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Catalytic biodiesel synthesis under supercritical conditions

Egle Sendzikiene* and Violeta Makareviciene

Vytautas Magnus University, Agriculture Academy, LT-44248 Kaunas, Lithuania.
E-mail: egle.sendzikiene@vdu.lt

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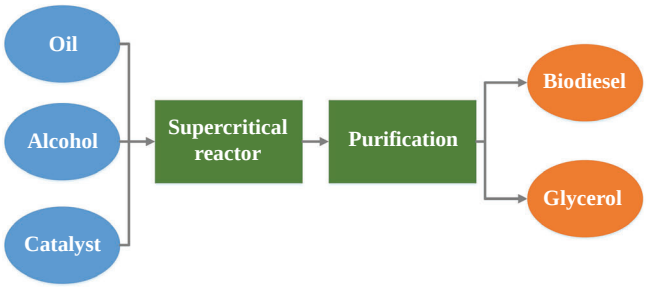
Increasing atmospheric pollution with greenhouse gases, a large proportion of which are transport pollutants, is forcing the search for new fuels from renewable sources. Biodiesel is currently produced by transesterification of plant oils over heterogeneous catalysts under gentle conditions. The other recent technology dealing with the transesterification with alcohols under supercritical conditions, *i.e.*, at high temperature and pressure, can be more efficient, the cost of the resulting biodiesel having been lower, and lower quality feedstocks having been used. Supercritical transesterification can be performed catalytically or catalyst-free. This paper provides an overview of the catalytic lipid transesterification under supercritical conditions. The influence of raw material, alcohol and catalyst, as well as process parameters on biodiesel yield is analyzed.



Keywords: plant oils, biodiesel, transesterification, esters, glycerides, methanol, ethanol, supercritical conditions.

Introduction

The biodiesel industry is developing because biodiesel is an environmentally friendly fuel with lower engine emissions and rapid biodegradation. In the production of biodiesel, triglycerides are transesterified with alcohols. Catalytic biodiesel production using alkaline[1–3] or acidic[4] catalysts, depending on the quality of the raw materials, have been studied and used in industry. In most cases, homogeneous catalysis requires two technological steps to access high-quality biodiesel. Homogeneous catalysts are difficult to remove from the reaction mixture and, as a result, the biodiesel is also contaminated with glycerol, the secondary product of the process. The biodiesel refining stage and reuse of catalyst are not so easy. Studies are also performed using heterogeneous enzymatic,[5–7] natural[8,9] and chemical[10,11] catalysts. However, the duration of heterogeneous procedures are usually long.

In 2001, Saka and Kusdiana[12] began search for biodiesel synthesis employing lower alcohols in supercritical state. Those studies have been continued by other scientific groups.[13–15] The main advantages of the supercritical biodiesel production comprise relatively short reaction times (4–30 min) and high (>95%) yields of esters, whereas the process is not hindered by the presence of free fatty acids and water, making it possible to use lower quality raw materials.[13] Supercritical non-catalytic and catalytic syntheses have been conducted,[16,17] and systematization of results from different researchers allows us to

Egle Sendzikiene has completed his PhD at the Lithuanian University of Agriculture (Lithuania) in 2005. She is the head research fellow and professor at Vytautas Magnus University, Agriculture Academy (Lithuania). She has published more than 60 papers in the scientific journals. E. Sendzikiene has also conducted a number of national and international projects. She has both scientific and practical knowledge of the analysis and usage of renewable energy, biodiesel fuel and biogas. E. Sendzikiene received Lithuania Republic state grant (Young Scientist) in 2008. She was awarded by National science award in 2011 for the cycle of work 'New raw materials and technologies for biodiesel fuel production'.

Violeta Makareviciene received her PhD in Environmental Engineering from Lithuanian University of Agriculture in 2001. Currently she is a professor and head research fellow of Institute of Environment and Ecology at Vytautas Magnus University, Agriculture Academy (Lithuania), head of Laboratory of Chemical and Biochemical Research for Environmental Technology at the same institute. Main research activities and responsibilities of V. Makareviciene – research in the field of biofuel and biolubricant production, usage and influence on environment. She has published more than 80 peer-reviewed papers in international scientific journals. She has coordinated and performed national and international research projects, is a member of editorial boards of scientific journals 'Environmental Research', 'Engineering and Management', 'International Scholarly Research Notices', 'Biofuels Engineering', 'Agricultural Engineering'. She was awarded by National science award in 2011 for the cycle of work 'New raw materials and technologies for biodiesel fuel production'.

state that the use of catalysts provides higher yields at lower temperatures and shorter processing times.[18–20]

This paper summarizes the results of biodiesel synthesis using catalytic supercritical processes. The effect of raw materials and catalyst type on biodiesel yield is analyzed. The optimal conditions found by individual authors are presented, namely, molar ratio of alcohol to oil or fatty acids, amount of catalyst, processing time, and temperature. The possibilities of reusing a heterogeneous catalyst are indicated, the economic aspects of catalytic biodiesel synthesis under supercritical alcohol conditions are discussed.

