Optimization of biodiesel production of fatty acid esterification using ion exchange resins

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To my beloved mother

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ABSTRACT

Due to energy crisis by depletion of fossil fuel and environmental concerns about air pollution caused by the combustion of fossil fuels, the search for alternative fuels has gained much attention. Biodiesel as a valuable alternative to petroleum-derived fuels is a renewable fuel of vegetal origin. Biodiesel is an oxygenated, renewable, biodegradable and environmentally friendly biofuel with similar flow and combustion properties and low emission profile. However, it is impractical to use refined edible oils to produce biodiesel due to its high cost and priority for food products, while waste oils with high free fatty acids (FFAs) can be considered as the raw materials. The esterification reaction of acid oils or fats can then be used both as biodiesel direct production (in the case of substrates with very high content of FFAs) and as pre-treatment step in the framework of a conventional transesterification process (for feedstock with moderate free acidity).

In this study optimization of esterification process of free fatty acids (FFA) in waste cooking oil with methanol in the presence of ion exchange resin is carried out. The esterification reaction was investigated in a Batch laboratory scale and effects of catalyst amount, temperature were studied. The model is optimized in order to maximize conversion of fatty acid to Methyl ester (biodiesel). The optimal conditions achieved at reaction temperature of 120□C and 4.48 g catalyst loading. All programming was employed in Matlab environment.

ABSTRAK

Oleh kerana krisis tenaga yang disebebkan oleh kehabisan bahan api fosil di samping juga pertimbangan terhadap pencemaran udara yang diakibatkan oleh pembakaran bahan api fosil, kajian terhadap bahan api alternatif telah menerima banyak perhatian. Biodiesel sebagai bahan api bernilai tinggi daripada tumbuh-tumbuhan adalah alternatif kepada petroleum yang boleh diperbaharui. Biodiesel adalah bahan api beroksigen, boleh diperbaharui, terbiodegradasikan dan tidak mencemarkan alam sekitar mempunyai aliran dan keadaan pembakaran yang lebih kurang sama dengan bahan api fosil dan juga profil pengurangan pengepulan. Tetapi, adalah tidak praktis dengan menggunakan minyak gred makan yang bertapis untuk menyediakan biodiesel disebabkan kos yang tinggi dan bertanding dengan keperluan makanan, manakala, minyak sisa dengan kandungan fatty asid yang tinggi boleh dipertimbangkan sebagai bahan ramuan. Tindak balas esterifikasi lemak dan minyak berasid boleh digunakan untuk penyediaan biodiesel (jika sampel mempunyai nilai fatty asid yang tinggi) dan sebagai rawatan awal untuk proses transesterifikasi (sampel dengan kandungan asid yang sederhana).

Dalam kajian ini, pengoptimuman proses esterifikasi yang melibatkan fatty asid dalam minyak masak sisa dengan menggunakan metanol dengan kehadiran resin penukaran ion telah dijalankan. Tindak balas esterifikasi telah dikaji secara sekumpulan dengan skala makmal dan kesan amaun mangkin, suhu telah dikaji. Pengoptimuman model adalah untuk memaksimumkan pertukaran metil ester (biodiesel). Keadaan optimum telah tercapai pada suhu tindak balas 120^{o}C dan kemasukan 4.48 gm mangkin. Pemprograman adalah dijalankan dengan menggunakan Matlab.

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LIST OF SYMBOLS

k , k_{-1}	-	Reaction constant of the forward and the reverse uncatalyzed reaction (cm^6 mol^{-2} min^{-1})
k^{ref}	-	Kinetic constant at a reference temperature
k_{cat}^{ref} , k_{-cat}^{ref}	-	Kinetic constants of the forward and the reverse reaction at a reference temperature (cm^3 gcat^{-1} min^{-1})
r_{un}	-	Rate of uncatalyzed reaction (mol min^{-1} cm^{-3})
r_{cat}	-	Rate of catalyzed reaction (mol min^{-1} gcat^{-1})
C_i	-	Liquid phase bulk concentrations(mol cm^{-3})
E_A	-	Activation energy (kcal/mol)
T^{ref}	-	Reference temperature (373.16 K)
T	-	Temperature (K)
R	-	Universal gas constant (kcal mol^{-1} K^{-1})
A	-	Pre-exponential factor (cm^6 mol^{-2} min^{-1})
b_i	-	Adsorption equilibrium constant ($cm^3 mol^{-1}$)
v_i	-	Stoichiometric coefficient
V_L	-	Reaction volume (cm^3)
W_{cat}	-	Mass of the catalyst (g)
n_i	-	Number of moles of the component (mole)
n	-	Number of components in a mixture
t	-	Time (min)
ρ_i	-	Density of the components (g cm^{-3})
ρ_n	-	Density of the mixture (g cm^{-3})
X_i	-	Mass fraction of component in a mixture

