Review

THE CURRENT STATUS OF BIODIESEL PRODUCTION TECHNOLOGY: A REVIEW

(Status Perkembangan Teknologi Produksi Biodiesel: Suatu Ulasan Ilmiah)

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ABSTRACT

Biodiesel is addressed to the name of fuel which consist of mono-alkyl ester that made from renewable and biodegradable resources, such as oils from plants (vegetable oils), waste or used cooking oil, and animal fats. Such oils or fats are chemically reacted with alcohols or methanol in producing chemical compounds called fatty acid methyl ester (FAME) and these reactions are called transesterification and esterification. Glycerol, used in the pharmaceutical and cosmetics industry is produced from biodiesel production as a by-product. Researches on biodiesel as an alternative petroleum diesel have been done for more than 20 years. Transesterification reaction can be acid-catalyzed, alkali-catalyzed, or enzyme-catalyzed. Commercially biodiesel is processed by transesterification with alkali catalyst. This process, however, requires refining of products and recovery of catalysts. Such biodiesel production accelerates researches on biodiesel to obtain simpler methods, better quality, and minimum production cost. Besides the catalytic production for biodiesel, there is a method for biodiesel production namely non-catalytic production. Non-catalytic tranesterification method was developed since catalytic transesterification still has two main problems associated with long reaction time and complicated purification. The first problem occurres because of the two phase nature of vegetable oil/methanol mixture, and the last problem is due to purification of catalyst and glycerol. The application of catalytic tranesterification method leads to condition of high biodiesel production cost and high energy consumption. This paper provides information of biodiesel production progress namely catalytic tranesterfification (acid, alkali, and enzymatic tranesterfification), and non-catalytic tranesterification (at sub-critical-supercritical temperature under pressurized conditions). It was found that every method of biodiesel production still has advantages and disadvantages. It means that there is a necessity to develop biodiesel processing method further in order to obtain high reaction rate, high reaction constant (k), high yield, safely process, and minimum energy consumption. In conclusion, there are some works should be undertaken in biodiesel research.

Keywords : biodiesel, methyl esters, transesterification, esterification, and FAME

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INTRODUCTION

It has been predicted that the petroleum oil will exhaust within 30 years in many part of the world (Saragih, 2001; Pakpahan 2001). So far the world heavily depends on the petroleum oils to fulfill the needs of the world energy consumptions such as for automotives, industry, generators, heating, agricultural machineries and others. The predicted shortage of fossil fuel encouraged the efforts for substitutes for petroleum derivatives. Among the efforts are developing engine with high fuel efficiency, using alternative energy like coal and gas. With the increase in awareness of environmental issues such as global warming and more environmental-friendly, bio-fuel and biomass are also being developed as alternatives to fossil fuel. Biofuel has promising prospect to be scaled up as the answer to the issue of energy crisis. Such considerations should be done in order to obtain energy security, to eliminate the dependence on petroleum fuel, to anticipate higher consumption of fossil fuel than its production, and to reduce the production of green house gas emission (CO_2). This policy is implemented in line with the international programs such as Kyoto Protocol (1997)

Biofuels include many fuels like bioethanol, pure plant oil (PPO), and biodiesel. Bioethanol is a renewable alcohol fuel made from products containing sugars and starches, through a process of fermentation and distilling (Anonymous, 2008). Bioethanol is a fuel which compatible with premium fuel due its similarity of chemical and physical characteristics. PPO and biodiesel can be produced from renewable sources such as palm oil, jatropha oil, crude palm oil, and any other vegetable oil. PPO is a kind of bio-fuels which is relatively cheaper than biodiesel since it can be directly used after oil extraction, degumming and neutralization. The advantage of PPO is that it can be produced without resulting by product (glycerol) and without alcohol and catalyst addition. It is however suitable for a low speed stationary diesel engine. Recent studies shows that the use of PPO for vehicles engine with additional heater and filter is still under research. Small modification or component addition should be done for diesel engine since first, engine should be started with solar fuel and continued by combination mix PPO and solar fuel (Priyanto, 2007; Niels, et al., 2001). Biodiesel is therefore more suitable for vehicle engine use since the properties or parameters of such fuel are compatible with solar fuel in terms of viscosity, cetane number, flash point, and related parameters

Biodiesel is a kind of petroleum diesel derived from biological product especially vegetable or animal oil, and is defined chemically as the mono-alkyl esters of long chain fatty acids derived from lipid sources (Darnoko, et al 2001; Tapasvi, et al, 2005; Ma and Hanna, 1999). To obtain biodiesel, the vegetable or animal oil is subjected to chemical reaction termed transesterification in the presence of catalyst (alkali or acid) with an alcohol (methanol or ethanol) to produce alkyl ester (biodiesel) and glycerol as represented in Figure 1. Triglycerides, as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triglycerides 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., fatty acid methyl esters or FAME). This alcoholysis reaction process is a three stepwise and reversible reactions that form three molars of FAME and one molar of glycerol (GL) from one molar of triglyceride (TG) and three molars of methanol (Figure 1.a). Diglycerides (DG) and monoglycerides (MG) are intermediates of the reaction (Figure 1.b).

There are two methods of transesterification reaction. One is the method using a catalyst and the other is without the help of a catalyst. The former method has a long story of development and now biodiesel produced by this method is in the market in some countries such as North America, Japan and some west European countries and Indonesia.

The name of biodiesel has been approved by The Department of Energy (DOE), The Environmental Protection Agency (EPA) and The American Society of Testing Materials (ASTM) as alternative energy for diesel engine. *Bio* represents its renewable and biological source in contrast to petroleum petroleum diesel, meanwhile *diesel* refers to its use in diesel engines. Biodiesel relates to: 1) a fuel obtained from mixtures, in different proportions of fossil diesel and methyl ester of vegetable oils or animal fats. In this case the notation of biodiesel is expressed as BXX which means any mixture of XX % of methyl ester with petroleum diesel, 2) a fuel obtained from pure or 100 % methyl ester, which is expressed as B100. Technically, biodiesel is the alkyl ester of fatty acids, made by the transesterification of oils or fats, from plants or animals, with short chain alcohols such as methanol and ethanol. Glycerol is, consequently, a by-product from biodiesel production.

