JHSS (Journal of Humanities and Social Studies)
https://journal.unpak.ac.id/index.php/jhss

Volume 08, Number 02, Page 513-520
e-ISSN: 2598-120X; p-ISSN: 2598-117X

A REVIEW: PRODUCTION PROCESS OF BIODIESEL MADE FROM WOSTEN OIL RAW

Anggi Anggreini Tanjung [a*)], Susila Arita Rahman [a)], Fitri Hadiah [a)]

[a)] Program Studi Magister Teknik Kimia, Fakultas Teknik, Universitas Sriwijaya, Palembang, Indonesia

[*)] Corresponding Author: anggitanjung2001@gmail.com

Article history: received 10 November 2024; revised 21 November 2024; accepted 27 December 2024 *DOI: https://doi.org/10.33751/jhss.v8i2.11017*

Abstract: The development of biodiesel in Indonesia is increasing judging from consumption and export data to meet energy and fuel needs. The high cost of the biodiesel production process can be overcome by using waste cooking oil as a raw material. The use of waste cooking oil as biodiesel is an environmentally friendly action because it reduces environmental pollution. The method used in writing this article is a literature study by collecting data and information from various journals with the aim of explaining the processing of waste cooking oil into biodiesel. The catalysts used are acid and base catalysts (homogeneous, heterogeneous) and enzyme catalysts. Waste cooking oil can be converted into biodiesel by going through the transesterification stage. Under optimal conditions, used cooking oil as a raw material for biodiesel produces the highest methyl ester content of 98.94% using a heterogeneous base catalyst, namely ATKKS. The final conversion of biodiesel is affected by several parameters such as reaction temperature, reaction time, molar ratio of alcohol to oil, amount of fatty acids, moisture content and catalyst used.

Keywords: Biodiesel, Waste cooking oil, Transesterification, Catalyst

I. INTRODUCTION

Energy consumption has increased, especially in the industrial, transportation and household sectors. Indonesia has abundant renewable energy sources but they have not been utilized optimally compared to the use of fossil fuels. It is time to reduce dependence on the use of fossil fuels by developing alternative energy sources that are renewable.[1] Indonesia as an agrarian country has a huge opportunity to develop biodiesel as an alternative energy source.[2]

Biodiesel is an alternative energy substitute for diesel engine fuel *non-toxic, renewable, biodegradable,* does not emit carbon into the atmosphere and has environmental advantages compared to *petroleum diesel*.[3] The development of biodiesel in Indonesia is increasing to meet energy and fuel needs. This increase is followed by consumption and exports which are getting bigger every year.

Table 1. Data on biodiesel development in Indonesia from 2018-2023 (Kilo Liters)

Development Data	2018	2019	2020	2021	2022	2023
Production	5,600	8,399	8,594	10,258	11,816	13,151
Export	1,772	1,319	36	147	371	187
Consumption	3,950	6,396	8,400	9,296	10,430	12,242

Source: Approbi, 2024

Regarding National Policy in Government Regulation no. 79, the cumulative need for oil, coal, gas and New and Renewable Energy (EBT) will increase almost 5 times during the 2015-2050 period. Biodiesel growth in Indonesia from 2018-2023 can be seen in Table 1.

Currently, the selling price of biodiesel is still almost as expensive as fossil fuels because the costs of the biodiesel production process are still high. Considering these conditions, used cooking oil is the most suitable type of vegetable oil as a raw material for biodiesel because its price is cheap so it can reduce the selling price of biodiesel.[4] Used cooking oil is household waste that has the potential to pollute the environment. Utilizing used cooking oil into biodiesel can overcome the problem of waste oil disposal.

Used cooking oil can be converted into biodiesel by going through the transesterification stage which reacts the oil molecules with alcohol and a catalyst to obtain methyl ester and glycerol as by-products. The success of the biodiesel production process can be influenced by several factors such as the catalyst, reaction temperature, alcohol molar ratio, water content in the raw material, reaction time and stirring speed.[5] This article discusses the biodiesel production process using used cooking oil as raw material and the use of several types of catalysts to speed up the production of biodiesel from used cooking oil.

II. RESEARCH METHODS

Methods used in the article *review* This is a literature study carried out by collecting data and information from various sources such as journals and books. The literature study begins with identifying a problem, analysis and discussion related to biodiesel synthesis.

III. RESEARCH RESULT

a. Used Cooking Oil

Used cooking oil is cooking oil that has been used many times so that its quality has decreased due to damage to the oil, which is characterized by the color changing to dark, the aroma becoming less pleasant and the nutritional value decreasing.[6] Used cooking oil contains compounds that are carcinogenic, which occur during the frying process. Repeated use of cooking oil will cause oxidation of unsaturated fatty acids which then form peroxide groups and cyclic monomers. This can have a negative impact on those who consume it, namely causing various symptoms of poisoning.[7] Apart from causing serious health problems, if used cooking oil is thrown away carelessly it can be a problem for the environment.[8]

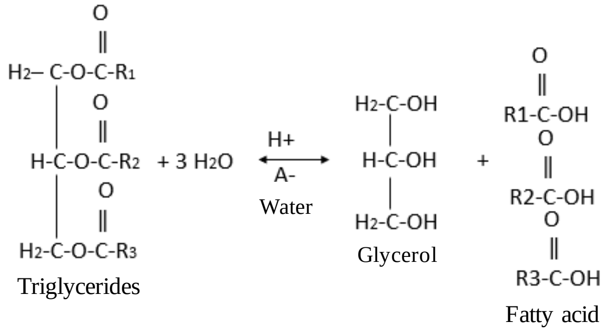

Figure 1. Hydrolysis Reaction

Used cooking oil is a glycerol tryester of saturated and unsaturated fatty acids produced from oxidation and hydrolysis reactions (Figure 1). Almost all pure cooking oils contain 98% triglycerides, while 2% are non-triglyceride components such as monoglycerides, tocopherols, free fatty acids, phospholipids, diglycerides, and a small amount of dye components. The free fatty acid content in used cooking oil ranges from 5-30% (w/w).[9]

