

**PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING  
SULFATED TIN OXIDE CATALYST**

**by**

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## LIST OF ABBREVIATIONS

AG	Acyglycerols
Al	Aluminium
Al <sub>2</sub> O <sub>3</sub>	Alumina oxide
Ar	Argon
BET	Brunauer-Emmett-Teller
CaCO <sub>3</sub>	Pulverized limestone
CaO	Calcium oxide
CO	Carbon oxide
CO <sub>2</sub>	Carbon dioxide
EU	European Union
FAEE	Fatty acid ethyl esters
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FID	Flame ionization detector
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
HCl	Hydrochloric acid
He	Helium
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
HSO <sub>3</sub> Cl	Chlorosulfonic acid
ICDD	International Center of Diffraction Data
IEA	International Energy Agency
KBr	Potassium bromide
KI	Potassium iodide
KOH	Potassium hydroxide
LCA	Life cycle assessment
Mg-Al	Magnesium-alumina
Mg <sub>6</sub> Al <sub>2</sub> (OH) <sub>16</sub> CO <sub>3</sub> 4H <sub>2</sub> O	Hydrotalcites
MgO	Magnesium oxide
NaOH	Sodium hydroxide
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Sodium thiosulphate
NH <sub>3</sub>	Ammonia
NH <sub>3</sub> -TPD	Nitrogen Adsorption-Desorption
PID	Proportional-Integral-Derivative
R <sup>•</sup>	Radicals- alkyl radicals
RH	Triacylglycerol
RO <sup>•</sup>	Alkoxy radicals
ROO <sup>•</sup>	Alkylperoxy radicals
ROOH	Hydroperoxides
SEM	Scanning Electron Microscopy
Si	Silicon
SiO <sub>2</sub>	Silicon dioxide
SnO <sub>2</sub>	Tin oxide
SnO.H <sub>2</sub> O	Meta-stannic acid
SO <sub>4</sub> <sup>2-</sup>	Sulfate group
SrO	Strontium oxide
SZA	Sulfated zirconia-alumina

THF	Tetrahydrofuran
TiO <sub>2</sub>	Titanium dioxide
WO <sub>3</sub>	Tungsten oxide
WZA	Tungstated zirconia-alumina
XRD	X-ray Diffraction
ZrO <sub>2</sub>	Zirconia oxide

## LIST OF SYMBOLS

$\alpha$	Reaction order with respect to reactant A
$\beta$	Reaction order with respect to reactant B
$\theta_B$	Ratio of $C_{BO}$ to $C_{AO}$
A	Frequency factor
$C_A$	Concentration of reactant A after time t ( $\text{mol}/\text{dm}^3$ )
$C_{AO}$	Initial concentration of reactant A ( $\text{mol}/\text{dm}^3$ )
$C_B$	Concentration of reactant B after time t ( $\text{mol}/\text{dm}^3$ )
$C_{BO}$	Initial concentration of reactant B ( $\text{mol}/\text{dm}^3$ )
$C_{IS}$	Concentration of IS (g/L)
DF	Dilution factor
$E_A$	Activation energy (J/mol)
k	Reaction rate constant
M	Molar ( $\text{mol}/\text{dm}^3$ )
$r_A$	Rate of reaction ( $\text{mol}/\text{dm}^3 \cdot \text{s}$ )
R	Gas constant (J/mol.K)
$R_f$	Ratio of peak area of individual methyl ester to peak area of IS in standard reference.
$R_s$	Ratio of peak area of individual methyl ester to peak area of internal standard (IS) in the sample.
T	Reaction temperature (K)
V	Volume of oil (mL)
x	Conversion



**PENGHASILAN BIODIESEL DARIPADA MINYAK MASAK SISA  
MENGUNAKAN MANGKIN TIMAH OKSIDA TERSULFAT**

**ABSTRAK**

Biodiesel adalah sejenis bahan api yang boleh diperbaharui, biodegradasi, tidak bertoksik dan boleh dihasilkan dengan mudah menerusi tindak balas transesterifikasi. Namun, penggunaan minyak masak sayuran tulen sebagai stok suapan biodiesel adalah tidak praktikal dan ekonomikal kerana harganya yang tinggi dan keutamaan sebagai sumber makanan. Minyak masak gred rendah, lazimnya minyak masak terpakai boleh dijadikan satu alternatif yang lebih baik; walaubagaimanapun, kandungan asid-asid lemak terbebas yang tinggi dalam minyak masak terpakai menyebabkan penghasilan biodiesel tidak efektif sekiranya dihasilkan melalui proses transesterifikasi homogen yang kini diaplikasikan dalam industri biodiesel. Oleh itu, dalam kajian semasa ini, mangkin oksida timah tersulfat,  $\text{SO}_4^{2-}/\text{SnO}_2$  telah disediakan melalui kaedah impregnasi untuk penghasilan biodiesel menerusi proses transesterifikasi heterogen. Kesan mangkin dwilogam juga dikaji, di mana  $\text{SnO}_2$  diadunkan dengan  $\text{SiO}_2$  atau  $\text{Al}_2\text{O}_3$ , masing-masing mengikut nisbah berat yang berbeza dengan tujuan untuk meningkatkan aktiviti mangkin  $\text{SnO}_2$ . Kesan parameter tindak balas seperti suhu dan tempoh pengkalsinan mangkin, suhu tindak balas, muatan mangkin, nisbah metanol kepada minyak dan masa tindak balas turut dikaji untuk mengoptimumkan keadaan tindak balas. Didapati bahawa  $\text{SO}_4^{2-}/\text{SnO}_2$ - $\text{SiO}_2$  (3) menunjukkan aktiviti mangkin yang tinggi dengan hasil optimum 92.3 %

pada suhu tindak balas 150°C, muatan mangkin 3 % berat (merujuk kepada keberatan minyak), nisbah metanol kepada minyak adalah 15 dan masa tindak balas 3 jam. Sifat-sifat fizikal dan kima mangkin juga ditentukan menggunakan analisis XRD, NH<sub>3</sub>-TPD, denyutan penjerapan kimia, pengimejan FT-IR dan SEM. Dalam kajian penyahaktifan dan penjanaan semula mangkin, didapati bahawa mangkin dinyahaktifkan disebabkan pengumpulan spesies karbon yang tinggi pada permukaan mangkin. Tambahan pula, spesies berkarbon itu didapati tidak dapat disingkirkan dengan sepenuhnya walaupun langkah penjanaan semula dilakukan. Selain itu, model kinetik transesterifikasi menggunakan pengubahsuaian mangkin SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> telah berjaya dilakukan, di mana keseluruhan tertib tindak balas ialah tiga, tertib kedua terhadap kepekatan trigliserida dan tertib satu terhadap kepekatan metanol. Lebih-lebih lagi, didapati bahawa tenaga pengaktifan yang diperolehi dalam kajian ini adalah setanding dengan tenaga pengaktifan yang diperolehi daripada tindak balas menggunakan mangkin homogen.