Advantages that can be obtained by a country when using biodiesel are: 1) improving domestic nation capability in agricultural and industrial technologies, 2) improving domestic nation capability in producing processing equipment, 3) opening job opportunities, 4) reducing income disparity among the regions/provinces and among the people, 5) domestic reducing the need of importing petroleum diesel oil, 6) strengthening security supply of petroleum diesels, 7) enlarging the resource base of liquid fuels, 8) reducing local air pollution as well as global warming tendency, and 9) nurturing a new/potentially exportable commodity (Soerawidjaja , 2004; Pakpahan, 2001; Saraglh, 2001) .

Indonesia consumes a lot of petroleum diesel and needs to produce biodiesel as substitute. There are some consideration to be undertaken e.g.: 1) the unsubsidized price of petroleum fuel is continually increasing along with the scarcity of crude oil, 2) Indonesia has been importing
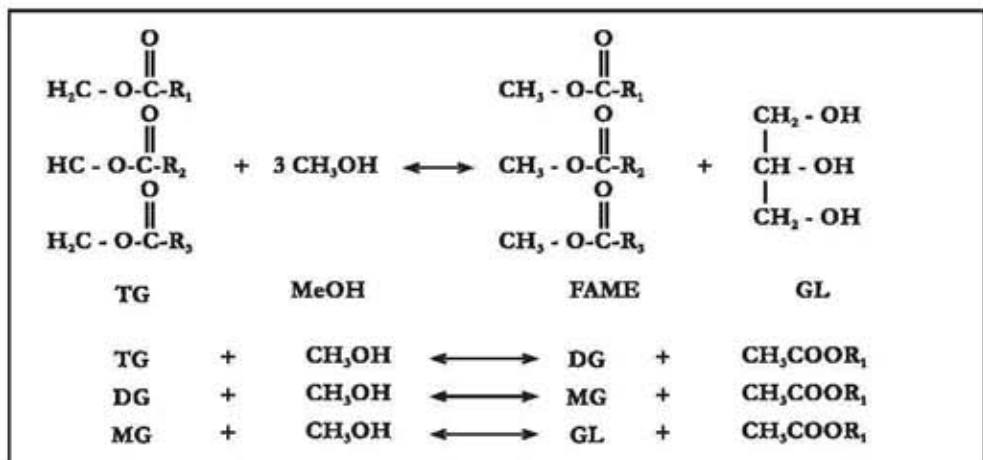

Figure 1. Alcoholysis of triglyceride with methanol. (a) overall reaction; (b) three consecutive and reversible reactions (Yamazaki, et al. 2006; Gerpen, 2005; Fredmen et al, 1986). $R_{1,2,3}$ = Fatty acid

petroleum diesel at a level higher than 30 % of national consumption, 3) security supply of petroleum fuels is alarmingly worsening, 4) biodiesel could be an excellent substitute, 5) biodiesel production technology is relatively simple so that it could be developed and mastered easily, and 6) the country is plentiful with the raw material sources (Soerawidjaja, 2004; Handaka, 2005). For Indonesia, production of biodiesel becomes more important due to the shortage of non-renewable energy, i.e. fossil fuels.

Biodiesel from vegetable oil has attracted increasing among the governments, industry sector, and general public. Research and development activities on biodiesel research, production and utilization have advanced to a such stage that its application as diesel supplement is feasible and practical. Relating to the development of biodiesel needs in Indonesia, Indonesian government has issued regulation (Inpres) on January 2006 concerning supply and the use bio-fuel as alternative energy or fuels. Furthermore, National Standardization Bureau (BSN) also has issued the standard for biodiesel produced in Indonesia which presented in SNI 04-7182-2006.

Based on the current method implemented in biodiesel plant, there is a need to assess and recheck the overall process and performance. A technical assessment of each process has to be evaluated and completely economic analysis in every step should be reviewed. This work has to be conducted to contribute in the process improvement of biodiesel production as well as its commercialization. This paper reviews the technologies as well as current research progresses of biodiesel productions including acid, alkali and, enzymatic transesterifiaction, and non catalytic alcoholysis methods.

SOURCE FOR BIODIESEL PRODUCTION

Biodiesel can be produced from several sources of vegetable or plant oils (feedstocks) and animal fats. The source for biodiesel production is chosen according to the availability in each country or location. The most common source of biodiesel in Europe is rapeseed oil while in the United States is soybean oil. Coconut oil, sunflower seed oil and used frying oil have been used to produce biodiesel in some countries. In tropical countries like Indonesia palm oil, jatropha oil, used or waste cooking oil and any other vegetable oil can be used to produce fatty-acid methyl ester or biodiesel. The advantage of being tropical region which makes possible to grow plant all year around should be utilized. The source of biodiesel (Indonesian name) which can be produced in Indonesia are *sawit/palm, jarak pagar, coconut, peanut, jarak kaliki, nimba, kelor, kemiri, kesambi* and other plant oils. It is important to know that only several of these tens of plant species (e.g. : palm, coconut, peanut) have been utilized as commercial sources of fatty-oils. From the Indonesian renewable energy policy, especially bio-fuels, it is stated that the target of biodiesel use in 2010 is 10% of the total diesel oil for transportation consumption (solar consumption will be 2.41 million kiloliters in 2010). To meet this target, Indonesia should develop 15 to 40 units biodiesel plant at commercial scales with the plant size of 30,000 to 100,000 tones per year (ESDM / DNEEC, 2006).

