Available online at www.elixirpublishers.com (Elixir International Journal)



Applied Chemistry



Elixir Appl. Chem. 120 (2018) 51235-51242

Comparative Study of Transesterification Processes for Biodiesel Production (A Review)

Montcho Papin S., Konfo T. R. Christian, Agbangnan D. C. Pascal, Sidouhounde Assou and Sohounhloue C. K.

Dominique

Laboratory Of Study And Research In Applied Chemistry, Polytechnic School Of Abomey-Calavi, University Of Abomey-Calavi, 01 PO Box: 2009 Cotonou, Benin.

ARTICLE INFO Article history: Received: 28 May 2018; Received in revised form: 1 July 2018; Accepted: 10 July 2018;

Keywords

Processes, Transesterification, Biodiesel, Benin.

ABSTRACT

Energy demand is increasing while fossil fuels, the main source of energy, threaten their depletion and consequently their market value increases. In addition to this crisis, climate change and air pollution caused by the combustion emissions of fossil fuels pose problems of increased greenhouse effect. Due to the environmental problems caused by the use of fossil fuels, attention has been paid to the production of biodiesel as an alternative to petrodiesel. Biodiesel is an environmentally friendly alternative diesel fuel made from renewable resources made from vegetable oils and animal fats. It is a renewable energy source that seems to be an ideal solution for global energy needs. The current method of biodiesel production is the transesterification of the inedible oil with an alcohol (methanol or ethanol) in the presence of a catalyst or not. The transesterification reaction is very sensitive to the parameters and oil nature such as the acid composition and the free fatty acid content. Other variables include reaction such as temperature, ratio of alcohol to vegetable oil, catalyst, and intensity of mixing, purity of reagents. The development of biofuels creates new agricultural sectors and could offer new niche markets for farmers in exploitable areas. This study aims to make a comparative study transesterification processes for biodiesel production.

© 2018 Elixir All rights reserved.

Introduction

The search for alternative fuels to replace petroleum derived fuels is currently a highly studied topic. Biofuels such as biodiesel and bioethanol are considered an appropriate alternative to traditional fuels. These petroleum derived fuels are not a long-term energy source. Indeed, oil reserves can be depleted by 2054 [1]. Biofuels have become one of the major solutions to the problems of sustainable development, energy security and the reduction of greenhouse gas emissions [2]. Biodiesel has properties very similar to those of fossil diesel, but with emissions of sulfur, carbon dioxide (CO_2) and much smaller particles [3]. The use of vegetable oils as alternative fuels has been around for a long time but has been set aside due to the availability of petroleum products that appears to be cheaper. Biodiesel is now recognized as an alternative because it has several advantages over conventional diesel [4]. It is safe, renewable and non-toxic (about 98% biodegradable in just a few weeks). It contains fewer sulfur compounds and has a high flash point (130°C). It is almost neutral with respect to carbon dioxide emissions and emits 80% less hydrocarbons and 50% fewer particles. It has a positive social impact, by reinforcing rural revitalization [5]. It is the only alternative fuel currently available with a generally positive energy balance, producing up to 3.2 units of energy for every unit of fossil energy consumed during its life cycle, compared with just 0.83 unit for fossil diesel [6]. Biodiesel does not contain any petroleum products, but can be mixed with conventional diesel. A mixture of petroleum (80%) and biodiesel (20%) (known as B20) can be used in unmodified diesel engines.

Biodiesel can also be used in its pure form (B100), but this requires minor engine modifications to avoid maintenance problems. With the inevitable depletion of non-renewable resources of fossil fuels and because of its favorable environmental characteristics, biodiesel promises to be the fuel of tomorrow. Nevertheless, there are many barriers to effective biodiesel production on an industrial scale. This review describes biodiesel production processes (transesterification), the most important variables that influence this reaction, and the advantages and disadvantages of transesterification processes.

Transesterification processes

Biodiesel synthesis by transesterification of oil can be carried out by various methods. Indeed, the reaction is feasible in the presence of a homogeneous catalyst, a heterogeneous catalyst but also in the presence of an enzymatic catalyst. Finally, it has been shown that the use of supercritical alcohols made it possible to dispense with these catalysts. The summary of the principle of use of the different transesterification processes is as follows (Figures 1, 2 and 3) [7].

Specificities of the main transesterification methods

Transesterification is a chemical reaction that consists of replacing the alcohol groups of an ester with other types of alcohol. Animal fat and vegetable oils consist mainly of triglycerides.

A triglyceride molecule is formed by the combination of a glycerin molecule with three molecules of long carboxylic acids chain called fatty acids.

© 2018 Elixir All rights reserved



Figure 1. Transesterification process in basic medium.





The resulting products of this reaction are glycerin and fatty acid esters. Indeed, there are various transesterification processes for the production of biodiesel. But its various processes the nature differ in of the catalyst Transesterification by homogeneous catalysis involves contacting the oil and the alcohol with a catalyst in the alcohol phase. The catalyst may be alkaline, acidic or enzymatic. The most common synthesis process at present is the homogeneous alkaline catalysis method, with sodium hydroxide, potassium hydroxide or sodium methanoate. This choice is linked, among other things, to economic reasons. With regard to heterogeneous catalysis, it is an alternative to the homogeneous catalysis of transesterification. The catalyst may be acidic or basic as in the homogeneous catalysis case.

