SIMULATION OF BIODIESEL PRODUCTION THROUGH HETEROGENEOUSLY CATALYSED TRANSESTERIFICATION OF VEGETABLE OIL BY CALCIUM ETHOXIDE

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ABSTRACT

Biodiesel is a clean burning alternative fuel, produced from domestic, renewable resources such as plant oils, animal fats, used cooking oil and even new sources such as algae. Biodiesel is also defined as fuel which has the same characteristics with commercial diesel in terms of its molecular formula. The transesterification reaction can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base, or enzymatic) catalyst. Homogeneous catalysts provide much faster reaction rates than heterogeneous catalysts, but it is considerably more costly to separate homogenous catalysts from the reaction mixture (Liu et al., 2008). Therefore, heterogeneously base catalysts are studied in this research. The objective of this study is to find the feasibility of new type of heterogeneous catalyst in determining the best operating parameters and design factors which affecting the performance of biodiesel production. Aspen Plus 12.1 is used to performed the simulation study for feasibility of the biodiesel production using heterogeneous catalyst through a plug flow reactor (PFR). The simulation was done by incorporating the reaction kinetics and thermodynamics model into the reactor model. The NRTL of thermodynamics model is used in this research in order to perform the separation process for two liquid phases in the transesterification of vegetable oil process. The simulation was run after all the important property data had been incorporated into Aspen Plus simulator. After running all the operating parameters, it shows that the best temperature is 65 ^{0}C, the best molar ratio of methanol to oil is 6:1, the best mass ratio of catalyst to oil is 3% and the best space velocity is 0.25 hr^{-1} on oil conversion and biodiesel yield percentage. The PFR reactor schemes which are in single PFR, two PFR in series and PFR to CSTR were proposed as a suitable scheme for the production of biodiesel. Hence that, at the optimum operating condition, the conversion is 91.5%.

ABSTRAK

Biodiesel adalah pembakaran bahan bakar alternatif yang bersih, yang dihasilkan dari dalam negeri, sumber terbaru seperti minyak tanaman, lemak haiwan, minyak masakan yang telah diguna serta sumber-sumber baru seperti rumpai. Biodiesel juga ditakrifkan sebagai bahan api yang memiliki ciri-ciri yang sama dengan diesel komersil dalam kajian formula molekulnya. Transesterifikasi tindak balas boleh dilaksanakan menggunakan kedua – dua homogen (asas atau berasid) dan heterogen (asid, asas atau berenzim) sebagai pemangkin. Mangkin homogeny menyediakan kadar reaksi lebih cepat daripada mangkin heterogen, tetapi ia sangat lebih mahal untuk memisah mangkin seragam daripada campuran tindak balas (Liu et al., 2008). Maka, mangkin heterogen dikaji dalam penyelidikan ini. Tujuan kajian ini adalah untuk mencari jenis keupayaan baru bagi mangkin heterogen dalam menentukan operasi parameter yang terbaik dan faktor yang mempengaruhi prestasi penghasilan biodiesel. Simulasi di Aspen Plus 12.1 digunakan untuk mengkaji keupayaan keputusan pengeluaran biodiesel dengan menggunakan mangkin heterogen melalui reaktor aliran plug (PFR). Simulasi dilakukan dengan memasukkan kinetika reaksi dan model termodinamik ke dalam reaktor model. Simulasi ini dijalankan selepas semua data penting dimasukkan ke dalam simulator Aspen Plus 12.1. Setelah semua parameter operasi dijalankan, simulasi menunjukkan bahawa pengaruh terbaik dari suhu adalah 65 ^{0}C, nisbah molar metanol terbaik untuk minyak adalah 6:1, nisbah jisim mangkin terbaik untuk minyak adalah 3% dan kelajuan ruangan terbaik adalah 0.25 hr-1 pada penukaran minyak dan peratusan penghasilan biodiesel. Susunan reaktor PFR iaitu dalam susunan satu reaktor, susunan dua reaktor dan susunan reaktor PFR kepada CSTR dicadangkan sebagai skim yang tepat dalam reaktor yang berterusan. Maka bahawasanya, keadaan optimum penukaran adalah 91.5%.

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ρb	-	Bulk Density
CSTR	-	Continuous Stirred Tank Reactor
^{o}C	-	Degree Celsius
K	-	Degree Kelvin
ρ	-	Density
hr	-	Hour
kmol	-	Kilo Mole
kg	-	Kilogram
m	-	Meter
MW	-	Molecular Weight
PFR	-	Plug Flow Reactor
P	-	Pressure
τ	-	Retention Time
s	-	Second
SV	-	Space Velocity
T	-	Temperature
Ø	-	Void Fraction

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CHAPTER 1

INTRODUCTION

1.1 Biodiesel

Biodiesel is a clean burning alternative fuel, produced from domestic, renewable resources such as plant oils, animal fats, used cooking oil and even new sources such as algae. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. Biodiesel blends can be used in most compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics.

