:2 | Methyl Linoleate |
| Linolenic acid | $R\text{-}(CH_2)_7\text{-}(CH{=}CH\text{-}CH_2)_3\text{-}CH_3$ | C18:3 | Methyl Linolenate |

Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains (Meher *et al.,* 2004). The effective area occupied by fatty acid molecules at solid liquid interfaces is the same as that occupied by these molecules in films on water. The area occupied by long chain fatty acid molecules increased from 0.192 to 0.702 $nm^2$ as the chain length increase irrespective of the adsorbent (Allen, 1997). Thus FAME refers to lower alkyl esters of long chain fatty acids which must diffuse well in the porous catalyst in transesterification process.

In addition, the various sources of vegetable oils will result in the different fuel properties. Although this diesel still can be used in conventional engine, it leads to a number of problems depending on the type and grade of oil and local climatic conditions. The high viscosity of vegetable oils interferes with the injection process and leads to poor fuel atomization. The inefficient mixing of oil with air contributes to incomplete combustion, leading to heavy smoke emission, and the high flash point attributes to lower volatility characteristics. These disadvantages, coupled with the reactivity of unsaturated vegetable oils, do not allow the engine to operate trouble free for longer period of time. These problems can be solved if the vegetable oils are chemically modified to biodiesel, which is similar characteristics with diesel (Barnwal and Sharma, 2005).

### 2.1.3 Waste cooking oil

The increasing production of waste cooking oils (WCOs) from household and industrial sources is a growing problem in all around the world. This residue is regularly poured down the drain, resulting problems for wastewater treatments plants and energy loss, or is integrated into the food chain through animal feeding, thus becoming a potential cause of human health problems (Felizardo *et al.*, 2006). The production of biodiesel from waste cooking oil is one of the better ways to utilize it efficiently and economically (Kulkarni and Dalai, 2006). Based on estimates from seven countries, a total of about 0.4 Mt is collected within the EU, mainly from the catering industry, while the amount that could be collected is estimated to be considerably higher, possibly from 0.7 to 1 Mt. Its price is variable, but in general is approximately half that of virgin oil (Gomez *et al*., 2002). Thus the used of waste cooking palm oil is expected to greatly reduce the cost of biodiesel (Kulkarni and Dalai, 2006).

However, the production of biodiesel from waste cooking oil is a challenging task due to the presence of undesirable components such as free fatty acids (FFAs) and water. The use of a homogeneous alkali catalyst for the transesterification of such feedstock suffers from serious limitation due to of the formation of undesirable side reaction such as saponification which creates the serious problem of product separation (Jacobson *et al*., 2008). However, the use of heterogeneous catalyst can overcome this problem. The heterogeneous catalyst creates no soap byproducts through the reaction with free fatty acid and is also easily separated from the reaction mixture (Guan *et al*., 2009).

Guan *et al*. (2009) investigated tri-potassium phosphate as a solid catalyst for the transesterification of waste cooking oil. They reported that transesterification of waste cooking oil was successfully carried out but it required approximately two times more solid catalyst than the transesterification of fresh oil. The fatty acid methyl ester yield reached was 93.7 % when the transesterification was performed with a catalyst concentration of 4 wt. % at 60 $^{o}$C for 120 min.

Thus, the biodiesel production from waste cooking oil will also be investigated using the most suitable mesoporous catalyst and the optimum conditions found in this study. Thus, the yield of biodiesel from refined and waste cooking oil will be compared to evaluate the effectiveness of the proposed mesoporous solid base catalyst.

### 2.1.4 Effect of operating variables.

#### 2.1.4(a) Effect of reaction temperature

Transesterification can occur at different temperatures, depending on the oil used. Temperature clearly influenced the reaction rate and yield of esters because the intrinsic rate constants are strong functions of temperature (Ma and Hanna, 1999; Meher *et al.,* 2004; Liu *et al.,* 2007b). The primary advantage of higher temperatures is a shorter reaction time. However, if the reaction temperature exceeds the boiling point of methanol, the methanol will vaporize and form a large number of bubbles, which will restrain the reaction on the three-phase interface.

Shu *et al*. (2007) studied the effect of reaction temperature in the range of 45 to 70 $^{o}$C. The highest conversion of triglyceride obtained was 38.9 % at 60 $^{o}$C. The obtained results showed that the higher temperatures resulted in higher reaction rate to produce more fatty acid methyl esters (FAME). However, it also formed more glycerol byproduct to enhance the solubility of glycerol in the fatty phase, and intensify the glycerolysis of FAME. They also found that the mass transfer between the two liquid phases was the rate determining step, and the temperature had small effect on it. Liu *et al*. (2007b) studied the reaction temperature from 40-65 $^{o}$C and found that the reaction rate was slow at low temperatures. The optimum reaction temperature is generally reached at 65 °C.