What supports the development of biodiesel from used cooking oil, apart from being more economical in terms of raw material costs, is the cooking oil consumption pattern of the community, most of which use palm oil for frying the food they consume. So this is the starting point in providing raw materials for continuous production of biodiesel.[10]

The total used cooking oil waste produced in Indonesia reaches 3.8 million tonnes each year, originating from the household sector, food processing industry, hotels and restaurants.[11] So the use of used cooking oil as a raw material in the production of abundant biodiesel is an effort to reduce environmental pollution.

b. Stages *Pretreatment* Used Cooking Oil

Used cooking oil contains free fatty acids (*Free Fatty Acid*, FFA) is high enough that processing is required *pretreatment* such as the adsorption process for reduce FFA levels. Research conducted by Setiorini et al (2023), *pretreatment* What is done is that the used cooking oil is settled, filtered using a filter *whatman* then natural zeolite adsorbent was added which had been activated for 24 hours to reduce the free fatty acid content. Used cooking oil that has been processed *pretreatment* produces FFA levels of 4.096%.

Process *pretreatment* Other aspects of used cooking oil include the filtering process, *bleaching*, and neutralization. The purpose of filtration is to remove particles from the oil. The filtering process can be done using filter paper. Process *Bleaching* In used cooking oil, the aim is to remove natural dyes which are the degradation of natural substances, the influence of metals and color due to oxidation.

Process *bleaching* This is done by mixing the filtered oil with activated carbon or charcoal at a temperature of 100^{the}C and stirred with *magnetic stirrer* for 1 hour. Next, it is filtered using filter paper, thus activated carbon is widely used in purification because it has so many pores that it can absorb various impurities. The neutralization process in used cooking oil aims to remove phosphate, color and reduce FFA levels. The neutralization process is carried out by mixing a 16% NaOH solution in used cooking oil and then heating it at a temperature of 40^{the}C and stirred for 10 minutes then the precipitate was filtered.[12]

Degumming is one method *pretreatment* which can be applied to used cooking oil.[13] This process aims to remove phosphatide compounds which can make the oil cloudy and contain excess water content. *Degumming* There are two methods, namely acid and water. The use of acid compounds mixed with oil so that the phosphatide content that is not soluble in oil can be removed.

The acid compound used is phosphoric acid because it has the ability to bind phosphorus which is a component of *gum* then settle it. The high phospholipid content in used cooking oil will react with phosphoric acid to produce gum phosphate and CaHPO.$_4$. The phosphoric acid used has a concentration of 85% and a reaction occurs *degumming* at a temperature of 70^{the}C. Process *degumming* with water is used to remove soluble phosphatides by mixing water with oil at a temperature of 60-90^{the}C is then separated by centrifugation.[14]

c. Biodiesel Production Process

Several biodiesel production processes, namely *dilution process*, microemulsion method, pyrolysis, esterification-transesterification.[15] The process that is often used on a home to industrial scale is the esterification-transesterification reaction.

1. *Dilution Process*

Dilution process the most common is mixing oil with diesel fuel to reduce oil viscosity and the use of diesel fuel. The oil used in this method is *peanut oil*, *rapeseed oil* And *sunflower oil*. *Dilution process* is a simple reaction process with low production costs. The disadvantages of this process are the high FFA content and high viscosity of the resulting solution.

2. Method Microemulsion

Microemulsions are defined as thermodynamically stable, isotropic liquid mixtures of oil, water, and surfactants (compounds that reduce surface tension in liquids).[16] The advantage of this process is that it has a good absorption process and can increase the cetane number. The microemulsion method can reduce the high viscosity of vegetable oils using short chain alcohols such as methanol, ethanol or 1-butanol. However, short chain alcohols have a weakness, namely that microemulsified vegetable oil has a lower calorific value than diesel fuel.[15] Microemulsion processes are also used to obtain properties *spry* which is good when injected into the engine at the nozzle. If microemulsion diesel is used in a diesel engine, several problems will arise such as incomplete combustion, carbon deposits and nozzle failure.

3. *Thermal Cracking* (Pyrolysis)

Pyrolysis is a process that converts complex hydrocarbon structures into the simplest structures with or without a catalyst. Due to this process the density and viscosity of the oil will decrease. The use of vegetable oil as fuel can affect engine atomization. So the fuel processed by this process can be used directly in diesel engines without any modification. Generally alumina, zeolite and *redmud* used as a catalyst in the pyrolysis process for biodiesel production. The pyrolysis process will occur at temperatures between 250^{THE}C and 350^{THE}C.[16] Fuel obtained by pyrolysis can be made cheaper than that obtained by transesterification.

In this method, vegetable oil molecules are broken down into smaller molecules in an airtight manner at high temperatures. This process occurs in the form of separation of C-C or C-H bonds. This process is divided into three parts: *hydro cracking*, *catalytic cracking* And *thermal cracking*. The amount of product produced depends on the method used and the reaction parameters. Solid products are obtained at low reaction rates at low temperatures and liquid products are obtained under operating conditions at fast reaction times and increased reaction temperatures.[15] The pyrolysis process uses high energy because the fuel properties of vegetable oil are close to those of diesel fuel. The pyrolysis process is a good method because it is easy and efficient among other processes because it can produce *yield* high.[8]

4. Esterification and Transesterification

Esterification and transesterification reactions are common methods for producing biodiesel. The esterification reaction is used to remove FFA by reacting FFA and alcohol with the help of a sulfuric acid catalyst. Esterification is the conversion stage of carboxylic acids or their derivatives into esters.[17] With esterification, the free fatty acid content can be minimized to 2% and additional esters can be obtained.[18]

The esterification reaction is a slow reaction so it requires a catalyst to support the reaction speed. The homogeneous catalyst commonly used in industry is sulfuric acid. H ion $^{+}$ from sulfuric acid as a strong acid encourages the carboxylic acid to be protonated so that the reaction can occur. Therefore, sulfuric acid has higher activity compared to heterogeneous catalysts such as resin or zeolite.[19]

Biodiesel is obtained from vegetable oil by transesterification reaction. The transesterification reaction is changing the triglycerides produced by the esterification reaction back into the reaction using methanol with the help of a catalyst.[20] The main purpose of transesterification is to break the chains in glycerol and produce *fatty acid alkyl ester*. This reaction is based on one mole of triglyceride with three moles of methanol which react to produce three moles of methyl ester (biodiesel) and also one mole of glycerol.

