

**TRANSESTERIFICATION OF CRUDE JATROPHA OIL BY
ULTRASOUND-ASSISTED PROCESS IN THE PRESENCE OF
HETEROPOLYACID BASED CATALYSTS**

by

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LIST OF SYMPOLS

A	The pre-exponential factor of Arrhenius equation.	
a	Specific surface area of the catalyst.	m ² /g
C	Molar concentration.	mol/L
DF	Dilution factor.	
E	Activation energy.	kJ/mol
k	Effective reaction rate constant.	
k _{app}	Apparent reaction rate constant.	
k _m	Mass transfer coefficient towards the catalyst surface.	
k _s	Mass transfer coefficient towards catalyst surface active sites.	
M	Molarity.	mol/L
n	Number of experiments.	
n _i	Number of moles of substance.	mol
R	The gas constant.	J/mol.K
R _i	Relative areas ratio of GC graph.	
R ²	Coefficient of determination.	
SS _i	Total sum of square.	
T	The reaction temperature.	K
v	Volume.	L or ml
w	Weight.	g
X _i	Variables corresponding to the reaction factor.	
x	Molar ratio of Cs ion to heteropoly anion.	

Y	The response generated by a mathematical expression.	
y	FAME yield.	
α	Distance from the center in the central composite design.	
$\gamma, \beta, \delta, \eta$	Reaction orders with respect to substances.	
ε	The error.	
θ	The ratio of initial concentration of methanol to the initial triglyceride concentration.	
κ	Number of variables.	
λ_i	The linear effect coefficient of 2 nd order equation of regression model.	
λ_{ii}	The quadratic effect coefficient of 2 nd order equation of regression model.	
λ_{ij}	The cross-product effect coefficient of 2 nd order equation of regression model.	
λ_0	The constant factor of 2 nd order equation of regression model.	
ρ	Mass concentration.	kg/L
φ	The fraction of the catalyst available active specific surface.	
χ	Conversion.	

LIST OF ABBREVIATIONS

AC	Activated carbon.
Al	Gamma-alumina.
ANOVA	Analysis of variance.
ASTM	American Standard for Testing and Materials.
BET	Brunauer-Emmet-Teller.
CCD	Central composite design.
CPO	Crude palm oil.
C.V.	The coefficient of variation.
DOE	Design of experiment.
EDAX	Energy dispersive X-ray.
ESG	Eruca sativa gars.
EU	European Union standards.
F	Fisher F-test.
FAME	Fatty acid methyl ester.
FFA	Free fatty acid.
FT-IR	Fourier Transformed Infrared Spectrometry.
FPO	Fresh palm oil.
GC	Gas chromatography.
HPA	Heteropoly acid.
ICP	Inductivity coupled plasma.
IUPAC	International union of pure and applied chemistry.
P	Pressure.
PMo	Molibdophosphoric acid.
Prob>F	Probability value.
RSM	Response surface methodology.

SEM	Scanning electron microscopy.
SiW	Tungstosilicic acid.
TEM	Transmission electron microscopy.
TPA	Tungstophosphoric acid.
UPO	Used cooking palm oil.
UV-vis	Ultra-violet visible.
VHCJO	Very high FFA content crude Jatropha oil.
XRD	X-ray diffraction.

SUBSCRIPTS

Adj	Adjusted value.
cat	Catalyst.
err	Error.
exp	Experimental value.
F	Fatty acids.
G	Glycerol.
IS	Internal standard.
M	Methanol.
mean	Mean value.
sam	Sample.
st	Standard material.
T	Triglyceride.
tot	Total.

**TRANSESTERIFIKASI MINYAK JATROPHA MENTAH
MELALUI KAEDAH ULTRABUNYI DENGAN KEHADIRAN
MANGKIN ASID HETEROPOLI**

ABSTRAK

Kajian ini memberi lebih tempuan terhadap penghasilan FAME daripada minyak *Jatropha* yang mengandungi kandungan air dan FFA yang tinggi melalui proses ultrasonifikasi. Proses ultrasonifikasi dilakukan bagi mengubahsui penghalang dalaman pemindahan jisim antara minyak dan metanol bagi mengurangkan masa tindakbalas dan suhu yang diperlukan. Mangkin berasid baru yang berasaskan asid heteropoli (TPA) telah dihasilkan, dicirikan dan digunakan di dalam proses transesterifikasi. TPA telah disekatgerak ke atas karbon teraktif dan alumina atau ditukarkan kepada garam cesium bagi memperbaiki kualiti untuk menghalang kebolehlarutan di dalam media berkutub. Kesan TPA yang berbeza ke atas penyokong dan nisbah molar sebanyak 1.5 telah dikaji dan dicirikan. TPA20-AC, TPA25-Al dan garam cesium dengan nisbah molar sebanyak 1.5 telah digunakan di dalam pengoptimuman process dengan kaedah rekabentuk eksperimen (DOE). Empat pengubahsui tindakbalas termasuk masa tindakbalas (10-50 min), nisbah molar bahan tindakbalas (5:1-25:1), amplitud ultrasonik (30-90%), dan jumlah kandungan mangkin (2.5-4.5 b/b minyak) telah dipilih and dioptimumkan bagi menghasilkan kefahaman menyeluruh berkenaan kelakuan sistem di bawah pengaruh ultrasonik. Mangkin tersebut juga dinilai dari segi kebolegunaan dan fenomena pegurasan di bawah pengaruh ultrasonik. Tindakbalas keseluruhannya adalah heterogen dan mangkin TPA yang disokong dengan Al dan garam Cs menunjukkan pengurangan yang minimum di dalam aktiviti selepas tiga kali

tindakbalas di bawah keadaan yang optimum. Mangkin Cs menunjukkan aktiviti ~ 90% dan menunjukkan potensi yang terbaik bagi penggunaan semula pada suhu 65 °C selama 34 minit. Mangkin tersebut telah digunakan dalam proses transesterifikasi bagi minyak tidak boleh makan yang berbeza dan telah diuji dalam beberapa sistem dengan kandungan FFA dan air yang tinggi dan menunjukkan keputusan yang memberangsangkan. Ujian tindakbalas kinetik telah dijalankan dan pengesanan FFA dan kandungan air semasa tindakbalas membuktikan mangkin tersebut mampu untuk mempercepatkan kedua-dua proses esterifikasi FFA dan transesterifikasi trigliserida secara serentak.