1. Catalytic supercritical transesterification of triglycerides using short-chain alcohols

1.1. Influence of raw material on transesterification effectiveness

The quality and type of raw materials affect the efficiency of the transesterification. Most of scientists explored edible oils in the catalytic synthesis of biodiesel in supercritical methanol (Table 1). The use of high quality oils in the synthesis of biodiesel was found not always result in a high product yield. Some publications report ester yields over 96%,[21] while others provide figures of 78–79%.[22]

Most research has been done with the most widespread world plant oils. Ester yields of 94–100% were obtained for soybean oil using methanol for transesterification.[15,21,23,26–29] Soybean oil is mainly consumed in America while rapeseed and sunflower oils are more popular in Europe. Demirbas[21] obtained high yield (96%) for 'rapeseed methyl esters' upon catalytic transesterification in supercritical methanol. Mazanov[37] reported 95–98% yield of 'rapeseed ethyl esters' depending on the catalyst, whereas Yoo[22] indicated a significantly lower yield of 68–79%. Santana[24] studied the transesterification of rapeseed oil with both supercritical alcohols under the same conditions and reported 90% yield of 'rapeseed methyl esters' while the yield of similar ethyl esters was only 80%. Supercritical transesterification of sunflower oil with methanol yielded 97–100% of methyl esters.[21] Lin[31] obtained 98% yield of methyl esters from coconut oil. Sawangkeaw[14] used supercritical hydrated ethanol for transesterification of palm oil and achieved 97–100% yield of the esters. The application of less popular oils was also studied: in case of rubber seed oil the methyl esters were obtained in 87% yield,[35] whereas for mahua oil this value reached 98%.[34]

Some researchers have turned attention to low-quality or non-food raw materials. The one-step methanolysis of waste cooking oil provided 95–100% yields of the methyl esters depending on the catalyst.[32,33] The single-stage synthesis of biodiesel using simulated feedstock consisting of 33% free fatty acids and 67% soybean oil gave more than 90% of methyl esters. This value was raised to 99% by employing a two-stage process in the packed bed reactor.[30] The lowest yield of methyl esters (3–5%) was obtained in the case of *Chlorella vulgaris* (64% moisture) microalgae biomass.[20]

Ethanolysis of oleic acid and its natural glycerides under supercritical conditions is outlined in Table 2.

Zhang[36] using supercritical methanol for esterification of free oleic acid obtained a 90% yield of methyl oleate. Liu[29] achieved as much as 99% yield of ethyl oleate in supercritical ethanol.

1.2. Influence of catalyst nature on the biodiesel yield

A number of studies on the variation of catalysts in the supercritical synthesis of biodiesel have been carried out. The most popular

Table 1 Catalytic production of biodiesel in supercritical methanol.

Raw material	Molar ratio MeOH/oil	Catalyst (wt%)	*P*/bar	*T*/°C	*t*/min	Yield (wt%)	References
Rapeseed oil	41 : 1	MgO (3)	240	251.85	23.33	~97	21
Rapeseed oil	40 : 1	ZnO (1)	105	250	10	96	21
Rapeseed oil	40 : 1	TiO_2 (1)	151	270	10	79	22
Rapeseed oil	40 : 1	ZrO_2 (1)	151	250	10	68	22
Sunflower oil	41 : 1	MgO (3)	240	251.85	23.33	~100	21
Sunflower oil	41 : 1	CaO (3)	SC[a]	251.85	6	~97	18
Soybean oil	24 : 1	KOH (0.1)	SC[a]	160	20	98	23
Sunflower oil	25 : 1	SAC-13[b]	250	200	2	90	24
Soybean oil	41 : 1	MgO (3)	240	251.85	20	~100	21
Soybean oil	60 : 1	AcOH[c]	200	280	90	98	25
Soybean oil	30 : 1	AcOH (3.125)	75.8	250	60	95	15
Soybean oil	18 : 1	$MnCO_3$/ZnO (4)	SC[a]	174.85	60	94	26
Soybean oil	n.d	Na_2SiO_3 (0.5)	SC[a]	220	30	96	27
Soybean oil	24 : 1	K_3PO_4 (1)	SC[a]	220	30	96	28
Soybean oil	15 : 1	$MnCO_3$/$NaSiO_3$ (5)	SC[a]	174.85	60	98	19
Soybean oil with fatty acids[d]	9.4 : 1	ZnO–TiO_2–Nd_2O_3/ZrO_2	SC[a]	200	69	95	30
Soybean oil with fatty acids[d]	9.4 : 1	ZnO–TiO_2–Nd_2O_3/ZrO_2	SC[a]	200	69	95	30
Soybean oil with fatty acids[d]	9.4 : 1	ZnO–Yb_2O_3–SiO_2/ZrO_2	SC[a]	230	69	93	30
Coconut oil	30 : 1	MnO_2	55.2	240	11	98	31
Waste cooking oil	41 : 1	KOH (6)	SC[a]	286.85	20	~100	32
Waste cooking oil	50 : 1	Aglomerated Zr–SBA-15/bentonite	70	210	30	95	33
Chlorella vulgaris (64% moisture)	9 : 1 to dry algae	α-Al_2O_3 (5) $Zr(WO_4)_2$ (5) ZrO_2 (5)	SC[a]	385	60	5 4 3	34
Rubber seed oil	28 : 1	KF/CaO–Fe_3O_4–Al (1.5)	SC[a]	220	49	87	35
Rubber seed oil	26 : 1	KF/CaO–Fe_3O_4–Li (1.5)	SC[a]	220	60	85	35
Rubber seed oil	34 : 1	KF/CaO–Fe_3O_4–Al (1.6)	SC[a]	220	60	69	35
Oleic acid	20 : 1	γ-Al_2O_3	200	275	0.5	90	36

[a] Value arising for supercritical conditions. [b] Solid acid. [c] Acetic acid/oil molar ratio 3:1. [d] Mixture of soybean oil (67 wt%) and free fatty acids (33 wt%).