BIODIESEL QUALITY

The quality for biodiesel should follow the appropriate standard otherwise there will be problems in vehicle or engine application. In the United States, this standard is ASTM D 6751-02 "Standard

Table 1. The Indonesian Biodiesel Standard (SNI Biodiesel No. 04-7182-2006)

Property	Method	SNI	ASTM	Units
Density at 40°C	ASTM D 1298	850 - 890 (40°C)	-	kg/m³
Kinematic viscosity, 40 ° C	ASTM D 445	2.3 – 6.0	9 – 6.0	mm²/s (cSt)
Cetane number	ASTM D 613	51 min	47 min	-
Flash point	ASTM D 93	100 min.	130 min	°C
Cloud point	ASTM D 2500	18 max	Report to customer	°C
Copper strip corrosion	ASTM D 130	no 3 max	No. 3 max	Rating (3 hours at 50°C)
Carbon residue - in undistilled sample, or - in 10 % distillation residue	ASTM D 4530	05 max. 0.3 max. 0	0.05 max	% (m/m) % (m/m)
Water and sediment	ASTM D 2709 or ASTM D-1796	0.05 max	0.050 max	%-vol.
90 % (v/v) recovered at distillation temperature	ASTM D 1160	360 max	-	°C
Ash content (sulfated ash)	ASTM D 874	0,02 max	0,02 max	%
Sulfated ash	ASTM D 874	0,02 maks	0.020 max	%-massa
Sulfur content	ASTM D 5453 or ASTM D-1266	100 max.	Total sulfur 0.05 max	ppm
Phosphorous content	AOCS Ca 12-55	10 max	10	ppm
Acid number	AOCS Cd 3d-63 or ASTM D-664	0.8 max	0.8 max	mg-KOH/g
Free glycerol	AOCS Ca 14-56 or ASTM D-6584	0.02 max	0.02	%
Total glycerol	AOCS Ca 14-56 or ASTM D-6584	0.24 max	0.24	%
Alkyl Ester content	calculated	96.5 min.	-	%
Iodine number	AOCS Cd 1-25	115 max	-	% (m/m) (g-I2/100g)
Halphen test	AOCS Cb 1-25	AOAC Cb 1-25	AOAC Cb 1-25	-

Specification for Biodiesel (B100) Blend Stock for Distillate Fuels". Mostly many countries in the world used this standard as a reference for their biodiesel national standards. Generally, the fuel quality of biodiesel can be influenced by several factors (Gerpen and Knothe, 2005): 1)The quality of the feedstock, 2) the fatty acid composition of the parent vegetable oil or animal fat, 3) the production process and other materials used in this process, and 4) post-production parameters.

Table 1 shows the property values of methyl esters issued by SNI 04-7182-2006 (Indonesian National Standard of Biodiesel). This table also shows biodiesel standard issued from ASTM D 674. When these limits are met, the biodiesel can be used in most modern engines without modifications while maintaining the engine's durability and reliability. Some properties in the standard, such as cetane number and density, reflect the properties of the chemical compounds that make up biodiesel, while other properties such as glycerol content, acid number, water sediment, and acid number provide indications of the quality of the production process. Generally, the parameters given in ASTM D6751 are defined by other ASTM standards. However, other test methods, such as those developed by the American Oil Chemists' Society (AOCS) may also be suitable (or even

more appropriate as they were developed for fats and oils and not for petroleum-derived materials addressed in the ASTM standards). GC (Gas chromatography) and HPLC (High Performance Liuid Chromatography) are the most commonly employed methods for characterization of biodiesel composition. HPLC is a technique that gives good results but the cost of the analysis is a little higher than GC. GC is preferred to quantify biodiesel (Fredmen et al, 1984 a; Knothe, 2005).

METHODS OF BIODIESEL PRODUCTION

1. Pretreatment Process For High Free Fatty Acids Oils

Vegetable oils as sources of biodiesel production can be classified into three groups depends on its free fatty acyd (FFA) content namely (Kinast, 2003): (1) refined oils which has FFA less than 1.5 %, (2) vegetable oils that have FFA less than 4 %, and (3) vegetable oils with FFA content higher than 20 %. Based on FFA content of the vegetable oils the method of biodiesel production can be

determined. The process can be one step reaction (tranesterification) or two steps reaction (esterification continued by transesterification).

According to Gerpen and Knothe (2005), a special process is required when the vegetable oil or fat contains significant amounts of FFA. Used or waste cooking oils mostly contain 2 – 7 % FFA and animal fats contain 5 – 30 % FFA. Some very low-quality feedstocks such as trap grease can approach 100 % FFA. When an alkali catalyst is added to these feedstocks, free fatty acids react with the catalyst to form soap and water. Up to about 5 % FFA, the reaction can still be catalyzed with an alkali catalyst but additional catalyst must be added to compensate for that lost by soap formation. The soap created during the reaction is either removed with glycerol or washed with water wash. When the FFA level is above 5 %, the soap formation inhibits separation of glycerol from methyl esters and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulfuric acid can be used to esterify the FFA to methyl esters.
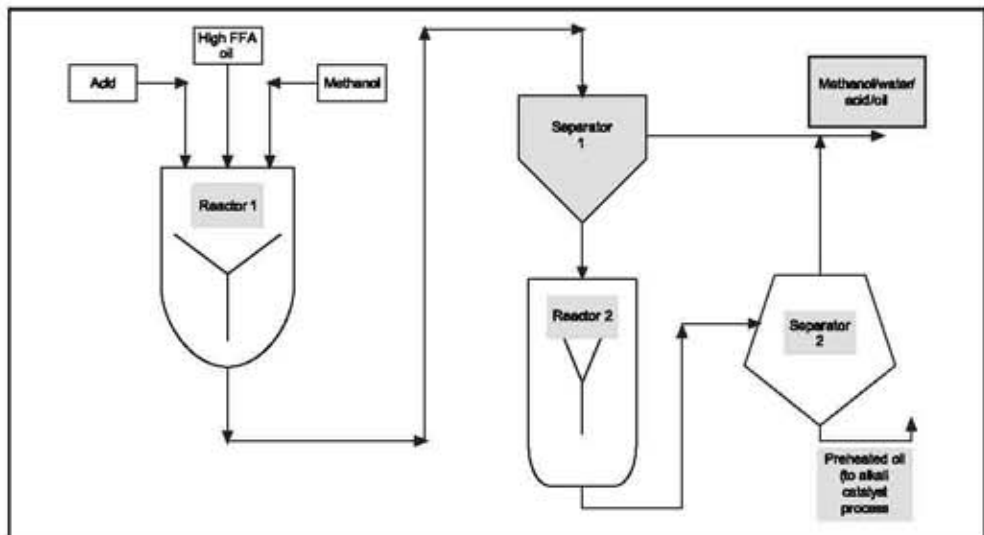