TRANSESTERIFICATION OF CRUDE JATROPHA OIL BY ULTRASOUND-ASSISTED PROCESS IN THE PRESENCE OF HETEROPOLYACID BASED CATALYSTS.

ABSTRACT

The current research work research work focused on the investigation of FAME production from high FFA and water content crude Jatropha oil through an ultrasound-assisted process. The ultrasonic energy was invested to overcome the barrier of poor contact between the oil and methanol due to the immiscible nature of them reducing the required reaction time and temperature. New heterogeneous acid catalysts based on heteropoly acid were synthesized, characterized and used in the transesterification reaction. Tungstophosphoric acid (TPA) was immobilized on activated carbon (AC) and gamma alumina (Al) or converted to its cesium (Cs) salt to improve its resistance against the solubility in the polar reaction media. Different TPA loadings on the supports and various molar ratios of cesium to TPA were studied and characterized. TPA20-AC, TPA25-Al and Cs salt with molar ratio of 1.5 were used in the investigation of the optimum reaction conditions with the aid of design of experiments software (DOE). Four reaction variables including reaction time (10-50 min), reactants molar ratio (5:1-25:1), ultrasonic amplitude (30-90 %) and catalyst amount (2.5-4.5 w/w oil) were chosen and optimized to generate thorough understanding on the behavior of the system under ultrasonic conditions. The catalysts were also investigated for possible reusability and leaching phenomenon under ultrasonic conditions. The reactions were mostly heterogeneous in nature and the TPA supported on Al and Cs salt catalysts showed minimal reduction in the activity after three successive reaction runs under the optimum

reaction conditions. The catalyst of Cs showed the activity of ~ 90% of FAME yield and the greatest potential of reusability within a reaction temperature of 65 °C in just 34 min. The catalysts were further investigated for transesterification of different non-edible oils and tested in high FFA and water content systems and they generally showed promising results. The reaction kinetics was investigated and the tracing of FFA and water contents during the reaction course proved that the catalysts were able to accelerate both esterification of FFA and transesterification of triglycerides simultaneously.

CHAPTER ONE

INTRODUCTION

1.1 Oleochemical Industry

The depletion of fossil resources and environmental pollution are among the most critical problems that threaten humanity. The attention is currently turned towards the use of biomass or biomass-derived materials as replacements to petroleum fuel. Chemical industries often rely on renewable resources such as carbohydrate, starch, cellulose, sucrose, proteins, natural oils and fats as the key feed stocks (Salimon *et al.*, 2012). Oleo chemical industry is a field of bioresource industry that involves the use of vegetable oil or animal fats as the feed stocks for the chemical reaction. Unlike petrochemicals that are derived from a non-renewable source, oleochemicals represent the chemicals that are derived from bio-based and renewable resources.

Great enhancement to the industrial sector on both economical and environmental perspective aspects can be provided by oleochemical industry (Murphy, 1992). In the environmental aspect, the emission of CO_x and NO_x that are usually associated with the petroleum based industries causes severe air pollution and greenhouse effects to be avoided. The world wide concerns have been dedicated recently to investigate appropriate solutions to these serious issues and oleochemicals provide promising alternatives (Kim *et al.*, 2004).

Switching from petrochemicals to oleochemicals has been the ultimate goal during the earlier decades due to the steady increase in the price of the crude oil and its downstream products (Abdullah *et al.*, 2009b). Meanwhile, the world's energy

demands still depend extensively on finite fossil resources such as petroleum, coal and natural gases. The accelerated rate of exhaustion of these resources is one of the serious problems facing the mankind (Abdullah *et al.*, 2009a, Meher *et al.*, 2006). As oleochemicals are identified as plausible alternatives to fossil fuels, rapid development in this area has been seen in the last few decades. For the conversions to value-added products, the development of innovative and effective catalysts and techniques are deemed indispensable. However, oleochemical reaction towards renewable biodiesel production through transesterification of vegetable oils is considered as one of the important roles of oleochemistry in the area of alternative energy (Leung *et al.*, 2010).

1.2 Biodiesel

Biodiesel, an alternative fuel that meets the greenhouse phenomena standards, is a mixture of mono alkyl esters (usually fatty acid methyl esters known as FAME) with long-chain fatty acids derived from animal fats or vegetable oils (Lou *et al.*, 2008). It has many good properties in comparison to diesel fuel. It is eco friendly, biodegradable, non toxic, and mainly free of sulfur-containing components and aromatics (Li *et al.*, 2012). Biodiesel can mix at any proportion with petroleum oil or itself can be used as a standalone fuel successfully (Vyas *et al.*, 2010).