Table 2 Catalytic production of biodiesel in supercritical ethanol.

Raw material	Catalyst (wt%)	Molar ratio EtOH/oil	*P*/bar	*T*/°C	*t*/min	Yield (wt%)	References
Rapeseed oil	Al_2O_3	20 : 1	300	349.85	30	97	37
	(2 wt%)			351.85		98	
Rapeseed oil	SrO/Al_2O_3 (2 wt% SrO)	12 : 1	300	349.85	30	97	37
Rapeseed oil	ZnO/Al_2O_3 (2 wt% ZnO)	12 : 1	300	349.85	30	97	37
Rapeseed oil	MgO/Al_2O (2 wt% MgO)	12 : 1	300	349.85	30	95	37
Sunflower oil	SAC-13[a]	25 : 1	200	200	6	80	24
Palm oil	CaO/Al_2O_3	30 : 1	200	285	4.84	97	14
Palm oil	La_2O_3/Al_2O_3	30 : 1	200	285	4.84	100	14
Oleic acid	γ-Al_2O_3	18 : 1	SC[b]	325	1	99	29
Waste soybean oil	[HMim][HSO_4]	40 : 1	96.2	254.85	45	98	38

[a] Solid acid. [b] Value arising for supercritical conditions.

catalysts were heterogeneous ones, which are easier to separate and reuse. However, homogeneous catalysts were also of attention. Potassium hydroxide as the homogeneous catalyst for supercritical methanolysis provided high product yields.[23,32] In the processing of soybean oil, the amount of catalyst was changed from 0 to 0.25%, the optimal KOH content was found to be 0.1% when 98% yield of the esters was reached in 10 min at 240 °C.[23] In the case of waste cooking oil, preparation of the methyl esters required significantly higher amount of catalyst when the yield of target material of 99.6% was achieved at 6% of KOH with processing at 286.85 °C for 20 min.[32] As for other homogeneous catalysts, at 220 °C the yield of 'soybean methyl esters' was 95.6% within 30 min with the application of 0.5% Na_2SiO_3[27] or 1% K_3PO_4.[28]

Acidic homogeneous catalysts were also tested for synthesis of 'soybean methyl esters' under supercritical conditions. Wei[25] used acetic acid to partially trap the glycerol byproduct and to promote the liberation of fatty acids under supercritical conditions. The optimum reaction temperature was determined to be 280 °C, the molar ratio of methanol to oil was 60 : 1, and the ratio of acetic acid to oil was 3 : 1. Under these conditions, the yield of 98% for fatty acid methyl esters was reached after 90 min at the reaction pressure of 200 bar and a supply of carbon dioxide. Go[15] obtained 'soybean methyl esters' in a yield of 95% using 3.125% acetic acid over 60 min at 250 °C and a pressure of 75.8 bar with the alcohol/oil molar ratio of 30 : 1. Caldas[38] successfully used ionic liquid [HMim][HSO_4] as a catalyst for the transesterification of waste soybean oil with supercritical ethanol. The process was not negatively affected by the presence of 1–3% moisture in the raw material, 98% yield of the esters was reached in 45 min.

However, most studies on oil transesterification under supercritical alcohol conditions have been performed using heterogeneous catalysts. Various metal oxides (MnO_2, CuO, ZnO, MgO, Al_2O_3) were tested as catalysts for the transesterification of coconut oil with supercritical methanol at 240, 280 and 320 °C. Alumina had the lowest activity, giving only 15% of 'coconut methyl ester' at 240 °C, which was similar to the yield obtained without the catalyst. The best results were obtained with MnO_2 at higher temperatures (280 and 320 °C). Oxides ZnO, MgO and CuO had lower catalytic efficiency than MnO_2 at 240 and 280 °C. The maximum yield of methyl esters was about 90%, but it was lower than that for MnO_2 when 98% yield of methyl esters was achieved.[31] Yoo[22] investigated the application of metal oxides (ZrO_2, TiO_2, ZnO, CaO, SrO) in the transesterification of rapeseed oil with supercritical methanol. The highest yield of the methyl esters was obtained with the use of ZnO. Meanwhile, the use of TiO_2 and ZrO_2 gave low ester yields of 79 and 68% (at 270 °C), respectively, which did not differ much from the yields obtained in the course of non-catalytic processes.

Detailed XRD analyzes of the products revealed that oxides CaO or SrO upon mixing with methanol (at 250 °C, 105 bar, 10 min) would form methoxides thus acting as homogeneous catalysts. Zinc oxide, on the contrary, acted as a heterogeneous catalyst. Examination of the transesterification with 0 to 5 wt% of ZnO showed that to obtain 96% yield of methyl esters at 250 °C, 105 bar, with 40 : 1 molar ratio of methanol to oil and 10 min of process time, application of 1% ZnO was required. Pugnet[38] investigated the transesterification of rapeseed oil with supercritical methanol and found, like Lamba,[34] that ZnO was not very efficient and stable, and the better results were obtained with $ZnAlO_4$. Demirbas[21] observed completely different picture and determined that the use of 1% ZnO provided 96% 'rapeseed methyl esters' in 10 min at 250 °C. Lamba[34] investigated the influence of ZnO on the transesterification of mahua oil with supercritical methanol. Zinc oxide was prepared using different fuels (ascorbic acid, urea, glycine, oxalyl dihydrazide and lactose) in solution combustion synthesis. Materials ZnO/ascorbic acid and ZnO–NR were found to best catalyze the process yielding 95–98% of methyl esters. Some authors have tried to improve the process efficiency using complexes of zinc oxide and other metal salts. Wan[26] found by the example of $MnCO_3$/ZnO catalyst that the molar ratio of Mn/Zn was an important factor in the production of an efficient catalyst. The best efficiency of the transesterification was achieved when the molar ratio of Mn/Zn was 1 : 1, the optimal heating time for the preparation of the catalyst was 0.5 h, temperature 300 °C. To determine the optimal amount of catalyst, transesterification was performed with 1 to 5% of the catalyst. The maximum (99%) conversion of triglycerides and 94% ester yield were achieved with the use of 4% of this catalyst.[26] Liu[19] successfully used $MnCO_3$/Na-silicate for soybean oil methanolysis when 98% yield of methyl esters was obtained in 60 min, with the molar ratio of methanol soybean oil having been 15 : 1, the amount of catalyst, 5%, and the process temperature, 174.85 °C.

