PRODUCTION OF BIODIESEL THROUGH TRANSESTERIFICATION OF SUNFLOWER OIL USING $SiO_2/50\%H_2SO_4$ SOLID ACIDIC CATALYST

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A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
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APRIL 2010

ABSTRACT

A renewable fuel such as biodiesel, with lesser exhaust emissions, is the need of the day. Hence, researchers and scientific community worldwide have focused on development of biodiesel and the optimization of the processes to meet the standards and specifications needed for the fuel to be used commercially without compromising on the durability of engine parts. Based on the intricacies associated with the homogeneously catalyzed transesterification process, the purpose of the present work is to study biodiesel production by transesterification of sunflower oil with methanol in a heterogeneous system, using silica gel loaded with sulfuric acid ($SiO_2/50\%H_2SO_4$) as a solid acidic catalyst. The catalyst prepared by loading of 50 v/v% H_2SO_4 on silica gel followed by drying it at 110°C. The catalysts were characterized by FTIR, TGA and SEM. The reaction between sunflower oil and methanol is carried out in a 3-necked round bottom flask heated by a rotamantle. The sample is withdrawn at certain time interval and is analyzed using gas chromatography. The dependence of the conversion of sunflower oil on the reaction variables such as the molar ratio of methanol to oil, reaction temperature and catalyst loading was studied. The catalyst has exhibited maximum oil conversion (84wt.%) under the conditions of 100°C, methanol/oil molar ratio of 6:1 and catalyst amount 10%. Kinetic study of reaction was also done. The experimental data is well fitted to the Pseudo-homogeneous model. This optimum operating condition and kinetic model are very important for producing biodiesel fuel effectively in a larger scale.

ABSTRAK

Pada masa kini, bahan bakar yang terbaru seperti biodiesel yang mempunyai pembebasan gas buangan yang lebih rendah diperlukan. Oleh itu, penyelidik and komuniti saintifik dunia telah tertumpu pada pembangunan biodiesel dengan mengoptimumkan proses untuk memenuhi piawaian dan spesifikasi yang diperlukan untuk bahan bakar yang akan digunakan secara komersial tanpa mengganggu jangka hayat sesuatu bahagian mesin. Berdasarkan perkara-perkara yang berkaitan dengan proses pengtransesterifikasi permangkin berhomogen, tujuan kerja ini adalah untuk mempelajari penghasilan biodiesel melalui transesterifikasi minyak bunga matahari dengan methanol di dalam system heterogen dengan menggunakan silika gel yang diisi dengan asid sulfuric ($SiO_2/50\%H_2SO_4$) sebagai pemangkin asid pejal. Pemangkin disediakan dengan menambahkan 50 v/v% H_2SO_4 ke dalam silika gel dan seterusnya dikeringkan pada suhu 110ºC. Ciri-ciri pemangkin telah dianalisa dengan menggunakan FTIR, TGA dan SEM. Tindak balas antara minyak bunga matahari dan methanol telah dilakukan di dalam kelalang bulat berleher-3 yang dipanaskan dengan menggunkan rotamantle. Bahan ujikaji dikeluarkan pada masa tertentu dan dianalisis menggunakan kromatografi gas. Penghubungan antara penukaran minyak bunga matahari terhadap parameter tindak balas telah dipelajari. Pemangkin ini telah menghasilkan penukaran minyak yang maksimum (84 wt%) dibawah keadaan 100ºC dan kadar molar methanol/minyak adalah 6:1 dan loading mangkin 10%. Pelajaran kinetik tindak balas juga telah dibuat. Data eksperimental juga sesuai dengan model Pseudo-homogeneouse. Keadaan operasi yang optimum ini dan model kinetic adalah paling penting dalam penghasilan bahan bakar biodiesel yang effektif di dalam skala yang lebih besar.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