Environmental aspects related to the production and use of biodiesel as an alternative and promising fuel can be explained in terms of reduction in the green house effects. Biodiesel cause less emission of CO₂ than fossil fuel as the CO₂ generated by the combustion of it and released to the atmosphere can be balanced by the rate of absorbed CO₂ by photosynthesis of the growing plant used as resources

for biodiesel itself (Santori *et al.*, 2012). Since it contains 10-15% oxygen by weight, biodiesel can be considered as an oxygenated fuel leading to complete combustion with less exhaust emissions than diesel fuel (Basha and Raja Gopal, 2012). There are four different methods to produce biofuel from bioresources i.e. direct use and blending of raw oils (Adams *et al.*, 1983, Engler *et al.*, 1983, Peterson *et al.*, 1983, Strayer *et al.*, 1983), micro-emulsions (Ziejewski *et al.*, 1984), thermal cracking (Luo *et al.*, 2010, Seames *et al.*, 2010) and finally, transesterification which is the most popular way to transfer vegetable oils or animal fats to biodiesel (Leung *et al.*, 2010).

1.3 Esterification and Transesterification

Esterification is a slow and reversible reaction at room temperature in which the reactants i.e. alcohol and fatty acids, will react in the presence of a suitable acid catalyst to produce ester and water as the products (Oliveira *et al.*, 2010). Usually, esterification process is carried out in batch mode using homogenous acid catalysts and excess amount of alcohol is used to shift the equilibrium towards forward reaction forming the desired product. Traditionally, strong Brönsted acids in liquid phase such as sulfuric acid and hydrochloric acid are used to catalyze the reaction (Caetano *et al.*, 2008). The general representation of an esterification reaction is shown in Scheme 1.1. In this reaction, stronger acid catalysts will lead to higher reaction rate and no issue with respect to product selectivity is generally encountered as a single product is produced.



Scheme 1.1 Esterification of fatty acid with alcohol (Leong *et al.*, 2010).

Converting fatty acids to a mixture of fatty acid alkyl esters is one of the basic reactions involved in biodiesel production (Borges and Díaz, 2012). Developing alternative energy resources based on vegetable oils through esterification is an important research field to overcome the problem of fossil fuel depletion and for better protection of environment towards polluting emissions associated with fossil fuels (Leung *et al.*, 2010, Sharma *et al.*, 2008).

Transesterification is an organic reaction involving the exchange of the organic group R^1 of an ester with the organic group R^2 of an alcohol. Generally, short chain alcohols (i.e. methanol, ethanol or propanol) are used in the tranesterification reaction. Usually, methanol is the most commonly used alcohol for producing biodiesel as it is relatively cheaper and has smaller carbon chain (Talebian-Kiakalaieh *et al.*, 2013a). When the original ester is reacted with an alcohol, the tranesterification reaction is generally called alcoholysis and in particular methanolysis if methanol is used. Scheme 1.2 illustrates the general representation of a tranesterification reaction (Marchetti *et al.*, 2007). Transesterification is a reversible reaction and the tendency to attain equilibrium depends on the operating variables.



Scheme 1.2 Transesterification of triglycerides with alcohol (Leong *et al.*, 2010).

The presence of excess alcohol in the reaction mixture and a catalyst (acid or base) could accelerate and control the equilibrium to achieve a high yield of the ester (Yin *et al.*, 2012). According to the reaction stoichiometry, one mol of esters reacts with three mol of alcohol to produce three mol of the desired product, methyl esters, and one mol of glycerol as the co-product. This reaction can be catalyzed by basic or acidic catalysts. However, basic catalysts can result in higher reaction rate but the free fatty acids (FFA) content in the oil should be low while acid catalysts are more preferred in the case of significant FFA present in the reactants (Leung *et al.*, 2010).

1.4 Catalysts for Transesterification Reaction

The production of biodiesel using homogenous catalyst has been investigated by many researchers using conventional batch process. Catalysts such as potassium hydroxide (Kulkarni and Dalai, 2006), sodium hydroxide (NaOH) (Georgogianni *et al.*, 2008) and other types of homogenous catalysts (Miao *et al.*, 2009) have been studied. Comparing with other types of catalysts, homogenous catalysts attract researchers and used widely in industries since they provide high conversion in a relatively short reaction time and low reaction temperature (Leung *et al.*, 2010). Also, homogenous catalysts are more preferred due to their availability and cheapness (Loterio *et al.*, 2005).

Unfortunately, there are some problems that can limit the success in the use of this type of catalyst. The significant disadvantage is that the catalysts cannot be reutilized because they are consumed in the reaction media and the separation process of this type of catalyst needs complicated equipment. This factor can affect the process economy and overall energy consumption (Zabeti *et al.*, 2009). So,

research efforts have been shifting towards investigating heterogeneous catalysts that can catalyze the reaction with the same efficiency without this kind of drawbacks.

Alkaline earth metal oxides especially CaO and SrO have achieved much interest due to their relatively high basic strength, low solubility in reaction media, and the possibility to be manufactured from cheap materials (Liu *et al.*, 2007, Vicente *et al.*, 2007). Other type of alkali catalyst that has been investigated is potassium catalyst supported on SBA-15 (Abdullah *et al.*, 2009a). In recent years, researchers' efforts have been shifted towards developing sustainable solid acid catalysts for transesterification reaction that have no sensitivity towards FFA in the feedstock and subsequently easy to be separated from the reaction products. Solid acid catalysts such as ZrO₂ (Jitputti *et al.*, 2006), sulfonic ion-exchange resin (Melero *et al.*, 2010), sulfonic modified silica (Melero *et al.*, 2010, Alba-Rubio *et al.*, 2010), sulfonic functionalized SBA-15 (Zuo *et al.*, 2013), carbon-based solid acid catalyst (Shu *et al.*, 2010) and heteropolyacids (Morin *et al.*, 2007) have been successfully used in transesterification reaction of different triglyceride sources.

