PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING ULTRASONIC TUBULAR REACTOR

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ABSTRACT

The aim of study is to produce the synthesis of biodiesel from waste cooking oil (WCO) using ultrasonic tubular reactor at laboratory scale. The experiment was used to determine the effect of ester contents by reaction time, molar ratio of WCO to Methanol (MeOH), amount of catalyst, frequency of ultrasonic and ultrasonic output power using ultrasonic tubular reactor. Based on the optimum process by ultrasonic tubular reactor, a comparisons study of three different processes (ultrasonic tubular reactor, conventional ultrasonic cleaner and mechanical stirring) were also investigated. The optimum results of biodiesel process using ultrasonic tubular reactor are the reaction time of 5 minute, sodium hydroxide (NaOH) catalyst 1%wt of WCO, molar ratio WCO to MeOH of 1:6, frequency ultrasonic of 20 KHz and ultrasonic output power of 650 Watt. The reaction time was reduced to 12-24 times (minute) compare to mechanical stirring and the ester contents was obtained at 96.54%wt. The ternary phase diagram ultrasonic tubular reactor was to find out the liquid liquid-equilibrium base on WCO- Fatty Acid Methyl Esters (FAME) -MeOH. The results show that by increasing the residence time of the whole reactant system within the two-phase zone is good for the reaction transesterification on ultrasonic tubular reactor. The semi continuous ultrasonic tubular reactor for biodiesel process of WCO gave conversion of WCO to FAME of 98%wt with flow rate of 5.56 ml/s. Meanwhile, the pilot plan of biodiesel facilities using mechanical stirring method (capacity of 100 kg WCO/batch) was designed and the transfer knowledge about biodiesel process was a success between the university with industry in Batu Pahat.
ABSTRAK

Tujuan kajian yang telah dijalankan adalah untuk menghasilkan sintesis biodiesel daripada minyak masak terpakai dengan menggunakan reaktor ultrasonik tubular didalam skala makmal. Rekabentuk eksperimen yang digunakan untuk mendapatkan kandungan ester dipengaruhi oleh masa tindakbalas, kadar kemolaran minyak masak terpakai kepada Metanol, jumlah pemangkin, frekuensi ultrasonik, dan output kuasa ultrasonik menggunakan reaktor ultrasonik tubular. Berdasarkan kepada proses reaktor ultrasonik tubular yang optimum, perbandingan antara tiga proses yang berbeza (reaktor ultrasonic tubular, permbersih ultrasonik konvensional dan pengadukan secara mekanikal) juga dikaji. Hasil optimum daripada proses biodiesel menggunakan reaktor ultrasonik tubular ialah masa tindakbalas lima (5) minit, 1%wt pemangkin NaOH bagi minyak masak terpakai, Nisbah kemolaran minyak masak terpakai kepada MeOH ialah 1:6, 20 KHz frekuensi ultrasonik dan 650 Watt output kuasa ultrasonik. Masa tindakbalas dikurangkan kepada 12-24 kali (minit) dibandingkan kepada dua (2) lagi kaedah dan kandungan ester yang diperolehi ialah 96.54 %wt. Rajah fasa ternary reaktor ultrasonik tubular adalah untuk mendapatkan keseimbangan cecair diantara minyak masak terpakai- asid lemak metil ester-MeOH. Keputusan menunjukkan peningkatan masa penghapusan bagi keseluruhan sistem tindakbalas dalam zon dua fasa adalah baik bagi tindakbalas pengtransesteran pada reaktor ultrasonik tubular. Reaktor ultrasonik tubular semi-berterusan bagi proses biodiesel daripada minyak masak terpakai memberi penukaran minyak masak terpakai kepada asid lemak metil sebanyak 98%wt dengan kadar alir sebanyak 5.56 ml/s. Sementara itu, loji pandu bagi kemudahan biodiesel menggunakan kaedah pengadukan secara mekanikal (kapasiti sebanyak 100 kg minyak masak terpakai/kelompok) telah direka dan pemindahan pengetahuan tentang proses biodiesel dilakukan antara universiti dengan industri di Batu Pahat telah berjaya.
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<tr>
<td>Al₂O₃</td>
<td>Aluminum Oxide</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society For Testing And Materials</td>
</tr>
<tr>
<td>ATR-IR</td>
<td>Attenuated Total Reflection Infrared Spectroscopy</td>
</tr>
<tr>
<td>-C–CH₂–O⁻</td>
<td>Alkoxide Ion</td>
</tr>
<tr>
<td>-CH₃</td>
<td>Methyl Group</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>CWCO</td>
<td>Crude Waste Cooking Oil</td>
</tr>
<tr>
<td>DEE</td>
<td>Diethyl Ether</td>
</tr>
<tr>
<td>DG</td>
<td>Diglyceride</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethyl Ether</td>
</tr>
<tr>
<td>EN</td>
<td>European Normalization</td>
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<tr>
<td>FAEE</td>
<td>Fatty Acid Ethyl Ester</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty Acid Methyl Ester</td>
</tr>
<tr>
<td>FFA</td>
<td>Free Fatty Acid</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>Potassium Carbonate</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium Hydroxide</td>
</tr>
<tr>
<td>LLE</td>
<td>Liquid – Liquid Equilibrium</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MG</td>
<td>Monoglyceride</td>
</tr>
<tr>
<td>MSTFA</td>
<td>N-Methyl-N-Trimethylsilyl Trifluoroacetamide</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>Naγ</td>
<td>Gamma Sodium</td>
</tr>
<tr>
<td>O–CH₃</td>
<td>Methoxide Group</td>
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<td>OFR</td>
<td>Oscillatory Flow Reactor</td>
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SCFs - Supercritical Fluid Continues
SFC - Supercritical Fluid
TBME - Tert-Butyl Methyl Ether
TG - Triglyceride
THF - Tetrahydrofuran
UTHM - Universiti Tun Hussein Onn Malaysia
WCO - Waste Cooking Oil
AV - Acid Value
C - Ester Contents
GT - The Percentage (m/m) of Total Glycerol (Free And Bound) In The Sample
ml - millimeter
ρ - Density
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CHAPTER 1

INTRODUCTION

1.1 Background of study

Biodiesel is an alternative diesel fuel derived from vegetable oils or animal fats (Ma & Hanna, 1999) or mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock. The main advantages of using biodiesel fuel are renewable, better quality of exhaust gas emissions, biodegradability and, given that all the organic carbon present is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere if all of the energy inputs for the biodiesel production are non-fossil-based, and consequently to the greenhouse effect (Barnwal & Sharma, 2005).

