

**BIODIESEL PRODUCTION USING ULTRASONIC-ASSISTED  
HETEROGENEOUS CATALYTIC PROCESS**

**by**

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**Thesis submitted in fulfillment of the  
requirements for the degree of  
Doctor of Philosophy**

**April 2011**

**BIODIESEL PRODUCTION USING ULTRASONIC-ASSISTED  
HETEROGENEOUS CATALYTIC PROCESS**

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**UNIVERSITI SAINS MALAYSIA  
2011**

## ACKNOWLEDGMENTS

First, I would like to thank the Almighty God for His infinite mercy and protection upon the accomplishment of my studies. I would like to express my genuine gratitude to my supervisor, Assoc. Prof. Dr. Ahmad Zuhairi Abdullah for his wonderful supervision and his unrelenting support, expert guidance, valuable comments and the enormous time and effort he rendered throughout my research work. I would not have better supervision and feel to be a lucky person to work with him. I would also like to extend my heartfelt thanks to Prof. Dr. Subhash Bhatia for his brilliant comments, encouragement and for providing me continuous advice throughout my studies. I really was honored to have the opportunity to work under the supervision of both of you.

I would also like to express my appreciation to the Dean, Prof. Dr. Azlina Harun @ Kamaruddin and Assoc. Prof. Dr. Lee Keat Teong, Assoc. Prof. Dr. Mohamad Zailani Bin Abu Bakar and Assoc. Prof. Dr. Ahmad Zuhairi Abdullah, Deputy Deans of the School of Chemical Engineering USM, for their continuous support and help rendered throughout my studies. My sincere thanks go to all the respective lecturers, staff and technicians in the School of Chemical Engineering for their cooperation and support. Great appreciation goes to the former Dean, Prof. Dr. Abdul Latif Ahmad and the Deputy Deans, Dr. Syamsul Abdul Syukor and Dr. Zinal Ahmad. Thousand thanks to Mr. Muhd Arif Mat Husin, Mr. Mohd. Faiza Ismail and Mrs. Latifah Abd. Latif for their valuable and kind help in laboratory works. I highly appreciate all the help and supports spared from Mrs. Aniza Abd. Ghani and Mrs. Normie Hana A.Rahim in smoothing my studies through their assistance in the official work throughout my studies. I am also indebted to School of Industrial

Technology and School of Material and Mineral Engineering in USM for their assistance in some of my analysis work in this study. The financial supports provided by Yayasan Felda (Project No. 6050115) And RU grants provided by Universiti Sains Malaysia are gratefully acknowledged.

I would like to extend my sincere and deepest gratitude to all my adored friends, in Malaysia and in Iran for their unparalleled help, kindness and moral support towards me. Thank you for always being there for me. I hope we all have a very bright future undertaking ahead. Very special thanks goes to my dear friend Mr. Hamed Mootabadi for his useful help and support in forwarding this thesis.

I also do wish to express my deepest appreciation to Universiti Sains Malaysia for providing me a warm environment to feel at home. The financial supports provided by Yayasan Felda (Project No. 6050115) And RU grants provided by Universiti Sains Malaysia are gratefully acknowledged.

Last but definitely not least, my deepest and most heart-felt gratitude to my beloved mum, Mrs. Nahid Foroughi and my adored dad, Mr. Mahmoud Salamati for their endless love and support. I would like to dedicate this PhD thesis to them. To my wonderful sister, Pantea, my kind brother in law Mr. Vahid Beheshti and my lovely nephew, Behrad for their love and care. To my lovely grandmother, who has always prayed for me towards my study, and those who are directly and indirectly involved in this research, your contribution given shall not be forgotten. My appreciation goes to all of you.

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## LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
BaO	Barium oxide
BET	Brunauer-Emmett-Teller
CaO	Calcium oxide
CCD	Central composite design
CCO	Coconut oil
CO <sub>2</sub>	Carbon dioxide
DF	Degree of freedom
DOE	Design of experiment
EN	European standard
FAME	Fatty acid methyl ester
FID	Flame ionization detector
FFAs	Free fatty acids
H <sub>2</sub> O	Water
HNO <sub>3</sub>	Nitric acid
ISO	International standard organization
KOH	Potassium hydroxide
MeOH	Methanol
MgO	Magnesium oxide
MPOB	Malaysian Palm Oil Board
MPOC	Malaysian Palm Oil Council
MS	Mean square
NaOH	Sodium hydroxide

NO <sub>x</sub>	Nitrogen dioxide
RSM	Response Surface Methodology
SEM	Scanning electron microscope
SrO	Strontium oxide
SS	Sum of square
TG	Triglyceride
UCOs	Used cooking oils

## LIST OF SYMBOLS

Symbols	Descriptions	Unit
$A$	Arrhenius factor (pre-exponential factor)	Dimensionless
$C_{TG}$	Concentration of triglyceride	$(\text{mol}/\text{dm}^3)$
$C_{TG,0}$	Concentration of initial triglyceride	$(\text{mol}/\text{dm}^3)$
$C_{FAME}$	Concentration of FAME	$(\text{mol}/\text{dm}^3)$
$C_{MG}$	Concentration of monoglyceride	$(\text{mol}/\text{dm}^3)$
$C_{DG}$	Concentration of diglyceride	
$C_{TG}$	Concentration of triglyceride	$(\text{mol}/\text{dm}^3)$
$C_{MeOH}$	Concentration of methanol	$(\text{mol}/\text{dm}^3)$
$d$	Weight percent of the catalyst	
$-dC_{TG}/dt$	Differential of $C_{TG}$ polynomial with respect to time (t)	$(\text{mol}/\text{dm}^3.\text{h})$
$dX/dt$	Differential of conversion of triglyceride with respect to time	$(\text{mol}/\text{h})$
$D_f$	Dilution factor	Dimensionless
$E_a$	Activation energy	$(\text{kJ}/\text{mol})$
$k$	Reaction rate constant	$(\text{dm}^3/\text{mol}.\text{h})$
$[\text{ME pure}]_{SD}$	Concentration of ester in the standard references	$(\text{g}/\text{l})$
$m_{oil}$	Weight of oil	$(\text{g})$
$m_{alc}$	Weight of alcohol	$(\text{g})$

$m_{\text{cat}}$	Weight of catalyst	(g)
$MW_{\text{oil}}$	Molecular weight of oil	
$MW_{\text{alc}}$	Molecular weight of alcohol	
$MW_{\text{cat}}$	Molecular weight of ccatalyst	
$n$	Order of reaction	Dimensionless
$N_A$	Initial numbers of moles	(mol)
$Q$	Amount of energy	(J)
$R$	Gas constant	(J/mol.K)
$R_{\text{SD}}$	Ratio of peak area of ester to peak area of internal standard references	Dimensionless
$R_{\text{SP}}$	Ratio of peak area to peak area of internal standard in the sample	Dimensionless
$-r_A$	Rate of reaction	(mol/dm <sup>3</sup> .h)
$-r_{\text{TG}}$	Rate of reaction of triglyceride	(mol/dm <sup>3</sup> .h)
$T$	Reaction temperature	(K)
$t$	Reaction time	(h)
$X$	Conversion of triglyceride	Dimensionless
$V$	Total volume	(dm <sup>3</sup> )