1.5 Ultrasonic Energy

Ultrasonic technology in biodiesel production process is new, attractive and effective procedure to solve problems that are related with conventional methods of production. The use of ultrasonic irradiation can enhance mass transfer rate between the reactants which are immiscible fluids. It has been functionalized in wide range of chemical processes causing reduction in reaction time and improvement in production yield (Ji *et al.*, 2006).

Ultrasound (US) is simply sound pitched above human hearing ability, usually above 20 kHz. It has plenty of applications in our daily life (Singh *et al.*, 2007). The use of ultrasound as a source of energy is common these days and recently it is used to provide large assistance to great number of industries. Figure 1.1 shows the general divisions of sound frequencies. Frequencies beyond 20 kHz till 100 kHz are widely used in industries but the range of industrial frequencies can be extended to 2 MHz according to the required power.

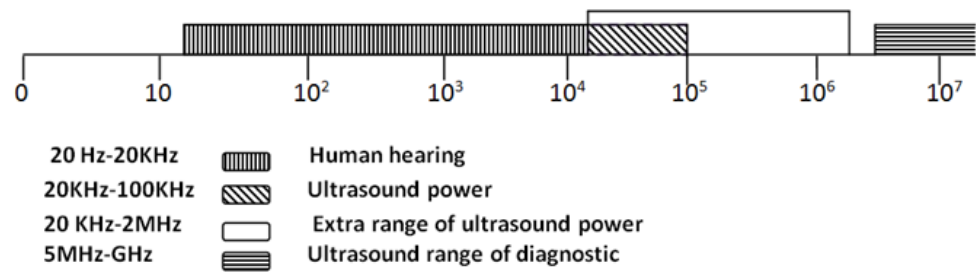


Figure 1.1 The general divisions of ultrasonic energy (De Castro and Capote, 2007).

1.6 Crude Jatropha Oil

Non-edible vegetables oils such as *Madhuca indica*, crude *Jatropha* and *Pongamia pinnata* oils have been found to be suitable for biodiesel production. These oils are not suitable for human consumption due to the presence of some toxic components. Among various non-edible oils, *Jatropha* oil is considered as a suitable source of triglycerides and possesses good potential for biodiesel production.

Crude *Jatropha* oil has no conflict with the food resources and it possesses high oil content (Koh and Mohd. Ghazi, 2011). *Jatropha* oil also has relatively high oil fraction in the range of 50-60% in comparison to other oils as well as high

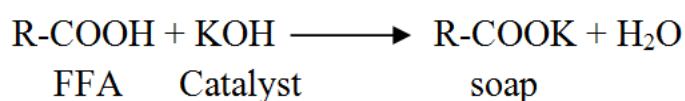
productivity per hectare of 2-3 tones/ ha/year. The high yield per hectare and high oil content are important parameters in selecting the potential renewable source of fuel (Juan *et al.*, 2011).

1.7 Problem Statement

In many oleochemical reactions such as transesterification of triglycerides with alcohols, serious problems and limitations can be noticed and identified. First of all, it is due to the immiscible nature of the involved reactants coupled with variations in viscosity and density. This is the main reason for the low contact between the reactants results in poor mass transfer rate, reduction in reaction rate and increasing in reaction time (Santos *et al.*, 2010). The reaction between two immiscible fluids makes it look like heterogeneous transport phenomenon (heat, mass and fluid) that is caused by the lag in the film between them. The use of ultrasound in reactions involving two immiscible reactants will be the basic technique to solve this problem. Ultrasonic energy will neglect the needs for vigorous mechanical mixing by improving the emulsification of the reactants and enhancing the mass transfer (Ramachandran *et al.*, 2013).

Due to better contact with the reactants, homogenous catalysts are generally more active than the heterogeneous ones. The disadvantage of homogenous catalyst is that the catalyst cannot be reutilized as it is consumed in the reaction media. The separation process of this type of catalyst is very complicated and requires further equipment (Zabeti *et al.*, 2009). On the other hand, the drawback with respect to the use of base catalyzed systems is the limitation towards the use of many oil feed stocks because of their sensitivity to the presence of free fatty acids (FFA). Amounts

of FFA larger than 1% wt can react with the base catalyst and lead to the formation of soap (Leung *et al.*, 2010) according to the reaction in Scheme 1.3. Even with low FFA under the level of soap formation, base homogenous catalysts itself are hard to be removed from the product and requires two or three times of washing with hot water (Janaun and Ellis, 2010). This process will generate large amount of wastewater that deserves further treatment before discharge.



Scheme 1.3. General equation for soap formation (Leung *et al.*, 2010).

Investigations of homogenous acid catalysts lead to the conclusion that they have no sensitivity towards FFA content in the feedstock but the reaction must be maintained at high temperature and the yield of the methyl esters could still be low (Zabeti *et al.*, 2009). Conventional process including mechanical stirring requires long reaction time for heterogeneous and homogenous acid catalysts. The reaction temperature and molar ratio between the reactants are usually higher than those used in the case of basic catalysts (Mootabadi *et al.*, 2010). This could affect the product quality and overall process economy because the feed stock can undergo serious degradations at high temperature especially when long reaction time is needed. Operating a system at high temperature also do requires huge amount of energy input (Yee *et al.*, 2009). The search for active solid acid catalysts that can possess the activity similar to that of basic catalysts and the tolerance of acidic catalysts towards FFA will be thoroughly investigated in the current research work. Yet, the use of

heteropolyacid catalysts as heterogeneous acid catalysts in transesterification is governed by the soluble nature of the catalyst in polar reaction mixture.

