

Review

Noncatalytic Biodiesel Synthesis under Supercritical Conditions

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Abstract: The constant increase in greenhouse gases in the environment is forcing people to look for different ways to reduce such pollution. One of these ways is the use of biodiesel for road transport. Conventional biodiesel production involves the catalytic triglyceride transesterification process. When using homogeneous two-stage catalysis, it is difficult to purify the resulting product from the by-products formed, and the catalysts cannot be reused. In the case of heterogeneous catalysis, the process costs are increased due to separation and regeneration of the catalysts. To solve these problems of catalytic synthesis, a noncatalytic process has been recently studied that which takes place under supercritical conditions for an alcohol or other acyl receptor. In such biodiesel production, fatty feedstocks and alcohols are used as raw materials, with the synthesis taking place at supercritical conditions for alcohol, i.e., high temperature and pressure, thus making the process quite simple. This paper reviews the results obtained from biodiesel synthesis using a noncatalytic supercritical process for transesterification using both alcohols and carboxylate esters of low molecular weight, evaluating the optimal conditions for these processes and biofuel stability at high temperatures.

Keywords: biodiesel; transesterification; noncatalytic supercritical process



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1. Introduction

Energy consumption is growing every year. Efforts must be made to meet the growing demand for energy from renewable sources, as one of the disadvantages of fossil fuels is that they are not renewable. The use of fossil fuels also has an impact on climate change and air pollution. Biodiesel has many advantages over conventional petroleum-derived mineral diesel. The biomass from which biodiesel is produced absorbs carbon dioxide from the atmosphere through photosynthesis. One of the positive environmental properties of biodiesel is its rapid biodegradation [1,2]. Compared to mineral diesel, the use of biodiesel or mixtures of mineral diesel and biodiesel in vehicles reduces CO, SO_x, particulate matter and unburnt hydrocarbon emissions [3–5].

Biodiesel is a mixture of alkyl esters of fatty acids, which is typically produced by transesterification of fatty feedstocks with alcohols using catalysts. Typically, oil of high quality is transesterified with methanol using sodium or potassium hydroxide as a catalyst [5,6]. Such a process is not suitable for biodiesel production when using non-edible raw materials with a higher content of free fatty acids and/or water [7], because soaps are formed during the reaction of alkali catalyst with free fatty acids and high-quality biodiesel is not obtained. This problem is solved by using acidic (usually H₂SO₄) or heterogeneous (biocatalysts, metal oxides, etc.) catalysts [8–12]. When using homogeneous catalysts, a one process step is usually not sufficient for obtaining a high yield of fatty acid alkyl esters; thus, a two-stage process is applied. When heterocatalysts are used, the process has a long process duration, but it is possible to produce the biodiesel in one stage [13]. Separation of heterogeneous catalysts increases the cost of the process. In the case of homogeneous catalysis, the catalysts cannot be reused after transesterification. Therefore, researchers have begun to look for alternative technologies that can solve problems encountered by catalytic reactions. One alternative is the supercritical process, where the reaction is carried

out at supercritical alcohol temperature and pressure. In this biodiesel production process, only a mixture of fatty feedstocks and alcohol is used and heated to supercritical alcohol conditions, making the process relatively simple and economical [14].

Recently, an increasing number of studies have been conducted for biodiesel synthesis in supercritical conditions for alcohol or other acyl receptors [15]. This paper reviews the results of biodiesel production applying a noncatalytic supercritical process for transesterification of oil or fat using alcohols and carboxylate esters of low molecular weight, evaluating the efficiency of these processes.

2. Noncatalytic Supercritical Transesterification of Triglycerides Using Short-Chain Alcohols

The supercritical process allows the use of lower quality feedstocks for biodiesel production: oils with higher levels of free fatty acids or moisture. In a supercritical process, triglycerides are converted to biodiesel directly. Neither free fatty acids (FFA) nor water has a negative effect on the process.

Because the process is noncatalytic, the separation and purification of the resulting biodiesel from glycerol is uncomplicated [16–18]. Optimization of the process for the production of biodiesel under supercritical conditions requires the selection of independent variables that influence the process effectiveness and biodiesel yield, such as temperature, pressure, molar ratio of alcohol to oil, and reaction duration [19,20].

Studies of the noncatalytic transesterification process with methanol and ethanol were carried out at temperatures ranging from 280 to 425 °C, pressures ranging from 8 to 43 MPa, a molar ratio of alcohol to oil ranging from 6:1 to 50:1, reaction times ranging from 4 to 90 min (Table 1) depending on the type of oil and equipment used. The majority of studies have been performed for transesterification using methanol, with fewer results obtained from studies for transesterification with ethanol. The results of transesterification with ethanol are presented in Table 2.

Table 1. Summary of reported experiment data for noncatalytic biodiesel production using supercritical methanol.

| Raw Material | Molar Ratio Alcohol/Oil, mol/mol | Pressure, Mpa | Temperature, °C | Duration, min | Yield, w% | References |
|-----------------------|----------------------------------|---------------|-----------------|---------------|-----------------------------------|------------|
| Coconut oil | 42:1 | 19 | 350 | 6.67 | 95 | [21] |
| Palm kernel oil | 42:1 | 19 | 350 | 667 | 96 | [21] |
| Palm oil | 40:1 | 15–25 | 372 | 16 | 81.5 | [22] |
| Refined palm oil | 12:1 | 15 | 400 | 18–20 | 90 ester content 99 conversion | [23] |
| Used Palm oil | 12:1 | 15 | 400 | 18–20 | 80 ester content | [23] |
| Crude castor oil | 43:1 | 21 | 300 | 90 | 96.5 | [24] |
| Castor oil | 40:1 | 20 | 350 | 40 | 100 conversion | [25] |
| Linseed oil | 40:1 | 20 | 350 | 40 | 100 conversion | [25] |
| Soybean oil | 40:1 | 35 | 310 | 25 | 77 | [26] |
| Soybean oil | 43:1 | 35 | 325 | 60 | 84 | [16,27] |
| Sunflower oil | 40:1 | 20 | 400 | 30 | 96 | [28] |
| Cottonseed oil | 41:1 | 8 | 240 | 10 | 95 | [29,30] |
| Hazelnut kernel oil | 41:1 | 8 | 240 | 5 | 95 | [29] |
| Canola oil Canola oil | 40:1 | 20 | 350 | 10 | 100 | [31] |
| | 40:1 | 20 | 400 | 3 | 100 | [31] |
| Waste canola oil | 2:1 w/w | 10 | 270 | 45 | 102 | [32] |
| Rapeseed oil | 42:1 | 43 | 350 | 6 | 97.7 | [33] |
| Rapeseed oil | 42:1 | 19 | 350 | 4 | 95 | [34] |