$\bar{X}$	-	Average of initial amount of components
w_i	-	Mass fraction of component in a mixture
m_i	-	Mass of component (g)
m_{tot}	-	Total mass of mixture (g)
x_i	-	Reaction temperature of experimental data (K)
y_i	-	Oleic acid Conversion % of experimental data
x'_i	-	Reaction temperature of predicted data (K)
y'_i	-	Oleic acid Conversion % of predicted data

LIST OF ABBREVIATIONS

WCO	-	Waste cooking oil
FAME	-	Fatty acid methyl ester
FFA	-	Free fatty acid
A	-	Oleic acid
M	-	Methanol
E	-	Ester
W	-	Water
TG	-	Triglyceride
DG	-	Diglyceride
MG	-	Monoglyceride
G		Glyceride
ANOVA		Analysis of variance
RMS		Root mean square
RSM		Response Surface Methodology

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CHAPTER 1

INTRODUCTION

1.1 Background

Biofuel is any fuel that is produced from biomass. Thus it could be from animal fat or vegetable oil. It is a renewable energy source, unlike other natural resources such as petroleum, coal and nuclear fuels.

Agricultural products specifically grown for use as biofuels include corn and soybeans, mainly in the United States, and flaxseed and rapeseed, primarily in Europe. Waste from industry, agriculture, forestry, and households can also be used to produce bioenergy; examples include straw, lumber, manure, sewage, garbage and food leftovers. Most biofuel is burned to release its stored chemical energy (Castor Oil, 2006)

The interest in biofuels production as among the most promising alternative to petroleum-based oil and natural gas has been rapidly growing in the last years. The carbon in biofuels was recently derived from atmospheric carbon dioxide through photosynthesis of plant, so burning it does not result in a net increase of carbon dioxide in the Earth's atmosphere. Biofuels consider as a way to lessen the amount of carbon dioxide released into the atmosphere by using them to replace non-renewable sources of energy.

Biofuel appears as a potential alternative to energy source. This renewable resource is also environmental friendly due to none of sulfur and nitrogen content. Biofuels appear in liquid form so it is easy to be handled and transported. Vegetable oils contain triglycerides of long chain fatty acids and glycerol, which are the best choice to obtain hydrocarbons fuel (Maher & Bressler, 2007). Thus, different vegetable oils such as palm oil, soybean oil, coconut and rapeseed oil are brake into smaller hydrocarbons in order to reduce their viscosity.

Biodiesel which is standardized as mono-alkyl ester in the United States refers to any diesel-equivalent biofuel made from the oil and methanol. It is usually produced by transesterification and esterification reaction of vegetable or waste oil respectively with a low molecular weight alcohol, such as ethanol and methanol. During this process, the triglyceride molecule from vegetable oil is removed in the form of glycerin (soap). Once the glycerin is removed from the oil, the remaining molecules are, to a diesel engine, somewhat similar to those of petroleum diesel fuel (CastorOil, 2006).

The concept of using vegetable oil as a fuel dates back to 1895 when Dr. Rudolf Diesel developed the first diesel engine to run on vegetable oil (Shay, 1993). Diesel demonstrated his engine at the World Exhibition in Paris in 1900 using peanut oil as fuel. Bio-diesel can be used in diesel engines either as a standalone or blended with petro diesel. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix. For example, fuel containing 20% biodiesel is labeled B20. Pure biodiesel is referred to as B100 (CastorOil, 2006).

In 1930s and 1940s vegetable oils were used as diesel fuels from time to time, but usually only in emergency situations. Recently, because of increases in crude oil prices, dwindling resources of fossil oil, steady increase in energy consumption and environmental concerns there has been a renewed focus on vegetable oils and animal fats to make biodiesel fuels. Continued and increasing use of petroleum will magnify environmental impacts such as local air pollution and global warming (Shay, 1993)**.**

The two common following methods have been reported to convert oil sources to biodiesel:

1) Thermal cracking (pyrolysis)

Pyrolysis is the degradation of one substance into another by means of heat or by heat with the aid of a catalyst in the absence of air or oxygen (Demirbas, 2003).

The equipment for thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produced some low value materials and, sometimes, more gasoline than diesel fuel (Ma & Hanna, 1999)

2) Transesterification

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl eters (i.e., biodiesel) and glycerol (Wang, Ou, & Zhang, 2007). Triacylglycerols, as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters or FAME). Glycerol is produced as a by-product. Methanol is the most commonly used alcohol because of its low cost and is the alcohol of choice in the processes. In general, a large excess of methanol is used to shift the equilibrium far to the right (Zhang, Dubé, McLean, & Kates, 2003) (Fig. 1.1).