Non-edible vegetable oils attract great attention in biodiesel production as these kinds of feedstock do not oppose the objections against the use of edible sources as feed stocks in fuel industry (Leong *et.al.*,2010). Crude vegetable oils and waste cooking oils are promising feedstock yet they possess high FFA and water content which forbidding the possibility of base catalysts usage. Waste cooking oil is considered hazardous materials that affect the environment. Serious water contamination may occur if no proper disposal method is implemented. Such scenario does not only contribute to pollution problems but is also harmful to human beings (Stavarache *et al.*, 2005). Combining with the need for cheap feedstock, the research work will focus on the use of non edible oils as well as used cooking oil. The use of heterogeneous acid catalysts in conjunction with ultrasound-assisted process will enable the feasible use of feedstocks containing high FFA and moisture content to produce fatty acid esters.

1.8 Objectives

The following objectives are planned to be addressed in the current research project:

- To synthesize various heteropolyacid based catalysts for ultrasound-assisted transesterification reaction between non-edible vegetable oil and methanol, and subsequently characterize using different characterization methods to study their physical and chemical properties.

- To elucidate the interplay between reaction variables and the limiting reactant conversion and yield of fatty acid methyl esters by studying various process parameters in the ultrasound-assisted transesterification process.
- To investigate the possible reusability potential of the prepared catalysts showing the desired effects in the ultrasound-assisted batch reaction as well as the nature of the reaction media on the catalysts stability.
- To investigate the catalytic performance towards various contents of FFA and water in the feedstock and for different types of non-edible oils.
- To study the reaction kinetics under ultrasound-assisted process to elucidate the influence of ultrasonic energy on the course of the reaction.

1.9 Scope of Study

The present study addresses the investigation on the use of an ultrasound-assisted transesterification process of a non-edible vegetable oil with methanol in the presence of heteropolyacid based catalysts. The catalysts have been developed by immobilizing the heteropolyacid active component on different supports or the use of a combination of co-precipitated heteropolyacid salt with cesium. The synthesized catalysts were characterized using different characterization techniques involving qualitative and quantitative processes to highlight their physical and chemical properties.

The production of FAME (fatty acid methyl ester) from crude *Jatropha* oil has been conducted using the synthesized catalysts and the yield of methyl ester was considered as the target in the establishment of the historical design describing the system. A preliminary study involving the determination of the effective catalyst

composition on the reaction yield has been conducted. Four reaction variables including reaction time (10-50 min), reactants molar ratio (5:1-25:1), ultrasonic amplitude (30-90 %) of the maximum sonifier power and catalyst amount (2.5-4.5 w/w oil) have been chosen and optimized to generate thorough understanding on the behavior of the system. Mathematical representation for the FAME production process has also been established. The significance of the model and the interaction between the reaction variables are meant to be validated statistically. The optimum reaction conditions have been subsequently used to investigate the catalysts in terms of reusability and leaching of active component to validate the stability of the developed catalysts in the polar reaction mixture under ultrasonic mixing effects. In addition, a mathematical model has been generated to represent the transesterification reaction and several significant kinetics parameters such as reaction order, reaction rate constant and activation energy will be determined.

The effects of the feedstock types and properties have been studied under the optimum reaction conditions for each catalyst. The quality of the crude Jatropha oil has purposely varied by increasing the water content and FFA content to test the tolerance of the different developed catalysts towards the changing oil quality. The catalysts have also been used in the transesterification of different types of non-edible oils such as crude palm oil, originally high FFA crude Jatropha oil as well as used palm oil. The data obtained from this study are expected to reveal the role of the prepared acid catalysts coupled with the effects of ultrasonic energy in conducting both esterification and transesterification simultaneously in a short reaction time. This will significantly highlight and justify the significance of the

current study in the future use of low grade, cheap price and non-edible vegetable oils in biodiesel production.

1.10 Impact Towards Society

This research has the potential impact to orient and promote further investigations in the direction of developing other heterogeneous catalysts that will promote a more sustainable biodiesel industry in Malaysia. Studying the application of ultrasonic energy in biodiesel production will generate further information about phenomena and changes that occur on reaction parameters. This will help to understand the role of ultrasonication in enhancing these parameters towards future scale up of the process into industrial scale.

The production of a biofuel from non-edible oil with low cost will encourage the biodiesel industry as an environmental friendly fuel. This will lead Malaysia to employ its natural resources in this direction. The use of cheap and reusable materials as catalysts and cheap feed stocks will cut down the production costs of biodiesel and avoid the dependence on expensive resources.

In addition, it is expected that the research will contribute towards future employment opportunities, thereby providing livelihood support (economic empowerment). It is also expected that more plantation of oil yielding plants such as *Jatropha* tree and palm tree (cash crop) and others for biodiesel production will help to create eco-restoration, environment sanity vis-a-vis environment security and reduce drought. Also, it is hoped that the sustainable application biodiesel technologies in the automobiles and industrial sectors will contribute to the

worldwide direction to minimize greenhouse effects. Finally, this research intends to promote and provide technical information required by the producers of biodiesel as well as researchers to push forward the growth of the process in a more sustainable manner.

1.11 Organization of the Thesis

This thesis has been organized to consist of five chapters. In Chapter One, the outlines for the whole thesis are given covering the definitions of the oleochemicals reaction, biodiesel, and ultrasonic energy. A brief discussion on the various catalysts used in transesterification reaction including the main advantages and disadvantages are also presented in this chapter. The problems that need to be addressed in the current research work and the objectives of the study are detailed out in the problem statement while the scopes of the current research are presented in the scope of the study section.

Chapter Two of this thesis presents the literature reviews related to the research scopes including oleochemical applications and biodiesel feed stock. The historical investments of the ultrasonic energy as well as the effects of ultrasonic waves on the transesterification reaction are thoroughly discussed. Different catalytic systems under ultrasonication are analyzed and discussed to highlight the advantageous role of the ultrasound-assisted process in enhancing the reaction parameters. The definition and application of heteropolyacids in the transesterification reaction are thoroughly reviewed presenting the earlier reported researches in the field. On the other hand, reaction mechanism and statistical approach are also defined and discussed in this chapter.