Biodiesel produced by the transesterification reaction has a high conversion percentage. The byproducts of the transesterification reaction and the homogeneous acid catalyst trigger corrosion in the reactor. and a homogeneous base catalyst causes saponification to occur.[8]

d. Purification Methods After Production

Crude Biodiesel must be purified to reach quality standards. Impurities in biodiesel can trigger engine damage. The aim of the purification stage is to remove impurities such as unconverted triglycerides, FFA, monoacylglycerol, diacylglycerol, glycerol, water, catalyst and soap.[21] Biodiesel purification methods can be carried out using *wet washing*, *dry washing*, distillation and membranes.[22]

The main technique used in industry today is the wet washing technique (*wet washing)* and dry washing techniques with adsorption (*dry washing)*. The wet washing technique is a method for removing biodiesel impurities such as soap, catalyst, glycerol and alcohol residue using water as a washing agent. Other cleaning agents that can be used are phosphoric acid, sulfuric acid and hydrochloric acid.[23] Using 10% phosphoric acid as a washing agent produces biodiesel products with brighter colors after purification.[24]

Washing *crude* biodiesel can also be made using *water washing machine*. Operating conditions with a volume ratio of 0.8:1 (water: *crude* biodiesel) and a flow rate of 4L/minute for 0.5 minutes, the density and viscosity of biodiesel meet international biodiesel standards. The washing technique used in *water washing machine* namely method *spray washing* for *crude* biodiesel. This technique is recommended for purification *crude* biodiesel because it saves water and short operating time.[25]

Method *dry washing* on purification *crude* biodiesel is a method for removing contaminants using adsorption or ion exchange resin. Several adsorbents that can be used include: *Amberlite*, *purolite*, *cellulosics*, *Magnesol*, *Trisy*, activated carbon, *activated fiber*, and clay. Adsorbents consist of basic and acidic adsorption sites that can easily attract polar compounds such as glycerol and methanol.[23]

Method *dry washing* can improve fuel quality, reduce washing time and does not produce waste water. In addition, method *dry washing* can also reduce production costs and reduce production time. This process produces quality biodiesel because no water is added, the resulting biodiesel contains water below 500 ppm as specified by ASTM D6751. Method *wet washing* produces biodiesel with a water content higher than 1000 ppm so this method requires a long time and uses a lot of water in its operation.[23]

Method application *dry washing* namely biodiesel made from used cooking oil which is purified using rice husk ash with varying concentrations which are then compared with the use of adsorbents in the form of 1% magnesol and 1% phosphoric acid. Purification of biodiesel using 4% rice husk ash produces biodiesel with good quality.[26]

Magnesol is effective for eliminating *impurities* such as metals, alcohol, diglycerides, glycerol and soap. Magnesol with a concentration of 1% and 600 rpm gives the best results because it meets international standards, EN 14214 in terms of density, acid number, free glycerol, methanol, triglyceride and mono-glyceride content.[27]

e. Biodiesel Quality Standards

Standardization of quality requirements for biodiesel is needed so that it complies with established specifications. Biodiesel specifications can be seen from viscosity, density, acid number, total glycerol and methyl ester content. Viscosity is a value that states the thickness of a liquid. Flow at a fast rate indicates that the viscosity of the liquid is low, whereas if the flow speed is slow, the viscosity of the liquid is higher.[28]

Density or density is the ratio of the weight of a volume such as the weight of water at the same volume and temperature.[29] Density is an indicator of the amount of impurities contained in biodiesel. The density of an oil will affect the performance of the engine because the ratio of the amount of air and energy in the engine combustion chamber is influenced by the density.

The acid number is the number of milligrams of KOH needed to neutralize free fatty acids from one gram of oil or fat. A high acid number is an indicator that biodiesel still has free fatty acids. According to Sangha et al (2004), stated that acid numbers that are too high are undesirable because at high temperatures free fatty acids can react with metals such as iron, zinc, lead, manganese, cobalt, tin and other metals, where this event can accelerate damage. diesel engine components.[30]

Glycerol and glycerides are by-products of biodiesel production which can be harmful to diesel engines because of the presence of OH groups which are chemically aggressive towards non-ferrous metals and chrome mixtures. A decrease in total glycerol levels due to the addition of methanol will encourage the reaction towards the formation of methyl ester as the main product and glycerol as a side product will decrease.[31]

The methyl ester content is calculated to determine the amount of methyl ester formed after the biodiesel synthesis process.[32] The amount of methyl ester in biodiesel is influenced by the reaction time and the amount of catalyst used. The longer the reaction time, the more methyl ester produced. However, if the reaction time is too long, a reverse reaction can occur which converts the methyl ester back into triglyceride.[33] The following is a table of standard biodiesel quality values in Indonesia.