One of the more promising and cheap heterogeneous catalysts is calcium oxide available from natural sources. However, the data obtained from CaO efficacy studies are quite contradictory. Some authors report high catalytic activity, whereas Demirbas[18] states that the catalytic transesterification capacity of CaO at ambient temperature is rather poor: at 61.85 °C, the yield of methyl esters is only about 5% in 3 h. Calcium oxide, meanwhile, has higher catalytic activity under supercritical transesterification conditions to provide 97% yield of methyl esters using 3% CaO in 6 min at 251.85 °C.[18] Magnesium oxide was also characterized by good catalytic efficiency in transesterification of rapeseed, soybean and sunflower oils with supercritical methanol. The optimum amount of catalyst was found to be 3% for all oils tested. At this amount, the yield of >97% of methyl esters was achieved in 20–23.33 min.[21]

Studies performed by Yoo[22] who used ZrO_2 in the transesterification of rapeseed oil with supercritical methanol were not successful as a moderate (68%) ester yield (270 °C) was obtained. Meanwhile, Kim[30] successfully employed zirconia supported mixed metal oxides ($ZnO–TiO_2–Nd_2O_3/ZrO_2$ and $ZnO–SiO_2–Yb_2O_3/ZrO_2$) to convert low quality soybean oil containing 33% of free fatty acids to biodiesel using methanol. Mixtures of metal oxides have been found to catalyze esterification and transesterification processes simultaneously and can therefore be used for the production of biodiesel from poor quality feedstocks containing much free fatty acids. With the catalysis by $ZnO–TiO_2–Nd_2O_3/ZrO_2$, low quality soybean oil was converted into biodiesel in 95% yield, while $ZnO–SiO_2–Yb_2O_3/ZrO_2$ provided 93% yield.

Some authors investigated the esterification of oil free fatty acids with supercritical ethanol and analyzed the efficiency of heterogeneous catalysts (see Table 2). Liu[29] used γ-Al_2O_3 to catalyze the esterification of oleic acid with ethanol when 99% yield of the product was obtained at a 18 : 1 molar ratio of ethanol to oleic acid, 325 °C and 1 min process time, while a non-catalytic process under the same conditions gave only 40% yield of the ethyl ester. Zhang[36] obtained similar results when 90% yield of esters was achieved using γ-Al_2O_3 oxide in the oleic acid ethanolysis at a molar ratio of ethanol to oleic acid of 20 : 1, the process was carried out at 275 °C for 0.5 min. Mazanov[37] also confirmed that Al_2O_3 was an effective catalyst in the ethanolysis process: the yield of 'rapeseed ethyl esters' was 97% at a catalyst content of 2%, the molar ratio of ethanol to oil was 18 : 1, and the temperature was 349.85 °C. Meantime, Lin[31] reported significantly worse results of transesterification of coconut oil with supercritical methanol using Al_2O_3. At 240 °C, the yield of the methyl esters was only 15%. This catalyst was not effective in the transesterification of high moisture feedstocks. Using *Chlorella vulgaris* biomass containing 64% moisture, the transesterification with supercritical methanol afforded only 5% methyl esters in 60 min.[20]

Mazanov[37] investigated the efficiency of Al_2O_3 in the production of 'rapeseed ethyl esters' under supercritical conditions (349.85 °C with molar ratio 18 : 1) and compared its efficiency with pure and impregnated aqueous metal nitrate solution. When the non-catalytic process was applied, the yield of ethyl esters was 94%, and with Al_2O_3 it grew to 97% and met the requirements of the standard.

Some researchers attempted to improve the catalytic efficiency of Al_2O_3 by its combination with other oxides. Sawangkeaw[14] for transesterification of palm oil with hydrated ethanol used CaO/Al_2O_3 and La_2O_3/Al_2O_3 and reported the ethyl ester yields of 97 and 100%, respectively (molar ratio 30 : 1, 285 °C, 4.84 min). The activity and durability of La_2O_3/Al_2O_3 are greater than those of CaO/Al_2O_3, but the price is about 800 times higher; therefore, the CaO/Al_2O_3 catalyst is more promising considering the technical and economic benefits. With the use of ZnO/Al_2O_3 and MgO/Al_2O_3 catalysts, the highest ester yield (97%) was obtained for MgO/Al_2O_3 containing 5% MgO. For a SrO/Al_2O_3 catalyst, the maximum conversion of 97% was achieved for the sample containing 2% SrO thus making this catalyst prospective.

