PRODUCTION OF BIODIESEL FROM *JATROPHA CURCAS* L. OIL CATALYZED BY SO_4^{2-}/ZrO_2

by

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LIST OF ABBREVIATIONS

Al_2O_3	Aluminium oxide
ASTM	American Society Testing and Materials standard
AV	Acid value
BET	Brunauer-Emmett-Teller
C_{IS}	Concentration of internal standard used
CCD	Central composite design
DF	Dilution factor
DOE	Design of experiment
FAME	Fatty acid methyl esters
FFA	Free fatty acid
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas chromatograph
HF	Hydrofluoric acid
HNO_3	Nitric acid
H_2S	Hydrogen sulfide
H_2SO_4	Sulfuric acid
IS	Internal standard
KBr	Potassium bromide
KF	Potassium fluoride
KNO3	Potassium nitrate
KOH	Potassium hydroxide
MCM-41	Matter no. 41
MPOB	Malaysian Palm Oil Board
N_2	Gas nitrogen
NaCl	Sodium chloride
Na_2SO_4	Sodium sulfate anhydrous
NH_4OH	Ammonium hydroxide
$(NH_4)_2SO_4$	Ammonium sulfate
RSM	Response surface methodology
R_f	Ratio of reference
R_s	Ratio of sample
R-Squared	Regression squared
SiO_2	Silicon dioxide
SO_2	Sulfur dioxide
SO_4^{2-}	Sulfate ion
SV	Saponification value
SZA	Sulphated zirconia alumina
TCP	Tricaprylin
V	Volume
XRD	X-ray diffraction
ZnO	Zinc oxide
$ZrCl_4$	Zirconium chloride
$Zr(NO_3)_2.5H_2O$	Zirconium nitrate pentahydrate
ZrO_2	Zirconia oxide
$Zr(OC_3H_7)_4.C_3H_7OH$	Zirconium isopropoxide
$ZrOCl_2.8H_2O$	Zirconyl chloride octahydrate
$Zr(OH)_4$	Zirconium hydroxide

LIST OF SYMBOLS

°	Degree
α	Distance of axial point from center
x	Independence variable
n	Number of independence variables
θ	Radiation angle
ε	Random error
λ	Radiation wavelength
β	Regression coefficient

PENGHASILAN BIODIESEL MENGGUNAKAN MINYAK *JATROPHA CURCAS* L. DENGAN MANGKIN SO_4^{2-}/ZrO_2

ABSTRAK

Biodiesel yang diterbit daripada minyak tidak boleh makan seperti minyak *Jatropha curcas* L. mempunyai potensi yang lebih besar berbanding dengan minyak boleh makan sebagai gantian petroleum diesel kerana ia tidak perlu bersaing dengan sumber makanan. Walau bagaimanapun, minyak *Jatropha curcas* L. menggandungi kandungan asid lemak bebas yang tinggi, dimana melebihi batasan yang boleh diterima oleh mangkin alkali dalam fasa bendalir. Oleh itu, mangkin asid dalam fasa pepejal amat diperlukan untuk mencegah penghasilan sabun dalam campuran produk. Dalam kajian ini, dua cara mudah untuk menyediakan mangkin zirconia yang disulfatkan dan dimuati alumina (SZA) yang digunakan dalam transesterifikasi minyak *Jatropha curcas* L. dan metanol kepada biodiesel telah dilaporkan. Mangkin ini telah disediakan dengan cara pensulfatan zirconia oksida secara langsung dan cara bebas bendalir. Mangkin ini telah dikaji melalui alatan Analisis Pembelauan Sinar-X (XRD), Spektroskopi Jelmaan Fourier Infra-merah (FTIR), FTIR-pyridine dan luas permukaan BET. Keputusan menunjukkan bahawa mangkin yang disediakan daripada kedua-dua cara tersebut mempunyai struktur berhablur yang baik dengan tapak-tapak berasid yang mencukupi untuk tindak balas transesterifikasi. Kesan daripada pembolehubah-pembolehubah bagi proses penyediaan mangkin SZA terhadap hasil biodiesel telah dikaji dengan menggunakan Rekabentuk Eksperiement (DOE). Bagi cara pensulfatan zirconia oksida secara langsung, 84.6 peratus berat hasil biodiesel yang optimum telah diperolehi dengan suhu pengkalsinan 400 °C selama 4 jam. Bagi cara bebas bendalir, keputusan menunjukkan 81.4 peratus berat hasil biodiesel yang optimum dapat diperolehi dengan suhu pengkalsinan 490 °C selama 4 jam. Disebabkan cara terdahulu memerlukan suhu pengkalsinan yang lebih rendah dalam proses penyediaan mangkin, mangkin yang dioptimumkan dengan cara tersebut telah dipilih untuk digunakan dalam kajian proses transesterifikasi yang seterusnya. Sekali lagi dengan menggunakan "DOE", didapati bahawa bagi syarat-syarat berikut: 150 °C suhu reaksi selama 4 jam, nisbah 9.88 bagi metanol dan minyak *Jatropha curcas* L. dan 7.61 peratus berat nisbah mangkin, dapat menghasilkan 90.32 peratus berat biodiesel. Daripada keempat-empat pembolehubah yang dikaji, suhu tindak balas menunjukkan kesan yang paling jelas terhadap hasil biodiesel diikuti dengan nisbah mangkin, nisbah metanol dan minyak *Jatropha curcas* L. dan akhir sekali jangka masa tindak balas. Keputusan telah menunjukkan bahawa dengan meningkatkan nilai pembolehubah-pembolehubah tersebut, hasil biodiesel dapat dipertingkatkan lagi. Selain daripada itu, interaksi pembolehubah-pembolehubah tersebut juga menunjukkan kesan yang jelas terhadap hasil biodiesel. Keupayaan mangkin ditebusguna dan jangka hayat mangkin terhadap proses transesterifikasi juga telah dikaji dan keputusan menunjukkan bahawa hasil biodiesel turun daripada 90.32 peratus berat kepada 74.57 peratus berat (kitar semula kali pertama). Hasil biodiesel terus turun kepada 52.04 peratus berat dalam kitar semula kali kedua, 32.07 peratus berat dalam kitar semula kali ketiga dan 30.86 peratus berat dalam kitar semula kali keempat. Ini adalah disebabkan mangkin tersebut telah hilang keaktifan. Oleh itu, penjanaan semula mangkin yang telah digunakan adalah penting. Ciri-ciri bahan api bagi biodiesel *Jatropha* telah dikaji dan biodiesel *Jatropha* dapat memenuhi biodiesel speksifikasi mengikut ASTM D6751.

PRODUCTION OF BIODIESEL FROM *JATROPHA CURCAS* L. OIL CATALYZED BY SO_4^{2-}/ZrO_2

ABSTRACT

Biodiesel which is derived from non-edible oil such as *Jatropha curcas* L. oil has a better potential compare to edible oil to replace petroleum-derived diesel fuel as it does not compete with food resources. However, *Jatropha curcas* L. oil contains high free fatty acids, which is far beyond the limit that can be tolerated by homogeneous alkaline catalyst. Therefore, heterogeneous acid catalyst is required to eliminate soap formation in the product mixture. In this study, two simplified methods to prepare sulfated zirconia loaded on alumina (SZA) catalyst for transesterification of *Jatropha curcas* L. oil with methanol to biodiesel is reported. The catalysts were prepared by direct sulfation of zirconia oxide method and solvent-free method. The catalysts were characterized by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), pyridine- FTIR and BET surface area measurement. The characterization results revealed that the catalysts prepared by these two different methods had good crystalline structure with sufficient acidic sites required for transesterification reaction. The effects of SZA catalyst preparation variables on the yield of biodiesel were investigated using Design of Experiment (DOE). For direct sulfation of zirconia oxide method, it was found that an optimum biodiesel yield of 84.6 wt% was obtained using catalyst prepared with calcination temperature and calcination duration at 400 °C and 4 hours, respectively. For solvent- free method, the results revealed that at the optimum condition, calcination temperature and calcination duration at 490 °C and 4 hours, respectively, an optimum biodiesel yield of 81.4 wt % was obtained. Since the former method requires lower calcination temperature for catalyst preparation, the optimized catalyst prepared using this method was selected for subsequent transesterification process study. Again using DOE, it was found that at the following conditions; 4 hours of reaction at 150 °C, methanol to oil molar ratio of 9.88 mol/mol and 7.61 wt% for catalyst loading, an optimum biodiesel yield of 90.32 wt% can be obtained. Among the four process variables studied, reaction temperature showed the greatest effect on the yield of biodiesel followed by catalyst loading, molar ratio of methanol to oil and reaction duration. The result revealed that an increase in each of the process variable led to an increase in biodiesel yield. Apart from that, the interaction between variables also showed significant effect on the yield of biodiesel. The reusability and life span of the catalyst for the transesterification process were also studied and it was found that the yield of biodiesel dropped from 90.32 wt% to 74.57 wt% (first cycle). The yields dropped further to 52.04 wt% in the second cycle, 32.07 wt% in the third cycle and 30.86 wt% in the fourth cycle. It was due to catalyst deactivation. Hence, regenerating the spent catalyst was important in order to reuse the catalyst. The fuel properties of *Jatropha* biodiesel were characterized and *Jatropha* biodiesel indeed met the specification for biodiesel according to ASTM D6751.

CHAPTER ONE

INTRODUCTION

This chapter gives an overall introduction to the entire research project. The current scenario of biodiesel (fatty acid methyl ester, FAME) and biodiesel related issues are outlined at the beginning of this chapter. Apart from that, information on *Jatropha curcas* L. oil used in this study and basic theory on transesterification reaction are given as well. Finally, this chapter concludes with the problem statement, project objectives, scope and the organization of thesis contents.

1.1 Biodiesel

At present, despite of the rapid decline in fossil fuel reserves, the demand for fossil fuels is still increasing very fast and this scenario has escalated the price of fossil fuel in the world market. It was estimated that remaining fossil fuel reserves for oil will last another 40 years if the world continues to consume fossil fuels at the rate recorded in 2006 (Shafiee and Topal, 2009). Therefore, the diminishing fossil fuel reserves and the negative environmental consequences of exhaust gases from petroleum-fuelled engines has given rise to the exploitation of renewable energy sources such as biodiesel.

Biodiesel, which consists of simple alkyl esters of fatty acids is synthesized by the transesterification of vegetable oils with alcohols. Biodiesel is now recognized as a “green fuel” that has several advantages over conventional diesel. It is safe, renewable, non-toxic and biodegradable in water. Furthermore, it contains less sulfur compounds (Demirbas, 2005), has a high flash point (>130°C) and has been successfully tested in unmodified diesel engines without effecting engine performance. Comparison between biodiesel and fossil-based diesel, biodiesel shows effectiveness in reducing exhaust emissions of carbon monoxide, emitting 80% fewer hydrocarbons and almost 50% less particulates and sulfur (National Biodiesel Board, 2004). Generally, renewable fuel always has an “intrinsic” perception of being environmentally friendly and sustainable (Niederl-Schmidinger and Narodoslawsky, 2008). Hence, there is a need to prove the sustainability credentials of biodiesel in a rigorous manner that can withstand the scrutiny of a competitive market. This can be achieved with the use of life cycle assessment (LCA) as one of the systematic approaches to investigate all upstream and downstream processes or cradle-to-grave analysis for the production of biodiesel to validate the benefits or “cleanliness” of this so called “green fuel” throughout the product lifespan.

In the recent decade, there were unprecedented rise of the biodiesel industry all over the world. As shown in **Figure 1.1**, production of biodiesel in the world has been increasing steadily from the year 1991 to 2005 (Worldwatch Institute, 2006). However, at the beginning of the year 2004, there was a drastic increase in the world biodiesel production from 2,196 million liters to 3,762 million liters in the year 2005. In the year 2006, biodiesel production further jumped 50% compared to the previous year to over 6,000 million liters globally (REN21, 2008). Biodiesel 2020 (2008) reported that the global production for biodiesel in the year of 2007 and 2008 reached over 9,000 million liters and 11,000 million liters, respectively. This is the consequence of the drastic increase in petroleum prices (shown in **Figure 1.2**) which has gained the world attention to find an alternative renewable fuel such as to convert cheaper vegetable oils and animal fats to biodiesel. However, the utilization of vegetable oils and fats for the production of biodiesel has affected the food and oleochemical sectors since these sectors compete for the same raw materials. Due to this circumstance, the issue on food security has been intensively debated all over the world focusing on issues encompassing adequacy, affordability and realiability of oils and fats supply. One possible solution to overcome this problem is to use non-edible oil sources for the production of biodiesel. Since non-edible oils derived from non-edible crops are by nature not consumable by human, it will not affect food security and thus will not lead to the shortage of food supply.

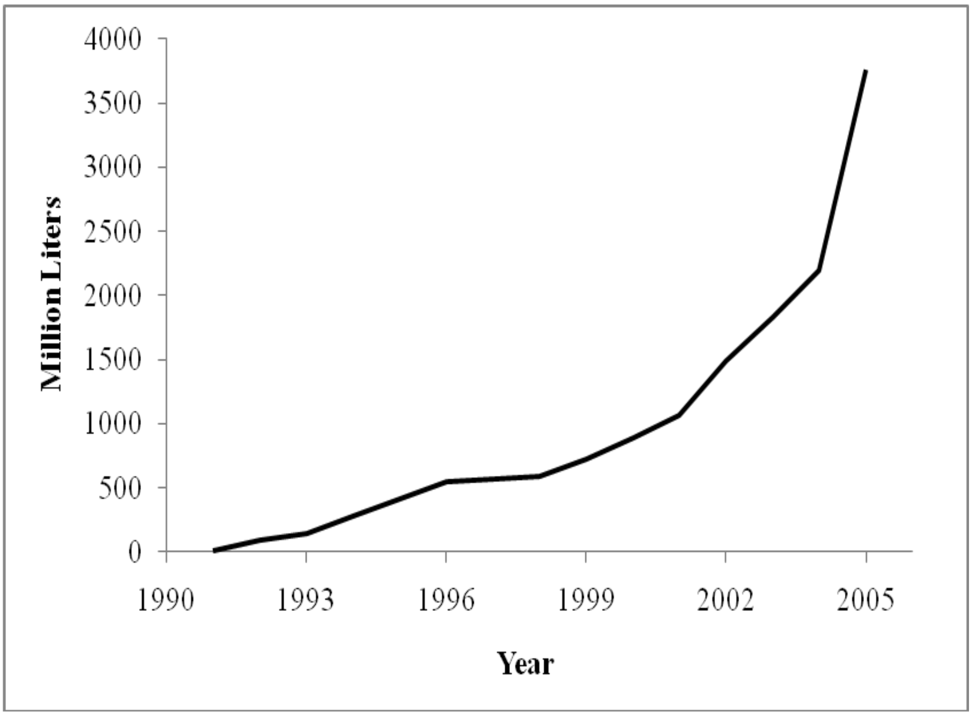


Figure 1.1: World biodiesel production from 1991 to 2005 (Worldwatch Institute, 2006).

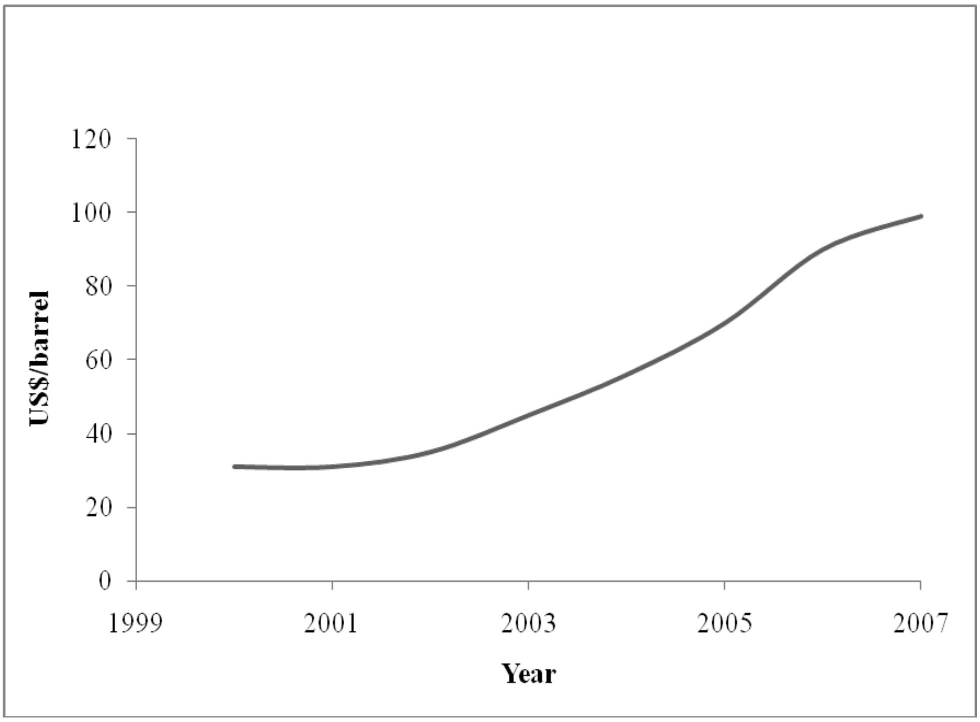


Figure 1.2: Crude petroleum price from 2000 to 2007 (Basiron, 2008).

1.2 Non-edible Oil as Feedstock

Feedstock for biodiesel production covers a wide variety of oil source which can be mainly classified into three types; vegetable oils, animal fats and non-edible oil. However, due to the food versus fuel debate, non-edible oils offer a better prospect as feedstocks. Example of non-edible oils are those derived from plant species such as *Pongamia pinnata* (karanji), *Calophyllum inophyllum* (nagchampa), *Rosa canina* L. (rosehip fruit), *Eribotrya japonica* (loquat fruit), *Cerbera odollam* (sea mango), sweet sorghum and castor. Lately, *Jatropha curcas* L. or physic nut has gained popularity as a potential source of non-edible oil due to its special characteristics. The plant has a lifespan of 30 to 40 years. It is a drought resistant large shrub or small plant tree belonging to the genus *Euphorbiaceae* which produces seeds containing oil. The seeds of *Jatropha curcas* L. are a good source of oil which can be used as a diesel substitute. The oil extracted from the seed can serve as fuel for diesel engines (Berchmans and Hirata, 2008). *Jatropha* seed and oil were found to be toxic to mice, rats, calves, sheep and goats, and human. The high concentration of phorbol esters present in *Jatropha* seed has been identified as the main toxic agent responsible for *Jatropha* toxicity (Kumar and Sharma, 2008). Hence, due to its toxicity, its utilization is limited only for traditional use such as manufacturing soap and medicinal applications and cannot be consumed by human and animal. Therefore, this non-food crop is very suitable to become the feedstock for the production of biodiesel.

Jatropha curcas L. has its native habitat distribution range in Mexico, Central America, Brazil, Bolivia, Peru, Argentina and Paraguay, but is now found abundantly in many tropical and sub-tropical climates across the developing world (Openshaw, 2000). It can grow in arid, semiarid and waste lands, which mean that it can be cultivated on non-agricultural land, and therefore, it does not compete with land for food crops plantation. Apart from that, it has a high-seed yield and high oil content. Under optimum conditions, *Jatropha curcas* L. seeds can yield up to 40 % oil content (The Energy Report, 2008). For extraction of the *Jatropha curcas* L. oil, two main methods are generally used; mechanical extraction and chemical extraction (Arhten *et al*., 2008). Mechanical press is able to extract 60-80 % of the available oil while chemical extraction can extract up to 95-99 % of available oil by using soxhlet apparatus in which n-hexane is used as the extraction solvent. *Jatropha curcas* L. oil contains 20.1 % saturated fatty acids and 79.9 % unsaturated acids. Its fatty acid content is similar to conventional oilseeds such as palm oil, which mainly contains palmitic acid, stearic acid, oleic acid and linoleic acid. Table 1.1 shows the typical properties and fatty acid compositions of *Jatropha curcas* L. oil (De Oliveira *et al*., 2008). Due to this characteristic, *Jatropha curcas* L. oil is seen as a very promising source of non-edible oil that can be used as feedstock for the production of biodiesel.

Table 1.1: Typical properties and fatty acid compositions of *Jatropha curcas* L. oil (De Oliveira *et al*., 2008)

Properties	Value
Calorific value (MJ/kg)	40.31
Acid value (mg KOH/g)	8.45
Kinematic viscosity at 40°C (C_{st})	30.686
Pour point (°C)	-2
Fatty acid composition (%)	
Lauric (C12:0)	5.9
Myristic (C14:0)	2.7
Palmitic (C16:0)	13.5
Stearic (C18:0)	6.1
Oleic (C18:1)	21.8
Linoleic (C18:2)	47.4
Others	2.7

1.3 Transesterification Reaction

Generally, transesterification reaction describes the process of exchanging alkoxy group of an ester compound with another alcohol. The transformation of ester compound occurs by mixing the reactants together. In the transesterification of vegetable oils, triglyceride reacts with alcohol in the presence catalyst, producing a mixture of fatty acids alkyl esters (fatty acid methyl esters) and glycerol. The overall process is a sequence of three reversible reactions, in which di- and monoglycerides are formed as intermediates. **Figure 1.3** shows the stoichiometric reaction which requires 1 mol of a triglyceride and 3 moles of alcohol to form a mixture of alkyl esters and glycerol. Excess amount of alcohol is normally used to increase the yield of alkyl esters and to facilitate easier phase separation from the glycerol formed.

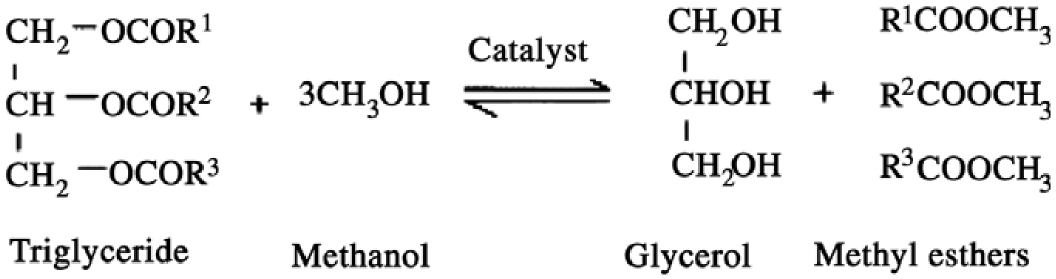


Figure 1.3: General equation for transesterification of triglycerides (Jitputti *et al.*, 2006).

Transesterification reaction requires catalyst in order to obtain reasonable conversion rates. Basically, the catalytic process is categorized based on the type of catalyst used such as homogeneous catalyst, heterogeneous catalyst or enzyme-based catalyst. Furthermore, homogeneous and heterogeneous catalysts can be further divided into base or acid catalyst. Besides that, there is also non-catalytic process for producing biodiesel such as transesterification in supercritical alcohol in which catalyst is not required under the critical reaction conditions.

1.3.1 Homogeneous Catalysis

Homogeneous catalysis uses catalyst which is in the same phase as the reactants. Currently, most biodiesel is produced using homogeneous base catalysts such as sodium and potassium methoxides and hydroxides in a batch process. In the industry, sodium hydroxide, NaOH and potassium hydroxide, KOH are preferred due to their wide availability and low cost (Lotero *et al*., 2005). Apart from that, homogeneous base-catalyzed transesterification proceeds faster and is less corrosive if compared with acid-catalyzed transesterification. Even though transesterification is feasible using homogeneous base catalysts, the process suffers limitations, both from the ecological and economical points of view. Oil that contains significant amounts of free fatty acid (FFA) reacts with homogeneous base catalyst to produce soaps and leads to difficulty in downstream separation process (Lu *et al*., 2009; Berchmans and Hirata 2008). Besides, removal of these catalysts appears to be technically challenging which brings additional cost to the final product (Helwani *et al*., 2009). One way to overcome this limitation is to use heterogeneous catalyst.

1.3.2 Heterogeneous Catalysis

Heterogeneous catalysis is defined as catalyst which is in different phase than the reactants and the catalyst provides a surface on which reaction may take place. An appropriate amount of heterogeneous catalyst could be easily incorporated into a packed bed continuous flow reactor, simplifying product separation and purification and reducing waste generation. There are two types of heterogeneous catalysts which are acid and base. Heterogeneous acid catalysts are preferable than heterogeneous base catalysts as the latter require a feedstock with higher purity. For heterogeneous base catalyst, the total FFA content associated with the lipid feedstock must not exceed 0.5 wt%, otherwise this might lead to undesired saponification side reaction that produces soap. Soap production is undesirable because it causes the emulsification between biodiesel and glycerol which makes the separation of biodiesel-glycerol mixture become more difficult (Shu *et al*., 2007). Heterogeneous acid catalysts can be further sub-categorized by their Bronsted or Lewis acidity. There are many types of heterogeneous acid systems such as heteropoly acids, ion exchange resins (Amberlyst and Nafion-H), zeolites and clays.

1.3.3 Enzyme-based Catalysis

Enzyme-based transesterification is typically catalyzed by lipase such as *Candida antartica*, *Candida rugasa*, *Pseudomonas cepacia*, immobilized lipase (Lipozyme RMIM), *Pseudomonas spp*. and *Rhizomucar miehei*. Both extracellular and intracellular lipases are favourable as they are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems (Helwani *et al*., 2009). However, the main problem with lipase-catalyzed process is the high cost of lipases. Apart from that, this enzyme-catalyzed system normally requires a much longer reaction time than base catalyzed systems (Helwani *et al*., 2009).

1.3.4 Supercritical Alcohol

Lately, non-catalytic transesterification reaction has been reported and continuous effort is being carried out to fully develop this technology for producing biodiesel using supercritical alcohol. A high temperature, high pressure vessels are used to physically catalyze the oil and alcohol into biodiesel. Methanol and ethanol are the alcohols used in this context. At supercritical condition, both the reaction temperature and pressure are above the thermodynamic critical point of alcohol and thus when mixed with oil, only one phase exists. This is because at supercritical condition, the properties of the alcohol are intermediate between those of gases and liquids and can be easily manipulated. The supercritical point for methanol is at a temperature of 240 °C and a pressure of 8.09 MPa (79.8 atm) whereas for ethanol is at a temperature of 243 °C and a pressure of 6.14 MPa (60.6 atm) (Warabi *et al.*, 2004).

1.4 Problem Statement

Biodiesel or fatty acid methyl ester as an alternative fuel for diesel engines has attracted considerable attention during the past decade as a renewable, biodegradable and non-toxic fuel to overcome the shortage of petroleum derived diesel in the coming era while protecting the environment. However, currently, more than 95 % of the biodiesel produced worldwide is from edible oil. Thus, fatty acid methyl ester which is derived from non-edible oil such as *Jatropha curcas* L. has a better potential to replace petroleum-derived diesel fuel as it does not compete with food resources.

Currently in the biofuel industry, biodiesel is mostly produced using a batch process with homogeneous catalyst such as sodium and potassium methoxides and hydroxides. However, homogeneous base catalyzed process suffers from many limitations that translate into high production costs for biodiesel. One of them is the base catalyst used have to be neutralized in the reconditioning step with inorganic acids like sulfuric acid, H_2SO_4. Subsequently, a significant amount of inorganic salts will be formed which must be removed in the purification step. These additional complex reconditioning and purification steps will increase the processing cost of biodiesel unnecessarily. Furthermore, the purification step will produce a lot of wastewater which must be disposed off properly, which again adds cost to the processing step. Another limitation of the homogeneous base catalytic process is the requirement of oil feedstock with high purity.

Non-edible oil normally contains FFA ranging from 3 % to 40 %. When the amount of FFA in the feedstocks exceeds 0.5 wt%, the use of base homogeneous technology for the production of biodiesel, which employs sodium hydroxide as catalysts, is not recommended due to soap formation in the product mixture leading to additional cost required for the separation of soap from the biodiesel. Soap is formed when metal hydroxide catalyst reacts with FFA in the feedstock. Apart from that, the formation of soap will also lead to the loss of triglycerides molecules that can otherwise be used to form biodiesel. Hence, it will make the downstream separation and purification of biodiesel more complex and difficult, making the cost of biodiesel not economical as compared to petroleum-derived diesel. *Jatropha* curcas L. oil contains about 14% FFA, which is far beyond the limit that can be tolerated by homogeneous alkaline catalyst.

Some researchers proposed the use of two step acid-base catalyzed transesterification for oil with high FFA such as *Jatropha curcas* L. oil. In the first step, acid catalyst is used to reduce the FFA in oil to less than 1% by esterifying it to biodiesel. In the subsequent step, transesterification reaction with an alkaline catalyst follows. However, the requirement of this two-step method is not efficient because if appropriate strong heterogeneous acid catalyst is used, the catalyst can catalyze transesterification and esterification reactions simultaneously for oil with high FFA content.

After summarizing all the problems faced by the biodiesel industry, production of biodiesel from *Jatropha curcas* L. oil using heterogeneous acid catalyst was chosen in this study. The use of *Jatropha curcas* L. oil provides an alternative non-edible oil feedstock to overcome the food security issue. Moreover, heterogeneous acid catalytic transesterification reaction provides a more promising solution to overcome the problem faced by homogeneous base catalytic transesterification reaction like complex separation, reconditioning and purification steps and the requirement of feedstocks with high purity.

1.5 Scope

This study consists of three major sections; oil extraction, synthesize of heterogeneous acid catalyst and transesterification process study. For the oil extraction, *Jatropha curcas* L. oil was extracted from the seeds using soxhlet hexane extraction base on the optimum conditions reported by Machmudah *et al*. (2008). The purpose of the extraction stage is to obtain the oil require throughout this study.

The extracted oil was then characterized based on Malaysian Palm Oil Board (MPOB) standard to acquire its basic properties such as density and fatty acid compositions.

For the preparation of heterogeneous acid catalyst, two different methods were used; direct sulfation of zirconia oxide method and solvent-free method. In this study, solvent-free method was used as a comparison with direct sulfation of zirconia oxide method since the use of solvents such as sulfuric acid is not environmentally friendly as they are very harmful to human and the environment and therefore is eliminated. Subsequently, only one of the optimized heterogeneous acid catalysts was selected from this two catalyst preparation methods for the transesterification process study. The life span of the heterogeneous acid catalyst was also investigated using the optimum transesterification process conditions obtained previously. Finally, the biodiesel obtained was characterized.

1.6 Objective

i. To synthesize heterogeneous acidic catalyst using direct sulfation of zirconia oxide method and solvent- free method.
ii. To study and optimize the calcination variables (temperature and duration) for the two different preparation methods and correlate the effect with characterization results.
iii. To study and optimize the transesterification process variables (temperature, duration, molar ratio of methanol to oil, catalyst loading).
iv. To study the reusability and lifespan of the catalyst and the possible regeneration route (re-sulfation method).
v. To characterize the biodiesel produced according to ASTM D6751.

1.7 Organization of the Thesis

This thesis consists of five chapters. Chapter One gives an outline of the overall research project covering some introduction of biodiesel, current scenario on the development of biodiesel, possible use of non-edible oil feedstock for the production of biodiesel and transesterification reaction. Problem statement is then defined after reviewing the existing limitations faced by the biodiesel industry. Hence, this stresses on the need of this research project to overcome the limitations. The objectives of this research project are carefully set with the aim to solve the problems faced by the biodiesel industry. Next the scope of this study is given. Finally, the organization of the thesis highlights the content and arrangement of each chapter.

Chapter Two gives an overall review of various research works reported in the literature in this area of research. The various research works reported include oil extraction, production of biodiesel from *Jatropha curcas* L. oil, types of heterogeneous acid catalyst used in the production of biodiesel and their preparation methods, catalyst recycling, biodiesel characterization and design of experiment. This review is aimed at reporting the feasibility and advantages of using *Jatropha curcas* L. oil and heterogeneous acid catalyst for the production of biodiesel. Meanwhile, the review on design of experiment is given to identify the suitable types of statistical method and model for this research project.

Chapter Three discusses the experimental materials and methodologies used in this research project. This chapter describes detail information on the overall flow of this research work and also several experimental methods used in conducting this research project. Besides, detail information on the materials and chemicals used in this study is also given. This chapter also includes the mathematical equation /information that is required for the calculation of yield and data analysis.