The real utility of heterogeneous catalysis lies in reducing the costs of neutralization at the reactor outlet. Indeed, the catalyst being solid, it does not have to be separated in a dedicated step, limiting polluted effluents leaving the process. The solid catalyst is often considered to be easily recoverable and reusable. On the other hand, these catalysts are less effective than homogeneous catalysts. Heterogeneous catalysis introduces among other things the problem of limitations by the transfer of matter. The triphasic nature of the problem, consisting of the alcohol phase, the oil phase and the catalytic solid phase, is also a brake on conversion and yield [8, 9]. The two preferred methods for the industrial production of biodiesel from oils are basecatalyzed transesterification and acids. For against, biodiesel production catalyzed by an acid has received less attention because it is 400 times slower than the production using an alkali catalyst. Nevertheless, conversion of oils to acidcatalyzed biodiesel is less sensitive to free fatty acids in the oil than the alkali-catalyzed process. In the conventional homogeneous process, removal of these catalysts is very difficult therefore conventional homogeneous catalysts should be replaced by environmentally friendly heterogeneous catalysts. The replacement of homogeneous catalysts with heterogeneous catalysts would have various advantages such as the ease of separating the catalyst from the reaction mixture, the purification of the product and the reduction of environmental pollutants [10, 11, 12, 13]. The resulting biodiesel must meet the ASTM standard. Ethyl esters and methyl esters have almost the same heat content [14]. The acidic catalysts commonly developed generally require more stringent temperature and pressure conditions than those required by homogeneous catalysts. In the same way, the molar ratios between alcohol and oil must be higher in order to reach the thermodynamic balance and to override the introduced limitations [15]. In return, they are less polluting and reduce production costs [8]. The basic catalysts used are generally metal oxides. They are more active than acid catalysts and require a shorter reaction time. Calcium oxide (CaO) in particular can be used, mainly because it does not require particularly severe conditions to be effective [8]. Studies have been conducted showing that it is possible to use calcium oxide from the calcination of calcium carbonates from eggshells or shells, making the process even more environmentally friendly [16, 17, 18]. Besides the processes by homogeneous and heterogeneous catalysis, there are two synthetic routes and less common still in development namely: syntheses with supercritical alcohol and syntheses by enzymatic catalysis. In fact, the transesterification with supercritical methanol makes it possible to modify the conventionally biphasic oil/alcohol system into a monophasic system. Indeed, the supercritical state of methanol decreases its dielectric constant, leading to the formation of a single phase [19]. The reaction is then extremely fast, and does not require catalyst addition, facilitating the separation steps. Indeed, under supercritical conditions, methanol itself becomes acidic, catalyzing the reaction [20]. The temperature must be high, as well as the pressure. In addition, the molar ratio between methanol and oil is also very high. The use of supercritical alcohols is possible with other alcohols, such as ethanol, propanol, butanol or even octanol [21]. In addition, enzymatic catalysis synthesis is still a flourishing and promising field. The main advantages of this method of synthesis are a simple separation of the products, a small quantity of process water,

Tuble II Comparison of various transcisterification processes [24, 20, 20].							
Process	Basic	Acid	Enzymatic	Supercritical			
Caracteristic	transesterification	transesterification	Transesterification	Transestérification			
Yield alkyls	high (> 94%)	high (> 94%)	high (> 90%)	high (>95%)			
esters							
Reaction	Moderate (50 -	High (60 – 120) °C	Low (30 – 60°C)	High (200 at 280 °C)			
Temperature	70°C)						
Ratio alcohol:	Excess Alcohol,	High excess Alcohol,	Excess Alcohol,	High,			
oil	molar ratio (6 – 12 :	molar ratio (10 – 166	stoichiometrically	Molar ratio (methanol			
	1)	:1)	ratio (3 – 4 : 1)	: brute oil) (40 : 1)			
Reaction time	Fat (average to 4 h)	Short (average to 12	Short (average to 28	Very short, fast			
		h)	h)	(average to 7 à 15			
				min)			
Catalyst	Cheaper,	Cheaper; low	Expensive, moderate	Without catalyst			
	low quantity	Low quantity	quantity (8% w/w				
	(1% w / w average)	(1% w/w	average), deactivated				
		average)	because of the				
			alcohol				
Energy	High, the product	High, high reaction	Moderate	Low, high reaction			
consumption	requires washing	temperature		temperature			
	with hot water						
Product	Difficult, several	Easy; the product	Easy, the product	biodiesel purification			
recovery	purification steps	does not require	does not require	and glycerol recovery			
		washing	washing	are much easier			
Environmental	Using high quantity	The process is	Ecological, no step	Using high quantity of			
impacts	of water to wash	corrosive; the acid	washing with	water to wash			
		catalyst is polluting	necessary				

Table 1. Comparison of various transesterification processes [24, 25, 26]

As regards the enzymatic catalysts, they are used in immobilized form (for example by adsorption on a resin or membrane) in order to maintain their catalytic activity and not to contaminate the final product, in which one could see the development of an enzymatic activity after the synthesis [23]. In addition, with enzymatic catalyzed reactions, further treatment of the wastewater is not necessary. The enzyme often used in the production of biodiesel is lipase. Indeed, there are two main problems regarding the effective use of lipase in the production of biodiesel. First, lipases are unstable in short chain alcohols. To avoid this problem, the amount of alcohol used must be below the solubility limit, so that it is not present as a separate phase. Staged addition of alcohol has been proposed to maintain the amount below the critical concentration. The use of an organic solvent has also been proposed as a means of increasing the alcohol concentration. Table 1 compares the various methods of transesterification.