# **PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING SULFATED TIN OXIDE CATALYST**

## **ABSTRACT**

Biodiesel is a renewable, biodegradable and non-toxic fuel which can be easily produced through transesterification reaction. However, current commercial usage of refined vegetable oils for biodiesel production is impractical and uneconomical due to high feedstock cost and priority as food resources. Low-grade oil, typically waste cooking oil can be a better alternative; however, the high free fatty acids (FFA) content in waste cooking oil does not allow efficient production of biodiesel via current commercial homogeneous transesterification process. Therefore, in the present study, superacid sulfated tin oxide catalyst,  $\text{SO}_4^{2-}/\text{SnO}_2$  has been prepared using impregnation method for biodiesel production via heterogeneous transesterification process. The bimetallic effect of the catalyst was also studied, in which  $\text{SnO}_2$  was mixed with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , respectively at different weight ratio in order to enhance the catalytic activity of  $\text{SnO}_2$ . The effect of different reaction parameters such as calcination temperature and period of the catalyst, reaction temperature, catalyst loading, methanol to oil ratio and reaction time were studied to optimize the reaction conditions. It was found that  $\text{SO}_4^{2-}/\text{SnO}_2\text{-SiO}_2$  with weight ratio of 3 exhibited an exceptional high activity with an optimum yield of 92.3% at reaction temperature of 150°C, catalyst loading of 3 wt % (referred to weight of oil), methanol to oil molar ratio of 15 and reaction time of 3 hours. The physical and chemical properties of the catalysts were also characterized using XRD analysis,

NH<sub>3</sub>-TPD, Pulse Chemisorptions, FT-IR and SEM imaging. On deactivation and regeneration study, the catalysts were found to deactivate after the first reaction cycle due to high accumulation of carbonaceous species on the catalyst surface. In addition, the carbonaceous species were not removed completely even after the regeneration step. Apart from that, a kinetic model has been developed and the overall order of the transesterification reaction catalyzed by modified SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> was found to be third order in which second order for triglyceride and first order for methanol. Furthermore, the activation energy obtained in the present work was comparable to reaction catalyzed by homogeneous base catalyst. This study therefore demonstrates that waste cooking oil can be a potential source of biodiesel via heterogeneous catalyst using modified SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>.

## **CHAPTER ONE: INTRODUCTION**

The world is currently facing the worst energy crisis in its entire history. Many countries in the world are still heavily dependent on crude petroleum as the source of electricity and transportation fuels and its price has been hitting record height every other day. Thus, the only possible solution to this crisis is to find a sustainable (renewable) and economically feasible source of alternative energies. There are many alternative energies that may fulfill the first criteria (sustainable) such as wind, solar, geothermal and biomass. However, not many of them can fulfill the second criteria (economically feasible). The best option that would fulfill both criteria is biofuel, particularly from readily available biomass feedstock such as sugarcane, corn, seed oil from soybean, rapeseed and palm. It has been proven scientifically that sugarcane and corn can be converted to bioethanol while the various oilseeds to biodiesel, efficiently. Apart from that, utilization of biofuels contributes to net zero carbon emission which subsequently would mitigate the effect of global warming and overcome the dwindling reserves of fossil fuel.

### **1.1 Current status of crude oil reserves and the potential of biodiesel**

To date, fossil fuels account over 82 % of the primary energy consumed in the world, and 60 % of that amount is used in transportation sector (International Energy Agency, 2008). On the other hand, global consumption of diesel fuel is estimated to be 934 million tonnes per year (Kulkarni and Dalai, 2006). Thus, there is no doubt that fossil oil will be exhausted in less than 10 decades as predicted by The World Energy Forum if no new oil well is found (Sharma and Singh, 2009). The main reason that caused the fast diminishing of energy resources is due to rapid

population and industrialization growth globally. Due to this phenomenon, the era of cheap crude oil is no longer exists leading to high rocketing price of petroleum, bellicose conflicts and increasing number of undernourished people especially from undeveloped countries. **Figure 1.1** presents the projection of world energy demand in the near future indicating that there is an urgent need to find more new renewable energies towards assuring energy security worldwide (Exxon Mobil, 2004).

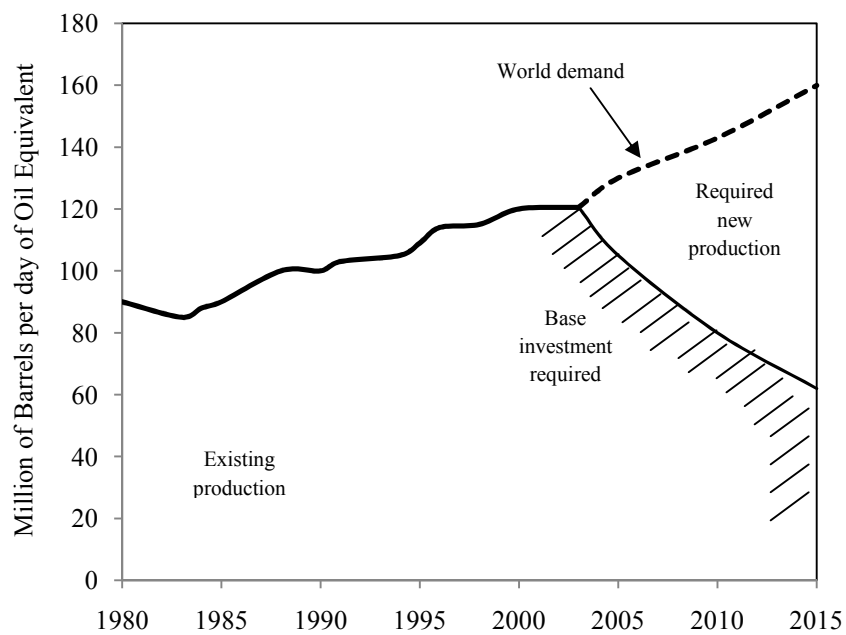


Figure 1.1: Projection of energy demand for the near future (Exxon Mobil, 2004).

Renewable energy has been highlighted in the last ten years due to its potential to replace fossil fuel especially for transportation. Renewable energy sources such as solar energy, wind energy, hydro energy, and energy from biomass and waste have been successfully developed and used by different nations to limit the use of fossil fuels. Nevertheless, based on recent study from International Energy Agency (IEA) (International Energy Agency, 2008), only energy produced from renewable sources and waste has the highest potential among other renewable

resources as shown in **Figure 1.2**. Combustible renewable and waste accounted for 10.1 %, compared to hydro energy 2.2 % and other 0.6 % (included geothermal, solar wind and heat) (International Energy Agency, 2008). Hence, it is predicted that renewable energy from combustible energies such as biodiesel will enter the energy market intensively in the near future to diversify the basket of global energy sources.