# **PENGHASILAN BIODIESEL MENGGUNAKAN PROSES BERMANGKIN HETEROGEN BERBANTUKAN ULTRABUNYI**

## **ABSTRAK**

Biodiesel adalah bahan alternatif kepada petroleum diesel yang dihasilkan daripada proses transesterifikasi antara alkohol dan minyak sayuran atau lemak haiwan. Proses penghasilan biodiesel berbantuan tenaga ultrabunyi telah dikaji dan mangkin oksida logam alkali bumi seperti MgO, CaO, BaO dan SrO telah digunakan untuk memangkin proses tersebut. Semua mangkin tersebut diuji dengan menggunakan cara pencampuran konvensional bagi mengetahui aktiviti yang paling baik sebagai data latarbelakang. Ultrabunyi mulanya digunakan bagi menggantikan pencampuran mekanikal. Kesan pembolehubah proses dengan dan tanpa penggunaan ultrabunyi termasuk suhu tindakbalas (50-70 °C), kandungan mangkin (0.5-3 wt.%), nisbah metanol kepada minyak (6:1-15:1) dan masa tindakbalas (10-240 min) telah dikaji. Keadaan operasi yang terbaik telah digunakan untuk mengkaji kesan kepelbagaian keadaan ultrabunyi seperti “pulse on” (1-9s), “pulse off” (1-9s), kuasa ultrasonik (20-70 % amplitud), masa tindakbalas (10-50 min) dan berat sampel (30-60 g). Kaedah sambutan permukaan (RSM) telah digunakan untuk mengoptimumkan pembolehubah-pembolehubah. Keadaan yang terbaik telah diuji dengan minyak jagung, minyak kanola, minyak bunga matahari dan minyak sawit terpakai. Hasil biodiesel tertinggi diperolehi pada nisbah metanol terhadap minyak 9:1. Bagi mangkin BaO, hasil biodiesel meningkat sedikit pada suhu melebihi 65 °C dan sebaliknya bagi dua mangkin yang lain. Hasil terbaik iaitu 95.4 % dicapai oleh BaO diikuti dengan SrO pada 86.4 %. Keadaan yang optimum yang diperolehi pada “pulse on” 9 s, “pulse off” 2 s, masa tindakbalas 30.7 minit, kuasa pada 130 Watt dan kandungan minyak sebanyak 52 g. Masa tindakbalas untuk mencapai hasil 96 % bagi proses berbantuan ultrabunyi ialah 30-50 min berbanding 120-180 min bagi proses

pencampuran mekanikal. Keperluan mangkin juga lebih rendah iaitu pada 2.8 %, berbanding 3-5 %. Peningkatan kadar tindakbalas disebabkan oleh pembinasaan buih kavitasi oleh ultrabunyi yang meningkatkan kadar campuran. Hasilnya, persenturan antara bahan tindakbalas meningkat. Kandungan Sr dalam biodiesel sebanyak 18.1 mg/L telah dikesan dan ia membuktikan kestabilan mangkin terhadap ultrabunyi. Sebuah model telah dihasilkan bagi meramal peningkatan haba semasa tindakbalas menggunakan minyak dan mangkin yang berbeza. Pematuhan kualiti biodiesel yang dihasilkan terhadap piawai ASTM dan EN juga dikaji. Selain itu, ia juga lebih jernih serta kurang kandungan asid lemak dan sisa mangkin yang tertinggal di dalam produk. Proses pembasuhan biodiesel didapati dapat meningkatkan kualiti biodiesel. Tindakbalas didapati mengikuti kinetik tertib kedua. Tenaga pengaktifan adalah berbeza antara 70.63 KJ/mol dan 136.93 KJ/mol dengan pekali penentuan yang tinggi. Sebagai rumusan, penggunaan ultrabunyi mengurangkan masa tindakbalas dan penggunaan mangkin. Biodiesel yang diperolehi juga menunjukkan kualiti produk yang lebih baik.

# **BIODIESEL PRODUCTION USING ULTRASONIC-ASSISTED HETEROGENEOUS CATALYTIC PROCESS**

## **ABSTRACT**

Biodiesel, a product from the transesterification of alcohol and vegetable oils or animal fats, is a greener alternative to petroleum diesel. Biodiesel production process assisted by means of ultrasonic energy has been investigated. Alkaline metal earth oxide catalysts i.e. MgO, CaO, BaO and SrO were employed to catalyze the transesterification process. Initially these catalysts were tested in conventional mixing method to find out the best catalytic activities and to serve as background data. Ultrasonic was initially introduced into the reaction as a replacement for mechanical mixing. Effects of process variables for the reaction in the case of both non-ultrasonic and ultrasonic-assisted biodiesel production were investigated. The process variables were the reaction temperature (50-70 °C), catalyst loading (0.5-3 % w/w.), methanol to oil ratio (6:1-15:1) and reaction time (10-240 min). The best operating conditions were used to study the effects of varying ultrasonic conditions such as pulse on (1-9 s), pulse off (1-9 s), ultrasonic power (20-70 % of amplitude), reaction time (10-50 min) and sample weight (30-60 g). Response surface methodology (RSM) was used to optimize the variables. The best conditions were verified using different oil sources i.e. corn oil, canola oil, sunflower oil and used palm oil. The highest biodiesel yield was achieved at a methanol to oil ratio of 9:1. For BaO catalyst, the biodiesel yield showed a graduate increase above 65 °C while for the other two catalysts, it dropped. The best yield was observed using BaO with 95.4% of yield followed by SrO with a yield of 86.4 %. The optimum conditions were achieved at pulse on for 9 s, pulse off of 2 s, reaction time of 30.7 min, at a power of 130 W and an oil amount of 52 g. Compared to stirrer mixing reaction, ultrasonic-assisted process showed significant reduction in time (from 120-180 min



to 30-50 min) and catalyst loading (from 3-5 % to less than 2.8 %) to reach up to 96 % yield. The increase in the reaction rate was attributed to the collapse of cavitation bubbles by ultrasonic which led to high intensity mixing. That improved the contact between the reactants. The stability of the catalyst was also tested to find out the amount of Sr dissolved in the biodiesel product. The trace amount of catalyst of 18.1 mg/L in the product proved the stability of the catalyst under ultrasonic conditions. A model was successfully developed to predict the heat increase in the reaction using ultrasonification. The results were verified using different oils and catalysts. The quality of the biodiesel from ultrasonic-assisted process showed great conformance with ASTM and EN standards besides having a better clarity, less FFA and trace amount of catalyst remaining in the product. Washing the biodiesel was found to be necessary for an even better quality biodiesel. The reaction followed a second-order kinetic. The activation energy varied between 70.63 KJ/mol and 136.93 KJ/mol with relatively high coefficient of determinations. As an overall conclusion, ultrasonic significantly reduced the reaction time and the catalyst requirement. The biodiesel produced by means of ultrasonic showed better qualities compared to that obtained using conventional mixing process.

