THE KINETIC STUDY OF BIODIESEL PRODUCTION BY USING TWO STEP METHOD

AHMAD SAFWAN BIN ABDUL HALIM

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University Malaysia Pahang

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ABSTRACT

This research is to do the kinetic study of the biodiesel producing process by using the two steps method. Firstly the rubber seed oil was extracted by using the Soxhlet extractor using hexane as a solvent. The FFA content of the oil is determined by the titration of NaOH in the sample of rubber seed oil by using isopropanol as solvent. The FFA content as found between 8 to 10%. So the FFA content need to be reduce less than 1% so that the two step method can be used. Then the catalyst was prepared by using cuprum nanoparticles to produce cuprum oxide. The process was done in the furnace at 673K for 6 hours. The cuprum oxide produced was characterized by using XRD. The esterification process was done afterwards by using cuprum oxide as the catalyst to reduce FFA content in the rubber seed oil. The process was conducted at the reaction temperature. The kinetic study was done on the esterification process. The biodiesel was produced by the base-catalyzed transesterification process of the yield from the esterification process by using NaOH as catalyst. The kinetic study was done on the tranesterification process.

ABSTRAK

Objektif penyelidikan ini adalah untuk menjalankan kajian kinetic ke atas proses penghasilan biodiesel menggunakan kaedah dua langkah. Pertama sekali didalam penyelidikan ini adalah pengekstrakan biji getah dengan menggunakan Soxhlet dengan menggunakan eksanal sebagai pelarut. Kandungan FFA didalam minyak ditentukan dengan cara pentitratan NaOH ke dalam campuran minyak bersama isopropyl alcohol dan beberapa titis fenolftalein. Kandungan FFA didalam minyak perlu dikurangkan kepada kurang dari 1% untuk membolehkan penggunaan kaedah dua langkah. Kemudian, mangkin untuk proses pengesteran disediakan dengan menggunakan hasil tindakbalas nanopartikel kuprum dengan karbon aktif untuk menghasilkan kuprum oksida. Proses ini dijalankan didalam relau pada suhu 400˚C selama 6 jam. Kuprum oksida yang terhasil diklasifikasikan dengan menggunakan XRD. Proses pengesteran seterusnya telah dijalankan dengan menggunakan kuprum oksida sebagai mangkin untuk menurunkan peratus FFA didalam minyak getah. Proses ini dijalankan pada suhu 80˚C. kajian kinetic telah dijalankan pada proses tersebut. Biodiesel dihasilkan menggunakan hasil proses pengesteran dengan menggunakan proses tranesteran menggunakan suhu sama tapi menggunakan larutan NaOH sebagai mangkin. Kajian kinetik telah dijalankan pada proses transesterifikasi tersebut.

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LIST OF SYMBOLS/ABBREVIATIONS

° C	-	degree celcius
mm	-	millimeter
ml	-	milliliter
L	-	liter
h	-	hour
g	-	gram
BD	-	biodiesel
BET	-	Brunauer-Emmett-Teller
FAME	-	free acid methyl ester
FFA	-	free fatty acid
GC	-	Gas chromatography
XRD	-	X-Ray diffraction

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

As energy demands increase and fossil fuels are limited, research is directed towards alternative renewable fuels. Biomass has been found to produce low-molecular-weight organic liquids, which can be used or proposed for vehicles. A potential diesel oil substitute is biodiesel, consisting of methyl esters of fatty acids produced by the two step method, hydrolysis reaction of triglycerides of vegetable oils, and then esterification reaction with methanol with the help of a catalyst. Due to the great molecular similarities of biodiesel to paraffinic diesel fuel compounds, this alternative fuel has a chance of fulfilling the demands that diesel engine makes of its fuel. Essentially, no engine modifications are required to substitute biodiesel for diesel fuel that can maintain the engine performance. In addition, biodiesel is better than diesel fuel in terms of sulphur content, flash point, aromatic content and biodegradability.