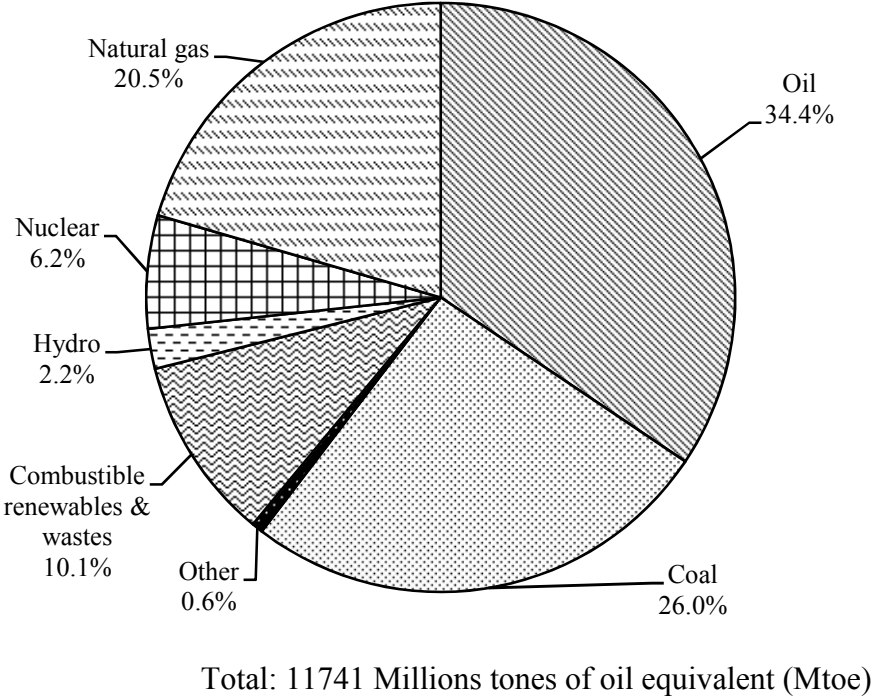


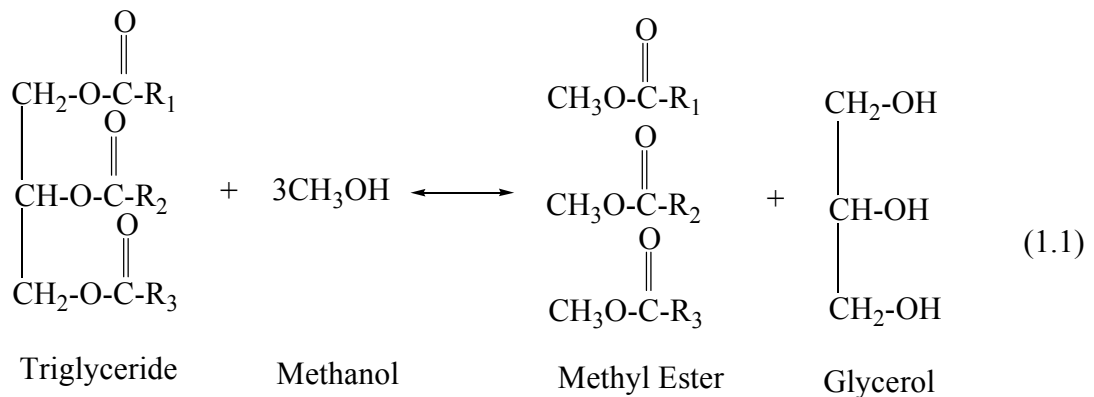
Figure 1.2: World total energy supply by fuel (Mtoe) in year 2006 (International Energy Agency, 2008).

**1.2 Biodiesel**

Biodiesel is an alternative diesel fuel derived from vegetable oils or animal fats (Vasudevan and Briggs, 2008). The main components of vegetable oils and animal fats are triglycerides or also known as esters of fatty acids attached to a glycerol. Normally, triglycerides of vegetable oils and animals fats consist of several different fatty acids. Different fatty acids have different physical and chemical

properties; the composition of fatty acids will be the most important parameters influencing the corresponding properties of a vegetable oils and animal fats (Gerhard Knothe, 2004).

Direct use of vegetable oils and animal fats as combustible fuel is not suitable due to their high kinematic viscosity and low volatility. Further more, its long term use posed serious problems such as deposition, ring sticking and injector chocking in engine (Muniyappa *et al.*, 1996). Therefore, vegetable oils and animal fats must be subjected to chemical reaction such as transesterification to reduce the viscosity of oils. In a transesterification reaction, triglycerides are converted into fatty acid methyl ester (FAME), in the presence of short chain alcohol, such as methanol or ethanol, and a catalyst, such as alkali or acid, with glycerol as a by-product (Vasudevan and Briggs, 2008). **Equation 1.1** depicts the transesterification reaction (Ma and Hanna, 1999). Another alternative way to produce biodiesel is through thermal process or pyrolysis. However, this process is rather complicated to operate and produce side products such as carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) that have no commercial value (Sharma and Singh, 2009).





### **1.2.1 Composition of vegetable oils and fats**

Vegetable oils and animal fats usually have hydrophobic properties, which mean they are insoluble in water. As mentioned earlier, triglycerides are made up of one mole glycerol and three moles fatty acids. Fatty acids vary in terms of carbon chain length and number of unsaturated bonds (double bonds). Typical fatty acid compositions found in several vegetable oils are summarized in **Table 1.1** (Ma and Hanna, 1999). Fatty acids that have no double bonds are termed "saturated" such as Stearic acid. These chains contain maximum number of possible hydrogen atoms per carbon atom. Fatty acids that have double bonds are termed "unsaturated" such as Linoleic acid. These chains do not contain maximum number of hydrogen atoms due to the presence of double bond(s) on some carbon atoms. Normally, natural vegetable oils and animal fats are obtained in the crude form through solvent extraction or mechanical pressing, containing a lot of impurities such as free fatty acids, sterols and water (Di Serio *et al.*, 2006). In fact, these free fatty acids and water content will have significant effect on the transesterification reaction, especially if an alkaline catalyst is used (Lotero *et al.*, 2005). They could also interfere with the separation of FAME and glycerol during water washing (purification step) because of soap formation (Kulkarni and Dalai, 2006).

### **1.2.2 Composition of biodiesel**

Biodiesel is a mixture of fatty acid alkyl esters. In the case when methanol is used as reactant, it will be a mixture of fatty acid methyl esters (FAME) whereas if ethanol is used as reactant, the mixture will be fatty acid ethyl esters (FAEE). However, methanol is commonly and widely used in biodiesel production due to their low cost and availability. Based on different feedstock, biodiesel will have

different composition of FAME. **Table 1.2** shows the common composition of FAME in biodiesel (Ma and Hanna, 1999).

Table 1.1: Typical fatty acid composition for different common oil source  
(Ma and Hanna, 1999).

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric (C12:0)	0.1	0.1	0.1	0.1	0.1	46.5
Myristic (C14:0)	0.1	0.7	1.0	1.4	0.8	19.2
Palmitic (C16:0)	0.2	20.1	42.8	23.6	23.3	9.8
Stearic (C18:0)	3.7	2.6	4.5	14.2	19.4	3.0
Oleic (C18:1)	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic (C18:2)	53.7	55.2	10.1	10.7	10.7	2.2
Linolenic (C18:3)	8.6	0.6	0.2	0.4	0.4	0.0

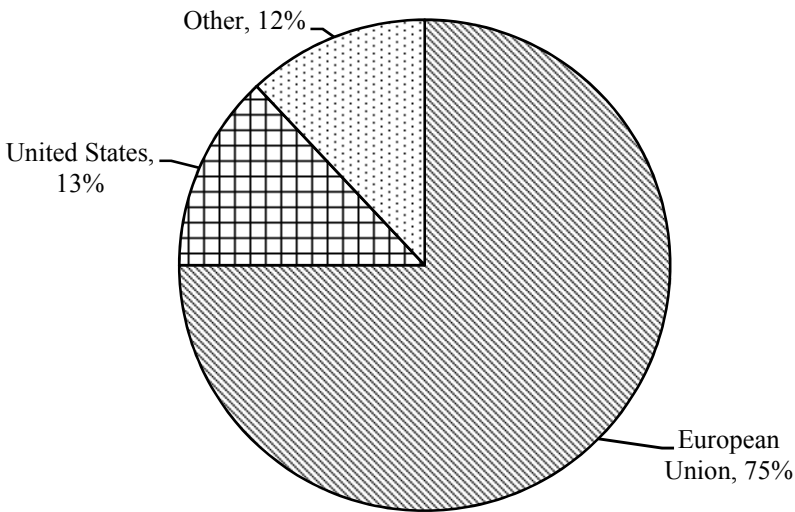
Table 1.2: Chemical structures of common FAME (Ma and Hanna, 1999).