Figure 2. Pretreatment process for high free fatty acid (Gerpen and Knothe, 2005)

Figure 2 shows a pretreatment process for high free fatty acids vegetable oils or feedstocks. This process can be used as a pretreatment to convert the FFA to methyl esters and reduce the FFA level. The low FFA pretreated oil can be transesterified with alkaline catalyst to convert the triglycerides to methyl esters. In this process water is formed and if it accumulates, it can stop the reaction before completion. Normally vegetable oils wtith high FFA are processed with esterification continued by transesterification. When an alkali catalyst is added to these feedstocks, the FFA reacts with the catalyst to form soap and water as shown in equation bellow.

2. Catalytic Method

2.1 Acid catalyst

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 esters (i.e., biodiesel) and glycerol. Acid catalysts such as sulfuric acid, phosphoric acid, chloric acid, and others are suitable for oils containing high free fatty acid (FFA). As for the enzyme-catalyzed system, it requires a much longer reaction time than the other two systems (Nelson et al., 1996; Watanabe et al., 2001).

Despite its insensitivity to free fatty acids in vegetable oil or feedstock, acid-catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate (Zhang et al, 2003). There are numbers of studies on biodiesel production by an acid-catalyzed transesterification of vegetable oils and fats (Freedman et al, 1986;Ripmeester, 1998; Canakci and Gerpen, 1999). Alamsyah et al (2006) studied biodiesel production from jatropha oil by implementing esterification-transesterification method and tranesterification method. The objective

of this study was to investigate effects of such method on methyl ester quality with additional of antioxidant. Methanol and HCl were used in esterification process and it was operated at 60°C during 2 hours. Meanwhile alkali tansesterification process was carried out at 75 °C during 1 hour. It was found that the previous method provide better result than transesterification method in term of viscosity, density, and iodine number.

Canakci and Gerpen (1999) studied the effect of variables process on acid-catalyzed tranesterification of soybean oil. The study has ben conducted to investigate the effects of process variable e.g. molar ratio, reaction temperature, reaction time, catalyst amount, water and free faty acid on the yield of acid-catalyzed methyl ester on biodiesel production using acid (sulfuric acid) catalyst. The experiments were designed to the best strategy for producing biodiesel. To do this, the transesterification process of soybean with , methanol and sulfuric acid oil were conducted using a 100 ml glass flask at 48 hours reaction time and 60°C reaction temperature. It was found that acid catalyst can provide high conversion rate but much longer times are required than for alkaline catalyst. The acid catalyst also requires the concentration of water to be less than 0.5 %, which is about the same as is required for alkaline catalyst. Water formed by the esterification of FFA limited their presence in the oil to 5 %.

2.2. Alkali catalyst

Alkali catalyzed transesetrifica-tion was addressed to produce biodiesel production from vegetable oils or feedstocks containing low content of free fatty acids (FFA). This includes palm oil, soybean oil, rapeseed oil, jatropha oil, and higher grades of waste restaurant oils. In general the biodiesel production process consist of transesterification reaction, glycerol separation from methyl ester, purification of methyl ester

(neutralization, methanol separation, methyl ester washing, and drying). Alcohol, catalyst, and oil are combined in a reactor and agitated for approximately one hour at 60 °C. Small production often use batch reactor but larger plants with more than 30.000 tones/year capacity use continuous flow process involving continuous stirred-tank reactors as presented in Figure 3 (Tapasvi, et al , 2005; Mittelbach and Reshmidt, 2004).. The overall process includes crude oil degumming, refining, transesterification reaction, purification of methyl esters from catalyst (ester washing), recovery of unreacted methanol and separation of glycerin as by product (glycerol refining). Therefore, this conventional methods still requires a high production cost and energy. So far there are some biodiesel industry using alkali catalyst such Lurgi Corporation (Germany) with capacities 250,000 tons per year and Biox Corporation (Canada) with 60-million-litre a year biodiesel production (Anonymous, 2007)

There are many studies of alkali-catalyzed transesterification on research scale have been conducted. A reaction temperature of transesterification near boiling point of alcohol (e.g., 60°C for methanol) and a 6 : 1 molar ratio of alcohol to soybean oil or vegetable oil were recommended (Freedman et al, 1984; Noureddini and Zhu, 1997). The kinetics study of alkali-catalyzed transesterification were conducted by Darnoko and Cheryan (2000), Freedman et al (1984), and Noureddini and Zhu (1997). Based on their results, approximately 90 – 98 % oil conversion to methyl esters was observed within 90 minutes. Purification of biodiesel study has been done by Karaosmanoglu et al (1996). It was found that the use of hot water washing at 50 °C was the best way to obtain a high purity (99 %) and yield (86 %) of the biodiesel product. The data of the above experiments have been used as reference for many biodiesel plants for both small and large capacity production.

Transesterification of soybean oil with zeolite and metal catalysts has been done by Suppes et al (2003). The transesterification of soybean oil with methanol was carried out at 60, 120, and 150 °C in the presence of series NaX zeolite, ETS-10 zeolite, and metal catalysts. It was found that the increased conversion was attributed to the higher basicity of ETS-10 zeolites and larger pore structure that catalysts improved intra-particle diffusion. Methyl ester yield increased with an increase in temperature from 60 to 150 °C. The metal catalysts increased conversion by one to over two orders of magnitude over the homogenous reaction with several of the zeolite catalysts performing better than metal catalyst (Suppes et al, 2003; Suppes et al, 2004).