## CHAPTER 1

### INTRODUCTION

#### 1.1. Current Fossil Fuel Situation

Recently, the increasing demand on fossil fuels leading to the depletion of these resources has turned into a challenging area of study. With the current rate of crude oil consumption, the reserves could be finished in less than 50 years (Crabbe *et al.*, 2001). The high usage of such fuels to generate energy has also caused environmental effects such as global warming (Kawashima *et al.*, 2008; Santos *et al.*, 2009), green house gas emissions and acid rain (Tan *et al.*, 2009), and other environmental pollutions (Kawashima *et al.*, 2009; Trakarnpruk and Porntangjitlikit, 2008). It is reported that emissions from the combustion of fossil fuels including carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>) and sulphur-containing residues are the main reasons for global warming (Crabbe *et al.*, 2001). It is expected that the world overall energy consumption and thus, the CO<sub>2</sub> emissions to the atmosphere could show 60 % increase as compared to 2008. Furthermore, oil and gas prices have been increasing in the past few years (Arzamendi *et al.*, 2008).

Due to the above mentioned issues, the necessity of replacing conventional fossil fuels with environmental friendly substitutes to fulfill the increasing energy demand has been of great concern (Kawashima *et al.*, 2009; Monteiro *et al.*, 2008; Yang and Xie, 2007). Alternatives to replace fossil fuels are such as biofuels, wind and solar energy (Meher *et al.*, 2006b; Santos *et al.*, 2009; Van Gerpen, 2005). The dependence on fossil fuels in transportation is 96 % of the current energy consumed in the sector (Arzamendi *et al.*, 2008). In view of the escalating petroleum price and

the depletion of petroleum feeds, the introduction of biofuel as the fifth source of energy is deemed critical.

## **1.2. Biodiesel**

Recently, fatty acid methyl esters derived from vegetable oil, known as biodiesel, has been considered as an alternative fuel to be used in diesel engines (Kalva *et al.*, 2009; Sharma *et al.*, 2008). Biodiesel fuel is produced by transesterification of vegetable oils and animal fats. This fuel is a biomass based alternative to fossil fuels due to its specifications (Kawashima *et al.*, 2008). It consists of monoalkyl esters and produced through a reaction between the triglycerides available in the vegetable oil or fat and a monohydric alcohol (Hanh *et al.*, 2007a). Biodiesel shows the following general advantages: (1) lower dependence on crude oil, (2) renewable fuel, (3) favorable energy balance, (4) reduction in greenhouse gas emission, (5) lower harmful emission, (6) biodegradable and non-toxic, (7) the use of agricultural surplus, and (8) safer handling (higher flash point than conventional diesel fuel) (Abdullah *et al.*, 2007).

The properties of biodiesel depend very much on the nature of its raw material as well as the technology or process used in its production. There are several methods of biodiesel production reported such as homogeneous acid-catalyzed process (Di Serio *et al.*, 2005; Lotero *et al.*, 2005; Mbaraka and Shanks, 2005), supercritical process (Bertoldi *et al.*, 2009; Tan *et al.*, 2009; Zhao *et al.*, 2009), enzymatic process (Liu *et al.*, 2009; Ognjanovic *et al.*, 2009) and homogenous base catalyzed process (Jeong *et al.*, 2008; Sinha *et al.*, 2008). Base catalysts are often more effective than acid catalysts and enzymes (Sakai *et al.*, 2009).

### 1.3. Transesterification

Biodiesel is generally produced by transesterification of oils and fats with short chain alcohols (i.e. methanol, ethanol, propanol and butanol) in the presence of suitable catalysts. Glycerol is produced as the by-product of the reaction. The transesterification process is shown in Figure 1.1. Stoichiometrically, the reaction requires 3 moles of alcohol and 1 mole of triglyceride in order to produce 3 moles of biodiesel and 1 mole of glycerol (Sinha *et al.*, 2008). However, due to the reversible nature of this reaction, in practice, a higher molar ratio is employed in order to shift the equilibrium towards favorable side to achieve higher ester production (Kalva *et al.*, 2009; Meher *et al.*, 2006b). In this reversible reaction, diglycerides and monoglycerides are intermediate products. The final product in step three would be fatty acid methyl esters (biodiesel) and glycerol.

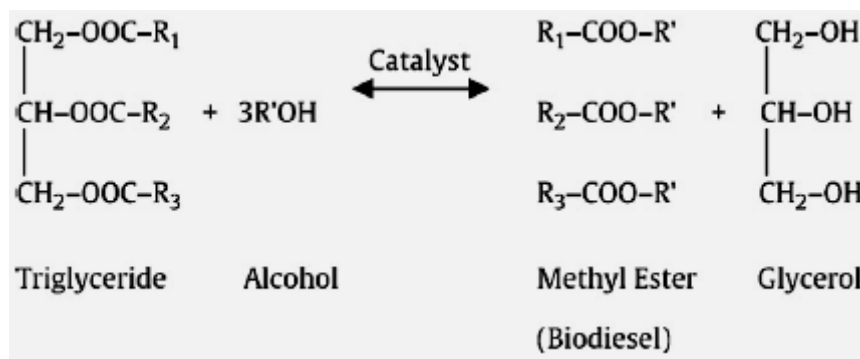


Figure 1.1 Transesterification of triglycerides for the production of biodiesel (Singh and Fernando, 2008)

Esters are the desired products of the transesterification reactions. After the reaction, glycerol is separated by settling or centrifugation and is purified to be used in traditional applications (pharmaceutical, cosmetic and food industries) or in recently developed applications in the fields of animal feed, carbon feedstock in fermentations, polymers, surfactants and lubricants (Ma and Hanna, 1999). Glycerol

recovery is also crucial because of its several applications in different industrial processes including CP/USP glycerin (Emery 916) and dynamite glycerol. Glycerol is separated by gravitational settling or centrifugation (Meher *et al.*, 2006b).

#### **1.4. Catalyst for the Transesterification Process**

Biodiesel production process is usually catalyzed by enzymatic, acidic or basic catalysts. Sulfuric acid and hydrochloric acids are usually used for the acid catalyzed process. These catalysts are used for oils with high free fatty acid and more water content. Acid-catalyzed processes require longer reaction time and higher ratio of alcohol to oil (Di Serio *et al.*, 2005; Furuta *et al.*, 2004). Biodiesel is mainly produced from refined/edible type oils using methanol and alkaline catalyst. The difficulty of alkaline-esterification of non-edible oils and fats is soap production which inhibits the separation of ester and glycerin. This phenomenon is attributed to large amounts of free fatty acids present in the non edible/not refined oils (Gerpen, 2005).