In the South East Asia, Malaysia is one of the countries which actively produce oil for the commercial production and usage biodiesel as fossil fuels replacement due to its rich palm oil resources. The current approved installed capacity for biodiesel production is about 10.2 million tons in Malaysia (Puah & Choo, 2008). Malaysia is now looked upon as the pioneer palm biofuel producer. Malaysia has embarked on a comprehensive palm biofuel programmed 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. Currently, the major concern for biodiesel production is economic feasibility. Biodiesel production will not be favored without tax exemption and subsidy from government; as the production cost is higher than fossil derived diesel (Demirbas & Balat, 2006). The overall biodiesel cost consists of raw material (production and processing), catalyst, biodiesel processing (energy,
consumables and labor), transportation (raw materials and final products) and local and national taxes (Haas et al., 2006). Most biodiesel plants are using refined vegetable oils as their main feedstock. Therefore, the cost of refined vegetable oils contributed 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.

In order to overcome this limitation, biodiesel manufacturer are focusing their attention on using low-cost feedstock such as waste cooking oil in order to ensure economic viability in biodiesel production. Waste cooking oil (WCO) 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 1.1 showed that, the estimation of waste cooking oil produced in selected countries (Gui, Lee & Bathia, 2008). Based on the table, waste cooking oil generated is more than 15 million tones. However, it is estimated that the WCO collected in Malaysia, is 0.5 million per year. This collected material is a good commercial choice to produce biodiesel due to its low cost. It should be noted that the actual amount of waste oil produced is much higher based on global production.

Table 1.1: Quality of waste cooking oil produces in selected countries. (Gui et al, 2008)

<table>
<thead>
<tr>
<th>Country</th>
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<tr>
<td>China</td>
<td>4.5</td>
</tr>
<tr>
<td>European</td>
<td>0.7 – 1.0</td>
</tr>
<tr>
<td>United States</td>
<td>10.0</td>
</tr>
<tr>
<td>Japan</td>
<td>0.45 – 0.57</td>
</tr>
<tr>
<td>Malaysia</td>
<td>0.5</td>
</tr>
<tr>
<td>Canada</td>
<td>0.12</td>
</tr>
<tr>
<td>Taiwan</td>
<td>0.07</td>
</tr>
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</table>

With the increase in the demand for biodiesel, new methods of increasing and enhancing biodiesel production are being researched. The commercial method of biodiesel production is time consuming and energy intensive. It is a conventional process that requires maintaining the reactants at a temperature of 60 °C for 1–2 h and yield of 97–98% (Chand, 2008). Al-Widyan & Al-Shouykh, (2002) reported the
transesterification process of waste palm oil to biodiesel with 2.25 M sulfuric acid as catalyst, 3 hours of time reaction and ester yields of 90%. Dias et al, (2008), established of biodiesel process using mechanical stirring gives yields of ester up to 97% in 60 minutes, molar ratio of 1:6 (oil to methanol) at 70°C. Veljkovic et al, (2006), reported the production of biodiesel from tobacco seed oil using two step reactions with optimum condition in 30 minute at 60°C of reaction temperature and yield of FAME about 91%.

1.2 Problem statement

The mechanical stirring method in transesterification reaction can only occur in the interfacial region between the liquids and also WCO and alcohols are not totally miscible, this is a very slow process. A vigorous mixing is required to increase the area of contact between the two immiscible phases, and thus produce an emulsion.

Ultrasonic is one of the alternative methods to high mixing. However, conventional ultrasonic systems are based on the relatively-fixed resonant frequency of the transducers used, small capacity and inefficient sonochemistry reactors. Therefore, an ultrasonic tubular reactor is one of modification tools for reaction of biodiesel. It is designed with piezoelectric transducers type at the tube to provide the longitudinal vibration. The tube is driven by the transducers and can effectively transform the longitudinal vibration into the radial vibration; moreover, the frequency and the output power can be adjustable. The key benefit to this tubular reactor system is the possibility to make batch or inline flow through production.

1.3 Objectives of study

The objective of this study was:

(a) To study the experimental variables for the production of biodiesel conversion using ultrasonic tubular reactor
(b) To design suitable plant for small-scale production of biodiesel process from waste cooking oil.

1.4 Scopes of study

In achieving the objective of the research, important tasks need to be carried out comprising of four research scopes such as:

(a) Comparison method of mechanical stirring and type of ultrasonic (ultrasonic tubular reactor and ultrasonic cleaner) in conversion of waste cooking oil to biodiesel. On other hand, to find the effect of reaction time and molar ratio oil to methanol in ultrasonic tubular reactor was conducted. The calculation of conversion WCO to biodiesel by means of acid value analysis.

(b) Transesterification of waste cooking oil was conducted using ultrasonic tubular reactor with close system at different reaction time, amount of catalyst, molar ratio oil to methanol, ultrasonic output power, and frequency.

(c) Liquid-liquid equilibrium (LLE) of three phases between FAME, methanol and WCO in different molar ratio oil to methanol, amount of catalyst and frequency of ultrasonic was investigated. Reaction time is base on variation in ternary diagram.