Methyl Ester	Formula	Common acronym	Molecular weight
Methy Palmitic	$C_{17}H_{34}O_2$	C16:0	270.46
Methy Stearate	$C_{19}H_{38}O_2$	C18:0	298.51
Methy Oleate	$C_{19}H_{36}O_2$	C18:1	296.50
Methy Linoleate	$C_{19}H_{34}O_2$	C18:2	294.48
Methy Linolenate	$C_{19}H_{32}O_2$	C18:3	292.46

### 1.3 Current status of biodiesel production

With uncertainty in the crude fossil fuel price and near all-time high, biodiesel has emerged as the fastest growing industries worldwide. Several countries

especially United State and members of European Union are actively supporting the production of biodiesel from the agriculture sector. In year 2006, nearly 6.5 billion liters of biodiesel was produced as shown in **Figure 1.3** (TBW, 2008). Based on this figure, European countries contributed the most which covered 75 % of the total biodiesel production. This is due to substantial support from government such as consumption incentives (fuel tax reduction) and production incentive (tax incentives and loan guarantees) that has and will further catalyzed the global market of biodiesel to grow explosively in the next ten years. For example, United States spent around US\$ 5.5 billion to 7.3 billion a year (TBW, 2008) to accelerate biofuels production. As a result, around 450 million gallons of biodiesel was produced in United States in the year 2007 compared to only 25 million gallons in year 2004 (Multi-Client, 2008). Thus, the 1700 % increment was indeed a shocking increase in the entire history of biodiesel production.



Total production: 6.5 billion liters

Figure 1.3: Biodiesel production in year 2006 (TBW, 2008).

However, by the year 2020, it is predicted that biodiesel production from Brazil, China, India and some Asian countries such as Malaysia and Indonesia could contribute as much as 20 % (Multi-Client, 2008). In Malaysian alone, total biodiesel production capacity was accounted to 10.5 million tonnes annually in the year 2008 (Lam *et al.*, 2009). The driving forces for development of biodiesel in these countries are economic, energy and environmental security, improving trade balances and expansion of agriculture sector (Zhou and Thomson, 2009). In addition, Brazil, China and India each have targets to replace 5 % to 20 % of total diesel with biodiesel (Multi-Client, 2008). If governments from these countries continue to aggressively promote biodiesel generation and continue to invest in research and development for non-edible feedstocks such as jatropha, castor, algae and grease, the prospects to achieve biodiesel targets will be realized faster than anticipated. **Figure 1.4** depicts a more recent world biodiesel production and capacity in the recent years (Multi-Client, 2008). However, total biodiesel production was lower than its actual plant capacity. It is strongly believe that high cost of vegetable oils in the global market is the main cause to this scenario.

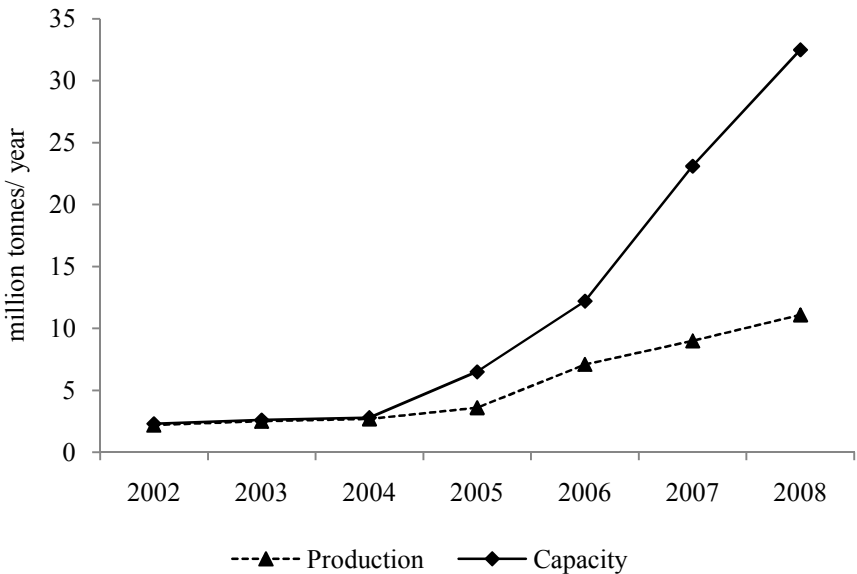


Figure 1.4: World biodiesel production and capacity (Multi-Client, 2008).

#### 1.4 Biodiesel and the environment

Generally, biodiesel is classified as an environment friendly combustible fuel. It is biodegradable and non toxic since it is produced from renewable sources such as vegetable oils and animal fats. In addition, it does not cause significant amount of sulfur-containing emissions upon combustion (Gerhard Knothe, 2004). Apart from that, emission of CO<sub>2</sub> during combustion is sequestered from the atmosphere during cultivation of the plants, resulting in a closed carbon cycle (Escobar *et al.*, 2009).

Recently, a useful tool to clearly describe the environmental impact of biodiesel utilization has been reported using Life Cycle Assessment (LCA). LCA is an internationally accepted method to determine the environment consequences over the entire period of a particular product, eg. biodiesel production. This systematic approach will eventually reveal the true potential of the product by evaluating and identifying the environmental hot spots in the product chains so that precaution steps can be suggested to reduce the negative environmental impact. Based on a LCA study for several oil crops as biodiesel feedstock reported by Quirin *et al.*, a few important findings were made (Quirin *et al.*, 2004). A summary of the LCA result is shown in **Figure 1.5** and **Figure 1.6**. It was reported that all types of biodiesel posed positive energy balance and significantly reduced green house gases emission if compared to fossil derived diesel. The positive effect was most significant for sunflower and rapeseed, followed by canola and coconut, whereas soybean was at the lower end. Nevertheless, the study only included mostly oil crops planted in temperate countries. For other countries with climate condition permitting the plantation of several other oil crops, they must also be considered as they could give better positive results (Gerhard Knothe, 2004).

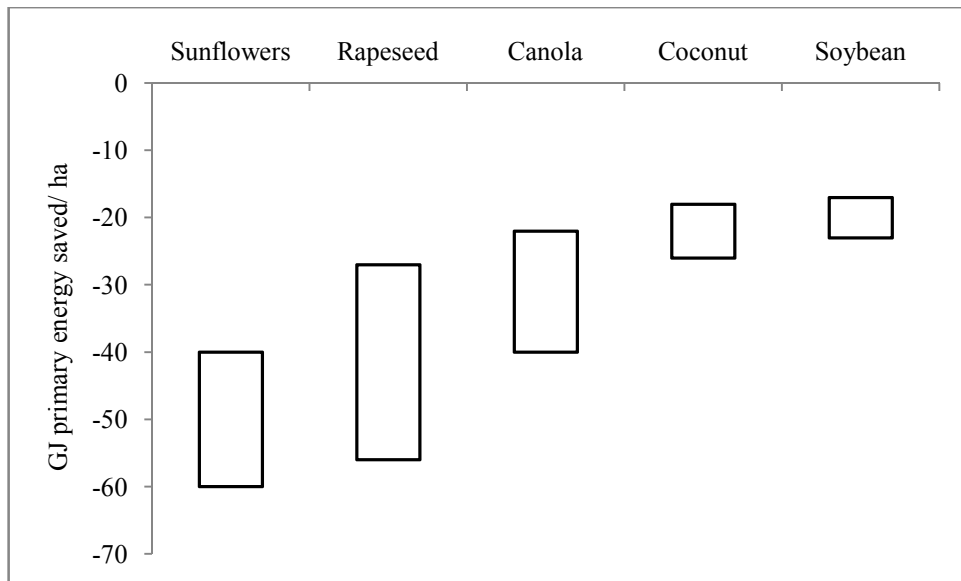


Figure 1.5: Energy saved for biodiesel from different vegetable oil compared with conventional diesel fuel. The negative value indicates the advantages for biodiesel (Quirin *et al.*, 2004).