2.3. Enzymatic catalyst

Enzymatic catalyst lipase easily converts FFA into FAME resulting in high conversions of FAME in alcoholysis of waste edible oils (Fukuda et al., 2001). Enzymatic alcoholysis requires low energy, but the cost of lipase is still too high compared to alkaline catalyst. Comparison between alkali-catalysis and lipase-catalysis methods for biodiesel production is shown in Table 2. In particular, it should be noted that the by product, glycerol, can be easily recovered without any complex process, and also that free fatty acids contained in waste oils and fats can be completely converted to methyl esters. On the other hand, in general the production cost of lipase catalyst is significantly greater than that of an alkali one.

Various types of alcohols-primary, secondary, and straight and branched chain can be employed in transesterification using lipases as catalyst as presented in Table 3. Linko et al (1998)

Table 2. Comparison between alkali-catalysis and lipase-catalysis methods for biodiesel production (Fukuda et al, 2001)

Parameters	Alkali catalysis process	Lipase-catalysis process
Reaction temperature	60 – 70 °C	30 – 40 °C
FFA in raw matyerials	Saponified products	Methyl esters
Water in raw materials	Interference with the reaction	No influence
Yield of methyl esters	Normal	higher
Recovery of glycerol	Difficult	Easy
Purification of methyl esters	Repeated washing	none
Production cost of catalyst	Cheap	Relatively expensive

have demonstrated the production of a variety of biodegradable esters and polyesters with lipase as the biocatalyst. In the transesterification of rapeseed oil with 2-ethyl-1-hexanol, 97 % conversion of esters was obtained using Candida rugosa lipase powder. De et al (1999) investigated the conversion of fatty alcohol esters (C4-C18-1) using immobilized Mucor mehei lipase (Lypozyme IM-20) in a solvent-free system. The percentage of molar conversion of all corresponding alcohol esters ranged from 86.8 to 99.2 %, while the slip melting points of the esters were found to increase steadily with increasing length of alcohol chain (from C4 to C18) and to decline with the incorporation of unsaturation for the same chain length (as from C18 to C18:1).

3. Non-catalytic Method

3.1. Non-catalytic Transesterification at Supercritical Condition

The main problems associated with the catalytic methods are: its relatively time consuming and severe steps of purification of the product for catalyst and saponified products are necessary. The first problem due to the two phase nature of vegetable oil–methanol mixture which requires vigorous stirring to proceed in the transesterification reaction . To solve the above problem, numbers of studies in non-catalytic transesterification have been conducted (Saka and Kusdiana, 2000; Yamazaki et al, 2006; Dermibas, 2003). The advantage of this method is that this new process just requires only a very short reaction time. In addition, because of the non-catalytic process, the purification of products after transesterification reaction reaction is much simpler and environmental friendlier. Compared with the common method in which the catalyst and saponified products have to be removed for biopetroleum diesels, it requires less energy for manufacturing process.

Saka and Kusdiana (2000) have been conducted study on transesterification tion of rapeseed oil in supercritical methanol without using any catalyst The schematic of its process is shown in figure 4. Dermibas (2002) studied biodesel from vegetable oils via transesterification in supercritical methanol. Transesterification was conducted using six vegetable oils (cotton seed, hazelnut kernel, poppy seed, rapeseed, safflower seed, and sunflower seed) in supercritical methanol without using any catalyst. The experiments were carried out using 100 ml cylindrical autoclave made 316 stainless steel at 100 MPa and 850°K. The autoclave was charged with a given amount of vegetable oil (20-30 g) and liquid methanol (30-50 g) with changed
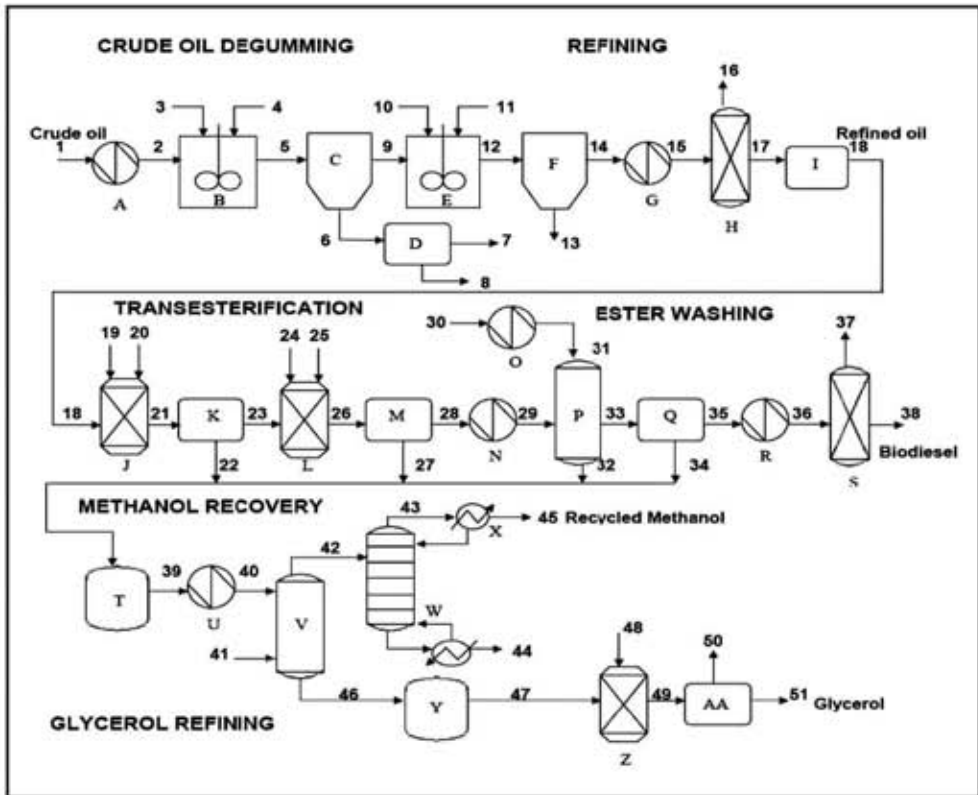
Figure 3. Continuous alakali-catalyzed biodiesel production process used for model development (Tapasvi, et al, 2005). Equipment: (A) heater, (B) mixing tank, (C) centrifuge, (D) gums/water separator, (E) refining tank, (F) centrifuge, (G) heater, (H) vacuum oil dryer, (I) surge tank, (J) continuous stirred tank reactor (CSTR) 1, (K) decanter 1, (L) CSTR 2, (M) decanter 2, (N) heater, (O) heater, (P) wash columns, (Q) settler tank, (R) heater, (S) vacuum ester dryer, (T) collecting tank, (U) heater, (V) glycerol-alcohol stripper, (W) distillation column/reboiler, (X) reflux condenser, (Y) glycerol hold tank, (Z) acidulation reactor, and (AA) decanter. Streams: (1) crude oil, (2) heated crude oil, (3) phosphoric acid, (4) soft water, (5) mixing tank outstream, (6) gums-water mix, (7) gums, (8) water, (9) degummed oil, (10) NaOH solution, (11) wash water, (12) refining tank outstream, (13) soapstock, (14) centrifuge outstream, (15) heater outstream, (16) water vapor, (17) hot oil, (18) refined oil, (19) sodium methoxide, (20) methanol, (21) CSTR 1 outstream, (22) glycerol phase, (23) methyl ester phase, (24) sodium methoxide, (25) methanol, (26) CSTR 2 outstream, (27) glycerol phase, (28) ester phase, (29) heater outstream, (30) soft water, (31) heated wash water, (32) waste stream, (33) washed esters, (34) aqueous phase, (35) esters, (36) heated esters, (37) water vapor, (38) biodiesel, (39) glycerol/aqueous phase, (40) heater outstream, (41) super heated steam, (42) saturated methanol vapors and saturated steam, (43) methanol vapor, (44) distillation column bottoms, (45) recycled methanol, (46) hot glycerol solution, (47) glycerol, (48) HCl solution, (49) acidulation reactor outstream, (50) waste, and (51) product glycerol.