In addition, enzymes, unlike basic and acidic catalysts, are not pollutants[27]. However, enzymatic transesterification also has some disadvantages (Tables 3). Due to the ability of methanol to denature the catalyst, the enzymatic transesterification process requires the presence of a cosolvent such as t-butanol or n-hexane [28, 29]. The presence of these solvents increases the solubility of the methanol in the reaction medium, thus decreasing the denaturation of the enzyme. However, the use of these solvents makes the process more expensive. Nevertheless, certain denaturationresistant enzymes, such as those produced by Candida antarctica can be used in the presence of methanol alone. During the transesterification of rapeseed oil in the presence of methanol and in the absence of co-solvent, lipase produced from Candida antarctica yielded methyl esters of 91% (m / m) [27, 30]. Another solution to avoid co-solvents is the use of long alkyl chain acceptors such as 1-butanol, 2-butanol, isobutanol or propanol [30]. The solubility of long alcohols chain such as propanol and butanol

in oils (hydrophobic substrates) is higher than those of short alcohols chain such as methanol or ethanol. Yields of alkyl esters close to 100% (w / w) can be obtained in the presence of long-chain alcohols and in the absence of co-solvents [30], but these alkyl acceptors are more expensive. Various studies were conducted for transesterification with different catalysts, alcohols and molar ratios at different temperatures. The summary of these studies is shown in Table 2.

According Arzamendi to et al. [42]. the transesterification of sunflower oil in the presence of methanol (MeOH) and potassium carbonate (K₂CO₃) provides a yield of alkyl esters that can reach 100%. During this reaction, the amount of soap varies depending on the oil free fatty acid content, the type of catalyst and the reaction temperature [7]. For example, sodium hydroxide tends to induce a higher soap formation than that obtained with potassium hydroxide (KOH). Thus, if the oil has a free fatty acid content greater than 0.5 mg KOH / g-oil, it must be pretreated before basic transesterification in order to remove free fatty acids and thus avoid the formation of soap [57]. The soap formed during basic transesterification consumes the catalyst and prevents the separation of alkyl esters and glycerol [57, 58].

Thus, during basic transesterification, if the oil used is rich in free fatty acids, a step of oil deacidification is required either by using of alcohols [59] or by liquid-liquid extraction of free fatty acids [60]. However, this treatment increases the production costs of biodiesel. After the basic transesterification reaction, it is necessary to cool the reaction mixture to separate the glycerol from the biodiesel. The transesterification of waste oil in the presence of methanol and sodium hydroxide (NaOH) for a reaction time of 0.5 h gives a yield of methyl esters of 85% (w/w) [32]. Even if the stoichiometric alcohol: triglyceride molar ratio is 3: 1, the basic transesterification reaction uses an excess of alcohol and the alcohol molar ratio to oil can vary between 5: 1 to 30: 1 [61, 62].

Table 2. Comparison of the different processes of transesterification.								
Basic Catalyst	Oil / alcohol	Molar ratio	Operating	Yield in alkyl	References			
		alcohol: Oil	condition	esters				
				(% m/m)				
Transesterification in basic medium								
Sodium hydroxide (NaOH)	Tournesol oil/ Methanol	6:1	60°C : 2h	97	[31]			
	Frving oil/Methanol	75.1	$70^{\circ}C \cdot 30 \text{ min}$	85	[32]			
	Frying oil / Méthanol	6:1	65°C · 1.5 h	77	[33]			
	Madhuaca	6:1	60°C: 2h	92	[34]			
	Indica Oil/Methanol	0.1	00 C, 211	12	[]+]			
Potassium hydroxida (KOH)	Enving oil / Methanol	6.1	65°C·2h	04	[33]			
r otassium nydroxide (KOII)	Pongamia	10.1	$60^{\circ}C; 1h 20min$	02	[35]			
	Fongamia Binnata cil/Methenol	10.1	00 C, 11 Solim	-92	[55]			
		06.01	(590.0)	0.0	[2(]			
	Karanja oli/Wethanol	06:01	65°C; 2h	98	[30]			
	Colza oil/Methanol	06:01	65°C; 2h	96	[31]			
oxide (KF/Eu ₂ O)	Colza oil / Methanol	12:01	65°C; 1h	92	[37]			
Potassium fluoride on aluminum $oxide (KE/ALO)$	Palm oil/Methanol	12:01	65°C; 3h	90	[38]			
Calcium ethoxide (Ca(OCH ₂ CH ₃))	Soybean oil / Ethanol	12:01	75°C; 3h	92	[39]			
Potassium iodida on ovida	Sovbaan oil/ Mathanol	15:01	65°C: 8h	06	[40]			
d'aluminium (KI/Al ₂ O ₃)		15.01	05 C, 81	90	[40]			
Potassium fluoride on zinc oxide (KF/ZnO)	Palm oil / Methanol	11,4 : 1	65°C; 9,7h	89	[41]			
Potassium carbonate (K2CO ₂)	Tournesol oil / Methanol	12.01	50°C · 7 5h	100	[42]			
Sodium carbonate (NaCO ₂)	Tournesol oil/ Methanol	12:01	50°C: 7.5h	92	[42]			
Sodium phosphate (Na PO)	Tournesol oil/ Methanol	12:01	50°C; 0h	00	[42]			
$\frac{1}{2} \frac{1}{2} \frac{1}$	Tournesol oil / Methanol	12.01	50°C; 11.5h	90	[42]			
		12.01	50 C, 11.51	97	[42]			
Potassium nitrate (KNO ₃)	Soybean oil / Methanol	15:01	60°C; 7h	87	[40]			
Transesterification in acid medium		1		1	1			
Sulfuric acid (H_2SO_4)	Soybean oil / Methanol	9:1	100°C; 12h	98	[43]			
	atropha oil / Methanol	166:1	60°C; 24h	99	[44]			
	Oil of <i>Chlorella</i>	164 : 1	110°C; 2h	95	[45]			
	Pyrenoidosa/ Methanol							
	Used oils / Methanol	16:1	95°C; 10h	93	[46]			
S-ZrO ₂	Soybean oil / Methanol	20:1	120°C; 1h	98	[47]			
ZnO	Oil of <i>Pongamia</i>	10:1	120°C; 24h	83	[35]			
	Pinnata/ Methanol							
Transesterification in enzymatic medi	um							
Novozim 435	Soybean oil / Methanol;	3:1	30°C ; 3,5h ; 150	97	[48, 49, 50,			
(C. antarctica)	Methyl acetate		rpm		51]			
incubated	Palm oil / Methanol	4:1	45°C ; 24h	87	[52]			
	Olive oil / Methanol	8:1	60°C ; 100 rpm ; 32h	93	[53]			
Novozym et lipozyme TLIM (T.	Colza oil of / Methanol	4:1	35°C ; 130 rpm ;	95	[11]			
lanuginosa)	Oil of tournesol/ Methanol	24 :1	20MPa ; 40°C ; 30	99	[54]			
			S					
Novozym 388 immobilized (A. oryzae)	Oil of Colza/ Methanol	4:1	pH=6; 40°C; 24h	85	[55]			
Candida sp.	Rice oil / Methanol	4:1	40°C: 170 rpm:	87	[56]			
99–125			12h		[20]			
Rhizopus orvzae	Sovbean oil / Methanol	1.5 : 1	130 bar	99	[11]			
(ROL) et Candida		-,	(supercritical)		[]			
rugosa (CRL)			45°C; 250 rpm: 3h					