(d) The results of biodiesel were subjected to comprehensive the chemical and physical tests using attenuated total reflection infrared spectroscopy (ATR-IR), gas chromatography (GC), acid value by titration, density at 40°C, kinematic viscosity at 40°C, water contents and flash point.

1.4 Significant of study

Biodiesel is a liquid transportation fuel that can be produced from renewable raw material such as waste cooking oil. The use of cooking oil as raw material for biodiesel production will enhance the viability of the food industry in Batu Pahat.
Technologies of transesterification of vegetable oils into Fatty Acid Methyl Esters (FAME) called Biodiesel, have been experimentally established and are well documented in the open literature. But, no previous work using ultrasonic tubular reactor in biodiesel process was explored. This study will provide useful data for society in the biodiesel process.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

For the last century, petroleum derived fuels have been the major source of the world’s energy. However, it is predicted that fossil oil will be depleted in the near future. In addition to that, environmental concerns have trigged the examination of alternative energy sources. Future projections indicate that economics and energy needs will increase the focus on the production of synthetic fuels derived from non-petroleum sources, including biomass and waste products among others (Ghassan, Al-Widyan & Al-Shyouck, 2002).

The higher public awareness in recent years of the impacts of fossil fuel emissions on the environment and their potential health hazards triggered the government to impose restrictions on fossil combustion emissions. One way to solve the problem mentioned above is to look for alternative and renewable energy sources. One of the most promising alternative energy sources is biomass (Peterson et al., 1995). It is renewable, available everywhere and contains much less sulfur and nitrogen, which makes it more environmentally friendly than fossil sources. Among the biomass sources, waste vegetable oils and animal fats have attracted much attention as a potential renewable resource for production of an alternative for petroleum based diesel fuel. Most of the investigations reported in the literature on the usage of vegetable oil as engine fuels have emphasized modifying the oil to work in existing engine designs. The primary problem associated with using straight vegetable oils as a fuel in a compression ignition engine is the high viscosity (Yahya & Marley, 1994). Among the methods that have been investigated was transforming...
the vegetable oils to their corresponding esters. The fuel characteristics of these esters are much closer to those of diesel fuel than those of the fresh vegetable oils (Clark et al., 1984). In the 1970s, it was found that the viscosity of vegetable oils could be decreased through a simple chemical process. The process yields a vegetable oil based fuel that works as efficiently as diesel fuel in modern diesel engines. This fuel is called biodiesel, and the process is called transesterification. It is a chemical process in which a triglyceride in the vegetable oils and fat reacts with alcohol in the presence of a strong acid or base to produce a mixture of fatty acids alkyl esters (FAME) and glycerol.

2.2 Biodiesel

Biodiesel is an alternative diesel fuel derived from vegetable oils or animal fats. 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 and the composition of these fatty acids will be the most important parameters influencing the corresponding properties of a vegetable oils and animal fats. The reaction of biodiesel was shown in the Figure 2.1.

\[
\text{Tri-Glyceride} + 3\text{MeOH} \xrightarrow{\text{Catalyst}} \text{FAME} + \text{Glycerol}
\]

where R denotes a hydrocarbon chain of carbon number 12~18.

Figure 2.1: Chemical reaction of biodiesel (Freedman et al., 1986).

The reaction associated with biodiesel production is a transesterification reaction. This is a reaction that converts one form of ester to another. Vegetable oils are triglyceride esters (esters of 3 molecules of fatty acids with one molecule of
They react with monohydroxy alcohols like methanol and ethanol, producing corresponding esters. Glycerol is the by-product.

### 2.2.1 Composition of biodiesel

Making Biodiesel is defined chemically as a reaction between an alcohol and a long chain fatty acid. 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. Ethanol or Ethyl Alcohol can also be used but with problems. It needs to be as pure (water free) as possible. Ethanol containing as little as 2% water will not make biodiesel. If you have dry ethyl alcohol, and make good biodiesel, the glycerin may not separate from the biodiesel without help (Alok, 2008).

Based on different feedstock, the biodiesel produced will have different composition of FAME. Table 2.1 is shown the common composition of FAME in biodiesel (Alok, 2008).

Table 2.1: Chemical structures of common FAME. (Alok, 2008)

<table>
<thead>
<tr>
<th>No</th>
<th>Components</th>
<th>Chemical Formula</th>
<th>Molecular weight (kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methyl Myristate</td>
<td>C_{14}H_{30}O_2</td>
<td>242.41</td>
</tr>
<tr>
<td>2</td>
<td>Methyl Pentadecanoate</td>
<td>C_{16}H_{32}O_2</td>
<td>256.42</td>
</tr>
<tr>
<td>3</td>
<td>Methyl Palmitate</td>
<td>C_{17}H_{34}O_2</td>
<td>270.457</td>
</tr>
<tr>
<td>4</td>
<td>Methyl Stearate</td>
<td>C_{18}H_{36}O_2</td>
<td>298.511</td>
</tr>
<tr>
<td>5</td>
<td>Methyl Oleate</td>
<td>C_{18}H_{36}O_2</td>
<td>296.495</td>
</tr>
<tr>
<td>6</td>
<td>Methyl Linoleate</td>
<td>C_{18}H_{36}O_2</td>
<td>294.479</td>
</tr>
<tr>
<td>7</td>
<td>Methyl Linolenate</td>
<td>C_{18}H_{36}O_2</td>
<td>292.463</td>
</tr>
</tbody>
</table>

### 2.2.2 Benefits of biodiesel

One of the main driving forces for biodiesel widespread use is the limitation of greenhouse gas emissions (CO₂ being the major one) by the Kyoto Protocol. Along
with ethanol and other biomass derived fuels, biodiesel is an important bio-energy. When plants photosynthesize, they use the sun's energy to pull CO\textsubscript{2} out of the atmosphere and incorporate it into biomass. Part of the solar energy is locked into the chemical structure within the biomass. There are a number of thermal, chemical or microbial processes that can be used to release this energy or convert it into a more convenient form for human use. As a form of bio-energy, biodiesel is nearly carbon-neutral, i.e., the CO\textsubscript{2} it produces on burning will be absorbed naturally from CO\textsubscript{2} in the air and recycled without an overall net increase in the atmospheric CO\textsubscript{2} inventory, thus making an almost zero contribution to global warming (Van Gerpen \textit{et al.}, 2004).