For an alkali-catalyzed transesterification process, the glycerides and alcohol must be substantially anhydrous as the undesired saponification reaction caused by water will result in the production of soap (Parlak *et al.*, 2008). The amount of catalyst used in the process has great environmental impact. High amounts of catalyst will have the tendency to produce larger amount of soap which is an undesired product. Besides, the remaining catalyst can end up in the increase of biodiesel pH (Santos *et al.*, 2009). The typical catalyst used for production of biodiesel is homogeneous base catalyst such as KOH and NaOH. This process can produce high methyl ester yield under atmospheric pressure and temperature of 50-65 °C which is

usually carried out in 1-4 hours (Kawashima *et al.*, 2008; Meher *et al.*, 2006b; Santos *et al.*, 2009). In order to improve the biodiesel quality to meet certain intentional standards, purification is required prior to its use. This could be achieved by removing impurities such as catalyst and glycerol by hot water washing and further purification processes which generates enormous amounts of wastewater (Sakai *et al.*, 2009; Xie *et al.*, 2006b). Thus, replacing conventional homogeneous catalysts with environmentally friendly heterogeneous catalysts seems to be essential for the benefit of lower production costs and environmental considerations.

### **1.5. Heterogeneous Catalysis in Biodiesel Production**

Due to environmental concerns, the interest in biodiesel production has shifted to the use of heterogeneous catalysts. This is due to easier catalyst removal without any need for solvents, reusability of the catalyst and less corrosive character of heterogeneous catalysts (Dossin *et al.*, 2006). They can also be designed to give higher activity, selectivity and longer catalyst lifetimes (Liu *et al.*, 2007). Heterogeneous catalyst can also be divided into two groups, i.e. acid catalysts and base catalysts. It has been reported that acid catalysts usually show weak activity and react at high temperatures with a longer reaction time as compared to base heterogeneous catalysts (Xie *et al.*, 2006b). Various types of heterogeneous catalysts for transesterification process have been reported by several researchers. It has been reported that alkaline and alkaline-earth metals compounds are recently used in biodiesel production to replace conventional homogenous catalysts (Arzamendi *et al.*, 2008; Dossin *et al.*, 2006; Yang and Xie, 2007). Alkaline and alkaline-earth metals supported on other materials such as alumina and silica can be considered as potential catalysts for transesterification. Zeolites are another group of catalysts

studied for transesterification process (Albuquerque *et al.*, 2009; Brito *et al.*, 2007). Clay minerals such as hydrotallic, chrysotile and sepiolite are considered to be the next group. These clay minerals are in the group of modest or weakly basic catalysts (Ono, 2003).

It is obvious that in recent years that the research focus has been shifted towards the use of solid base catalyst in biodiesel production due to its benefits. Yet, there are a lot more to understand about the natures of these catalysts. Clarifying the nature of the interaction between the support and the catalytically active component in the process is still worthy of further research. In this new process, the catalyst promotes the transesterification reaction without catalyst loss. Yet, it is known that solid base catalysts can be easily poisoned by water or carbon dioxide. Poisoning is the loss of activity due to strong chemisorption on the active sites by impurities present in the feed stream. When solid bases are used in liquid phase organic reactions, the reaction rate may decrease due to the diffusion of reactants and products. One of the main drawbacks of heterogeneous catalysts is lower catalytic activity as compared to that of homogeneous catalysts such as KOH (Kawashima *et al.*, 2008). Consequently, the reaction needs to be performed at higher temperature and pressure than those in homogeneous processes with an excess of methanol. This will certainly increase the production costs and, therefore, more research work is needed to improve this technology to make it more interesting economically and favorable environmentally.

## 1.6. Immiscibility of the Reactants

Oil and alcohol as the 2 main reactants in the transesterification process are mutually immiscible. This reaction is therefore a mass-transfer-limited one due to this immiscibility (Cintas *et al.*, 2010). The rate of the reaction is very much dependent on the mixing ability of the reactants providing a better contact area. The main reason for low reaction rates of transesterification process is the mass transfer limitations since the oil and alcohol form immiscible phases in the system (Kelkar *et al.*, 2008). To overcome this problem, researchers have recently introduced new methods to make rigorous mixing in the system. One of the techniques is the use of cavitation which result in conditions of local intense turbulence and liquid circulation currents. These cavitations are expected to increase the rates of chemical reactions which are limited by mass transfer resistances (Deshmane *et al.*, 2009; Kelkar *et al.*, 2008).

Ultrasonic is one of the approaches that attract much attention in this process to overcome the immiscibility of the reactants (Fan *et al.*, 2010; Hingu *et al.*, 2010; Kumar *et al.*, 2010). Ultrasound is cyclic sound pressure with a frequency greater than the upper limit of human hearing. Although this limit varies from person to person, it is approximately 20 kilohertz (20,000 hertz) in healthy, young adults and thus, 20 kHz serves as a useful lower limit in describing ultrasound. Figure 1.2 demonstrates the approximate frequency ranges corresponding to ultrasound, with rough guide of some applications (Novelline, 1997).

Sonochemical techniques involve the use of ultrasonic waves to produce an oxidative environment via cavitation bubbles generated during the rarefaction period



of sound waves. The formation, growth, and collapse of cavitation bubbles, in the presence of ultrasonic waves leading to high local temperatures and pressures, are considered the main mechanism through which chemical reactions occur in sonochemistry. This leads to the increase the efficiency and reduce the time required for the reaction (Ghodbane and Hamdaoui, 2009). In a homogeneous aqueous system, three different reaction sites have been postulated: (i) the gaseous interiors of collapsing (ii) the interfacial liquid region between cavitation bubbles and the bulk solution (iii) the bulk solution region (Adewuyi, 2001; Thompson and Doraiswamy, 1999).

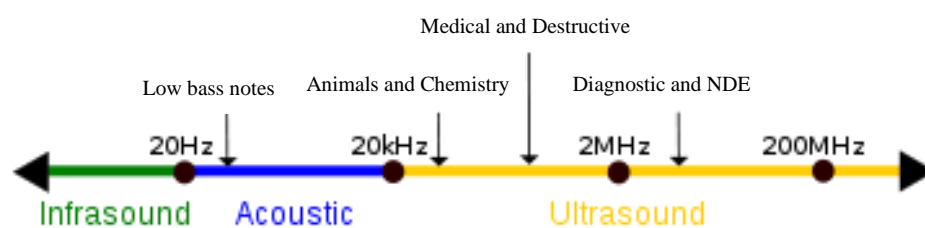


Figure 1.2 Approximate frequency ranges corresponding to ultrasound, with rough guide of some applications (Novelline, 1997)

### 1.7. Biodiesel Oil Source

The source for biodiesel production is usually chosen according to the availability in each region or country. In Brazil, biodiesel production has been adjusted to the available crop in each region of the country. In the north, palm kernel and soybean are the most commonly used oil sources while in the northeast, castor bean, palm oil, palm kernel, babassu, soybean and cotton seed are more popular. In the central west, soybean, cotton seed, castor bean and sunflower seed are more preferred while in the southeast, soybean, castor bean, cotton seed and sunflower seed are more suitable (Pinto *et al.*, 2005). There are different oil sources reported in

scientific articles showing their suitability for biodiesel production. Soybean oil (Kim *et al.*, 2004), sunflower oil (Stamenkovic *et al.*, 2007), rubber seed oil (Ramadhas *et al.*, 2005), palm kernel oil (Chongkhong *et al.*, 2007), canola oil (Strayer *et al.*, 1983), rapeseed oil (Rashid and Anwar, 2008; Strayer *et al.*, 1983), coffee oil (Oliveira *et al.*, 2008), are some examples of oil sources investigated for biodiesel production. Figure 1.3 summarizes the number of technical reports on various vegetable oils that have been used to produce biodiesel and mostly soy, sunflower and rapeseed oils have been reported to be the feedstocks (Pinto *et al.*, 2005).