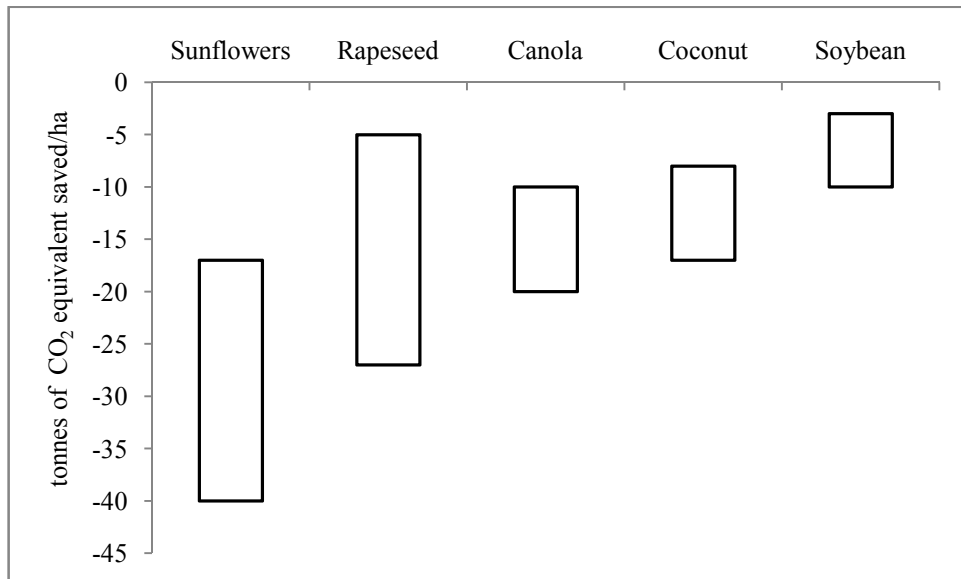


Figure 1.6: CO<sub>2</sub> equivalent saved for biodiesel from different vegetable oil compared with conventional diesel fuel. The negative value indicates the advantages for biodiesel (Quirin *et al.*, 2004).

## 1.5 Cost and potential of waste cooking oil as feedstock

Currently, the major concern of biodiesel production is the economic feasibility issue. In a reality scenario, biodiesel production will not be favored without tax exemption and subsidy from government; as the production cost is higher than fossil derived diesel. The overall biodiesel cost consists of raw material (production and processing), catalyst, biodiesel processing (energy, consumables and labour), transportation (raw materials and final products) and local and national taxes (Haas *et al.*, 2006). To date, most biodiesel plants are using refined vegetable oils as their main feedstock to avoid any undesirable product (soap) produced and to meet the international standard of biodiesel (ASTM D 6751 or EN 14214). In fact, the cost of refined vegetable oils contribute nearly 80 % of the overall biodiesel production cost (Lam *et al.*, 2009). Thus, it is undeniable that feedstock will be the most crucial variable affecting the price of biodiesel in the global market.

A generic process model to estimate biodiesel capital and operating cost had been developed by Haas *et al.* and is shown in **Figure 1.7** (Haas *et al.*, 2006). The model was designed on the basis of continuous transesterification process using crude, degummed soybean oil as the main feedstock and is dependent on the price of feedstock. In addition, the model was based on a processing plant with an annual production capacity 378,541,181 liter ( $10 \times 10^6$  gallon). However, some economic factors were excluded, such as internal rate of return, economic life span, corporate tax rate, salvage value, debt fracture, construction interest rate and long term interest rate, working capital, environment control equipment, marketing and distribution expenses, the cost of capital, and the existence of governmental credits or subsidies. Based on **Figure 1.7**, when the feedstock cost is at US\$ 0.52/kg (US\$ 0.236/lb)

(ideal cost of feedstock), the model estimated a final biodiesel production cost of US\$ 0.53/L (\$ 2.00/gal). From the study, the cost of feedstock contributed the most, which accounted 88 % of the total production cost. In addition, the model also estimated the economic potential from the recovery of co-product, glycerol as illustrated in **Figure 1.8**. Assuming that glycerol is sold as low commercial grade glycerol with purity 80 % w/w aqueous solution, the price is \$0.33/kg. It can be noted that returns from selling glycerol was not significant, only accounted to 6 % reduction in the overall biodiesel production cost.

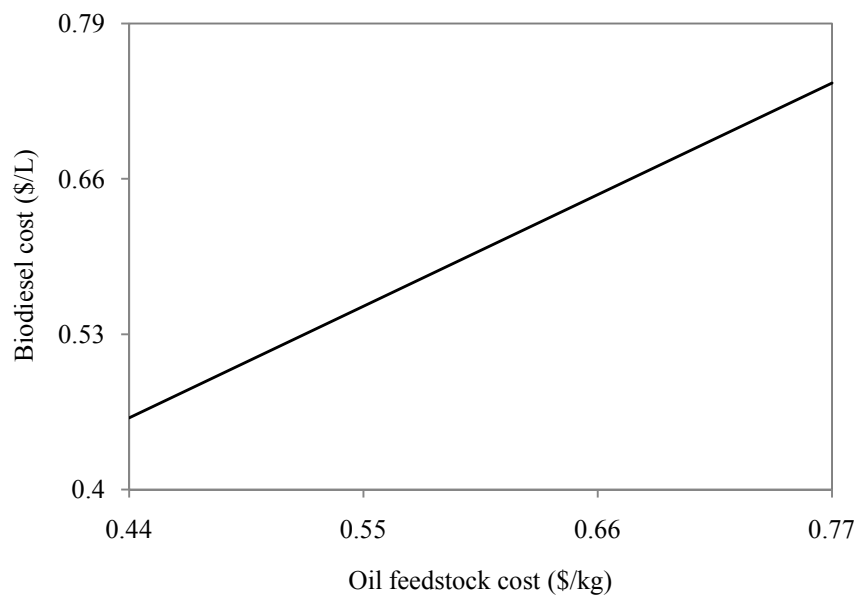


Figure 1.7: Impact of feedstock prices on the predicted unit cost of biodiesel production from crude degummed soybean oil with crude glycerol coproduct assigned a value of \$0.33/kg (\$0.15/lb) (Haas *et al.*, 2006).



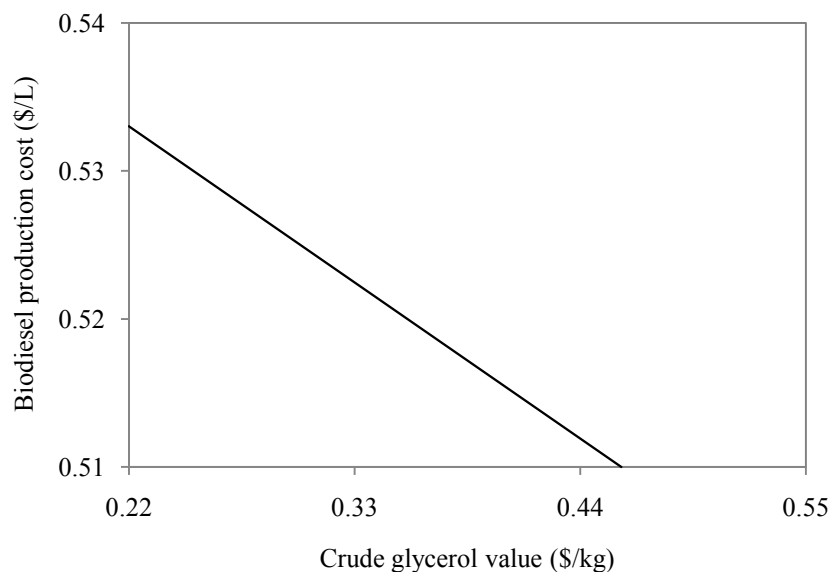


Figure 1.8: Impact of crude glycerol market value on the unit cost of biodiesel production with soy oil feedstock assigned a value of \$0.520/kg \$0.236/lb (Haas *et al.*, 2006).