Chapter Four is the most important chapter in this thesis. It encompasses detail discussion in the results obtained in the present research work. This chapter consists of six sections which have been divided according to the stages of this research work. First section of this chapter presents the results of characterization of *Jatropha curcas* L. oil from the seeds. The second and third section reports the effect of calcination variables on catalyst characteristics and the yield of biodiesel through two different catalyst preparation methods; (i) direct sulfation of zirconia oxide method and (ii) solvent-free method. Also, the analysis results of catalyst characterization using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and BET surface area and the optimization of the calcination variables are presented. This is then followed by the fourth section which presents the process study used to optimize the transesterification variables for optimum yield of biodiesel using the optimum catalyst. Section five covers the study on reusability and the life span of the catalyst for the transesterification process. At the end of this chapter, characterization of biodiesel sample obtained in this project is reported.

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

CHAPTER TWO

LITERATURE REVIEW

This chapter reports the literature review related to this research project. Possible oil extraction methods and different oil sources used for the production of biodiesel were reviewed. Then, the suitability of *Jatropha curcas* L. oil as non-edible oil feedstock for transesterification reaction was discussed. Apart from that, reviews on different types of common heterogeneous catalyst used for biodiesel production were also reported. This was followed by the review on sulfated zirconia catalyst which is claimed as the most promising heterogeneous acid catalyst, highlighting its advantages compared with other types of heterogeneous acid catalyst. Besides that, the preparation methods to synthesize sulfated zirconia were also reported in detail. Then the review on catalyst recycling and biodiesel quality were reported subsequently. Review on statistical design of experiment (DOE) was covered at the end of this chapter.

2.1 Oil Extraction

Generally, there are three different methods to be used for extracting oil from oil-containing seed, which are mechanical extraction using screw-presses or ram presses, direct solvent extraction and supercritical carbon dioxide (SC-CO_2) extraction. In recent years, there has been a resurgence of interest in the use of continuous, mechanical screw-presses to recover oil from oilseeds. This is a reliable extraction method which consists of a number of unit operations such as cleaning, cracking, cooking, and drying of the seed followed by pressing. However, according to Marcela *et al*. (2008), the oil recovery of this extraction method is rather low. This statement was supported by Henning (2000) in which it was reported that engine driven screw presses extract 75 % to 80 % of the available oil while manual ram presses only achieved 60 % to 65 % recovery of oil. Marcela *et al*. (2008) further reported that the thermal treatment before or during pressing and the seed moisture content at the time of pressing are the key process variables that effect extraction efficiency. Generally the application of thermal treatment improves oil recovery but it may adversely influence the oil quality by increasing oxidative parameters. However, high moisture content may result in poor oil recovery due to insufficient friction during pressing. Hence, the optimum pressing temperature and moisture content of seed for highest oil recovery (89.3 %) was reported at 50 °C and 7.5 %, respectively.

Another type of conventional oil extraction method is direct solvent extraction by using soxhlet hexane apparatus. In solvent extraction, the duration and amount of hexane used for extraction are the important factors that must be controlled to ensure maximum possible extraction yield. Zaidul *et al*. (2007) reported the use of soxhlet apparatus for the extraction of palm kernel oil from palm kernel using 15 g of palm kernel seed with 200 ml hexane as the extraction solvent. The whole extraction process was carried on for 6 hours. The content of oil in the palm kernel was found to be 50.1 g oil extracted/ 100 g palm kernel on dry basis. In another study, Machmudah *et al*. (2008) reported that the extraction time for hundred percent extraction yield is minimum 8 hours. Apart from that, the amount of hexane required varies based on the amount of grounded seed loaded in the extraction vessel

(Machmudah *et al*.; 2008, Zaidul *et al*., 2007; Molero and Martinez, 2002). Machmudah *et al*. (2008) conducted the extraction process using 35 g grounded seed with 250 ml hexane. However, Zaidul *et al*. (2007) only utilized 15 g seed with 200 ml hexane in the study.

Lately, supercritical carbon dioxide extraction is another extraction method used which utilizes CO_2 above its critical point. The critical temperature and pressure for carbon dioxide are 31.1 °C and 73.8 atm (7.48 MPa), respectively. Study on supercritical carbon dioxide extraction mainly focus on the crucial process variables such as pressure and temperature. Machmudah *et al*. (2008) studied the effect of pressure (15 MPa to 19 MPa) on the extraction yield of rosehip, loquat and physic nut seeds using supercritical carbon dioxide and subsequently predicted the extraction rate using two different models. The results showed that the recovery of rosehip seed oil increased with increasing pressure at short extraction time but decreased as extraction time progress longer. However, the recovery of loquat seed oil increased with decreasing pressure at 60 and 80 °C, but at 40 °C, extraction recovery was independent of pressure. For physic nut, increasing pressure allows high extraction recovery from 83.7 to 88.7 % at constant temperature. Meanwhile, Marcela *et al*. (2008) studied the extraction process of oil from walnut seeds by mechanical pressing followed by supercritical carbon dioxide. The best result for this type of extraction (92.6 %) was obtained at 40 MPa, 50 °C and 7.5 % seed moisture. Apart from that, Westerman *et al.* (2006) also investigated the effect of solvent flow rate and sample pre-treatment (shell disruption) on the extraction rate and yield. It was found that the rate of extraction was only dependent on the solvent flow rate, while the yield is dependent on the solvent flow rate and sample pre-treatment.

Besides that, Louli *et al*. (2004) studied the effect of particle sizes on the extraction rate. It was shown that an increase of particle size in the seeds decrease the extraction rate. Based on all these studies reported, it was found that the operating pressure and temperature for supercritical carbon dioxide normally range from 15 MPa to 40 MPa and 35 °C to 50 °C, respectively.

Based on the literature review on the various oil extraction methods, it can be summarized that mechanical screw-press is not suitable due to the requirement of many processing steps and low oil recovery rate. On the other hand, supercritical carbon dioxide is not suitable as it requires high operating pressure. Hence, in this study, conventional soxhlet hexane extraction method was selected to extract *Jatropha curcas* L. oil from the seed.

2.2 Oil Feedstocks

Up until today, the common approach for biodiesel production is by transesterification of vegetable oils and animal fats. A variety of vegetable oils has been exploited for biodiesel production with varying but promising results. The oils used include soybean (Garcia *et al*., 2008; Xie *et al*., 2006; Suppes *et al*. 2004), rapeseed (Georgogianni *et al*., 2009; Kwiecien *et al*., 2009; Zhang *et al*., 2006), sunflower seed (Lukic *et al*., 2009), cotton seed (Nabi *et al*., 2009; Selvi and Rajan, 2008) and palm oil (Abdullah *et al*., 2009; Noiroj *et al*. 2009; Kansedo *et al*, 2009). Different types of vegetable oils have different types of fatty acids which vary in terms of their carbon chain length and in the number of double bonds.

According to Gubitz *et al*. (1999), *Jatropha curcas* L. oil can be used directly as fuel in diesel engines or by blending it with methanol. Takeda (1982) also reported that *Jatropha curcas* L. oil shows a satisfactory engine performance in Thailand during an engine test. However, direct use of *Jatropha curcas* L. oil in engine may cause problem in a long run, and therefore, recently researchers have been putting a lot of effort to use this non-edible oil for biodiesel production through transesterification process. Besides that, the life cycle energy balance of biodiesel derived from *Jatropha curcas* L. oil is reported to be positive (Tobin and Fulford, 2005). These results showed that it is possible to use *Jatropha curcas* L. oil as oil feedstock for the production of biodiesel.

Bechmans and Hirata (2008) and Tiwari *et al*. (2007) have developed a technique to produce biodiesel from *Jatropha curcas* L. oil with high FFA content (15 % FFA). Two stages transesterification process was selected to improve methyl ester yield. The first stage involved sulfuric acid pretreatment process to reduce the FFA level of crude *Jatropha* seed oil to less than 1 % (1.43 % v/v H_2SO_4, 0.28 v/v methanol to oil ratio, 88 minutes reaction time, reaction temperature at 60 °C) and second stage was the alkali base catalyzed transesterification process that can give 90 % methyl ester yield (0.16 v/v methanol to oil ratio, 24 minutes reaction time, reaction temperature at 60 °C). In the pretreatment stage, maximum conversion of FFA was obtained at high acid concentration and methanol to oil ratio. Reaction time showed an insignificant effect on the conversion of FFA. In transesterification stage, methanol to pretreat oil ratio showed the most significant effect on the conversion follow by reaction time. However, the interactions of variables for both stages also affect the conversion of FFA and conversion of oil.

Apart from that, Lu *et al*. (2009) also studied biodiesel production from *Jatropha curcas* L. oil in a two-step process consisting of pre-esterification and transesterification. In the first step, FFA in the oil was converted to methyl esters using sulfuric acid or sulfated titanium oxide as catalyst. The yield of biodiesel was compared between both types of catalyst in the pre-esterification step. Then, KOH was used as the catalyst in the transesterification process and 98 % of biodiesel yield was achieved. In the pre-esterification step using sulphuric acid as catalyst, increased reaction temperature, time, methanol to oil ratio could reduce the acid value of oil to below 1 mg KOH/ g. The optimum conditions were at 70 °C, 2 hours reaction time, 12 wt% methanol and 1 wt% H_2SO_4. Apart from that, in the pre-esterification step using sulfated titanium oxide, the yield increased when reaction time and catalyst loading increase, however, reaction time longer than 3 hours and catalyst loading over 4 wt% did not change the yield anymore. Apart from that, increasing reaction temperature from 70 °C to 90 °C increased the yield but further increase of reaction temperature reduces the yield. The use of excessive methanol was also reported to increase the reaction rate and promote the completion of reaction. Hence, the optimal conditions obtained were at 90 °C, 2 hours, methanol to oil ratio at 20 and 4 wt% catalyst loading. In the transesterification reaction, the results showed that higher methanol to oil ratio led to greater yield for a given reaction time. Also, higher yield was obtained at a higher reaction temperature between 35 °C to 65 °C. Therefore, an optimal yield over 90 % was reported at the following optimum conditions at 64 °C in 20 minutes with 1.3 % KOH as catalyst and methanol to oil ratio at 6.

Amish *et al*. (2009) studied the transesterification of *Jatropha curcas* L. oil with methanol catalyzed by potassium nitrate loaded on alumina, KNO_3/Al_2O_3. In addition, the effect of various variables was also studied such as reaction time, catalyst loading, methanol to oil molar ratio and the agitation speed. The result showed that the effect of reaction time on yield of biodiesel become insignificant after the process had reached equilibrium. Besides that, the yield of biodiesel was reported to increase with initial increase in catalyst loading, but further increase in the catalyst amount decreased the yield of biodiesel. Also, the yield of biodiesel increased when higher methanol loading was used. Apart from that, the results showed that an efficient mixing of the reagents was essential to reach a high yield of biodiesel. Therefore, under optimum conditions, biodiesel yield of 84 % was attained (70 °C, 6 hours, 6 wt% catalyst, methanol to oil molar ratio of 12, agitation speed at 600 rpm) by using *Jatropha curcas* L. oil as oil feedstock. Hence, *Jatropha curcas* L. oil is a potential candidate in the production of biodiesel replacing edible oil which has been heavily criticized due to the food security issue. **Table 2.1** summarized the work done by the researchers.

Table 2.1: Production of biodiesel with different routes using *Jatropha curcas* L. oil.

Optimum condition	Researchers			
	Tiwari *et al.* (2007)	Lu *et al.* (2009)		Amish *et al.* (2009)
Pre-treatment				
Temperature	60 °C	70 °C	90 °C	-
Time	88 minutes	120 minutes	120 minutes	-
Methanol	0.29 % v/v	12 wt%	20 molar ratio methanol to FFA	-
Sulfuric acid	1.43 % v/v	1 wt%	4 wt% (sulfated titanium oxide)	-
Conversion of FFA	Acid value below 1.0 mg KOH/ g	Acid value below 1.0 mg KOH/ g	97%	-
Transesterification				
Temperature	60 °C	64 °C		70 °C
Time	24 minutes	20 minutes		6 hours
Methanol to oil molar ratio	0.16 % v/v	6		12
Catalyst	5.5 g KOH/ liter oil	1.3 wt% KOH		6 wt% KNO_3/Al_2O_3
Yield of biodiesel	99 %	98 %		84 %

2.3 Heterogeneous Catalyst

There are two types of heterogeneous catalysts which are acid and base. Heterogeneous acid catalyst is preferable than heterogeneous base catalyst as the latter require oil with higher purity or otherwise it could lead to undesire saponification side reaction. Soap production is undesirable because it reduces the ester yields and makes the recovery of glycerol considerably more difficult, due to the formation of emulsions (Vicente *et al*., 2004). In the case when the amount of FFA in the feedstock exceeds 0.5 %, the use of heterogeneous base catalyst is not recommended (Xie *et al*., 2007). However, heterogeneous acid catalyst allows the transesterification of vegetable oils or animal fats even with high content of FFA (Tiwari *et al*., 2007).

There are many types of heterogeneous acid catalyst such heteropoly acids, ion exchange resins (Amberlyst and Nafion-H) and zeolites. However, each of these catalysts has its own limitations towards the transesterification reaction (Ahmed *et al*., 2008; Reddy *et al*., 2005). Ahmed *et al*. (2008) reported that heteropoly acids easily loose their activity at higher temperature due to collapse in structure and thus is not suitable for use in biodiesel production where high reaction temperature is required. Another researcher, Kiss *et al*. (2006) investigated various heterogeneous acid catalysts which included ion exchange resins and zeolites in the esterification of dodecanoic acid with 2-ethylhexanol, 1-propanol and methanol at 130-180 °C. The results showed that ion exchange resins only showed high initial activity and deactivated after 2 hours reaction duration. This made ion exchange resins not suitable for continuous industrial process, where a long catalyst lifetime is essential. Besides that, zeolites showed only a small increase of conversion (1-4 %) compared to non-catalyzed reaction. It was suggested that zeolites are not suitable for production of biodiesel due to its small pores (micropores) that caused diffusion limitations of large fatty acid molecules. Thus the catalytic reaction probably takes place only on the external surface. Moreover, the hydrophilic catalyst surface leads to deactivation of catalytic sites due to strong adsorption of polar by products such as glycerol and water.

Due to all these limitations, there are ongoing efforts to develop stronger heterogeneous acid catalyst which have better characteristics such as water tolerant, stable at high temperature and suitable for both liquid and vapor phase reaction conditions. Among various heterogeneous superacid catalysts reported, sulfated zirconia is a catalyst that possesses strong acid site and possesses all the advantages of heterogeneous catalysts (Zhao *et al*., 2008). This catalyst has been found to exhibit high catalytic activity for skeletal isomerization of light paraffins, n-alkane isomerization, alkylation, acylation, dehydration of ethanol, esterification, etc. (Ahmed *et al*., 2008; Zhao *et al*., 2008; Ardizzone *et al*., 2004). Sulfated zirconia is a potential replacement for mineral acids like sulfuric acid, H_2SO_4, nitric acid, HNO_3 and hydrofluoric acid, HF in esterification and transesterification reactions since it has superacid sites that could contribute to high catalytic activity (Ni and Meunier, 2007; Jitputti *et al*., 2006; López *et al*., 2005).

Apart from that, under appropriate reaction conditions, sulfated zirconia allows the simultaneous esterification of FFA and transesterification of triglycerides for oil with high FFA content (Suwannakarn *et al*., 2008). This will eliminate the requirement of complicated two-step process for the production of biodiesel which includes acid-catalyzed esterification process and alkali base catalyzed transesterification process as reported by some of the researches (Tiwari *et al*., 2007; Berchmans and Hirata, 2008). The catalytic behavior of sulfated zirconia is controlled by its surface phenomenon and generally larger surface area will have higher catalytic activity. Against all the positive points of sulfated zirconia, its relatively small surface area and non-uniform pore size limit its potential applications in catalytic reactions. Therefore, sulfated zirconia must be supported on materials with high surface area to improve its textural properties, such as alumina. Alumina was more preferred as a support than other supports in the production of biodiesel through transesterification reaction (Zabeti *et al*., 2009).

Several studies have been conducted concerning the preparation method, catalyst characterization and possible application of sulfated zirconia in the production of biodiesel. In particular, it has been shown that acidic and catalytic properties of sulfated zirconia catalyst depend heavily on sulfation procedure (Comeli *et al*., 1995) and calcination temperature (Monterra *et al*., 1996). Variation in any of these variables can drastically affect the resultant catalytic activity of sulfated zirconia.

Ahmed *et al*. (2008) studied the effect of calcination temperature and the effect of incorporation of sulfate ion (SO_4^{2-}) in zirconia oxide (ZrO_2) (wet impregnation method) on the structural properties of the catalyst using X-ray diffraction, nitrogen adsorption at -196 °C and adsorption of pyridine at room temperature. XRD showed that the sample contain mixture of tetragonal and monoclinic zirconia phases. The percentage of tetragonal zirconia phase was found to depend on sulfate content and calcination temperature. **Figure 2.1** showed the x-ray diffraction patterns of sulfated zirconia catalyst (10% polyvinyl alcohol, 30 wt% sulfates) at different calcination temperature. The monoclinic phase peaks were located at $2\theta = 28.16$ °, 31.44 ° and that for tetragonal phase peaks at $2\theta = 30.15$ °.

The sample calcined at 400 °C was mainly amorphous. For samples calcined at 500 °C the predominant phase is the tetragonal phase. By increasing calcination temperature to 600 °C and 700 °C, the percentage of tetragonal phase decreased gradually up to 700 °C at which monoclinic phase become the predominant phase. Apart from that, the surface area of the investigated samples was influenced with the sulfate content and calcination temperature as well. A continuous decrease in surface area was observed with the rise of calcination temperature from 400 °C to 700 °C. Besides that, acidity studies demonstrated the presence of mixture of Brónsted and Lewis acid sites. In summary, it was reported that sulfate ions concentration and calcination temperature at 15 wt% and 500 °C, respectively, resulted to the highest content of tetragonal phase and largest surface area in sulfated zirconia catalyst.

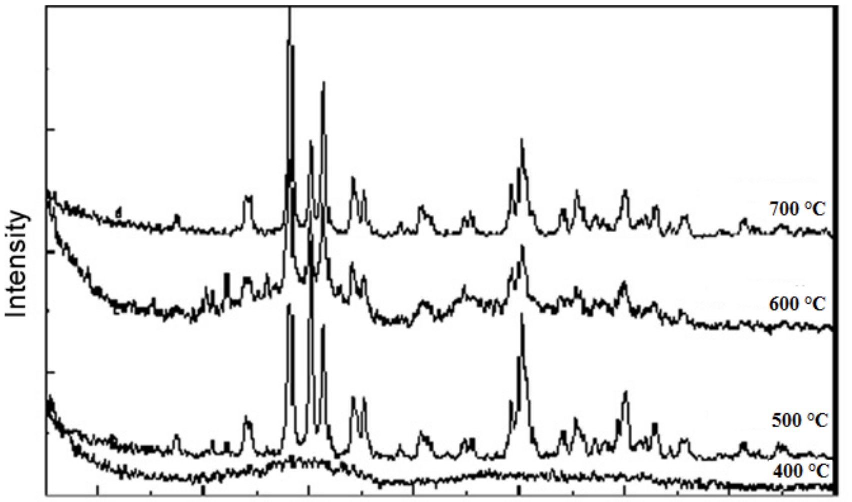


Figure 2.1: X-ray diffraction patterns of sulfated zirconia catalyst (10% polyvinyl alcohol, 30 wt% sulfates) at different calcination temperature (Ahmed *et al.*, 2008).

Mekhemer (2006) investigated the effect of calcination temperature (500 °C to 800 °C) on pure zirconia oxide and sulfated zirconia which was prepared by wet impregnation method. The samples were analysed using X-ray powder diffractometry, N_2 sorptiometry and FTIR spectroscopy of adsorbed pyridine molecules. **Figure 2.2** showed the x-ray powder diffractogram of sulfated zirconia as a function of calcination temperature. It was obvious that the tetragonal phase peak was formed at 500 °C and 600 °C with a few weak peaks assignable to a minor proportion of monoclinic phase. At temperature higher than 700 °C, the monoclinic phase peak was dominant. **Table 2.2** showed the surface area and particle size of pure and sulfated zirconia. Sulfated zirconia showed higher surface area than pure zirconia oxide within the range of calcination temperature studied. Apart from that, increasing calcination temperature from 500 °C to 700 °C, surface area for both pure and sulfated zirconia decreased but with increasing of particle size. These results may indicate that the presence of sulphate ions was capable to stabilize the surface area of sulfated zirconia and these incorporated sulphate ions retard the formation of larger crystalline of zirconia. Apart from that, acidity studies revealed that pure zirconia oxide has no Brónsted acidic sites which indicate that the surface only contains Lewis acid sites. However, sulfated zirconia showed both Brónsted and Lewis acid sites that enhanced its acidic strength.

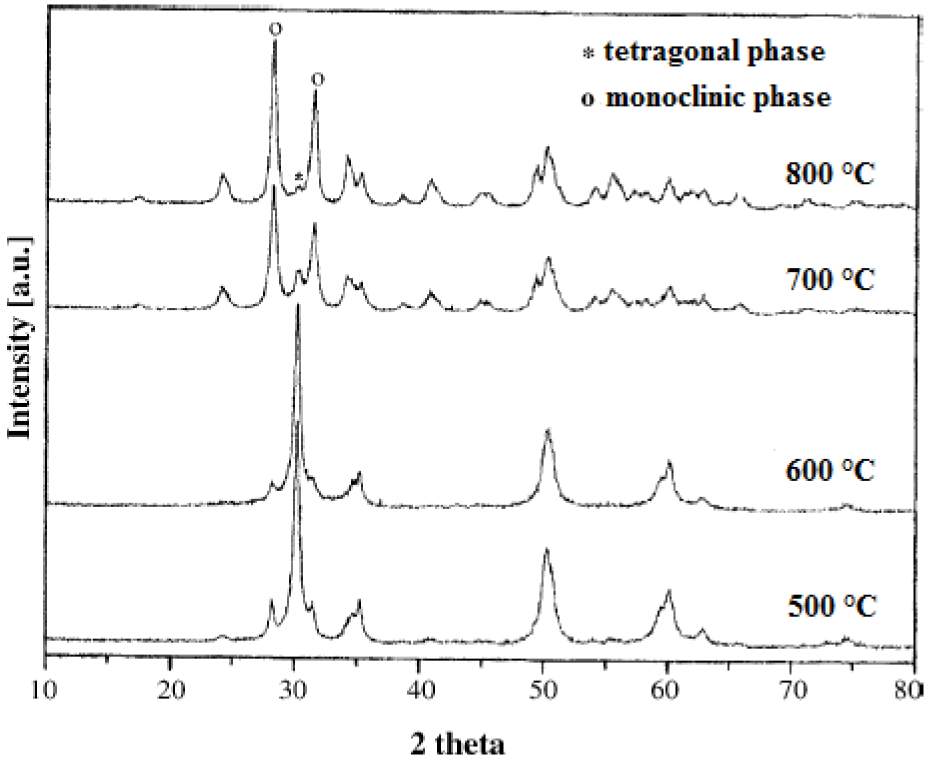


Figure 2.2: X-ray powder diffractogram of sulfated zirconia as a function of calcination temperature (Mekhemer, 2006).

Table 2.2: Surface area and particle size of pure and sulfated zirconia with different calcination temperature (Mekhemer, 2006).

	Calcination temperature							
	500 °C		600 °C		700 °C		800 °C	
	Pure	Sulfated	Pure	Sulfated	Pure	Sulfated	Pure	Sulfated
S_{BET} (m^2/g)	88	110	54	100	38	72	21	39
Particle size (nm)	13.0	12.2	20.3	13.6	30.5	17.5	37.3	23.0

Li and Li (2002) studied on the phase transformation of sulfated zirconia which was calcined at different temperature by investigating the XRD patterns of sulfated zirconia sample. As shown in **Figure 2.3**, broad peaks of the tetragonal phase were detected for sample calcined at 500 °C. These indicated that the sample was in an intermediate amorphous to tetragonal form. The peaks of tetragonal phase become stronger when the sample was calcined at 600 °C as that of the peaks of monoclinic phase. The peak intensities of the monoclinic phase grow steadily and those of the tetragonal phase decline with the increase in calcination temperature from 700 °C to 800 °C. For the sample calcined at 800 °C, the monoclinic phase was predominant. Hence, it was revealed that the increase of calcination temperature leds to crystalline growth due to loss of sulfate group, which leads to instability of tetragonal phase. The phase change of sulfated zirconia was significantly retarded with the presence of surface sulfate groups.

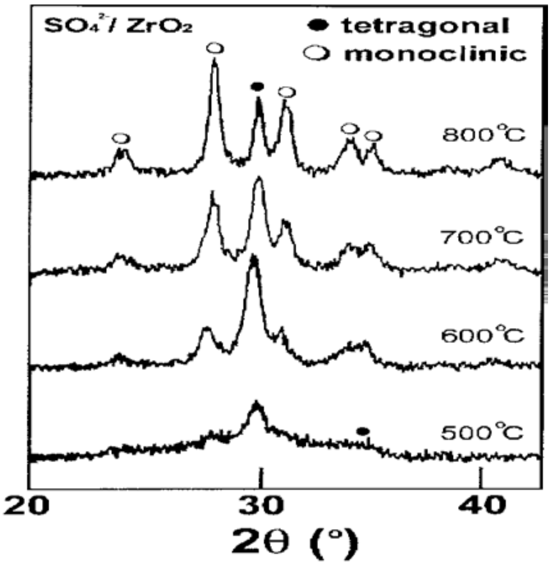


Figure 2.3: XRD patterns of sulfated zirconia calcined at 500 °C, 600 °C, 700 °C, 800 °C (Li and Li, 2002).

Zhao *et al*. (2008) prepared a novel mesoporous heterogeneous acid catalyst system by loading sulfated zirconia into mesostructured γ-Al_2O_3 and mobil composition of matter no. 41 (MCM-41). The textural and structural properties as well as acid properties of the catalysts were characterized. The results showed that a novel mesoporous solid acid with large surface area and pore volume were successfully synthesized by loading sulfated zirconia into mesostructural γ-Al_2O_3. This catalyst has equivalent acid strength to sulfated zirconia but with more acid sites (with both Lewis and Bronsted acid sites). Besides that, zirconia in the mesoporous catalysts exhibits only tetragonal phase. It was also shown that sulfated zirconia supported with alumina exhibits a better textural and structural properties than supported with MCM-41. Hence, the novel mesoporous solid acids are more active than sulfated zirconia and MCM-41 supported zirconia. Besides that, Prescott *et al*. (2004) studied the preparation, physical surface properties, surface acidity and catalytic activity of sulfated zirconia catalysts supported on silicon dioxide (SiO_2), γ-Al_2O_3 and montmorillonite K-10. It was reported that the catalytic activity was higher than that of bulk sulfated zirconia with the use of a support. Apart from that, it was revealed that the physical surface properties play a secondary role in the catalytic activity in comparison to other factors, such as surface acidity. Also, it was shown that Brónsted acid sites have a greater effect on the catalytic activity compared to Lewis acid sites.

Apart from that, Kiss *et al*. (2006) reported that sulfated zirconia was found to be a good candidate for the esterification of fatty acids with a variety of alcohols (2-ethlyhexanol, 1-propanol, and methanol) under specific process conditions due to its active, selective and stable state. The catalyst was prepared using two-step synthesis procedure with modification and calcined for 3 hours at 650 °C. The following characteristics were reported; 118 m^2/g surface area, 0.099 cm^3/g of specific pore volume and 3 nm of average pore size. The initial rate of the catalyzed reaction was about three times higher compared to that of non-catalyzed reaction. Even after 20 minutes of reaction, the conversion of the catalyzed reaction was double to that of non-catalyzed reaction. Apart from that, the catalyst has high reusability where by even after five consecutive runs, with no treatment between the runs, the activity only dropped to 90 % of the original value and remained constant thereafter. Recalcination of this (slightly) deactivated catalyst can restore it to the original activity.

Kansedo *et al*. (2009) investigated the performance of sulfated zirconia supported by alumina as a heterogeneous catalyst in the transesterification of sea mango oil. The yield of biodiesel obtained under optimized conditions (180 °C, 3 hours, methanol to oil molar ratio at 8, 6wt% of catalyst) was 83.8 %. Suwannakarn *et al*. (2008) studied the use of sulfated zirconia in the acid catalyzed alcoholysis of triglycerides using a model triglyceride compound, tricaprylin (TCP) and three low molecular weight alcohols; methanol, ethanol and n-butanol. The reaction was carried out for 2 hours at 120 °C and 6.8 atm in a Parr batch reactor with typical molar ratio of alcohols to TCP at 12:1 and catalyst concentration at 10 wt% based on the weight of TCP. It was found that the catalytic activity for TCP conversion decreased as the number of carbons in the alkyl chain of alcohol increased from methanol (84 %), ethanol (45 %) to butanol (37 %), most likely as a result of increased steric hindrance.

Chen and Wang (2006) studied the production of biodiesel from cottonseed oil using sulfated zirconia catalyst. Sulfated zirconia was prepared by mounting immersed H_2SO_4 on zirconium hydroxide ($Zr(OH)_4$) and then followed by calcining at 550 °C. In the case of using 2 wt% of the catalyst with methanol to oil molar ratio at 12 to 1, an optimum yield of biodiesel (80.0 wt%) can be obtained under desired reaction temperature at 230 °C for 7 hour. **Table 2.3** shows the comparison of biodiesel yield obtained with sulfated zirconia catalyst under different reaction conditions.

Table 2.3: Comparisons of biodiesel yield obtained with sulfated zirconia catalyst under different reaction conditions.

Optimum reaction condition	Researchers		
	Chen and Wang (2006)	Kansedo *et al.* (2007)	Suwannakarn *et al.* (2009)
Oil feedstock	Cottonseed oil	Sea mango oil	Tricaprylin (TCP)
Alumina supported	no	yes	no
Temperature	230 °C	180 °C	120 °C
Duration	7 hours	3 hours	2 hours
Methanol to oil molar ratio	12	8	12
Catalyst loading	2 wt%	6 wt%	10 wt%
Yield of biodiesel	80.0 %	83.8 %	84 %

2.4 Preparation of Sulfated Zirconia Catalyst

The acidic and catalytic properties of sulfated zirconia highly depends on the preparation method, preparation procedure and calcination conditions (Reddy *et al*., 2005; Ahmed *et al*., 2008). There are various methods for the preparation of sulfated zirconia catalyst, which can be generally classified into two types. The first one is a two steps process starting from precipitation followed by impregnation. The other one is sol-gel method, which is a single step method.

In the two steps method, zirconium hydroxide, $Zr(OH)_4$ is synthesized during the first step followed by sulfate impregnation in the second step. In the first step, precipitation process is carried out by using precipitated agents to precipitate starting material (which is zirconium compounds) to $Zr(OH)_4$. There are various zirconium compounds that can be used such as zirconium nitrate, $Zr(NO_3)_2.5H_2O$, zirconium chloride, $ZrCl_4$, zirconyl chloride octahydrate, $ZrOCl_2.8H_2O$ and zirconium isopropoxide, $Zr(OC_3H_7)_4.C_3H_7OH$. Ammonium hydroxide, NH_4OH and urea are normally use as the precipitating agents. In the second step, sulfate impregnation is carried out by introducing sulfating agent to $Zr(OH)_4$. The most commonly used sulfating agent is H_2SO_4 and ammonium sulfate, $(NH_4)_2SO_4$. Some sulfur compounds such as hydrogen sulfide, H_2S and sulfur dioxide, SO_2 have also been used. However, it has been observed that the use of H_2SO_4 as the sulfating agent shows higher sulfate concentrations and higher specific surface area. **Figure 2.4** shows the schematic diagram which summarize this method.

Tichit *et al*. (1996) synthesized sulfated zirconia using this preparation method for the isomerization of n-hexane. $Zr(OH)_4$ with specific area in the range of

60 to 300 m^2/g were obtained in aqueous media by hydrolysis of $ZrOCl_2.8H_2O$ salt solutions (0.4 *M*) with adjusted quantities of NH_4OH (6 *M*). These compounds were then sulfated by impregnation with 15 and 35 ml of aqueous 0.5 *M* H_2SO_4. It was reported that the solids remain amorphous up to at least 400 °C and then crystallize in the tetragonal and monoclinic phases. However, Kiss *et al*. (2006) performed a modification on the two-step catalyst synthesis method for the esterification of dodecanoic acid with alcohol. 50 g of $ZrOCl_2.8H_2O$ was dissolved in 500 ml water followed by precipitation of $Zr(OH)_4$ at pH 9 using 25 wt% NH_3 solution. The resulting $Zr(OH)_4$ was washed with water to remove the chloride salts. In the second step, $Zr(OH)_4$ was dried for 16 hours at 120 °C, impregnated with 1 N H_2SO_4 (15ml H_2SO_4 per 1g $Zr(OH)_4$) and calcined in air for 3 hours at 650 °C. The result showed that sulfated zirconia synthesis by this method is appropriate to apply in the production of biodiesel under appropriate process conditions. However, optimization of the process variables was not performed in this study.