Biodiesel is methyl or ethyl ester of fatty acid made from virgin or used vegetable oils (both edible and non-edible) and animal fats. Since edible oils are in short supply, the main raw materials for manufacture of biodiesel can be non-edible oils obtained from plant species such as *Jatropha cucas, Pongamia Pinnata, Calophyllum inophyllum, Hevca brasiliensis* and etc. Just like petroleum diesel, biodiesel operates in compression ignition (diesel) engine, which essentially require very little or no engine modifications because biodiesel has properties similar to petroleum diesel fuels. It can be stored just like the petroleum diesel and hence does not require separate handling or storage infrastructure. (Demirhas, 2001)

The use of biodiesel in conventional diesel engines results in substantial reduction of unburnt hydrocarbons, carbon monoxide and particulate matters. Biodiesel is considered clean fuel since it has almost no sulphur, no aromatics and has about 10% built-in oxygen, which helps it to burn fully. Its higher cetane number improves the ignition quality even when blended in the petroleum diesel. (Demirhas, 2001)

There are several methods to produce biofuels from renewable sources and among the earliest is based on pyrolysis process whereby heavy molecules such as vegetable oils or animal fats are converted to smaller one by means of heat or heat and catalyst. The fuel obtained through this process was called “diesel-like fuels” since there were variety of components such as olefins and paraffin which are similar to the petroleum-based diesel. However, this process requires high temperatures between 300 and 500 °C and products characterization is difficult due to the variety of reaction products. Biodiesel can also be produced by a variety of esterification technologies but transesterification is one of the most commercially useable methods to produce biodiesel. (Demirhas, 2001)

1.1.1 Transesterification

Transesterification also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis. This process has been widely used to reduce the viscosity of triglycerides. It is the reaction of vegetable oil or animal fat with an alcohol to form esters and glycerol. A catalyst is used to improve the reaction rate and yield. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side. Alcohols are the primary and secondary monohydric aliphatic compounds having 1–8 carbon atoms. Methanol and ethanol are used most frequently in the transesterification process. Methanol is preferred because of its lower cost and its physical and chemical advantages (polar and shortest chain alcohol) over ethanol. Fatty acid methyl esters are known as the sources of biodiesel, which is synthesized by the direct transesterification of vegetable oils with a short-chain alcohol in the presence of a catalyst.

1.1.2 Type of Catalyst

Biodiesel is composed of long-chain fatty acids with an alcohol attached, often derived from vegetable oils. It is produced through the reaction of a vegetable oil with methyl alcohol or ethyl alcohol in the presence of a catalyst. Animal fats are another potential source. Commonly used catalysts are potassium hydroxide (KOH) or sodium hydroxide (NaOH).

Nowadays, the transesterification reaction can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base, or enzymatic) catalysts. Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts, but it is considerably more costly to separate homogeneous catalysts from the reaction mixture.

Heterogeneous catalysis has many advantages, such as being noncorrosive, being environmentally benign, and presenting fewer disposal problems. These catalysts are also much easier to separate from liquid products, and they can be designed to give a higher activity and selectivity and to have longer catalyst lifetimes. Many types of heterogeneous catalysts, such as alkaline earth metal oxides, anion exchange resins, and various alkali metal compounds supported on alumina or zeolite, can catalyze many types of chemical reactions, such as isomerization, aldol condensation, Knoevenagel condensation, Michael condensation, oxidation, and transesterification. In transesterification of vegetable oils to biodiesel, most supported alkali catalysts and anion exchange resins exhibit a short catalyst lifetime because the active ingredients are easily corroded by methanol. (Masoud, 2009)

From the commercial point of view, solid base catalysts are seen more effective than acid catalysts and enzymes. However, more researches on solid base catalysis are needed to substantiate this because the favorable results from previously reported works were at the expense of high temperatures and high pressures. From the economic standpoint, it would be ideal if solid base catalysts could work efficiently at temperatures below 150 ^{0}C and low pressure. On the other hand, solid acid catalysts, enzymes and non-catalytic supercritical transesterification have been largely ignored in biodiesel research due to pessimistic expectations in terms of reaction rates, undesirable side reactions and high costs. (Masoud, 2009)

1.1.3 Simulation

Simulation is the imitation of some real thing, state of affairs, or process. The act of simulating something generally entails representing certain key characteristics or behaviours of a selected physical or abstract system.