In order to overcome this limitation and to ensure economic viability in biodiesel production, biodiesel manufacturers are focusing their attention on using cheap feedstock such as waste cooking oil in order to ensure economic viability in biodiesel production. Waste cooking oil is far less expensive than refined vegetable oils and therefore has become a promising alternative feedstock to produce biodiesel. In fact, generation of waste cooking oil in any country in the world is huge, and may result to environmental contamination if no proper disposal method is implemented. **Table 1.3** shows the estimated waste cooking oil produced in some selected countries including Malaysia (Gui *et al.*, 2008). Based on the table, the total amount of waste cooking generated is more than 15 million tonnes. However, it should be noted that the actual amount of waste oil produced is much higher than that amount based on global production. If such amount of waste oil is successfully collected and converted to biodiesel, it will be sufficient to meet the European biodiesel production target at 10 million tonnes in year 2010 (Lam *et al.*, 2009).

Table 1.3: Quantity of waste cooking oil produced in selected countries (Gui *et al.*, 2008).

Country	Quantity (million tonnes/ year)
United States	10.0
China	4.5
Japan	0.45-0.57
Malaysia	0.5
Canada	0.12
Taiwan	0.07

Apart from that, a recent study on the production cost of biodiesel using waste cooking oil as feedstock shows that the overall production costs of biodiesel can be reduced by more than half compared to virgin vegetable oil (Escobar *et al.*, 2009). This was then resulted in production cost were even lower than fossil derived diesel as illustrated in **Figure 1.9**. Hence, the high cost of feedstock can be overcome if waste cooking oil is used for biodiesel production.

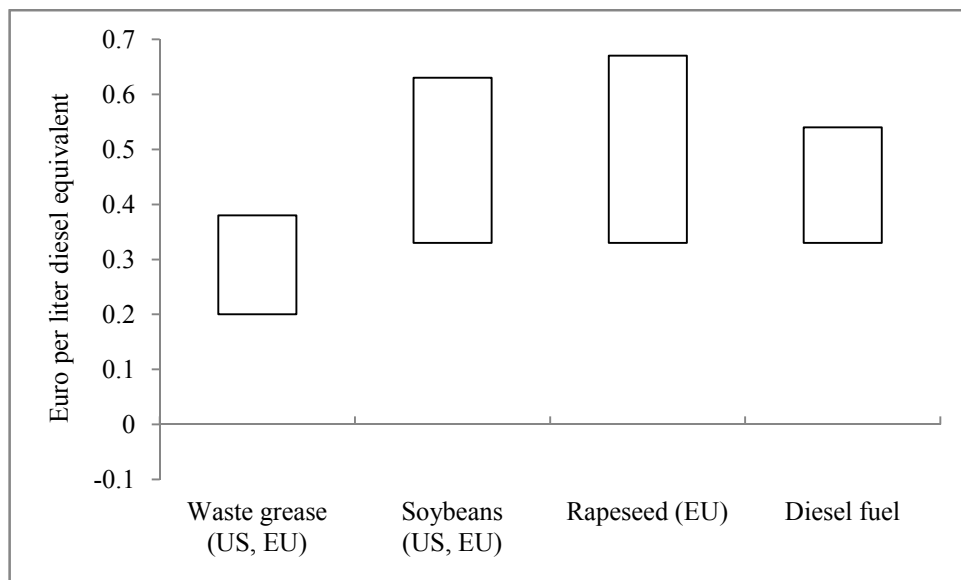


Figure 1.9: Range of production cost for biodiesel and diesel in year 2006 (Escobar *et al.*, 2009).

## **1.6 Objectives**

1. To synthesize and modify SnO<sub>2</sub> as solid acid catalyst.
2. To characterize the synthesized and modified SnO<sub>2</sub> catalyst.
3. To use the modified SnO<sub>2</sub> catalyst in transesterification of waste cooking oil and to optimize the process.
4. To study the catalyst deactivation and regeneration.
4. To develop a kinetic model for the heterogeneous catalyzed transesterification reaction catalyzed by modified SnO<sub>2</sub>.

## **1.7 Organization of Thesis**

This thesis consists of five chapters. Chapter one gives an outline of the overall research project covering introduction on biodiesel, current status of biodiesel production and potential of waste cooking oil as an alternative feedstock. Problem statement was then written after reviewing the scenario for the biodiesel market. The problem statement therefore reveals current problem faced by the biodiesel industry and the need of this research project. The objectives of this research project were then carefully devised with the aim to solve the problems faced by the biodiesel industry. Finally, the organization of thesis highlights the content of each chapter.

Chapter two gives an overall review of various research works reported in the literature in this area of research. The various research works include report on the properties of waste cooking oil and reactions occurring during frying process, homogeneous and heterogeneous catalysis in transesterification, reviews on some potential solid acid catalysts in biodiesel production and lastly reaction kinetic modeling. From the review, sulfated tin oxide (SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>) was determined as an

potential alternative solid acid catalyst especially in transesterification of high free fatty acid (FFA) oil, due to the presence of strong acid strength on the surface of the catalyst. However, only a handful study reported on the technical information of this catalyst and its application in transesterification is still limited.

In Chapter three, experimental materials and methodology were discussed. This chapter described detail information on the overall flow of this research work and also several experimental methods in conducting this research project. Besides, detail of the materials and chemicals used in this study were also reported. This chapter also consists of information that is required for the calculation of yield and data analysis. Apart from that, kinetic modelling of transesterification catalyzed by heterogeneous catalyst is proposed at the last part of this chapter.

Chapter four is the most important chapter in the thesis. It encompasses detail discussion on the results obtained in the present research work. This chapter consists of five sections which have been divided according to the stages of this research work. The first section of this chapter presents the characterization of raw materials that was carried out before any further experimental work. This was then followed by process optimization on the transesterification of waste cooking oil. The parameters studied were calcination temperature, calcination period and bi-metallic effect of the catalyst, reaction temperature, methanol to oil molar ratio, catalyst loading and reaction time. Section three reports the characterization of catalyst, such as X-ray Diffraction (XRD), Fourier Transform Infrared (FT-IR), Scanning Electron Microscopy (SEM), Nitrogen Adsorption-Desorption ( $\text{NH}_3$ -TPD) and Brunauer-Emmett-Teller (BET) surface area and pulse chemisorption. On the other hand,

deactivation and regeneration of the catalysts were studied in section four to determine the catalyst lifespan. At the end of this chapter, reaction studies and kinetic model developed for the transestrification of waste cooking oil were presented.

Chapter five, the last chapter in this thesis, gives a summary on the results obtained in this research work. This chapter concludes the overall research project and gives recommendations for future studies related to this research project.

## **CHAPTER 2:**

### **LITERATURE REVIEW**

This chapter reports the literature review related to this research project. Initially, suitability of waste cooking oil as an alternative feedstock for the production of biodiesel was reported in this chapter. Subsequently, homogeneous and heterogeneous catalysis in transesterification are discussed in detail, including their advantages and limitations. Then, several types of solid acid catalysts are reviewed in this chapter to address their possibility as heterogeneous catalyst in biodiesel production. Review on kinetic study is reported at the end of this chapter.