Table 1. Cont.

| Raw Material | Molar Ratio Alcohol/Oil, mol/mol | Pressure, Mpa | Temperature, °C | Duration, min | Yield, w% | References |
|---|----------------------------------|---------------|-----------------|---------------|------------|------------|
| <i>Jatropha curcas</i> oil | 44:1 | | 358 | 27 | 89.4 | [35] |
| Neem oil | 50:1 | 30 | 425 | 15 | 83 | [36] |
| Mahua oil | | | | 10 | 99 | |
| Waste vegetable oil | 33.8:1 | 23.1 | 271.1 | 20.4 | 95.27 | [37] |
| Tobacco (<i>Nicotiana tabacum</i>) seed oil | 43:1 | 26 | 300 | 90 | 92.8 ± 2.1 | [15] |
| <i>Calophyllum inophyllum</i> oil | 40:1 | 30 | 400 | 30 | 80 | [38] |
| <i>Chlorella protothecoides</i> oil | 19:1 | 15.2 | 320 | 31 | 90.8 | [39] |
| Chicken fat | 6:1 | 41.1 | 400 | 6 | 88 | [40] |

Table 2. Summary of reported experiment data of non-catalytic biodiesel production using supercritical ethanol.

| Raw Material | Molar Ratio Alcohol/Oil, mol/mol | Pressure, Mpa | Temperature, °C | Duration, min | Yield, w% | References |
|-------------------------------------|----------------------------------|---------------|-----------------|---------------|------------|------------|
| Soybean oil | 40:1 | 20 | 350 | n.d. | 77.5 | [41] |
| Canola oil | 40:1 | 20 | 350 | 30 | 100 | [31] |
| Canola oil | 40:1 | 20 | 400 | 10 | 100 | [31] |
| Soybean oil | 40:1 | 20 | 350 | 15 | n.d. | [42] |
| Soybean oil | 15:1 | n.d. | 320 | 50 | 62.5 | [43] |
| Sunflower oil | 40:1 | 20 | 350 | 40 | ~100 | [28] |
| Sunflower oil | 40:1 | 20 | 400 | 30 | ~99 | [28] |
| Palm oil | 33:1 | 15–25 | 349 | 29 | 79.2 | [22] |
| Castor oil | 40:1 | 20 | 350 | 40 | ~100 | [25] |
| Linseed oil | 40:1 | 20 | 350 | 40 | conversion | [25] |
| <i>Chlorella protothecoides</i> oil | 33:1 | 17 | 340 | 35 | 87.8 | [39] |

The process of biodiesel synthesis for transesterification using both conventional oils: rapeseed, sunflower, soybean, palm, and rarer oils such as microalgae, tobacco, neem, mahua oil and oily waste were investigated. The data in the table show that in almost all cases comparatively high yields of fatty acid methyl/ethyl esters were obtained.

2.1. Influence of Alcohol to Oil Molar Ratio on the Biodiesel Yield

The yield of transesterification under supercritical conditions depends on four main independent variables. One of them is the amount of alcohol, which is usually expressed in terms of the molar ratio of alcohol to oil. Stoichiometrically, in order for a triglyceride molecule to react completely to form three moieties of fatty acid alkyl esters, three molecules of alcohol are required, i.e., the molar ratio of alcohol to oil must be at least 3:1. Given that the transesterification reaction is reversible, in order to increase the rate of the direct reaction and shift the equilibrium to the right (side of the reaction product), transesterification usually requires more than the stoichiometric alcohol content. The molar ratio of alcohol to oil in conventional biodiesel synthesis is approximately 6:1. In supercritical conditions, the synthesis of biodiesel results in a high ester yield at an even higher molar ratio of alcohol to oil. Kusdiana and Saka [34] investigated the process of transesterification of rapeseed oil with methanol under supercritical conditions by varying the molar ratio of alcohol to oil 3.5:1 to 42:1. An ester yield of 95 wt% was determined at a molar ratio of 42:1. A crude castor oil methyl ester yield of 96.5 wt% was observed at a molar ratio of

43:1 [24]. The maximum yields for neem oil and mahua oil methyl esters (83 wt% and 99 wt% accordingly) were obtained at a molar ratio of 50:1 [36].

Varma and Madras [25] investigated the influence of raw material molar ratio on the effectiveness of castor oil and linseed oil supercritical transesterification with methanol and ethanol. The molar ratio of alcohol to oil was varied from 10:1 to 70:1. Maximum triglyceride conversion was achieved in all analysed cases at a molar ratio of 40:1. Very similar results have been obtained by other scientists using different types of oils and the same molar ratio of raw materials. The process of canola oil transesterification with methanol resulted in a 100 wt% yield for methyl esters [31]. A biodiesel yield of 96 w% was obtained by transesterification of sunflower oil [28]. A lower yield of 81.5 wt% was observed by performing the process of supercritical transesterification for palm oil [22]. A biodiesel yield of 80 w% was determined after transesterification of *Calophyllum inophyllum* oil [38]. Only 77 wt% ester yield was reported for soybean oil [26].

