Biodiesel

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Biodiesel (mono alkyl esters) is the most attractive alternative fuel to diesel, with numerous environmental advantages over petroleum-based fuel. The most practicable method for converting triglycerides to biodiesel with viscosities comparable to diesel fuel is transesterification.

Keywords: triglycerides ; biodiesel ; esterification ; transesterification ; biodiesel feedstock

1. Introduction

The conversion of renewable energy sources to alternative fuels has been at the forefront of sustainable energy research due to the increased environmental awareness and worries from the expected depletion of fossil fuel resources [1][2][3]. Biodiesel is among the most promising alternative fuels produced from virgin and waste cooking vegetable oils or animal fats [4][5]. Due to its renewability, biodegradability, low emission profile, nontoxicity, and high flash point, biodiesel has a number of advantages over petroleum-based diesel [6][7][8][9][10]. In addition, biodiesel increases the operational lifetime of the compression engine and reduces the consumption of the engine spare parts due to the high lubricity of biodiesel [11][12]. Therefore, biodiesel is an alternative fuel with the high potentiality to compete with petroleum fuel from environmental and economic points of view [7][13][14][15]. Using vegetable oil as a fuel dates back to the 1900s when Adolf Diesel used peanut oil as fuel in a diesel engine [16][17]. The main problem regarding vegetable oil as fuel is its greater viscosity besides its low volatility and bad cold flow properties, which affect the proper operation of the diesel engine [18][19]. The properties of vegetable oils can be improved in different ways, such as pyrolysis, dilution with liquid hydrocarbon (blending), micro emulsification, and transesterification process [20][21][22][23]. Transesterification is the most practicable process, among these four ways, for reducing the viscosities of vegetable oils and producing alkyl esters with characteristics comparable to diesel. This is the reason why transesterified vegetable oils are popularized as “biodiesel” [24][25].

The transesterification reaction modifies one ester to another by changing its alkoxy part [26][27][28]. This is similar to hydrolysis; however, alcohol is used in this process instead of water and is thus known as alcoholysis [29]. Biodiesel is produced through transesterification by the reaction of lipids with alcohol. The major components of lipids (oil/fats) are triglycerides. Triglycerides are esters of three fatty acids and one glycerol. Thus, the alcoholysis of lipids produces monoalkyl esters, commonly named biodiesel, and glycerol as a by-product. The overall process of transesterification is a sequence of three consecutive and reversible reactions in which di and monoglycerides are formed as intermediates. The stoichiometric reaction requires one mol of triglyceride and three moles of alcohol. However, to maximize the yield of the alkyl ester, alcohol should be used in an excess amount. However, an excessive amount of alcohol makes the separation of the yields difficult. Therefore, the alcohol/oil molar ratio, besides the type of catalyst, temperature, and purity of the reactant, are the factors that affect the process of transesterification [30]. The purity of the reactants, mainly water content and free fatty acids, is the crucial factor that determines the convenient route of transesterification [31][32].

Commonly, the transesterification of lipids is applied by using a short-chain alcohol (C1 to C4). However, methanol is the most common alcohol because it is cheaper, and it is easier to recover unreacted methanol. On the other hand, ethyl esters are more renewable because ethanol is produced from agricultural resources [33]. In addition, ethyl esters were proved to have lower emissions of green gases and more biodegradability in the aquatic environment [34][35]. However, there are practical difficulties associated with the production of ethyl esters, as it suffers due to the fast saponification and solubility of ethyl esters in glycerol, which increases at a high oil/ethanol molar ratio [36].

The cost of biodiesel production is high because more than 75% of its total cost is related to conventional raw materials, such as edible oils and animal fat [37]. On the other hand, using edible vegetable oils for biodiesel production leads to a food crisis [16]. A practical, sustainable transesterification route should produce biodiesel from low-cost feedstocks such as non-edible oils, waste cooking oils, or animal fats, increasing the cost-effectiveness of biodiesel production. Generally, the transesterification process is classified into catalytic and non-catalytic methods. Catalytic methods are categorized into

homogenous and heterogeneous processes [38]. The transesterification reaction's route determines the biodiesel industry's feasibility, considering economic and environmental constraints. Therefore, this paper aimed to review the progress in research, based on a bench scale, concerning the latest technologies of transesterification. The modifications to the conventional homogenous methods and the most promising innovative catalytic or non-catalytic technologies were critically reviewed.