There are many distinct benefits of using biodiesel compare to diesel fuel (Cao, 2008):

(a) Considered to be environmental friendly, biodiesel is one of the most renewable fuels compare to diesel fuel.

(b) It is biodegradable.

(c) It is derived from a renewable domestic resource, thus reducing dependence on and preserving petroleum. It can be domestically produced, offering the possibility of reducing petroleum imports,

(d) Reductions of most exhaust emissions relative to conventional diesel fuel, generating lower emissions of hydrocarbons, particulates and carbon monoxide;

(e) Biodiesel has a relatively higher flash point, >150 °C, indicating that it presents a very low fire hazard; leading to safer handling and storage,

(f) Biodiesel provides greater lubricity than petroleum diesel, thus reducing engine wear. In fact, biodiesel can be used as a lubricity enhancer for low-sulphur petroleum diesel formulations,

(g) Toxicity tests show that biodiesel is considerably less toxic than diesel fuel (Haws, 1997).

(h) Biodiesel can be used directly in most diesel engines without requiring extensive engine modifications.
2.3. Composition of vegetable oil

Vegetable oils and animal fats usually have hydrophobic properties, which mean they are insoluble in water. As mentioned earlier, triglycerides are made up of 1 mol glycerol and 3 mol fatty acids. Fatty acids vary in terms of carbon chain length and number of unsaturated bonds (double bonds). Typical fatty acids compositions found in several vegetable oils are summarized in Table 2.2 (Alok, 2008). Fatty acids that have no double bonds are termed “saturated” such as stearic acid. These chains contain the maximum number of possible hydrogen atoms per atom carbon. Fatty acids that have double bonds are termed “unsaturated” such as linoleic acid. These chains do not contain the 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 extracting or mechanically pressing, containing a lot of impurities such as free fatty acids, sterols and water. In fact, these free fatty acids and water content will have a significant effect on the transesterification reaction, especially if a base catalyst is used. They could also interfere with the separation of FAME and glycerol during water washing (purification step) because of soap formation.

Table 2.2: Typical fatty acid composition (%) for different common oil source. (Alok, 2008)

<table>
<thead>
<tr>
<th>Fatty Acid composition (%)</th>
<th>Soybean oil</th>
<th>Cottonseed oil</th>
<th>Palm oil</th>
<th>Lard oil</th>
<th>Tallow oil</th>
<th>Coconut oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric (C12:0)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>46.5</td>
</tr>
<tr>
<td>Myristic (C14:0)</td>
<td>0.1</td>
<td>0.7</td>
<td>1.0</td>
<td>1.4</td>
<td>0.8</td>
<td>19.2</td>
</tr>
<tr>
<td>Palmitic (C16:0)</td>
<td>0.2</td>
<td>20.1</td>
<td>42.8</td>
<td>23.6</td>
<td>23.3</td>
<td>9.8</td>
</tr>
<tr>
<td>Stearic (C18:1)</td>
<td>3.7</td>
<td>2.6</td>
<td>4.5</td>
<td>14.2</td>
<td>19.4</td>
<td>3.0</td>
</tr>
<tr>
<td>Oleic (C18:2)</td>
<td>22.8</td>
<td>19.2</td>
<td>40.5</td>
<td>44.2</td>
<td>42.4</td>
<td>6.9</td>
</tr>
<tr>
<td>Linoleic (C18:2)</td>
<td>53.7</td>
<td>55.2</td>
<td>10.1</td>
<td>10.7</td>
<td>10.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Linolenic (C18:3)</td>
<td>8.6</td>
<td>0.6</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
<td>0.0</td>
</tr>
</tbody>
</table>
2.4 Waste cooking oil as feedstock of biodiesel

The term “waste cooking oil” (WCO) refers to vegetable oil which has been used in food production and which is no longer viable for its intended use. WCO arises from many different sources, including domestic, commercial and industrial. WCO is a potentially problematic waste stream which requires to be properly managed. The disposal of WCO can be problematic when disposed, incorrectly, down kitchen sinks, where it can quickly cause blockages of sewer pipes when the oil solidifies. Properties of degraded used frying oil after it gets into sewage system are conducive to corrosion of metal and concrete elements. It also affects installations in waste water treatment plants. Thus, it adds to the cost of treating effluent or pollutes waterways (Szmigielski, Maniak & Piekarski, 2008).

Any fatty acid source may be used to prepare biodiesel. Thus, any animal or plant lipid should be a ready substrate for the production of biodiesel. The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials - the food versus fuel dispute (Pimentel et al., 2009; Srinivasan, 2009). There are concerns that biodiesel feedstock may compete with food supply in the long-term (Lam et al., 2009; Metzger, 2009).

From an economic point of view; the production of biodiesel is very feedstock sensitive. Many previous reports estimated the cost of biodiesel production based on assumptions, made by their authors, regarding production volume, feedstock and chemical technology (Canakci & Van Gerpen, 2003; Zhang et al., 2003; Kulkarni & Dalai, 2006). In all these reports, feedstock cost comprises a very substantial portion of overall biodiesel cost.