Table 2. Biodiesel Quality Requirements

Parameter Test	Units, min/max	Condition
Density at 40^{the}C	Kg/m3	850-890
Kinematic viscosity at 40^{the}C	mm^2/s (cSt)	2,3-6,0
Demon number	min	51
Flash point	^{the}C, min	100
Acid number	mg-KOH/g, maks	0,5
Glycerol free	% mass, max	0,02
Gliserol total	% mass, max	0,24
up to methyl ester	% mass, min	96,5
Monogliserida	% mass, max	0,8

(Source: *SNI 7182-2015).*

f. Biodiesel Transesterification Process Factors

Transesterification reactions generally involve several critical parameters that can significantly influence the final conversion and yield.[34] Factors that can influence the transesterification process are reaction temperature, reaction time, alcohol to oil molar ratio, amount of fatty acids, water content, stirring, and the catalyst used.

The reaction temperature greatly influences the reaction speed. The faster molecular movement and the increasing reaction rate are the effect of increasing temperature so that the conversion increases. An increase in temperature causes the reactants to get more energy to reach the activation energy so that the reaction takes place more quickly. Temperatures that are too high can cause the oil to foam.[35]

A longer reaction time provides more time for methanol and triglycerides to react with each other. Research conducted by Hikmah and Zuliyana (2010) stated that the longer the transesterification time, the longer the transesterification time *yield* the output is getting bigger.[36] If the reaction time is too long, the remaining free fatty acids that do not participate in the esterification process will react with NaOH to form soap *yield* formed did not experience a significant increase.

The transesterification process is a reaction *reversible*. Increasing alcohol content can shift the equilibrium towards the product. The molar ratio influences the viscosity of biodiesel. The more biodiesel yield produced, the higher the molar ratio of alcohol provided. Research conducted by Ahmad et al. (2019), using variations in the methanol ratio of 4.5, and to the oil ratio.[37] *Yield* The biodiesel produced is 99.54% with variations in the methanol 6 to oil ratio so that adding the methanol molar ratio can increase the percentage *yield* from the biodiesel synthesis reaction.

The fatty acids contained in used cooking oil can cause a saponification reaction, which will interfere with the reaction. The saponification reaction can result in the formation of an emulsion which has the potential to thwart the synthesis reaction and reduce biodiesel yield, as well as making it difficult to separate the product from glycerol. The transesterification process requires oil with high purity, namely with an FFA content of less than 5%, to avoid the possibility of side reactions.[38]

The presence of water can also have a negative influence on the biodiesel synthesis reaction because it can result in the hydrolysis of triglycerides into FFA. The high water content in biodiesel can cause a decrease in combustion heat, foaming, is corrosive if it reacts with sulfur because it will form acid, and provides space for microbes to grow so that it will become an impurity for biodiesel.[39]

The stirring process can increase the movement of material particles. As the movement of material particles increases, collisions and contact between material particles will become more frequent. That way, the chemical reaction will take place more quickly. In order for chemical reactions to occur more quickly, the substances that react require stirring.[40]

The transesterification process is influenced by catalysts such as homogeneous catalysts, heterogeneous catalysts, and biocatalysts. The more catalysts are used, the more methoxide ions are formed so that more oil is converted. Too much catalyst is also not good. Too much quantity encourages side reactions. Research conducted by Mantovi (2017) used a 6% CaO catalyst to produce *yield* amounting to 88.62%.[41] Increasing the number of catalysts has the effect of increasing the conversion of fatty acids into esters. The greater the number of catalysts in the transesterification reaction will reduce the biodiesel conversion, this is because the reaction tends to return to normal.

g. Types of Catalysts

The rate of transesterification is generally slow. The addition of a catalyst increases the contact area between reactants thereby increasing the reaction rate. Catalytic transesterification reactions use chemical or biological catalysts. Chemical catalysts consist of homogeneous and heterogeneous catalysts, while biological catalysts are enzyme catalysts.[42]

The choice of catalyst depends on the quality of the oil, quantity of FFA content in the oil, operating conditions, cost and availability.[43]

1. Homogeneous Catalyst

A homogeneous catalyst is a catalyst that is in the same phase as the reactants. Homogeneous catalysts consist of base catalysts and acid catalysts. On a laboratory and industrial scale, the most commonly used catalysts are homogeneous base catalysts such as NaOH, KOH and metal hydroxides such as NaOCH.$_3$, Archeology$_3$The serta NaOC$_2$H$_5$. Homogeneous base catalysts are most widely used because of their operating conditions and fast reactions.[44] The use of a homogeneous base catalyst produces *yield* high biodiesel. The NaOH catalyst is used in the biodiesel production process using raw materials in the form of *virgin oils* and used cooking oil. *Yield* produced on *virgin oils* and used cooking oil produces 97% and 92% biodiesel.[45]

Sodium-based catalysts are better than KOH catalysts when methanol is the solvent because of their rapid solubility in methanol and higher yields.[46] A significant advantage of homogeneous base catalysts is that they are cheap and produce high quality products in a short time.[47] The reaction rate of the reaction with a base catalyst is 4000 times faster than that with an acid catalyst.[48] Alkaline catalysts have limited use of raw materials due to side reactions, namely the formation of soap if the FFA content is >0.5% and the water content is >0.06%. Another major drawback, the catalyst used cannot be recovered so it can cause environmental problems.[49]

The acid catalyst is not affected by the FFA content in *crude oil* so that it can catalyze esterification and transesterification reactions simultaneously. So, raw materials with high FFA content such as used cooking oil can use an acid catalyst.[47] The use of acid catalysts such as H_2SO_4, H_2SO_3, HCl, and $Fe_2(SO_4)_3$. The most commonly used acid catalyst is H_2SO_4 with moderate reaction temperature and atmospheric pressure.