2. Transesterification by Ultrasonic and Microwave Irradiation

Ultrasound-assisted lipase-catalyzed transesterification of triglycerides has also emerged as one of the latest trends in the research efforts concerning the application of ultrasound irradiation for biodiesel production. Batistella et al. [39] studied the influence of ultrasound irradiation on lipase-catalyzed ethanolysis of soybean oil, without agitation, in the presence of hexane as a solvent. They were able to obtain high biodiesel yield (≈90 wt%) at reaction temperature 60 °C in a relatively short reaction time, 4 h, by using Lipozyme RM IM as a catalyst. The catalyst was reused successfully for two cycles without significant decay in its activity. The effect of ultrasound irradiation on lipase-catalyzed transesterification in the presence of different solvents and in the absence of solvent, as well as the behavior of the lipase in the ultrasound systems, are hot topics to be investigated by researchers.

Microwave radiation can change the magnetic field of weak polar molecules, such as alcohols. As a result, the rotational movement of the molecules is accelerated, and heat is generated. In chemical reactions, microwave irradiation leads to more effective heat transfer than conventional heating in a much shorter reaction time. The major disadvantage or restriction of microwave heating is its shallow penetration depth. The microwave has a few millimeters of penetration depth, indicating a fast reduction in microwave intensity in a reaction setting. The non-thermal effect associated with microwave heating is also debatable. Another difficult issue is choosing suitable building materials because microwave susceptibility in some materials, sparks in metal, and high-temperature zones at welded or sharp edges may all be lethal.

Combining ultrasound mixing with microwave heating in transesterification of triglycerides increases the mass transfer and heat transfer in the reaction media simultaneously. Therefore, a discrete two-step process was proposed by Hiaso et al. [40] to attain high biodiesel yield and conversion from soybean oil in the presence of methanol and alkaline catalyst. The authors aimed to obtain the optimal ultrasonic mixing and closed microwave irradiation. In the first step, the reaction of reagents was assisted by ultrasound mixing. In the second step, the reaction of reagents was assisted by closed microwave irradiation. A high rate of conversion (97.7%) was achieved by 1 min ultrasound mixing followed by 2 min closed microwave irradiation at optimal conditions: methanol to oil molar ratio, 6:1; the amount of catalyst, 1.0 wt%; and reaction temperature of 333 K. It is worth mentioning that assisting the reaction in one step within a short time, by ultrasound mixing without microwave irradiation or by microwave irradiation without ultrasound mixing, led to very poor methyl ester conversion. A comparative study of the sequential effect of microwave and ultrasound compared to individual approaches of microwave and ultrasound was carried out by Gole and Gogate [41] to produce biodiesel from high acid value Nagchampa oil. By an individual approach of ultrasound, the initial acid value of the oil was reduced from 18.9 to 1.7 mg KOH/g of oil by the optimized condition: methanol to oil molar ratio 1:4, 3 wt% H 2SO 4 to oil, and 60 min reaction time.

In contrast, the individual microwave approach required a 1:3 methanol to oil molar ratio, t3 wt% H 2SO 4 to oil, and a 25 min reaction time to achieve the same result. However, the sequential approach of microwave followed by ultrasound, to reduce the acid value in the range, required a considerably smaller methanol to oil ratio, amount of catalyst, and reaction time (1:2 M, 2 wt%, and 15 min), respectively. For the transesterification reaction, ultrasound, microwave, and the sequential approach required (1:6, methanol to oil molar ratio, 1 wt% NaOH to oil, and a reaction time of 20 min at 50 °C reaction temperature), (1:6 methanol to oil molar ratio, 1 wt% NaOH to oil, 350 rpm, and 15 min), (1:4 methanol to oil molar ratio, 1 wt% NaOH to oil, and 6 min reaction time), respectively. The sequential process should start with the microwave since the heat released by the microwave effect accelerates the ultrasonic mixing. In their study, Gole and Gogate [41] illustrated that a sequential combination of microwave and ultrasound is economically more feasible in producing biodiesel because it reduces the amount of the catalyst and the reaction time. Moreover, the requirement of less amount of methanol reduces the consumption of energy in methanol recovery.

3. Non-Catalytic Biodiesel Production

Saka and Kusdaina [42] studied the production of methyl esters from rapeseed oil using supercritical methanol instead of sodium hydroxide as a catalyst. The authors reported that methyl esters produced in supercritical methanol have similar fatty acid composition comparable to that of the conventional method. Moreover, they reported higher biodiesel yield for the supercritical method compared to biodiesel yield derived using an alkaline catalyst; this can be attributed to

simultaneous transesterification and esterification of FFAs. As supercritical alcohol transesterification required a more straightforward purification process, the authors claimed the process to be more environmentally friendly. Alcohol to oil molar ratio, temperature, and alcohol type are the factors that affect this process. Saka and Kusdaina [43] carried out a detailed kinetic study in free catalyst transesterification of rapeseed oil using supercritical methanol. The authors varied the controlling factors, such as temperature and reaction time and methanol to oil molar ratio. The authors reported maximum biodiesel yield at 350 °C, 43 MPa, and 1:42 methanol to oil molar ratio. Warabi et al. [44] reported that, by using supercritical conditions, short-alkyl chain alcohols could achieve 100% conversion of triglycerides to biodiesel. They also reported a higher FFAs esterification reaction rate compared to triglycerides transesterification rate.