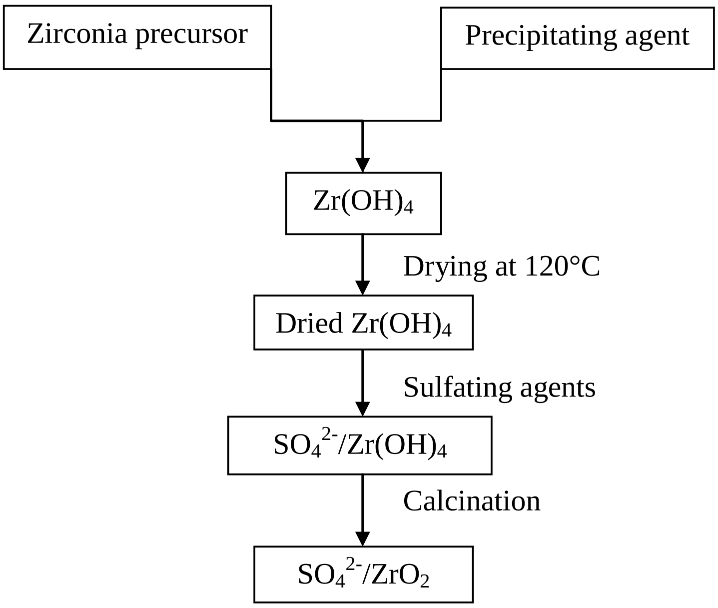


Figure 2.4: Two step preparation procedure for sulfated zirconia (Reddy and Patil, 2009).

Apart from that, sol gel technique is another way to produce sulfated zirconia. This method has the advantage of high chemical homogeneity, require low processing temperature and offers possibility of controlling the size and morphology of the resulting particles. Furthermore, the sol gel-derived materials provide excellent matrixes for a variety of organic and inorganic compounds. Due to these huge advantages, it has attracted a lot of researchers to study the preparation of sulfated zirconia via sol gel method (Melada *et al*, 2004; Ben Hamouda *et al*., 2000; Armendariz *et al*., 1997). However, the procedures employed by each researcher may differ slightly from one to another to suite specific needs.

Ward and Ko (1994) reported an efficient method to synthesize sulfated zirconia aerogels in a one step synthesis through sol gel method followed by supercritical drying for n-butane isomerization. During the sol gel formation of the aecogel, sulfuric acid solution was added to the zirconium n-propoxide in n-propanol and reacted with water and nitric acid, in order to incorporate sulfate functional group into the alcogel network, leading to the formation of a zirconium sulphate cogel. Then, sulfated zirconia aerogel was obtained after supercritical drying with carbon dioxide which was used to remove the alcohol solvent.

Apart from that, Melada *et al*. (2004) investigated the effect of preparative variable (water/ alkoxide molar ratio) in the preparation of sulfated zirconia xerogels by a single step sol gel method. Zirconium n-propoxide (as precursor) was mixed with 2-propanol (as solvent) and sulfuric acid was added dropwise with stirring. Sulfuric acid was used both as the sulfating agent and as the catalyst of the polycondensation reaction in the gel formation. When the exothermic reaction was accomplished, a water/ 2-propanol solution was introduced drop by drop with stirring for 2 hours. The water/ alkoxide molar ratio was varied in the starting mixtures at 1.4, 14, 60 and 143. After ageing and drying process, the dried xerogels were calcined. The characterization results showed that water/ alkoxide molar ratio is an important factor in the development of a high surface area and in the retention of sulfur after the calcination step. However, it does not influence the final structure of the catalyst.

Although a lot of researchers preferentially use sol gel method for the synthesis of sulfated zirconia, but modifications are made to the standard method in order to get specific catalytic characteristics such as larger surface area or to produce mesoporous structure of sulfated zirconia. Sun *et al*. (2005) used a solvent free preparation method to synthesis nanosized sulfated zirconia with brønsted acidic sites using a simple calcination step. In this method, zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$) and ammonium sulfate ($(NH_4)_2SO_4$) were grounded in an agate mortar for 20 minutes at room temperature (25 °C) with a molar ratio of 1:6. After placement for 18 hours at room temperature, the sample was calcined for 5 hours at 600 °C. By using this preparation route, an average size of 7 nm of sulfated zirconia was obtained and the catalyst also exhibited high surface area (165-193 m^2/g). The catalytic tests showed that the sulfated zirconia synthesis by solvent free method exhibits much higher activity than conventional sulfated zirconia in catalytic esterification of cyclohexanol with acetic acid. Conventional sulfated zirconia gives 40 % conversion of cyclohexanol, while the sulfated zirconia synthesis by solvent free method exhibits 62 % conversion, both for 300 minutes reaction duration.

2.5 Catalyst Recycling

One of the main advantages of heterogeneous acid catalysts over liquid acids is that the former can be easily recovered from the reaction mixture. Apart from that, it can be regenerated and reused. Thus, the life span of sulfated zirconia can then be evaluated.

Suwannakarn *et al*. (2008) carried out the recycling studies of sulfated zirconia catalyst by recovering the used catalysts after 2 hours transesterification reaction and reusing them (without pretreatment) with fresh reagents in the subsequent reaction cycle. The reaction were carried out using Tricaprylin (TCP) with three different types of alcohol; methanol, ethanol and butanol. However, the result showed continuous activity loss for all reactions. The TCP conversion dropped significantly from the initially run to the third run of alcoholysis; 80 % to 30 % (with methanol), 45 % to 5 % (with ethanol) and 38 % to 3 % (with butanol). The sulfated zirconia catalyst was deactivated with subsequent reaction runs in all cases due to the leaching of sulfate ion species. However, the degree of sulfur removal was dependent on the alcohol size. Larger alcohol size leads to higher degree of catalyst deactivation.

Garcia *et al*. (2008) investigated the reusability of sulfated zirconia catalyst in the transesterification of soybean oil with methanol. The reaction product was filtered to separate the catalyst. Then, the separated catalyst sample was exhaustively washed with hexane, dried for 1 hour at 60 °C and reuse in the subsequence reaction with fresh reagents. The results showed that yield of biodiesel dropped significantly when using recycle catalyst. After the fourth reaction run, the yield of biodiesel was only 14 % compared to 90 % at the initial run. This revealed that the activity of sulfated zirconia was limited due to its rapid deactivation. The catalysts could be recycled, however, they start losing their catalytic activities after the second reuse. Hence, a more effective catalyst regeneration route should be studied.

Jitputti *et al*. (2006) studied the life span of sulfated zirconia with and without pretreatment. The used catalyst obtained from transesterification was tested to determine whether the one-time used sulfated zirconia was fully deactivated. The used catalyst was recovered by filtering the product mixture with nylon membrane filter. The recovered catalyst was then dried at 100 °C and directly added to the reactor to test for crude palm kernel oil transesterification with fresh reactants. However, the results showed that the reaction catalyzed by spent sulfated zirconia only gave a biodiesel yields of 27.7 wt%, which was much lower than biodiesel produced by fresh sulfated zirconia catalyst (90 wt%). This indicates that the used catalyst was fully deactivated and cannot be directly reused for transesterification without further treatment. Therefore, the used catalyst was regenerated by immersing the reused catalyst in a 0.5 M H_2SO_4 solution for 30 minutes, filtered and dried at 110 °C for 24 hours to form the sulfated sample again. Then, the regenerated catalyst was calcined at 500 °C for 2 hours prior to use. In this case, the regenerated catalyst gave high biodiesel yield (90 wt%) as in the case of freshly prepared catalyst. Hence, this showed that the used catalyst from transesterification can be easily regenerated and results in the same activity as in fresh catalyst.

2.6 Biodiesel Quality

The properties of biodiesel vary with their production methods and ways of handling. Hence, biodiesel produced should be compare with the international standard and the properties should falls within the range of specification. There are two major standards including ASTM International D6751 and European standard EN 14214.

Tiwari *et al*. (2007) studied the production of biodiesel from *Jatropha curcas* L. oil with two-step process consisting of pre-esterification and transesterification using sulfuric acid and potassium hydroxide as catalyst. The product obtained was subjected to biodiesel property test and the results compared with the American Society Testing and Materials standard (ASTM D6751) and European standards (DIN EN 14214). The properties tested include density, kinematic viscosity at 40 °C, flash point, water content, ash content, carbon residue and acid value. **Table 2.4** shows the fuel properties and the biodiesel standards.

Amish *et al*. (2009) studied the production of biodiesel through transesterification of *Jatropha curcas* L. oil using potassium nitrate as heterogeneous catalyst. Apart from that, Lu *et al*. (2009) also studied the production of biodiesel from *Jatropha curcas* L. oil with two-step process using sulfuric acid and potassium hydroxide as catalyst. Both of the biodiesel fuel properties were tested and summarized in **Table 2.4**.

Table 2.4: Fuel properties of *Jatropha* biodiesel and biodiesel standards.

Property	Unit	*Jatropha* biodiesel			Biodiesel standards	
		Tiwari *et al.* (2007)	Amish *et al.* (2009)	Lu *et al.* (2009)	ASTM D6751	DIN EN 14214
Density	kg m^{-3}	880	862	881	860-900	860-900
Viscosity at 40 °C	mm^2 s^{-1}	4.8	4.5	5.13	1.9-6.0	3.5-5.0
Flash point	°C	135	110	164	>130	>120
Water content	%	0.025	-	-	<0.03	<0.05
Ash content	%	0.012	-	-	<0.02	<0.02
Carbon residue	%	0.20	-	-	-	<0.03
Acid value	mg KOH g^{-1}	0.40	-	0.29	<0.80	<0.50

2.7 Statistical Design of Experiment

Statistical design of experiment refers to the process of planning experiment so that appropriate data will be collected and analyzed by statistical methods, resulting in valid and meaningful conclusions. Apart from that, the application of statistical experiment design techniques followed by optimization can results in enhanced yields, close conformance of the process response to target requirements and reduced process variability, development time and cost. A statistical design of experiment is a combination of two aspects which includes the design of experiment and statistical analysis of the data (Montromery, 2001).

2.7.1 Response Surface Methodology (RSM)

RSM is a collection of mathematical and statistical techniques employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously. The graphical representations of these equations are called response surfaces, which can be used as tools to understand complex processes and to describe the individual, cumulative and interactive effects of the variables on the process yield. Thus, it is useful for modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize the response. Based on Montgomery (2001), the ultimate objective of RSM is to determine the optimum operating conditions for the system or to determine a region of the factor space in which operating requirements are satisfied. In most RSM problems, the form of relationship between variables and response are unknown. Therefore, figuring out a suitable approximation for the true functional relationship between variables and response is one of the important functions in RSM and the approximate function is expressed in polynomial model. Usually, a lower-order polynomial in some region of the independent variables is employed. The general form of the first-order model for linear function of the variables is as follow:

$$y = \beta_{\circ} + \beta_1 x_1 + \beta_2 x_2 + \ \dots \ + \beta_n x_n + \varepsilon \qquad (2.1)$$

Besides that, polynomial model is employed for curvature system. In most cases, once experiments are performed, second-order model is used where the coefficient of polynomial model is calculated using the equation shown in **Equation**

2.2. The term *i* and *j* are linear, quadratic coefficients, respectively, while '*β*' is regression coefficient, *n* is the number of variables studied and optimized in the experiment and '*ε*' is random error (Balusu *et al*., 2005).

$$y = \beta_{\circ} + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i_{i<j}}^{n} \sum_{j}^{n} \beta_{ij} x_i x_j + \varepsilon \qquad (2.2)$$

The coefficients in the approximating polynomial are estimated using least square method. The surface response is then performed using the fitted surface. If the fitted surface is an adequate approximation of the true function, then the analysis of the fitted surface will be approximately the analysis of the actual system. The model variables can be approximated effectively with a proper experimental design using variables with appropriate range.

2.7.2 Central Composite Design (CCD)

A full factorial central composite experimental design is used to acquire the data required to fit an empirical quadratic polynomial model involving several factors. Researchers apply this standard RSM design in different area of interest and it has become the most favourable design for fitting a quadratic surface. Generally, CCD consists of three groups of design points, first is the two-level (2^n) factorial or fractional factorial design points, where *n* is the design factor or number of independent variables in the design system, second is the axial points and the third is the center points (Montgomery, 2001)

The two-level factorial design points consist of all possible combinations of the high coded (+1) and the low coded (-1) levels of the factors. The axial points are located at ($\pm\alpha$, 0, 0), (0, $\pm\alpha$, 0) and (0, 0, $\pm\alpha$) where α is the distance of the axial point from center and makes the design rotatable. The center points are use to estimate the overall curvature effect and in the position of (0, 0, 0). The distance α of the axial runs from the design center and the number of center points have to be specific when designing a CCD system. The choice of α determines the rotatability of the CCD. The value for α for rotatability depends on the number of points in the factorial portion of the design. Rotatability is a reasonable basis for the selection of a response surface design. Rotatability in the CCD is important to provide equal precision of estimation in all directions in the design system.

Up until now, there is no study in the literature that reports on the use of statistical design of experiments for the optimization of transesterification of *Jatropha curcas* L. oil with heterogeneous acid catalyst. Most of the optimization studies reported were done manually using the conventional optimizing procedure in which one single variable is optimize at one time while remaining the rest constant. However, statistical design of experiment has been applied in the process optimization for transesterification reaction of other oil feedstocks such as palm oil and waste rapeseed oil. Yuan *et al.* (2008) investigated biodiesel production by alkaline catalyst using response surface methodology and 2^4 full-factorial central composite design. The objectives were to optimize the reaction conditions for maximum yield of biodiesel and understand the significance and interaction of the factors affecting biodiesel production. The results showed that catalyst loading and reaction duration were the limiting factors and little variation in their value would alter the yield of biodiesel significantly. At the same time, there was a significant mutual interaction between catalyst loading and reaction duration. The maximum yield of biodiesel (83.3 %) was obtained at reaction temperature of 48.2 °C, reaction duration of 65.4 minutes, methanol to oil molar ratio of 6.5 and catalyst loading of 1 %.

Apart from that, Hammed *et al*. (2009) applied RSM based on CCD to optimize three important reaction variables; methanol to oil molar ratio, reaction duration and catalyst loading for the production of biodiesel from palm oil using potassium fluoride supported by zinc oxide (KF/ZnO) catalyst. The reaction temperature was controlled at 65 °C by heater. The optimum conditions for biodiesel production were found as follows: methanol to oil molar ratio of 11.43, reaction duration of 9.72 hours and catalyst loading of 5.52 wt%. The optimum biodiesel yield was 89.23 %. Abdullah *et al*. (2009) reported the optimization of mesoporous K/SBA-15 catalyzed transesterification of palm oil using RSM. The influence of reaction variables on biodiesel yield were studied using CCD. It was found that at optimum conditions (reaction temperature at 70 °C, 5 hours reaction duration, methanol to oil molar ratio of 11.6, catalyst loading of 3.91 wt%), 93 % of biodiesel yield can be achieved. Apart from that, the results reveals that the effect of catalyst loading and reaction duration were relatively more dominant in affecting the biodiesel yield.

2.8 Summary

From the literature review, it is clear that *Jatropha curcas* L. oil can be used as an oil feedstock for production of biodiesel. Its non-edible characteristics offer possible replacement for the current edible oil used in biofuel production and ultimately resolve the food versus fuel issue. The fatty acid compositions of *Jatropha curcas* L. oil which is similar to edible oil such as palm oil, positive life cycle energy balance and satisfactory engine performance test has further make it a promising candidate to replace edible oil as biofuel feedstock.

Among the extraction methods, conventional soxhlet hexane extraction method is selected to extract *Jatropha curcas* L. oil from the seed. Mechanical screw-press is not selected since this method requires a lot of machinery for the extraction process and thus is not applicable in a lab-scale project. Besides that, from the literature review, it was reported that supercritical carbon dioxide extraction could not completely extract oil from the seed as compared to soxhlet extraction using hexane. The extracted oil yield was less than 90 % even a very high pressure was applied on the extraction process. Hence, conventional soxhlet extraction method is selected which can completely extract the oil from seed within an acceptable duration.

Currently, most of the biodiesel industries are using homogeneous base catalyst to catalyze the transesterification reaction. However, there are limitations of using such type of catalyst such as soap formation. Thus, the limitation of homogeneous catalyst in the production of biodiesel has caused an increase in the development of heterogeneous catalyst. There are two types of heterogeneous catalysts, which are base and acid catalyst. Since base catalyst is not suitable for oil with high FFA content such as *Jatropha curcas* L. oil. Therefore, heterogeneous acid catalyst has been chosen in this study for the transesterification reaction of *Jatropha curcas* L. oil. Based on the literature review, among heterogeneous acid catalyst, sulfated zirconia has shown promising results in the production of biodiesel.

Generally, there are two methods to prepare sulfated zirconia which are precipitation followed by impregnation method and sol-gel method. Besides that, there are also a lot of modifications done by researchers on these catalyst preparation methods. In this study, a direct sulfation of zirconia oxide method and solvent-free method are selected in the synthesizing of sulfated zirconia. Alumina is being use as the support for both of the methods. The use of both simple and direct preparation methods is attempted to minimize the quantity of chemicals used and to reduce the preparation variables, such as pH. Involving less preparation variables would mean that it is easier to control the final texture and performance of the catalyst.

In this research work, statistical design of experiment is used in the planning of experiments data collection and analysis. The results obtained are then use to optimize the yield of biodiesel. Response surface methodology (RSM) is the technique applied in this study in which the complex transesterification process is then presented graphically. The individual, cumulative and interactive effects of the variables on the process yield are then investigated. A central composite design (CCD) which is one of the standard RSM design was applied to study the process.

This method is suitable for fitting a quadratic surface and it helps to optimize the effective variables with a minimum number of experiments. Hence, the process study and optimization are then performed systematically by using this mathematical and statistical technique.

CHAPTER THREE

MATERIALS AND METHODOLOGY

This chapter describes in detail the experimental works carried out in this study covering raw materials and chemicals, reactor system, characterization of raw materials and products, experimental procedures, analytical method and design of experiments. This chapter is divided into seven sections according to these categories. First section gives information on the raw materials and chemicals used in the study. The reactor system used to conduct the transesterification reaction is presented subsequently; including the schematic diagram of the reactor. Experimental procedures to conduct the experiment work are presented next. In the following section, it gives the type of characterization performed on the raw materials and products samples obtained from this present work. Then, the analysis of samples and sample calculation method are presented. Lastly, at the end of the chapter, the design of experiment gives detail information on the process variables studied and experimental matrix designed using Design-Expert software.

3.1 Raw Materials and Chemicals

In this study, there are several different types of raw materials and chemicals required at different stages of experiment such as for the oil extraction, synthesis of heterogeneous catalyst, transesterification reaction and gas chromatography analysis.

3.1.1 Raw Materials

Jatropha curcas L. seed is the major and the most important raw material required in this study especially for the oil extraction process. Planting grade seed was purchased from a local company in Malaysia, Misi Bumi Alam Sdn. Bhd. The extracted oil was then used in the transesterification reaction for the production of biodiesel after evaporation of n-hexane and filtration steps.

3.1.2 Chemicals

For catalyst preparation, the chemicals used were zirconium oxide, alumina and sulfuric acid for the direct sulfation method, while zirconyl chloride octahydrate and ammonium sulfate were used for the solvent-free method. Apart from that, in the transesterification reaction, methanol was used as the reagent and nitrogen gas was used as an inert gas to pressurize the reactor. Reference standards, such as methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl heptadecanoate were used as the internal standards for gas chromatography analysis. Apart from that, n-hexane was used as extraction solvent in the oil extraction process and also used as a solvent for gas chromatography analysis. All the chemicals used were of analytical reagent grade. The list of raw materials and chemicals used is summarized in **Table 3.1**.

Table 3.1: Source and purity of raw materials and chemicals used in this study.

No	Chemicals	Purity (%)	Source	Purpose of use
1	*Jatropha curcas* L. seed	-	Misi Bumi Alam Sdn. Bhd.	Extracted to obtain *Jatropha curcas* L. oil
2	Zirconium oxide, ZrO_2	97.0	R & M Marketing, Essex, U.K	As active metal in direct sulfation method
3	Alumina, Al_2O_3	98.0	R & M Marketing, Essex, U.K	As catalyst’s support in direct sulfation and solvent-free method
4	Zirconyl chloride octahydrate, $ZrOCl_2.8H_2O$	$\geq$ 99.0	Sigma-Aldrich Chemie GmbH	As zirconia precursor in solvent-free method
5	Ammonium sulfate, $(NH_4)_2SO_4$	$\geq$ 99.0	Sigma-Aldrich Chemie GmbH	As sulfating agent in solvent-free method
6	Sulfuric acid, H_2SO_4	95.0-97.0	Sigma-Aldrich Chemie GmbH	As sulfating agent in direct sulfation method
7	Nitrogen gas	99.999	Air Products STB Sdn. Bhd.	As inert gas to pressurize reactor
8	Methanol	99.8	R & M Marketing, Essex, U.K	As reactant for transesterification reaction
9	n-Hexane	96.0	Merck KGaA	As solvent in dilution of sample prior to GC analysis
10	Sodium chloride, NaCl	pure	Fisher Scientific	As washing solvent in biodiesel purification

Table 3-1. Continued

No	Chemicals	Purity (%)	Source	Purpose of use
11	Sodium sulfate anhydrous, Na_2SO_4	>99.5	Fisher Scientific	As drying agent in biodiesel purification
12	Methyl heptadecanoate	≥ 99.5	Fluka Chemie, Germany	As internal standard
13	Methyl palmitate	≥ 99.5	Fluka Chemie, Germany	As standard reference
14	Methyl stearate	≥ 99.5	Fluka Chemie, Germany	As standard reference
15	Methyl oleate	≥ 99.5	Fluka Chemie, Germany	As standard reference
16	Methyl linoleate	≥ 99.5	Fluka Chemie, Germany	As standard reference

3.2 Experimental Procedure

The experimental procedure in this section will be described according to the flow of this study. **Figure 3.1** shows the overall research methodology used in this study. Initially, oil will be extracted from *Jatropha curcas* L. seed using conventional soxhlet hexane extraction method to obtain *Jatropha curcas* L. oil as the oil feedstock for the whole research work. Subsequently, two different catalyst preparation methods (direct sulfation of zirconia oxide and solvent-free method) were used to synthesize the catalyst required in this study. During catalyst preparation, calcination variables (calcination temperature and duration) were optimized for both preparation methods to obtain catalyst with the highest catalytic activity for transesterification reaction. At this stage of study, only the calcination variables were varied while the process variables for the transesterification reaction were held constant. After optimization, only one of the optimized catalysts which have the highest activity in the transesterification process was selected for the subsequent part of this study. In the transesterification process study, the following reaction variables were studied and subsequently optimized; reaction temperature, duration, molar ratio of methanol to oil and catalyst loading. Finally, the reusability of the catalyst was tested. Apart from that, characterization on the catalyst used and biodiesel obtained were conducted whenever appropriate.

3.2.1 Oil Extraction

Jatropha curcas L. oil was extracted from *Jatropha curcas* L. seed using soxhlet hexane extraction. **Figure 3.2** shows the schematic diagram of the oil extraction apparatus. The process variables for the extraction process namely extraction temperature, extraction duration, weight of grounded seed and amount of solvent used were selected base on the optimum conditions reported by Marchmudah *et al*. (2008). The values were fixed for all batches of extraction. Initially, 30 g of grounded seed was loaded into a cellulose thimble and then inserted into the inner tube of the soxhlet extractor. Then, it was connected to a reflux condenser and a round bottom flask, which contained the extraction solvent (150 ml hexane). The whole apparatus then placed on a heater where the solvent was boiled in the round bottom flask to a temperature above its boiling point (approximately 80 °C). After 8 hours, hexane was separated from the extracted oil by using rotary evaporator and subsequently reused.

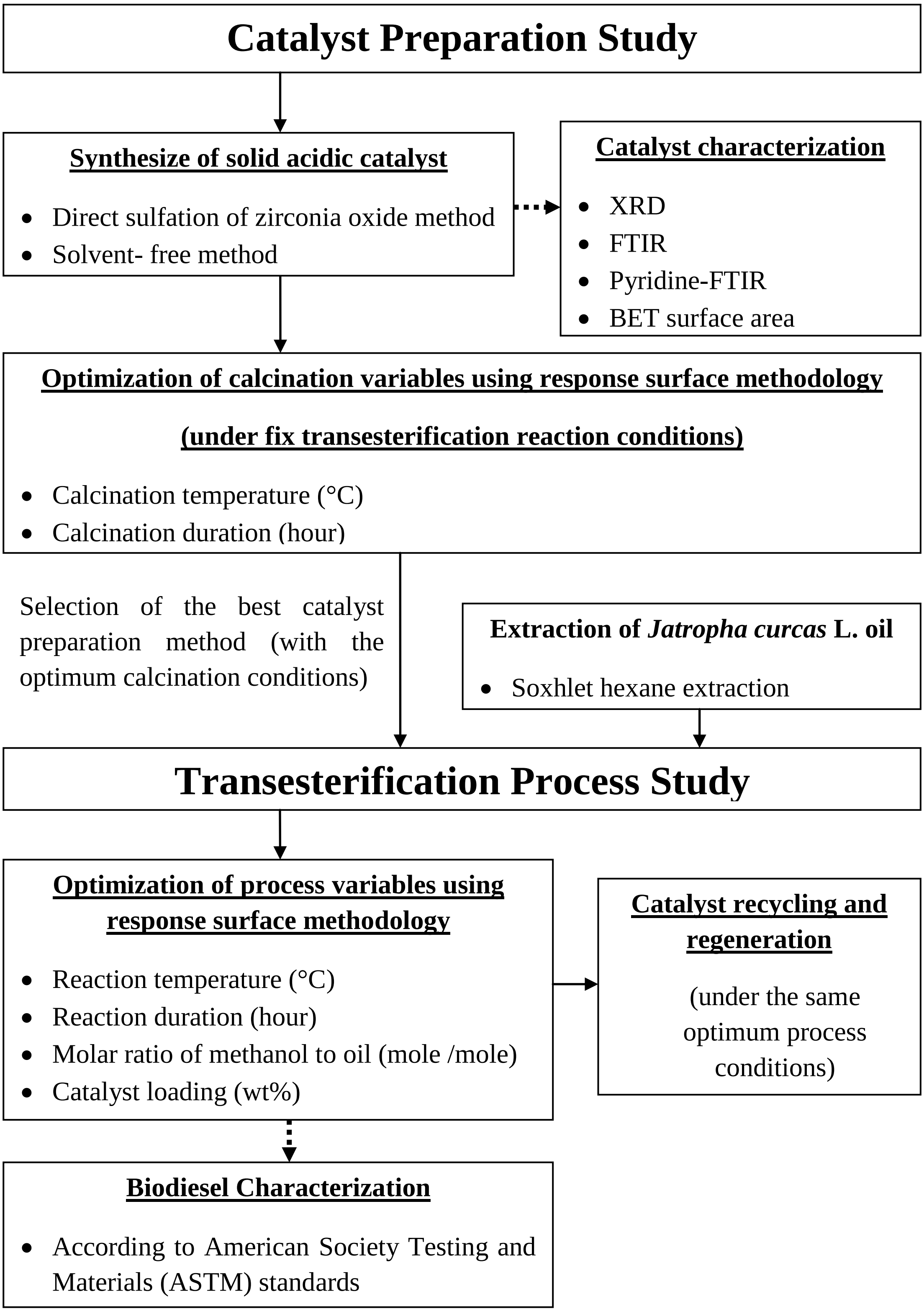


Figure 3.1: Overall research methodology flow diagram.

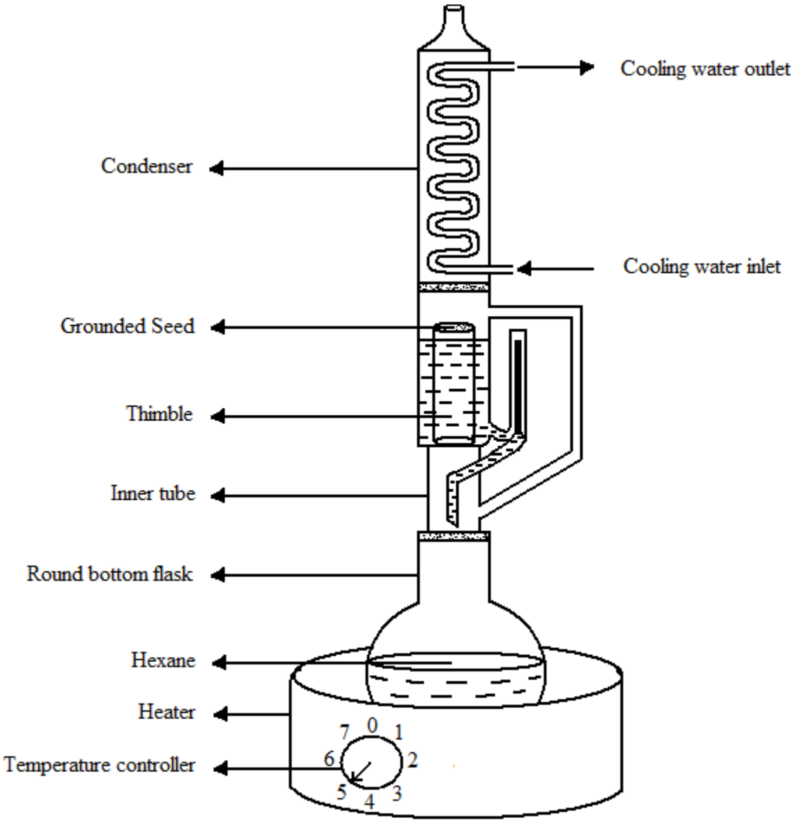


Figure 3.2: Schematic diagram of soxhlet hexane extraction apparatus.

3.2.2 Catalyst Preparation

Sulfated zirconia loaded on alumina was synthesized using two different preparation methods i.e. direct sulfation of zirconia oxide and solvent- free method.

3.2.2 (a) Direct Sulfation of Zirconia Oxide Method

8 g of commercial zirconia oxide, ZrO_2 was dipped into 60 ml of 2.5 M sulfuric acid, H_2SO_4. After continuous stirring for 20 hours, 4 g of alumina, Al_2O_3 was introduced into the mixture and stirring was continued for 2 hours. The mass ratio of zirconia oxide to alumina was 2:1. The mixture was then filtered using a

vacuum pump. Subsequently, the filtrate was calcined in a furnace for a specific temperature and duration. After calcination, the sulfated zirconia supported on alumina catalyst was grounded in a mortar. The calcination temperature and calcination duration were varied from 300 °C to 700 °C and 1 hour to 5 hour, respectively according to the experiment matrix obtained from design expert software, which all will be discussed in the later part of this chapter.

3.2.2 (b) Solvent- free Method

The preparation of sulfated zirconia using the solvent-free method was accomplished according to the procedure described by Sun *et al*. (2005) but with the addition of alumina as support. 1 g of Zirconyl chloride octahydrate, $ZrOCl_2.8H_2O$ (molecular weight of 322.25 g/mole) and 2.46 g of ammonium sulfate, $(NH_4)_2SO_4$ (molecular weight of 132.14 g/mole) were grounded in an agate mortar for 20 minutes at room temperature (25 °C) using a molar ratio of 1:6. Then, 1.73 g of alumina, Al_2O_3 was introduced. The mixture was grounded for another 20 minutes. The mass ratio of alumina and the mixture of zirconyl chloride octahydrate with ammonium sulfate is 1:2. After leaving for 18 hours at room temperature, the mixture was calcined using a furnace at a specific temperature and duration. Similar as for the direct sulfation method, the calcination temperature and calcination duration were varied from 300 °C to 700 °C and 1 hour to 5 hour, respectively according to the experiment matrix obtained from design expert software.