Nanomagnetic catalysts can also be used in the synthesis of biodiesel under supercritical conditions. Winoto[35] analyzed the CaO-based samples such as $KF/CaO–Fe_3O_4$ and $KF/CaO–Fe_3O_4$–Li (Li additives) as well as $KF/CaO–Fe_3O_4$–Al (Al additives) for transesterification of rubber seed oil with methanol under constant temperature of 220 °C. The most efficient catalyst was found to be $KF/CaO–Fe_3O_4$–Al, which at 1.5% loading gave a 87% yield of the methyl esters (methanol to rubber seed oil molar ratio of 28 : 1, 60 min). The usage of catalyst with lithium additive $KF/CaO–Fe_3O_4$–Li yielded 85% methyl esters at the catalyst loading of was 1.5%. When 1.6% $KF/CaO–Fe_3O_4$ was used without additives, the yield of methyl esters was only 69%.[35]

The results of sunflower oil transesterification using a solid acid catalyst SAC-13 show that this catalyst is more efficient for the case of supercritical methanol compared to ethanol. The yield of esters was 90% in 2 min with methanol, and 80% with ethanol in 6 min at 200 °C and molar ratio of alcohol to oil 25 : 1.[24] Material Zr–SBA-15 has been agglomerated with bentonite clay to form a macroscopic structured catalyst. With the use of this catalyst, processing of waste cooking oil gave 96% of the methyl esters at 210 °C, 70 bar, molar ratio of methanol to oil 50 : 1, and 30 min.[33]

1.3. Influence of alcohol to oil molar ratio on the biodiesel yield

The theoretical stoichiometric molar ratio for the reaction between any monatomic alcohol to triglyceride is 3 : 1. However, the reaction is equilibrium and with this ratio it does not occur completely, so an excess of alcohol is generally required. The higher the molar ratio, the higher the reaction rate, the more equilibrium is shifted to the products and the higher the yield. However, it is important to select the optimal molar ratio, as the higher the excess alcohol used, the higher the material and energy consumption for alcohol separation and recovery into the process.[40] In catalytic supercritical alcohol transesterification process, the alcohol to oil molar ratio used ranged from 9 : 1 to 60 : 1.[25,30] To determine the optimal molar ratio of methanol to oil, the synthesis of 'soybean methyl esters' was performed at a fixed KOH percentage of 0.1% for a set duration of 30 min. Raising the molar ratio of methanol to oil from 6 : 1 to 24 : 1 at a reaction temperature of 160 °C caused the product yield rise from 38 to 100%.[23] Lin[31] for the transesterification of coconut oil with supercritical methanol varied the reactant ratio from 3 : 1 to 60 : 1 with a reaction time of 1.38–11 min. The optimum molar ratio was determined to be 30 : 1 giving the ester yield of 98% in 11 min. For the transesterification of palm oil with hydrated ethanol, the optimal molar ratio was 30 : 1, while 4.84 min was sufficient to reach maximum 100% yield.[14] Kim[30] processed low quality soybean oil (containing 33% of free fatty acids) with variation of the methanol to oil molar ratio from 4.2 : 1 to 13.3 : 1, with the optimal molar ratio of 9.4 : 1 having provided 93–95% of the esters. Mazanov[37] obtained 97% yields of 'rapeseed ethyl esters' when the molar ratio was 20 : 1 and the Al_2O_3 catalyst was used. At a molar ratio of 12 : 1 and with ZnO/Al_2O_3 catalysts, the ester yield was higher than 97% in 30 min.

For esterification of free oleic acid with supercritical ethanol, the optimum molar ratio of the starting materials was found to be 18 : 1, which provided 99% yield of ethyl oleate.[29] In the case of esterification with methanol, a yield of 90% was achieved at a molar ratio of 20 : 1. The similar results were obtained on moving to soybean oil when its 60 min transesterification with methanol at 18 : 1 molar ratio afforded the esters in 94% yield.

Contradictory results were obtained by Santana[24] at a molar ratio of ethanol to sunflower oil of 30 : 1 when only 80% yield of the ethyl esters was achieved. Go[15] found that the optimal molar ratio of alcohol to oil is directly dependent on the reaction time. In the course of transesterification of soybean oil with supercritical methanol, the yield of the esters was about 90% after 30 min, when the molar ratio of alcohol oil was 35 : 1. The yield of 95% was achieved in 60 min at a molar ratio of 30 : 1 with the same amount of catalyst.

The process of transesterification using moist microalgae biomass is somewhat more complicated. Han[20] used a fixed 9 : 1 molar ratio of alcohol to oil calculated for methanol to dry

Chlorella vulgaris algae (64% moisture), but these studies were not successful due to the low yield of esters of 3–5%.

Although the results obtained by many researchers show that a yield of more than 90% of methyl and ethyl esters is achieved at a molar ratio of alcohol to oil of about 20 : 1, some researchers claim that a significantly higher excess of alcohol is required to achieve a high yield of esters. The molar ratio of methanol to rapeseed oil of 40 : 1 was determined to be optimal, but only 96% ester yield was obtained in 10 min.[22] At the same molar ratio, a 98% yield of 'mahua methyl esters' was achieved.[34] Demirbas[18,21,32] tested different types of oils under supercritical methanol conditions and found that the optimal molar ratio should be 40 : 1–41 : 1 to provide more than 97% yields. A large excess of methanol was found to be important for supercritical transesterification of cooking oil. These studies were performed using molar ratios from 10 : 1 to 50 : 1, and a 96% biodiesel yield was obtained at a molar ratio of 50 : 1.[33] An even higher molar ratio of 60 : 1 methanol to soybean oil was used in the study by Wei[25] when only after 90 min the methyl esters were produced in 98% yield.