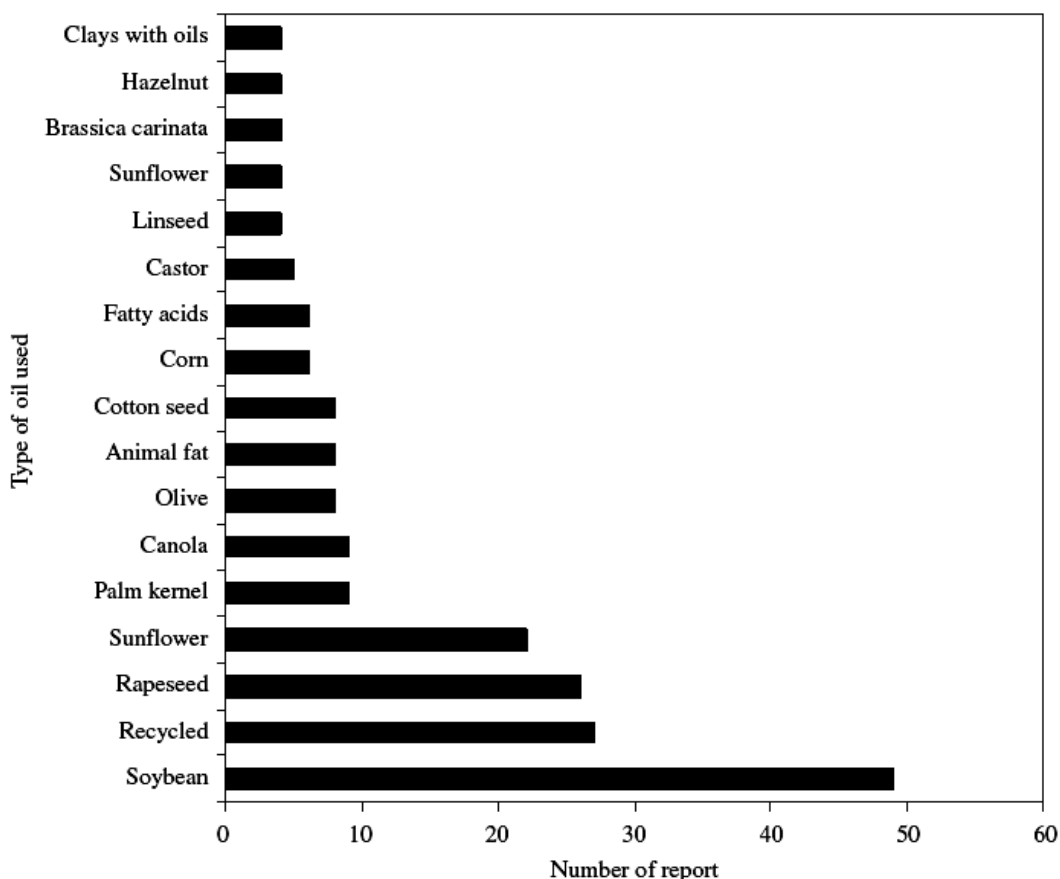


Figure 1.3 Number of scientific articles in 2005 on oils used as feedstock for biodiesel production (Pinto *et al.*, 2005)

## **1.8. Palm Oil a Potential Feedstock**

Despite rarely reported, palm oil possesses high potential due to high production rate to meet the future demand as well as having high oil content as shown in Figure 1.4 (Sumathi *et al.*, 2008). As noted in the figure, the oil productivity per hectare of oil palm is about 14 times better than that of soy oil and the nearest rival is coconut oil with a productivity of about 22 % lower. Life cycle analysis (LCA) conducted on various biodiesels revealed that palm oil-based biodiesel can reduce the current emission rate of greenhouse gases (GHG) by 62 % as compared to that of soy-based (40 %), rapeseed-based (45 %) and sunflower-based (58 %) (Sani, 2009b). Thus, leading producers of palm oil like Malaysia are looked upon to be the anchors to produce palm oil-based biodiesel and exporters to other regions of the world.

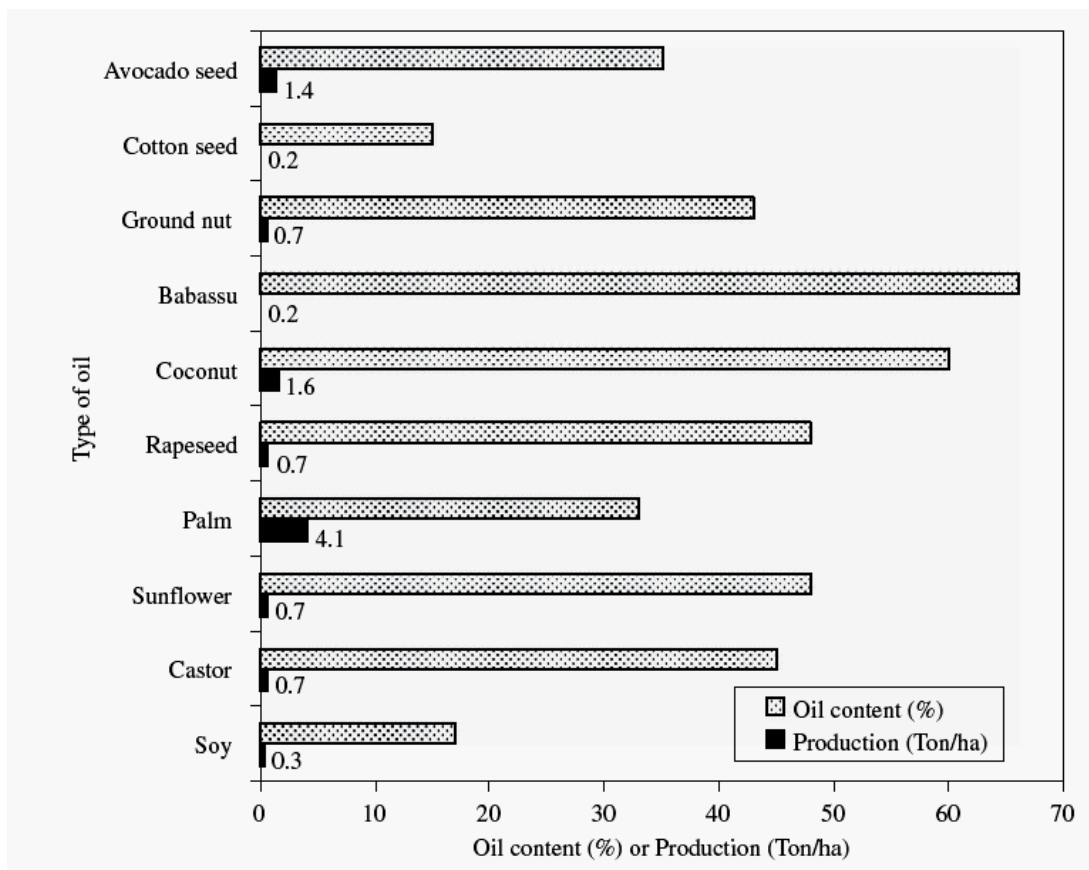


Figure 1.4 Production rate and oil content of various oil sources for biodiesel feed stocks (Sumathi *et al.*, 2008)