In Chapter Three, the experimental methodology and instrumental analysis are presented. The descriptions of the materials used in the current research work are listed in details. The methods conducted to synthesize the catalysts as well as the methods of characterization of the feedstock, the product and the catalysts were explained. The experimental set-up for the reactions, the statistical approach and the product analysis are elaborated in detail.

The results and their discussion for the characteristics of the catalysts and their catalytic reactions are presented in Chapters Four. The results of the preliminary study for the catalysts followed by the design of experiments (DOE) to identify the optimum conditions are thoroughly explained. This chapter also includes discussions on the catalysts stability, reusability and leaching effects for the synthesized catalysts as well as the results of the reaction kinetics and modeling. The effects of feedstock properties and the investment of different feedstock types in the presence of the prepared catalysts under the ultrasonic conditions are explained. This is conducted to investigate the validity of the heterogeneous catalysts in conducting the transesterification reaction for a wide range of non-edible triglycerides resources. Mathematical approach to represent the process is also accomplished and the study of the reaction kinetics is explained in Chapter Four. The conclusions of the results obtained in this study are listed in Chapter Five. The overall recommendations for the future work are also listed in this chapter.

CHAPTER TWO LITRATURE REVIEW

2.1 Introduction

In this chapter, the overview and background of the topics and fields that related to the current study are presented. The nature and benefit of the oleochemical reactions and the role of heteropolyacids in catalyze the transesterification reaction will be detailed out. The role of ultrasonic irradiation in enhancing the biodiesel production process for both homogenous and heterogeneous systems will be reviewed. The statistics for developing mathematical approach for describing the system and kinetics of the reaction will be addressed.

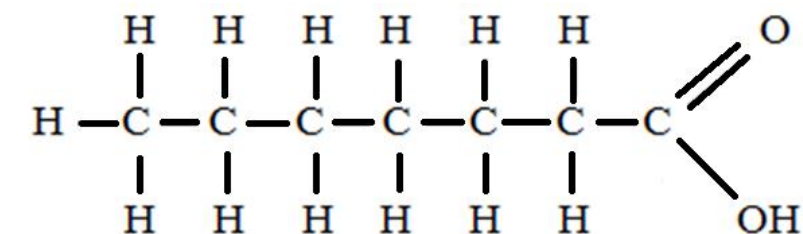
2.2 Vegetable Oil for Biodiesel Production

One of the common feedstock for oleochemical industry is the vegetable oils. The nature of the vegetable oils differs from one source to another. However, they share the same general individual components of free fatty acids and generally contain water in various proportions, depending on the oil source (Koh and Mohd. Ghazi, 2011). Oils and fats can be converted to other oleochemicals such as fatty acids and glycerol that, in turn, can be further converted to value-added substances through suitable reactions with other biomaterials. Table 2.1 shows the common distribution of the fatty acids for a range of vegetable oils.

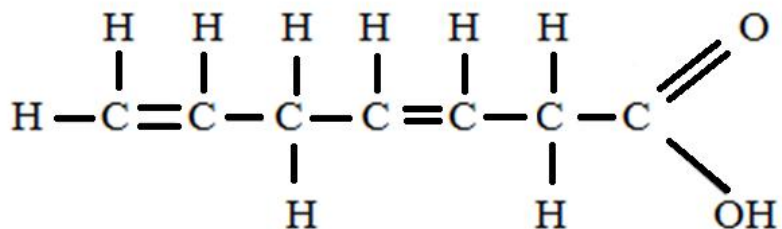
Table 2.1 The chemical structure of the common fatty acids (w%) (Lam *et al.*, 2010).

Name	Structure	Formula	Common oil source					
			Palm	Soy bean	Cotton seed	Coconut	Rape seed	Jatropha
Lauric	12:0	C ₁₂ H ₂₄ O ₂	0.1	0.1	0.1	46.5	-	0.14
Myristic	14:0	C ₁₄ H ₂₈ O ₂	1.0	0.1	0.7	19.2	-	0.17
palmitic	16:0	C ₁₆ H ₃₂ O ₂	42.8	0.2	20.1	9.8	3.5	14.8
Stearic	18:0	C ₁₈ H ₃₆ O ₂	4.5	3.7	2.6	3.0	0.9	7.2
Oleic	18:1	C ₁₈ H ₃₄ O ₂	40.5	22.8	19.2	6.9	64.1	42.5
Linoleic	18:2	C ₁₈ H ₃₂ O ₂	10.1	53.7	55.2	2.2	22.3	32.7
Linolenic	18:3	C ₁₈ H ₃₀ O ₂	0.2	8.6	0.6	-	8.2	0.17

Free fatty acids that exist in the vegetable oil can be classified into two type's i.e. saturated and unsaturated fatty acids as shown in Scheme 2.1 Saturated free fatty acids consist of straight organic chains that do not contain any double bonds or other functional groups in the chain. Usually, these fatty acids have higher melting and boiling points and predominantly found in animal fats rather than vegetable oils.



Saturated fatty acid



Unsaturated fatty acid

Scheme 2.1. Typical examples of saturated and unsaturated fatty acids.

Meanwhile, unsaturated fatty acids possess one or more C=C double bands that exist in the hydrocarbon chain (Hou, 2000).

Oleochemical reaction towards the production of renewable fuel through different processes is considered as one of the important sectors of oleochemistry in the area of alternative energy (Leung *et al.*, 2010). There are four different processes that can be conducted to produce biofuel from vegetable oil i.e. dilution, microemulsion, pyrolysis and transesterification.