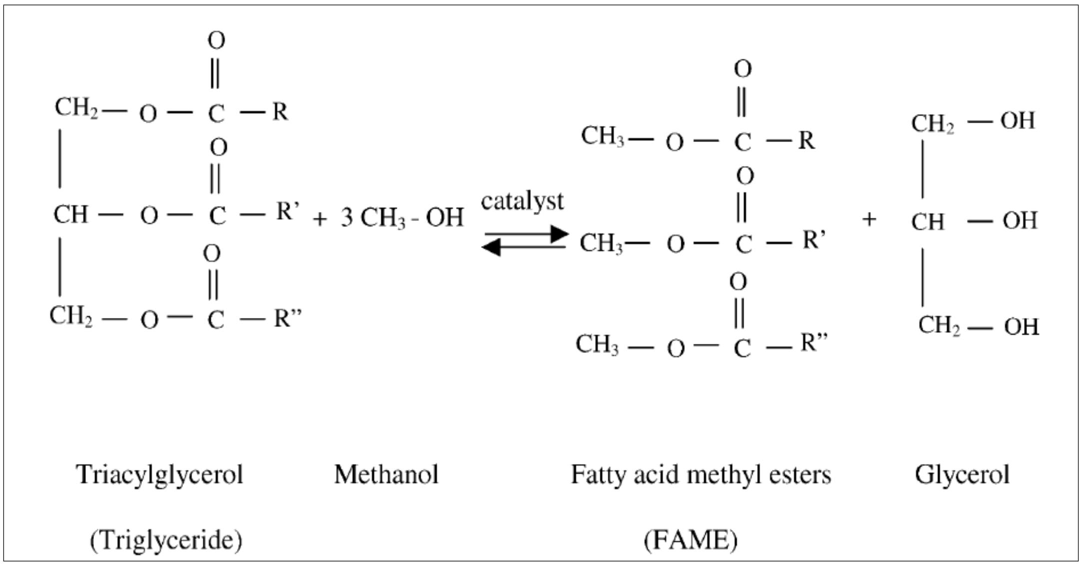

Fig.1.1. A schematic of the transesterification of triglycerides (vegetable oil) with methanol to produce fatty acid methyl esters (biodiesel) (Zhang, et al., 2003).

A lot of advantages of biodiesel make it a good alternative to petroleum based fuel and have led to its use in many countries, especially in environmentally sensitive areas. However, the raw material costs and limited availability of vegetable oil feedstocks due to the requirement of large land for plantation always hinder to foster market competitiveness for biodiesel. The relatively high cost of vegetable oils affect up to 75% of the total manufacturing cost, resulted in the production costs of biodiesel becoming approximately 1.5 times higher than that for diesel. A possible solution to this drawback could be using waste cooking oils (WCO) which its price is 2–3 times cheaper than virgin vegetable oils. Consequently, the total manufacturing cost of biodiesel can be significantly reduced. (Phan & Phan, 2008).

Besides low price, using WCO as feedstock for producing biodiesel has some benefits such as solving the disposal problem that causes environmental impacts as well as producing significant quantity of fuel. Therefore, biodiesel from WCO (or used frying oils) has been recently investigated.

In producing biodiesel, waste cooking oil cannot be treated in the conventional process for their high content in free fatty acids This viewpoint shows how we can develop innovative biodiesel production processes such as the two-stage process (esterification and transesterification. The esterification reaction of acid oils or fats can then be used both as biodiesel direct production (in the case of substrates with very high content of FFAs) and as pre-treatment step in the framework of a conventional transesterification process (for feedstock with moderate free acidity) (Tesser, Casale, Verde, Di Serio, & Santacesaria, 2009). The generic esterification reaction of a carboxylic acid with methanol, producing methylester and water, is schematically shown below:

$$\text{RCOOH (A)} + \text{CH3OH (M)} \rightleftharpoons \text{RCOOCH3 (E)} + \text{H2O (W)} \qquad (1)$$

It is clear that producing biodiesel from WCO can cover all advantages of a biofuel discussed before and solve the economical obstacles. Therefore, it is supposed that in the future, the industrial scale of such units absorb the attention of the investors. In order to scale up and commercializing the production process, optimization of the kinetic model is required which are scarce in the literature. In this research according to the available kinetic model in the literature, it is tried to satiate the mentioned problem and to develop an optimization to predict the optimum operational condition due to maximizing the conversion of waste cooking oil to biodiesel.

1.2 Problem statement

Converting vegetable oils to biodiesel is very well known for its benefits especially with regards to low sulfur and low carbonaceous emission fuel. But from economically point, using of waste cooking oil instead of vegetable oil is more attractive. However, there is still no optimization study concerning kinetic model in the literature which is important for scale-up and commercialization purposes. All optimization are carried out base of response surface methodology. Because a model is an abstraction, modeling allows us to avoid repetitive experimentation and measurements and subsequently optimization of a kinetic model allows us to have a better understanding of optimal operational condition in order to maximize conversion and yield of products.

1.3 Objectives

The objective of this study is to optimize a kinetic-based model for biodiesel production from artificially acidified soybean with oleic acid which is simulation of waste cooking oil contains high free fatty acid. The optimization process should be able to predict the best operational conditions based on maximum conversion of acid oil to biodiesel.

1.4 Scope of Study

i. Validation of model with experimental data according to comparison between the model output and the experimental data. To do so, ANOVA methods were applied.
ii. Development of an optimization program using Matlab optimization toolbox to find out best operational condition according to maximize conversion of fatty acid. The complete process is programmed and simulated in MATLAB R2010a.

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