### 1.9. Ultrasonic-Assisted Biodiesel Production Process

Lately, the use of ultrasonic energy for biodiesel production has become an area of interest to so many researchers (Deshmane *et al.*, 2009; Hanh *et al.*, 2007a; Ji *et al.*, 2006; Kalva *et al.*, 2009; Santos *et al.*, 2009; Wu *et al.*, 2007). Because of the immiscibility of a liquid-liquid heterogeneous system, the reaction between oil and alcohol only occurs in the interface of the two phases (Kalva *et al.*, 2009). Conventionally, vigorous mechanical stirring or agitation is used to homogenize the reactants to enhance the interfacial area between the two phases (Arzamendi *et al.*, 2008; Jeong *et al.*, 2009; Yang and Xie, 2007). In conventional stirring method to achieve high yields (>90 %), a temperature of 50-65 °C in presence of catalyst 0.5-3.0 % and reaction times of longer than 2 h are required (Kawashima *et al.*, 2009;

Yuan *et al.*, 2008). According to (Kalva *et al.*, 2009), the reaction rate was very dependent on the interfacial contact of two phases and also the alcohol anions which initiated the biodiesel production reaction.

The use of ultrasonic energy as the source of mixing has become a great interest by two means. It can produce a homogeneous mixture in a very short time and at the same time, it can increase the biodiesel production yield. Ultrasonic has been reported to show its effects in accelerating a liquid-liquid immiscible reaction system through cavitation bubbles (Santos *et al.*, 2009; Stavarache *et al.*, 2007a; Wu and Zong, 2005). The asymmetric collapse of the cavitation bubbles disrupts the phase boundary and impinging of the liquids creates micro jets, leading to intensive mixing of the system near the phase boundary. Cavitation may also lead to a localized increase in temperature at the phase boundary, thus, enhancing the transesterification reaction. Ultrasonic irradiation has been used to accelerate many heterogeneous catalytic processes. It has been reported that the use of ultrasonic energy in biodiesel production process using homogeneous catalyst can lead to a shorter reaction times of 10-40 min with 2 to 3 times lower amount of catalyst needed as compared to those in normal mechanical stirring reactor (Thanh *et al.*, 2010).

#### **1.10. Problem Statement**

Biodiesel is one of the alternatives that researchers are showing great interest to investigate it more. Conventional biodiesel production processes are still more expensive as compared to those of fossil diesel. The cost of the biodiesel as compared to diesel does not make it favorable alternative to fossil fuels. One of the

important issues which can directly reduce the cost is the reduction in the production costs. These expenses are such as the heating, labor work, mixing, raw material use etc. On the other hand, generally biodiesel is produced from refined vegetable oils. These oils are expensive and at the same time can be used for edible purposes.

Homogeneous catalyst has many environmental impacts due to production of wastewater during the separation process. Alcohol and oil are also immiscible and as the reaction only happens in the interface of the phases. Thus, the production of biodiesel requires a lot time and excess catalyst to assure high yields. This aspect can increase the biodiesel production costs. Therefore, as an ultimate objective, alternative method to decrease the process costs and time should be identified. Long reaction time will directly and indirectly affect the production cost of biodiesel. Effective transesterification process usually occurs at temperatures higher than 60 °C. Thus, reduction in the reaction time can cause less time of energy consumption for heating the system. This highlights the importance of finding technologies which are less costly and less energy consumption. Time reduction can also reduce the labour work for production of the same amount of biodiesel which will reduce the overall biodiesel production cost. Ultrasonic has recently been introduced to intensify the immiscible reactions such as transesterification. Yet, there are aspects of the ultrasonic use in biodiesel production which require further investigations. The areas which are not fully investigated yet are such as behaviour of the ultrasonic-assisted process, effects of ultrasonic on the reactants and the catalysts, effects on biodiesel quality, optimization of the reaction based on different aspects and also the kinetic modeling of the reaction.

Biodiesel needs to meet strict requirements according to ASTM D6751-07 or EN 14212:2003 to be used as a substitute for fossil diesel. This compliance is a very challenging task. In order to produce biodiesel that consistently fulfills the technical regulation, a strict procedure for the raw material, conditions and catalyst should be followed. This technology should also have the feasibility to be scaled up. Thus, the reaction rates and optimized operating conditions are also of great concern in this study. The use of ultrasonic is expected to intensify the reaction due to the better mixing effects caused by the cavitations produced by this energy. Thus, it will be fully investigated in this work. It is necessary to evaluate the quality of the biodiesel produced to make sure that also ultrasonic cavitations has no adverse effect on the quality to make it not suitable engine use.

### **1.11. Impacts Towards Society and Country**

Palm oil possesses high potential due to high production rate to meet the future demand of biodiesel industries as well as having high oil content. The development of the oil palm sector in Malaysia is best described as having been most colourful. Malaysia is currently the world's second top producer of palm oil (after Indonesia) in 2008/09 (Mamat, 2009). By increasing the demand on energy and the intensified production and usage of this renewable energy source, Malaysia could find itself as a potent country in this area. In Malaysia, biodiesel is included in the list of products/activities that are encouraged under the Promotion of Investment Act 1986. The positive growth of industries related to biodiesel can directly and indirectly affect job opportunities in Malaysia. Besides, it is also in line with the global efforts to reduce the green house gasses. All these factors will contribute to the Malaysian

palm oil-based biodiesel development. This new method can enhance and accelerate the biodiesel production in Malaysia.

The use of ultrasonic energy in biodiesel production can provide a solution towards a cheaper and simpler process. This technology can reduce the biodiesel production cost by reducing costs involved in the production process such as the amount of raw material, reaction time, labour work and heating energy required. This cost reduction can benefit Malaysia as the world leading palm oil to emerge as a leading country in biodiesel production. By reducing the biodiesel price, the technical issues with respect to the cost of this product compared to fossil diesel in the market will also be easier to deal with.