1.4. Influence of temperature on the biodiesel yield

Temperature is a very important parameter influencing the effectiveness of biodiesel synthesis. As the temperature is raised, the reaction rate increases, resulting in a higher product yield in a shorter time. However, when selecting the optimal temperature, it is important to consider what is more cost-effective and economically or a higher temperature and a shorter reaction time, or a slightly lower temperature and a longer duration. The risk of thermal decomposition of biodiesel also increases at elevated temperatures.

Some researchers have obtained high ester yields when the temperatures were below the critical point. The influence of temperature on the outcome of $MnCO_3$/ZnO-catalyzed transesterification of soybean oil with methanol by changing the temperature from 160 to 182 °C was investigated. Triglyceride conversion varied from 27 to 99% with the temperature growth from 160 to 174.85 °C while the further temperature raising was not important. At the optimal temperature of 174.85 °C, the yield of 'soybean methyl esters' was 94%.[26] Liu[19] confirmed that 98% yield of such esters was obtained at 174.85 °C using $MnCO_3$/Na-silicate catalyst.

Lin[31] performed detailed kinetic calculations to evaluate the optimal temperature for transesterification of coconut oil with supercritical methanol (catalyst MnO_2). A nonlinear dependence of ln$k$ on 1/T was observed when the temperature varied from 160 to 300 °C, however, the linearity existed in two temperature ranges, namely, from 160 to 200 °C and from 200 to 300 °C. This is inconsistent with other studies[40] claiming good linearity below the critical point of methanol (239.8 °C).

Studies[33] on transesterification of cooking oil with methanol at relatively low temperatures (150–210 °C) revealed that the optimal temperature should be 210 °C thus providing the biodiesel yield of 96% (70 bar, 30 min, catalyst Zr–SBA-15). Kim[30] analyzed the methanol transesterification of low quality oils containing 33% free fatty acids. The optimum temperature was found to be 200 °C to give 95% yield of the methyl esters with the use of ZnO–TiO_2–Nd_2O_3/ZrO_2 catalyst. Using ZnO–Yb_2O_3–SiO_2/ZrO_2 as the catalyst, 93% yield of esters was achieved at 230 °C. For transesterification of sunflower oil with methanol and ethanol at 250 bar, the optimum temperature is 200 °C. When solid acid SAC-13 was employed as the catalyst, the yields of methyl and ethyl esters were 90 and 80%, respectively.[24]

Yin[28] found that raising the temperature from 200 to 220 °C significantly increased the yield of esters. The optimum temperature for transesterification of soybean oil with methanol is 220 °C, the use of different catalysts Na_2SiO_3 and K_3PO_4 resulting in the same 96% yield of the esters.[27,28] The 220 °C temperature as optimal was reported by Winoto[35] for the rubber seed oil methanolysis with different catalysts. Lin[31] found that the optimum temperature of the coconut oil methanolysis process was 240 °C providing the ester yield of 98%. This is also consistent with studies by Wang[42] who found that a mixture of methanol and soybean oil became homogeneous only when the critical temperature of methanol was reached.

Similar results were obtained in the transesterification of rapeseed oil with methanol using the ZnO catalyst when the reaction proceeded most efficiently at 250 °C to give 96% of the esters.[21] The results of other studies by Demirbas[18,21] confirm that the temperature of 251.85 °C is the most suitable for soybean and sunflower oil methanolysis using MgO or CaO as catalysts. At this temperature, yields of the methyl esters were higher than 97%.

Less encouraging results were reported by Yoo[22] who used ZrO_2 and TiO_2 at 250–270 °C and obtained only 68 and 79% of the methyl esters. Go[15] confirmed that the temperature of 250 °C was also optimal in the production of 'soybean methyl esters' with a yield of 95%. The yield of 'mahua methyl esters' reached as high as 98% at 249.85 °C in 45 min using the ZnO–NR catalyst.[34] Conversion of 90% of mahua oil was achieved in 65 min at 229.85 °C, and this value was higher than 95% in 20 min at 309.86 °C using ZnO/ascorbic acid as the catalyst.

Zhang[36] optimized the process of oleic acid methanolysis by varying the temperature from 175 to 325 °C and the pressure from 10 to 200 bar. At the optimum temperature of 275 °C and the pressure of 200 bar, the 90% yield of methyl oleate in 0.5 min using γ-Al_2O_3 catalyst was obtained. Yield of 98% of 'soybean methyl esters' was reached in 90 min using acetic acid catalyst at 200 bar and 280 °C.[25] A slightly higher temperature of 286.85 °C is required to obtain ~100% 'waste cooking methyl esters'.[32] Methanolysis studies of *Chlorella vulgaris* (64% moisture) were performed at a very high temperature of 385 °C using various catalysts, but very low ester yields of only 3–5% were obtained.[20]

Since the critical temperature of ethanol is higher than that of methanol, the transesterification of oils with ethanol at higher temperatures was the challenge. Mazanov[37] performed ethanolysis of rapeseed oil at temperatures from 349.85 to 379.85 °C using 2% of non-impregnated and impregnated Al_2O_3 as a catalyst with a molar ratio of ethanol to oil of 18 : 1. When the process temperature increased to 379.85 °C the ester yields decreased from 97 to 92%. The yield of ethyl oleate with the temperature growth decreased, which is thought to be due to the thermal decomposition of esters at temperatures above 374.85 °C, as confirmed by Olivares–Carilo and Quesada–Medina.[43] Liu[29] determined the optimum oleic acid ethanolysis temperature of 325 °C at which 99% yield of ethyl esters was obtained in 1 min.