1.2 PROBLEM STATEMENT

For this biodiesel fuel, there have been various studies in Europe, US and Japan and most of the conventional methods for biodiesel production use a basic or acidic catalyst. With an acid catalyst, a reaction of 1–45 h was necessary for the formation of the respective esters and by basic catalyst, it is somewhat faster depending on the temperature and pressure, but it still takes 1–8 h for a reaction. The reaction is initially slow because of the two-phase nature of the methanol/oil system, and slows even further because of polarity problem. In addition, a removal of both the catalyst and the saponified products after the reaction is essential for its purification.

1.3 RESEARCH OBJECTIVE

The objectives of this research are;

a) Preparation and characterization of oil.
b) Activity of the catalyst for esterification reaction to produce biodiesel.
c) Optimization of the process parameter esterification and tranesterification.
d) Kinetic study of esterification and tranesterification.

1.4 SCOPE OF STUDY

The scopes of this research are;

a) Preparation of biodiesel from rubber seed oil by two step method.
b) Preparation and characterization of catalyst for esterification of oil.
c) Kinetic study of FFA production by base catalyzed esterification.

1.5 SIGNIFICANCE OF STUDY

Biodiesel is a substance contains of esters of fatty acid with short-chained alcohol (methanol or ethanol). This biodiesel can be used as alternative fuel which obtained from renewable sources such as vegetable oil, or animal fats. Biodiesel is good because it emits fewer atmospheric pollutants than petroleum diesel. Biodiesel fuel can be used at the diesel engine without required any mechanical modification to the engine because of its similar properties with petroleum fuel. So to fit with the increasing demands of biodiesel, this study can lead to ways to produce biodiesel in large scale with lower cost and the yield produce is purified, safe to use and nature friendly.

CHAPTER 2

LITERATURE REVIEW

2.1 BASIC CONCEPT ON BIODIESEL

For over a decade, world is depending on petroleum to generate life, daily routine. When it comes to the problems of increasing cost and rapidly decrease supply of petroleum, people seems to align focused attentions on biodiesel fuel as an alternative way to reduce dependence on foreign oil, as well as to decrease emission of hazardous material to the environment. Biodiesel is obtained from renewable sources, has lower emissions than regular diesel, does not contribute to an increase in carbon dioxide in the atmosphere since all the material come from the plants, and extends the life of the engine due to its good lubricity (Mallory, 2007). Biodiesel is the name of clean burning alternative fuel, produced from domestic, renewable resources such as rubber seed oil, recycled restaurant greases, and animal fats. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition also known as diesel engines with little or no modification. Biodiesel is simple to use biodegradable, nontoxic and essentially free of sulphur and aromatics. Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the 1990 clean Air Act Amendments (Busari, 2005).

2.2 CONVENTIONAL METHOD OF PRODUCTION

The first method of processes in the production of biodiesel seems to have a few of main problems. One of the main problems is the availability of raw materials and the costs of refined vegetables oil. The process of producing biodiesel is so called transesterification. The process is quite simple, having work at low temperature and low cost of catalyst, having conversions near 100%.

However, it seems to be a few problems with the process:

a) The separation of glycerol/ biodiesel is long and costly
b) The cost of feed stocks is about 80% of the biodiesel production cost.
c) Industrial tranesterification process occurs by means of basic homogenous catalysis always producing soap and demanding refined oils (more expensive than crude ones) to minimize saponification.

The research now turned towards the improvement of chemical and biological process necessary to achieve second generation's biofuel, using waste materials such as exhausted vegetable oils.

In the hydroesterification process, hydrolysis is a chemical reaction between triglycerides and water, Producing fatty acids and glycerol (Fig.2.1). Thus, hydrolysis increases the acidity of the fatty material Instead of free fatty acid removal through refining. Moreover, glycerol obtained from hydrolysis is cleaner than one using transesterification process. After hydrolysis, fatty acids are esterificated with methanol or ethanol producing pure esters. There is no contact between glycerol (removed during hydrolysis) and biodiesel. Water, a by-product in the esterification (Fig. 2.2) is re-used in the hydrolysis step in a continuous way.