3.2.3 Transesterification Process Study

In this study, a batch- type reactor was used to carry out the transesterification reaction. It consists of a metal cup, a metal cover, a magnetic stirrer, a heater and jacket and a thermocouple. **Figure 3.3** shows the schematic diagram of the reactor. Initially, mixture of *Jatropha curcas* L. oil, sulfated zirconia loaded on alumina catalyst and methanol was charged into the reactor. Then, the reactor was pressurized to ensure that most of the reactants remain in liquid phase. The mixing speed of the magnetic stirrer was set at 350-400 rpm, which was sufficient to ensure uniform temperature and suspension. After the reaction, the mixture was filtered and residual methanol was separated from the liquid phase by using rotary evaporator. The upper layer of the liquid phase was separated from the bottom layer by using decanter and was analyzed to detect biodiesel content. The process variables (reaction temperature, reaction duration, molar ratio of methanol to oil and catalyst loading) were varied according to the experiment matrix obtained from design expert software.

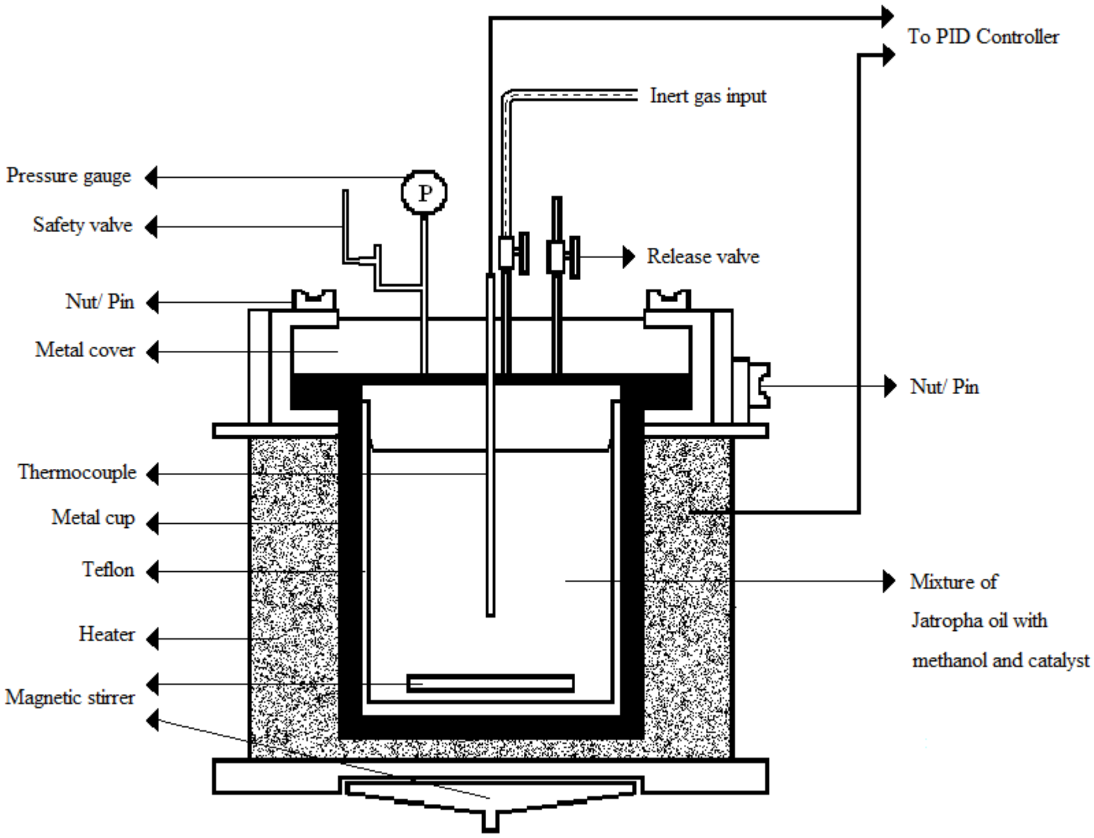


Figure 3.3: Schematic diagram of reactor.

3.2.4 Catalyst Reusability

The life span or reusability of the catalyst for transesterification was tested by subjecting the used catalyst (catalyst after the first run of reaction and without pretreatment) with repeated transesterification reaction and measuring the resulting yield. The conditions for the transesterification was the optimize condition obtained in the transesterification process study. After each transesterification reaction, the reaction mixture was filtered to separate out the wet heterogeneous acid catalyst. Then, the used catalyst was exhaustively washed with hexane and dried at 70 °C for 1 hour to evaporate the remaining hexane attach on the catalyst. After drying, the used catalyst was subjected to transesterification with fresh *Jatropha curcas* L. oil and methanol under the same conditions as the initial reaction. This was repeated for several runs to investigate the life span of the heterogeneous acid catalyst. Apart from that, regeneration of the used catalyst was also investigated. The catalyst regeneration study was carried out by recovering the used catalyst and reusing them with fresh reagents in a subsequent reaction cycle after pretreatment steps. In the pretreatment steps, the used catalyst was dipped into 2.5 M sulfuric acid with continuous stirring for 2 hours after washing with hexane and dried at 70 °C. Subsequently, the catalyst was filtered using vacuum pump and calcined in a furnace at the optimum calcination condition determined previously at 400 °C for 4 hours.

3.3 Characterization

3.3.1 *Jatropha curcas* L. Oil

The properties of the extracted *Jatropha curcas* L. oil used in this study were characterized based on fatty acid composition (%), moisture content (%w/w), free fatty acid (%w/w), acid value (m_{KOH}/m_{oil}, mg/g), saponification value (m_{KOH}/m_{oil}, mg/g), density, flash point (°C), kinematic viscosity (mm^2/s) and ash content (%w/w) of *Jatropha curcas* L. oil according to Malaysian Palm Oil Board (MPOB) standard by My CO_2 Sdn. Bhd., Malaysia. The average molecular weight was then calculated from the acid value and saponification value of *Jatropha curcas* L. oil. The average molecular weight of *Jatropha curcas* L. oil is calculated using **Equation 3.1**.

$$M = 56.1 \times 1000 \times 3 / (SV - AV) \tag{3.1}$$

where; AV is the acid value and SV is the saponification value.

3.3.2 Sulfated Zirconia loaded on Alumina Catalyst

The catalyst prepared in this study was characterized based on the following analysis.

3.3.2 (a) X-ray diffraction (XRD)

The sulfated zirconia loaded on alumina were characterized by X-ray diffraction (XRD), recorded on a Siemens D-5000 diffractomer, employing Cu Kα radiation (λ= 1.5412) generated at 40 kV and 40 mA and a graphite secondary beam monochromator. The radiation angle used is in the 5° to 70° 2θ range. Intensity was measured by step scanning in the 2µ range of 108-808 with a step of 0.028 and a measuring time of 2s per point.

3.3.2. (b) Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) measurements were performed to investigate the presence of acidic functional group in the catalyst. This was performed using Perkin Elmer System 2000 spectrometer with potassium bromide (KBr) pellet technique. In this technique, catalyst was mixed with KBr with a mass ratio of 1:10. Then, the mixture was grounded to a fine, homogeneous powder which was then poured into a mould. The powder was densified and compacted using a hydraulic press applying pressure of 8 tons to form thin pellet (thickness ≈ 100µm). Finally, the thin and transparent pellet was placed on a sample holder for analysis. Before analysis, calibration of the spectrometer was performed by using polystyrene as control sample. Each spectrum was obtained in the transmission mode over 32 scans, in the range from 4000 to 400cm^{-1} with a resolution of 1cm^{-1}. Background spectra were obtained before each sampling. Data analyses were carried out using the spectrum BX II.

3.3.2. (c) Pyridine FTIR

Characterization on the type of acid sites (Bronsted or Lewis acidic sites) on the surface of catalyst was determined by pyridine adsorption at room temperature. 0.06 g of catalyst sample was degassed for 1 hour at 200 °C to reduce the amount of adsorbed molecular water. Then, it was cooled to room temperature and subsequently 2 drops of pyridine were dropped on the samples and left for 1 hour to facilitate the adsorption process. After that, the samples were heated for 1 hour at 150 °C, prior to analysis by FTIR.

3.3.2 (d) BET Surface Area

The catalyst was also subjected to nitrogen adsorption measurement performed at -196 °C by using a Micromeritis ASAP2010 surface area and porosity analyzer to determine the specific surface area of the catalyst. The calculation for the specific surface area of the catalyst was determined from the adsorption isotherms using the Brunauer-Emmett-Teller (BET) method.

3.3.3 Biodiesel Characterization

The properties of biodiesel fuel are closely related to the fatty acid content in the *Jatropha* curcas L. oil. After the transesterification reaction and separation steps, the upper layer of the product which contains biodiesel was subjected to purification steps; biodiesel was washed with 20 wt% sodium chloride (double the volume of biodiesel) for three times (Binney *et al*., 2005; Mondala *et al*., 2009). After washing, the upper layer of the liquid phase was separated from the bottom layer using decanter. The upper layer was dried over sodium sulfate anhydrous and the mixture was stirred for 3 minutes (Qian *et al*., 2008). Then, the mixture was filtered to separate hydrated sodium sulfate. After the purification steps, the biodiesel was ready for characterization. The properties of biodiesel obtained including density, kinematic viscosity, flash point, water content, ash content and acid value were measured and compared with the American Society Testing and Materials (ASTM) standard. The properties of the biodiesel were characterized by My CO_2 Sdn. Bhd., Malaysia. Biodiesel properties not complying with the standard could lead to problems in the fuel system (Lu *et al*., 2009).

3.4 Sample Analysis using Gas Chromatograph

The resulting products from the transesterification process were analyzed using Gas Chromatography (GC) which was equipped with Nukol^{TM} column (15 m x 0.53 mm, 0.5 μm film) to identify the presence of fatty acid methyl esters (biodiesel) in the sample. Helium was used as the carrier gas. Oven temperature at 110 °C was initially hold for 0.5 minute and then increased to 220 °C (held for 8 minutes) at a rate of 10 °C min^{-1}. The temperature of the injector and detector were set at 220 °C and 250 °C respectively. A quantity of 1 µl from each sample was injected into the column. Methyl heptadecanoate was used as internal standard for the calculation of yield.

3.5 Calculation of Biodiesel Yield

Methyl esters yield in this study was calculated based on the peak areas of the methyl esters recorded in the GC chromatogram. **Figure C.1** (refer to Appendix C) shows a typical GC chromatogram for biodiesel sample. The individual peak of the spectrum was identified by comparing the retention time of reference compound and shown in **Table C.4**. The weight of methyl esters was calculated using the basis of ratio of peak area to each standard according to **Equation 3.2**. The yield of the transesterification processes were calculated as sum of weight of biodiesel produced to weight of *Jatropha* oil used, multiplied by 100. The formula is given by **Equation 3.3**.

$$Weight\ of\ Methyl\ Esters\ (g) = \frac{R_s}{R_f} \times C_{IS} \times V \times DF \tag{3.2}$$

$$Yield\ of\ Biodiesel = \frac{\sum Weight\ of\ Fatty\ Acid\ Methyl\ Esters\ (g)}{Weight\ of\ Jatropha\ Oil\ used\ (g)} \times 100\% \tag{3.3}$$

where;

$$Ratio\ Sample, R_s = \frac{Peak\ Area\ of\ Methyl\ Esters\ in\ sample}{Peak\ Area\ of\ Internal\ Standard\ in\ sample}$$

$$Ratio\ Reference, R_f = \frac{Peak\ Area\ of\ Methyl\ Esters\ in\ Reference}{Peak\ Area\ of\ Internal\ Standard\ in\ Reference}$$

C_{IS} = Concentration of internal standard used which is 1.00g/L.

V = Volume of *Jatropha* oil used (mL)

DF= Dilution factor

3.6 Design of Experiment

In this research work, statistical design of experiment was used throughout the experiment planning and data collection according to the experimental matrix generated by design expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA). The data obtained were subsequently analyzed and used for optimization purpose, again using the same software. There were two main sections in this study that utilized design of experiment; one was to study the effect of catalyst calcination variables on the yield of biodiesel and the other one on the effect of transesterification process variables on the yield of biodiesel. The types of DOE selected were the factorial design of experiments and Response Surface Methodology (RSM), originally developed by Box and Wilson (1951). The experimental design selected for this study was Central Composite Design (CCD) and the yield of biodiesel was the selected response for both studies. Regression model equation was developed to correlates the response to the variables studied and the adequacy of the model developed were evaluated based on the coefficients of correlation and analysis of variance (ANOVA).

3.6.1 Effect of Catalyst Calcination Variables

Two sets of DOE were used in this section, one set for each preparation method: (a) Direct sulfation of zirconia oxide, (b) Solvent-free method. Two calcination variables were studied; calcination temperature and calcination duration. The range of both the calcination variables for both preparation methods are given in **Table 3.2**. It was fixed based on literature review and preliminary studies. The value of α for this CCD was fixed at 2 and there are 5 levels for each of the calcination variable studied (-2, -1, 0, +1, +2). **Table 3.3** shows the complete experimental matrix. Generally, the experimental matrix consists of 2^n factorial runs with 2n axial runs and n_c center runs. Therefore, for two variables (n=2), the total number of experiments were 13 (4 factorial points, 4 axial points, 5 center points). Factorial points are variables which at the level of -1.0 and +1.0. All variables at zero level constitute to the center points and the combination of each of the variables at either its lowest (-2.0) level or highest (+2.0) level with the other variables at zero constitute the axial points. Experimental runs were randomized. In this section, the conditions for the transesterification reaction were fixed as follows; reaction temperature of 150 °C, duration of 3 hours, methanol to oil molar ratio of 8 and catalyst loading of 8 wt% with respect to *Jatropha curcas* L. oil. 40 ml *Jatropha curcas* L. oil was used in each experimental run.

Table 3.2: Independent variables and levels used for the Central Composite Design (CCD) for direct sulfation of zirconia oxide method and solvent- free methods.

Variable	Symbols	Unit	Levels				
			(-α)	(-1)	0	(+1)	(+α)
Calcination temperature	x_1	°C	300	400	500	600	700
Calcination duration	x_2	hour	1	2	3	4	5

Table 3.3: Experiment design matrix for direct sulfation of zirconia oxide method.

Run	Point type	Coded independent variable levels	
		Calcination temperature, x_1 (°C)	Calcination duration, x_2 (hour)
1	Fact	-1	-1
2	Fact	+1	-1
3	Fact	-1	+1
4	Fact	+1	+1
5	Axial	-2	0
6	Axial	+2	0
7	Axial	0	-2
8	Axial	0	+2
9	Center	0	0
10	Center	0	0
11	Center	0	0
12	Center	0	0
13	Center	0	0

3.6.2 Effect of Transesterification Process Variables

In this section, the four transesterification process variables studied were reaction temperature, reaction duration, methanol to oil ratio and catalyst loading. **Table 3.4** lists the range and levels of the four independent variables studied. It was fixed based on literature review and preliminary studies. The value of α for this CCD was fixed at 2. **Table 3.5** shows the complete experimental matrix. For four variables (n=4), the total number of experiments is 30 calculated from **Equation 3.4**. The order in which the runs were made was randomized to avoid systematic errors. In this study, 40ml *Jatropha curcas* L. oil was used in each experimental runs.

$$N = 2^n + 2n + n_c = 2^4 + 2x4 + 6 = 30 \qquad (3.4)$$

Table 3.4: Independent variables and levels used for the Central Composite Design (CCD) for transesterification process study.

Variable	Symbols	Unit	Levels				
			(-α)	(-1)	0	(+1)	(+α)
Reaction temperature	x_1	°C	60	90	120	150	180
Reaction duration	x_2	hour	1	2	3	4	5
Molar ratio of methanol to oil	x_3	mole mole^{-1}	4	6	8	10	12
Catalyst loading	x_4	wt%	2	4	6	8	10

Table 3.5: Experimental design matrix for transesterification process study.

Run	Point type	Coded independent variable levels			
		Temperature, x_1	Duration, x_2	Molar ratio methanol/oil, x_3	Catalyst loading, x_4
		(°C)	(hour)	(mole mole^{-1})	(wt%)
1	Fact	-1	-1	-1	-1
2	Fact	+1	-1	-1	-1
3	Fact	-1	+1	-1	-1
4	Fact	+1	+1	-1	-1
5	Fact	-1	-1	+1	-1
6	Fact	+1	-1	+1	-1
7	Fact	-1	+1	+1	-1
8	Fact	+1	+1	+1	-1
9	Fact	-1	-1	-1	+1
10	Fact	+1	-1	-1	+1
11	Fact	-1	+1	-1	+1

Table 3-5. Continued

Run	Point type	Coded independent variable levels			
		Temperature, x_1	Duration, x_2	Ratio methanol/oil, x_3	Catalyst loading, x_4
		(°C)	(hour)	(mole $mole^{-1}$)	(wt%)
12	Fact	+1	+1	-1	+1
13	Fact	-1	-1	+1	+1
14	Fact	+1	-1	+1	+1
15	Fact	-1	+1	+1	+1
16	Fact	+1	+1	+1	+1
17	Axial	-2	0	0	0
18	Axial	+2	0	0	0
19	Axial	0	-2	0	0
20	Axial	0	+2	0	0
21	Axial	0	0	-2	0
22	Axial	0	0	+2	0
23	Axial	0	0	0	-2
24	Axial	0	0	0	+2
25	Center	0	0	0	0
26	Center	0	0	0	0
27	Center	0	0	0	0
28	Center	0	0	0	0
29	Center	0	0	0	0
30	Center	0	0	0	0

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter is divided into six main sub-sections. In the first sub-section, characterization results of *Jatropha curcas* L. oil will be presented. Then, the following two sub-sections will discuss the effect of calcination variables on catalyst characteristics and the yield of biodiesel through two different catalyst preparation method; (i) direct sulfation of zirconia oxide method and (ii) solvent-free method. When appropriate, catalyst characterization results using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and BET surface area will be given. The catalyst calcination variables were then optimized. Next sub-section presents the process study used to optimize the transesterification variables for optimum yield of biodiesel. Then, the study on reusability and the life span of the catalyst for transesterification process is presented. The final sub-section presents the results for characterization of biodiesel.

4.1 Properties of *Jatropha Curcas* L. Oil

Table 4.1 shows the properties for *Jatropha curcas* L. oil. On the basis that the measured acid value is 10.37 m_{KOH}/m_{oil} and saponification value is 195.5 m_{KOH}/m_{oil}, average molecular weight of *Jatropha curcas* L. oil was calculated as 909.09 g/mol. The saponification value of *Jatropha curcas* L. oil was found to be small, indicating high concentration of triglycerides, and therefore *Jatropha curcas* L. oil can be a suitable feedstock for the production of FAME (biodiesel). Nevertheless, the high content of free fatty acids (4.73 %w/w) shows that conventional biodiesel production technology using homogeneous base catalytic system is not suitable for *Jatropha curcas* L. oil. Therefore, acidic catalyst is required in transesterification reaction for oil with high content of free fatty acid to avoid soap formation problem.

Table 4.1: Properties of extracted *Jatropha curcas* L.oil.

Flash point	60 °C
Kinematic viscosity	48.2 mm^2/s
Ash content	0.09 %w/w
Moisture content	0.05 %w/w
Free fatty acid	4.73 %w/w
Acid value	10.37 m_{KOH}/m_{oil}
Saponification value	195.5 m_{KOH}/m_{oil}
Density	0.9220 g/ml
Fatty acid composition	
Palmitic acid, C16:0	14.4%
Palmitoleic acid, C16:1	0.1%
Stearic acid, C18:0	3.6%
Oleic acid, C18:1	43.2%
Linolenic acid, C18:2	38.7%

4.2 Catalyst Preparation Study- Direct Sulfation of Zirconia Oxide Method

4.2.1 Design of Experiment (DOE)

Design of experiment was used to study the effect of calcination variables on the catalyst characteristics and their effect on the yield of biodiesel. Subsequently, optimization on the catalyst calcination variables was carried out. **Table 4.2** shows the experimental design matrix and result with different combination of calcination variables obtained from DOE.

Table 4.2: Experimental design matrix and results for direct sulfation of zirconia oxide method.

Catalyst code	Level of variables [actual (coded)]		Yield of biodiesel (%)
	Calcination temperature, x_1 (°C)	Calcination duration, x_2 (hour)	
SZA 01	400 (-1)	2 (-1)	71.41
SZA 02	600 (+1)	2 (-1)	55.64
SZA 03	400 (-1)	4 (+1)	84.40
SZA 04	600 (+1)	4 (+1)	51.12
SZA 05	300 (-2)	3 (0)	64.76
SZA 06	700 (+2)	3 (0)	13.36
SZA 07	500 (0)	1 (-2)	68.64
SZA 08	500 (0)	5 (+2)	75.54
SZA 09	500 (0)	3 (0)	64.53
SZA 10	500 (0)	3 (0)	64.21
SZA 11	500 (0)	3 (0)	64.16
SZA 12	500 (0)	3 (0)	64.38
SZA 13	500 (0)	3 (0)	64.24

4.2.2 Development of Regression Model Equation

The model equation that correlates the response, Y (yield of biodiesel) to the calcination variables (x_1, x_2) by eliminating the insignificant variable is:

$$Y = +65.88 - 12.65x_1 - 6.21x_1^2 + 2.04x_2^2 - 4.38x_1x_2 \qquad (4.1)$$

4.2.3 Statistical Analysis of Results

The quality of the model developed was evaluated based on the coefficients of correlation. The value of R-squared for the developed correlation is 0.9729. It implies that 97.29 % of the total variation in the yield of biodiesel is attributed to the experimental variables studied. Besides that, **Figure 4.1** demonstrated that the regression model equation provided a very accurate description of the experimental data, indicating that it was successful in capturing the correlation between the two calcination variables to the yield of biodiesel.

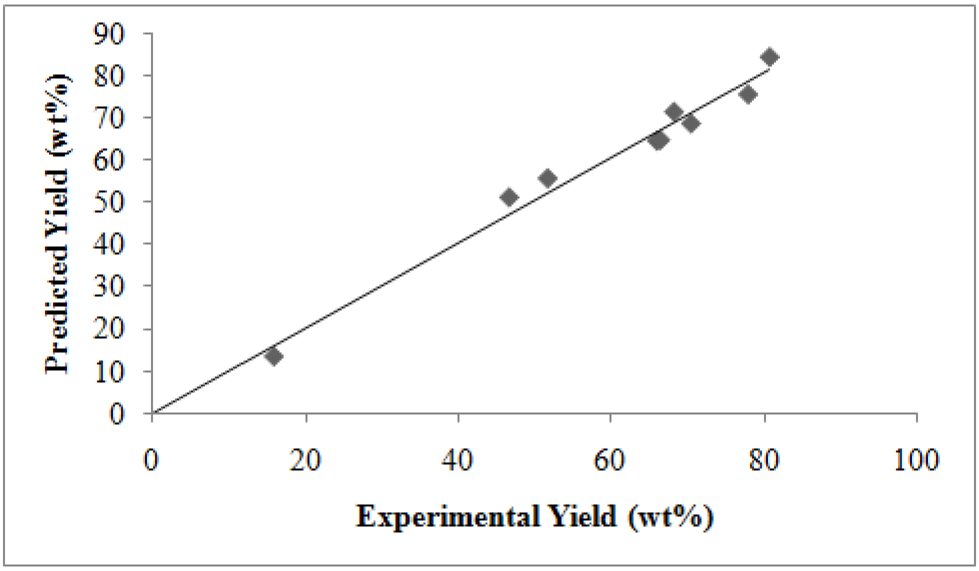


Figure 4.1: A comparative plot between experimental yield of biodiesel and predicted yield of biodiesel for direct sulfation of zirconia oxide method.

The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in **Table 4.3**. Based on 95 % confidence level, the model was tested to be significant as the computed F value (50.26) is much higher than the theoretical $F_{0.05\,(5,7)}$ value (3.97) and the p value was less than 0.05. Apart from that, all terms in the model except calcination duration (x_2) was tested to be significant at a 95 % confidence level as the computed F values for x_1 (147.07), x_1^2 (67.69), x_2^2(7.27) and x_1x_2 (5.87) terms were higher than the theoretical $F_{0.05\,(1,\,7)}$ value (5.59) and the p values were also less than 0.05. On the other hand, the computed F value for x_2 is 3.12 and the p value was more than 0.05. Value of p greater than 0.05 indicates that the model term is not significant.

Therefore, from these statistical tests, it was found that the model is adequate for predicting the yield of biodiesel within the range of variables studied and calcination temperature (x_1) is the significant variable that affects the yield of biodiesel while calcination duration (x_2) gave insignificant effect.

Table 4.3: Analysis of Variance (ANOVA) for the regression model equation and Coefficients (direct sulfation of zirconia oxide method).

Source	Sum of squares	Degree of freedom	Mean of squares	F-Test	p value
Model	3283.30	5	656.66	50.26	<0.0001
x_1	1921.54	1	1921.54	147.07	<0.0001
x_2	40.81	1	40.81	3.12	0.1205
x_1^2	884.36	1	884.36	67.69	<0.0001
x_2^2	95.00	1	95.00	7.27	0.0308
x_1x_2	76.65	1	76.65	5.87	0.0459
Residual	91.46	7	13.07	-	-

4.2.4 Effect of Calcination Variables

4.2.4 (a) Single Variable Effect

Based on the developed model, calcination temperature was found to have the most significant negative effect on the yield of biodiesel as indicated by the negative value of the regression coefficient estimates. Contrary, calcination duration brings insignificant effect on the yield of biodiesel. Apart from that, the degree of significance of each variables can also be evaluated according to the F-test value obtained using ANOVA. The highest F-test value indicates the most significant effect on the yield of biodiesel. By referring to **Table 4.3**, calcination temperature (x_1) has the highest F-test value (147.07) while the value for calcination duration (x_2) was merely 3.12.

Besides that, these results can also be easily verified by visually inspecting **Table 4.2**. For instance, comparison between runs 1 and 2 (and also for all comparable runs), an increase in calcination temperature (while calcination duration remain constant) always resulted in lower yield of biodiesel which is in agreement with the highest F-test value obtained for calcination temperature in the ANOVA. However, an increase in calcination duration was not always resulted in higher yield of biodiesel. Based on visual inspection on the results in **Table 4.2**, an increase in the calcination duration (runs 1 and 3, runs 7 and 8) resulted in an increase in the yield of biodiesel. But, for runs 2 and 4 and runs 7 and 9, the yield of biodiesel decreases as calcination duration increase. This is again consistent with the ANOVA results, whereby the F-test value for the term calcination duration is not that high as compared to calcination temperature.

These results showed that the effect of calcination duration on the yield of biodiesel is not solely dependent on its individual effect, but its interaction effect with calcination temperature must also be considered. Therefore, the need of using design of experiment approach is important in order to study the interaction effect between variables efficiently, which will be presented in the subsequent section.

(i) Effect of Calcination Temperature

As discussed in the previous section, calcination temperature was found to have a negative effect on the yield of biodiesel in which higher calcination temperature led to lower yield of biodiesel (**Figure 4.2**). This is most probably due to the drop in acidic sites in the SZA catalyst. In order to verify this explanation, SZA catalyst calcined at different temperatures were subjected to XRD analysis as shown in **Figure 4.3**. It is obvious that the XRD spectrum for all catalyst exhibited the diffraction peaks correspond to crystalline structure of SZA. This finding shows that this catalyst preparation method is successful in synthesizing SZA with good crystalline structure.

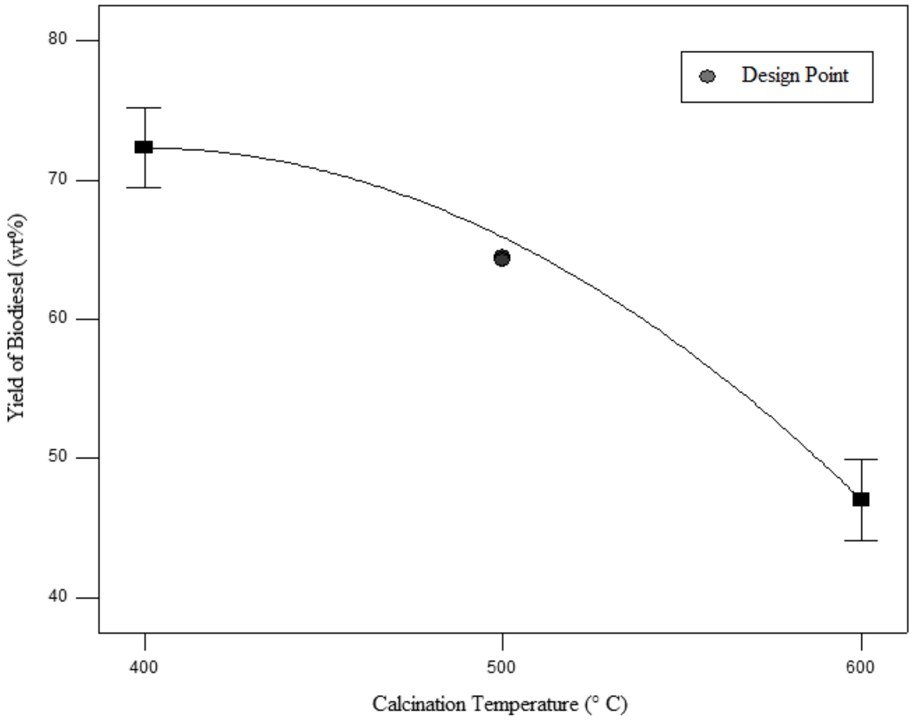


Figure 4.2: Yield of biodiesel against calcination temperature (Calcination duration at 3 hours) (direct sulfation of zirconia oxide method).

Apart from that, it was also found that zirconia oxide successfully reacts with sulfuric acid to form zirconia sulfate tetrahydrate, $Zr(SO_4)_2.4H_2O$. This sulfated compound will supply the acidic sites required for the transesterification reaction. The catalyst shows higher crystallinity at lower calcination temperature compare with higher calcination temperature (referring to the peak for $Zr(SO_4)_2.4H_2O$). Beyond 500 °C, the crystalline peaks almost disappeared. This shows that at higher temperature, the sulfated groups will decompose leading to a significant drop in the acidic sites in the catalyst which subsequently lower the yield of biodiesel. This finding is indeed consistent with those reported in literature in which decomposition of sulfated groups was reported to begin at around 500 °C (Funamoto *et al.*, 2005; Matsuhashi *et al.*, 2004).

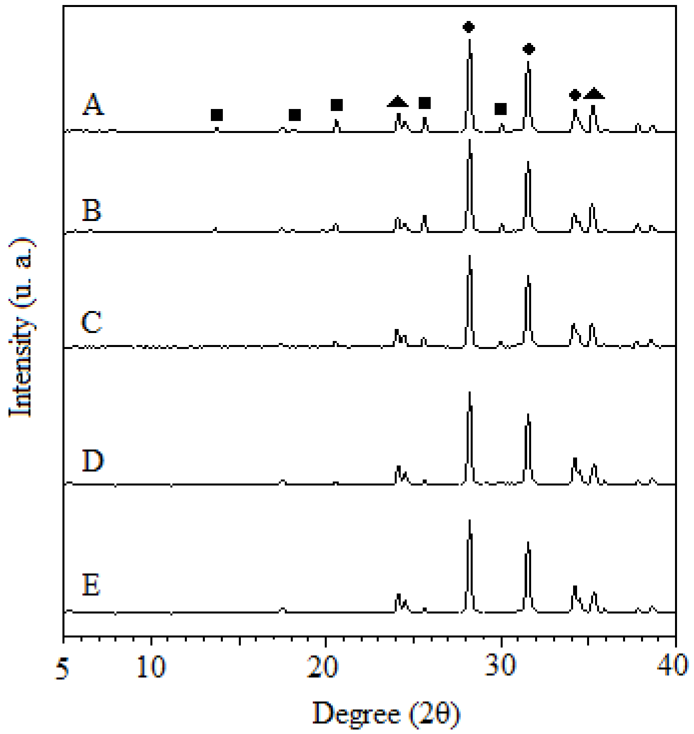


Figure 4.3: XRD patterns of SZA for direct sulfation of zirconia oxide method; calcination duration at 3 hours with different temperatures; (A) 300 °C, (B) 400 °C, (C) 500 °C, (D) 600 °C, (E) 700 °C

(■) zirconia sulfate tetrahydrate, (◆) zirconia oxide and (▲) aluminium oxide

Apart from that, the decrease in the yield of biodiesel at higher catalyst calcination temperature can be further explained by IR spectra shown in **Figure 4.4**. The IR spectra of SZA calcined at 300 °C and 600 °C exhibited obvious bands at 1,030 and 1108 cm^{-1} which are typical bands assigned to chelating bidetate sulfate ion coordinated to zirconium cation (Sun *et al*. 2005; Garcia *et al*. 2008). However these characteristic bands become weaker at higher calcination temperature, again supporting the fact that sulfate group in the catalyst decomposed at higher temperature.