### 2.1.4(b) Effect of methanol to oil ratio

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. Higher molar ratios result in higher ester conversion in a shorter time (Ma and Hanna, 1999). Stoichiometrically, the ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, other reports have shown that at this stoichiometry, the reaction rate is slow and rarely proceeds to completion necessitating the use of excess methanol (Crabbe *et al.,* 2001). In practice, a higher molar ratio is employed in order to drive the forward reaction towards completion and produce more methyl esters as products (Meher *et al.,* 2004). Xie and Li (2006) found that the conversion to FAME from soybean oil increased with the increasing molar ratio of methanol to oil and achieved the optimum at 15:1. However, Kim *et al*. (2004) found that the optimum molar ratio of methanol to oil was 9:1, and beyond that the excessive added methanol had no significant effect on the production yield. They concluded that to elevate the biodiesel yield, an excess methanol feed was effective to a certain extent.

A study by Yang and Xie (2007) revealed that due to the presence of heterogeneous solid catalysts, the reaction mixture initially constitutes a three-phase system, oil-ethanol-catalyst, which for diffusion reasons inhibits the reaction. When the mass transfer is limited, the rate of mass transfer seems to be much slower than the reaction rate. Therefore, the usage of excess methanol is one of the better options for improving the rate of reaction. They found that the maximum conversion of about 95 % was obtained when the molar ratio was very close to 12:1 from a study range of 6:1-18:1.

Noiroj *et al*. (2008) come out with the investigation of the molar ratio of methanol to oil varied in a range between 6:1 and 21:1. The obtained results showed that when the molar ratio of methanol to oil increased, the biodiesel yield also increased and the highest yield (91.1 %) was obtained at a methanol to oil molar ratio of 15:1. It has been reported that when the amount of methanol was over 15:1, glycerol separation became difficult, resulting in a decrease of biodiesel yield.

Since methanol to oil ratio has a significant impact on the FAME production and glycerol produce depending the oil and catalyst used, this effect will be further investigated in this study.

#### 2.1.4(c) Effect of catalyst loading

Yang and Xie (2007) studied the effect of catalyst loading on the conversion of soybean oil in the range of 1.0-9.0 % with reference to the starting oil weight. They found that when the amount of catalyst was increased from 1.0-4.0 %, the conversion to methyl esters showed a gradual increase. The maximum value of 94.7 % of biodiesel yield was achieved at 5 % of catalyst loading. Xie and Li (2006) reported that the transesterification reaction was strongly dependent upon the catalyst used. Without the addition of a catalyst, transesterification did not occur, while the presence of the supported catalyst significantly increased the reaction rate. High conversion of biodiesel was obtained at 2.5 % of catalyst loading.

Results by Liu *et al*. (2007b) indicate that with more catalyst addition, reaction rate become faster and reached equilibrium at 4.0 % of catalyst amount because of the increase in the total number of available active catalytic sites for the reaction. Xie *et al*. (2007) varied the catalyst amount in the range of between 1.0-6.0 % with reference to the starting oil weight. Kim *et al*. (2004) revealed that with increasing catalyst loading, the slurry (mixture of catalyst and reactants) became more viscous. This gave rise to a problem of mixing and a demand of higher power consumption for adequate stirring. From the reported literature, the optimum catalyst loading is defined as the loading that will give high FAME yield and does not contribute to the mixing problem in the reaction mixture at the same time. Thus, the optimum loading will be further investigated in this study as well.

#### 2.1.4(d) Effect of reaction time

The result from a study by Xie and Li (2006) revealed the dependence of the conversion to methyl esters in the range of 1-10 h of the reaction time. Their results showed that the conversion increased steadily in the reaction time range between 4-8 h, and thereafter, remained nearly constant as a result of a nearly equilibrium conversion. The maximum conversion of soybean oil was achieved after 8 h. A similar behaviour was reported by Yang and Xie (2007). The optimum reaction time for the production of biodiesel was determined by performing reaction at varying reaction times (1-6 h). The experimental results indicated that the conversion increased steadily in the reaction time range between 1-4 h, and thereafter, remained almost constant as a result of a nearly equilibrium conversion. Thus, the maximum conversion of soybean oil was achieved after 4 h of the reaction time. Noiroj *et al*. (2008) studied the effect of reaction time to the yield of biodiesel in a range of 1-6 h.