Simulation is used in many contexts, including the modeling of natural systems or human systems in order to gain insight into their functioning. Other context includes simulation of technology for performance optimization, safety engineering, testing, training and education. Simulation can be used to show the eventual real effects of alternative conditions and courses of action.

In a chemical engineering prospect, there is a flow sheet of simulation which is use of a computer program to quantitatively model the characteristic equations of a chemical process. Simulation uses underlying physical relationship with mass and energy balance, equilibrium relationship and rate correlations (reaction and mass/heat transfer). Therefore, it will help engineer to predict stream flow rates, compositions and properties also the operating conditions.

Simulation has many advantages, such as reduces plant design time which allows designer to quickly test various plant configurations. These simulations also helps engineer to improve current process which determines the optimal process conditions within given constrain and assist in locating the constraining parts of a process (debottlenecking).

1.1.4 Kinetic Model

A homogenous reaction is one that involves only one phase. A heterogeneous reaction involves more than one phase, and the reaction usually occurs at the interface between the phases. An irreversible reaction is one that proceeds in only one direction and continues in that reaction until the reactants are exhausted. A reversible reaction, on the other hand, can proceed in either direction, depending on the concentrations of reactants and products relative to the corresponding equilibrium concentrations. An irreversible reaction behaves as if no equilibrium condition exists.

There are several types of kinetic model such as pseudo homogeneous, Langmuir- Hinshelwood equation and Eley-Rideal equation. Langmuir derived a relationship for q and C based on some quite reasonable assumptions. These are: a uniform surface, a single layer of adsorbed material, and constant temperature. The rate of attachment to the surface should be proportional to a driving force times an area. The driving force is the concentration in the fluid, and the area is the amount of bare surface. (Liang, 2006)

1.1.5 Thermodynamics Model

Proper selection of thermodynamic models during process simulation is absolutely necessary as a starting point for accurate process simulation. A process that is otherwise fully optimized in terms of equipment selection, configuration, and operation can be rendered essentially worthless if the process simulation is based on inaccurate thermodynamic models. Because of this, good heuristics and appropriate priority should be placed on both selecting thermodynamic models and reporting the selections in process reports. Simulation generally differs from hand calculations in two ways:

i. The simulator allows use of more sophisticated models without significantly expending more of the engineer’s time.

ii. Simulations in chemical engineering typically involve VLE (vapor-liquid equilibrium) where the ideal gas EOS (equation of state) is inaccurate.

Productivity is rarely diminished by selecting rigorous thermodynamic models as compared to models that make for easy calculations, and so, criteria for selecting thermodynamic models during simulation are based primarily on accuracy and not the optimal combination of accuracy and effort. However, acquiring accurate binary interaction coefficients or data still fall within the realm of increasing accuracy at the expense of increased effort.

During process simulation, thermodynamic model selection should be performed in at least two steps. Firstly, as with initial process configurations, the thermodynamic model should be chosen based on heuristics (heuristics) that provide for a good base case but may or may not provide the desired level of accuracy. Secondly, based on the results of the base case simulation (complete with cost estimate), improving the accuracy of the thermodynamic models should be prioritized relative to optimizing other design parameters such as the configuration of unit operations, optimization of specific unit operations, heat integration, and other degrees of freedom used to optimize processes. Optimization includes both economic and simulation accuracy aspects. Thermodynamic model definition should be revisited as often as necessary during process optimization.

Therefore, thermodynamic modeling including the selection of the best models for use with process simulation is a recognized topic is chemical engineering that is held in the same regard as process simulation. However, richness and complexity of the phase equilibrium topic should not prevent engineers from using heuristics as a starting point for tapping into the ability of powerful simulation packages.

1.2 Background of Research and Problem Statement

Fatty acid methyl esters are known as the sources of biodiesel, which is synthesized by the direct transesterification of vegetable oils with a short-chain alcohol in the presence of a catalyst. The transesterification reaction can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base, or enzymatic) catalyst. Homogeneous catalysts provide much faster reaction rates than heterogeneous catalysts, but it is considerably more costly to separate homogenous catalysts from the reaction mixture (Liu et al., 2008). Therefore, heterogeneously base catalysts are studied in this research.

Biodiesel is renewable fuel that can be used to power up the conventional diesel engines with little or no modifications. Biodiesel is composed of mono-alkyl esters of fatty acid chain from animal fat or vegetable oils. Waste vegetable oil will reduce the cost of biodiesel production, and will give the world a way to reuse the total production cost of biodiesel results from the cost raw materials. The price of biodiesel is much higher compare to conventional diesel makes it is less chosen by the customer.