B100 - Pure Biodiesl

HSA - High Surface Area

FAME - Fatty acid methyl esters

GC - Gas chromatography

SEM - Scanning Electron Microscopy

TGA - Thermogravimetric Analyses

FT-IR - Fourier Transform Infrared Spectroscopy

SSA - Silica sulfuric acid

LIST OF SYMBOLS

$-r_A = -\frac{dC_A}{dt}$	-	The consumption of reactant A per unit time
k’	-	Rate constant
C_A	-	Concentration of A after time t
C_B	-	Concentration of B after time t
	-	Reaction order of reactant A
	-	Reaction order of reactant B
C_{AO}	-	Initial concentration of A
C_{BO}	-	Initial concentration of B
X	-	Conversion
θ_B	-	Ratio of C_{BO} to C_{AO}
A	-	Pre-exponential factor or frequency factor
E	-	Activation energy
R	-	Gas constant
T	-	Absolute temperature

CHAPTER 1

INTRODUCTION

The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). The status of present consumption of crude oil is about 79 million barrels per day. The tremendous increasing need of oil, which is predicted to be about 119 million barrels per day by 2020's and the shortage of oil thereafter (after 10-15 years), predicted based on the total reserves in hand, urgently to focus the research in finding alternative means to fulfill world's energy needs. The alternative sources of new and renewable energy such as hydro, biomass, wind, solar, geothermal, hydrogen and nuclear is of vital importance. Alternative new and renewable fuels have the potential to solve many of the current social problems and concerns, from air pollution and global warming to other environmental improvements and sustainability issues (Mackenzie, 2008).

Among liquid biofuels, biodiesel derived from vegetable oils is gaining acceptance and market share as Diesel fuel in Europe and the United States. Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources (Hanna, 1999). The development of energy efficient biofuel production technologies in aiming at reducing the reagent costs and increasing the production efficiency is becoming important in a world that is increasingly becoming “green”.

There are more than 350 oil-bearing crops identified, researchers have been led in using different sources of vegetable oil such as peanut, rapeseed, corn, soybean or sunflower seed because there are considered as potential alternative fuels for diesel engines. Table 1.1 shows the oil species that can be used in biodiesel production. Vegetable oil is one of the renewable fuels and potentially inexhaustible sources of energy with an energetic content close to diesel fuel.

Table 1.1: Oil species for biodiesel production (Ayhan, 2009)

Group	**Source of oil**
Major oils	Coconut (copra), corn (maize), cottonseed, canola (a variety of rape seed), olive, peanut (groundnut), safflower, sesame, soybean, and sunflower.
Nut oils	Almond, cashew, hazelnut, macadamia, pecan, pistachio and walnut.
Other edible oils	Amaranth, apricot, argan, artichoke, avocado, babassu, baylaurel, beechnut, ben, Borneotallownut, carobpod(algaroba), cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit(Acrocomia sclerocarpa), meadow foam seed, mustard, okra seed(hibiscus seed), perilla seed, pequi (Caryocar brasiliensis seed), pinenut, poppy seed, prune kernel, quinoa, ramtil(Guizotia abyssinica seed or Niger pea), rice bran, tallow, tea(camellia), thistle(Silybum marianum seed), and wheat germ.
Inedible oils	Algae, babassu tree, copaiba, honge, jatropha or ratanjyote, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, and tall.
Other oils	Castor and radish

The vegetable oil fuels were not acceptable because they were more expensive than petroleum fuels. However, with recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines (Demirbas, 2003). The use of vegetable oils as alternative renewable fuel competing with petroleum was proposed in the beginning of 1980s. The advantages of vegetable oils as diesel fuel are:

- Liquid nature-portability
- Ready availability
- Renewability
- Higher heat content (about 88% of no. 2 diesel fuel)
- Lower sulfur content
- Lower aromatic content
- Biodegradability

The disadvantages of vegetable oils as diesel fuel are:

- Higher viscosity
- Lower volatility
- The reactivity of unsaturated hydrocarbon chains

The major problem associated with the use of pure vegetable oils as fuels, for diesel engines are caused by high fuel viscosity in compression ignition. Diesel boiling range material is of particular interest because it has been shown to significantly reduce particulate emissions relative to petroleum diesel (Giannelos, 2002).