Table 3. Enzymatic transesterification reactions using various types of alcohol and lipases

Oil	Alcohol	Lipase	Conversion (%)	Solvent	Reference
Rapeseed	2-Ethyl-1hexanol	C rugosa	97	None	Linko, et al (1998)
Mowrah, mango, kernel	4-C18, alcohols	M.miehei (Lipozome IM - 20)	86.8 – 99.2	None	De, et al (1999)
Sunflower	Ethanol	M.miehei (Lipozome)	83	None	Selmi and Thomas (1998)
Fish	Ethanol	C. antarcita	100	None	Breivik et al (1997)
Recycled restaurant grease	Ethanol	P.cepacia (Lipase PS-30) + C. antarcita (Lipase SP435)	85.4	None	Wu, et al (1999)
Tallow, soybean, rapseed	Primary alcohols[a] Secondary alcohols[b] Methanol Ethanol	M.miehei (Lipozome IM60) C. antarcita (SP435) M.miehei (Lipozome IM60) M.miehei (Lipozome IM60)	94.8 – 98.5 61.2 -83.8 19.4 65.5	None	Nelson, et al (1996)
Sunflower	Methanol Methanol Ethanol	P. fluoresence	3 79 82	None	Mittelbach (1990)
Palam kernel	Methanol ethanol	P. cepacia (Lipase PS-30)	15 72	None	Abigor, et al (2000)

[a] Methanol, ethanol, propanol, and isobutanol
[b] Isopropanol and 2-butanol

molar ratios. Molar ratio used were 1:1, 1:3, 1: 9, 1: 20, and 1 : 41).

Kusdiana and Saka (2000) have also conducted a kinetic study on non-catalytic subcritical and supercritical methanol with different reaction temperature and reaction times. Experiments were made in bath-type reaction vessel ranging from 200 °C in subcritical temperature to 500 °C at supercritical state with different molar ratios of methanol using rapeseed oil to determine reaction rate constant by employing a simple method. It was shown that, the conversion rate of rapeseed oil to its methyl esters increased dramatically in the supercritical state, and the reaction temperature of 350 °C was considered as the best conditions, with the molar ratio of methanol in rapeseed oil being 42. The experimental data were further analyzed in terms of kinetics of rapeseed oil to methyl esters, and the rate constant of the reaction was evaluated as function of unmethyl esterfied compounds (μME) and times (t).

3.2. Noncatalytic Alcoholysis of Semi-batch Process using buble column reactor

Research on non catalytic alcoholysis of oils for biodiesel production also has been carried out by Yamazaki et al (2006). In this study, a new semi-batch reactor was developed to produce FAME by blowing superheated methanol gas continuously into oils without using any catalysts (Figure 5). The reactor was used to produce biodiesel from sun flower. This study was conducted to investigate the effects of reaction temperature (250, 270, 290, 310, and 340°C), feed flow rate of methanol (0.6, 0.9, 5 mL/minute), operating pressure, stirring rat (300, 700, 100 rpm) and initial oil volume (150, 200, and 250 mL) on mass flow rate of methyl ester gas (g./minute). It was found that the increase in methanol feed flow rate and initial oil volume, and decrease in stirring rate all increased the outflow rate of FAME. Increase in outflow rate of FAME with methanol feed flow rate indicated

the large effect of product inhibition in this reaction. Decrease in outflow rate and total production rate of FAME with increase in stirring rate shows the effect of methanol bubble residence time in the liquid phase. Effect of initial oil volume on reaction also indicates the same effect. These correlation were presented in equation below:

$$k = \frac{\ln [\mu ME, t] - [\mu ME, 0]}{T}$$

Where: k is constant of reaction rate (1/mimute), μME is unmethyl esterified compounds e.g unreacted of TG, DG, MG and FFA, t is time (minute), and T is temperature (°C)

3.3. Noncatalytic Alcoholysis of Semi-batch Process using buble column reactor (at atmospheric pressure)

Research on kinetics of semi-batch non catalytic transesterification using palm oil at atmospheric pressure has been conducted by Joelianingsih, et al

(2006). The effect of reaction temperature (250, 270, 290°C) on constant and conversion rate were observed at a feed flow rate of methanol (4 g/minute) and initial volume of (200 g) the reaction was occurred among contact area of methanol bubble and palm oil and its product (gas phase) was exhausted and then condensed. Un-reacted methanol was also evaporated in order to yield methyl ester (biodiesel) and glycerol as by product.