Generally, the reaction temperature and the yield of alkyl esters during basic transesterification is high (generally above 90%) (Table 2).

The acidity and free fatty acid composition of fat has led researchers to use acid catalysts. In 1986, Freedman et al. [63] studied the transesterification of soybean oil with methanol using 1% by weight concentrated sulfuric acid. They found that at 65°C and a molar ratio of 30: 1 methanol to oil, it took 69 hours to obtain more than 90% oil conversion of the methyl esters. Canakci et al. [64] investigated the effects of the molar ratio of alcohol to soybean oil, reaction temperature, catalyst quantity and reaction time on conversion to esters by acid-catalyzed

found that transesterification. They increased ester conversions could be obtained at higher molar ratios between alcohol and oil, increased reaction temperatures, increased sulfuric acid concentrations, and longer reaction times.

In 2006, Wang et al. [46] studied the acid transesterification of waste oils in the presence of methanol and sulfuric acid (H₂SO₄). This study enabled them to find a vield of 93% (w/w) methyl esters (temperature of 95°C, reaction time of 10 h and alcohol to oil molar ratio of 16: 1). On the other hand, during the acid transesterification of Chlorella pyrenoidosa in the presence of methanol and sulfuric acid (H₂SO₄), 95% (w/w) of the oil is transformed

into biodiesel (at 90 ° C, during 2 hours and alcohol: oil molar ratio of 165: 1) [56]. The acid transesterification requires a higher alcohol excess than that used during the reaction in basic medium, alcohol molar ratios: oil of the basic transesterification and acid ranging between 5: 1 and 30: 1 (basic) and between 9: 1 and 166: 1 (acid) (Tables 1 and 2) The kinetics of acid-catalyzed transesterification with butanol was also studied [63]. Studies on the acid-catalyzed system have been very limited, and no commercial biodiesel plant has been described as using the acid-catalyzed process, despite its relatively slow reaction rate. The acid-catalyzed derivative has advantages in terms of its independence from free fatty acid content and the subsequent absence of a pretreatment step. These advantages favor the use of the acid catalyzed process when spent cooking oil is used as the raw material, which usually has free fatty acid contents of greater than 2% by weight [48, 64, 65]. This process is particularly suitable for raw materials such as unrefined or spent cooking oils that are rich in free fatty acids. This process does not require pretreatment of the oil with alkali to reduce its free fatty acid content. However, this transesterification process has drawbacks. It is very slow and requires a very high molar ratio methanol-oil (Table 3). Adding a large proportion of acid would burn the oil, reducing the overall biodiesel yield [66]. Another disadvantage of the acidic process is the temperature (generally between 60 and 120 ° C), higher than that required during basic transesterification (about 65 $^{\circ}$ C) (Table 3). In acid transesterification, large part of alcohol are needed to use the lowest possible temperatures. For example, the transesterification temperature of jatropha oil in the presence of sulfuric acid (H_2SO_4) is low (60 ° C), but the excess alcohol is high (molar ratio alcohol: oil of 166: 1) [67].