Haas et al., (2006) developed a computer model to estimate the capital and operating costs of a moderately-sized industrial biodiesel production facility. Calculated production costs included the cost of the feedstock and of its conversion to biodiesel. The model is flexible in that it can be modified to calculate the effects on capital and production costs of changes in feedstock cost, changes in the type of feedstock employed, changes in the value of the glycerol co-product and changes in process chemistry and technology. The authors reported that for biodiesel produced from soybean oil, the cost of the oil feedstock accounted for 88 % of total estimated production costs (Haas et al., 2006).
Marchetti, Miguel & Errazu, (2008) used a conceptual design of alternative production plants with a techno-economic analysis in order to compare these alternatives. In all cases, more than 80% of the production cost is associated with the feedstock itself and consequently, efforts should be focused on developing technologies capable of using lower-cost feedstock, such as recycled cooking oils. Reusing of these waste greases not only reduce the burden of the government in disposing the waste, maintaining public sewers and treating the oily wastewater, but also lower the production cost of biodiesel significantly. (Refaat, 2010)

2.5 Current of biodiesel technologies

Several alternatives are been employed to increase the conversion rates and the yields of esters in order to lower production costs and improve biodiesel product quality and presented as follows;

2.5.1 Catalytic conversion

The problems associated with the homogeneous catalysts are the high consumption of energy and expensive separation of the homogeneous catalyst from the reaction mixture. Alternative heterogeneous catalysts have been successfully explored (Ma & Hanna, 1999) to circumvent the difficulties with homogeneous catalysts for transesterification of high FFA-containing oils.

Heterogeneous catalyst developed to eliminate the need for aqueous quenching and elimination metal salts (soaps) (Zhou & Boocock, 2006) but the conversion for most of the heterogeneous are not high enough to be used for industrial based production (Xie, Pen & Chen, 2006) and relatively prolonged reaction period. There have also been experiments aimed at replacing the sodium and potassium compounds with basic ammonium compounds as catalysts or reactants such as amines, amino guanidines, nitro guanidine’s and triamino (imino) phosphoranes. The guanidines are the more active catalysts, the activity following their relative basicity. At a concentration of 3% was similar to that of potassium carbonate at the same concentration. The saturated aqueous solution of guanidine
carbonate has a pH of 11 to 11.5. The aqueous solution of free guanidine, on the other hand, gives just as strong an alkaline reaction (Schuchardt et al., 1998). KOH loaded on Al₂O₃ and Naγ zeolite supported as heterogeneous catalysts, though leaching of potassium species in both spent catalysts was observed, biodiesel yield of 91.07% was reported (Noiroj et al., 2009) at temperatures below 70°C within 2–3 h at a 1:15 molar ratio of palm oil to MeOH and a catalyst amount of 3–6 wt%.

2.5.2 Supercritical process

Triglyceride (TG) utilization in the presence of a acid or alkali catalyst is affected by high level of water content and free fatty acid (FFA) with undesirable saponified products. Hence the study to reduce catalyst has attracted interest in water-added supercritical method with a feature of easier product separation. The glycerol (side reaction in biodiesel process) is more soluble in water than in MeOH (Kusdiana & Saka, 2004; Georgogiannia et al., 2008). Single phase medium using supercritical fluid (SCF) due to the creation of a single phase environment has some unique advantages including increased species mixing, heat and mass transfer, fast reaction typically at a few minutes level. These systems are environmentally benign, and have good scalability, as well as being simple and easy for continuous production. The SCFs is ideal for separation and extraction of useful products and for oxidation of organic materials (Wen, Jiang & Zhang, 2009). For most of the supercritical methods of biodiesel production, the reaction requires temperatures of 340–400°C and pressures of 20–70 MPa. Rapeseed oil was treated at 250-350°C, 43 MPa and 240 s with a molar ratio of 42 in MeOH for transesterification to biodiesel fuel. By this MeOH approach, crude vegetable oil as well as its wastes could be readily used for biodiesel fuel production in a simple preparation. Regardless of the content of water supercritical MeOH method does not require a catalyst and the FFA in the oils are esterified at once (Kusdiana & Saka, 2004).
2.5.3 Co-solvent

Enhancing solubility, addition of a co-solvent is to create a single phase greatly accelerated the reaction so that it reached substantial completion in a few minutes (Royon et al., 2007). The technique is applicable for use with other alcohols and for acid-catalyzed pretreatment of high free fatty acid feed stocks. Comparison of various co-solvent dimethyl ether (DME), diethyl ether (DEE), tert-butyl methyl ether (TBME) and tetrahydrofuran (THF) (Guan, Sakurai & Kusakabe, 2009) to synthesize biodiesel from sunflower oil by using a KOH catalyst at 25°C in a closed batch reactor was reported (Wen et al., 2009). Addition of a co-solvent enhanced the transesterification rate at the MeOH/oil molar ratio of 6 at 25°C, and sunflower oil was almost completely converted into biodiesel after 20 min reaction while only approximately 78% conversion was reached in the absence of a cosolvent. The oil conversion was influenced by the cosolvent/ MeOH molar ratio, MeOH/oil molar ratio, and catalyst concentration. However, the homogeneous flow was broken with the formation of immiscible glycerol, and transformed to a dispersed flow of fine glycerol droplets. The problem of immiscibility of MeOH and vegetable oil leading to a mass-transfer resistance in the transesterification of vegetable oil (Kusdiana & Saka, 2004) can be overcome by this method amongst many other techniques being developed like membrane separation and inert dopant (Disselkamp et al., 2006)

2.5.4 Microwave method

Microwave irradiation is a well-established methodology to improve extraction and accelerate chemical reactions such as those of hydrolysis and esterification (Ipsita & Gupta, 2003) because of its convenience, rapidity, and economy advances in equipment design, trends in electrical energy costs, and research on food properties have provided a basis for modeling microwave heating patterns that should stimulate the development of new and improved commercial food processes (Tan et al., 2001).