Research by Dewati et al (2013), using the H catalyst$_2$SO$_4$ in the esterification reaction of biodiesel made from used cooking oil.[50] The reaction temperature used was 65^{the}C with a catalyst amount of 2% by weight of oil obtained a biodiesel conversion of 43.2%. The weakness of the acid catalyst is the formation of water during the esterification process from the reaction of FFA and alcohol, thereby inhibiting the transesterification reaction. Catalyst reuse is a challenge in the biodiesel production process because it can result in contamination, corrosion and difficulties in product separation and purification. *Loss* biodiesel occurs significantly during product washing so that extra energy is required when refining the product which consequently increases the overall cost of biodiesel production.[14]

2. Heterogeneous Catalysts

A heterogeneous catalyst is a catalyst that has a phase that is not the same as the substance to be reacted. Heterogeneous catalysts have the advantages of more practical separation of catalyst and product, high activation energy, non-corrosiveness, and long service life.[51] Heterogeneous catalysts can reduce soap formation, are economical because they can be reused in biodiesel production so their use can be carried out continuously in *fixed bed reactor* which can be used on an industrial scale.[52]

Heterogeneous catalysts are categorized into heterogeneous acid catalysts and heterogeneous base catalysts. Heterogeneous acid catalysts can synthesize biodiesel through esterification and transesterification while replacing homogeneous acid catalysts. The advantages of a heterogeneous acid catalyst are that it eliminates the biodiesel washing step, the process of separating the catalyst from the product is simpler, it can be reused and reduces corrosion.[53]

The properties of a solid acid catalyst must have a large pore size, strong acidity and hydrophobicity. Some solid heterogeneous acid catalysts such as metal oxides, mixed oxides, sulfated metal oxides, sulfonated carbon, cation exchange resins, *heteropolyacids* and zeolite.[54] The biodiesel production process is carried out using a solid catalyst with a strong acid, S$_2$THE$_8$$^{2-}$ /ZrO$_2$. Biodiesel is produced using expired soybean oil with a methanol to oil ratio of 20:1 at 100^{the}C and a reaction time of 4 hours produces *yield* 100% biodiesel. The catalyst used shows high stability.[55]

Heterogeneous acid catalysts are catalysts with slower reactions than heterogeneous base catalysts, in addition to requiring higher temperatures, a high amount of catalyst and a higher methanol to oil ratio. Heterogeneous base catalysts such as alkali oxides, alkaline earth metal oxides, *hydrotalcite*, *metallic salt*, anion exchange resin and zeolite.[48] Alkaline earth oxide catalysts are widely used because they are cheap and have high alkaline properties, but for the catalytic activity of metal oxide catalysts they are effective for biodiesel production.

The biodiesel process is carried out by mixing used palm oil with methanol and adding the CaOZnO catalyst where CaO is calcined at a temperature of 800^{the}C for 6 hours. The transesterification reaction was carried out with CaOZnO under N gas$_2$ in a tube at 800^{the}C for 1 hour then the mixture is heated to a temperature of 65^{the}C for 3 hours. The methyl ester produced with the CaO catalyst was 96.49%. The use of a heterogeneous base catalyst produces *yield* which is high with a fast reaction rate and is environmentally friendly, non-corrosive and potentially cheaper. However, the use of a base catalyst means that the molar ratio of methanol to oil is high and side reactions occur if the FFA content is> 2% by weight. There is a need for comprehensive exploration and development to reduce saponification and diffusion limitations so as to produce better yields.

3. Enzyme Catalyst

Enzyme catalysts or biocatalysts come from lipase enzymes produced by microorganisms, animals and plants. Enzyme catalyst is a potential catalyst for industrial scale biodiesel production because it is non-toxic, tolerant to organic solvents, can be used on raw materials with high FFA levels and can be reused.

The application of an enzyme catalyst to used cooking oil was carried out by Jayaraman et al (2020), the enzyme catalyst used was lipase with a weight of 1.5% by weight of the oil. The biodiesel production reaction takes 4 hours with a molar ratio of methanol to used cooking oil of 3:1 with a reaction temperature of 60^{the}C. The conversion of biodiesel produced was 88%. The biodiesel produced was subjected to an engine test where a mixture of 40% biodiesel made from used cooking oil and diesel produced a low CO emission value of 0.11% with an engine workload of 100%.

Enzyme catalysts have disadvantages, including that the reaction is limited to a certain temperature range. If the temperature is too high, the proteins in the enzyme will be denatured and the enzyme will not be able to work optimally. The use of enzyme catalysts is still limited because they are expensive, unstable, the reaction speed is relatively slow and enzymes experience deactivation. The development of enzyme catalysts is needed so that the process is more environmentally friendly and meets environmental needs. This process has the potential to produce high quality products that can compete with petrodiesel fuel.

h. Related Research

Several studies relate to the production of biodiesel from used cooking oil using various types of catalysts.

Table 3. Production of Biodiesel from Used Cooking Oil

Raw material	**Catalyst**	**Operating Conditions**	**Results**	**Reference**
Used cooking oil	K_2CO_3 /$_{\gamma}$-To_2THE_3	Reaction temperature 45, 55, 65^{the}C. The mole ratio of used cooking oil to biethanol is 1:9 for 120 minutes.	The conversion was 86.39% at a temperature of 65^{the}C and time 60 minutes	Handayani et al (2023)
Used coconut oil (used cooking oil)	Esterification reaction: H_2SO_4 Transesterification Reaction: KOH	Reaction temperature 60^{the}C was carried out for 30, 45, 60 and 75 minutes.	Conversion of 80.28%	Yuniwati and Karim (2009)
Used cooking oil	NaOH	Reaction molar ratio 1:6. The reaction time consists of 0.25-10 minutes with a reaction temperature variation of 30-55^{the}C	The highest biodiesel yield was 78.44% at a temperature of 55^{the}C with a reaction time of 10 minutes	Gita dkk (2018)
Used Cooking Oil	NaOH/CaO/C	Reaction temperature 60^{the}C for 3 hours	The yield of biodiesel produced was 84.2610% with a catalyst amount of 4.5% and a methanol:used cooking oil ratio of 0.5:1	About dkk, 2021
Used cooking oil	Gismondine zeolite	Reaction time 6 hours with reaction temperature 65^{the}C. The ratio of catalyst: used cooking oil: methanol is 1:20: 13.3	The percentage of methyl ester formed is 85%	Salim, 2020
Used Cooking Oil	Biocatalyst of crude	The enzyme: substrate ratio is 1:1 to 1:7 with a	The esterification	Nenobahan et