Similarly, during the acidic transesterification of soybean, the molar ratio of alcohol to oil is low (9: 1), but the temperature is high (100 $^{\circ}$ C). [43]. This process is rarely used in industry since acids such as sulfuric acid (the most used) are corrosive [68]. The different limits encountered when using transesterification processes in homogeneous and heterogeneous catalysis, gave rise to another type of catalyst such as enzymatic catalysis. Indeed, the enzymatic production

of biodiesel has been the subject of extensive discussions in the literature. Shimada et al. [69] reported that biodiesel production increased with increasing methanol concentration to an oil-to-methanol ratio of 3: 1, and then decreased when the methanol concentration was further increased. The same observation was also made by Noureddini et al. [70] although the ratio is higher (7.5: 1). In general, it is widely accepted that the methanol completely dissolved in the substrate mixture must not inactivate lipases [11, 71, 69]. Proteins are generally unstable in short alcohols chain such as methanol and ethanol. Therefore, the lipases are inactivated by contact with insoluble methanol, which exists as drops in the oil. To avoid this problem, the amount of methanol used must be less than its solubility limits in the oil. To achieve this goal, a gradual addition of methanol to maintain the quantity less than its solubility has been proposed [11, 69]. In addition, the use of organic solvent to dissolve methanol has also been suggested. However, this is not recommended as it requires the addition of a solvent recovery unit. Also, methyl acetate has been proposed to replace alcohols as an acyl acceptor for the production of biodiesel from soybean oil using Novozym 435 [51]. Methyl acetate has been shown to have no negative effect on enzymatic activity after use. However, when the methanol was used at an appropriate concentration, its reaction rate remained much faster. Moreover, the use of alcohol in the supercritical phase for the conversion of oils into fatty acid esters comes to solve the disadvantages observed in other methods of transesterification. But the main disadvantage of this method of synthesis comes from the drastic operating conditions (temperatures of 300-350°C., pressures greater than 200 bars), the sizes of the necessary installations as well as their costs, putting a brake on the industrial use of the synthèse avec alcool supercritique [72, 73[. The method is however adaptable with co-solvents such as carbon dioxide (CO_2) or hexane and a catalyst, which makes it possible to reduce temperature conditions and molar ratios [74]. Supercritical transesterification is very fast and gives pure products without resorting to the separation of catalyst or soap, this reaction is sensitive to neither water nor free fatty acids which spares the pretreatment step.

Example of catalyst	Advantages	disadvantages				
Homogeneous						
Basic (NaOH, KOH)	Low cost, speeds of High reaction, advantageous operating conditions, high activity.	Incompatible with free fatty acids - formation of soaps, incompatible with water - formation of free fatty acids, polluted separation effects.				
Acid (H ₂ SO ₄ concentrate)	No soap formation, catalyzes the esterification of free fatty acids and the transesterification of glycerides simultaneously.	Corrosion, polluted separation effects, low catalytic activity, high reaction temperature, long reaction time.				
Heterogeneous						
Basic (CaO, CaCo ₃ , KOH- Al ₂ O ₃ , Al ₂ O ₃ -KI, Zeolite ETS-10)	Recyclable, non-corrosive, easy separation, better selectivity, long catalyst life cycle.	Incompatible with free fatty acids -formation of soaps, incompatible with water-formation of free fatty acids, high molar ratio of alcohol / oil required, high temperature and high pressure, diffusional limitation, higher costs.				
Acid (ZnO-I2, ZrO2-SO4-2, Tio2-SO4-2, solid catalysts based on carbon or carbohydrates) Supercritical	No soap formation, catalyzes the esterification of free fatty acids and the transesterification of glycerides simultaneously, recyclable.	Low acid site concentration, low catalytic activity, diffusional limitations due to low microporosity, high cost.				
Without catalyst	Very low reaction time, no limitation to transfers due to uniqueness of phase, no catalyst to recycle.	Drastic operating conditions (high temperature, high pressure, high molar ratios), high operating costs.				
Enzymatic						
Candida antartica, Pseudomonas fluorescens	No parasitic reactions, easy separation, no pollutant.	Risk of denaturation of the enzyme, very slow.				

 Table 3. Compares homogeneous, heterogeneous catalysis, supercritical alcohol use and basic enzyme catalysis in terms of advantages and disadvantages [7, 81].

In addition this reaction can esterify free fatty acids [75, 76, 77, 78]. During this reaction, a better conversion rate was noted when the temperature of the reaction was increased in the supercritical state and the methyl ester content increased with the molar ratio of the alcohol/oil [78, 77]. He et al. [77] conducted a supercritical transesterification reaction of soybean oil in the presence of methanol. They observed that from 310°C side reactions were triggered. In 2008, Permsuwan et al. [79] have tested the supercritical transesterification of palm oil at atmospheric pressure. They recorded a maximum oil conversion at 290°C after 5 hours, but the methyl ester content was 87%, which was far from the specification of the European standard EN 14214 [80]. They recorded at 250 ° C a 95% methyl esters but the conversion rate was 55% by weight. These different processes have advantages and disadvantages. Table 3 summarizes the advantages and disadvantages of the various transesterification processes with respect to the various catalysts used.

Conclusion

Biodiesel is a good alternative fuel for diesel engines because it is environmentally friendly and renewable. There are different methods of producing biodiesel, but the vegetable oil transesterification and fats is the method mostly used nowadays. Researchers are focusing more on producing biodiesel using edible oils, but their use for biodiesel production has contributed enormously to reducing its costs. It is an effective alternative with the potential to significantly improve the environment. Biodiesel is an excellent diesel alternative fuel and is probably the best solution to greenhouse gas and urban pollution problems. The major advantage of Biodiesel compared to other alternatives such as natural gas or electricity, is that it can be used without modification in various fuel-based applications especially in existing diesel engines. Governments should make full use of these biodiesel resources and ensure the international safety of diesel as a sustainable complement. The combustion characteristics of biodiesel are similar to those of diesel and the engine power of biodiesel is equivalent to that of diesel. In addition, the use of biodiesel in the diesel engine results in a drastic reduction in engine emissions. Therefore, based on this review, we concluded that biodiesel is a better renewable fuel for diesel.