1.5. Influence of process duration on the biodiesel yield

The duration of the transesterification process is a significant parameter affecting the yield of biodiesel. The influence of duration (20–70 min) on the process efficiency was exemplified[26] by transesterification of soybean oil with supercritical methanol (catalyst $MnCO_3$/ZnO, $MnCO_3$/ZnO, temperature 174.85 °C, molar ratio 18 : 1). The optimal time was found to be 60 min when the ester yield was 94% at the triglyceride conversion of 99%. When the duration was prolonged, the yield of esters decreased.[26]

The same optimal duration was found for supercritical methanolysis of soybean oil,[15,19] robber seed oil,[35] and *Chlorella vulgaris* (64% moisture).[20] A close 69 min duration was found

by Kim[30] who analyzed the methanol transesterification of low quality oils (with 33% free fatty acids). The yield of esters varied from 93 to 95% depending on the catalyst used ($ZnO–Yb_2O_3–SiO_2/ZrO_2$ and $ZnO–TiO_2–Nd_2O_3/ZrO_2$, respectively). The optimal reaction time of 45 min was determined for transesterification of waste soybean oil with ethanol with the use of ionic liquid [HMim][HSO_4] as the catalyst, and a 98% ester yield was obtained.[38]

Lamba[34] reported the yields of 95 and 98% for 'mahua methyl esters' after 20 and 45 min of the same processing with different catalysts such as ZnO–NR and KF/CaO–Fe_3O_4–Al. The optimal duration of the transesterification of the cooking oil with methanol using the catalyst Zr–SBA-15 was 30 min at 210 °C and molar ratio of methanol to oil of 50 : 1. Under these conditions, a 96% yield of methyl esters was obtained.[33] The same duration for the 'soybean methyl ester' production using Na_2SiO_3 and K_3PO_4 catalysts was documented.[27] Mazanov[37] also selected the same (30 min) optimal duration of 'rapeseed ethyl ester' production in 95–98% yields. However, Wei[25] reported longer (90 min) time for supercritical methanolysis of soybean oil required to reach 98% yield of the methyl esters.

Some studies show that high ester yields can be obtained with shorter process times. Waste cooking oil and soybean oil were nearly quantitatively transformed into the methyl esters in 20 min, while for sunflower oil this time was 23.33 min.[21] The highest reaction rate was detected within the first 10 min when the oil conversion grew from 50 to 90% during that time. Lin[31] aimed to determine the optimal duration of transesterification of coconut oil with methanol using MnO_2 as a catalyst. The optimal process time was found to be 11 min at 240 °C at the methanol to oil molar ratio of 30 : 1. Under these conditions, a yield of 98% of methyl esters was obtained. Yoo[22] determined a similar optimal duration of 10 min of transesterification of rapeseed oil with supercritical methanol and obtained a 96% yield of the product at 250 °C and the methanol to oil molar ratio of 40 : 1. Demirbas[21] also found that 96% yield of 'rapeseed methyl esters' was obtained within 10 min. The same value was optimal for the case of 'soybean methyl esters' (98% yield) as reported by Yin.[23] Comparison of catalytic and non-catalytic processes showed that with 0.1% KOH the reaction time was 10 min while without the catalyst the processing required 120 min. These results are useful to optimize the process and reduce production costs.

Santana[24] investigated the effect of process time (2–10 min) on the transesterification of sunflower oil with methanol and ethanol using solid acid catalyst SAC-13. It was found that at 200 °C and a molar ratio of methanol to oil of 25 : 1, 90% yield of esters was obtained in 2 min. Transesterification with ethanol yielded 80% of ethyl esters in 6 min, and higher yields were never achieved. Similar studies were performed by Demirbas[18] who searched for the optimal duration of 'sunflower methyl ester' synthesis, varying it from 1.67 to 26.67 min. It was determined that it took 6 min to reach 97% ester yield using a CaO catalyst at a molar ratio of methanol to oil of 41 : 1 at 251.85 °C.

Studies on the esterification of free fatty acids under supercritical conditions have been relatively scarce. The alcoholysis of oleic acid under supercritical conditions is particularly efficient in a short time. The 90% yield of methyl oleate was achieved in 0.5 min at 278 °C with 20 : 1 molar ratio of alcohol to acid.[36] Esterification with ethanol gave 99% ethyl esters in 1 min at 325 °C and a molar ratio of ethanol to oleic acid of 18 : 1.[29] In both cases, a γ-Al_2O_3 catalyst was used. Liu[29] treated oleic acid with supercritical ethanol for 1 min and obtained the product in 99% yield. However, other researchers failed to achieve such results when 96–98% yields were obtained in just 30–90 min.[25,27]

In summary, the transesterification process is affected by four variables, the interaction of which is important for the yield of esters. In addition, the catalyst used for the synthesis of biodiesel and the feedstocks used are very important, because in the case of high oil acidity, the esterification of free fatty acids and the transesterification of triglycerides should occur simultaneously. When more active catalysts are used, a higher ester yield is obtained under milder process conditions. In any case, after selecting the catalyst and feedstocks, it is necessary to optimize the process by selecting the optimal values of the variables in order to obtain the desired biodiesel yield.

2. Catalyst reuse

Reusing catalysts would reduce the cost of biodiesel production. However, only a few researchers who studied the supercritical biodiesel production process also analyzed the reusability of the catalyst (Table 3).