	extract of lipase from kesambi seeds (*Schleicheraoleosal*)	temperature of 40^{the}C	process produces quite high activity of 366.67 U/mL.	al, (2020)
Used Cooking Oil	Lipase from bacteria *Candida* sp.	The weight ratio of lipase:hexane:water: used cooking oil is 25:15:10:100 at a temperature of 45^{the}C and flow rate 1.2 ml/min	*Yield* FAME produced 91.08%	Chen dkk (2009).
Used Cooking Oil	CaO/KI/ γ-Al$_2$THE$_3$	The amount of catalyst is 6% by weight with a temperature of 35-65^{the}C for 5 hours. The molar ratio of oil to methanol is 1:15	*Yield* FAME of 83.08%	Asri et al (2015).
Used cooking oil	Ferric suphate + Acid catalyst	Reaction temperature 60^{the}C for 3 hours with a methanol to oil molar ratio of 7:1	*Yield* FAME of 81.3%	Omar dkk, (2009).
Used cooking oil	Ash Tandan Koong Sawit Palm (ATKKS)	Reaction time varies from 1-5 hours with a temperature of 70^{the}C	Methyl ester levels from 1-5 hours are 98.42% - 98.94%	Manik et al, (2017).

From several studies above, the highest methyl ester content was using an empty palm fruit bunch ash (ATKKS) catalyst of 98.94% for 5 hours of reaction time. Research conducted by Desi (2024), produces biodiesel through a transesterification reaction using a potassium glycerolate catalyst from a DES catalyst (*Deep Eutectic Solvent* – K$_2$CO$_3$-glycerol). The raw materials used are *Refined Bleached Deodorized Palm Oi* (RBDPO) produced a conversion of 96.77% with a methyl ester content of 97.81% during 4 hours of reaction at a temperature of 65^{the}C.

IV. CONCLUSION

Pretreatment used cooking oil needs to be done to reduce the FFA content and water content. Biodiesel production methods generally use esterification and transesterification reactions because the process is simple and more economical. There are types of catalysts that can be used during the transesterification reaction, namely homogeneous catalysts, heterogeneous catalysts and enzyme catalysts.

Based on data from various literature, biodiesel made from used cooking oil produces the highest methyl ester content of 98.94% using a heterogeneous base catalyst, namely ATKKS. The final conversion of biodiesel is influenced by several parameters such as reaction temperature, reaction time, alcohol to oil molar ratio, amount of fatty acids, water content and catalyst used.

REFERENCES

[1] Hidayati, N., Ariyanto, T.S., dan Septiawan H. 2017. Transesterifikasi Minyak Goreng Bekas Menjadi Biodiesel dengan Katalis Kalsium Oksida. *Jurnal Teknologi Bahan Alam*. Vol.1(1): 1-5.

[2] Trisnaliani, L., Fatria., dan Sari, I.M. 2018. Proses Produksi Biodiesel dari Minyak Jelantah Menggunakan *Microwave Hydro Distillation* dan Separasi Tegangan Tinggi. *Politeknik Negeri Sriwijaya, Jurnal Kinetika*. Vol. 9 (2): 25-30.

[3] Sulistianingsih., dan Wahyuningtyas, D. 2019. Optimasi Pembuatan Biodiesel dari Minyak Jelantah Dengan Katalisator Kalsium Oksida (CaO) dengan Proses Metanolisis (Variabel Suhu Reaksi). *Jurnal Inovasi Proses*. Vol. 4(2): 81-87.

[4] Kapuji, A. Hadi, S., dan Arifin, Z. 2021. Proses Pembuatan Biodiesel dari Minyak Jelantah. *Jurnal Chemtech*. Vol. 7(1): 1-6.

[5] Mathiyazhagan, M., dan Ganapathi, A. 2011. Factors Affecting Biodiesel Production. *Research in Plant Biology*. Vol.1(2):1-5.

[6] Kusumastuti. 2004. Kinerja Zeolit dalam Memperbaiki Mutu Minyak Goreng Bekas. *Jurnal Teknologi dan Industri Pangan*. Vol. 15(2): 141-144.

[7] Sarungu, S., Lukman., dan Paelongan, S. L.P. 2020. Analisa Karakteristik Biodiesel Hasil Tranesterifikasi Minyak Jelantah Menggunakan Katalis KOH. *Petrogas*. Vol. 2(1): 57-76.

[8] Budiman, A. A., dan Samik, S. 2023. Review Artikel: Produksi Biodiesel dari Minyak Goreng Bekas dengan Metode Transesterifikasi Menggunakan Katalis. *UNESA Journal of Chemistry*. Vol. 12(2): 36-48.

[9] Kartika, D. dan Widyaningsih, S. 2012. Konsentrasi Katalis Dan Suhu Optimum Pada Reaksi Esterifikasi Menggunakan Katalis Zeolit Alam Aktif (ZAH) Dalam Pembuatan Biodiesel Dari Minyak Jelantah. *Jurnal Natur Indonesia*. Vol. 14(3): 219-226.

[10] Sutanto, C. F., Wiryawan, F. P., dan Kurniawansyah, F. 2021. Pra Rancangan Pabrik Biodiesel dari Minyak Jelantah Menggunakan Metode Transesterifikasi dengan Kapasitas 50.000 Ton/Tahun. *Jurnal Teknik ITS*. Vol. 10(2): F210- F215.

[11] Almagribi, I. Q., Dzakiyy, A. H., dan Hafizh, H. 2022. Pemanfaatan Kulit Pisang sebagai Penjernihan Minyak Jelantah Solusi untuk Kelangkaan Minyak Goreng bagi Masyarakat. *Esabi*. Vol.4(2): 1-8.