References

[1]V. Maltitz, Graham P., and Kevin A. Setzkorn. "A typology of Southern African biofuel feedstock production projects." Biomass and bioenergy 59 (2013): 33-49.

[2]S. Izah, Sylvester C., and Elijah I. Ohimain. "The challenge of biodiesel production from oil palm feedstock in Nigeria." Greener journal of Biological sciences 3.1 (2013): 001-012.

[3]J. Dhainaut, Jérémy, et al. "Hierarchical macroporousmesoporous SBA-15 sulfonic acid catalysts for biodiesel synthesis." Green Chemistry 12.2 (2010): 296-303.

[4]O. Aworanti, S. E. Agarry, and A. O. Ajani. "Statistical Optimization of Process Variables for Biodiesel Production from Waste Cooking Oil Using Heterogeneous Base Catalyst." (2013).

[5]P. Chitra, P. Venkatachalam, and A. Sampathrajan. "Optimisation of experimental conditions for biodiesel production from alkali-catalysed transesterification of Jatropha curcus oil." Energy for sustainable development 9.3 (2005): 13-18.

[6]A. Demirbas, Ayhan. "Importance of biodiesel as transportation fuel." Energy policy 35.9 (2007): 4661-4670.

[7]D. Leung, Dennis YC, Xuan Wu, and M. K. H. Leung. "A review on biodiesel production using catalyzed transesterification." Applied energy 87.4 (2010): 1083-1095. [8]A. Borges, Aline, et al. "Changes in spatial and temporal gene expression during incompatible interaction between common bean and anthracnose pathogen." Journal of plant

physiology 169.12 (2012): 1216-1220.

[9]A. Chouhan, AP Singh, and A. K. Sarma. "Modern heterogeneous catalysts for biodiesel production: A comprehensive review." Renewable and Sustainable Energy Reviews 15.9 (2011): 4378-4399.

[10]L. Liu, Liang. "BEST: Bayesian estimation of species trees under the coalescent model." Bioinformatics 24.21 (2008): 2542-2543.

[11]Y. Shimada, Yuji, et al. "Enzymatic alcoholysis for biodiesel fuel production and application of the reaction to oil processing." Journal of Molecular Catalysis B: Enzymatic 17.3-5 (2002): 133-142.

[12]M. Kulkarni, Mangesh G., et al. "Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification." Green Chemistry 8.12 (2006): 1056-1062.

[13]D. Serio, Martino, et al. "Heterogeneous catalysts for biodiesel production." Energy & Fuels 22.1 (2007): 207-217.

[14]A. Gashaw, Alemayehu, and Amanu Lakachew. "Production of biodiesel from non edible oil and its properties." International Journal of Science, Environment and Technology 3.4 (2014): 1544-1562.

[15]M. Lam, Man Kee, Keat Teong Lee, and Abdul Rahman Mohamed. "Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review." Biotechnology advances 28.4 (2010): 500-518.

[16]J. Boro, Jutika, Dhanapati Deka, and Ashim J. Thakur. "A review on solid oxide derived from waste shells as catalyst for biodiesel production." Renewable and Sustainable Energy Reviews 16.1 (2012): 904-910.

[17]N. Viriya-Empikul, N., et al. "Waste shells of mollusk and egg as biodiesel production catalysts." Bioresource technology 101.10 (2010): 3765-3767.

[18]N. Viriya-Empikul, N., et al. "Biodiesel production over Ca-based solid catalysts derived from industrial wastes." Fuel 92.1 (2012): 239-244.

[19]D. Kusdiana, Dadan, and Shiro Saka. "Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol." Fuel 80.5 (2001): 693-698.

[20]A. Vyas, Amish P., Jaswant L. Verma, and N. Subrahmanyam. "A review on FAME production processes." Fuel 89.1 (2010): 1-9.

[21]Y. Warabi, Yuichiro, Dadan Kusdiana, and Shiro Saka. "Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols." Bioresource technology 91.3 (2004): 283-287.

[22]K. Jegannathan, Kenthorai Raman, et al. "Production of biodiesel using immobilized lipase—a critical review." Critical Reviews in Biotechnology 28.4 (2008): 253-264.

[23]K. Tan, Bee K., Raghu Adya, and Harpal S. Randeva. "Omentin: a novel link between inflammation, diabesity, and cardiovascular disease." Trends in cardiovascular medicine 20.5 (2010): 143-148.

[24]E. Shahid, Ejaz M., and Younis Jamal. "Production of biodiesel: a technical review." Renewable and Sustainable Energy Reviews 15.9 (2011): 4732-4745.

[25]S. Al-Zuhair, Sulaiman. "Production of biodiesel: possibilities and challenges." Biofuels, Bioproducts and Biorefining 1.1 (2007): 57-66.

[26]Y. Gong, Yan, Lu Lin, and Zhipei Yan. "Catalytic hydrogenation and oxidation of biomass-derived levulinic acid." BioResources 6.1 (2011): 686-699.

[27]M. Antczak, Mirosława Szczęsna, et al. "Enzymatic biodiesel synthesis-key factors affecting efficiency of the process." Renewable energy 34.5 (2009): 1185-1194.

[28]M. Raita, Marisa, Verawat Champreda, and Navadol Laosiripojana. "Biocatalytic ethanolysis of palm oil for biodiesel production using microcrystalline lipase in tertbutanol system." Process Biochemistry 45.6 (2010): 829-834.
[29]C. Gao, Chunfang, et al. "Rapid quantitation of lipid in microalgae by time-domain nuclear magnetic resonance." Journal of microbiological methods 75.3 (2008): 437-440.