Successful results at a molar ratio of alcohol to oil of 40:1 were obtained using ethanol for transesterification. The reported yield for ethyl esters of sunflower oil and canola oil was 100 wt% [28,31], and a yield of 77.5 wt% was determined for soybean oil transesterification with ethanol [41].

Nan et al. [39] investigated a molar ratio from 10:1 to 42:1 by optimizing the transesterification process of microalgae *Chlorella protothecoides* oil with methanol and ethanol. Using a methanol to oil molar ratio of 19:1, an ester yield of 90.8 wt% was obtained, and by using a molar ratio of 33:1, the yield for *Chlorella protothecoides* fatty acid ethyl esters was determined to be 87.8 wt%.

Although most authors point out that high transesterification effectiveness is obtained using a large excess of alcohol, some studies have shown that a high ester content is obtained using a lower excess of alcohol, but with different process conditions. Sakdasri et al. [23] performed studies on the transesterification of palm oil with methanol under supercritical conditions using a lower molar ratio of alcohol to oil, which ranged from 6:1 to 15:1. Triglyceride conversion and ester content were higher at a 9:1 molar ratio (300–450 °C and 10.0–12.0 MPa) than that at a 12:1 molar ratio of methanol to oil (250–370 °C and 8.0–11.0 MPa). Similar results were observed at a molar ratio of 15:1 compared to a molar ratio of alcohol to oil of 12:1. Taking into account other process parameters, a molar ratio of 12:1 methanol to oil was chosen as optimal, achieving 90% ester content and 99% triglyceride conversion. A lower yield of 65.5% was reported for soybean oil ethyl esters at a molar ratio of 15:1 [43]. Using an even lower amount of alcohol, the efficiency of the process is significantly reduced: Marulanda et al. [40] obtained an ester yield of 88 wt% at a molar ratio of methanol to chicken fat of 6:1.

Only a few researchers have obtained sufficiently high ester yields at very low molar ratios. Surprising results were reported by Lee et al. [32], who obtained a 102 wt% yield for methyl esters from waste canola oil using a methanol to oil molar ratio of 2:1.

2.2. Influence of Pressure and Temperature on the Product Yield

The critical temperature and pressure for methanol and ethanol are 239 °C and 8.1 MPa and 243 °C and 6.3 MPa, respectively. Studies of noncatalytic transesterification under supercritical conditions have been performed under a variety of conditions. Some of these studies have been conducted at relatively low temperatures and pressures, others have been carried out at significantly higher temperatures and pressures compared to the critical point of alcohols.

Relatively low ester yields were found at temperatures of 200–300 °C. Kusdiana and Saka [34] reported 68 wt% and 70 wt% conversion of rapeseed oil with methanol at a temperatures of 200 °C and 230 °C and a duration of 3600 s. Demirbas et al. [29,30] obtained better results when studying the transesterification process of cottonseed and hazelnut kernel oil under conditions near supercritical temperature and pressure. It has been found that a 95 wt% yield for methyl esters can be achieved at a process temperature

of 240 °C and a pressure of 8 MPa. By optimizing the waste vegetable oil methyl ester production process, a yield of 95.27 wt% was obtained at 271.1 °C and 23.1 MPa [37].

Nan et al. [39] optimized the transesterification process for *Chlorella protothecoides* oil with methanol and ethanol by varying the pressure and temperature from 0.8 MPa to 20 MPa and 270 °C to 350 °C, and found that the optimal pressure and temperature using methanol is 15.2 MPa and 320 °C, respectively. Under these conditions, a yield of 90.8 wt% for *Chlorella protothecoides* oil methyl esters was obtained. The optimum conditions for transesterification with ethanol were determined to be 17 MPa and 340 °C. A yield of 87.8 wt% for ethyl esters of *Chlorella protothecoides* oil was obtained under these conditions.

Other authors point out that relatively low yields of esters are obtained at relatively low temperatures. Varma and Madras [25] reported that at a process temperature of 200 °C, castor oil conversion shows yields of only 55 wt% and 27 wt% using methanol and ethanol accordingly at an alcohol to oil molar ratio of 40:1, a process duration of 40 min, and a pressure of 20 MPa. An even lower conversion yield for flaxseed oil of 29 wt% and 11 wt% was obtained under the same process conditions. Increasing the temperature to 350 °C resulted in an approximately 100% conversion [25]. A temperature of 350 °C was confirmed as optimal from results obtained by researchers investigating the transesterification of coconut oil, palm kernel oil [21] rapeseed oil [33], soybean oil [41], palm oil [22] under supercritical conditions without the use of a catalyst.

Even higher optimal temperatures have been reported by Madras et al. [28] and Farobie and Matsumura [31]. It was found that increasing the temperature from 200 °C to 400 °C for transesterification of sunflower oil with methanol at a constant pressure of 20 MPa increases the triglyceride conversion from 78 wt% to 96 wt%. Similar trends have been observed with ethanol, with almost 100 wt% conversion determined at 350–400 °C [28]. The results showed that temperatures of 350–400 °C are optimal for the transesterification of canola oil with both methanol and ethanol, although, at lower temperatures, the reaction proceeds more slowly, but in all cases the conversion reaches 100 wt% [31].

Although many scientists have obtained yields greater than 95 wt% at temperatures close to 400 °C, the results from some studies are contradictory: Marulanda et al. [40] performed transesterification studies of chicken fat at a temperature of 400 °C and a pressure of 41.1 MPa with an ester yield of 88 wt%. Lamba et al. [38] also obtained a relatively low yield of 83 wt% at the same temperature for the transesterification of *Calophyllum inophyllum* oil with methanol.