#### **1.12. Expected Output and Application**

The main goal of this study is to develop a suitable method which can be used to accelerate the conversion of palm oil to a high quality biodiesel. For this purpose, an ultrasonic-assisted heterogeneously catalyzed reactor is used to speed up the process. Ultrasonic-assisted biodiesel production is expected to be an energy saving process as compared to conventional methods. This process aims at a more cleaner and environment friendly process. The physical properties of the biodiesel are also aimed to be improved so that the product can be used in diesel engine based on available standards. The conditions involving the reaction in different aspects are expected to be optimized to obtain a high quality low cost biodiesel. Kinetics of the ultrasonic-assisted process will also be investigated in this study. The capability of the system will be extended to different types of vegetable oils and used palm oil. It



is also expected to use the ultrasonic energy as the heating source in the reaction system.

### **1.13. Scopes of the Study**

In this study, 4 different types of alkaline metal earth oxide catalysts i.e. MgO, CaO, BaO and SrO are employed to catalyze the transesterification process. Initially these catalysts are tested in conventional method to find out the best catalytic activities and to serve as background data. Ultrasonic is initially introduced into the reaction as a replacement for mechanical mixing. Process variables for the reaction in the case of both non-ultrasonic and ultrasonic assisted biodiesel production are studied and compared. The process variables investigated include reaction temperature (50-70 °C), catalyst loading (0.5-3 % w/w.), methanol to oil ratio (6:1-15:1) and reaction time (10-240 min). The optimized operating conditions from the first part are used to study the effects of varying ultrasonic conditions such as pulse on (1-9 s), pulse off (1-9 s), ultrasonic power (20-70 % of Amplitude), reaction time (10-50 min) and sample weight (30-60 g). Response surface methodology is a statistical method that is employed to optimize the above mentioned variables. The best conditions are to be used for different oil sources i.e. corn oil, canola oil, sunflower oil and used palm oil. The free fatty acid and moisture content of these oils are also studied to check their effect on the yield.

As ultrasonic is expected to disperse energy and act as a heat source. Thus, studies on its use as a heat source are also attempted. Different ultrasonic parameters were used to model the final reaction temperature created by ultrasonic irradiation. Kinetic studies are carried out considering each of the three steps of

transesterification individually. Selected samples of biodiesel obtained from ultrasonic-assisted and non ultrasonic biodiesel production process catalyzed by the most suitable catalyst in the form of pure and blend of B10 are also tested for the compliance with international biodiesel standards. The characterizations of the catalyst are performed by means of scanning electron microscopy (SEM) surface analysis, atomic adsorption spectrophotometer (AAS) and Hammet indicator methods.

#### **1.14. Objectives**

This research project is planned and carried out to address the following objectives:

- To identify the most active and stable heterogeneous catalyst among the metal earth oxides (group 2) to replace conventional homogeneous catalysts;
- To optimize the conditions affecting biodiesel production such as time, molar ratio, catalyst loading and temperature under various ultrasonic conditions and testing with different oils;
- To utilize and optimize ultrasonic as the heat source for transesterification process;
- To characterize the physical properties of the biodiesel produced and the performance.
- To study the kinetics of the ultrasonic-assisted biodiesel production process.

### **1.15. Organization of the Thesis**

This thesis contains six main chapters. The first chapter (Introduction) will briefly introduce the research project, the problem statement, and the scope of the study. In the Literature Review section (Chapter 2), an overview of the reported results related to this study and the main basic knowledge about this project such as ultrasonic application, transesterification, kinetic modeling and others are discussed in detail. Chapter Three (Materials and Methods) includes descriptions on the materials, experimental procedures and instrumental analyses used in this study. The response surface methodology (RSM) designs used including the ranges of variables and the codes used are introduced and discussed in this section. This chapter is presented in great detail and arranged in such a way that other researchers can get sufficient details to repeat the experimental works. Discussions on the results generated in this project are covered in Chapter Four. This chapter is sectionalized into different parts to fully cover the objectives of this study. In Chapter Five (Conclusions and Recommendations), the overall conclusions based on results and findings made in the present study are given in brief. Recommendations for future research based on the understanding and knowledge generated in the present study are also given in this chapter.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1. Introduction

This chapter provides an overview and the background of the study which are crucial to the understanding of this area. Related literature and findings by other researchers are reviewed in this chapter.

#### 2.2. Biofuel Production

##### 2.2.1. Direct Use and Blending

In early 1980s, the use of vegetable oils as a substitute for fossil fuels attracted a lot of discussion. Substituting 100 % of vegetable oil for diesel fuel at that time was not practical. Thus, the use a blend of 5-20 % of vegetable oil and diesel were suggested. Physical properties of biodiesel blends with diesel are illustrated in Table 2.1. As observed in the table, increasing percentage of the biodiesel in the blend results in a reduction in calorific value with corresponding increase in other parameters such as acid number, viscosity and flash point. The reduction in calorific value for the biofuel and its blends compared to diesel is due to the presence of oxygen in the biofuel (Phan and Phan, 2008).

There are several advantages to utilize vegetable oils as diesel fuels. These advantages are such as (1) liquid nature-portability, (2) heat content (80% of diesel fuel), (3) ready availability and (4) renewability. Some disadvantages are also been reported for the use of vegetable oils as fuel including (1) higher viscosity, (2) lower volatility and (3) the reactivity of unsaturated hydrocarbon chains. Some problems may also occur after a longer engine run using vegetable oils. Problems which

mostly occur in direct-injection engines are (1) coking and trumpet formation on the injectors, (2) carbon deposits, (3) oil ring sticking and (4) thickening and gelling of the lubricating oil as a result of contamination by vegetable oils (Ma and Hanna, 1999). Due to this disadvantages, direct use of vegetable oils and/or use of blends of oils are generally considered impractical and unfeasible for both direct and indirect diesel engines (Sharma *et al.*, 2008).

Table 2.1 Physical properties of FAME blends with diesel (Phan and Phan, 2008).

Quantity	Unit	Samples							
		B5	B10	B15	B20	B25	B30	B50	B75
Density	g/ml	0.85	0.85	0.85	0.85	0.85	0.86	0.86	0.88
Viscosity at 40°C	mm <sup>2</sup> /s	3.56	3.72	3.72	3.75	3.82	3.90	4.25	4.64
Cloud point	°C	0	0	0	0	0	0	0	0
Pour point	°C	-12	-11.5	-9.5	-9	-8.5	-8	-6	-4.5
Flash point	°C	74	80.5	81	82	85	86	91	106.5
Calorific value	kcal/kg	10845	10750	10683	10615	10545	10462	10180	10100
Water content	wt%	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Acid number	mg KOH/g	0.11	0.12	0.13	0.16	0.20	0.23	0.32	0.35

### 2.2.2. Emulsification (Microemulsions)

A microemulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1±150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles (Meher *et al.*, 2006b; Sharma *et al.*, 2008).

### **2.2.3. Thermal Cracking (Pyrolysis)**

Strictly defined, pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. Pyrolysis typically occurs under pressure and at operating temperatures above 430 °C (800 °F). It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield smaller molecules (Meher *et al.*, 2006, Demirbas, 2009).