In conventional heating of transesterification process (batch, continuous, and super critical MeOH process), heat energy is transferred to the raw material through convection, conduction, and radiation from surfaces of the raw material as shown
when triglyceride (TG) in soaked soybeans were already hydrolyzed into diglyceride (DG) and free fatty acids during soaking and were further hydrolyzed by microwaves. Satisfactory transesterification was achieved in a short time (30s), with alcohol to oil molar ratio 12:1 and the continuous conversion of waste frying palm oil to ethyl ester was over 97%. Although, the mechanism of the microwave effect on a chemical reaction, whether thermal or non-thermal, is debatable (Saifuddin & Chua, 2004), however the transesterification results clearly establish that there is considerable enhancement in reaction rates. This brings about considerable time saving as well as cost (Kusdiana & Saka, 2001). 100% biodiesel yield by applying microwave irradiation for two minutes compared to one hour with the conventional technique, with adjusted temperature to 65°C, a MeOH/oil molar ratio of 6:1 and potassium hydroxide (1%) used as a catalyst has been reported (Refaat & El Sheltawy, 2008) and showed that microwave-enhanced biodiesel is not, at least, inferior to that produced by the conventional technique (Yoshida & Takagi, 1997).

2.5.5 Ultrasonic reactor method

An ultrasonic field is known to produce unique chemical and physical effects that arise from the collapse of the cavitation bubbles (Bondy & Sollner, 1935). Their uses have been cited in synthesis of nanostructured materials, processing of biomass, sonofusion, sonodynamic therapy, and sonochemical degradation of pollutants (Hanh et al., 2007) and hazardous chemicals (Schuchardt, Sercheli & Vargas, 1998). A low frequency ultrasonic irradiation can be used to produce emulsions from immiscibility liquids and help generate small droplets and large interfacial areas if the ultrasonication device is placed near the liquid–liquid interface in a two phase reaction system (Bondy C & Sollner, 1935; Sivakumar et al., 2002).

Disselkamp et al., 2006, contrasted differences in a heterogeneous catalytic reaction for cavitating and non cavitating ultrasound incorporating an inert dopant, which does not partake in solution chemistry to enable facile transition from high power non cavitating to cavitating condition as not all liquid readily cavitation. The mechanism for discriminating between physical and chemical effects of ultrasound with different conditions have been coupled to a bubble dynamics mode (Kalva,
Sivasankar & Moholkar, 2009) and the result is attributed to the difference in intensity of microturbulence produced by cavitation bubbles in oil and MeOH. This effect is a low intensity of microturbulence generated by cavitation bubbles in oil, which restrict an intimate dispersion of oil in MeOH for high alcohol to oil molar ratios.

The optimum alcohol to oil molar ratio for the experimental system used in this study is 12:1. Transesterification of TG with various alcohols has been shown (Vasudevan & Briggs, 2008), under the low frequency ultrasonic irradiation (24KHz), stirring conditions (600 rpm). The optimal reaction condition was obtained with an alcohol to TG ratio of 6:1 (Hanh et al., 2007) low frequency ultrasonication (24KHz) and mechanical stirring (600 rpm) with MeOH gave high yields of methyl esters (95%) after a short reaction time (20 min) similar to those using mechanical stirring. Use of ultrasonication in conventional transesterification with ethanol gave similar yields to those using mechanical stirring but significantly lower than respective yields using MeOH. This also showed the alcohol-dependency of the operation. Gogate, Tayal & Pandit, (2006) review presented this method as very efficient for intensification of chemical processing and the analysis, fabrication, design of cavitational reactors would offer realistic solution to conventional transesterification.

2.5.6 Oscillatory flow reactor for transesterification reaction

Oscillatory flow reactor (OFR) was first introduced by Harvey, Mackley & Seliger, (2003) to produce biodiesel through some improvement in mixing intensity between reactants. OFR is a novel type of continues flow reactor, consisting of tubes containing equally spaced orifice plate baffles. Therefore, an oscillatory motion is superimposed upon the net flow of the process fluid, creating flow patterns conducive for efficient heat and mass transfer, whilst maintaining plug flow regime (Harvey et al., 2003).

In addition, each baffle essentially behaves as a stirred tank that lead to excellent mixing and suspension by creating vortices between orifice baffles and oscillating fluid (Zheng, Skelton & Mackley, 2007). This is an essential element in
designing a biodiesel reactor especially when heterogeneous catalysts are used due to the presence of three immiscible phases (oil–alcohol–catalyst) at the initial stage of reaction. Thus, improvement in mixing and suspension of catalysts tend to produce higher yield of biodiesel in a shorter reaction time compared to conventional batch-type stirred tank reactor.

Apart from that, OFR allows longer residence time as the mixing is independent of the net flow and hence the reactor length-to-diameter ratio can be reduced. This is an important plus point if the process is scaled up for commercial application in order to reduce the overall capital and pumping cost. Harvey et al., (2003) applied OFR in the production of biodiesel from waste cooking oil and pure rapeseed oil. The reaction was performed at temperature of 20–70 °C, residence time of 10–30 min and molar ratio of methanol to oil was maintained at 1.5. Pure sodium hydroxide (32.4 g) was dissolved in pure methanol initially at 40°C for 1 h. It was found that at 50°C and 30 min of reaction time, nearly 99% of biodiesel was produced. Moreover, the product contains negligible amount of triglyceride and diglyceride. However, some traces of monoglyceride were detected (Noureddini & Zhu, 1997). Nevertheless, Harvey et al., (2003) concluded that in-depth study on OFR in transesterification with heterogeneous catalyst is promptly required as OFR is ideal for suspending solid catalysts or polymer supported catalysts.

### 2.5.7 Mechanical stirring method

Several commercial processes for FAME production have been developed. In conventional (mechanical stirring method) industrial biodiesel processes, vegetable oil methanolysis is achieved using a homogeneous catalyst system operated in either batch or continuous mode. Sodium hydroxide or sodium methylate is often used as catalyst. Sodium is recovered after the transesterification reaction as sodium glycerate, sodium methylate, and sodium soaps in the glycerol phase.