1.1 Biodiesel history

Transesterification of triglycerides are in oils is not a new process. Scientists E. Duffy and J. Patrick conducted it as early as 1853. Life for the diesel engine began in 1893 when the famous German inventor Rudolph Diesel published a paper entitled *‘The theory and construction of a rational heat engine’*. What the paper described was a revolutionary engine in which air would be compressed by a piston to a very high pressure thereby causing a high temperature. Dr. Rudolph Diesel designed the original diesel engine to run on vegetable oil. Dr. Rudolph Diesel used peanut oils to fuel on of this his engines at the Paris Exposition of 1900 (Nitschke, 1965). Because of high temperature created, the engine was able to run a variety of vegetable oils including hemp and peanut oil. At the 1911 World’s Fair in Paris, Dr. Rudolph Diesel ran his engine on peanut oils and declared ‘the diesel engine can be fed with vegetable oils and will help considerably in the development of the agriculture of the countries which use it. One of the first uses of transesterified vegetable oil was powering heavy-duty vehicles in South Africa before World War II. The name ‘biodiesel’ has been given to transesterified vegetable oil to describe its use as a diesel fuel (Demirbas, 2002).

1.2 Properties of biodiesel fuels

Biodiesels are characterized by their viscosity, density, cetane number, cloud and pour points, distillation range, flash point, ash content, sulfur content, carbon residue, copper corrosion, and higher heating value (HHV). The most important parameters affecting the ester yield during the trainsesterification reaction are the molar ratio of alcohol to vegetable oil and reaction temperature. The viscosity values of vegetable oil methyl esters decrease sharply after transesterification. Compared to D2 fuel, all of the vegetable oil methyl esters are slightly viscous. The flash point values of vegetable oil methyl esters are significantly lower than those of vegetable oils. There is high regression between the density and viscosity values of vegetable oil methyl esters. The relationships between viscosity and flash point for vegetable oil methyl esters are considerably regular. These parameters are all specified through the biodiesel standard, ASTMD 6751. This standard identifies the parameters the pure biodiesel (B100) must meet before being used as a pure fuel or being blended with petroleum-based diesel fuel. Biodiesel, B100, specifications (ASTMD6751–02requirements) are given in Table 1.2.

Table 1.2: Biodiesel, B100, specifications (ASTMD6751–02requirements) (Ayhan. 2009)

Property	**Method**	**Limits**	**Units**
Flash point	D 93	130 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity at 40 °C	D 445	1.9- 6.0	mm²/s
Sulfated ash	D 874	0.020 max	wt%
Total sulful	D 5453	0.05 max	wt%
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report	°C
Carbon residue	D 4530	0.050 max	wt%
Acid number	D 664	0.80 max	mg KOH/g
Free glycerine	D 6584	0.020	wt%
Total glycerine	D 6584	0.240	wt%
Phosphorus	D 4951	0.0010	wt%
Vacuum distillation end point	D 1160	360°C max, at 90°C distilled	°C

1.2.1 Composition of biodiesel

Biodiesel is mixture of fatty acid alkyl esters. If methanol is used as a reactant, it will be a mixture of fatty acid methyl esters (FAME). Based on the feed stock, biodiesel has different proportions of fatty acid methyl esters. Table 1.3 shows the chemical composition of common fatty acids and their methyl esters present in the biodiesel.

Table 1.3: Chemical structures of common fatty acid and their methyl esters

Fatty acid/ Formula/ Molecular weight	**Common acronym**	**Methyl ester/ Formula/ Molecular weight**
Palmitic acid/ $C_{16}H_{32}0_2$/ 256.428	C16:0	Methyl Palmitate/ $C_{17}H_{34}0_2$/ 270.457
Stearic acid/ $C_{18}H_{36}0_2$/ 284.481	C18:0	Methyl Stearate/ $C_{19}H_{38}0_2$/ 298.511
Oleic acid/ $C_{18}H_{34}0_2$/ 282.465	C18:1	Methyl Oleate/ $C_{19}H_{36}0_2$/ 296.495
Linoleic acid/ $C_{18}H_{32}0_2$/ 280.450	C18:2	Methyl Linoleate/ $C_{19}H_{34}0_2$/ 294.479
Linolenic acid/ $C_{18}H_{30}0_2$/ 278.434	C18:3	Methyl Linolenate/ $C_{19}H_{24}0_2$/ 292.463

1.3 The use of vegetable oils and their derivatives as alternative diesel fuels

Problems appear only after the engine has been operating on vegetable oils for longer periods of time, especially with direct-injection engines. Due to their high viscosity and low volatility, the direct use of vegetable oils in fuel engines is problematic. The problems are:

(a) Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices.
(b) Carbon deposits
(c) Oil ring sticking
(d) Thickening and gelling of the lubricating oil as result of contamination by the vegetable oils (Hanna, 1999).