However, Sakdasri et al. [23] obtained a much higher ester yield of 99 wt% by transesterification of refined palm oil and an 80 wt% yield for used palm oil at a process temperature of 400 °C and pressure of 15 MPa. Less positive results have been published confirming the positive effect of temperatures higher than 400 °C on ester yield. Lamba et al. [36] performed transesterification studies at 425 °C and 30 MPa to obtain an 83 wt% yield for neem oil methyl ether. Transesterification of mahua oil under the same conditions gave a yield of 99 wt% for methyl esters.

Contradictory results were obtained by evaluating the influence of temperature on the effectiveness of transesterification. The results obtained from tests performed at pressures ranging from 8 to 41.1 MPa at different temperatures show that both at low pressure (8 MPa) and 240 °C, a yield of approximately 95 wt% for methyl esters can be obtained [29,30] and that at an increased pressure of 20 MPa and temperature of 400 °C, a yield of approximately 100 wt% for methyl ester can be found [31]. In contrast, at a pressure of 41.1 MPa and a temperature of 400 °C, only 88 wt% yield for chicken fat methyl esters was obtained [39]; an even lower yield of 77 wt% for soybean oil methyl esters was obtained at a pressure of 35 MPa and temperature of 310 °C.

2.3. Influence of Process Duration on Ester Yield

The rate of transesterification in supercritical conditions is high. Most authors have reported that high ester yields are obtained in a relatively short period of time, although studies have been performed over a wider range of time periods. Varma and Madras [25]

evaluated the ester yield in the process of transesterification of castor oil and linseed oil by varying the duration up to 300 min and found that a process time of 40 min was sufficient to achieve an approximately 100 wt% conversion.

Nan et al. [39] determined a yield of 90.8 wt% for fatty acid methyl esters from *Chlorella protothecoides* after a 31 min process duration; a yield of 87.8 wt% was determined after 35 min of transesterification with ethanol. Similar trends have been observed for the transesterification of palm oil with methanol and ethanol; the reaction proceeds faster with methanol and a slightly higher product yield is obtained. A yield of 81.5 wt% and 79.2 wt% has been reported for palm oil methyl esters and ethyl esters with a reaction time of 16 min and 29 min, respectively [22]. Farobie and Matsumura [31] confirm that the reaction with ethanol proceeds more slowly. After 5 min, the biodiesel yield reached 59.6 wt%, and, after only 30 min, full conversion was determined at a process temperature of 350 °C.

However, the statement that conversion with methanol occurs faster than with ethanol at the same reaction temperatures was contradicted by Madras et al. [28] and Varma and Madras [25], who stated that the same or very similar degree of transesterification is achieved with the same process duration. Transesterification of sunflower oil with methanol and ethanol after 30 min results in conversion rates of 96 wt% and 99 wt%, respectively [28].

Some researchers have achieved high ester yields in a very short time (up to 10 min). Using methanol, the biodiesel yield can reach 68.3 wt and 97.7 wt% after 3 and 5 min, and within 10 min, all canola oil can be converted to biodiesel at a temperature of 350 °C. After raising the temperature to 400 °C, a reaction time of 3 min was found to be sufficient to obtain a conversion rate of 100 wt% [31]. Bunyakiat et al. [21] obtained 95 wt% conversion of coconut and 96 w% conversion of palm kernel oils after 400 s (6.67 min). Over a similar process time (6 min), Marulanda et al. [40] achieved a yield of 88 wt% for chicken fat methyl esters (40:1, 41.1 MPa, 400 °C). Yields of 95 wt% for hazelnut kernel and cottonseed oil methyl esters were obtained after 5 min and 10 min, respectively [29,30]. A 95 wt% yield for rapeseed oil methyl esters was reached in 4 min [34]. A higher yield of 97.7 wt% for rapeseed oil methyl esters was achieved within 6 min [33]. Lamba et al. [36] reported that a yield of 99 wt% was reached in 10 min for mahua oil methyl esters; a yield of only 83 wt% was obtained for neem oil methyl esters after 15 min.

Although most scientists point out that the transesterification rate in supercritical conditions is high, studies by some scientists show that the process requires a longer time, even up to 90 min, and that a high product yield is not obtained in all cases. Transesterification of soybean oil with ethanol gave a yield of only 62.5 wt% with a process time of 50 min. [43]. A yield of 84 wt% after 60 min was observed when using methanol [16,27]. Successful transesterification of crude castor oil [24] and tobacco seed oil [15] with supercritical methanol took as long as 90 min, yielding 96.5 wt% and 92.8 wt% of esters, respectively.

Some researchers achieved high ester yields in a very short time (up to 10 min). Using methanol, a biodiesel yield of 68.3 wt% and 97.7 wt% was obtained after 3 min and 5 min, respectively, and, within 10 min, all canola oil was converted to biodiesel at a temperature of 350 °C. After raising the temperature to 400 °C, a reaction time of 3 min was found to be sufficient to obtain a conversion rate of 100 wt% [31].

2.4. Influence of Raw Material on Transesterification Effectiveness

The raw materials used in the conventional production of biodiesel must contain only small amounts of water and free fatty acids. This is due to the use of alkaline homogeneous catalysts, which form soaps with free acids, and the possibility of lipid hydrolysis to form free fatty acids. Given that no catalyst is used in the supercritical noncatalytic process, the negative effects of water and free fatty acids should be reduced. To evaluate this, studies were performed using different types and qualities of oils. Sakdasri et al. [23] conducted studies on the transesterification of refined palm oil (RPO) and used palm oil (UPO) with methanol. The raw materials differed in their content of water and free fatty

acids: refined palm oil contained less than 0.01% free fatty acids and less than 0.01% water, while the used palm oil contained 4.56% free fatty acids and 0.18% water. Under the same process conditions (molar ratio of methanol to oil 12:1, pressure of 15 MPa, temperature of 400 °C, duration of 18–20 min), 90 wt% of refined palm oil methyl esters and 80 wt% of used palm oil methyl esters were obtained. It can be assumed that transesterification under supercritical conditions is more difficult for raw materials containing a higher content of free fatty acids and water. However, the negative effect of free fatty acids is negated by Marulanda et al. [40], who achieved a yield of 88 wt% for chicken fat methyl esters (40:1, 41.1 MPa, 400 °C, 6 min) for raw material containing approximately 4 wt% of free fatty acids. The negative effect of water on the transesterification efficiency was denied by Nan et al. [39], who obtained ester yields of 90.8 wt% and 87.8 wt% in oil by transesterification of 7.5 wt% of water containing microalgae *Chlorella protothecoides* oil.