[30] A. Salis, Andrea, et al. "Biodiesel production from triolein and short chain alcohols through biocatalysis." Journal of Biotechnology 119.3 (2005): 291-299.

[31]U. Rashid, Umer, and Farooq Anwar. "Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil." Fuel 87.3 (2008): 265-273.

[32]D. Leung, D. Y. C., and Y. Guo. "Transesterification of neat and used frying oil: optimization for biodiesel production." Fuel processing technology 87.10 (2006): 883-890.

[33]J. Encinar, Jose M., Juan F. Gonzalez, and Antonio Rodríguez-Reinares. "Biodiesel from used frying oil. Variables affecting the yields and characteristics of the biodiesel." Industrial & Engineering Chemistry Research 44.15 (2005): 5491-5499.

[34]S. Puhan, Sukumar, et al. "Mahua oil (Madhuca Indica seed oil) methyl ester as biodiesel-preparation and emission characterstics." Biomass and Bioenergy 28.1 (2005): 87-93.

[35]S. Karmee, Sanjib Kumar, and Anju Chadha. "Preparation of biodiesel from crude oil of Pongamia pinnata." Bioresource technology 96.13 (2005): 1425-1429.

[36]L. Meher, Vidya SS Dharmagadda, and S. N. Naik. "Optimization of alkali-catalyzed transesterification of Pongamia pinnata oil for production of biodiesel." Bioresource technology 97.12 (2006): 1392-1397.

[37] H. Sun, Hui, HU, Kai, LOU, Hui, et al. Biodiesel Production from Transesterification of Rapeseed Oil Using KF/Eu 2O 3 as a Catalyst. Energy & Fuels, 2008, vol. 22, no 4, p. 2756-2760.

[38]X. Bo, Xu, et al. "Transesterification of palm oil with methanol to biodiesel over a KF/Al2O3 heterogeneous base catalyst." Energy & Fuels 21.6 (2007): 3109-3112.

[39]X. Liu, Xuejun, PIAO, Xianglan, WANG, Yujun, et al. Calcium ethoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel. Energy & Fuels, 2008, vol. 22, no 2, p. 1313-1317.

[40]W. Xie, Wenlei, Hong Peng, and Ligong Chen. "Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst." Applied Catalysis A: General 300.1 (2006): 67-74.

[41]B. Hameed, Bassim H., L. F. Lai, and L. H. Chin. "Production of biodiesel from palm oil (Elaeis guineensis) using heterogeneous catalyst: an optimized process." Fuel Processing Technology 90.4 (2009): 606-610.

[42]G. Arzamendi, E. Arguinarena, I. Campo, S. Zabala & L. M. Gandía, "Alkaline and alkaline-earth metals compounds as catalysts for the methanolysis of sunflower oil." Catalysis Today 133 (2008): 305-313.

[43]M. J. Goff, N. S. Bauer, S. Lopes, W. R. Sutterlin, & G. J. Suppes, "Acid-catalyzed alcoholysis of soybean oil." Journal of the American Oil Chemists' Society 81.4 (2004): 415-420.

[44]S. H. Shuit, K. T. Lee, A. H. Kamaruddin & S. Yusup, "Reactive extraction and in situ esterification of Jatropha curcas L. seeds for the production of biodiesel." Fuel 89.2 (2010): 527-530.

[45]P. Li, X. Miao, R. Li, & J. Zhong, "In situ biodiesel production from fast-growing and high oil content Chlorella pyrenoidosa in rice straw hydrolysate." BioMed Research International 2011 (2011).

[46]Wang, Yong, et al. "Comparison of two different processes to synthesize biodiesel by waste cooking oil." Journal of Molecular Catalysis A: Chemical 252.1-2 (2006): 107-112.

[47]C.M. Garcia, S. Teixeira, L.L. Marciniuk, U. Schuchardt, (2008). Transesterification of soybean oil catalyzed by sulfated zirconia. Bioresource Technology, volume 99, n° 14, p. 6608-6613.

[48]Y. Watanabe, Y. Shimada, A. Sugihara, & Y. Tominaga "Enzymatic conversion of waste edible oil to biodiesel fuel in a fixed-bed bioreactor." Journal of the American Oil Chemists' Society 78.7 (2001): 703-707.

[49]T. Samukawa, M. Kaieda, T. Matsumoto, K. Ban, A. Kondo, Y. Shimada, & H. Fukuda, Pretreatment of immobilized Candida antarctica lipase for biodiesel fuel production from plant oil. Journal of bioscience and bioengineering, 2000, vol. 90, no 2, p. 180-183.

[50]M. Kaieda, T. Samukawa, A. Kondo, & H. Fukuda, "Effect of methanol and water contents on production of biodiesel fuel from plant oil catalyzed by various lipases in a solvent-free system." Journal of Bioscience and Bioengineering 91.1 (2001): 12-15.

[51]W. Du, Y. Xu, D. Liu, & J. Zeng, "Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors." Journal of Molecular Catalysis B: Enzymatic 30.3-4 (2004): 125-129.

[52]H. M. Chang, H. F. Liao, C. C. Lee, & C. J. Shieh, "Optimized synthesis of lipase-catalyzed biodiesel by Novozym 435." Journal of Chemical Technology and Biotechnology 80.3 (2005): 307-312.

[53]F. Sanchez, & P. T. Vasudevan, "Enzyme catalyzed production of biodiesel from olive oil." Applied biochemistry and biotechnology 135.1 (2006): 1-14.