Different ways have been considered to reduce the high viscosity of vegetable oils:

(a) Dilution of 25 parts of vegetable oil with 75 parts of diesel fuel,
(b) Microemulsions with short chain alcohols such as ethanol or methanol,
(c) Thermal decomposition, which produces alkanes, alkenes, carboxylic acids and aromatic compounds,
(d) Catalytic cracking, which produces alkanes, cycloakanes and alkybenzenes, and
(e) Transesterification with ethanol or methanol.

Dilution of oils with solvents and microemulsions of vegetable oils lowers the viscosity, some engine performance problems, such as injector coking and more carbon deposits still exist. At present, the most common way to produce biodiesel is to transesterification of vegetable oil or animal fats with an alcohol in the presence of an alkali or acid catalyst. Among all these alternatives, the transesterification seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of those of diesel fuel and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation.

1.3.1 Composition of oils

Fats and oils are primarily water-insoluble hydrophobic substances of plant and animal origin and are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides. Fatty acids vary in carbon chain length and in the number of unsaturated bonds. The fatty acids found in vegetable oils are summarized in Table 1.4. Natural vegetable oils and animal fats are solvent extracted or mechanically pressed to obtain crude oil or fat. These usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Even refined oils and fats contain small amounts of free fatty acids and water. The free fatty acid and water contents have significant effects on the transesterification of glycerides with alcohols using alkaline or acid catalysts. They also interfere with the separation of fatty acid alkyl esters and glycerol because of salt formation in the product.

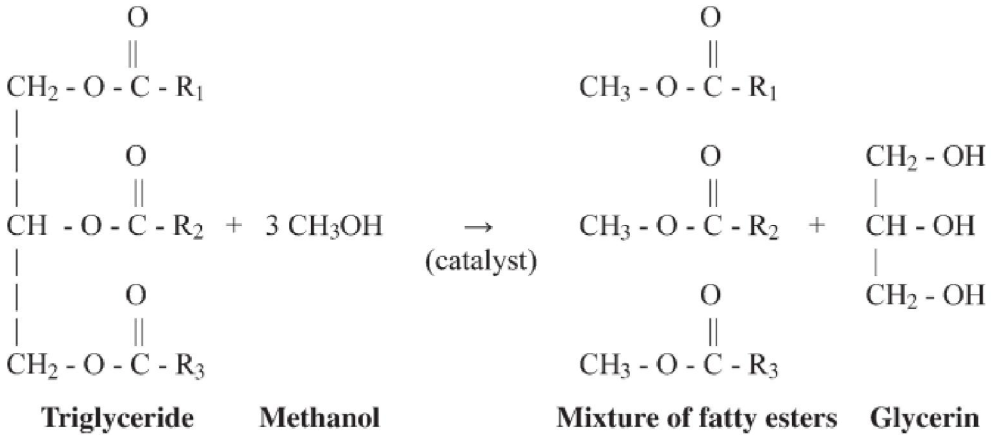
Table 1.4 Fatty acid compositions of vegetable oil samples (Gunstone, 2007)

Vegetable Oil	**16:0**	**18:0**	**18:1**	**18:2**	**18:3**	**Other**
Sunflower oil	7.0±0.2	3.5±0.1	33.3±0.6	55.2±0.4	0.00	1.0±0.1
Rapeseed	4	2	56	26	10	2
Soybean oil	11	4	33	53	8	2
Palm oil	44	4	40	10	0	2
Values are means± SD of triplicate determinations.						