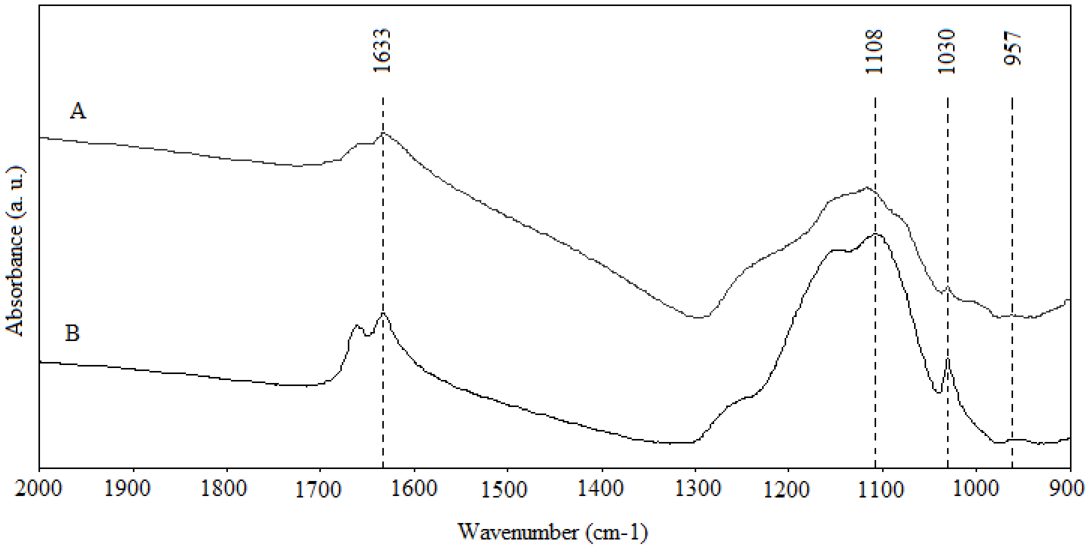


Figure 4.4: IR spectra of SZA for direct sulfation of zirconia oxide method; calcination duration at 3 hours with different temperatures; (A) 600 °C and (B) 300 °C.

Besides that, a broad band at 1633 cm^{-1} can be ascribed to the bending mode (δHOH) or coordinated molecular water due to its interaction with sulfated zirconia catalysts (Funamoto at al., 2005; Matsuhashi at al., 2004). In order to further characterize the types of acidic sites in the catalyst, pyridine adsorption was carried out as shown in **Figure 4.5**. Both samples were found to contain the Lewis and Brónsted acidic sites at the characteristic band of 1486 cm^{-1} and 1537 cm^{-1}, respectively (Ahmed *et al*. 2008; Zhao *et al*. 2008; Funamoto *et al*., 2005; Sun *et al*. 2005). However, one interesting finding is that when the catalyst was calcined at higher temperature, the type of acidic site shifted from Brónsted to Lewis. Therefore, Lewis acidic site might not be effective for transesterification reaction.

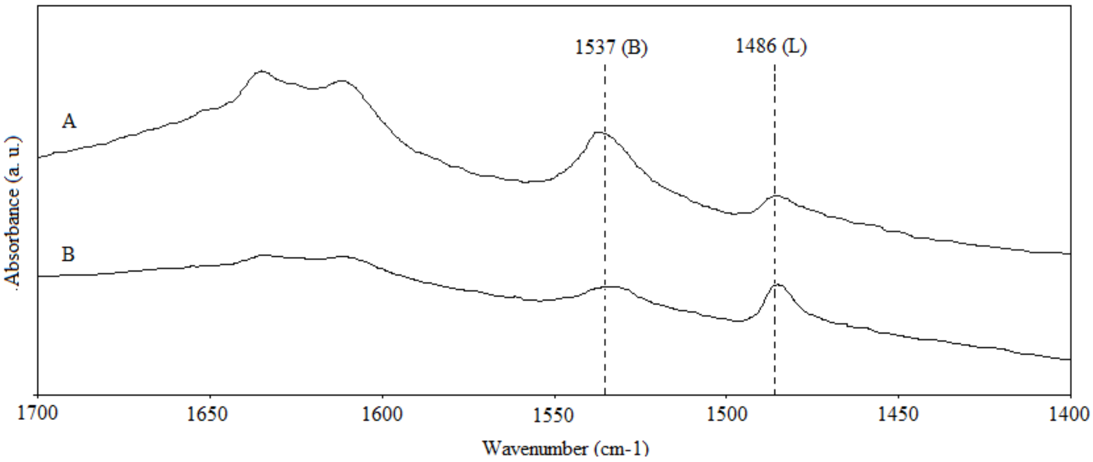


Figure 4.5: IR spectra of pyridine adsorption for SZA for direct sulfation of zirconia oxide method; calcination duration at 3 hours with different temperature; (A): 300 °C (B): 600 °C.

As discussed earlier, in this study, increase of calcination temperature from 300°C to 700°C leads to decrease of the biodiesel yield. This may be due to the change in surface area of SZA catalyst when varying calcination temperature. The surface area was increase from 0.73 m^2/g to 19.20 m^2/g when the calcination temperature was increase from 300 °C to 400 °C. However, further increase of the calcination temperature cause a drop of surface area to 9.97 m^2/g (500 °C) and to 1.62 m^2/g (700 °C). The largest surface area (19.20 m^2/g) occurs at calcination temperature 400°C. However, the surface area of the sulfated catalyst was still much better than un-sulfated catalyst at the same calcination temperature (400 °C). The surface area of the catalyst was 0.24 m^2/g. These results may indicates that the presence of sulfate groups lead to a better physicochemical properties of heterogeneous acidic catalysts by stabilize the surface area and retard the formation of larger crystalline of zirconia (Mekhemer, 2006). Hence, heterogeneous acidic catalyst with high calcination temperature resulting in having small surface area and less acidic sites (due to decomposition of the sulfate groups) that brings to low yield of biodiesel.

(ii) Effect of Calcination Duration

Figure 4.6 shows the effect of calcination duration on the yield of biodiesel. In accordance with the low F-test value, the yield of biodiesel did not change much with higher calcination duration. When SZA was calcined for 2 hours, the yield obtained is about 66 %, but when the calcination temperature was increased to 4 hours, the yield of biodiesel only increased marginally to 70 %. **Figure 4.7- 4.9** show the XRD spectra, IR spectra and IR spectra for pyridine adsorption respectively for catalyst prepared with different calcination duration. All the results were found to be consistence and revealed that there is no significant difference between SZA catalyst prepared at different calcination duration. The results indicate that as long as the calcination temperature is sufficient, crystallization process occurs almost instantaneously to form the sulfated compounds.

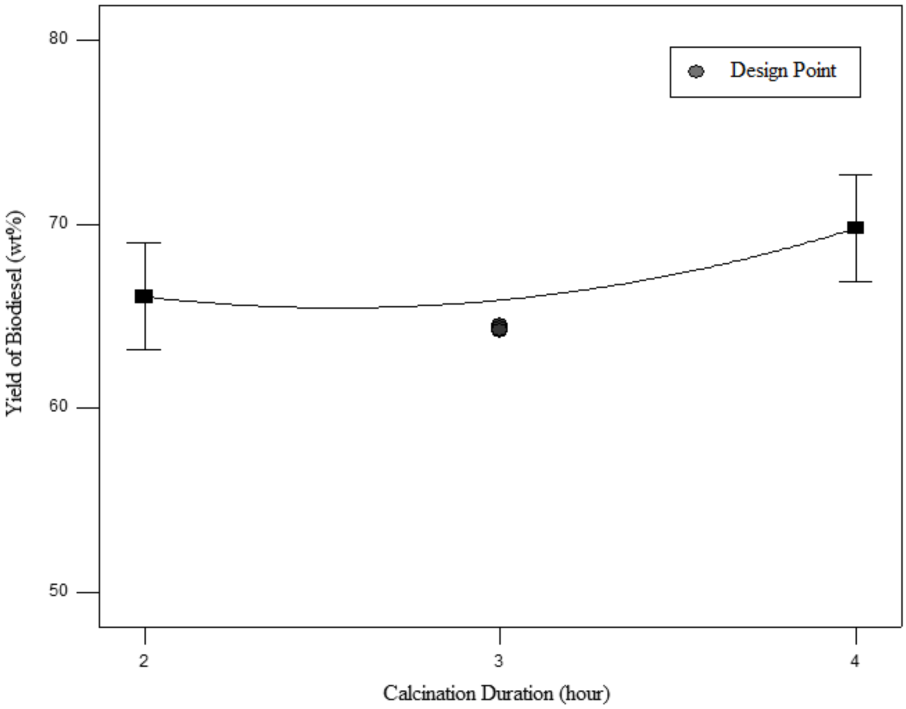


Figure 4.6: Yield of biodiesel against calcination duration (Calcination temperature at 500 °C) (direct sulfation of zirconia oxide method).

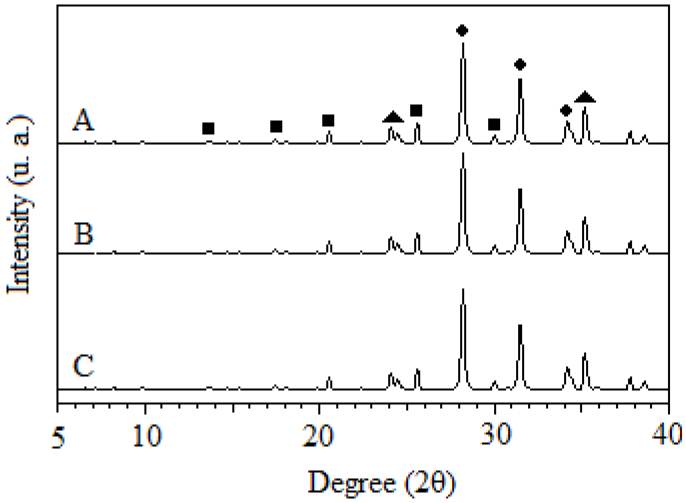


Figure 4.7: XRD patterns of SZA for direct sulfation of zirconia oxide method; calcination temperature at 400 °C with different duration; (A): 5 hour (B): 2 hour (C): 1 hour.

(■) zirconia sulfate tetrahydrate, (◆) zirconia oxide and (▲) aluminium oxide

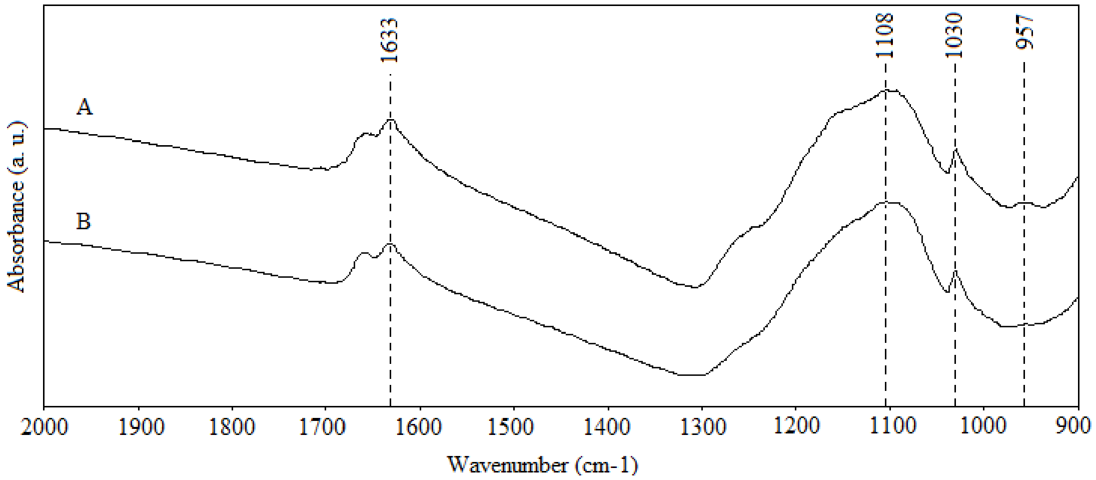


Figure 4.8: IR spectra of SZA for direct sulfation of zirconia oxide method; calcination temperature at 500 °C with different duration; (A): 1 hour (B): 3 hour.

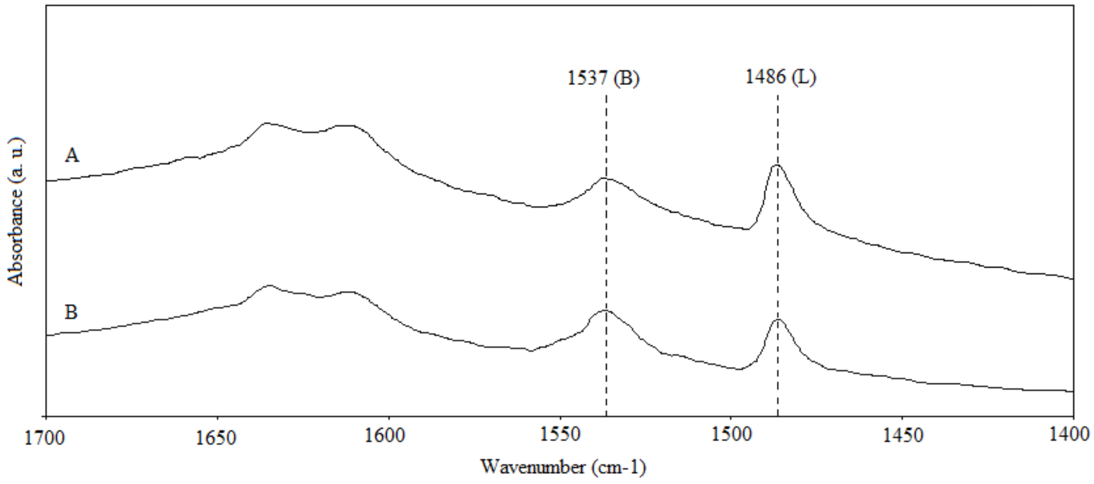


Figure 4.9: IR spectra of pyridine adsorption for SZA for direct sulfation of zirconia oxide method; calcination temperature at 500 °C with different duration; (A): 4 hour (B): 1 hour.

4.2.4 (b) Effect of Interaction between Variables

According to the ANOVA presented in **Table 4.3**, the interaction between calcination temperature and duration was found to give significant effect on the yield of biodiesel as shown in **Figure 4.10**. As expected and explained in the previous section, generally higher calcination temperature leds to lower yield of biodiesel. In addition, **Figure 4.10** shows that the effect of calcination temperature is more prominent at higher calcination duration as compared to lower calcination duration indicating the significant interaction between both variables. When the calcination duration was fix at 4 hours, the yield of biodiesel drops rapidly with higher calcination temperature; on the other hand, the yield of biodiesel drops much slower when the calcination duration was fixed at 2 hours.

In other words, longer calcination duration was required to obtain higher yield at lower calcination temperature (<540 °C); however, at higher calcination temperature (>540 °C), longer calcination duration led to lower yield of biodiesel. This can be explained as follows. At lower calcination temperature, more time is required for the formation of active compounds (sulfate groups) in the catalyst; therefore calcinations duration of 4 hours gave higher yield as compared to 2 hours. However, at higher calcination temperature, perhaps the decomposition of the sulfate group which begin at around 500 °C becomes too fast until it caused a drop in the yield of biodiesel. This finding therefore shows that a combination of high calcination temperature and long calcination duration is not favourable towards the yield of biodiesel.

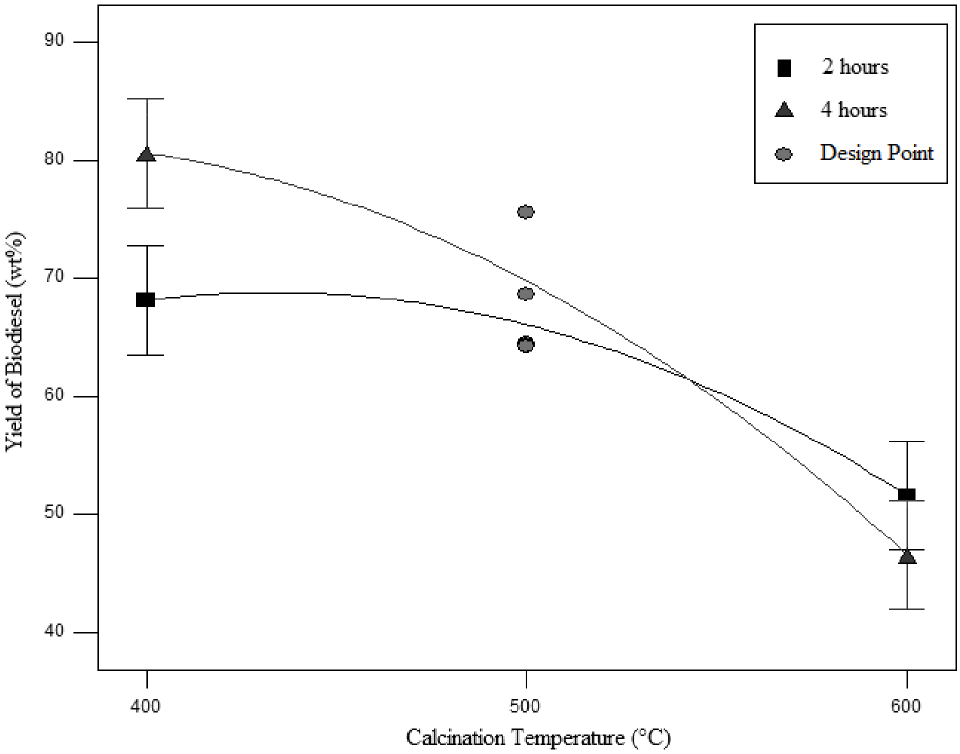


Figure 4.10: Yield of biodiesel against calcination temperature and calcination duration for direct sulfation of zirconia oxide method.

As discussed earlier, calcination duration shows insignificant effect on the yield of biodiesel. However, it is only acceptable for a particular calcination temperature (540 °C). **Figure 4.10** reveals that at lower calcination temperature (<540 °C), higher calcination duration leads to higher yield of biodiesel. But, at higher calcination temperature (>540 °C), yield of biodiesel is higher for lower calcination duration. The results indicate that crystallization process require much longer time to form the sulfated compounds in the case of insufficient calcination temperature. In terms of energy consumption, calcination temperature at 540 °C could be the optimum temperature since increase of calcination duration does not bring significant effect on the yield of biodiesel. However, the decomposition of sulfated compounds begins at around 500 °C which leads to decrease the yield of biodiesel. Lower calcination temperature is preferable to obtain high yield of biodiesel but require longer calcination duration.

Hence, this result stress the importance and need of using design of experiment approach in order to be able to study the interaction effect between variables efficiently and to obtain the optimum calcination variables towards achieving high yield of biodiesel.

4.2.5 Optimization of Calcination Variables

Based on the previous discussion, the results stressed that apart from the individual variables, interaction between calcination variables were also found to have significant effect on the yield of biodiesel. Higher calcination temperature led to lower yield of biodiesel. Furthermore, the effect of calcination duration is based on its interaction with calcination temperature. Therefore, the optimization process for the calcination variables to obtain the optimum yield for the transesterification process must be able to take into account all the effects of the individual variables and also the interaction between variables.

Thus, in order to perform this task, the mathematical model developed earlier was used to obtain the calcination variables that can give the optimum yield of biodiesel. This was carried out with the aid of the optimization function embedded in Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA). Specifically, numerical optimization was selected as it has a comprehensive and up-to-date description and it focus on the methods that are best suited to practical problems in engineering, science and business (Ahn *et al*., 2008). In this method, the yield of biodiesel was set to a maximum range whereas calcination variables were set in a range between low and high levels with the coded values of -1 and +1 respectively.

It was predicted that an optimum yield of biodiesel of 80.58 wt% can be achieved by using SZA prepared with calcination temperature at 400°C and calcination duration of 4 hours. In order to verify this prediction, experiments were repeated three times using the suggested optimum conditions and it was found that the results obtained (84.60 wt%) were comparable with the prediction with less than 5% error. This shows that the predicted optimum calcination conditions are valid for this study. Hence, sulfated zirconia supported with alumina prepared by direct sulfation of zirconia oxide method is a potential catalyst for the production of biodiesel from *Jatropha curcas* L. oil via heterogeneous transesterification.

4.3 Catalyst Preparation Study- Solvent- free Method

4.3.1 Design of Experiment (DOE)

Similar to section 4.2, design of experiment was used again to study the effect of calcination variables on the yield of biodiesel and subsequently for optimization. However, this time the catalyst is prepared using solvent- free method. Solvent- free method is another alternative route to synthesize sulfated zirconia without using precipitating agents. This direct use of sulfating agents with the zirconia precursor has eliminated the formation of intermediate product (zirconia hydroxide) which reduces the preparation variables that must be controlled such as pH of the solution. **Table 4.4** shows the experimental design matrix and result with different combination of calcination variables obtained from DOE.

Table 4.4: Experimental design matrix and results for solvent- free method.

Catalyst code	Level of variables [actual (coded)]		Yield of biodiesel (%)	Predicted value
	Calcination temperature (°C)	Calcination duration (hour)		
SZA 01	400 (-1)	2 (-1)	46.42	49.14
SZA 02	600 (+1)	2 (-1)	59.43	60.03
SZA 03	400 (-1)	4 (+1)	71.18	71.09
SZA 04	600 (+1)	4 (+1)	70.18	67.96
SZA 05	300 (-2)	3 (0)	33.86	32.67

Table 4-4. Continued.

Catalyst code	Level of variables [actual (coded)]		Yield of biodiesel (%)	Predicted value
	Calcination temperature (°C)	Calcination duration (hour)		
SZA 06	700 (+2)	3 (0)	39.49	40.42
SZA 07	500 (0)	1 (-2)	56.52	54.99
SZA 08	500 (0)	5 (+2)	83.59	84.87
SZA 09	500 (0)	3 (0)	70.80	70.87
SZA 10	500 (0)	3 (0)	71.23	70.87
SZA 11	500 (0)	3 (0)	71.05	70.87
SZA 12	500 (0)	3 (0)	70.96	70.87
SZA 13	500 (0)	3 (0)	70.82	70.87

4.3.2 Development of Regression Model Equation

The model equation that correlates the response, Y (yield of biodiesel) to the calcination variables (x_1, x_2) by eliminating the insignificant variables was:

$$Y = +70.87 + 1.94\,x_1 + 7.47x_2 - 8.58x_1^{\,2} - 3.50x_1x_2 \qquad (4.2)$$

4.3.3 Statistical Analysis of Results

The R-squared value for the developed correlation was found to be 0.9926, implying that 99.26 % of the total variation in the yield of biodiesel is attributed to the experimental variables studied. To further support this finding, **Figure 4.11** shows the predicted vs. experimental yield of biodiesel. The regression model equation was found to provide a very accurate description of the experimental data, indicating that it was successful in capturing the correlation between the two calcination variables to the yield of biodiesel.

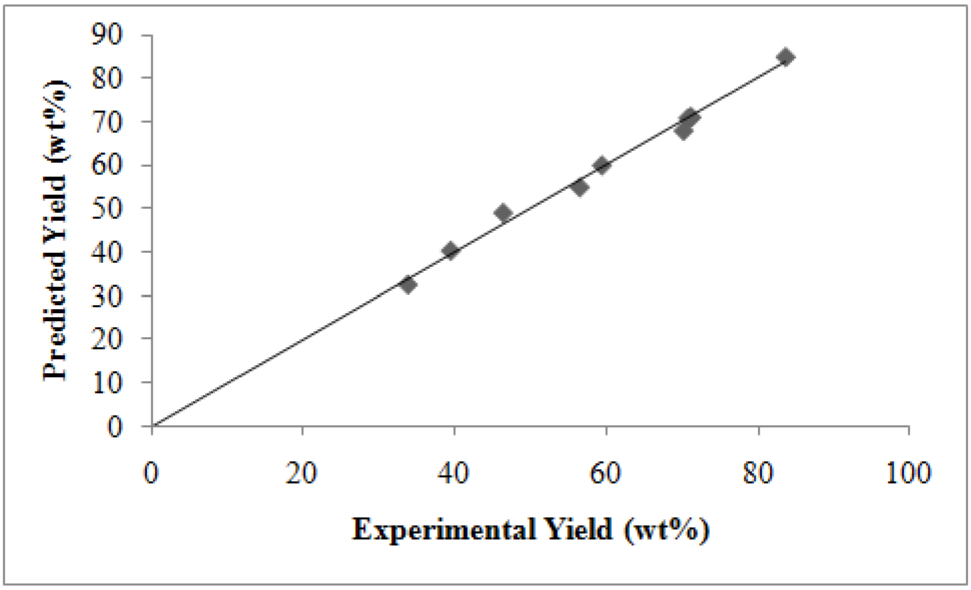


Figure 4.11: A comparative plot between experimental yield of biodiesel and predicted yield of biodiesel for solvent- free method.

The adequacy of the model was also checked with analysis of variance (ANOVA) as shown in **Table 4.5**. Based on 95 % confidence level, the model was tested to be significant as the computed F value (187.80) is much higher than the theoretical $F_{0.05\ (5,7)}$ value (3.97) and the p value is less than 0.05. Besides that, all terms in the model except x_2^2 was tested to be significant at a 95% confidence level as the computed F values for x_1 (16.46), x_2 (244.52), x_1^2 (616.00) and x_1x_2 (17.93) terms are higher than the theoretical $F_{0.05\ (1,\ 7)}$ value (5.59) and the p values are also less than 0.05. Thus, from these statistical tests, it was found that the model is adequate for predicting the yield of biodiesel within the range of variables studied.

Table 4.5: Analysis of Variance (ANOVA) for the regression model equation and coefficients (solvent- free method).

Source	Sum of Squares	Degree of Freedom	Mean of Squares	F-Test	p value
Model	2571.50	5	514.30	187.80	<0.0001
x_1	45.09	1	45.09	16.46	0.0048
x_2	669.65	1	669.65	244.52	<0.0001
x_1^2	1686.97	1	1686.97	616.00	<0.0001
x_2^2	1.28	1	1.28	0.47	0.5169
x_1x_2	49.11	1	49.11	17.93	0.0039
Residual	19.17	7	2.74		

4.3.4 Effect of Calcination Variables

4.3.4 (a) Single Variable Effect

Up to this point, it is clear that both the calcination variables studied have significant effect on the yield of biodiesel. This can be easily verified by observing **Table 4.4**, in which experiments were carried out with SZA catalyst prepared using various combination of calcination variables but with fix transesterification variables. The yield of biodiesel was found to range from 33.86 wt% to 83.59 wt%. Based on ANOVA shown in **Table 4.5**, there are two prominent significant terms that affect the yield of biodiesel, one is the linear effect of calcination duration (x_2) and the other one is the quadratic effect of calcination temperature (x_1) as indicated by the relatively large value of F-Test value.

(i) Effect of Calcination Temperature

Figure 4.12 shows the quadratic effect of calcination temperature on the yield of biodiesel. It was found that the yield of biodiesel increased from 60.3 wt% to 70.8 wt% when calcination temperature increased from 400 °C to 500 °C. However, further increase in calcination temperature led to a drop in the yield of biodiesel. The yield of biodiesel decreases to 64.2 wt% at a calcination temperature of 600 °C. This data trend was found to be consistent with the characterization results of catalyst which will be presented in the subsequent section.

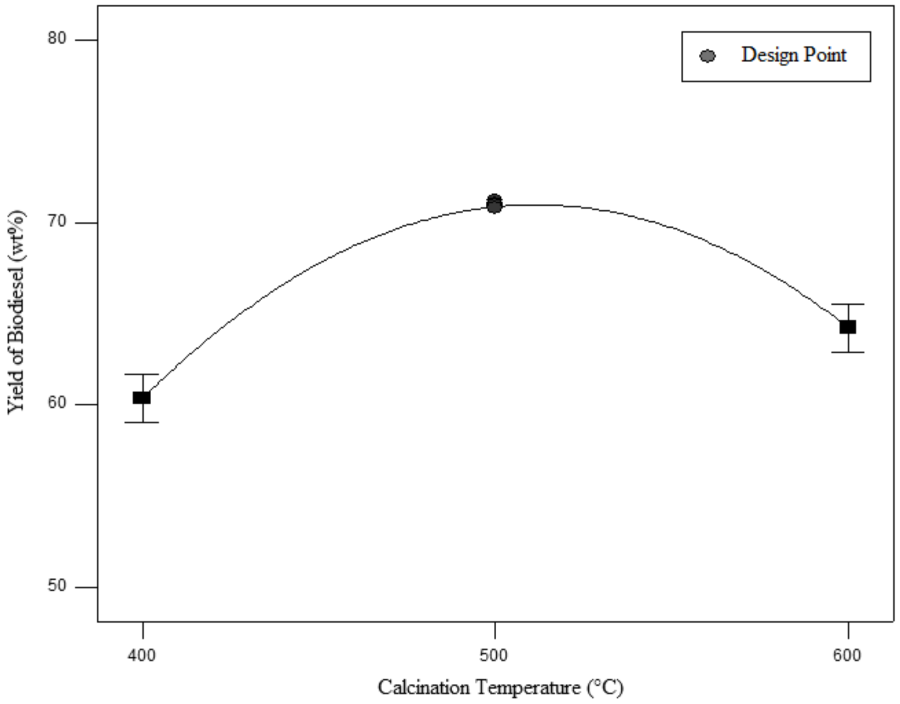


Figure 4.12: Plot of biodiesel yield against calcination temperature (Calcination duration at 3 hours) (solvent- free method).

Based on X-ray diffractograms (XRD) shown in **Figure 4.13**, the peaks assign to tetragonal phase and monoclinic phase of zirconia can be clearly detected for catalyst prepared at 500 °C. The presence of zirconia with a tetragonal structure is basically due to the stabilization role of sulfate groups (Ahmed *et al.*, 2008) and the presence of sulfate groups is the requirement for the formation of acidic sites (Sun *et al.*, 2005). Apart from that, catalyst prepared at 500 °C also showed dominant peaks assigned to tetragonal crystalline of zirconia (as compared to monoclinic).

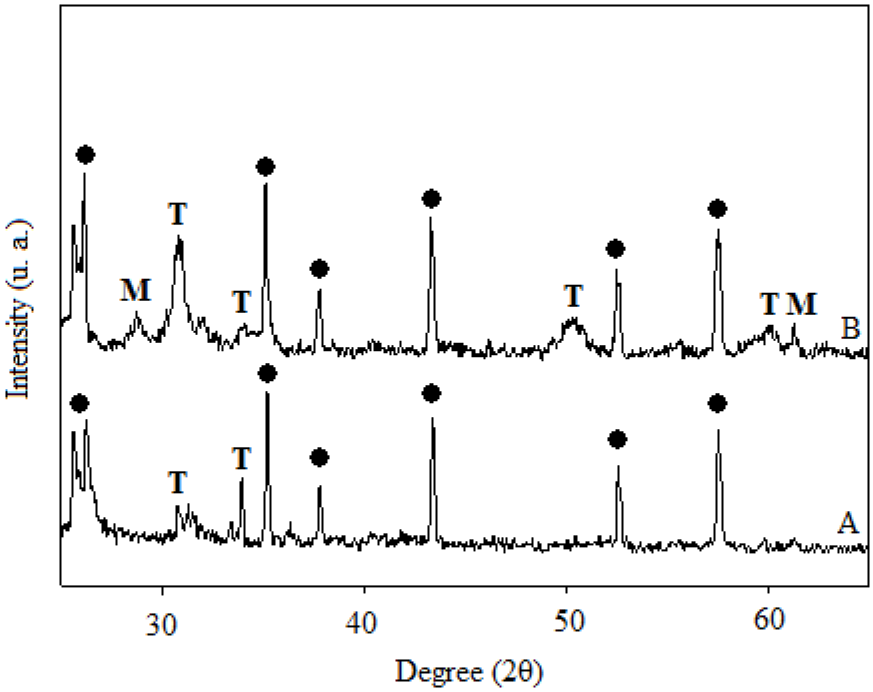


Figure 4.13: XRD patterns of SZA for solvent- free method; calcination duration at 3 hours with different temperatures (A), 300 °C (B), 500 °C

(**T**) tetragonal phase of zirconia, (**M**) monoclinic phase of zirconia and (●) aluminium oxide.