[12] Ariyani, S. B., Asmawit., dan Hidayati. 2016. Karakteristik Biodiesel dari Minyak Jelantah Menggunakan Katalis Abu Tandan Kosong Sawit. *Jurnal Penelitian dan Pengembangan Borneo Akcaya*. Hal. 38-47.

[13] Latief, M., Mahendra, I., Nurmawati, A., Saputro, W., dan Saputro, E. A. 2023. Uji Efektifitas Adsorpsi dan Degumming Pada Minyak Jelantah Sebagai Bahan Baku Pembuatan Biodiesel. *Seminar Nasional Teknik Kimia Soebardjo Brotohardkono XIX*. Hal.: 49-54.

[14] Singh, D., Sharma, D., Soni, S. L., Sharma, S., Sharma, P.K., dan Jhalani, A. 2020. A review on feedstocks, production processes, and yield for different generations of biodiesel. *Fuel*. Vol. 262: 1-15.

[15] Aktas, E. S., Demir, O., dan Ucar, D. 2020. A Review Of The Biodiesel Sources and Production Methods. *International Journal of Energy and Smart Grid*. Vol. 5(1): 1-10.

[16] Rajalingam, A., Jani, S.P., Kumar, A. S., dan Khan, M. A. 2016. Review Article: Production Method of Biodiesel. *Journal of Chemical and Pharmaceutical Research*. Vol. 8(3): 170-173.

[17] Otera, J. 2003. *Esterification: Methods, Reaction, And Application*. Weinheim: Wiley-VCR Verlag GmbH And Co.

[18] Ramadhas, 2005, Pembuatan Biodiesel dari Minyak Sawit dengan Esterifikasi Dua Tahap, Laporan Penelitian, Laboraturium Proses Kimia, Jurusan Teknik Kimia, Universitas Gadjah Mada, Yogyakarta.

[19] Fakhry, M. N., dan Rahayu, S. S. 2016. Pengaruh Suhu pada Esterifikasi Amil Alkohol dengan Asam Asetat Menggunakan Asam Sulfat sebagai Katalisator. Jurnal Rekayasa Proses. Vol. 10(2): 64-69.

[20] Sarandon, K. A., Siregar, A. L., dan Rahardja, I. B. 2019. Pembentukan Biodiesel Melalui Proses Transesterifikasi dengan Katalis Abu Tandan Kosong Kelapa Sawit (ATKKS). Seminar Nasional Sains dan Teknologi. Hal. 1-7.

[21] Niawanti, H. 2020. Review Perkembangan Metode Produksi dan Teknologi Pemurnian dalam Pembuatan Biodiesel. *J. Chemurg.* Vol.4(1): 27.

[22] Berrios, M., dan Skelton, R. L. 2008. Comparison of Purification Methods For Biodiesel. *Chemical Engineering Journal.* Vol. 144(3): 459-465.

[23] Atadashi, I. M. 2015. Review: Purification Of Crude Biodiesel Using Dry Washing And Membrane Technologies. *Alexandria Engineering Journal.* 54: 1265-1272.

[24] Srivastava, P. K., dan Verma, M. 2008. Methyl Ester Of Karanja Oil As An Alternative Renewable Source Energy. *Fuel.* Hal: 1673-1677.

[25] Limmun, W., dan Sansiribhan, S. 2020. Water-Spray Washing Techique As A Purification Process In The Production Of Biodiesel. *TSAE.* Hal: 1-8.

[26] Manique, M.C., Faccini, C.S., Onorevoli, B., Benvenutti, E. V., dan Caramao, E. B. 2012. Rice Husk Ash As An Adsorbent For Purifying Biodiesel From Waste Frying Oil. *Fuel.* Vol. 92(1): 56-61.

[27] Berrios, M., Martin, M.A., Chica, A.F., dan Martin, A. 2011. Purification Of Biodiesel From Used Cooking Oils. *Energy*. Vol. 88(11): 3625-3631.

[28] Sutiah, K., S. Firdaus, dan W. S. Budi. 2008. Studi Kualitas Minyak Goreng Dengan Parameter Viskositas dan Indeks Bias. *Berkala Fisika.* Vol. 11: 53 -58.

[29] Ketaren, S. 2005. Pengantar Teknologi: Minyak dan Lemak Pangan. Jakarta: UI- Press.

[30] Sangha, M. K., Gupta. P. K., Thapar, V. K., dan Verma. 2004. Storage Studies on Plants Oil and Their Methyls Esters. Agricultural Engineering International: the CIGR Journal of Scientific Research and Development Manuscript EE 03 005. Vol. (6): 1-15.

[31] Zalfiatri, Y., Ratuhadi, F., dan Zulhardi, R. 2019. Karakteristik Biodiesel dari Minyak Menggunakan Katalis Abu Gosok dengan Variasi Penambahan Metanol. Chempublish Journal. Vol. 4(1): 1-8.

[32] Dimawarnita, F., Emha, Z. M. F., Koto, A., dan Faramitha, Y. 2023. Karakteristik Sifat Fisika Kimia Biodiesel Berbasis Minyak Nabati. Warta PPKS. Vol. 28(1): 15-26.

[33] Faizal, U.M., Maftuchah, dan Auriyani, W. A. 2013. Pengaruh Kadar Metanol, Jumlah Katalis, Dan Waktu Reaksi Pada Pembuatan Biodiesel Dari Lemak Sapi Melalui Proses Transesterifikasi, Jurnal Teknik Kimia. Vol. 19(4): 29 37.

[34] Talebian-Kiakalaieh, A., Amin, N. A. S., dan Mazaheri, H. 2013. A Review on Novel Processes of Biodiesel Production from Waste Cooking Oil. Applied Energy. 104: 683–710.