#### **2.1 Waste cooking oil**

Currently, world oil and fats production stand at about 154 million tons (MPOC, 2008). This figure refers to the production of 17 major oils and fats, comprising from vegetable oils (i.e. soybean, cottonseed, groundnut, sunflower, rapeseed, sesame, corn, olive, palm, palm kernel, coconut, linseed, and castor) and animal fats/oils (i.e. butter, lard, tallow, grease and fish oil). Most of this oil is used for deep-frying processes, after which could cause disposal problem. Serious contamination of environmental water may occur if no proper disposal method is implemented. Such scenario does not only contribute to pollution problems but is also harmful to human beings. In fact, European Union (EU) has enforced a ban on the utilization of all waste oils as domestic animal feed because during frying process many harmful compounds are formed. Eventually, these harmful compounds will enter the human food chain during meat consumption (Kulkarni and Dalai, 2006).

Since frying improves the taste of food, it has become a popular way in food preparation. During frying, oil is heated under atmospheric condition at temperature of 160-190°C (Gazmuri and Bouchon, 2009) for relative long period of time. In addition, the same oil or fat is repeatedly used for several times, mainly because of economical reasons. However, continuously using the same oil or fat for frying will causes various physical and chemical changes in the oil, depending on the type of oil and oil composition. Some physical changes observed in vegetable oil after frying are (i) an increase in viscosity, (ii) an increase in specific heat, (iii) a change in surface tension, and (iv) a change in color (Cvengros and Cvengrosova, 2004). Apart from that, oils are also subjected to three types of reactions during frying, mainly thermolytic, oxidative and hydrolytic (Mittelbach and Enzelsberger, 1999; Nawar, 1984).

### **2.1.1 Thermolytic reaction**

A thermolytic reaction occurs in the absence of oxygen at high temperatures. A series of alkanes, alkenes, lower fatty acids, symmetric ketones, oxopropyl esters, carbon oxide (CO), carbon dioxide (CO<sub>2</sub>) are produced from the saturated fatty acids in the oil. For unsaturated fatty acids, basically diametric compounds including dehydrodimers, saturated dimers and polycyclic compounds are formed. In addition, dimmers and trimers may be formed when unsaturated fatty acids react with other unsaturated fatty acids through Diels-Alder reaction (Kulkarni and Dalai, 2006).

### **2.1.2 Oxidative reaction**

Oxidative reaction occurs when oxygen in air dissolved in the oil or fat and reacts mainly with unsaturated acyglycerols (AG) resulting in the formation of

various oxidation products. The main reactions involved in the oxidation reactions are summarized in **Figure 2.1** (Velasco and Dobarganes, 2002). RH represents triacylglycerol undergoing oxidation in one of its unsaturated fatty acyl groups. Initially, radicals- alkyl radicals ( $R^\bullet$ ) are formed. By the addition of oxygen, alkylperoxyl radicals ( $ROO^\bullet$ ) are produced eventually. Finally, alkoxy radicals ( $RO^\bullet$ ) are formed due to the decomposition of hydroperoxides ( $ROOH$ ) which produce various saturated and unsaturated aldehydes, ketones, hydrocarbons, lactones, alcohols, acids and esters. Most of these compounds will remain within the oil or fat, e.g. dimeric and polymeric acid, dimeric AG and polyglycerols as products of the radical reactions and increase the viscosity of the frying oil. Other compounds might be further decomposed through alkoxyradicals to volatile polar compounds, e.g. hydroxyl- and epoxyacids that could evaporate from the oil (Cvengros and Cvengrosova, 2004).

### **2.1.3 Hydrolytic reaction**

Triglycerides will be hydrolyzed when it reacts with steam produced during the preparation of food. Part of the water quickly evaporates, but a certain part will dissolved in the oil or fat and induces its cleavage to give higher fatty acids, glycerol, monoglycerides and diglycerides concentration (Kulkarni and Dalai, 2006).



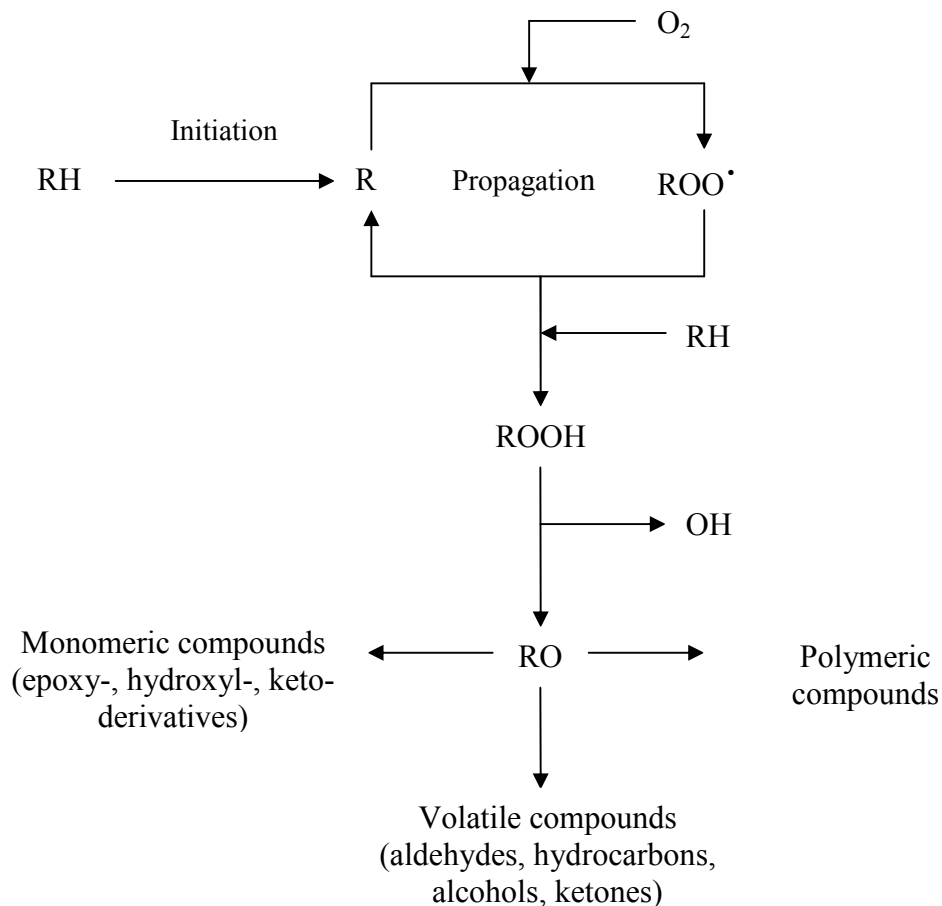


Figure 2.1: Simplified mechanism for oil oxidation reaction during frying (Velasco and Dobarganes, 2002).

Since oils are normally used repeatedly for frying, and therefore these three reactions will continuously cause the formation of many undesired and harmful compounds. The toxicological effects of these compounds upon human consumption are still not completely known. However, if waste frying oil is to be made feedstock for biodiesel production, the amount of polar compound in the waste frying oil, especially free fatty acid (FFA) must be taken into consideration as it will greatly affect the transesterification reaction. Refined oil usually contains less than 0.5 wt % FFA whereas for waste cooking oil, FFA contents range between 0.5-15 wt % (Gerhard Knothe, 2004).

## 2.2 Catalysis in transesterification

The following section describes various catalysis methods for transesterification reaction of high FFA oil, especially waste cooking oil and the potential of heterogeneous acid catalysts towards sustainable energy production in the biodiesel industry.