[54]J. K. Poppe, R. Fernandez-Lafuente, R. C. Rodrigues, & M. A. Z. Ayub, "Enzymatic reactors for biodiesel synthesis: present status and future prospects." Biotechnology advances 33.5 (2015): 511-525.

[55]Y. Yücel, "Biodiesel production from pomace oil by using lipase immobilized onto olive pomace." Bioresource technology 102.4 (2011): 3977-3980.

[56]P. Li, X. Miao, R. Li, & J. Zhong, "In situ biodiesel production from fast-growing and high oil content Chlorella pyrenoidosa in rice straw hydrolysate." BioMed Research International 2011 (2011).

[57]G. Vicente, M. Martınez & J. Aracil, "Integrated biodiesel production: a comparison of different homogeneous catalysts systems." Bioresource technology 92.3 (2004): 297-305.

[58]G. Huang, F. Chen, D. Wei, X. Zhang, & G. Chen, "Biodiesel production by microalgal biotechnology." Applied energy 87.1 (2010): 38-46.

[59]S. Turkay, & H. Civelekoglu, "Deacidification of sulfur olive oil. I. Single-stage liquid-liquid extraction of miscella

51241

with ethyl alcohol." Journal of the American Oil Chemists Society 68.2 (1991): 83-86.

[60] C.G. Pina, A.J.A. Meirelles, Deacidification of corn oil by solvent ex-traction in a perforated rotating disc column. JAOCS, Journal of the American Oil Chemists' Society, volume 77, n° 5, (2000) p. 553-559.

[63] B. Freedman, R. O. Butterfield, & E. H. Pryde, Transesterification kinetics of soybean oil 1. Journal of the American Oil Chemists' Society, 63(10) (1986), 1375-1380.

[64]M. Canakci, & J. Van Gerpen, Biodiesel production from oils and fats with high free fatty acids. Transactions of the ASAE, 44(6) (2001), 1429.

[65]F. André, Young, Fernando LP Pessoa, and Eduardo M. Queiroz. "Design and economic evaluation of alternatives to effluents treatment on biodiesel production from soybean oil and palm oil." Computer Aided Chemical Engineering. Vol. 37. Elsevier, 2015. 1067-1072.

[66]O. S. Tyagi, N. Atray, B. Kumar, & A. Datta, "Production, characterization and development of standards for biodiesel—a review." Mapan 25.3 (2010): 197-218.

[67]S. H. Shuit, Lee, K. T., A. H. Kamaruddin, & S. Yusup, "Reactive extraction and in situ esterification of Jatropha curcas L. seeds for the production of biodiesel." Fuel 89.2 (2010): 527-530.

[68]A. Robles-Medina, P. A. González-Moreno, L. Esteban-Cerdán, & E. Molina-Grima, "Biocatalysis: towards ever greener biodiesel production." Biotechnology advances 27.4 (2009): 398-408.

[69]Y. Shimada, Y. Watanabe, T. Samukawa, A. Sugihara, H. Noda, H. Fukuda, & Y. Tominaga, Conversion of vegetable oil to biodiesel using immobilized Candida antarctica lipase. Journal of the American Oil Chemists' Society, (1999): 76(7), 789-793.

[70]H. Noureddini, X. Gao, & R. S. Philkana, Immobilized Pseudomonas cepacia lipase for biodiesel fuel production from soybean oil. Bioresource technology, (2005): 96(7), 769-777.

[71] Al-Zuhair, S., Jayaraman, K. V., Krishnan, S., & Chan, W. H. (2006). The effect of fatty acid concentration and water content on the production of biodiesel by lipase. Biochemical Engineering Journal, 30(2), 212-217.

[72]E. Lotero, Y. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce, & J. G. Goodwin, Synthesis of biodiesel via acid catalysis. Industrial & engineering chemistry research, (2005): 44(14), 5353-5363.

[73]A. Demirbas, Progress and recent trends in biodiesel fuels. Energy conversion and management, (2009): 50(1), 14-34

[74]C. Kiwjaroun, C. Tubtimdee, & P. Piumsomboon, LCA studies comparing biodiesel synthesized by conventional and supercritical methanol methods. Journal of Cleaner Production, (2009): 17(2), 143-153.

[75]A. Deshpande, G. Anitescu, P. A. Rice, & L. L. Tavlarides, Supercritical biodiesel production and power cogeneration: technical and economic feasibilities. Bioresource technology, (2010): 101(6), 1834-1843.

[76]J. Y. Lee, C. Yoo, S. Y. Jun, C. Y. Ahn, & H. M. Oh, Comparison of several methods for effective lipid extraction from microalgae. Bioresource technology, (2010): 101(1), S75-S77.

[77]H. He, S. Sun, T. Wang, & S. Zhu, Transesterification kinetics of soybean oil for production of biodiesel in supercritical methanol. Journal of the American Oil Chemists' Society, (2007): 84(4), 399-404.

[78]A. Demirbas, Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. Progress in energy and combustion science, (2005): 31(5-6), 466-487.

[79]A. Permsuwan, N. Tippayawong, T. Kiatsiriroat, C. Thararux, & S. Wangkarn, Reaction kinetics of transesterification between palm oil and methanol under subcritical conditions. Energy Science and Technology, (2011): 2(1), 35-42.

[80]EN 14214: European Committee for Standardization, 2003 (E) Automotive fuels - fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods

[81]M. K. Lam, K. T. Lee, & A. R. Mohamed, Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. Biotechnology advances, (2010): 28(4), 500-518.

51242