It was reported, the time required to obtain complete conversion of methyl ester was 7.25 hours at 290°C (palm oil was completely converted into methyl ester). This means that the time required to convert palm oil was longer than those with catalytic process . It means 7 times longer than catalytic process e.g. 1 hour at 60°C where is the long reaction times can happen since the value of frequency factor which expressed amount collision between methanol and palm oil is still relatively low and reaction rate was influenced mass transfer on surface
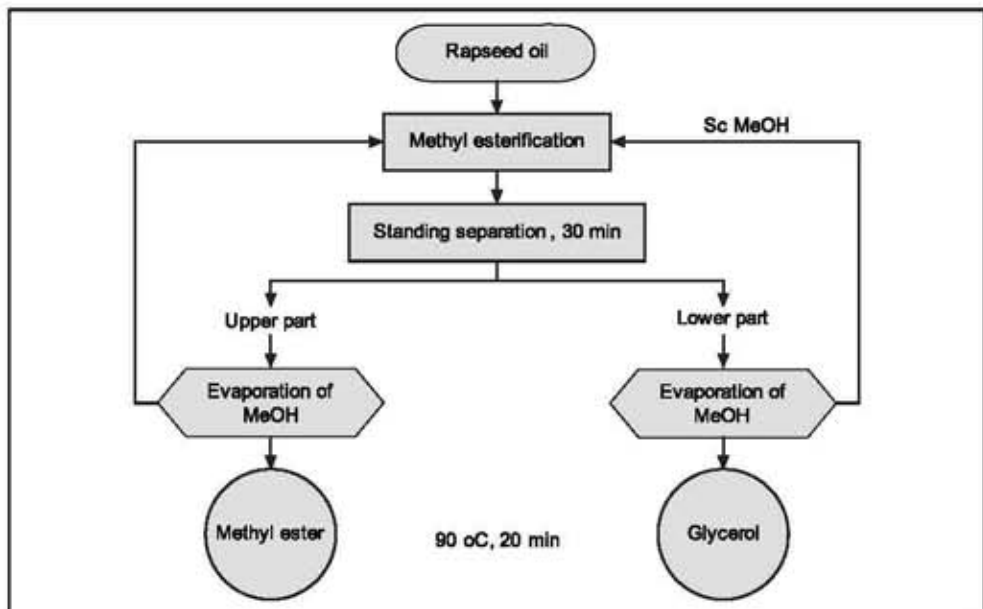

Figure 4. Schematic prosess of biodiesel fuel production by supercritical method (Saka and Kusdiana, 2000)

contact area. To reduce reaction time it is suggested to enlarge surface contact area, and to increase bubble quantity. In conclusion, the bigger surface contact area is the better the shorter reaction time.

PARAMETERS CONTROLLED REACTIONS

Transesterification consists of a number of consecutive and reversible reactions (Schwab et al, 1987; Fredmean et al, 1986). The triglyceride is converted stepwise to diglyceride, monoglyceride, and finally glycerol. A mole of ester is liberated at each step. The reaction itself are reversible, although at the equilibrium it produce fatty acid esters and glycerol. There are many parameters controlled transesterification process namely 1) molar ratio between methanol and oil, 2) type of catalyst, 3) reaction temperature, 4) homogenization of the reaction mixture, 5) reaction pressure, and 6) reaction time.

1. Molar ratio

The molar ratio between methanol and oil depends on catalyst used. To shift the reaction to the product side, an excess of the alcohol is recommended. According to Fredman et al (1986), comparison of 6 : 1 molar ratio of methanol to oil for alkali-catalyzed tranesterification can be used to obtain maximum ester yields. This ratio is usually not exceeded in the conventional alkaline catalyst. When higher amount of alcohol exceed in the reaction, it can lead to interfere in the separation of glycerol phase (Srivasta and Prasad, 2000). It was reported that for acid catalyzed transesterification methanol to oil ratio is up to 30 : 1.

2. Type of catalyst

To achieve satisfactory ester yields under mild reaction conditions, biodiesel production is generally conducted in the presence of some types of catalyst, including alkaline and acidic material. Catalyst from metal compound, silicates and lipase enzyme also can be used (Mittelbach and Remshcmidt, 2004). The
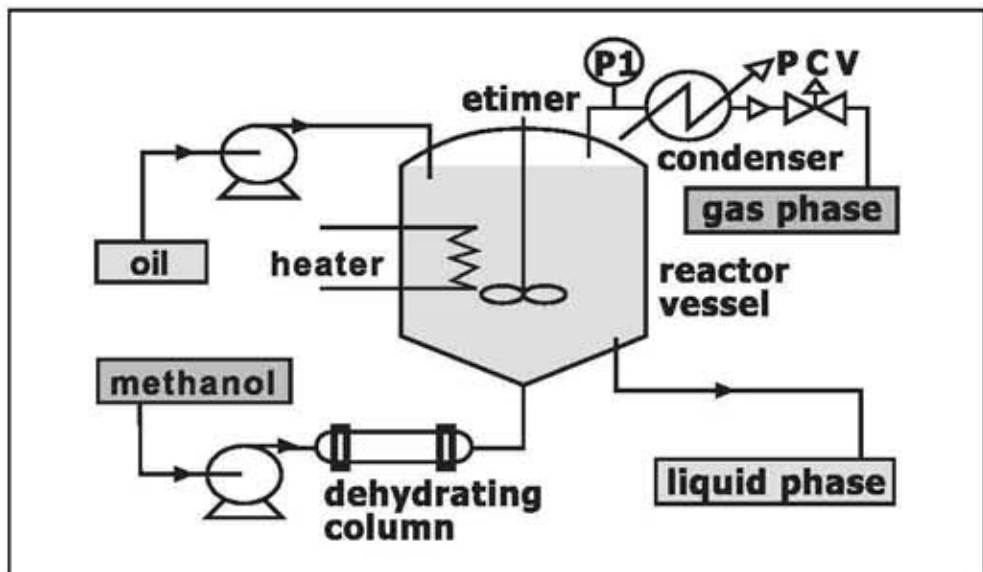