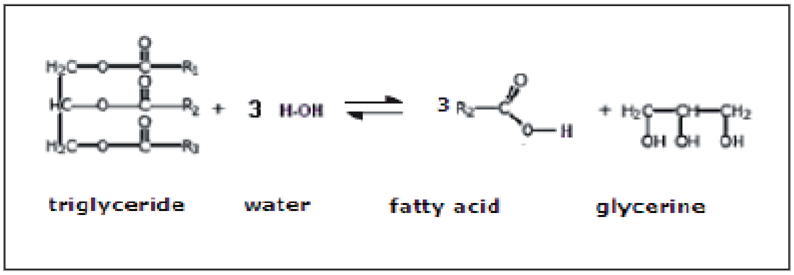

Figure 2.1: Diagram of reaction of hydrolysis

Source:

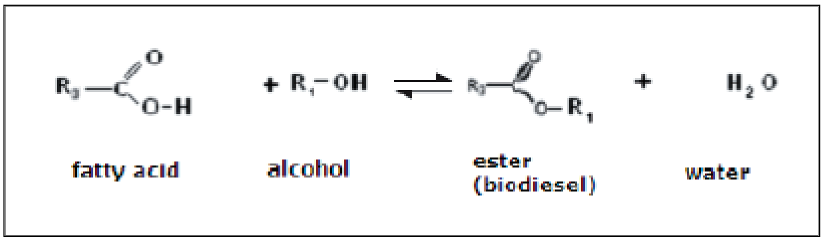

Figure 2.2: Diagram of reaction of esterification

Source:

Manco I. (Manco I, 2008) optimized the biodiesel production, obtained by esterification of the fatty acid derived from hydrolysis of rapeseed oil. Double-metal cyanide (DMC) was used as catalyst. The temperature and the mixing velocity remained constant during all reaction. The best conversion yields for the hydrolysis were observed at 300°C with 20% of catalyst: at the highest molar ratio the yield was 88.49% and at the lowest molar ratio the yield was 84.53%. The best conversion yield obtained in the esterification was observed working in the excess of methanol and at a temperature of 200°C; the concentration of catalyst is only relevant in the first 40 minutes of reaction. After one hour, even non-catalytic reaction produced high conversions at 200 ° C.

2.3 FREE FATTY ACID

Biodiesel is basically prepared from the triglycerides sources such as vegetable oils, animal fats and waste greases such as yellow and brown greases. Oils and fats came from a complete family of chemicals called lipids. Typically, fats come from animals and oils come from vegetable sources. Triglycerides are the primarily formed the fats and oils. Triglycerides molecules are basically a triester of glycerol and three fatty acid with long alkyl chain carboxylic acid (Lotero *et al.*, 2005). The main raw material that used to produce biodiesel and the vegetables oil extracted from the oleaginous plants due to economic and environment issue. The cost of these raw materials is 70% of its total production costs (Behzadi *et al.*, 2007). It is very important to note that vegetable oils are mixture of triglycerides from the various fatty acids. The free fatty acids composition is different for every plant sources.