In tetragonal form, each bulk phase zirconium atom is coordinated to eight different oxygen atoms. Four Zr-O bonds are significantly shorter than the other four, the short Zr-O bonds constitute one distorted tetrahedron and the four longer Zr-O bonds constitute another distorted tetrahedron. However, at the surface, zirconium atoms of tetragonal ZrO_2 are coordinated to only six oxygen atoms. These two anionic vacancies in active sulfated zirconia catalyst produce the stabilization of the tetragonal phase by oxygenated sulfur species (Srinivasan *et al.*, 1995). Therefore, the presence of tetragonal phase of zirconia shows the formation of acidic sites on the catalyst, indirectly. However, for catalyst prepared at 300 °C, only little of the peaks assign to tetragonal phase zirconia was detected and at a lower intensity. This results revealed that increasing calcination temperature from 300 °C to 500 °C favors the formation of tetragonal phase zirconia and is in agreement with other studies using SZA but prepared using different methods utilizing solvent (Ahmed *et al.*, 2008; Mekhemer 2006).

Apart from that, it was also reported that further increase in calcination temperature (>500 °C) leads to instability of tetragonal zirconia phase due to decomposition of sulfate groups and therefore it rapidly transformed into monoclinic zirconia phase. Sulfated zirconia is not stable in the monoclinic phase suggests that the acid site structure is sensitive to the spacing between zirconium and oxygen atoms at the oxide surface. Such anionic vacancies defects would be absent in monoclinic catalysts (Vera *et al.*, 2002). Thus, at calcination temperature above 700 °C, monoclinic zirconia phase will be dominant. Hence, the increment in the yield of biodiesel up to calcination temperature of 500 °C is due to the formation of more prominent tetragonal crystalline phase of zirconia and sulphated groups.

In a typical catalytic process, surface area of the catalyst plays a very crucial role in determining its catalytic activity, in which generally catalyst with larger surface area leads to higher catalytic activity. In this study, the surface area of SZA catalyst was found to increase from 0.735 m^2/g to 20.6 m^2/g when the calcination temperature was increased from 300 °C to 500 °C. However, subsequently increase in calcination temperature to 700 °C caused a drop in surface area to 1.92 m^2/g. The increment in the surface area of the catalyst up to a calcination temperature 500 °C also contributes to the higher yield of biodiesel. However, for calcination temperature above 500 °C, the yield of biodiesel decreases gradually. This is in tandem with the drop in catalyst surface area and the decomposition of sulphated groups.

(ii) Effect of Calcination Duration

Figure 4.14 shows the effect of calcination duration on the yield of biodiesel in which the yield was found to increase linearly with calcination duration. From the figure, the highest yield of biodiesel (71.1 wt%) was obtained at a calcination duration of 4 hours as compared to merely 49.1 wt% at 2 hours. **Figure 4.15** shows the XRD patterns of SZA with different calcination duration. It reveals that catalyst prepared at higher calcination duration (5 hours) favors the formation of tetragonal phase zirconia that can aid the formation of acidic sites. Catalyst which prepared with shorter calcination duration (1 hour) does not exhibits much peaks assign to tetragonal phase of zirconia. On the other hand, increasing the calcination duration from 2 hours to 4 hours led to an increase of catalyst surface area from 4.18 m^2/g to 18.6 m^2/g. This BET specific surface area results revealed that the increase in catalyst surface area contributed to the higher conversion of triglycerides into biodiesel.

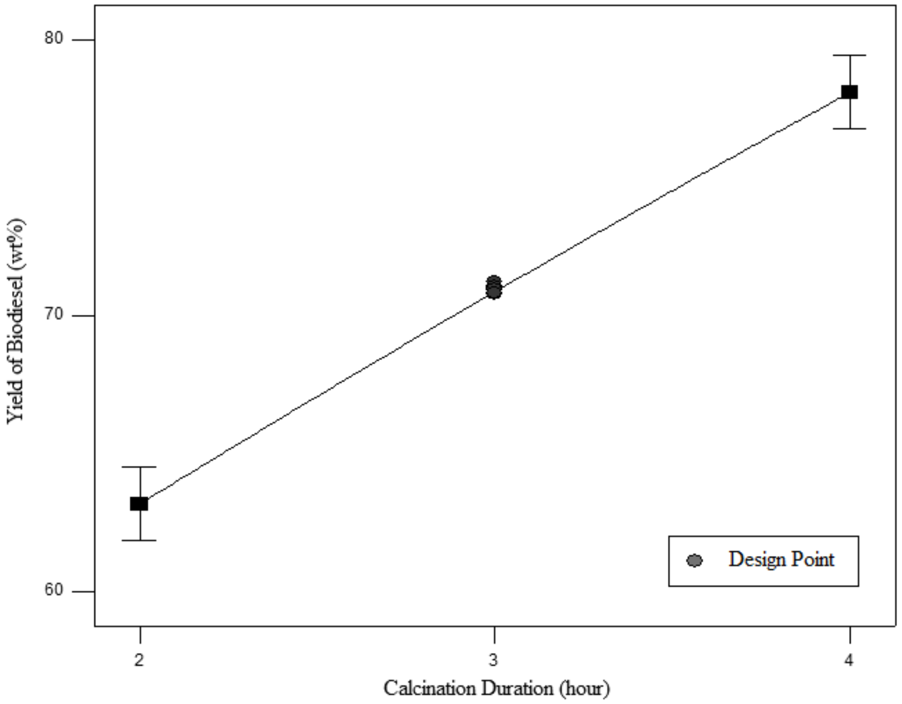


Figure 4.14: Plot of biodiesel yield against calcination duration (calcination temperature at 500 °C) (solvent- free method).

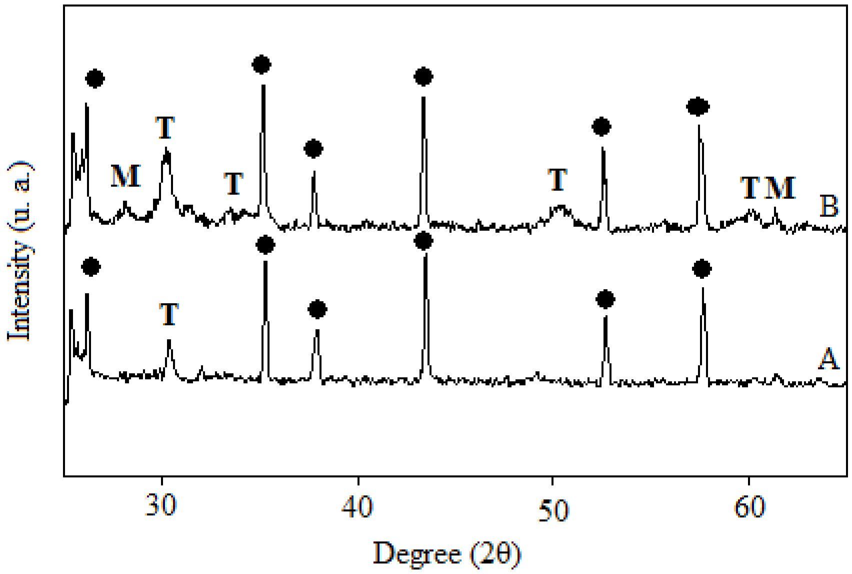


Figure 4.15: XRD patterns of SZA for solvent- free method; calcination temperature at 500 °C with different duration (A), 1 hour (B), 5 hour

(**T**) tetragonal phase of zirconia, (**M**) monoclinic phase of zirconia and (●) aluminium oxide.

Comparison between both catalyst preparation methods, calcination temperature was found to have a negative effect on the yield of biodiesel obtained using catalyst prepare by direct sulfation of zirconia oxide method. For solvent- free method, calcination temperature gives quadratic effect on the yield of biodiesel. The difference in the effect of calcinations temperature on the yield of biodiesel showed that different catalyst preparation methods led to catalyst with different sulfate groups strength where by catalyst prepare by solvent- free method decompose at much higher temperature (after 500 °C) than direct sulfation of zirconia oxide method (before 500 °C). However, it should be noted that higher yield of biodiesel can be obtained at lower calcination temperature for catalyst prepared by direct sulfation of zirconia (400 °C) compare to solvent- free method (500 °C).

This may be due to the different structure and behavior of the sulfated zirconia compound form with different preparation methods. As can be seen from the XRD analysis for both methods, zirconia sulfate tetrahydrate, $Zr(SO_4)_2.4H_2O$ was successfully detected using direct sulfation of zirconia oxide. For solvent- free method, the presence of sulfate groups within the catalyst cannot be detected directly but through the formation of tetragonal phase of zirconia which represents their presence availability since sulfate groups create the stabilization required for zirconia with tetragonal structure.

On the other hand, the yield of biodiesel did not change much with an increase in calcination duration for catalyst prepare by direct sulfation of zirconia oxide. However, catalyst prepared by solvent- free method shows a linear effect of calcination duration on the yield of biodiesel. This shows that the crystallization process for catalyst prepared by direct sulfation of zirconia oxide method occurs spontaneously and the crystal can fully grow as long as the calcination temperature is sufficient. However, for catalyst prepared by solvent- free method, both sufficient temperature and time are required for the crystal to grow fully. Again, as discussed earlier, this may be due to the different structure and behavior of the sulfated zirconia compound formed. Another possible reason is as follows; for solvent- free method which involves grinding the intermediate catalyst sample before calcination may reduce the catalyst particle size and also might leads to the destruction of surface sulfated groups (Li and Li, 2002). Therefore, calcination duration plays a significant role for the re-construction of the surface sulfated groups for catalyst prepared using solvent- free method.

4.3.4 (b) Effect of Interaction between Variables

The results so far illustrate the effect of individual effect of calcination temperature and duration on the yield of biodiesel. An added advantage of using design of experiment approach is that the interaction between both variables can also be studied systematically and efficiently. Based on the ANOVA presented in **Table 4.5**, apart from the individual calcination variables, the interaction between calcination temperature and duration was also found to significantly affect the yield of biodiesel. Therefore, this reflects the importance of using design of experiment approach.

Figure 4.16 shows the effect of interaction between calcination temperature and calcination duration on the yield of biodiesel. Two important findings can be extracted from **Figure 4.16**. Firstly, the optimum calcination temperature was found to vary, depending on the calcination duration. Referring to **Figure 4.16**, at calcination duration of 2 hours, the optimum calcination temperature was found to roughly range between 500 °C to 550 °C, but the optimum range reduces to 450 °C to 500 °C for calcination duration of 4 hours. The second finding is as follows; although longer calcination duration leads to higher yield of biodiesel (at fixed calcination temperature), however, the significance of the effect of calcination duration decreases with higher calcination temperature. For example, at 400 °C, the percentage difference in the yield of biodiesel when increasing calcination duration from 2 hours to 4 hours was 53.4 %, but at 600 °C, the percentage difference drop to merely 14.4 % for similar increment in calcination duration.

The reason for this phenomenon could be as follows. At lower calcination temperature, longer calcination duration is required for the formation of more tetragonal crystalline zirconia phase which subsequently leads to formation of more acidic sites and larger catalyst specific surface area. However, at higher calcination temperature, longer calcination duration is no longer required to promote the formation of tetragonal crystalline zirconia phase. Instead, longer calcination duration could cause the decomposition of sulfate groups that led to the drop in the yield of biodiesel.

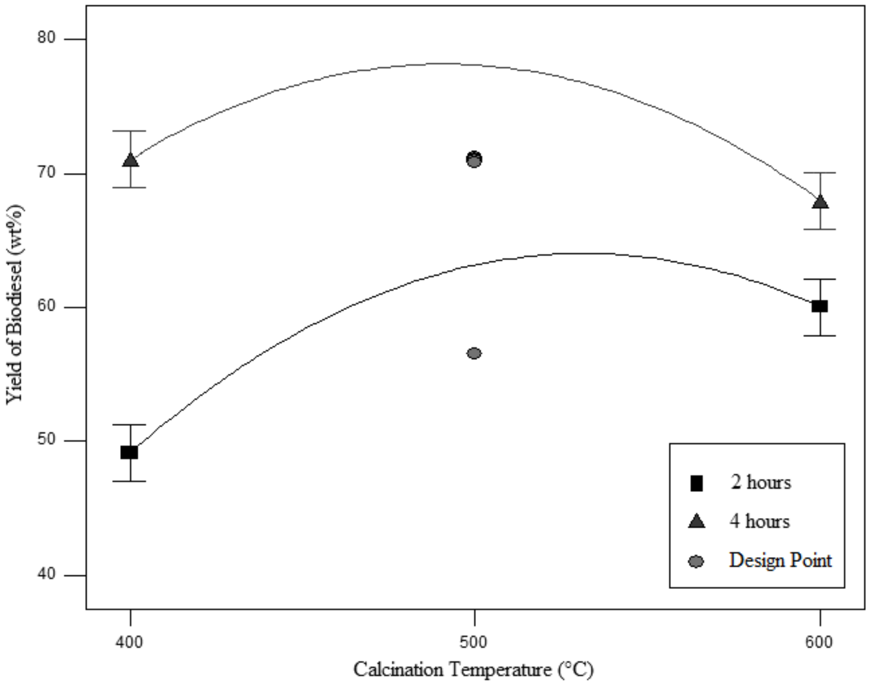


Figure 4.16: Plot of yield of biodiesel against calcination temperature and calcination duration for solvent- free method.

4.3.5 Optimization of Calcination Variables

In the production of biodiesel, an effective catalyst is one of the integral requirements for obtaining a high yield for economical feasibility. An effective catalyst, can be normally obtain by optimizing the preparation variables of catalyst such as calcination conditions including temperature and duration. Based on the results presented earlier, apart from individual variables, interaction between the calcination variables were also found to have significant effect on the yield of biodiesel. Therefore, the optimization process must be able to take into account all the effects of the individual variables and also the interaction between variables, in order to maximize the yield of biodiesel of the transesterification process. This was carried out with the aid of the optimization function embedded in the Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) using the mathematical equation developed. Specifically, numerical optimization was selected as it has a comprehensive and up-to-date description and it focus on the methods that are best suited to practical problems in engineering, science and business (Ahn *et al*., 2008). In this method, the yield of biodiesel was set to a maximum range whereas calcination variables were set in a range between low and high levels with the coded values of -1 and +1 respectively.

The software predicted that an optimum biodiesel yield of 78.2 wt% can be obtained with the following calcination temperature and duration of 490 °C and 4 hours respectively. The predicted optimum yield was then verified by carrying out 3 repeated experimental runs using the suggested optimum condition. The repeated experiments gave an average optimum yield of 81.4 wt% which is very close to the predicted value (less than 5 % error) indicating that the predicted optimum process conditions are valid for this study.

Table 4.6 shows the optimum calcination conditions and yield of biodiesel with two different catalyst preparation methods (direct sulfation of zirconia oxide method and solvent- free method). It was clearly shown that the yield of biodiesel obtained for direct sulfation of zirconia oxide method were slightly higher than solvent- free method. Apart from that, direct sulfation of zirconia oxide method gives a lower optimum calcination temperature compared to solvent- free method although both methods give the same optimum calcination duration. Since direct sulfation of zirconia oxide method requires lower calcination temperature for catalyst preparation, the optimized catalyst prepared using this method was selected for subsequent transesterification process study.

Table 4.6: Comparison between direct sulfation of zirconia oxide method and solvent- free method.

	Direct sulfation of zirconia oxide method	Solvent- free method
Optimum calcination temperature (°C)	400	490
Optimum calcination duration (hour)	4	4
Optimum yield of biodiesel (wt %)	84.60	81.40

4.4 Process Study for Transesterification of *Jatropha* C*urcas* L. Oil

4.4.1 Design of Experiment (DOE)

Design of experiment was used to study the effect of transesterification process variables on the yield of biodiesel. In addition to that, the process variables were then optimized. Sulfated zirconia loaded on alumina catalyst was required throughout the whole process study as the heterogeneous acidic catalyst to catalyze the transesterification reaction and was synthesized via direct sulfation of zirconia oxide method with optimum calcination conditions. **Table 4.7** shows the experimental design matrix and result with different combination of process variables obtained from DOE. **Table 4.8** shows the detail calculation for the molar ratio of methanol to oil and weight percentage of catalyst.

Table 4.7: Experimental design matrix by CCD for the four independent variables used for process study.

Run	Point type	Level of variables [actual (coded)]				Yield of biodiesel
		Temperature, x_1	Duration, x_2	Molar ratio methanol/oil, x_3	Catalyst loading, x_4	
		(°C)	(hour)	(mole mole^{-1})	(wt%)	(%)
1	Fact	90 (-1)	2 (-1)	6 (-1)	4 (-1)	13.22
2	Fact	150 (+1)	2 (-1)	6 (-1)	4 (-1)	42.93
3	Fact	90 (-1)	4 (+1)	6 (-1)	4 (-1)	16.22
4	Fact	150 (+1)	4 (+1)	6 (-1)	4 (-1)	58.58
5	Fact	90 (-1)	2 (-1)	10 (+1)	4 (-1)	18.82
6	Fact	150 (+1)	2 (-1)	10 (+1)	4 (-1)	54.39
7	Fact	90 (-1)	4 (+1)	10 (+1)	4 (-1)	20.54
8	Fact	150 (+1)	4 (+1)	10 (+1)	4 (-1)	77.61
9	Fact	90 (-1)	2 (-1)	6 (-1)	8 (+1)	26.46
10	Fact	150 (+1)	2 (-1)	6 (-1)	8 (+1)	58.31
11	Fact	90 (-1)	4 (+1)	6 (-1)	8 (+1)	24.66
12	Fact	150 (+1)	4 (+1)	6 (-1)	8 (+1)	63.04
13	Fact	90 (-1)	2 (-1)	10 (+1)	8 (+1)	30.65
14	Fact	150 (+1)	2 (-1)	10 (+1)	8 (+1)	74.48
15	Fact	90 (-1)	4 (+1)	10 (+1)	8 (+1)	32.65
16	Fact	150 (+1)	4 (+1)	10 (+1)	8 (+1)	85.52
17	Axial	60 (-2)	3 (0)	8 (0)	6 (0)	9.67
18	Axial	180 (+2)	3 (0)	8 (0)	6 (0)	88.90
19	Axial	120 (0)	1 (-2)	8 (0)	6 (0)	41.79
20	Axial	120 (0)	5 (+2)	8 (0)	6 (0)	61.86
21	Axial	120 (0)	3 (0)	4 (-2)	6 (0)	35.56
22	Axial	120 (0)	3 (0)	12 (+2)	6 (0)	61.83

Table 4-7. Continued.

Run	Point type	Level of variables [actual (coded)]				Yield of biodiesel
		Temperature, x_1	Duration, x_2	Molar ratio methanol/oil, x_3	Catalyst loading, x_4	
		(°C)	(hour)	(mole mole^{-1})	(wt%)	(%)
23	Axial	120 (0)	3 (0)	8 (0)	2 (-2)	17.51
24	Axial	120 (0)	3 (0)	8 (0)	10 (+2)	50.71
25	Center	120 (0)	3 (0)	8 (0)	6 (0)	44.93
26	Center	120 (0)	3 (0)	8 (0)	6 (0)	43.16
27	Center	120 (0)	3 (0)	8 (0)	6 (0)	43.07
28	Center	120 (0)	3 (0)	8 (0)	6 (0)	44.52
29	Center	120 (0)	3 (0)	8 (0)	6 (0)	44.38
30	Center	120 (0)	3 (0)	8 (0)	6 (0)	43.76

Table 4.8: Exact measurement for molar ratio of methanol to oil and weight percentage of catalyst for data used in Table 4.7.

Oil (ml)	Methanol/Oil ratio (mol/mol)		Catalyst	
	Ratio	Methanol (ml)	% wt	Gram, g
40	4	6.62	2	0.7376
40	6	9.94	4	1.4752
40	8	13.25	6	2.2128
40	10	16.56	8	2.9504
40	12	19.87	10	3.688

*Basis volume of *Jatropha curcas* L. oil used = 40 ml or 36.88 g with density = 0.9220 g/ml

4.4.2 Development of Regression Model Equation

By using multiple regression analysis, data in **Table 4.7** was used to develop a mathematical model that correlates the response (yield of biodiesel) to the transesterification process variables. By using Design-Expert 6.0.6 software, the model equation in terms of actual value after excluding the insignificant terms is:

$$\begin{aligned} Y = {} & +45.70 + 20.42x_1 + 4.15x_2 + 5.99x_3 + 6.66x_4 + 1.36x_2^{\ 2} - 3.07x_4^{\ 2} + 3.11x_1x_2 \\ & + 2.94x_1x_3 - 1.73x_2x_4 \end{aligned} \qquad (4.3)$$

4.4.3 Statistical Analysis of Results

The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-squared for **Equation 4.3** is 0.9866. It implies that 98.66 % of the total variation in the yield of biodiesel response is attributed to the experimental variables studied. The deviation is only 1.34 % from the ideal value. Besides that, **Figure 4.17** demonstrated that the regression model equation provided a very accurate description of the experimental data, indicating that it was successful in capturing the correlation among the four process variables to the yield of biodiesel.

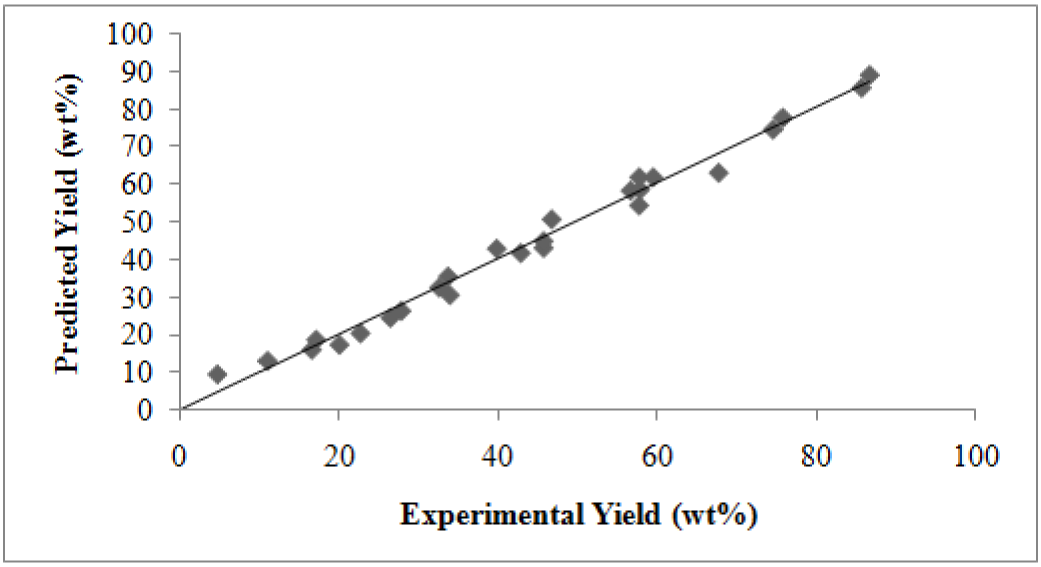


Figure 4.17: A comparative plot between experimental yield of biodiesel and predicted yield of biodiesel for process study.

The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in **Table 4.9**. Based on a 95 % confidence level, the model was tested to be significant as the computed F value (163.44) was much higher than the theoretical $F_{0.05\ (9,\ 20)}$ value (2.39) and the p value was less than 0.05. Thus, this indicates that the model was adequate for predicting the yield of biodiesel within the range of variables studied. Besides that, the significance of each term in the model was tested at 95 % confidence level by comparing the computed F values for the respective terms with the theoretical $F_{0.05\ (1,\ 20)}$ value (4.35) and checking the p values. Values greater than 0.05 indicate the model terms are not significant. From **Table 4.9**, the significant process variables that affect the yield of biodiesel were reaction temperature (x_1), reaction duration (x_2), molar ratio of methanol to oil (x_3) and catalyst loading (x_4). Interactions among some of the four variables also affect the yield of biodiesel.

Table 4.9: Analysis of Variance (ANOVA) for the regression model equation and Coefficients (process study).

Source	Sum of squares	Degree of freedom	Mean of squares	F-Test	p value
Model	13040.58	9	1448.95	163.44	<0.0001
x_1	10008.25	1	10008.25	1128.94	<0.0001
x_2	414.17	1	414.17	46.72	<0.0001
x_3	861.36	1	861.36	97.16	<0.0001
x_4	1064.80	1	1064.80	120.11	<0.0001
x_2^2	52.33	1	52.33	5.90	0.0247
x_4^2	268.50	1	268.50	30.29	<0.0001
x_1x_2	154.50	1	154.50	17.43	0.0005
x_1x_3	138.30	1	138.30	15.60	0.0008
x_2x_4	47.68	1	47.68	5.38	0.0311
Residual	177.30	20	8.87	-	-

4.4.4 Effect of Process Variables

4.4.4 (a) Single Variable Effect

The individual effects of reaction temperature, reaction duration, molar ratio of methanol to oil and catalyst loading towards the yield of biodiesel can be graphically seen from **Figure 4.18** to **Figure 4.21**, respectively. These four individual variables show positive influence towards the yield of biodiesel as shown in **Equation 4.3**. From **Table 4.9**, it was observed that among the four variables studied, reaction temperature (x_1) has the greatest effect on the yield of biodiesel (due to the highest F value) followed by catalyst loading (x_4), molar ratio of methanol to oil (x_3) and reaction duration (x_2).

Figure 4.18 indicates that an increase in the reaction temperature led to an increase in yield of biodiesel. In this study, the range of reaction temperature studied was from 60 °C to 180 °C. The results indicated that the reaction rate is slow at lower temperatures as the yield of biodiesel yield was only 9.67 wt% at 60 °C after 3 hours of reaction. The yield of biodiesel increases with higher reaction temperature and it reached 88.90 wt% at 180 °C. The mechanism of acid catalyzed transesterification is different from that of base catalyzed transesterification which comparatively required high reaction temperature to facilitate the slow reaction rate of acid catalyzed transesterification (Shu *et al*., 2009).

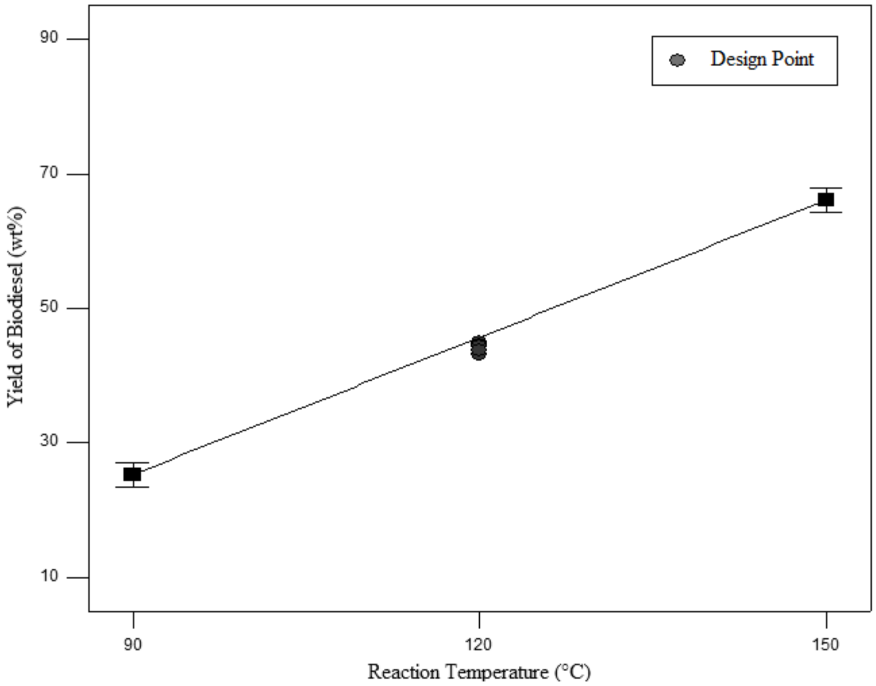


Figure 4.18: Yield of biodiesel against reaction temperature for process study (reaction duration at 3 hours, molar ratio of methanol to oil at 8, catalyst loading at 6 wt%).

As describe by the Arrhenius equation, rate constant is strongly dependent on temperature. An increase in reaction temperature will increase the rate of reaction where more particles will have the necessary activation energy resulting in more successful collisions (when new bonds are formed between reactants). Hence, transesterification reaction should take place at high reaction temperature since reaction temperature influence the reaction rate and the yield of biodiesel.

In **Figure 4.19**, the yield of biodiesel against reaction duration is presented. It can be clearly seen that the yield of biodiesel increased at higher reaction duration within the range studied. In a three phase system which involves oil, methanol and heterogeneous catalyst, reaction is usually limited by the diffusion of reactants. The presence of heterogeneous catalyst leads to slower mass transfer rate due to limited contact between catalyst and the liquid reactants (as compared to homogeneous catalyst). Hence, longer reaction duration is required for the reactants to diffuse to the active sites of the catalyst and therefore higher yield of biodiesel can only be obtained at longer reaction duration. Apart from that, the conversion of triglycerides involves three consecutive reactions with intermediates (monoglyceride and diglyceride) (Chen & Wang, 2006). Therefore, longer reaction duration was acquired to complete this sequence of fatty acids substitution from the triglyceride molecules and to obtain biodiesel as the desired product (Abdullah, Razali & Lee, 2009).

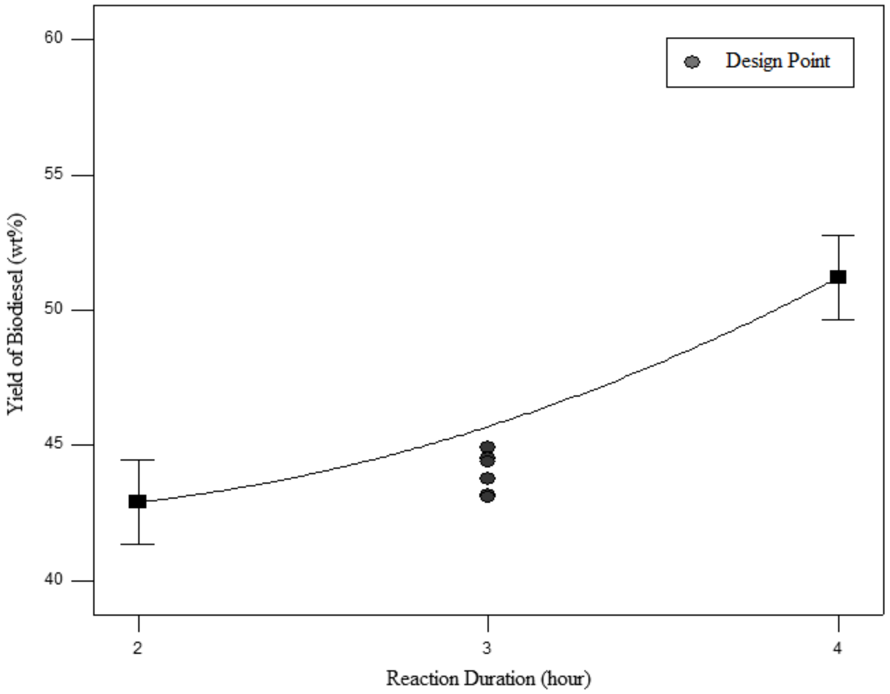


Figure 4.19: Yield of biodiesel against reaction duration for process study (reaction temperature at 120 °C, molar ratio of methanol to oil at 8, catalyst loading at 6 wt%).

Transesterification process consists of a sequence of three consecutive reversible reactions where by triglyceride is successively transformed into diglyceride, monoglyceride and finally into fatty acid methyl esters and glycerin. The molar ratio of methanol to oil is one of the important factors that affect the yield of biodiesel. Stoichiometrically, three moles of methanol are required for each mole of triglyceride, but in practice, a higher molar ratio is employed in the reversible reaction in order to shift the equilibrium towards the direction of biodiesel formation (Shu *et al.*, 2007; Abdullah *et al.*, 2009).