### **2.2.4. Transesterification (Alcoholysis)**

The most commonly used method is the transesterification of vegetable oils and animal fats. This method is more suitable and the by-product (glycerol) has commercial value (Ma and Hanna, 1999). Transesterification (alcoholysis) is the chemical reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters. Transesterification process consists of a sequence of three consecutive reversible reactions. That is, conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides (Meher *et al.*, 2006, Basha *et al.*, 2008).

## **2.3. Biodiesel**

### **2.3.1. Introduction**

Biodiesel is a combination of a Greek word (bio) meaning life and diesel taken from Rudolf Diesel as the inventor of diesel engines. It is referred to a diesel-equivalent processed fuel derived from biological sources. Recently, biodiesel has attracted lots of attention worldwide in blends with diesel or directly replaced with petroleum diesel fuel in vehicle engines. In 1895, Rudolf Diesel developed a new engine with the intention that it could use a variety of fuels, including vegetable oil.

However, vegetable oils got neglected as a source of fuel at that time due to the fact that readily available fossil fuels were available then. Recently, due to limited reserve of crude oil and threat to well being of mankind from emissions of exhaust gases, vegetable oil has been reconsidered as potential substitute as a fuel in various engines (Muniyappa *et al.*, 1996).

Unprocessed vegetable oil can also be used in diesel engines, but it requires extensive engine adjustments and modifications due to its high viscosity and low volatility (Xie and Li, 2006). Unlike diesel fuel, saturated hydrocarbons are one of the main components of vegetable oils. They mostly consist of triglycerides, glycerol and esters of fatty acids. The fatty acids vary in their carbon chain length and in the number of double bonds. To solve these issues, pure vegetable oils have to undergo some modification to fulfill the combustion-related properties required more closer to those of petroleum diesel (Enweremadu and Mbarawa, 2009). Technical properties and general characteristics of biodiesel are tabulated in Table 2.2 based on ASTM D 6751.

Table 2.2 Technical properties and selected general characteristics of biodiesel according to ASTM D 6751

Common name	Biodiesel (bio-diesel)
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	$C_{14}-C_{24}$ methyl esters or $C_{15-25}H_{28-48}O_2$
Kinematic viscosity range ( $mm^2/s$ , at 313 K)	3.3–5.2
Density range ( $kg/m^3$ , at 288 K)	860–894
Boiling point range (K)	>475
Flash point range (K)	420–450
Distillation range (K)	470–600

Vapor pressure (mm Hg, at 295 K)	<5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

Biodiesel, an alternative diesel fuel, originate from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic has low emission profiles and is environmentally beneficial. In general, it is composed of fatty acid methyl esters and prepared through transesterification of triglycerides in vegetable oils or animal fats with methanol (Kouzu *et al.*, 2009a). The resulting biodiesel has almost the same specifications as conventional diesel fuel in its main characteristics. Most biodiesel, are produced from refined/edible types of oil using methanol and alkaline catalysts (Xie *et al.*, 2006b).

### 2.3.2. Biodiesel Raw Materials

Typically, biodiesel is produced from different raw material sources i.e. rapeseed oil, canola oil, soybean oil, sunflower oil and palm oil. Beef and sheep tallow and poultry oil from animal sources and cooking oil are also possible sources of raw materials. Various oils have been in use in different countries as raw materials for biodiesel production depending to its availability. Soybean oil is commonly used in the United States, rapeseed oil is used in many European countries for biodiesel production while, coconut and palm oils are used in Malaysia and Indonesia (Demirbas, 2006; Ghadge and Raheman, 2006; Sarin *et al.*, 2007). Rapid increase in biodiesel production capacity and governmental mandates for alternative fuel usage around the world, recently, has intensified the development of alternative biodiesel



feedstocks. This is because meeting the increasing production capacity and mandated demand is not really possible using traditional sources for biodiesel production (soybeans, rapeseed/canola, palm, and various greases and used cooking oils, for instance).

Alternative feedstocks normally arise out of necessity from regions of the world where the above materials are not locally available or as part of a concerted effort to reduce dependence on imported petroleum. As an example, non-edible *Jatropha curcas* (Jatropha) oil has recently attracted considerable interest as a feedstock for biodiesel production in India and other climatically similar regions of the world (Azam *et al.*, 2005; Kumar Tiwari *et al.*, 2007). The Jatropha tree is a perpetual poisonous oilseed bush (up to 5 m) belonging to the Euphorbiaceae family which its seeds contain up to 30 wt % oil. It can be found in tropical and subtropical regions such as Central America, Africa, the Indian subcontinent, and other countries in Asia (Azam *et al.*, 2005).

Another non-edible feedstock is *Pongamia pinnata* (Karanja or Honge), mostly originated from India. It is a medium-sized (18 m) deciduous tree that grows fast in humid and subtropical environments. After 4 to 7 years, it is mature enough to provide fruit consisting of one to two kidney-shaped kernels (Azam *et al.*, 2005). The oil content of Karanja kernels varies between 30 and 40 wt % (Karmee and Chadha, 2005). Oleic acid is the main fatty acid found in Karanja oil (45–70 wt %), followed by linoleic, palmitic, and stearic acids (Karmee and Chadha, 2005; Naik *et al.*, 2008).

*Madhuca indica*, commonly known as Mahua, is a tropical tree found largely in the central and northern plains and forests of India. It belongs to the Sapotaceae family and grows quickly to approximately 20 m in height, possesses evergreen or semi-evergreen foliage, and is adapted to arid environments (Ghadge and Raheman, 2006; Kumari *et al.*, 2007). Consisting of one to two kidney-shaped kernels, the non-edible fruit is obtained from the tree after 4 to 7 years. The oil content of dried Mahua seeds is around 50 wt %. Mahua oil is characterized by an FFA content of around 20 wt % and a relatively high percentage of saturated fatty acids which makes it suitable as a feedstock for biodiesel production (Ghadge and Raheman, 2005, 2006). *Melia azedarach*, generally known as syringa or Persian lilac, is a deciduous tree which grows between 7 and 12 m in height in the mahogany family of Meliaceae that is native to India, southern China, and Australia (Stavarache *et al.*, 2008). The oil content of dried syringa berries, which are unedible due to poisonous nature of them, is around 10 wt %. Syringa oil is characterized by a high percentage of unsaturated fatty acids such as oleic (21.8 wt %) and linoleic (64.1 wt %) acids. Other constituents that are present in greater than 1 wt % are saturated species such as palmitic (10.1 wt %) and stearic (3.5 wt %) acids (Stavarache *et al.*, 2008).

*Moringa oleifera*, commonly known as Moringa, is an oilseed tree that grows in height from 5 to 10 m and is the most widely known and distributed of the Moringaceae family (Rashid *et al.*, 2008). The Moringa tree, indigenous to sub-Himalayan regions of northwest India, Africa, Arabia, Southeast Asia, the Pacific and Caribbean islands, and South America, is now also distributed in the Philippines, Cambodia, and Central and North America. It thrives best in a tropical insular climate and is plentiful near the sandy beds of rivers and streams (Rashid *et al.*, 2008). *Nicotiana tabacum*, commonly referred to as tobacco, is a common oilseed