Water affects the formation of biodiesel in the catalyst-free supercritical methanol process positively. Vegetable oils that contain water, transesterification, hydrolysis of triglycerides, and methyl esterification of fatty acids proceed simultaneously during the treatment and result in high yields [45]. Thus, supercritical methanol transesterification technology is deemed economically more feasible due to higher biodiesel yield in a short reaction time with lower methanol consumption from low feedstock with high FFAs or water contents. Palm fatty acids distillate (PFAD), which is a by-product from palm oil refineries, consists of 93% FFAs and is esterified by Yujaroen et al. [46] in supercritical methanol conditions. A high biodiesel yield was obtained (95%) at 300 °C with 1:6 PFAD to methanol molar ratio and a 30 min reaction time. Compared to the transesterification of pure palm oil (PPO) in supercritical methanol, a relatively low biodiesel yield (80%) was reached at 300 °C with higher methanol requirements (1:45 PPO to methanol) and 50 min reaction time. Acid-catalyzed-esterification of the PFAD produced only 75% biodiesel yield in a 5 h reaction time. Wet algae biomass containing 90% water was converted to biodiesel at much milder reaction conditions, a wet algae to methanol (wt./vol) ratio of 1:9, with a reaction temperature and reaction time of 255 °C and 25 min, respectively [47]. Hegel et al. [48] used free-catalyst supercritical ethanol transesterification of the bio-oil to obtain biodiesel. The authors reported higher lipid extraction yields using ethanol with respect to n-hexane. The authors further reported that the transesterification of crude lipids extracted with ethanol as the solvent at 305 °C and 40 min produced up to 15.9 wt% of biodiesel with respect to dried biomass processed.

Conventional free catalyst supercritical methanol treatment of triglycerides (lipids/oils) is economically not feasible, although they achieve high conversion to FAME, because of the harsh conditions, of high temperature and pressure required, besides the thermal degradation of FAME, especially those with a high unsaturation degree and isomerization of fatty acids to trans-type at high temperatures. Imahara et al. [49] investigated the effect of high temperature and pressure (270 °C/17 MPa to 380 °C/56 MPa) on the thermal stability of biodiesel derived from supercritical methanol conditions for various plant oils. Temperatures lower than 300 °C, preferably 270 °C, with a minimum pressure of 8.09 MPa, were proven to be appropriate to maintain the maximum yields and thermal stabilization of biodiesel. Therefore, researchers were motivated to develop new supercritical fluid technology to produce biodiesel at mild reaction conditions.

A novel two-step process to convert triglycerides to biodiesel at mild reaction conditions without glycerol production was developed by Saka et al. [50]. It includes treatment of triglycerides with subcritical acetic acids followed by supercritical methanol treatment. Rapeseed oil was converted in the first step to FA and triacetin by subcritical acetic acid under optimal conditions (300 °C/20 MPa, 30 min reaction time, and 1:54 oil to acetic acid molar ratio equivalent to 1:3.2 volumetric ratio). After removal of triacetin from the reaction mixture, supercritical methanol treatment required 270 °C/17 MPa for 15 min at a molar ratio of FAs to methanol 1:14 (1:1.6 volumetric ratio) the yield of FAME was 97 wt% and that for triacetin was 20 wt% totally being 117 wt% out of theoretical value 125 wt%.

4. In Situ Transesterification

Production of biodiesel by direct alkali-catalyzed transesterification of soybeans was examined by Haas et al. [51]. With the aid of thin-layer chromatography, it was apparent that even the brief incubation (2.5 h) of soy flakes (5 g) in 15 mL of alkaline solution (0.33 N NaOH) and simple alcohol (methanol, ethanol, isopropanol) at 60 °C resulted in fatty acid alkyl ester, suggesting that this phenomenon is a general one. Quain et al. [52] investigated the in situ transesterification of cottonseed oil by sodium hydroxide. Their study revealed that extraction and conversion of cottonseed oil increased significantly by increasing the amount of the catalyst, methanol loading, reaction time, and decreasing the moisture content and the size of the seed particles. The effect of temperature on biodiesel yield was not significant. A total of 99% and 98% of cottonseed oil extraction and conversion, respectively, were achieved by the optimal condition: less than 2% moisture content in cottonseed flour, 0.3–0.335 mm particle solid size, 0.1 mole/L methanolic sodium hydroxide solution, 135:1 methanol/oil molar ratio, 40 °C reaction temperature, and a 3 h reaction time. The presence of petroleum ether as a co-solvent substantially increased the extraction and conversion of the oil, with the optimal volume ratio of 1:3 ether/methanol. Moreover, the cottonseed oil extraction and conversion remained constant by using a mixture of fresh methanol and recycled methanol with 0.2 ratios (of recycled methanol/total reaction methanol, v / v).