The efficiency of the noncatalytic transesterification process under supercritical conditions is also influenced by the type of lipids used. Transesterification of coconut and palm kernel oils with methanol yield 95 wt% and 96 wt% conversion at a molar ratio of 42:1, pressure of 19 MPa, duration of 400 s (6.67 min), and temperature of 350 °C [21]. A similarly high yield of 95 wt% was obtained in the production of cottonseed oil and hazelnut kernel oil methyl esters at a molar ratio of 42:1, pressure of 8 MPa, temperature of 240 °C and process time of 5–10 min. [29]. Varma and Madras [25] studied the transesterification of castor oil and linseed oil with supercritical methanol and ethanol and reported a maximum conversion of approximately 100 wt% under the same process conditions (molar ratio of 40:1 at 20 MPa, 350 °C, and reaction time of 40 min).

Transesterification of microalgae oil (*Chlorella protothecoides*) with supercritical methanol and ethanol gave ester yields of 90.8 wt% and 87.8 wt%. Methanol gave higher yields at milder process conditions (320 °C, 152 bar, 19:1 molar ratio, 31 min, water content of 7.5 wt%) compared to ethanol (340 °C, 170 bar, 33:1 molar ratio, 35 min, 7.5 wt%) [39]. A high yield of esters (95.27 wt%) was obtained using waste vegetable oil with a methanol to oil molar ratio of 33.8:1, pressure of 23.1 MPa, reaction temperature of 271.1 °C, and duration of 20.4 min [37].

2.5. Thermal Stability of Fatty Acid Alkyl Esters

During the production of biodiesel under supercritical conditions, it is very important to select such process parameters that can be used to not only obtain a high yield of biodiesel but can also maintain the thermal stability of biodiesel, because the decomposition of esters takes place at high temperatures.

Román-Figueroa et al. [24] investigated the degradation process of castor oil methyl esters. The decomposition of the ester started at 325 °C after 15 min (0.56 wt% decomposition degree), and, at 90 °C, the decomposition degree reached 80.89 wt% at 90 min. Other researchers have found that the degradation of castor oil methyl esters begins at 300 °C [44]. It was determined that thermal decomposition of castor oil ethyl esters starts at 300 °C and 20 MPa; the decomposition of soybean oil esters begins between 300 °C and 325 °C [45].

Olivares-Carrillo and Quesada-Medina [16] studied the thermal decomposition of soybean oil methyl esters and found that at 300 °C, decomposition begins only after 75 min; at higher temperatures the decomposition of esters starts after a shorter time: after 30 min at 325 °C and after 15 min at 350 °C. Silva et al. [46] obtained a high yield of soybean oil ethyl esters at 325 °C and observed a low degree of thermal decomposition (<5.0 wt%).

The composition of the fatty acids of oil or fat used for transesterification are of great importance for the thermal stability of the produced fatty acid alkyl esters. Imahara et al. [47] investigated the thermal stability of methyl palmitate (C16:0), methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), and methyl linolenate (C18:3). Esters of saturated fatty acids (C16:0 and C18:0) were found to be thermally stable at 300 °C, but decomposed after 60 min at 350 °C.

The degradation rates for methyl esters of unsaturated fatty acids varied quite significantly. Approximately 10 wt% of methyl oleate (C18:1) decomposes at 300 °C and 19 MPa after 20 min. Temperature has a great influence on the stability of methyl linolenate (C18:3), 25% of which decomposes in 5 min at 350 °C. Research results demonstrate that esters of polyunsaturated fatty acid esters are much more sensitive to temperature than esters of monounsaturated or saturated acids. However, the results are stable at temperatures of 270 °C and below.

Vegetable and animal fats differ in their composition of fatty acids. Animal fats contain more saturated fatty acids and vegetable fats contain more unsaturated fatty acids. As a result, fatty acid methyl or ethyl esters derived from vegetable oils show a lower thermal stability and decompose at lower temperatures. Meanwhile, esters with an animal origin show a higher thermal stability. This is also evidenced by the thermal stability studies of chicken fat methyl esters performed by Marulanda et al. [40]: it was found that a temperature of 350 °C does not have a greater effect on the thermal decomposition.

3. Noncatalytic Interesterification with Carboxylate Esters of Low Molecular Weight under Supercritical Conditions

Conventional biodiesel (fatty acid methyl or ethyl esters) is obtained by transesterification of fatty feedstocks (triglycerides) with short-chain alcohols. A by-product of the transesterification process is crude glycerol, which is formed up to 10% [48]. Recently, there has been interest in a biofuel production process that can produce a blend of biodiesel and triacylglycerol (TAG), thus reducing production costs, eliminating the need to separate glycerol from the reaction product, and improving the quality of the biodiesel [49]. This is achieved by the use of carboxylate esters of low molecular weight for triglyceride interesterification, resulting in a mixture of fatty acid alkyl esters (FAME) and triacylglycerol (TAG) [50,51]. Theoretically, such a mixture contains about 80% of FAME and about 20% of TAG. This not only solves the problem of glycerol formation and separation but also results in a higher biofuel yield. The resulting mixture theoretically yields 25% more fuel than biodiesel obtained applying conventional transesterification because the TAG generated during the process is inseparable from the reaction mixture and can be used as fuel [52]. Additionally, a blend of FAME and TAG has better low-temperature properties than pure biodiesel and can be used as fuel in diesel engines [53,54]. The interesterification process for triglycerides is carried out without the use of a catalyst, but in the presence of acyl receptors in a supercritical state at high temperature and pressure. The results from interesterification studies using different types of oils and methyl and ethyl acetates are presented in Table 3.