In the mechanical stirring reaction, the temperature is 60-70°C, and it takes about an hour and half for the reaction to proceed to completion (Ma & Hanna, 1999). The alcohol and the alkali metal hydroxide catalyst are first mixed before the reaction in a separate unit to form the metal alkoxide. The alcohol and the alkoxide
catalyst are then mixed with oil in the reactor. The reactor is a batch reactor with stirrer, or a continuous or semi-continuous stirred tank reactor. A condenser is used to condense the alcohol continuously. The boiling point of the alcohol is in the range of the reaction temperature. Oil and alcohol are immiscible; they are constantly stirred, and the reaction takes place at the interface of two phases. The reaction is described by second order reaction kinetics (Freedman, Butterfield & Pryde, 1986). The stoichiometric ratio of triglyceride and alcohol for the reaction is 3:1, but 6:1 molar ratio is the optimal molar ratio used to push equilibrium to one side for maximum biodiesel conversion (97–98 %) (Freedman et al., 1986) and 0.5 wt % of catalyst is considered optimal for maximum activity.

2.5.7.1 Drawbacks Mechanical stirring

Transesterification reactions involve reactions between WCO and methanol in the presence of a catalyst. WCO and methyl alcohol are immiscible liquids and form separate layers when mixed together in a reactor. However conventional transesterification reaction requires mixing continuously for long periods of time to facilitate the reaction between oil and alcohol, due to the reaction can takes place only in the interfacial region between the two liquids. Therefore, this mixture is sonicated, ultrasonic waves produce cavitation at these interfacial areas. As a result, an emulsion of oil and alcohol forms, providing large surface areas for reaction. It is observed that reaction time is reduced significantly.

2.6 The biodiesel process

2.6.1 Esterification process

Esterification, as it applies to biodiesel production, is the chemical reaction by which a fatty acid, typically a free fatty acid in degraded or second-use oil, reacts with an alcohol to produce an alkyl ester and water. The process differs from the
transesterification reaction in that the reaction is occurring directly between the alcohol and the fatty acid molecule. The intermediate steps of cleaving the fatty acid chains from the glycerin backbone are not present. For this reason, no glycerin is produced during the esterification reaction (Altic, 2010).

The following formula shows the basic esterification reaction with methanol. A fatty acid molecule reacts with a methanol molecule to form a methyl ester plus a water molecule:

\[
R_1\text{COOH} + \text{CH}_3\text{OH} \rightarrow R_1\text{COOCH}_3 + \text{H}_2\text{O}
\]

Free fatty acid (FFA) Methanol Methyl ester Water

The above formula was adopted from Deshmane, Gogate & Pandit, (2009) and represents the basic chemical reaction for all industrial esterification reactions using methanol as the alcohol.

Conventionally, virgin vegetable oils and high-grade animal fats are the feedstock of choice for biodiesel production due to low levels of impurities, such as free fatty acids and sulfated proteins, which can cause problems with processing and final product quality. Rapeseed alone comprises of roughly 84% of the lipid stocks used for biodiesel production. By comparison, sunflower and palm oil each represent 13% of the feedstocks with soybean trailing with a 1% share. All other feedstock such as waste cooking oils, animal fats, jatropha, peanut, mustard, etc. make up the remaining 2% (Pahl, 2005). Second use oils such as yellow or brown grease are thermally or chemically degraded waste oils that primarily contain grease collected from restaurant or industrial grease traps. Most of this oil is spent cooking oil from restaurants that has been thermally degraded by sustained high temperatures. It further degrades when in contact with water in the grease trap through a process known as hydrolysis. This degradation produces molecules known as free fatty acids. Fatty acids will chemically react with the typical alkaline catalysts used in base catalyzed biodiesel reactions to form soap. Free fatty acids are always present in oils, however mass concentrations above 4% will generate more soap than can be dealt with reasonably in a conventional base-catalyzed reaction and will prevent the reaction from going to completion in almost all cases. (Tyson, 2002)
2.6.2 Transesterification reaction

The chemical reaction by which a lower alcohol reacts with a triglyceride to yield a fatty acid alkyl ester is known as transesterification. It occurs easily with the lower alcohols such as methanol or ethanol. The process is slow under normal conditions without the presence of a catalyst. Traditionally, an alkaline catalyst such as sodium or potassium hydroxide is used to catalyze and accelerate the reaction at standard temperatures and pressures. The catalytic reaction is complicated; however the necessity for a catalyst arises from the relative insolubility of alcohol in oils. Catalysts provide a phase-transfer as well as an ion exchange effect which reduces reaction times by many orders of magnitude (Mittelbach & Remschmidt, 2004).

Transesterification consists of a number of consecutive, reversible reactions (Schwab, Bagby & Freedman, 1987; Freedman et al., 1986). The triglyceride is converted stepwise to diglyceride, monoglyceride and glycerol (Figure 2.2). A mole of ester is liberated at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol.

\[
\begin{align*}
\text{Triglyceride (TG) + R'OH} & \rightarrow \text{Diglyceride (DG) + R'COOR}_1 \\
\text{Diglyceride (DG) + R'OH} & \rightarrow \text{Monoglyceride (MG) + R'COOR}_2 \\
\text{Monoglyceride (MG) + R'OH} & \rightarrow \text{Glycerol (GL) + R'COOR}_3
\end{align*}
\]

Figure 2.2: The transesterification reactions of vegetable oil with alcohol to esters and glycerol. (Freedman et al., 1986)

The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps (Eckey, 1956). The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. The catalyst such as NaOH, KOH, K₂CO₃ or other similar catalysts were mixed with alcohol and alkoxide group is formed (Sridharan & Mathai, 1974). A small amount of water, generated in the reaction, may cause soap
formation during transesterification. Figure 2.3 summarizes the mechanism of alkali-catalyzed transesterification.