1.4 Transesterification

The main component of sunflower oil is besides small amounts of stearic acid (1-7%), palmitic acid (4-9%), oleic acid (14-40%) and linoleic acid (48-74%). The demand of renewable combustible derived from vegetable oils increased and has led to the development of oils with methanol and ethanol, involving acidic and base catalysis. More recently, several solid acid catalysts, including H_2SO_4/SiO_2 employed in the organic synthesis are found as efficient and reusable catalysts.

Biodiesel is produced through a process known as transesterification, as shown in the equation below,



Where R1, R2, and R3 are long hydrocarbon chains, sometimes called fatty acid chains. There are only five chains that are most common in soybean oil and animal fats (others are present in small amounts).

Transesterification means taking a triglyceride molecule or a complex fatty acid, neutralizing the free fatty acids, removing the glycerin, and creating an alcohol ester. Theoretically, transesterification reaction is an equilibrium reaction. In this reaction, however, more amount of methanol was used to shift the reaction equilibrium to the right side and produce more methyl esters as the proposed product. A catalyst is usually used to improve the reaction rate and yield.

Alcohols are primary or secondary monohydric aliphatic alcohols having 1-8 carbon atoms. Among the alcohols that can be used in the transesterification reaction are methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are used most frequently; ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment. However methanol is preferable because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol).

In the conventional transesterification of vegetable oils for biodiesel production, free fatty acids and water always produce negative effects, since the presence of free fatty acids and water causes soap formation, consumes catalyst and reduces catalyst effectiveness, all of which resulting in a low conversion (Formo, 1997).

1.4.1 Homogeneous catalysts for transesterification

1.4.1 (a) Alkaline catalysis

Alkaline or basic catalysis is by far the most commonly used reaction type for biodiesel production. The main advantage of this form of catalysis over acid-catalyzed transesterifications is high conversion under mild conditions in comparatively short reaction times (Freedman, 1998). It was estimated that under the same temperature conditions and catalyst concentrations methanolysis might proceed about 4000 times faster in the presence of an alkaline catalyst than in the presence of the same amount of an acidic equivalent (Formo, 1997). Moreover, alkaline catalysts are less corrosive to industrial equipment, and thus enable the use of less expensive carbon-steel reactor material. The main drawback of the technology is the sensitivity of alkaline catalysts to free fatty acids contained in the feedstock material. Therefore alkali-catalyzed transesterifications optimally work with high-quality, low-acidic vegetable oils, which are however more expensive than waste oils. If low-cost materials, such as waste fats with a high amount of free fatty acids, are to be processed by alkaline catalysis, deacidification or preesterification steps are required.

Today most of the commercial biodiesel production plants are utilizing homogeneous, alkaline catalysts. Traditionally the alkoxide anion required for the reaction is produced either by using directly sodium or potassium methoxide or by dissolving sodium or potassium hydroxide in methanol. The advantage of using sodium or potassium methoxide is the fact that no additional water is formed and therefore side reactions like saponification can be avoided. The use of the cheaper catalysts sodium or potassium hydroxide leads to the formation of methanolate and water, which can lead to increased amounts of soaps. However, because of the fact that glycerol separates during alcoholysis reactions, also water is removed out of the equilibrium, so under controlled reaction conditions, saponification can be kept to a minimum.

The amount of alkaline catalyst depends on the quality of the oil, especially on the content of free fatty acids. Under alkaline catalysis free fatty acids are immediately converted into soaps, which can prevent the separation of glycerol and finally can lead to total saponification of all fatty acid material. So the alkaline catalysis is limited to feedstock up to a content of approx. 3 % of fatty acids. There are also other alkaline catalysts like guanidines or anion exchange resins described in literature, however, no commercial application in production plants is known so far. Table 1.5 shows the overview of homogenous alkaline catalysts.

Table 1.5: Overview of homogenous alkaline catalysts (Mustafa, 2010).

Type of Catalyst	**Comments**
Sodium hydroxide	Cheap, disposal of residual salts necessary
Potassium hydroxide	Reuse as fertilizer possible, fast reaction rate, better separation of glycerol
Sodium methoxide	No dissolution of catalyst necessary, disposal of salts necessary.
Potassium methoxide	No dissolution of catalyst necessary, use as fertilizer possible, better separation of glycerol, higher price.