Table 3. Summary of reported experiment data of catalytic biodiesel production using supercritical carboxylate esters of low molecular weight.

| Raw Material | Interesterification Agent | Molar Ratio mol/mol | Pressure, Mpa | Temperature, °C | Duration, min | FAME Yield, w% | References |
|---------------------|---------------------------|---------------------|---------------|-----------------|---------------|----------------|------------|
| Palm oil | Methyl acetate | 30:1 | n.d. | 399 | 59 | 97.6 | [55] |
| Palm oi | Methyl acetate | 30:1 | 22 | 400 | 60 | 99 | [49] |
| Palm oil | Methyl acetate | 42:1 | 20 | 300 | 45 | 95.0 | [53] |
| Jatropha curcas oil | Methyl acetate | 50:1 | | 400 | 32 | 71.9 | [35] |
| Jatropha curcas oil | | | | | | | |
| Soybean oil | Methyl acetate | 42:1 | 20 | 345 | 50 | 100 | [56] |
| Sunflower seed oil | Methyl acetate | | | | | | |
| Waste soybean oil | | | | | | | |
| Rapeseed oil | Methyl acetate | 42:1 | 20 | 350 | 45 | 96.7 | [57] |
| Rapeseed oil | Methyl acetate | 42:1 | 17.8 | 350 | 45 | 97.7 | [33] |
| Rapeseed oil | Methyl acetate | 42:1 | 20 | 350 | 45 | 97.0 | [52] |
| Olein acid | Methyl acetate | 42:1 | 20 | 350 | 20 | 91.0 | |
| Canola oil | Methyl acetate | 40:1 | 20 | 380 | 10 | 80.0 | [58] |

Table 3. Cont.

| Raw Material | Interesterification Agent | Molar Ratio mol/mol | Pressure, Mpa | Temperature, °C | Duration, min | FAME Yield, w% | References |
|--------------------------------------|---------------------------|---------------------|---------------|-----------------|---------------|----------------|------------|
| Macauba oil | Methyl acetate | 5:1 <i>w/w</i> | n.d. | 325 | 45 | 83.0 | [59] |
| Macauba pulp oil | Methyl acetate | 1:1 | 20 | 325 | 40 | 96.7 | [60] |
| Soybean oil | Methyl acetate | 5:1 <i>w/w</i> | n.d. | 350 | 45 | 44.0 | [59] |
| Pongamia pinata oil | Methyl acetate | 42:1 | 20 | 300 | 45 | 96.6 | [61] |
| <i>Nanochloropsis Salina</i> sp. oil | Methyl acetate | 40:1 | 10 | 310 | 60 | 70.0 | [62] |
| <i>Calophyllum inophyllum</i> oil | Methyl acetate | 40:1 | 30 | 400 | 30 | 70.0 | [38] |
| Palm oil | Ethyl acetate | 50:1 | 20 | 350 | 20 | 78.3 | [63] |
| Palm oil | Ethyl acetate + 10% water | 30:1 | 16 | 380 | 42.4 | 90.9 | [64] |

The possibilities for the transesterification of rapeseed oil with various types of carboxylate esters (methyl, ethyl, propyl and butyl acetates, propionates and butyrates) under supercritical conditions were investigated by Goembira et al. [33]. It was found that at 350 °C and up to 17.8 MPa, transesterification takes place without a catalyst, and, among the carboxylate esters studied, the highest yield of 97.7 wt% was obtained when using methyl acetate. The yield of the product decreases with the use of carboxylate esters in the following order: methyl > ethyl > propyl and butyl acetates.

3.1. Influence of the Carboxylate Esters to Oil Molar Ratio on Biodiesel Yield

Most studies have been performed for single-step transesterification using methyl acetate. Stoichiometrically, 3 moles of methyl acetate are required to convert 1 mole of triglycerides to 3 moles of fatty acid methyl esters (FAME) and 1 mole of triacylglycerol (TAG). Goembira et al. [53] found that the formation of FAME was observed to occur only for a molar ratio of methyl acetate to oil of 6:1.

Some researchers have used particularly low molar ratios of raw materials ranging from 1:1 to 5:1. Visioli et al. [60] obtained a 96.7 wt% yield for macauba pulp oil methyl esters at a molar ratio of 1:1. Doná et al. [59] investigated and optimized the molar ratio of methyl acetate to oil ranging from 1:1 to 5:1. The optimum molar ratio was found to be 5:1, yielding 83 wt% macauba oil and 44 wt% soybean oil methyl ester yields. Campanelli et al. [56] analysed the process of transesterification of various raw materials with methyl acetate by changing the molar ratio of methyl acetate to oil from 25:1 to 59:1. A maximum yield of 100 wt% FAME was found to be achieved at a molar ratio of methyl acetate to oil of 42:1. The same optimal molar ratio for raw materials was reported by Goembira et al. [53], who investigated the transesterification process of palm oil by varying the molar ratio from 3.5:1 to 54:1. Increasing the molar ratio from 42:1 to 54:1 led to an insignificant increase in the yield of FAME from 96.7 wt% to 97.2 wt% and that of triacetin from 8.8 wt% to 9.0 wt%, respectively. A similar molar ratio of 40:1 for raw materials was used by researchers in the production of canola oil methyl esters: an 80 wt% yield was obtained [58] and a 70 wt% yield for algal oil methyl esters was reported [38,63]. However, Tan et al. [49], obtained different results, and stated that a molar ratio greater than 30:1 results in a lower yield for esters. It was reported that at this molar ratio, a 97.6 wt% and 99 wt% yield for palm oil methyl esters was achieved [49,55].