Su et al. [53] examined the feasibility of biological in situ reactive extraction of oilseed with short-chain alkyl acetate for alkyl ester production. Firstly, they demonstrated that methyl acetate and ethyl acetate were capable of extracting oil from Pistacia chinensis Bunge seed and Jatropha curcas L, as well as n-hexane. Crude oil extracted by alkyl acetates had, remarkably, a lower phospholipids content compared to extract of hexane. Afterward, they compared the in situ transesterification versus conventional two-step extraction/transesterification in the presence of Novozyme 435 in both cases. The yields of methyl esters and ethyl esters in reactive extraction were considerably higher than those obtained by methanolysis and ethanolysis of the hexane extracted oil. The losses in yields may be attributed to the multi-step operations in the conventional extraction and transesterification, or the possible inhibition of lipase by methanol or ethanol and phospholipids. Furthermore, the effects of solvent, seeds, and seed water content on in situ reactive extraction were investigated. Methyl/ethyl esters' yields decreased by incomplete oil extraction due to the too low ratio of solvent/seed or the excessive dilution caused by higher ratios. Regardless of the kind of seeds or alkyl acetates used, the optimum solvent/seed ratio for high yields was 7.5 mL/g at the fixed condition of 5 g oilseed, 50 °C, 30% (w/w) Nophozyme 435 to theoretical oil content, 10 h, and 180 rpm.

The presence of water in the reaction medium enhances biological activity. However, the excess of water leads to hydrolytic reaction and, consequently, decreases the esters' yields. The highest ester yields were achieved at 4.26% and 4.62% water contents for Pistacia chinensis and Jatropha curcas L. seeds, respectively, regardless of the kind of alkyl acetate used, at the established solvent/seed ratio. Su et al. [54], in their further investigations on in situ reactive extraction of Pistacia chinensis and Jatropha curcas L. seeds, demonstrated that short-chain dialkyl carbonates act as not only an extraction solvent but also as a transesterification agent. The optimum solvent/seed ratio for the highest biodiesel yields was 10 mL/g, at fixed conditions: 5 g oilseed, 50 °C, 10% (w/w) Novozyme 435 to oil content, 10 h, and 180 rpm, regardless of the kinds of seeds and dialkyl carbonates used. Regarding the effect of water content at the optimized solvent/seed ratio, for Pistacia chinensis Bunge seed by using dimethyl carbonate, the highest methyl ester yields were attained at 3.14% water content. In comparison, the highest ethyl ester yields were attained at 2.34% by using diethyl carbonate. However, the highest ester yields were achieved at 3.02% of water content for Jatropha curcas L. seeds regardless of the kind of dialkyl carbonates used. At these optimized conditions, for both seeds, the yields of methyl esters and ethyl esters were almost constant after 24 h, with a rapid increase in the first 16 h.

A combination of supercritical methanol technology with reactive extraction was present as a novel method for producing biodiesel by Lim et al. [55]. They aimed to investigate the feasibility of non-catalytic reactive extraction of Jatropha curcas L. seeds in a high-pressure batch reactor in the presence of n-hexane as a co-solvent. The effects of temperature and the size of the solid particles of Jatropha curcas L. seeds on the FAME yields and the oil extraction efficiency were investigated extensively. The particle size of the seeds varied in the range of 0.5–2.0 mm, and the temperature varied in the range of 200–300 °C. Their study revealed that ≤ 1.0 mm particle solid size, the reaction temperature of 300 °C, and 240 MPa operational pressure are optimal conditions to achieve maximum extraction efficiency and FAME yield at 10 mL/g solvent to seed ratio, 2.5 mL /g co-solvent to seed ratio, and relatively short reaction time (45 to 80 min). The maximum FAME yield (103.5%) beyond the theoretical value (100%) was due to the excess oil being extracted based on n-hexane soxhlet extraction of Jatropha oilseeds due to the significant effect of the co-solvent at the low temperature.

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