This phenomenon was also reported by Shu *et al*. (2009). It was assumed that transesterification begins when triglycerides were chemisorbed on the catalyst active sites. These were then protonated at the carbonyl group to give a carbocation which can undergo attack by methanol to form methyl esters. When methanol was in excess, the approach of methanol molecules to the carbocation was enhanced and there was an increase in the yield of biodiesel. In another word, the presence of excess methanol in the transesterification reaction leads to essentially breaking the glycerine-fatty acid linkages (Miao *et al*., 2009). In this study, the plot of biodiesel yield versus molar ratio of methanol to oil (**Figure 4.20**) shows that the higher the molar ratio of methanol to oil, the greater the yield of biodiesel.

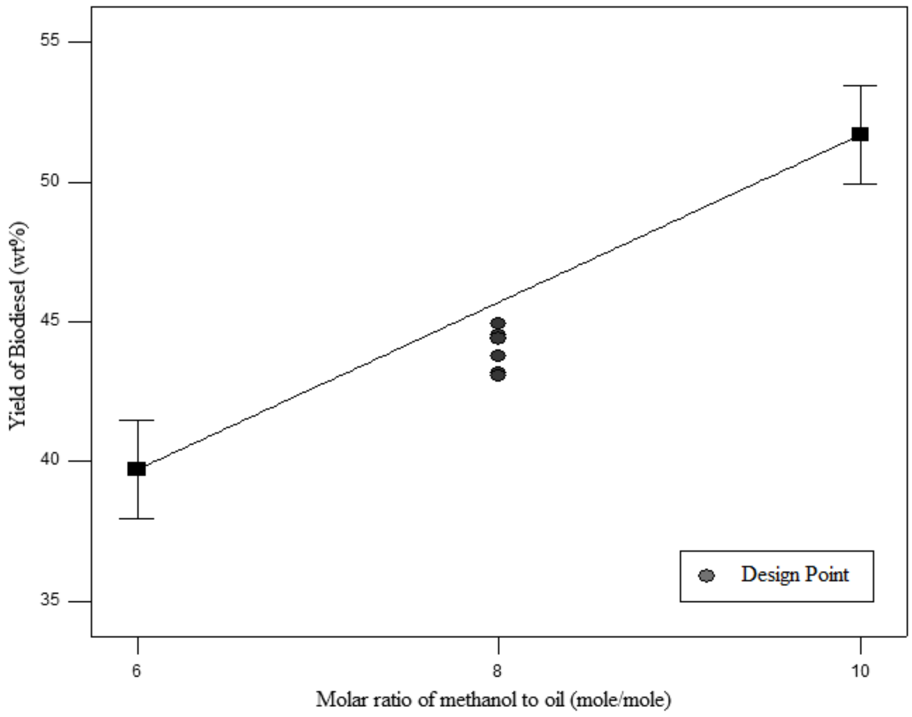


Figure 4.20: Yield of biodiesel against molar ratio of methanol to oil for process study (reaction temperature at 120 °C, reaction duration at 3 hours, catalyst loading at 6 wt%).

In a typical heterogeneous acid catalyst such as sulfated zirconia used in this study, the presence of sulfate group provides the acidity that is required for transesterification of *Jatropha curcas* L. oil with high free fatty acid content. As noted in **Figure 4.21**, it was found that higher catalyst loading directly increases the yield of biodiesel. This is due to the increase in the total number of available active acidic sites resulted in faster reaction rate to reach equilibrium. The active sites provided by catalyst were the locations where the reaction takes place and were proportional to the amount of catalyst (Li *et al*, 2010). However, it was noted that the yield of biodiesel increased with higher catalyst loading just up until a value in which higher increment no longer increased the yield of biodiesel. Further increase in catalyst loading beyond its optimum value will have negligible increase in the yield of biodiesel.

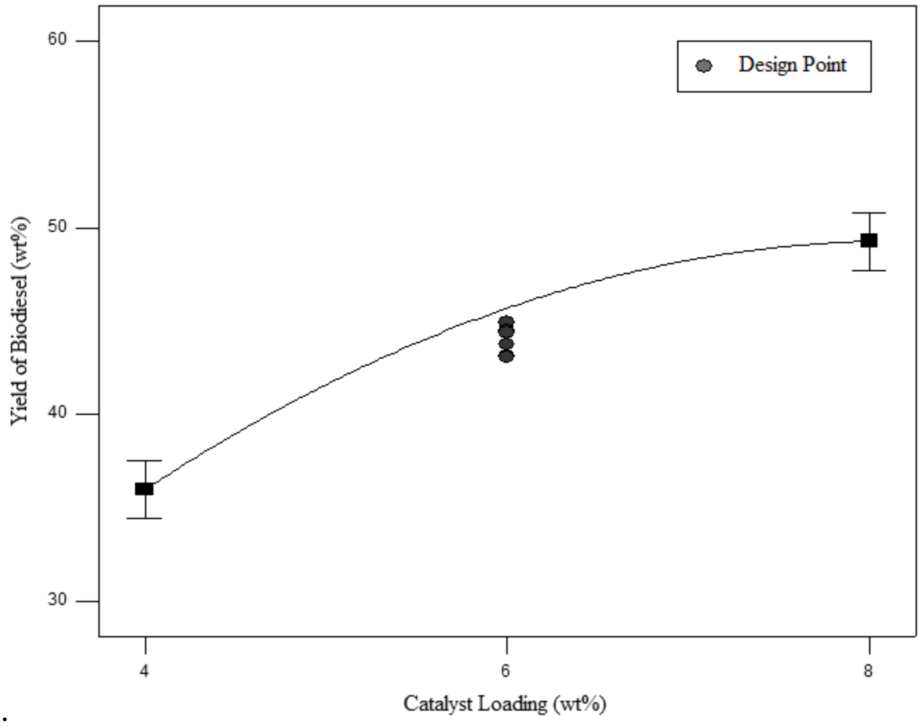


Figure 4.21: Yield of biodiesel against catalyst loading for process study (reaction temperature at 120 °C, reaction duration at 3 hours, molar ratio of methanol to oil at 8).

At the beginning of the reaction, the reaction was rate limiting due to the immiscibility of *Jatropha curcas* L. oil and methanol. However, as catalyst is introduced in the reaction mixture, it provides an external contact surface area that facilitates the formation of biodiesel. As more biodiesel is produced, it eventually acted as co-solvent, by dissolving both reactants to become a single-phase reaction system (Shu *et al*., 2007). Subsequently the reaction rate is being controlled by the diffusion of the reactants to the active sites, instead of catalyst loading. Hence, increasing the catalyst loading in the reaction mixture will have an insignificant effect on the yield of biodiesel.

4.4.4 (b) Effect of Interaction between Variables

The regression model shown in **Equation 4.3** indicates that the yield of biodiesel is not solely dependent on the individual process variables but also the interaction between variable. **Equation 4.3** suggested that three interaction terms show significant effect on the yield of biodiesel, which are: the interactions between reaction temperature (x_1) and reaction duration (x_2); reaction temperature (x_1) and molar ratio of methanol to oil (x_3) as well as reaction duration (x_2) and catalyst loading (x_4). Hence, it is of great interest to further study these interactions effect within the range of process variables studied. The developed model was then used to construct an interaction plot to facilitate a straightforward investigation on the interaction between variables.

Figure 4.22 shows the interaction between reaction temperature and reaction duration (molar ratio of methanol to oil was fixed at 8, catalyst loading was fixed at 6 wt%). At shorter reaction duration (2 hours), when the transesterification reaction was carried out at 90 °C, the yield of biodiesel was only 25.59 wt%. However, the yield of biodiesel increased to 60.21 wt% with increasing reaction temperature to 150 °C. The same trend was observed at 4 hours of reaction duration but the magnitude of the increase in biodiesel yield was more pronounced at this longer reaction duration which is from 27.68 wt% to 74.74 wt%. In another words, reaction duration has a more significant effect on the yield of biodiesel at higher reaction temperature than lower reaction temperature.

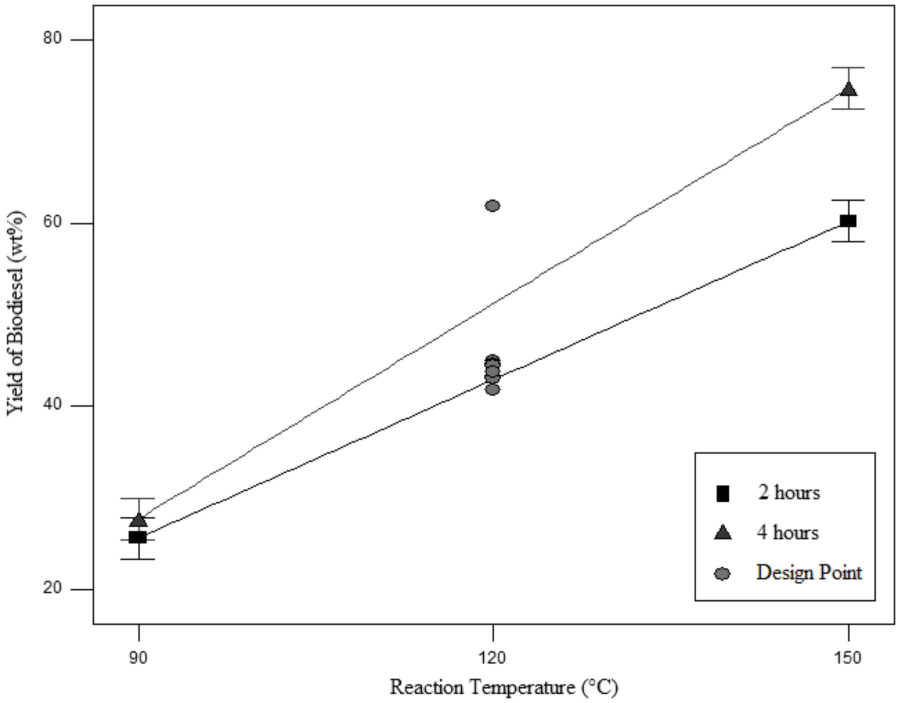


Figure 4.22: Yield of biodiesel against reaction temperature and reaction duration for process study (molar ratio of methanol to oil at 8, catalyst loading at 6 wt%).

Similar to the explanation given in the previous section, an increase in reaction temperature and reaction duration were found to increase the yield of biodiesel. At lower reaction temperature, the yield of biodiesel was slightly the same and less dependent on reaction duration since reaction temperature (x_1) is the major regressor variable affecting the yield of biodiesel (greatest coefficients) compare to reaction duration (x_2) as observed in **Equation 4.3**. The regression coefficients were 20.42 and 4.15 for both individual effects, respectively. At lower reaction temperature, there is insufficient energy to promote extensive collisions among reactant particles. Therefore, increasing the reaction duration do not contribute to any significant increase in the yield of biodiesel.

However, at higher reaction temperature, the possibility of collision among reactant particles became greater since now reactants can easily obtain the necessary activation energy. Thus if given longer contact time, most of the reactants will collide and react to give higher yield of biodiesel.

Figure 4.23 shows the interaction between reaction temperature and molar ratio of methanol to oil (reaction duration was fixed at 3 hours, catalyst loading was fixed at 6 wt%). The yield of biodiesel was found to increase with increasing reaction temperature and molar ratio of methanol to oil. However, similar to the interaction between reaction temperature (x_1) and reaction duration (x_2), the effect of molar ratio of methanol to oil is greater at higher reaction temperature. This is again probably because reaction temperature is the most significant variable affecting the yield of biodiesel compare to molar ratio of methanol to oil (x_3) since it has the largest coefficients in the model equation. The regression coefficients were 20.42 and 5.99 for the both individual effect of reaction temperature and molar ratio of methanol to oil, respectively. Hence, at lower reaction temperature, the yield of biodiesel obtained was only 22.23 wt% and 28.32 wt% for molar ratio of methanol to oil at 6 and 10, respectively. There is only 6.09 wt% increase in the yield of biodiesel when increasing the molar ratio of methanol to oil. However, at higher reaction temperature, the yield of biodiesel increases from 57.19 wt% to 75.05 wt% by increasing molar ratio of methanol to oil from 6 to 10. There is a 17.86 wt% increase in the yield of biodiesel.

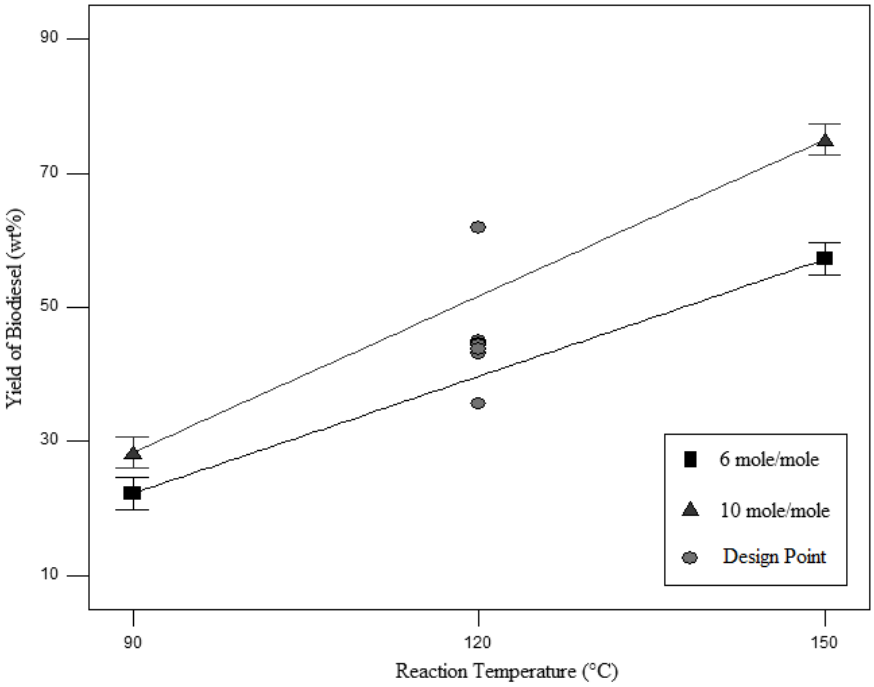


Figure 4.23: Yield of biodiesel against reaction temperature and molar ratio of methanol to oil for process study (reaction duration at 3 hours, catalyst loading at 6 wt%).

At lower reaction temperature, again there is not sufficient energy to promote extensive collision among the reactants to collide and rect. Therefore, even by increasing the amount of reactants available by increasing the molar ratio of methanol to oil do not bring much benefit to the yield of biodiesel. However, at higher reaction temperature, now most of the reactants have more energy, resulting to more collisions and reaction and therefore increasing the amount of reactants now have more positive effect on the yield of biodiesel.

Figure 4.24 shows the interaction between reaction duration and catalyst loading (reaction temperature was fixed at 120 °C, molar ratio of methanol to oil was fixed at 8). As can be seen from the model equation, catalyst loading (x_4) is a more significant regressor variable affecting the yield of biodiesel compared with reaction duration (x_2). The regression coefficients were 6.66 and 4.15 for the both individual effects of catalyst loading and reaction duration, respectively. This can be observed in **Figure 4.24** where the yield of biodiesel increases more significantly by increasing catalyst loading as compared with increasing reaction duration.

Apart from that, it was noticed that at shorter reaction duration, yield of biodiesel was significantly increased from 31.44 wt% to 48.21 wt% (increase by 16.77 wt%) with increasing catalyst loading from 4 wt% to 8 wt%, respectively. However, the increase was less pronounced at longer reaction duration (only increase by 9.87 wt%). In another words, the effect of catalyst loading reduced with the increment of reaction duration. This is a result of negative interaction which was correctly reflected by the negative value of regression coefficients for x_2x_4 interaction in **Equation 4.3** (-1.73).

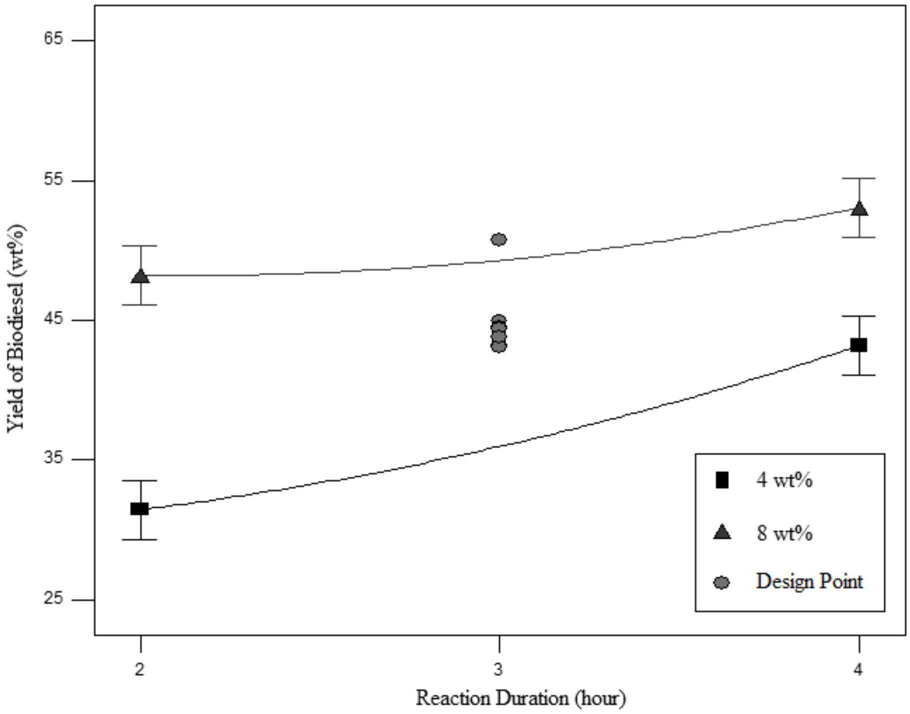


Figure 4.24: Yield of biodiesel against reaction duration and catalyst loading for process study (reaction temperature at 120 °C, molar ratio of methanol to oil at 8).

This finding can be explained as follows: the solubility of methanol in *Jatropha curcas* L. oil is limited and thus transesterification reaction can only occur at the interface of these two-phases or on the catalyst active sites. Therefore, at shorter reaction duration, there is not sufficient time for all the reactants to access the active sites especially at low catalyst loading. Thus, when the catalyst loading was increased, the yield of biodiesel significantly increases as now the reactants have better access to the active sites. However, at longer reaction duration, the amount of catalyst is no longer the limiting factor, as the reactants have more time to access the active sites. Therefore, increasing the catalyst loading at longer reaction duration, do not cause that much significant effect on the yield of biodiesel.

4.4.5 Optimization of Transesterification Process Variables

Up to this point, apart from the four individual variables, the interactions between variables were also found to have significant effect on the yield of biodiesel. Therefore, the optimization process must be able to take into account all the effects of the individual variables and also the interaction between variables, in order to maximize the yield of biodiesel of the transesterification process. In this study, the optimization of biodiesel yield was performed using Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) to search for an optimum combination of conditions that give maximum yield of biodiesel.

In this method, the yield of biodiesel was set to a maximum range whereas transesterification variables were set in a range between low and high levels with the coded values of -1 and +1 respectively. The software predicted that at the following optimum conditions; 150 °C, 4 hours for reaction duration, 9.88 mol/mol for the molar ratio of methanol to oil and 7.61 wt% for catalyst loading, an optimum biodiesel yield of 85.09 wt% can be obtained. The predicted optimum yield was then verified by carrying out 3 repeated experimental runs using the suggested optimum condition. The repeated experiments gave an average optimum yield of 90.32 wt% which is very close to the predicted value (less than 5 % error) indicating that the predicted optimum process conditions are valid for this study.

The result obtained in this optimization study was compared with the results reported by other researchers for the production of biodiesel from different oil feedstocks with sulfated zirconia catalyst as shown in **Table 4.10.** It was found that the yield obtained in this study is the highest as compared to those reported by other researchers. In addition to that, the transesterification process variables used for obtaining the optimum yield was only moderate, in between the conditions reported by other researchers. This result therefore show the superiority of the findings in this study in synthesizing sulfated zirconia loaded on alumina catalyst and utilizing it to convert *Jatropha curcas* L. oil to biodiesel with high yield.

Table 4.10: Comparisons of biodiesel yield obtained in this study and other researchers with the optimum transesterification process conditions.

Optimum reaction condition	Researchers			
	Chen and Wang (2006)	Kansedo *et al.* (2007)	Suwannakarn *et al.* (2009)	This study
Oil feedstock	Cottonseed oil	Sea mango oil	Tricaprylin (TCP)	*Jatropha curcas* L. oil
Alumina supported	no	yes	no	yes
Temperature	230 °C	180 °C	120 °C	150 °C
Duration	7 hours	3 hours	2 hours	4 hours
Methanol to oil molar ratio	12	8	12	9.88
Catalyst loading	2 wt%	6 wt%	10 wt%	7.61wt%
Yield of biodiesel	80.0 %	83.8 %	84.0 %	90.3 %

4.5 Catalyst Recycling and Regeneration

The catalysts used for transesterification reaction were recycled and re-utilized after the first run by washing with hexane for several times without any pretreatment. **Figure 4.25** shows that the yield of biodiesel dropped after the first cycle of reaction. Initially, when using the fresh SZA catalyst, the yield of biodiesel is 90.32 wt%. However, after recycling the catalyst for the first time, the yield of biodiesel decreased to 74.57 wt%, 52.04 wt% in the second cycle, 32.07 wt% in the third cycle and 30.86 wt% in the fourth cycle. After the third cycle and onwards, the yield of biodiesel remains constant at about 30 wt%, which is similar to the yield of biodiesel that would have been obtained without the use of sulfated catalyst.

Thus, it is clear that, the drop in the yield of biodiesel was due to catalyst deactivation. Generally, the deactivation process is caused by the free water or alcohol which is present in the reaction mixture. Kiss *et al*. (2006) reported that the ionic sulfur species supported on the catalyst surface could be hydrolyze into H_2SO_4, HSO_4^- and SO_4^{2-} by the presence of free water in the aqueous phase. The accumulation of free water on hydrophilic acidic sites will hydrolyze sulfate groups leading to the loss of active sites from the solid surface.

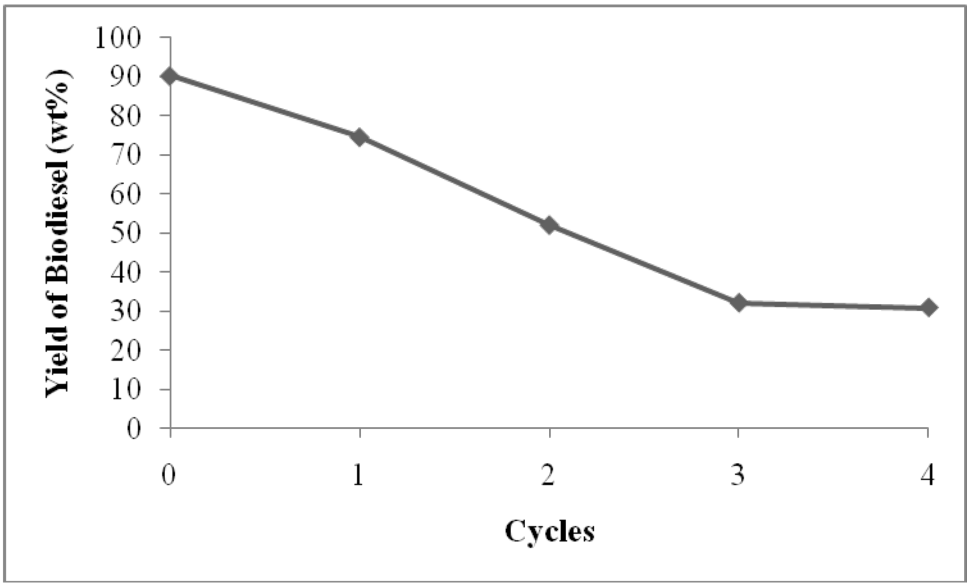


Figure 4.25: Effect of the recycling of sulfated zirconia alumina on yield of biodiesel (reaction temperature at 150 °C, reaction duration at 4 hours, molar ratio of methanol to oil at 9.88, catalyst loading at 7.61 wt%).

Another possible reason that could have cause catalyst deactivation is leaching of the sulfate groups. Leaching process could occurs in the organic phase even with the presence of a small amount of water and also alcohol (Suwannakarn *et al*., 2008), which are used as reactants in transesterification of *Jatropha curcas* L. oil. However, water is more efficient in removing sulfate groups from the catalyst surface, likely due to its higher polarity and stronger hydrogen bonding capacity compare to alcohol (Suwannakarn *et al*., 2008). Thus, it is suggested that even a small amount of water present in the reaction mixture, the sulfate groups still could be leached out continuously depending on the contact time with water. In short, the catalyst deactivation process is due to the presence of water and alcohol in the reaction mixture and the degree of sulfur removal depends on the contact time with water and alcohol. Thus in this study, it was found that the limitation of SZA catalyst was its fast deactivation and pretretment is necessary to regenerate the catalyst and to enhance its performance on the yield of biodiesel.

Regenerating the spent catalyst is important in order to recycle, reactivate and reuse the catalyst. Regeneration of spent catalyst was carried out by washing with hexane and stirring with sulfuric acid follow by calcination after every reaction cycles. **Figure 4.26** shows that the performance of the regenerated catalyst was better than the results obtained for catalyst without pretreatment. The yield of biodiesel was maintained at an average of 87.1 wt% after the first cycle of regeneration. It may be due to the reforming of sulfated groups on the catalyst which plays the role as the active component for increasing the yield of biodiesel. Hence, pretreatment step was important to overcome the limitation of fast deactivation of the catalyst.

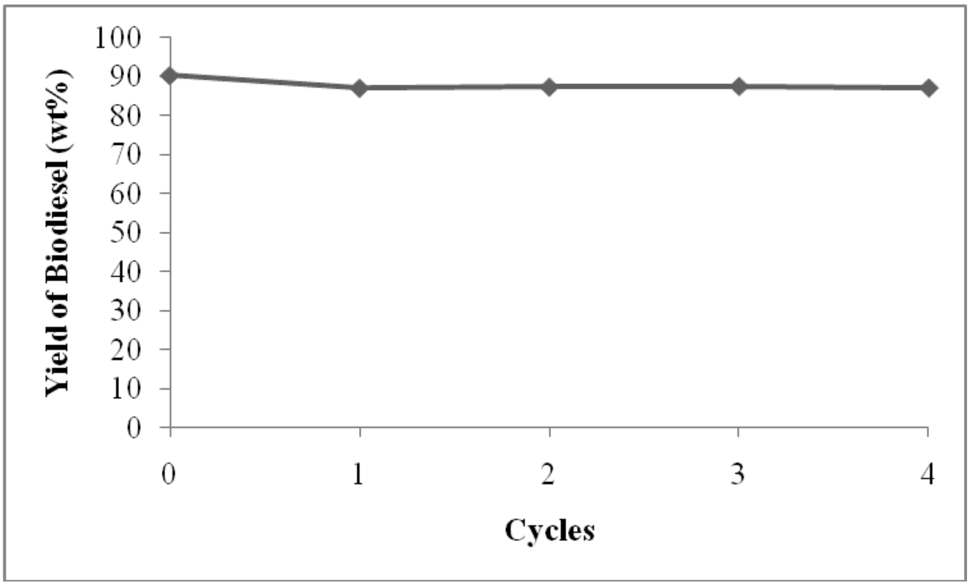


Figure 4.26: Effect of regeneration of sulfated zirconia alumina on yield of biodiesel (reaction temperature at 150 °C, reaction duration at 4 hours, molar ratio of methanol to oil at 9.88, catalyst loading at 7.61 wt%).

4.6 Characterization of Biodiesel

The properties of extracted *Jatropha curcas* L. oil, *Jatropha* biodiesel, conventional diesel and biodiesel standard are summarized in **Table 4.11**. It can be seen from this table that the property of *Jatropha curcas* L. oil was found to have values beyond the boundaries of normal range of biodiesel properties, especially acid value and kinematic viscosity, thus restricting its direct use as a fuel for diesel engines. The kinematic viscosity of the oil was found more than that of conventional diesel determined at 40 °C. However, after transesterification reaction, the acid value and kinematic viscosity of the oil decreased significantly.

On another note, the resulting flash point of *Jatropha* biodiesel was found much higher than those of conventional diesel which was greater than 100 °C leading to safer storage and handling (Amish, Subrahmanyam & Payal, 2009). Acid value for biodiesel is primarily an indicator for free fatty acid. Acid value higher than 0.8 mg KOH/g might cause deposition of FFA on fuel system leading to shorter fuel pumps and filters life span. Also, higher viscosity fuels can cause poor fuel combustion that leads to deposit formation. However, the properties of *Jatropha* biodiesel such as acid value, kinematic viscosity, flash point, specific gravity, water content and ash content had comparable fuel properties with those of conventional diesel and met the biodiesel standard of ASTM D6751 as shown in **Table 4.11**.

Table 4.11: Fuel properties of *Jatropha* biodiesel with ASTM D6751 standard.

Property	Unit	Extracted *Jatropha* oil	*Jatropha* biodiesel	Diesel	Biodiesel standards ASTM D 6751
Acid value	mg KOH g^{-1}	10.37	0.29	-	<0.80
Kinematic viscosity at 40 °C	$mm^2\ s^{-1}$	48.2	2.9	2.6	1.9- 6.0
Flash point	°C	60	140	68	>130
Specific gravity	g ml^{-1}	0.92	0.89	0.85	0.86- 0.90
Water content	%	0.05	0.01	0.02	<0.03
Ash content	%	0.09	0.01	0.01	<0.02

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, *Jatropha curcas* L. oil was successfully extracted from *Jatropha curcas* L. seed using soxhlet extraction with hexane and converted to biodiesel using sulfated zirconia loaded on alumina catalysts. The catalysts were synthesized using two different methods; direct sulfation of zirconia oxide method and solvent-free method. The characterization results revealed that the catalyst prepared by these two different methods had good crystalline structure with sufficient acidic sites required for the transesterification reaction.

However, the effects of calcination variables on the yield of biodiesel were different for both catalyst preparation methods. For the direct sulfation of zirconia oxide method, calcination temperature was found to have significant negative effect on the yield of biodiesel while calcination duration brings insignificant effect. On the other hand, for solvent- free method, calcination temperature shows quadratic effect on the yield of biodiesel while the yield of biodiesel was found to increase linearly with an increase in calcination duration. The different effect of calcination variables on the yield of biodiesel was due to the different acidic strength, chemical structure and behavior of the sulfated zirconia catalyst with different preparation methods.

Furthermore, the calcination variables for both catalyst preparation methods were then optimized in order to obtain the highest yield of biodiesel. The yield of biodiesel obtained for direct sulfation of zirconia oxide method (84.60 wt%) was slightly higher than that of solvent- free method (81.40 wt%). Apart from that, direct sulfation of zirconia oxide method require lower optimum calcination temperature (400 °C) compared to solvent- free method (490 °C) although both methods require similar optimum calcination duration (4 hours). This was again due to the different acidic strength of the sulfated groups that was formed with different catalyst preparation methods. Therefore, this led to different catalytic behaviors on the transesterification reaction.

The transesterification process variables were studied and optimized for sulfated zirconia loaded on alumina catalyst prepared using the direct sulfation of zirconia oxide method. The results revealed that reaction temperature have the greatest effect on the yield of biodiesel among the four process variables studied. Also, the interaction effect between the variables also showed significant effect on the yield of biodiesel. At the following conditions; 4 hours reaction duration at 150 °C, methanol to oil molar ratio of 9.88 mol/mol, 7.61 wt% for catalyst loading, an optimum biodiesel yield of 90.32 wt% was obtained.

The reusability and life span of the catalyst for the transesterification process were also studied and it was found that after recycling the catalyst for the first time, the yield of biodiesel decreased from 90.32 wt% to 74.57 wt%. The yields dropped further to 52.04 wt% in the second cycle, 32.07 wt% in the third cycle and 30.86

wt% in the fourth cycle. It was due to catalyst deactivation caused by leaching of sulfate compounds. However, the catalyst was successfully regenerated by re-sulfation method. The yield of biodiesel was maintained at an average of 87.1 wt% after the first cycle of regeneration.