Noncatalytic transesterification of triglycerides with ethyl acetate has been less studied. Sootchiewcharn et al. [63] used an ethyl acetate to refined palm oil molar ratio of 50:1 to obtain a 78.3 wt% yield for biodiesel. Komintarachat et al. [64] investigated the process of transesterification of palm oil with supercritical ethyl acetate by changing the molar ratio of raw materials from 10:1 to 35:1 and found that the optimal molar ratio is 30:1; under these conditions, a 90.9 wt% biofuel (FAME and TAG) yield was obtained. The influence of water content on the efficiency of the process was also investigated and it was found that the addition of 10% water in the reaction medium increases the yield of the product due to

acetic acid formation during the hydrolysis of ethyl acetate. Therefore, lower quality fatty feedstocks can be used for interesterification with supercritical ethyl acetate.

3.2. Influence of Pressure and Temperature on the Process Effectiveness

Process pressure and temperature have a significant effect on product yield and depend on the acyl receptor critical temperature and pressure. The critical temperature for methyl acetate and ethyl acetate is 233.85 °C and 250 °C, and the critical pressure for methyl acetate and ethyl acetate is 4.69 MPa and 3.83 MPa, respectively. Most studies have been performed for one-step interesterification using methyl acetate at temperatures ranging from 270–400 °C and a pressure of 20 MPa. Various types of vegetable oil (jatropha curcas, soybean, sunflower seed, waste soybean oil) have been used to study the conditions for the supercritical interesterification process. Approximately 100 wt% conversion of jatropha curcas oil was achieved at a temperature and pressure of 345 °C and 20 MPa, respectively [56]. Similar results were obtained by Tan et al. [49] for palm oil interesterification at 400 °C and 22 MPa. Visioli et al. [60] achieved a macauba oil methyl ester yield of 96.7 wt%, and Doná et al. [59] obtained a yield of only 83 wt% for macauba oil methyl esters at the same temperature of 325 °C. Goembira and Saka [61] obtained a 96.6 wt% yield for methyl esters of Pongamia pinata oil (300 °C, 20 MPa.).

The efficiency of interesterification using microalgae is lower. The yield of *Nanochloropsis Salina* sp. methyl esters is only 70 wt% under milder conditions: 10 MPa and 310 °C [62]. The same yield was obtained from *Calophyllum inophyllum* oil at 30 MPa and 400 °C [38].

Some studies have also been performed using ethyl acetate as an interesterifying agent. They were carried out by varying the reaction temperature from 330 °C to 370 °C at a pressure of 20 MPa. Maximum triglyceride conversion was found to be achieved at 370 °C and 350 °C [63]. Komintarachat et al. [64] used palm oil and ethyl acetate and varied the process temperature and pressure from 320 °C to 400 °C and 14 MPa to 20 MPa, respectively, and found a yield of only 60 wt% for esters at a pressure of 14 MPa. A maximum product yield of 90.9 wt% was achieved at a process temperature of 380 °C and a pressure of 16 MPa.

3.3. Influence of Process Duration on the Product Yield

The interesterification process under supercritical conditions takes place fairly quickly, with the duration of the process ranging from 15 min to 60 min, obtaining a fatty acid methyl ester yield of 44–100 wt%. Choosing the optimal duration for the process is very important, because at high temperatures and pressures the products formed begin to decompose.

Campanelli et al. [56] conducted interesterification studies of various types of oil (waste soybean, Jatropha curcas, soybean, sunflower seed oil) using methyl acetate under supercritical conditions and reported that approximately 100 wt% conversion is achieved with a relatively short reaction time of 50 min. Other authors report that high product yields are obtained within 45 min: 96.7 wt% for rapeseed oil methyl esters, 95 wt% for palm oil methyl esters [53], and 96.6% for pongamia pinata oil methyl esters [61]. Saka and Isayama [52] obtained a 97 wt% yield for rapeseed oil methyl esters. A slightly lower yield was obtained for macauba oil methyl (83 wt%) [59]. Researchers analysing the process of interesterification of palm oil with methyl acetate reported a longer process duration of 59–60 min obtaining ester yields ranging from 97.6–99 wt% [49,55]. A process time of less than 40 min is not recommended due to lower ester yields of less than 95 wt%. In 32 min, a yield of only 71.9 wt% was achieved for Jatropha curcas oil methyl esters [35]. In 10 min, a yield of 80.0 wt% was obtained for canola oil methyl esters [58].

Intesterification of microalgae oil with methyl acetate is not as effective as other types of oil. Even for a process duration of 60 min, a product yield of only 70 wt% was obtained by interesterification of the microalga *Nanochloropsis Salina* sp. and *Calophyllum inophyllum* oil with methyl acetate [38,62].

The optimal duration of interesterification with ethyl acetate is similar to that using methyl acetate. Komintarachat et al. [64] performed kinetic studies of the continuous interesterification process for palm oil with supercritical ethyl acetate and found that

a maximum biofuel yield of 90.9 wt% was obtained after 42.4 min. Contradictory results were reported by Sootchiewcharn et al. [63]. The highest yields of 63.6 wt% and 78.3 wt% were obtained for ethyl esters and methyl esters, respectively, for a reaction time of 20 min, while an even greater increase in time resulted in a lower product yield.

3.4. Influence of Raw Material on the Effectiveness of Interesterification

Campanelli et al. [56] investigated the interesterification of *Jatropha curcas*, soybean, sunflower seed and waste soybean oils with methyl acetate and found no effect of raw materials on product yield. Under the same conditions, the maximum product yield (100 wt%) was obtained from all tested raw materials. Goembira et al. [33,57,61] conducted many studies using rapeseed oil and methylacetate, and obtained product yields ranging from 96.6 wt% to 97.7 wt%, which met the standards. Rapeseed oil is dominated by oleic acid. Studies of interesterification of rapeseed oil and oleic acid with methyl acetate have shown that, under the same process conditions, high product yields of 97.0 wt% and 91.0 wt% are obtained, respectively, but that the interesterification of oleic acid is more complex and its efficiency is slightly lower [52].