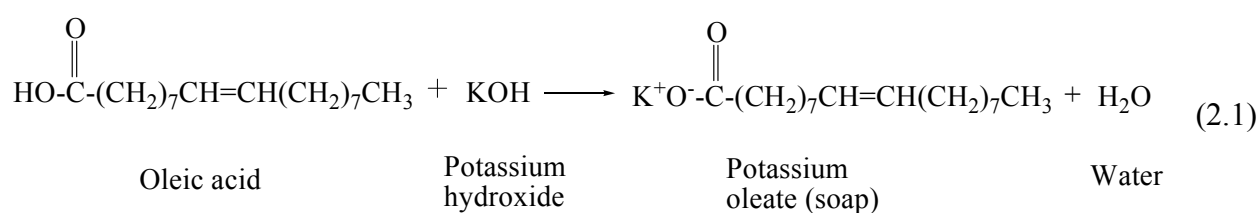
### 2.2.1 Homogeneous alkaline-catalyzed transesterification

Currently, biodiesel is produced using homogeneous base catalyst, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Felizardo *et al.*, 2006; Kulkarni and Dalai, 2006). These catalysts are commonly used in the industries due to several reasons: (i) able to catalyze reaction at low reaction temperature and atmosphere pressure; (ii) high conversion can be achieved in a minimal time, (iii) widely available and low cost (Lotero *et al.*, 2005). In fact, it was reported that the rate for alkaline-catalyzed reaction would be 4000 times faster compared to acidic catalyst (Fukuda *et al.*, 2001; Kulkarni and Dalai, 2006). However, the use of this catalyst is limited only for refined vegetable oil with less than 0.5 wt % FFA (Wang *et al.*, 2006) or acid value less than 2 mg KOH/g (Felizardo *et al.*, 2006). Some researchers reported that alkaline catalyst can tolerate higher content of FFA as shown in **Table 2.1**. Nevertheless, it is clear that the FFA content in oil feedstock should be as low as possible (ranging from less than 0.5 wt % to less than 2 wt %) for alkaline-catalyzed transesterification reaction. Thus, if waste frying oil with an average FFA content more than 2 wt %, alkaline catalyst is definitely not suitable to be used (Lotero *et al.*, 2005).

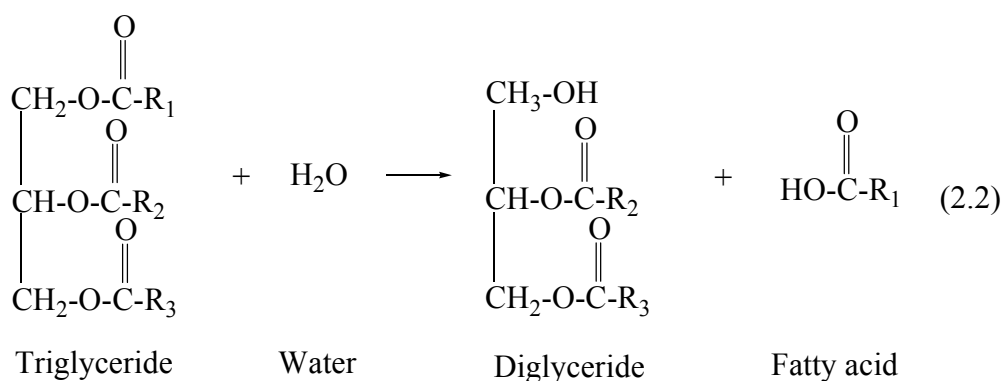
Table 2.1: Level of FFA recommended for homogeneous alkaline transesterification.

Author/Reference	Recommended FFA (wt %)
Freedman <i>et al.</i> (1984)	<1
Ma and Hanna, (1999)	< 1
Zhang <i>et al.</i> (2003a)	<0.5
Ramadhas <i>et al.</i> (2005)	≤ 2
Kumar Tiwari <i>et al.</i> (2007)	< 1
Sahoo <i>et al.</i> (2007)	≤ 2

FFA consists of long carbon chain that is disconnected from glycerol backbone. They are sometimes called carboxylic acids. If an oil or fat containing high FFA such as oleic acid is used to produce biodiesel, alkali catalyst will typically react with FFA to form soap, which is highly undesirable (Nag, 2008; Yan *et al.*, 2009; Kulkarni and Dalai, 2006). **Equation 2.1** shows a typical reaction between FFA (oleic acid) and alkaline catalyst (potassium hydroxide). This reaction is highly undesirable because it will reduce the amount of catalyst available to accelerate the transesterification reaction. Furthermore, excessive soap in the products can drastically reduce the fatty acid methyl ester (FAME) yield and inhibit subsequent purification process of biodiesel, including glycerol separation and water washing (Nag, 2008; Kulkarni and Dalai, 2006).



Apart from that, high water content in waste cooking oil also affects the methyl ester yield. When water is present, particularly at high temperature, it can hydrolyze triglycerides to diglycerides and form free fatty acid. **Equation 2.2** shows the hydrolysis reaction. With the presence of alkaline catalyst, the FFA will continuously react to form soap as shown in **Equation 2.1**. Thus, when water is present in the reactant, it generally manifests itself through excessive soap production. Apart from that, the soaps of saturated fatty acids tend to solidify at ambient temperatures and thus a reaction mixture with excessive soap may gel-up and form a semi-solid mass which is very difficult to recover (Felizardo *et al.*, 2006).



### 2.2.2 Homogeneous acid-catalyzed transesterification

Since liquid alkaline-catalyzed transesterification process faces a lot of problems especially for oil or fat with high FFAs concentration, liquid acid catalysts are proposed in order to overcome this limitation. To date, the most investigated catalysts for acid-catalyzed system are sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrochloric acid (HCl). Acid-catalyzed transesterification holds an important advantage with respect to alkali-catalyzed process: acid catalyst is insensitive to the presence of FFAs in the feedstock (Kulkarni and Dalai, 2006) and can catalyze esterification and

transesterification simultaneously (Jacobson *et al.*, 2008). Esterification is a chemical reaction in which two reactants, typically an alcohol (e.g. methanol) and an acid (e.g. FFA) react to form an ester as the reaction product. It was reported that acid catalyst is more efficient when the amount of FFA in the oil exceeds 1 wt % (Zhang *et al.*, 2003a; Canakci and Van Gerpen, 1999; Freedman *et al.*, 1984). In addition, economic analysis has proven that acid-catalyzed procedure, being a one-step process, is more economical than the alkaline-catalyzed process which requires an extra step to convert FFA to methyl esters (Zhang *et al.*, 2003a; Zhang *et al.*, 2003b). (Zhang *et al.*, 2003a; Zhang *et al.*, 2003b).

However, acid-catalyzed system is not a popular choice for commercial applications due to slower reaction rate, requirement of high reaction temperature, high molar ratio of alcohol to oil, difficulty in separation of the catalyst, serious environmental and corrosion related problem (Jacobson *et al.*, 2008; Wang *et al.*, 2006). In a study of acid-catalysed transesterification of waste frying oil using H<sub>2</sub>SO<sub>4</sub>, Wang *et al.*, 2006 reported that the yield of FAME increased with longer reaction time, higher methanol to oil ratio and higher catalyst loading. The conversion of waste cooking oil was more than 90 % at a reaction time of 10 hours with molar ratio of methanol to oil at 20:1 and 4 wt % H<sub>2</sub>SO<sub>4</sub> (with reference to weight of oil) (Wang *et al.*, 2006). In another study, Freedman *et al.*, 1984 reported 99 % oil conversion by using 1 mol % of H<sub>2</sub>SO<sub>4</sub> and methanol to oil molar ratio of 30:1 for 50 hours reaction time. These data indicates that acid-catalyzed transesterification process requires more severe reaction conditions such as long reaction time than alkaline-catalyzed reaction.