Hence, in the present research work, it discovered that direct sulfation of zirconia oxide method was a simple catalyst preparation method which provide an easy route for synthesizing sulfated zirconia supported on alumina, but yet with high catalytic activity in the production of biodiesel from *Jatropha curcas* L. oil. Apart from that, the fuel properties of *Jatropha* biodiesel were characterized and it was found to meet the biodiesel standard of ASTM D6751. Hence, *Jatropha* biodiesel can be commercially used as biodiesel throughout the world.

5.2 Recommendations

This study has shown the potential of using *Jatropha curcas* L. oil as feedstock for the production of biodiesel catalyzed by sulfated zirconia loaded on alumina. Some recommendations have been made for further improvement of this project in the future.

1. Different types of heterogeneous acidic catalysts should be used for comparison study. Other types of heterogeneous acidic catalyst that could be

used in transesterification of *Jatropha curcas* L. oil include tungsten oxides, Amberlyst 115, Lewatit GF 101, Nafion 1 resins and organosulphonic functionalized mesoporous silicas.

2. More variables should be studied during catalyst preparation which includes the effect of catalyst particle size and the effect of sulfuric acid concentration on the yield of biodiesel. Apart from that, other various types of non-edible oil feedstocks should also be studied. *Cerbera odollam* oil (sea mango oil) could be one of the choices as this feedstock can be found in Malaysia.

3. The study to pro-long the life span of the SZA catalyst should be carried out in order to overcome the fast deactivation of the catalyst. The study could consists of a new or modified route on catalyst preparation which to synthesize catalyst with good acidic characteristics and high reusability.

4. Another possible route for the production of biodiesel is through reactive extraction or in situ esterification of *Jatropha curcas* L. seed. For this method, the reactants required are *Jatropha curcas* L. grounded seed, methanol and sulfuric acid. The mode of this study involves both oil extraction step and transesterification reaction step to occur simultaneously in a round bottom flask equipped with reflux system. Methanol acts as both extraction solvent and reaction reagent. This single step reactive reaction process has the potential to reduce processing steps and cost. However, the total experiment time for each run might become longer as it involves both oil extraction and reaction to occur simultaneously.

REFERENCES

Abdullah A. Z., Razali N. & Lee K. T. (2009) Optimization of mesoporous K/SBA-15 catalyzed transesterification of palm oil using response surface methodology. *Fuel Processing Technology*, 90, 958-964.

Achten W. M. J., Verchot L., Franken Y. J., Mathijs E., Singh V. P., Aerts R. & Muys B. (2008) Jatropha bio-diesel production and use. *Biomass and Bioenergy*, 32, 1063-1084.

Ahmed A. I., El-Hakam S. A., Samra S. E., EL-Khouly A. A. & Khder A. S. (2008) Structural Characterization of Sulfated Zirconia and Their Catalytic Activity in Dehydration of Ethanol, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 317, 62-70.

Ahn J., Kim Y., Lee Y., Seo E., Lee K., Kim H. (2008) Optimization of microencapsulation of seed oil by response surface methodology. Food Chemistry, 107, 98-105.

Amish P. V., Subrahmanyam N. & Payal A. P. (2009) Production of biodiesel through transesterification of jatropha oil using KNO_3/Al_2O_3 solid catalyst. *Fuel*, 88, 625-628.

Ardizzone, S., Bianchi, C.L., Cappelletti, G. & Porta, F. (2004) Liquid-phase catalytic activity of sulfated zirconia from sol-gel precursors: The role of the surface features. *Journal of Catalysis*. 227, 470-478.

Armendariz H., Coq B., Tichit D., Dutartre R. & Figueras F. (1997) Influence of some synthesis parameters and activation procedures on the one-step sol-gel synthesis of sulphated-zirconia catalysts, followed by TG-DSC and mass spectrometry, *Journal of Catalysis*, 173, 345-354.

ASTM. American Standards for Testing of Materials. St. Joseph, MI: ASAE; 2003.

Balusu R., Paduru R. R., Kuravi S. K., Seenayya G. & Reddy G. (2005) Optimization of critical medium components using response surface methodology for ethanol production from cellulosic biomass by Clostridium thermocellum SS19. *Process Biochemistry*, 40, 3025-3030.

Basiron Y. (2008) Global oils and fats, Business magazine, vol.5 issue 3 (july-sept).

Ben Hamouda L., Ghorbel A. & Figueras F. (2000) Study of acidic and catalytic properties of sulfated zirconia prepared by sol-gel process influence of preparation conditions. *Studies in Surface Science and Catalysis*, 130, 971-976.

Berchmans H. J. & Hirata S. (2008) Biodiesel production from crude jatropha curcas L. seed oil with a high content of free fatty acids. *Bioresource Technology*, 99, 1716-1721.

Binney T., Solano R. & Montero G. (March 31, 2005) Continuous washing of biodiesel.

Biodiesel 2020: Global Market Survey, Feedstock Trends and Forecasts, 2nd Edition, Multi- Client Study, 1-685, Emerging Market Online [Online], [Accessed 20th November 2009]. Available from world wide web:

http://www.emerging-markets.com/PDF/Biodiesel2020Study.pdf

Chen H. & Wang J. F. (2006) Biodiesel from transesterification of cottonseed oil by heterogeneous catalysis. *Studies in Surface Science and Catalysis*, 159, 153-156.

Comeli R. A., Vera C. R. & Parera J. M. (1995) Influence of ZrO_2 crystalline structure and sulfate ion concentration on the catalytic activity of SO_4^{2-}-ZrO_2. *Journal of Catalysis*, 151, 96-101.

Demirbas, A. (2005) Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science*, 31, 466-468.

De Oliveira, J. S., Leite, P. M., De Souza, L. B., Mello, V. M., Silva, E. C., Rubim, J. C., Meneghetti, S. M. P. & Suarez, P. A. Z. (2009) Characteristics and composition of Jatropha gossyypiifoliaand Jatropha curcas L. Oils and application for biodiesel production. *Biomass and Bioenergy*, 33, 449-453.

DIN EN 14214. European Standards for biodiesel 2003. [Online], [Accessed 2nd September 2009]. Available from world wide web:

http://www.din.de

Funamoto, T., T. Nakagawa & Segawa K. (2005) Isomerization of n-butane over sulfated zirconia catalyst under supercritical conditions. *Apply Catalysis A: General*, 286, 79-84.

Furuta S., Matsuhashi H. & Arata K. (2004) Biodiesel fuel production with solod superacid catalysis in fixed bed reactor under atmospheric pressure. *Catalysis Communications*, 5, 721-723.

Garcia, C. M., Teixeira S., Marciniuk L. L. & Schuchardt U. (2008) Transesterification of soybean oil catalyzed by sulfated zirconia. *Bioresource Technology*, 99, 6608-6613.

Georgogianni K. G., Katsoulidis A. K., Pomonis P. J., Manos G. & Kontominas M. G. (2009) Transesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis. *Fuel Processing Technology*, 90, 1016-1022.

Gubitz G. M., Mittelbech M. & Trabi M. (1999) Exploitation of tropical oil seed plant Jatropha curcas L.. *Bioresource Technology*, 67, 73-82.

Hameed B. H., Lai L. F. & Chin L. H. (2009) Production of biodiesel from palm oil (*Elaeis guineensis*) using heterogeneous catalyst: An optimized process. *Fuel Processing technology*, 90, 606-610.

Helwani Z., Othman M. R., Aziz N., Kim J. & Fernando W. J. N. (2009) Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. *Applied Catalysis A: General*, 363, 1-10.

Henning R. K. (2000) The jatropha booklet- a guide to the jatropha system and its dissemination in Zambia. First edition. Weissensberg: bagani GbR.

Iiies V., Daood H. G., Perneczki S., Szokonya L. & Then M. (1999) Extraction of coriander seed oil by CO_2 and propane at super- and subcritical conditions. *The Journal of Supercritical Fluids*, 17, 177-186.

Jitputti, J., Kitiyanan, B., Rangsunvigt, P., Bunyakiat, K., Attanatho, L. & Jenvanitpanjakul, P. (2006) Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. *Chemical Engineering Journal*, 116, 61-66.

Kansedo J., Lee K. T. & Bhatia S. (2009) Biodiesel production from palm oil via heterogeneous transesterification. *Biomass and Bioenergy,* 33, 271-276.

Kansedo J., Lee K. T. & Bhatia S. (2009) *Cerbera odollam* (sea mango) oil as a promising non-edible feedstock for biodiesel production. *Fuel*, 88, 1148-1150.

Kiss A. A., Dimian A. C., Rothenberg G. (2006) Solid acid catalysts for biodiesel production- towards sustainable energy. *Advanced Synthesis and Catalysis,* 348, 75-81.

Kumar A. & Sharma S. (2008) An evaluation of multipurpose oil seed crop for industrial uses (*Jatropha Curcas* L. oil): an review. *Industrial Crops and Products*, 28, 1-10.

Kwiecien J., Hajek, M. & Skopal, F. (2009). The effect of the acidity of rapeseed oil on its transesterification. *Bioresource technology,* 100, 5555-5559.

Li C. & Li M. (2002) UV raman spectroscopic study on the phase transformation of ZrO_2, Y_2O_3-ZrO_2 and $SO_4^{2-/}ZrO_2$. *Journal of Raman Spectroscopy,* 33, 301-308.

Li X., Nagaoka K., Simon L. J., Olindo R., Lercher J. A., Hofmann A., Sauer J. (2005) Oxidative activation of n-butane on sulfated zirconia. *Journal of the American Chemical Society*, 127, 16159-16166.

Li Y., Zhang X. D., Sun L., Zhang J. & Xu H. P. (2010) Fatty acid methyl ester synthesis catalyzed by solid superacid catalyst SO_4^{2-}/ZrO_2-TiO_2/La^{3+}. *Applied Energy*, 87, 156-159.

López, D.E., Goodwin JR., J.G., Bruce, D.A. & Lotero, E. (2005) Transesterification of triacetin with methanol on solid acid and base catalysts. *Applied Catalysis A: General*, 295, 97-105.

Lotero, E., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D. A. & Goodwin Jr., J. G. (2005) Synthesis of biodiesel via acid catalysis. *Industrial and Engineering Chemistry Research,* 44, 5353-5363.

Louli V., Folas G., Voutsas E. & Magoulas K. (2004) Extraction of parsley seed oil by supercritical CO_2. *The Journal of Supercritical Fluids*, 30, 163-174.

Lu H. F., Liu Y. Y. Zhou H., Yang Y., Chen M. Y. & Liang B. (2009) Production of biodiesel from jatropha *curcas* L. oil. *Computers and chemical engineering*, 33, 1091-1096.

Lukic I., Krstic J., Jovanovic D. & Skala D. (2009) Alumina/ silica supported K_2CO_3 as a catalyst for biodiesel synthesis from sunflower oil. Bioresource Technology, 100, 4690- 4696.

Machmudah S., Kondo M., Sasaki M., Goto M., Munemasa J. & Yamagata M. (2008) Pressure effect in supercritical CO_2 extraction of plant seeds. *The Journal of Supercritical Fluids*, 44, 301-307.

Matsuhashi, H., D. Sato & Arata K. (2004) Influence of calcination temperature on the surface acidity of the solid superacid of sulfated alumina. *Reaction Kinetics and Catalysis Letters,* 81, 183-188.

Marcela L. M., Miguel A. M. & Damian M. M. (2008) Pressing and supercritical carbon dioxide extraction of walnut oil. *Journal of food engineering*, 88, 399-404.

Mekhemer G. A. H. (2006) Surface characterization of zirconia, holmium oxide/zirconia and sulfated zirconia catalysts. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 274, 211-218.

Melada S., Ardizzone S. A. & Bianchi C. L. (2004) Sulfated zirconia by sol-gel route. The effects of the preparative variables. *Microporous and Mesoporous Materials*, 73, 203-209.

Miao X., Li R. & Yao H. (2009) Effective acid-catalyzed transesterification for biodiesel production. *Energy Conversion and Management*, 50, 2680-2684.

Molero G. A. & Martinez de la Ossa E. (2002) Quality of borage seed oil extracted by liquid and supercritical carbon dioxide. *Chemical Engineering Journal*, 88, 103-109.

Mondala A., Liang K., Togniani H., Hernandez R. & French T. (2009) Biodiesel production by in situ transesterification of municipal primary and secondary sludges. *Bioresource Technology*, 100, 1203-1210.

Montgomery D. C. (2001) Design and Analysis of Experiments, 5th edition. New York, USA, John Wiley and Sons.

Monterra C., Cerrato G. & Signoretto M. (1996) On the role of the calcinations step in the preparation of active (superacid) sulfated zirconia catalysts. *Catalysis Letters*, 41, 101-109.

Nabi Md. N., Rahman Md. M. & Akhter Md. S. (2009) Biodiesel from cotton seed oil and its effect on engine performance and exhaust emissions. *Applied Thermal Engineering*, 29, 2265- 2270.

National biodiesel board. (2004) [Online], [Accessed 2nd September 2009]. Available from world wide web:

http://www.biodiesel.org/pdf_files/back-grounder.PDF;2004.

Ni, J. & Meunier, F.C.(2007) Esterification of free fatty acids in sunflower oil over solid acid catalysts using batch and fixed bed-reactors. *Applied Catalysis A: General*, 333, 122-130.

Niederl-Schmidinger, A. & Narodoslawsky, M. (2008) Life Cycle Assessment as an engineer's tool?. *Journal of Cleaner Production*, 16, 245-252.

Noiroj K., Intarapong P., Luengnaruemitchai A., Jai-in S. (2009) A comparative study of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. *Renewable Energy*, 34, 1145-1150.

Openshaw K. (2000) A Review of Jatropha Curcas: An Oil Plant of Unfulfilled Promise. *Biomass and Bioenergy*, 19, 1-15.

Prescott H. A., Wloka M. & Kemnitz E. (2004) Supported sulfated zirconia catalysts and their properties. *Journal of Molecular Catalysis A: Chemical*, 223, 67-74.

Qian J., Wang F., Liu S. & Yun Z. (2008) In situ alkaline transesterification of cottonseed oil for production of biodiesel and nontoxic cottonseed meal. *Bioresource Technology*, 99, 9009-9012.

Reddy B. M. & Patil M. K. (2009) Organic syntheses and transformation catalyzed by sulfated zirconia. *Chemical Reviews*, 109, 2185- 2208.

Reddy B. M., Sreekanth P. M. & Reddy V. R. (2005) Modified Zirconia Solid Acid Catalysts for Organic Synthesis and Transformations, *Journal of Molecular Catalysis A: Chemical*, 225, 71-78.

Renewable Energy Policy Network for the 21st Century (2008) Renewables 2007 Global Status Report, 1-54.

Selvi J. T. & Rajan R. (2008) Biofuel production from cotton seed oil. *Ecology, Environment and Conservation*, 14, 699- 701.

Shafiee S. & Topal E. (2009) When will fossil fuel reserves be diminished? *Energy Policy*, 37, 181-189.

Shu Q., Yang B., Yuan H., Qing S. & Zhu G. (2007) Synthesis of biodiesel from soybean oil and methanol catalyzed by zeolite beta modified with La^{3+}. *Catalysis Communication*, 8, 2159-2165.

Shu Q., Zhang Q., Xu G., Nawaz Z., Wang D. & Wang J. (2009) Synthesis of biodiesel from cottonseed oil and methanol using a carbon-based solid acid catalyst. *Fuel Processing Technology*, 90, 1002-1008.

Srinivasan, R., Keogh, R. A., Milburn, D. R. & Davis, B. H. (1995) Sulfated zirconia catalysis: Characterization by TGA/ DTA Mass Spectrometry. *Journal of Catalysis*, 153, 123-130.

Stat-Ease (2002) Version 6.0.6. User's Guide, Design Expert Software, Inc., Minneapolis, USA.

Sun, Y., Ma, S., Du, Y., Yuan, L., Wang, S., Yang, J., Deng, F. & Xiao, F. (2005) Solvent-free preparation of nanosized sulfated zirconia with brønsted acidic sites from a simple calcination. *Journal of Physical Chemistry B*, 109, 2567-2572.

Suppes G. J., Dasari M. A., Doskocil E. J., Mankidy P. J. & Goff M. J. (2004) Transesterification of soybean oil with zeolite and metal catalysts. *Applied Catalysis A: General*, 257, 213-223.

Suwannakarn, K., Lotero, E., Goodwin JR., J.G. & Lu, C. (2008) Stability of sulfated zirconia and the nature of the catalytically active species in the transesterification of triglycerides. *Journal of Catalysis*, 255, 279-286.

Takeda Y. (1982) Development study on jatropha curcas (sabu dum) oil as a substitute for diesel engine oil in Thailand. Interim report of the Ministry of Agricultural, Thailand.

The Energy Report, Chapter 14 Biodiesel (2008), [Online], [Accessed 3rd September 2009]. Available from World Wide Web:

http://www.window.state.tx.us/specialrpt/energy/pdf/14-Biodiesel.pdf

Tichit D., El Alami D. & Figueras F. (1996) Influence of the preparation and of the activation treatments on the catalytic activity of mechanical mixtures of sulfated zirconia and Pt/ Al_2O_3. *Journal of Catalysis*, 163, 18- 27.

Tiwari K. A., Kumar A. & Raheman H. (2007) Biodiesel production from jatropha oil (jatropha curcas) with high free fatty acids: an optimized process. *Biomass and Bioenergy*, 31, 569-575.

Tobin J. and Fulford D. J. (2005) Life cycle assessment of the production of biodiesel from jatropha. MSc dissertation, The University of Reading.

Vera, C. R., Pieck, C. L., Shimizu, K. & Parera, J. M. (2002) Tetragonal structure, anionic vacancies and catalytic activity of SO_4^{2-}-ZrO_2 catalysts for n- butane isomerization. *Applied Catalysis A: General*, 230, 137-151.

Vicente G., Martinez M. & Aracil J. (2004) Integrated Biodiesel Production: A Comparison of Different Homogeneous Catalysts Systems. *Bioresource Technology*, 92, 297-305.

Warabi, Y., Kusdiana, D. & Saka, S. (2004) Reactive of triglycerides and fatty acids of rapeseed oil in supercritical alcohols. *Bioresource Technology*, 91, 283-287.

Ward D. A. & Ko E. I. (1994) One-step synthesis and characterization of zirconia-sulfate aerogels as solid superacids. *Journal of catalysis*, 150, 18-33.

Westerman D., Santos R. C. D., Bosley J. A., Rogers J. S. & Al-Duri B. (2006) Extraction of amaranth seed oil by supercritical carbon dioxide. *The Journal of Supercritical Fluids*, 37, 38-52.

Worldwatch Institute, Biofuels For Transportation (2006), [Online], [Accessed 3rd September 2009]. Available from World Wide Web:

http://www.worldwatch.org/system/files/EBF038.pdf

Xie W., Huang X. & Li H. (2007) Soybean Oil Methyl Esters Preparation Using NaX Zeolites Loaded with KOH as a Heterogeneous Catalyst. *Bioresource Technology*, 98, 936-939.

Xie W., Peng H. & Chen L. (2006) Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst. *Applied Catalysis A: General*, 300, 67-74.

Yuan X., Liu J., Zeng G., Shi J., Tong J. & Huang G. (2008) Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology. *Renewable Energy*, 33, 1678-1684.

Zabeti M., Wan Daud W. M. A. & Aroua M. K. (2009) Activity of solid catalysts for biodiesel production: A review. *Fuel Processing Technology*, 90, 770-777.

Zaidul I. S. M., Norulaini N. A. N., Omar A. K. M. & Smith Jr. R. L. (2007) Supercritical carbon dioxide (SC-CO_2) extraction of palm kernel oil from palm kernel. *Journal of Food Engineering*, 79, 1007-1014.

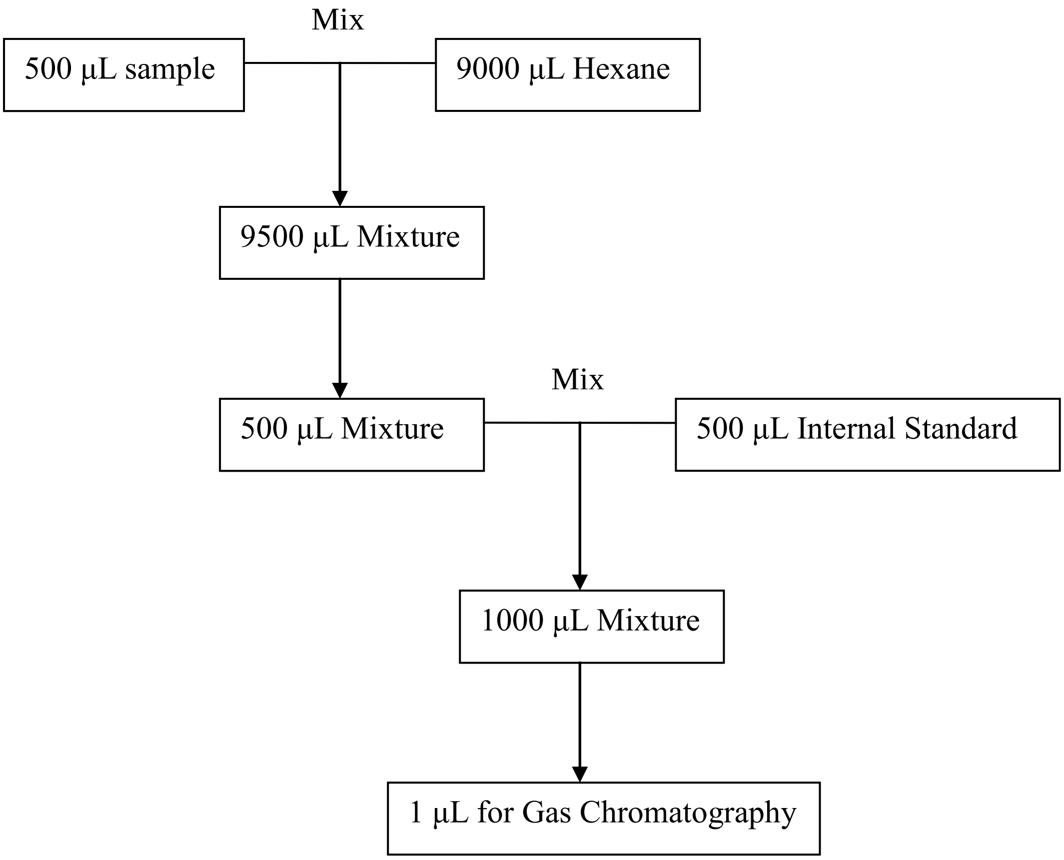
Zhang W., Liu S., Yin F., Guan H., Li J., Gao X. & Mao Y. (2006) Technology for production of biodiesel through the transesterification reaction of rapeseed oil. *Nongye Gongcheng Xuebao/ Transactions of the Chinese Society of Agricultural Engineering*, 22, 131- 134.

Zhao, J., Yue, Y., Hua, W., He, H. & Gao, Z. (2008). Catalytic activities and properties of sulfated zirconia supported on mesostructured γ-Al2O3. *Applied Catalysis A: General*, 336, 133-139.

APPENDICES

APPENDIX A

CALCULATION OF DILUTION FACTOR



Dilution Factor, DF = Dilution with Hexane x Dilution with Internal Standard

$$= \frac{9500\ \mu\text{L}}{500\ \mu\text{L}} x \frac{1000\ \mu\text{L}}{500\ \mu\text{L}}$$

$$= 19 \text{ x } 2$$

$$= 38$$

APPENDIX B

SULFURIC ACID PREPARATION

$$\mathbf{ZrO_2 + 2\ H_2SO_4 \rightarrow Zr(SO_4)_2 + 2H_2O} \quad \text{(B.1)}$$

Basis : For 1 sample, 8g of ZrO_2 used

Number of Mole for 8g of ZrO_2 = $\frac{1\,\text{mole}}{123.22\,\text{g ZrO}_2}\,x\,8\,\text{g} = 0.0649\,\text{mole ZrO}_2$

From Stoichiometry, 1 mole of ZrO_2 reacted with 2 mole of H_2SO_4

Thus, 0.0649 mole of ZrO_2 reacted with (0.0649 x 2 = 0.1298) mole of H_2SO_4

Weight of H_2SO_4 = $\frac{98.08\,\text{g}}{\text{mole}}\,x\,0.1298\,\text{mole} = 12.7307\,\text{g}$

For 2.5 M of H_2SO_4, Weight of H_2SO_4 = $\frac{2.5\,\text{mole}}{1000\,\text{cm}^3}\,x\,\frac{98.08\,\text{g}}{\text{mole}} = 0.2452\,\text{g/cm}^3$

Thus, Volume of H_2SO_4 needed = $\frac{1\,\text{cm}^3}{0.2452\,\text{g}}\,x\,12.7307\,\text{g} = 51.9197\,\text{cm}^3$

APPENDIX C

CALCULATION OF BIODIESEL YIELD

$$Yield\ of\ Biodiesel = \frac{\sum Weight\ of\ Fatty\ Acid\ Methyl\ Esters\ (g)}{Weight\ of\ Jatropha\ Oil\ used\ (g)} \times 100\%$$ From (3.3)

In order to calculate the total weight of methyl esters, area under each peaks of the results from Gas Chromatograph are needed. For example, the result of run 18 from the transesterification process study is used in the sample of calculation.

(A) Calculate ratio area for each of the standard reference methyl esters.

$$Ratio\ Reference, R_f = \frac{Peak\ Area\ of\ Methyl\ Esters\ in\ Reference}{Peak\ Area\ of\ Internal\ Standard\ in\ Reference} \tag{C.1}$$

Table C.1: Ratio area for each of standard reference methyl esters.

Fatty Acid Methyl Ester	Molecular Weight (g/mole)	Ratio, R_f	Concentration (mg/mL)
Methyl Palmitate	270.45	0.891384761	1.00
Methyl Stearate	298.50	0.986604560	1.00
Methyl Oleate	296.49	0.983110062	1.00
Methyl Linoleate	294.47	0.558205670	1.00
Internal Standard		1.000000000	

(B) Calculate ratio area for each of methyl esters of the samples

$$Ratio\ Sample, R_s = \frac{Peak\ Area\ of\ Methyl\ Esters\ in\ sample}{Peak\ Area\ of\ Internal\ Standard\ in\ sample} \qquad (C.2)$$

Table C.2: Ratio area for each of sample methyl esters.

Fatty Acid Methyl Ester	Molecular Weight (g/mole)	Area	Ratio, R_s
Methyl Palmitate	270.45	1082469.92	2.42393458
Methyl Stearate	298.50	477254.63	1.06869852
Methyl Oleate	296.49	3066123.88	6.86585703
Methyl Linoleate	294.47	2688206.89	6.01960159
Internal Standard		446575.55	1.00000000

(C) Calculate yield for each of the methyl esters

$$Weight\ of\ Methyl\ Esters\ (g) = \frac{R_s}{R_f} \times C_{IS} \times V \times DF \qquad \text{From (3.2)}$$

Dilution Factor, DF = 38

Volume of *Jatropha* Oil used, V = 40 mL

Concentration of internal standard used, C_{IS} = 1 mg/ml

Thus, for Methyl Palmitate:

$$\text{Weight of Methyl Palmitate} = \frac{2.42393458}{0.891384761}\ x\ 38 \text{ x } 40 \text{ mL x } \frac{1\,\text{mg}}{\text{mL}}$$

$$= 4133.3224 \text{ mg}$$

$$= 4.13332236 \text{ g}$$

Table C.3: Weight of each methyl esters.

Fatty Acid Methyl Ester	Weight (g)
Methyl Palmitate	4.13332236
Methyl Stearate	1.64647704
Methyl Oleate	10.6153961
Methyl Linoleate	16.3914394
Total Weight	32.7866349

Total Weight = 4.13332236 + 1.64647704 + 10.6153961 + 16.3914394

= 32.7866349 g

(D) Calculate % yield of biodiesel

$$Yield\ of\ Biodiesel = \frac{\sum Weight\ of\ Fatty\ Acid\ Methyl\ Esters\ (g)}{Weight\ of\ Jatropha\ Oil\ used\ (g)} \times 100\% \qquad \text{From (3.3)}$$

$$= \frac{32.7866349\ \text{g}}{36.88\ \text{g}} x100\%$$

= 88.90 %

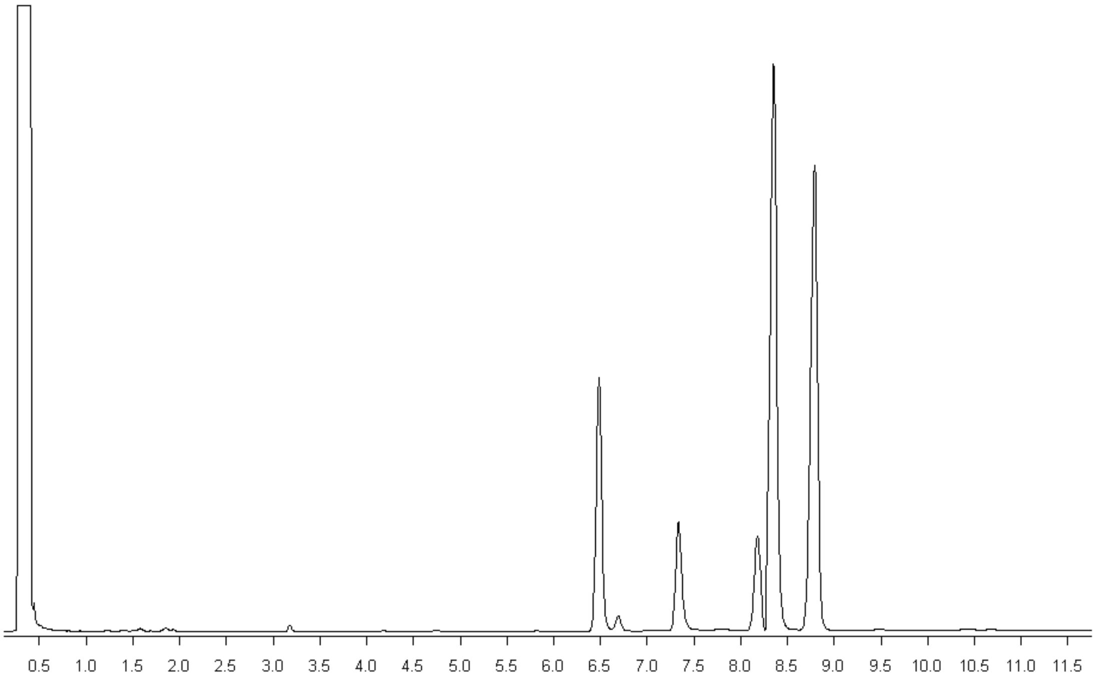


Figure C.1: A typical GC chromatogram for biodiesel sample.

Table C.4: Retention time for each methyl ester peak in GC chromatogram.

Retention time	Type of fatty acid methyl esters
6.49	Methyl palmitate
7.34	Methyl heptadecanoate (as internal standard)
8.19	Methyl stearate
8.36	Methyl oleate
8.80	Methyl linoleate

APPENDIX D

METHANOL VAPOR PRESSURE FOR ANTOINE'S EQUATION

$$Log\ P = A - \frac{B}{C + T} \tag{D.1}$$

Where A = 7.9701, B = 1521.23, C = 234 (valid for temperature range from 65°C to 214°C). Unit for Pressure, P in mmHg, Temperature, T in °C.

Table D.1: Methanol vapor pressure according to operating temperature.

Temperature (°C)	**Pressure (bar)**
60	0.8332
70	1.2330
80	1.7796
90	2.5110
100	3.4707
110	4.7078
120	6.2769
130	8.2376
140	10.6547
150	13.5977
160	17.1400
170	21.3590
180	26.3350
190	32.1511
200	38.8923

LIST OF PUBLICATIONS

Journals:

Yee, K. F., Tan, K. T., Abdullah A. Z. & Lee, K. T. (2009) Life cycle assessment of palm biodiesel: revealing facts and benefits for sustainability. *Applied Energy*, 86, S189-S196.

Yee, K. F., Kansedo J. & Lee, K. T. (2009) Optimization of biodiesel production from palm oil. *Chemical Engineering Communications*, 197 (12).

Conference:

Yee K. F. & Lee K. T. (2008) Palm oil as feedstocks for biodiesel production via heterogeneous transesterification: optimization study. International Conference on Environment 2008 (ICENV 2008), Penang, Malaysia.