Results of studies performed with macauba oil have shown that interesterification with methyl acetate is sufficient for milder process conditions compared to soybean oil [59]. Visioli et al. [60] reported that interesterification of macauba pulp oil with methyl acetate at a molar ratio of 1:1 gave a product yield of 96.7 wt%. However, the results from interesterification studies in microalgae oil show that this process is more complex compared to other types of oil. The highest product yield obtained so far is only 70 wt% [38,62].

3.5. Thermal Stability of Biofuel Produced by Interesterification in Supercritical Conditions

As with the process of transesterification under supercritical conditions, it is very important for the process of high-temperature interesterification that the products formed are stable at high temperatures and do not decompose with reduced biofuel yields and undesirable decomposition products in the fuel.

The interesterification produces triacylglycerol in the mixture in addition to the alkyl esters, the thermal stability of which may differ from the stability of the alkyl esters of fatty acids. This was observed by Campanelli et al. [56], which indicates that the triacylglycerol content in the interesterification product decreased by a factor of two after 50 min at 345 °C and 20 MPa. Thermal stability studies of palm and rapeseed oil methyl esters and triacylglycerol have shown that palm and rapeseed oil methyl esters and triacylglycerol do not degrade at 300 °C and 20 MPa. The decomposition of these products begins at 350 °C in 45 min. At 380 °C, the degradation of both methyl esters occurs, although a significant proportion of palm methyl ester consists of saturated fatty acids [53]. Studies of the thermal stability of biodiesel produced from microalgae oil in a nitrogen environment have shown that it is not stable even at low temperatures. At a temperature of 205 °C, a 10% decomposition was observed; at 300 °C, 50% of the product degraded, and at 475 °C, decomposition of 90% of the biodiesel was determined [62].

However, contradictory results have been reported by Tan et al. [49,55] who performed interesterification of palm oil with methyl acetate and determined the optimal process conditions. It was found that at 400 °C and 399 °C and after a duration of 60 min and 59 min, the reaction product yield was 99 wt% and 97.6 wt%, respectively, and that no thermal decomposition process was recorded under these conditions.

3.6. Process Economics for Supercritical Transesterification

It was found that biodiesel synthesis at supercritical conditions is technologically feasible however, it is necessary to estimate the production cost of the biodiesel obtained under supercritical conditions and compare it with the production cost of conventional biodiesel. Although the supercritical process does not involve additional processes for the preparation of raw materials and the purification of the resulting product from catalyst and soap, the high process temperature requires additional energy resources and at the

same time increases the cost price of biodiesel. Most scientists who have studied this process indicate that transesterification under supercritical conditions can compete with the existing alkali and acid catalyzed processes in the case when cheap raw materials including waste oil are used for biodiesel production. Kasteren and Nisworo [65] studied the supercritical transesterification process for biodiesel continuous production from waste cooking oil for three plant capacities and determined that supercritical process is an interesting technical and economical alternative for the conversion of waste cooking oil to biodiesel. The economic assessment of the biodiesel plant showed that biodiesel produced via non-catalytic methods is 5 US cent cheaper than biodiesel produced with acid catalyst process. The major contributor to the price is the price of raw material. Feedstock-related costs are responsible for 90% of the costs associated with the supercritical process. Micic et al. [66] found that using different types of alcohols for transesterification, the cost of biodiesel is also different. The lowest cost is obtained for the transesterification using methanol while transesterification in supercritical propanol has the highest direct costs. It was observed that direct costs decrease with the increase in biodiesel yields and they are the lowest at the highest yields.

4. Conclusions

The yield of transesterification with short-chain alcohols under supercritical conditions depends on four main variables. One of them is the amount of alcohol, which is usually expressed in terms of the molar ratio of alcohol to oil. The synthesis of biodiesel under supercritical conditions results in a high ester yield with a higher molar ratio of alcohol to oil compared to the conventional biodiesel synthesis process using chemical catalysts. The majority of research results indicate that the optimal molar ratio of methanol to oil for high ester yields is 40:1.

The process is performed under supercritical alcohol conditions: high temperature and pressure. It has been found that high ester yields can be obtained at 350 °C and 20 MPa. The high temperature is limited by the thermal decomposition of fatty acid alkyl esters, which takes place at a temperature higher than 350 °C for a longer process time.

The thermal stability of biodiesel, produced from different types of oil depends on the fatty acid composition of the oil. Alkyl esters of unsaturated and polyunsaturated fatty acids are less thermally stable than alkyl esters of saturated fatty acids.

The rate of transesterification under supercritical conditions is relatively high. Some authors point out that high ester yields can be achieved in a short time of up to 10 min. The reaction is faster with methanol than with ethanol. Various types of oil can be used for supercritical transesterification, but the process efficiency using microalgae oil is lower.

Under supercritical conditions, interesterification of oil with carboxylate esters of low molecular weight yields a product containing alkyl esters of fatty acids (biodiesel) and a glycerol derivative, triacylglycerol, which is soluble in biodiesel and can be used as a fuel.

Methyl acetate is the most commonly used acyl receptor in this process, resulting in high product yields. The optimum molar ratio of methyl acetate to oil has been determined to range from 30:1 to 42:1. Water in the reaction medium increases the yield of the product, with a yield of more than 90 wt% obtained at temperatures above 350 °C and pressures ranging from 16–20 MPa.

The duration of the process was found to be at least 40 min. The maximum yield is obtained in 60 min. The results from interesterification studies of microalgae oil show that this process is more complicated compared to other types of oil. Thermal decomposition of biofuels obtained by interesterification of lipids with carboxylate esters of low molecular weight starts at 350 °C in 45 min.

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