2.2.1 Dilution (blending)

Direct use and blending of raw oils is the technique where vegetable oils are diluted with petroleum diesel to run the engine (Adams *et al.*, 1983, Engler *et al.*, 1983, Peterson *et al.*, 1983, Strayer *et al.*, 1983). In early 1980s, experiments were conducted to use a blend of 10% of vegetable oil without significant adjustments on the combustion engine. The results showed that the same engine efficiency was achieved and the same total gain power was maintained (Strayer *et al.*, 1983). Short-term experiments using blend of up to 50:50 oil to diesel mixtures had been tested and good results were achieved. However, increasing the proportion of vegetable oil in the fuel mixture will lead to an increase in the viscosity. This causes a drawback since high viscosity fuel is undesirable in injection engines (Abbaszaadeh *et al.*, 2012).

2.2.2 Pyrolysis

Pyrolysis or thermal cracking is the conversion of triglyceride to biodiesel with or without the presence of catalyst by using heat in the absence of air or oxygen

(Luo *et al.*, 2010, Seames *et al.*, 2010). This method is simple, pollution-free and effective in comparison to other thermal cracking processes yielding FAME (Singh and Singh, 2010).

2.2.3 Microemulsion

Microemulsion is defined as colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the range of 1-150 nm formed spontaneously from two normally immiscible liquids (Ziejewski *et al.*, 1984). Microemulsions with solvents such as methanol and ethanol have been studied to overcome the problem of vegetable oils high viscosity. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles (Sharma *et al.*, 2008).

2.2.4 Transesterification

Transesterification is the most popular way to transfer vegetable oils or animal fats to biofuel (Leung *et al.*, 2010). The long and branched chain triglyceride molecules are transformed into monoesters and glycerin. Sometimes, this reaction is known as "ester interchange". The main product is a mixture of fatty acid methyl esters (FAME) better known as biodiesel. The composition of FAME is influenced by the type of oil or fat used as the feedstock.

As a rough estimation, the molecular weight of a typical ester molecule is one third that of typical oil molecule and therefore has a very low viscosity as compared to oil. Theoretically, 3:1 molar ratio of alcohol to triglyceride is needed to complete a

transesterification process, while practically, high molar ratio of alcohol to oil is required to obtain high FAME yield (Lam *et al.*, 2010).

2.3 Biodiesel Feed Stock and Economics

A wide range of studies have been dedicated to the production process of biodiesel using various methods and some of them could achieve good yields and look promising for large scale production. Some researchers' focus their study on the economic aspects of the process with respect to the types of feed stock, their availability and price that could influence the economy of the process (Abdullah *et al.*, 2009b). Figure 2.1 shows the distribution of biodiesel production cost. The main contributor to the overall cost of the process is the feed stock cost (the vegetable oil or animal fats) while the second one is the chemicals that are used in the reaction such as the catalyst and alcohol.

Investments of cheap recourses of triglyceride and efforts to reduce the amounts of the chemicals used should be considered. These days, some researchers are actively investigating the enhancements on the process to eliminate or reduce these problems or drawbacks. The aim is always to produce the desired product at an optimum rate that possesses high quality while at the same time demonstrates good process economy (Abdullah *et al.*, 2007).

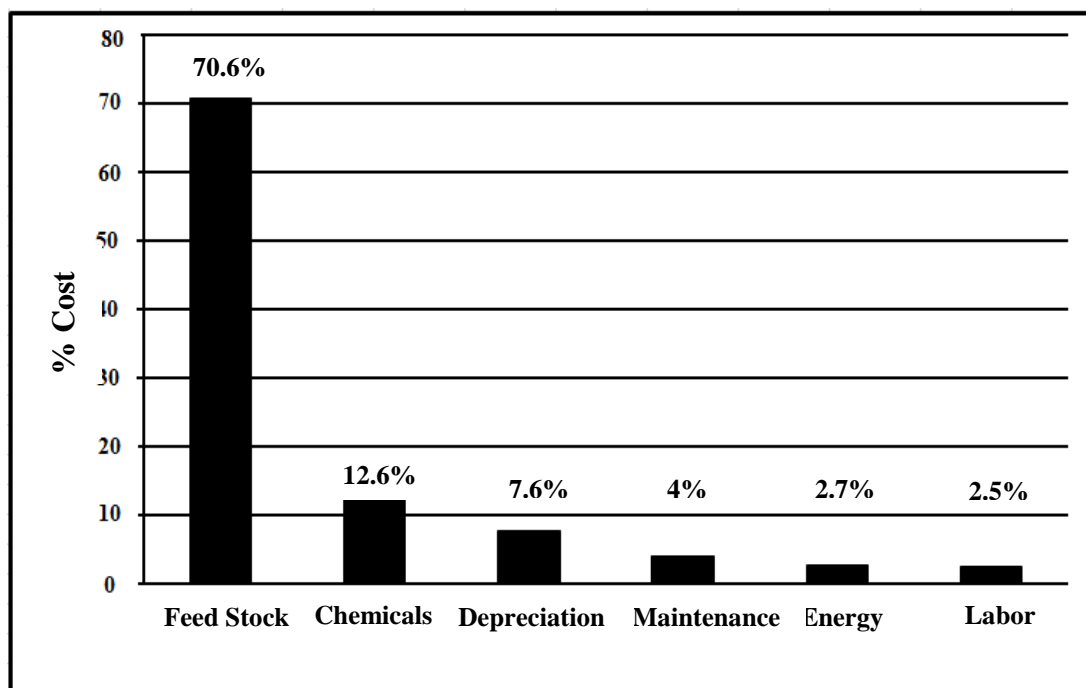


Figure 2.1. Costs of biodiesel production (Math *et al.*, 2010).