Table 2.1: Fatty Acid Compositions of Vegetable Oil Samples

Sampel							
Cotton Seed	28.7	0	0.9	13	57.4	0	0
Poppy Seed	12.6	0.1	4	22.3	60.2	0.5	0
Rapeseed	3.5	0	0.9	64.1	22.3	8.2	0
Safflowerseed	7.3	0	1.9	13.6	77.2	0	0
Sunflowerseed	6.4	0.1	2.9	17.7	72.9	0	0
Sesameseed	13.1	0	3.9	52.8	30.2	0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Wheat Grain	20.6	1	1.1	16.6	56	2.9	1.8
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Corn Marrow	11.8	0	2	24.8	61.3	0	0.3
Castor	1.1	0	3.1	4.9	1.3	0	89.6
Tallow	23.3	0.1	19.3	42.4	2.9	0.9	2.9
Soybean	13.9	0.3	2.1	23.2	56.2	4.3	0
Bay Laurel	25.9	0.3	3.1	10.8	11.3	17.6	31
Peanut Kernel	11.4	0	2.4	48.3	32	0.9	4
Hazelnut	4.9	0.2	2.6	83.6	8.5	0.2	0
Walnut Kernel	7.2	0.2	1.9	18.5	56	16.2	0
Almond	6.5	0.5	1.4	70.7	20	0	0.9
Olive Kernel	5	0.3	1.6	74.7	17.6	0	0.8
Coconut	7.8	0.1	3	4.4	0.8	0	65.7

Source: Immacota, (2008)

The fats and oils is characterized according to their physical such as density, viscosity, melting point, refractive index or chemical properties such as acidity, iodine index, peroxide index, saponification index. These parameters will determine the biodiesel quality. As an example, the iodine index is related to the grade of oil unsaturation and in general, biodiesel is produced from high unsaturated fatty acid containing oils are less viscous, show greater cloud point, the temperature at which fuel become cloudy due to solidification and pour points, temperature at which fuel stops flowing which makes this biodiesel more suitable for cold weather conditions. However, it is prone to oxidation, has lower cetane index which related to the reaction efficiency within the engine and lower the combustion heats. In contrast, the biodiesel produced from oils with high proportion in long chain fatty acids have higher cetane index and combustion heat, but also lower clouds and our points and greater viscosity (Knothe, 2005)

2.4 FEATURES OF RUBBER SEED OIL

Hevea Brasiliensis, the Pará rubber tree, often simply called rubber tree, is a tree belonging to the family *Euphorbiaceae* and the most economically important member of the genus Hevea. It is of major economic importance because its sap-like extract (known as latex) can be collected and is the primary source of natural rubber. In the wilderness, the tree can reach a height of up to 144 feet (44 m). The white or yellow latex occurs in latex vessels in the bark, mostly outside the phloem. These vessels spiral up the tree in a right-handed helix which forms an angle of about 30 degrees with the horizontal, and can grow as high as 45 ft (Berrios M.,2007) .

In plantations, the trees are kept smaller, up to 78 feet (24 m) tall, so as to use most of the available carbon dioxide for latex production.

The tree requires a climate with heavy rainfall and without frost (Elastomer-The rubber tree, *Encyclopaedia Britannica*, 2008). If frost does occur, the results can be disastrous for production. One frost can cause the rubber from an entire plantation to become brittle and break once it has been refined.

Figure 2.3: Rubber seed

Source: Juanhua, (2008)

Figure 2.4: Rubber seed

Source: Juanhua, (2008)

2.5 RUBBER SEED OIL AS ALTERNATIVE FUEL

Peninsular Malaysia, comprising 12 of the 14 states in the Malaysian federation is among the world's most important rubber growing area. Rubber is also grown in Sabah (formerly North Borneo) and Sarawak, which, known together as East Malaysia. Altogether Malaysia produces almost 20% of the world's natural rubber. More than half Malaysia's rubber comes from thousands of privately owned small landholdings, which are usually about 2 hectares. The rest is grown on big estates owned by various companies; each can cover over a thousand hectares. Altogether, Malaysia has 1.7 million hectares of rubber plantation (Alves and Figuereido,1989)

Rubber seeds are ellipsoidal, variable in size, 2.5–3 cm long, mottled brown, lustrous, weighing 2–4 g each. Capsules are spread over the ground. These are collected and kernels are separated by breaking the capsules. These kernels are dried to remove the moisture. The kernels are crushed in the crushers and the oil is filtered. At present rubber seed oil does not find any major applications and hence even the natural production of seeds itself remain underutilized. The filtered oil is used as feedstock for the biodiesel production in this study (Ramadhas *et al*., 2005),

The fatty acid composition and the important properties of rubber seed oil in comparison with other oils is given in Table 2.2.