Pre-step:

\[ \text{OH}^- + \text{R'OH} \quad \Leftrightarrow \quad \text{R'O}^- + \text{H}_2\text{O} \quad \text{or} \quad \text{NaOR'} \quad \Leftrightarrow \quad \text{R'O}^- + \text{Na}^+ \]

Step 1

\[ \text{ROOCR}_1 + \text{´OR'} \quad \Leftrightarrow \quad \text{R}_1\text{C} = \text{O}^- \quad \text{OR'} \]

Step 2

\[ \text{R}_1\text{C} = \text{O}^- + \text{HOR'} \quad \Leftrightarrow \quad \text{R}_1\text{C} = \text{O}^- + \text{´OR'} \]

Step 3

\[ \text{R}_1\text{C} = \text{O}^- \quad \Leftrightarrow \quad \text{R}_1\text{COOR'} + \text{HOR'} \]

where R-OH diglyceride, R$_1$ long chain alkyl group, and R' short alkyl group

Figure 2.3: The mechanism of alkali-catalyzed transesterification of triglycerides with alcohol. (Eckey, 1956)

2.7 Variables influencing the transesterification reaction

2.7.1 Molar ratio of vegetable oil to methanol

Methanol is a commonly used alcohol for transesterification because of its low price and highly reactive nature (Lang et al., 2001). The stoichiometric ratio required for transesterification is 1:3 moles of vegetable oil to alcohol. However, it has been found that the molar ratio of vegetable oil to alcohol depends on the type of catalyst used for the reaction. For example, the molar ratio of 1:6 moles of soybean oil to
methanol has been found to be the most suitable in the case of alkali-catalyzed transesterification because an excess of alcohol is required to drive the reaction (Freedman et al., 1986). For acid-catalyzed transesterification, a 1:30 vegetable oil to alcohol ratio is generally used (Freedman, Pryde & Mounts, 1984).

2.7.2 Moisture contents

Water content promotes the formation of soap during the reaction and reduces catalyst efficiency. The presence of water in acid catalyzed transesterification reduces the percentage of biodiesel produced to a greater extent compared to an alkaline catalyst. For example, in a reaction mixture of soybean oil, methanol and sulfuric acid, 0.5% water content reduces the resultant biodiesel conversion from 95% to 90% (Canacki & Van Garpen, 1999).

2.7.3 Free fatty acid

For an alkali catalyzed transesterification reaction, vegetable oil should not contain any free fatty acids. If any free fatty acids are present in the vegetable oil, an alkaline catalyst (e.g. NaOH) is utilized in neutralizing these free fatty acids which only consumes the catalyst and slows down the reaction. The acid value of glycerides should be less than 1 for a NaOH catalyzed transesterification reaction (Wright et al., 1944). Acid value is the milligrams of potassium hydroxide (KOH) required for neutralizing the free fatty acids present in 1 g of vegetable oil.

2.7.4 Catalyst

Transesterification reactions can occur in the absence of catalysts, (Diasakou, Louloudi & Papayannakos, 1998) however, it requires high temperature, pressure and long reaction times. If all these requirements are met, the process cost is
relatively high. This method produces relatively high purity esters and soap-free glycerol, but because it is un-economical, it is typically not considered for industrial production of biodiesel. Three types of catalysts are generally used for biodiesel production: alkaline catalysts, acidic catalysts, and enzymes.

2.7.4.1 Alkaline catalysts

Alkaline catalysis is the most commonly used process for biodiesel production. Its main advantage is that a high ester yield is obtained in short reaction times under mild reaction conditions (Canacki & Van Garpen, 1999). However, alkaline catalysts are highly sensitive to free fatty acids in vegetable oils. Therefore only low acidic vegetable oils produce high ester yields after transesterification. However, de-acidification of vegetable oil prior to transesterification reduces this issue. Examples of alkali catalysts are: sodium hydroxide, potassium hydroxide, alkali metals (such as sodium), alkali metal carbonates (such as sodium carbonate, and potassium carbonate).

2.7.4.2 Acidic catalysts

Acid–catalyzed transesterification requires a relatively high temperature (~100 °C), pressure (~5 bars) and large amounts of alcohol. It is also slower in comparison to alkaline catalysis. The only advantage of this type of catalytic conversion is that it can efficiently esterifies free fatty acids in vegetable oils and is therefore used to transesterify high free–acid–containing feedstock, such as waste edible oil (Mittelbach & Remschmidt, 2004).
2.7.4.3 Enzymes

Enzymes or lipases extracted from microorganisms can also be used as catalysts for the transesterification reaction (Mittelbach & Remschmidt, 2004). The advantages of these biocatalysts are:

(a) Biodiesel conversion under mild temperature, pressure, and pH conditions.
(b) No catalyst residues or soap in the final product.
(c) High quality glycerol is produced.
(d) These catalysts efficiently esterify free fatty acids and thus can be used for transesterification of oils or fats containing high free fatty acid contents.

The disadvantages of these catalysts include:

(a) Long reaction times and higher catalyst concentrations are required.
(b) These catalysts are expensive and not economical for commercial use.
(c) Enzymes are typically difficult to remove from the final products (i.e., biodiesel and glycerol) after the reaction is complete.

2.7.5 Reaction temperature

Temperature has no detectable effect on the ultimate conversion to ester. However, higher temperatures decrease the time required to reach maximum conversion (Pinto et al., 2005). Transesterification can be conducted at various temperatures ranging from room temperature to the boiling point of the alcohol employed (68°C in case of methanol) so that the reactor does not need to be pressurized. Thus, the usual temperature used during transesterification in most literature is 60-65°C. When the reaction temperature closes or exceeds the boiling point of methanol (68 °C), the methanol will vaporize and form a large number of bubbles which may inhibit the reaction.
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