The sensitivity of oil palm price resulted in instability of oil palm price. The higher price of crude petroleum oil will shift the market trend favorable towards the palm oil. Thus, the high market demand of palm oil makes the prices more volatile. Even though the price of palm oil is much cheaper than crude petroleum oil, the Malaysia government gives subsidized to petroleum oil in transportation sector resulted in lower prices compare to biodiesel. The main reason of high prices in production of biodiesel is because of its raw material. Thus, using vegetable oil as raw material will make the biodiesel price more comparable than subsidized petroleum diesel. The availability, cost and continuity are the main criteria for good raw material. The easy the availability of vegetable oil and continuity of supply make it as a good choice of raw material.

In recent years, most existing plants currently rely upon the use of a homogeneous catalyst in a continuous reactor system, using the transesterification of soybean or rapeseed oil with methanol into alkyl esters. Diglycerides and monoglycerides are the intermediate in this process, and glycerol is a major byproduct. To generate the experimental data, continuous reactor pilot plant should be build first. However, to build a pilot plant, the feasibility and operating parameters need to be studied so that a suitable configuration can be proposed to build the continuous reactor for heterogeneously catalysed process.

In fact, the previous study by Liu et al., (2009) has done to determine the influence of important operating and design factor of batch reactor for transesterification of vegetable oil with methanol to produce methyl esters by using sodium hydroxide as catalyst. Hence, the simulations need to be performed in order to attain the result for feasibility of the biodiesel production using heterogeneous catalyst through a continuous reactor. The simulation was done by incorporating the reaction kinetics and thermodynamics model in the reactor model.

1.3 Objectives of Study

The specific objectives of this study are:

i. To evaluate the feasibility of producing biodiesel using new type of heterogeneous catalyst.
ii. To determine the operating parameters and design factors which affecting the performance of biodiesel production using the new catalyst.
iii. To propose a suitable schemes for the continuous reactor.

1.4 Scope of Study

This research is a simulation study for the production of biodiesel using vegetable oil as the raw material. In order to realize the research objective, two scopes has been identified to be studied in this simulation.

i. To setup base case simulation in continuous reactor by using the existing reaction kinetics for heterogeneous catalyst and thermodynamic model in the ASPEN Plus 12.1.
ii. To determine the important parameters of heterogeneous catalyst by studying the effect of temperature, molar ratio of methanol to oil, mass ratio of catalyst to oil, space velocity and suitable reactor schemes for the continuous reactor.

1.5 Rational and Significant

Rationally, in this present study, simulation should be considered before setting up the biodiesel plant, this will prevent from building an inappropriate plant. The simulation study also can reduce the cost of building the plant. Significantly, the main purpose of this study can be achieved by finding the important parameters that can affect the continuous reactor before building up the plant in producing the biodiesel.

Thus the aim of this project is to produce biodiesel as diesel substitute with using solid base catalyst as a catalyst to minimum the production cost and in other words it will save the separation cost of producing biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Biodiesel could be an excellent renewable fuel for diesel engines. It is derived from vegetable oils that are chemically converted into biodiesel. As the name implies, it is similar to diesel fuel except that it is produced from crops commonly grown in North Dakota, including canola, soybean, sunflower and safflower. These crops are all capable of producing several gallons of fuel per acre that can power an unmodified diesel engine. Vegetable oil is converted into biodiesel through a chemical process that produces methyl or ethyl ester. After washing and filtering to meet American Society for Testing and Materials (ASTM) standards, it is usable as an alternate renewable fuel.

2.1.1 Biodiesel Cost

The cost of biodiesel is higher than diesel fuel. Currently, there are seven producers of biodiesel in the United States. Pure biodiesel (100%) sells for about $1.50 to $2.00 per gallon before taxes. Fuel taxes will add approximately $0.50 per gallon. A mix of 20% biodiesel and 80% diesel will cost about 15¢ to 20¢ more per gallon over the cost of 100% diesel. Some suppliers are selling a 2% biodiesel mix at the same price as diesel, but this price will probably not continue into the future. A more realistic price would be about 1 to 2 cents more per gallon than diesel. These prices would be more attractive to people. The U.S. Department of Energy is working with the biodiesel industry to reduce the cost of biodiesel. A subsidy for the industry similar to that for other alternate fuels may be needed to promote the fuel. Improvements in processing along with the use of waste cooking oil as a raw material may help reduce costs. Currently, there are several service stations selling a mix of biodiesel and diesel in North Dakota.