Three types of feedstocks have been used as potential sources for biodiesel industry i.e. animal lipids, waste cooking oils and vegetable oils. The production of biodiesel from renewable lipid sources has gained international attention, and the use of animal fats as raw material has been considered as a viable alternative (Teixeira *et al.*, 2009). Biodiesel that is produced from animal fats generally has particular drawbacks with respect to low pour point and poor resistance against oxidation (Encinar *et al.*, 2011). Waste cooking oils that are generated from deep frying processes have been used as a potential feed stock for biodiesel production (Chen *et al.*, 2012). Subjecting the vegetable oil to high temperature for long time during the cooking process can lead to significant changes in its chemical and physical properties. Waste cooking oils usually contain high amount of polar compound, especially free fatty acid (FFA) that must be taken into consideration as it will greatly affect the transesterification reaction. Usually the amount of FFA in the waste

cooking oils varies within the range of 0.5-15 wt % which does not justify the use of these feed stocks in base catalyzed reactions (Lam *et al.*, 2010).

Due to renewability in nature and environmentally friendly, various vegetable oils have been considered as promising potential feed stocks for biodiesel production. Major sources of oil for biodiesel production comes from edible oils such as sunflower oil, palm oil, rapeseed oil and soybean oil (Helwani *et al.*, 2009). However, wide rejections against the use of food source in fuel industry have been raised all over the world. The competition between the human use of the edible oil and the needs of biodiesel production may lead to significant increment in the feed stock price (Jain and Sharma, 2010).

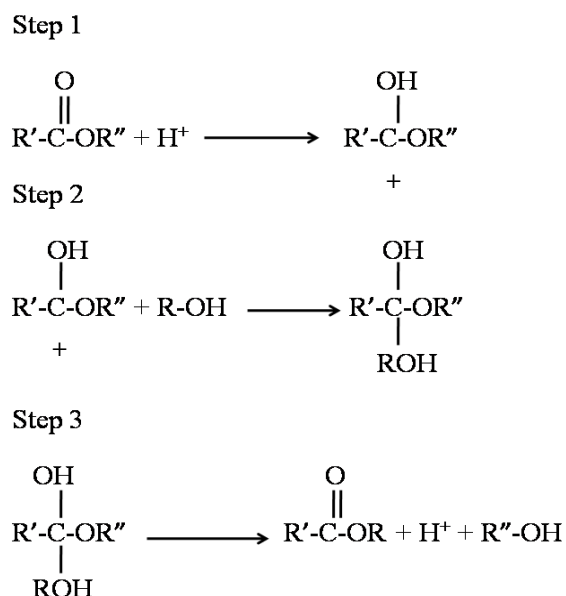
2.4 Transesterification of Crude Jatropha Oil

Two-step process consisted of pre-esterification and transesterification was developed to produce biodiesel from crude *Jatropha curcas* L. oil by Lu *et al.* (2009). By using sulfuric acid or solid acid, the FFAs were esterified with alcohol first to esters in order to reduce the acid value of the feed stock to the limit of base catalyst usage. The second step involved transesterification using KOH achieving higher than 98 % of biodiesel yield. It was recorded that for the esterification step, 2 h was required for the reaction while the reaction time for the transesterification was only 20 min. Endalew *et al.* (2011a) prepared and tested solid base and acid catalysts for the transesterification of *Jatropha curcas* oil in a batch reactor under mild reaction conditions. Two catalysts of CaO and Fe₂(SO₄)₃ were used together for one step reaction to achieve the esterification and transesterification simultaneously. This

mixture of acid-base catalysts showed complete conversion to biodiesel which was better in comparison to that of base catalyst alone. Sulfated zirconia alumina (SZA) catalyst was prepared and tested by Yee *et al.* (2011) who studied the effects of the catalyst preparation parameters on the transesterification reaction. At optimum reaction condition; calcination temperature and calcination duration at 490 °C and 4 h, respectively, achieved an optimum FAME yield of 78.2 % by converting *Jatropha* oil with 11.41% w/w FFA content.

2.5 Transesterification Mechanism

The acid catalyzed transesterification mechanism consists of three steps as shown in Scheme 2.2 for the process catalyzed by Brønsted acid catalysts such as sulfuric or sulfonic acids. The scheme explains the mechanism of single step monoglyceride formation and can be further extended to conclude diglyceride and triglyceride as well. In the first step, carbocation II will be generated as a result of the attack of the proton from the catalyst to the carbonyl group of the monoglyceride. This carbocation II will react with alcohol forming tetrahedral intermediate III in step 2 of the reaction. The final step involved the extraction of H⁺ and glycerol from the skeleton of the tetrahedral leaving the molecule of alkyl ester. Large amount of alcohol is usually required to shift the equilibrium point of the reaction to the formation of more alkyl esters as all these steps are reversible.



Scheme 2.2. The mechanism of acid catalyzed transesterification (Meher *et al.*, 2006).

The mechanism of base catalyzed transesterification is shown in Scheme 2.3. It consists of a pre-step where the base catalyst reacts with alcohol to form an alkoxide followed by three reaction steps. The first step involves the formation of tetrahedral intermediate due to the reaction of the alkoxide group with the carbonyl group of the triglyceride. In the second step, the tetrahedral intermediate will dissolve to produce alkyl ester and the diglyceride corresponding anion. Finally, the deprotonation of the base catalyst will be done donating the proton to the corresponding anion leading to the regeneration of the catalyst and the formation of glycerol molecule. The same mechanism can be applied for diglyceride and monoglyceride to produce a mixture of alkyl esters (Meher *et al.*, 2006, Demirbas, 2008).