Figure 5. Schematic diagram of Noncatalytic Alcoholysis of Oils for Biodiesel Fuel Production by Semi-batch Prosess (Yamazaki, et al, 2006)

optimum of homogeneous alkalinecatalyst range from 0.5 to 1.0 % by weight of the oil (Fredman et al, 1984). Acid catalyst also can be used for biodiesel production. Transesterification by acid catalysis is much slower than by alkali catalysis. Acid catalyzed transesterification is much more suitable for glycerides that have high relatively free fatty acid and more water. Aksoy et al (1988) reported that it was necessary to perform acid transesterification under an acidic condition when the oil components was low grade material such as sulphur olive oil. In general the ethyl esters mono-saturated or short chain fatty acid with 2 % sulfuric acid should make good alternative fuels (Klopfeinstein et al, 1983)

3. Reaction temperature

Transesterification can be conducted at different temperature, and it depends on the oil used. In methanolysis of castor oil to methyl ricinoleate the reaction proceeded most satisfactory at $20-35^{\circ}C$ with molar ratio 6 :1 and 12 : 1 with NaOH catalyst (Fredman et al, 1984). For transesterification of refined soybean oil with methanol (6:1) using 1 % NaOH, three different temperatures were used (Fredman et al, 1986). Ester produced after 0.1 h was 94.87 %, and 64 % , for 45, and $32^{\circ}C$ respectively. After 1 hours, ester formation was identical for the 60 and $45^{\circ}C$ runs and only slightly slower for the $32^{\circ}C$ run. In conclusion temperature clearly influenced the reaction rate and yields of esters.

4. Reaction time

The production rate of methyl ester strongly correlates with reaction time. Fredman et al (1984) reported transesterified peanut, cotton-seed, sunflower and soybean oils under condition of methanol to oil ratio of 6 : 1, 0,5 sodium methoxide catalyst and $60^{\circ}C$. It was observed that after 1 minute the yield was 80 %, and the conversion was 93 – 98 % after 1 hour. Ma et al (1998) also reported the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to mixing and dispersion of methanol into beef tallow. It was shown that the production of methyl esters were between 1 – 38 %. The production rate of methyl ester reached the maximum yield at about 15 minutes.

5. Homogenization of the reaction mixture

Homogenization is one of the important parameters that can affect the yield of methyl esters in tranesterification process. Transesterification does not run properly when the mixture is not homogenized effectively, especially during the initial stages of the process. Vigorous mixing of the components is one method of homogenization, which has been found successful for both batch process (Assmann et al, 2004) and continuous operation (Damoko and Cheryan, 2000).

6. Reaction pressure

Methyl esters can be produced under low pressure and low reaction pressure. Commercially biodiesel production from vegetable oil was produced by low pressure due to low process cost and safety factor and it is normally operated at atmospheric pressure. High pressure biodiesel production can be conducted with pressures up to 100 bars and temperatures about $250^{\circ}C$ with $7-8$ fold molar excess of methanol in the presence of alkaline or transient metal catalyst (Gerpen and Knothe, 2005.). The advantages using high pressure tranesterifications are that raw materials containing more than 20 % free fatty acid (FFA) can be used without pre-treatment and that high purity glycerol can be resulted as a by product (Mittelbach and Remshcmidt, 2004). However this method is not appropriate to biodiesel production because of high process cost.

CONCLUSION

The number of research on biodiesel production have been conducted to reach a good technological level for biodiesel production. There has been a continuous development of new catalysts for biodiesel production. The use of different available acid and alkali catalysts has been reviewed and particular attention has been given to the more recently developed ones.

There are at least two problems associated with catalytic process. The first problem due to the two phase nature of vegetable oil/MeOH mixture requires vigorous stirring to proceed in the transesterification reaction. The second problem is products purification because the reaction product contains residual catalyst, unreacted MeOH and saponified products. To solve this problem there is a need to some research on how increase homogenization in relatively short time with design of mixing mechanism to accelerate reaction rate as well as constant of reaction rate (k).

One of the research kinds need to be developed in biodiesel production is energy analysis. Since biodiesel can be produced by various methods, it is important to know how much energy required in each method. Biodiesel production includes many process steps, therefore there is a need to design a complete energy analysis in terms of exergy analysis. Another biodoesel research need to be elaborated is to increase reaction rate as well as constant of reaction rate (k). This can lead to reduce energy consumption for biodiesel production. It is hope the results of this work can be used to obtain process improvement. In conclusion there is a necessity to develop biodiesel processing method using low energy consumption. Therefore, in order to obtain economical product, better yield, and safely process, there are some work should be undertaken in biodiesel research.

Due to the rapid decline in crude oil reserves, the use of vegetable oils as diesel fuels is should be promoted in many countries. Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soybean oil in the United States, rapeseed an sunflower oils in Europe, palm oil or jatropha oil in Southeast Asia (mainly Indonesia and Malaysia), and coconut oil in the Philippines are being considered as substitutes for diesel fuels. Besides that micro algae as a marine product and renewable materials has to be elaborated for biodiesel feedstock.

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