2.1.2 Biodiesel and Air Pollution

There is a summary of engine tests completed at the University of Idaho shown in Table 2.1. These tests were performed with a 100% and a 20% mix of ethyl and methyl ester of rapeseed oil. A U.S. Department of Energy publication indicates reductions in most emission components except for an increase in nitrous oxide. Biodiesel use could provide reductions in several air pollutants. This could provide significant improvements in cities where air quality is a concern.

Table 2.1 Engine emission results from the University of Idaho

Emission	100% Ester Fuel (B100)	20/80 Mix (B20)
Hydrocarbons	-52.4%	-19.0%
Carbon Monoxide	-47.6%	-26.1%
Nitrous Oxides	-10.0%	-3.7%
Carbon Dioxide	+ 0.9%	+ 0.7%
Particulates	+ 9.9%	-2.8%

2.1.3 Characteristics of Biodiesel

There are some characteristics of biodiesel which is having high quality fuel. Biodiesel that adheres to the European biofuel norm EN 14214 is a high-grade fuel that meets the high requirements of the mineral oil industry and automobile manufacturers. Biodiesel is an adequate substitute fuel for traditional mineral diesel.

The accolade ignitability is also one of the biodiesel characteristic. In diesel fuels, the Cetane no. is the benchmark for measuring the ignition performance of diesel fuels. The higher the Cetane no. of a diesel fuel is, the better ignition and combustion function, the more smoothly an engine runs and the less wear and tear there is on the engine. As far as ignition performance is concerned biodiesel is an equal match to diesel. Its main components are similar to cetane, and as such it naturally has a Cetane no. of 56-58, thereby easily meeting engine manufacturers' requirements for high quality fuels with good ignition performance, even without additives.

Biodiesel is also known as a smooth operator. As opposed to mineral diesel, biodiesel contains practically no sulphur but, in itself, particularly high lubricating qualities, thereby reducing wear and tear on engines and injection pumps. Test plant investigations revealed a reduction in wear and tear of around 60%. As its sulphuric content gets lower, diesel produced from mineral oil loses its lubricating qualities, prompting the blending of synthetic additives. Lubrication tests revealed that the addition of 1% biodiesel to low-sulphur mineral oil diesel achieves the required lubrication effect again. For this reason, in future biodiesel will also be used as an environmentally friendly additive to mineral diesel fuels.

Moreover, biodiesel is also clean burning diesel fuel replacement made from natural, renewable source, such as new and used vegetable oils or animal fats. It will run in any diesel engine with a little or no modification and can be mixed with regular diesel fuel in any ratio. Biodiesel is non-toxic and biodegradable.

2.2 Vegetable Oil

Vegetable oils serve various Industrial applications such as plasticizers, emulsifiers, surfactants, plastics and resins. Research and development approaches may take advantage of natural properties of the oils. More often it is advantageous to modify those properties for specific applications. One example is the preparation of ink vehicles using vegetable oils in the absence of petroleum. They are cost competitive with petroleum-based inks with similar quality factors. Vegetable oils have potential as renewable sources of fuels for the diesel engine. However, several characteristics can restrict their use. These include poor cold-engine startup, misfire and for selected fuels, high pour point and cloud point temperatures. Other characteristics include incomplete combustion causing carbon buildup, lube oil dilution and degradation, and elevated NOx emissions. Precombustion and fuel quality data are presented as a tool for understanding and solving these operational and durability problems. (Peng et al., 2007)

2.3 Transesterification

In the transesterification, triglyceride reacts with an alcohol, generally methanol or ethanol to produced ester and glycerol. Catalyst is added to make it possible. In the Tanguy et.,al (2006) research, the transesterification of ethyl acetate with methanol was used as a model reaction to simulate fine-chemical production in batch slurry reactor at industrial conditions. The transesterification reaction occurs between methanol adsorbed on a magnesium oxide free basic site and ethyl acetate or the glyceride from the liquid phase. Methanol adsorption is assumed to be rate determining in both process.

Most of existing biodiesel plants currently relies upon the use of a homogeneous catalyst in a continuous reactor system, using the transesterification of soybean or rapeseed oil with methanol into alkyl esters. Diglycerides and monoglycerides are the intermediates in this process, and glycerol is a major byproduct. These reactions are affected by alcohol/oil feed ratio, free fatty acids, moisture, catalyst concentration, space velocity, temperature and mixing. Several studies have been carried out for soybean oil transesterification. Optimization of the amount of alcohol and base catalyst was studied, aiming for reduced alcohol usage, varying all other reactor and process parameters. There is a clear incentive for minimizing alcohol handling because of downstream separation costs. (Stiefel and Dassori, 2009)