[35] Pramitha, R. I., Haryanto, A., dan Triyono, S. 2016. Pengaruh Perbandingan Molar Dan Durasi Reaksi Terhadap Rendemen Biodiesel Dari Minyak Kelapa (Coconut Oil) Effect Of Molar and Comparative duration Reaction To Rendemen From Coconut Oil Biodiesel (Coconut Oil). Jurnal Teknik Pertanian Lampung. Vol 5(3): 157–166.

[36] Hikmah, M. N., dan Zuliyana. 2010. Pembuatan Metil Ester (Biodiesel) dari Minyak Dedak dan Metanol dengan Proses Esterifikasi dan Transesterifikasi. Jurnal Teknik Kimia. Vol.1(1): 1-7.

[37] Ahmad, T., Danish, M., Kale, P., Geremew, B., Adeloju, S. B., Nizami, M., dan Ayoub, M. 2019. Optimization of Process Variables for Biodiesel Production by Transesterification of Flaxseed Oil and Produced Biodiesel Characterizations. Renewable Energy. 139:1271-1280.

[38] Aziz, I., Nurbayti, S., dan Ulum, B. 2011. Esterifikasi Asam Lemak Bebas Dari Minyak Goreng Bekas. Jurnal Kimia VALENSI. Vol. 2(2): 384–388.

[39] Adhani, L., Aziz, I., Nurbayati, S., dan Oktaviana, C. O. 2016. Pembuatan Biodiesel dengan Cara Adsorpsi dan Transesterifikasi dari Minyak Goreng Bekas. Jurnal Kimia VALENSI. Vol.2(1): 71-80.

[40] Miskah, S., Apriani, R., dan Miranda, D. 2017. Pengaruh Waktu Reaksi dan Kecepatan Pengadukan Terhadap Konversi Biodiesel dari Lemak Ayam dengan Proses Transesterifikasi. Jurnal Teknik Kimia. Vol. 23(1): 57-67.

[41] Mantovi, S. A. 2017. Pengaruh Jumlah Katalis dan Waktu Reaksi Terhadap Konversi Biodiesel dari Minyak Jelantah dengan Katalis CaO dari Kulit Telur. [SKRIPSI]. Universitas Muhamadiyah Surakarta.

[42] Mandari, V., dan Devarai, S. K. 2022. Biodiesel Production Using Homogeneous, Heterogeneous, and Enzyme Catalysts via Transesterification and Esterification Reactions: a Critical Review. *Bioenergy Research.* 15: 935-961.

[43] Pascacio, T., Sanchez., dan T. Magro. D. 2019. Comparison of Acid, Basic and Enzymatic Catalysis On The Production Of Biodiesel After RSM Optimization. *Renew Energy.* 135: 1-9.

[44] Abelniece, Z., Laipniece, L., dan Kampars, V. 2020. Biodiesel Production By Interesterification Of Rapeseed Oil With Methyl Formate in Presence of Potassium Alkoxides. *Biomass Convers Biorefinery.* 10:1-9.

[45] Dias, J.M., Alvim-Ferraz, M.C.M., dan Almeida, M.F. 2008. Comparison of The Performance of Different Homogeneous Alkali Catalysts During Transesterification of Waste and Virgin Oils and Evaluation of Biodiesel Quality. *Fuel.* 87: 3572-3578.

[46] Thangaraj. B., dan Solomon P.R. 2019. Immobilization of lipases – a review Part I: Enzyme Immobilization. *ChemBioEng.* 6:157–166.

[47] Lam, M.K., Lee, K.T., dan Mohammed, A.R. 2010. Homogeneous, Heteregeneous, and Enzymatic Catalysis for Transesterification of High Free Fatty Acid Oil (Waste Cooking Oil) to Biodiesel, A review. *Biotechnol.* 28: 500-518.

[48] Talha, N.S., dan Sulaiman, S. 2016. Overview of catalysts in biodiesel production. *ARPN J Eng Appl Sci.* 11:439–442.

[49] Selvakumar, P., dan Sivashanmugam, P. 2017. Optimization of lipase production from organic solid waste by anaerobic digestion and its application in biodiesel production. *Fuel Process Technol.* 165:1–8.

[50] Dewati, P. R., 2013. Optimasi Proses dan Studi Kinetika Reaksi Pada Sintesa Biodiesel Dari *Used Cooking Oil* (CPO) Dengan Reaksi Etanolisis. *[TESIS]:* Fakultas Pascasarjana UGM, Yogyakarta.

[51] Ruhaiya, F., Nisa, H. C., Hafidh, M., dan Kurniasih, E. 2020. Jurnal Review : Transesterifikasi Minyak Kelapa Sawit pada Produksi Biodiesel dengan Katalis Heterogen CaO. *Jurnal Teknik dan Teknologi.* Vol.15(3):23-29.

[52] Malani, R. S., Sardar, H., dan Malviya, Y. 2018. Ultrasound-Inten Sified Biodiesel Production From Mixed Nonedible Oil Feedstock Using Heterogeneous Acid Catalyst Supported On Rubber De-Oiled Cake. *Ind Eng Chem Res.* 57:14926–14938.

[53] Shu, Q., Gao, Z., Nawaz, Y., Liao, D., Wang., dan Wang, J. 2010. Synthesis of Biodiesel From Waste Vegetable Oil With Large Amounts of Free Fatty Acid Using A Carbon-Based Solid Acid Catalyst. *Appl Energy.* Vol. 87(8): 2589-2596.

[54] Carvalho, A.K.F., Conceicao, L.R.V., dan Silva, J.P.V. 2017. Biodiesel Production From Mucor circinelloides Using Ethanol and Heteropolyacid In One and Two Step Transesterification. *Fuel.* 202:503-511.

[55] Wang, H.G., Shi, G.L., Yu, F., dan Li, R.F. 2016. Mild Synthesis of Biofuel Over a Microcrystalline $S_2O_8^{2-}/ZrO_2$ Catalyst. *Fuel Process Technol.* 145:9-13.