Table 2.2: Properties of rubber seed oil in comparison with the other oils

Property	**Rubber seed oil**	**Sunflower oil**	**Rapeseed oil**	**Cotton seed oil**	**Soybean oil**
Fatty acid composition (%)					
(i) Palmitic acid $C_{16:0}$	10.2	6.8	3.49	11.67	11.75
(ii) Stearic acid $C_{18:0}$	8.7	3.26	0.85	0.89	3.15
(iii) Oleic acid $C_{18:1}$	24.6	16.93	64.4	13.27	23.26
(iv) Linoleic acid $C_{18:2}$	39.6	73.73	22.3	57.51	55.53
(v) Linolenic acid $C_{18:3}$	16.3	0	8.23	0	6.31
Specific gravity	0.91	0.918	0.914	0.912	0.92
Viscosity (mm^2/s) at 40 °C	66.2	58	39. 5	50	65
Flash point (°C)	198	220	280	210	230
Calorific value (MJ/kg)	37.5	39.5	37.6	39.6	39.6
Acid value	34	0.15	1.14	0.11	0.2

Source:Dennis Y.C., (2010)

It contains of 18.9% saturation contains of palmateic and stearic acids and comprising mainly about 80.5% unsaturating of oleic, linoleic, and linoleic acids. The cloud point, the cetane numbers is increasing due to existence of saturation fatty acid methyl esters and the stability is improved whereas more polyunsaturated reduce the cloud points and cetane number and stability. The type and percentage of fatty acid consists in vegetable oils depends on the plant species and the growth condition of the plants. Even though vegetable oils are very low of volatility in nature; it quickly produces volatile combustible compounds upon heating.

The free fatty acid content of unrefined rubber seed oil was about 17%, i.e. acid value of 34. The yield of esterification process decreases considerably if FFA value is greater than 2%. Canakci and Gerpan (2001) found that transesterification would not occur if FFA content in the oil were about 3% .Biodiesel production from oils and fats with high free fatty acids.

2.6 ENVIRONMENTAL AND ECONOMICAL ANALYSIS ON RUBBER SEED OIL

Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the Clean Air Act. The used rubber seed biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter compared to emission from diesel fuel. In addition, the exhaust emissions of sulphur oxides and sulphates, one of major component of acid rain, from rubber seed biodiesel are essentially eliminated compared to diesel. The use of rubber seed biodiesel results in substantial reduction of unburned hydrocarbons. Emission of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used. Based on engine testing, using the straightest emissions testing protocols required by EPA for certification of fuels or fuel additives in the US, the overall ozone forming potential of the speciated hydrocarbon emission from Rubber Seed Biodiesel was nearly 50 percent less than that measured for diesel fuel.

Biodiesel cost more per gallon than conventional diesel fuel. While the price of both fuels can fluctuate and impact the incremental difference biodiesel has generally sold for approximately $1.00/gallon more than conventional diesel. The incremental cost associated with biodiesel blends with rubber seed biodiesel is lower than that of neat biodiesel. For example, with a 20% rubber seed biodiesel blend have historically seen an incremental cost differences with conventional diesel in the $0.10 - $0.20 cents/gallon range but the cost of biodiesel can be brought down by mass production and massive feedstock in producing rubber seed biodiesel (Joshi, 2003).

2.7 TWO STEP METHOD FOR BIODIESEL PRODUCTION

The main difficulty to produce biodiesel from the rubber seed oil is the high free fatty acid (FFA) content in the oil which is unfavorable for the use of base catalyzed transesterification. FFA produces soap with the base catalyst which is difficult to separate and results to a high loss of the product. Ramadash et al. reported the production of biodiesel from the rubber seed oil by a two-step method. (Ramadhas et al., 2005) where in the first step FFA was converted to FAME by acid catalyzed (H2SO4) esterification and in the second step, base catalyzed transesterification was conducted to convert the triglyceride to FAME.