Wan[26] investigated the reusability of $MnCO_3$/ZnO in the transesterification process of soybean oil with supercritical methanol and found that the catalyst can be used for 17 times without further treatment and without losing its catalytic activity. Liu[29] and Zhang[36] investigated the efficacy of γ-Al_2O_3 as a catalyst in the oleic acid transesterification process. Liu[29] found that the catalyst does not lose efficiency for 25 h when ethanol is used for transesterification, and Zhang[36] reported that the catalyst can be used in a 30 h methanolysis process.

Liu[19] performed pilot plant studies (100 dm^3 biodiesel per day) for the production of biodiesel from soybean oil employing supercritical methanol with $MnCO_3$/Na-silicate as the catalyst. No structural changes of catalyst were observed after 85 h performance in a continuous operation reactor. System $ZnO–Yb_2O_3–Nd_2O_3/ZrO_2$ can be used as a catalyst in the esterification and transesterification process of up to 150 h of soybean oil containing 15% free fatty acids. Even after 150 days, 89% ester yield is obtained.[30] Even better results were obtained using the Zr–SBA-15 catalyst for transesterification of waste cooking oil with supercritical methanol. The catalyst was insignificantly inactivated after 260 h while the ester yield was more than 96% over the entire period.[33]

The data presented in the Table 3 show that there are no positive results on the reusability of widely used pure metal oxides as catalysts. Only alumina which did not have high reusability among the other mixed catalysts studied was further investigated. The reuse of pure metal oxides is limited due to their solubility in oil, biodiesel and glycerol. Yoo[22] for the synthesis of biodiesel under supercritical conditions tested ZrO_2, TiO_2, ZnO, CaO and SrO and found that some catalysts would completely dissolve during the transesterification. Some others have lower solubility, but even they can be partially lost. It was observed that SrO, CaO and TiO were soluble in biodiesel and glycerol, while ZnO is soluble only in biodiesel, and ZrO_2 is insoluble in either biodiesel or glycerol. The high solubility of

Table 3 Reuse of catalysts in biodiesel synthesis under supercritical alcohol conditions.

Catalyst	Raw material	Number of cycles or hours	References
$MnCO_3$/ZnO	soybean oil	17 cycles	26
γ-Al_2O_3	oleic acid	25 h	29
γ-Al_2O_3	oleic acid	30 h	36
$MnCO_3$/Na-silicate	soybean oil	85 h	19
ZrSBA-15/bentonite	waste cooking oil	260 h	33
$ZnO–Yb_2O_3–Nd_2O_3/ZrO_2$	soybean oil containing 15% FFA	150 h	30

CaO and SrO is explained by the formation of strontium and calcium methoxides in their reaction with methanol, and these methoxides are completely soluble in biodiesel.

Kim[30] observed that ZnO is soluble in oil with a high content of free fatty acids, while the mixed oxide ZnO/ZrO_2 is more stable in an acidic medium. Mixtures of oxides containing acidic oxides have been found to be much more stable and therefore have the potential for reuse in biodiesel synthesis. Acidic oxides TiO_2, SiO_2, Nd_2O_3 and Yb_2O_3 were added to ZnO/ZrO_2 during catalyst production.[30] The use of $ZnO–SiO_2/ZrO_2$ not only gave a high yield of esters, but also provided small content of zinc dissolved in the product. When studying the possibilities of using ZnO, it was observed that much of the catalyst was decomposed and adsorbed in the reactor, while $ZnAl_2O_4$ was sufficiently stable and very small amounts were leached.[39] The available results of La_2O_3/Al_2O_3 and CaO/Al_2O_3 application showed that La_2O_3/Al_2O_3 was slightly more active and durable than essentially cheaper CaO/Al_2O_3.[14]

3. Advantages of heterogeneous catalysis in biodiesel synthesis with supercritical alcohols

When introducing new technologies, it is necessary to compare them with those already used in assessing material and energy costs and the competitiveness of the resulting product with the products on the market. Achieving Sustainable Development goals and reducing greenhouse gas emissions require the introduction of less energy-intensive technologies. This must also be achieved in the production of biofuels.

Conventional alkaline transesterification used in biodiesel production proceeds at relatively low temperatures, mostly at boiling point of alcohol, while transesterification in supercritical conditions occurs at significantly higher temperatures and pressures. The optimum process parameters were found as follows: temperature 300 °C, pressure 200 bar. The supercritical process is characterized by high speed even during non-catalytic transesterification, ester yields of 97% are reached in 2–7 min. However, unlike alkaline transesterification, supercritical transesterification requires a significantly higher excess of methanol. The optimal molar ratio of methanol to oil was found to be 42 : 1 (Table 4). Nevertheless, a number of research results suggest that the non-catalytic supercritical process can be more profitable than the conventional catalytic transesterification.[44,45]

Lim[47] determined that the non-catalytic supercritical process applied at 310 °C and 350 bar with a 40 : 1 molar ratio of methanol to oil and a process time of 25 min was more efficient than the alkali-catalyzed process.

Some authors compared the efficiency of the catalytic process at the boiling point of alcohol and under supercritical conditions using the same heterogeneous catalyst and found that the transesterification rate was significantly higher at high temperatures and pressures. Comparative studies of transesterification of sunflower oil with methanol using CaO as a catalyst were performed. It was found that at 61.85 °C after 3 h only 5% of the product was obtained at the 3% catalyst content. With the same amount of catalyst, methanol oil molar ratio 41 : 1, temperature 251.85 °C the ester yield was about 97% in 6 min.[18] Similar results were obtained for transesterification of soybean oil with methanol using MgO as catalyst. The reaction under ambient conditions gives only 5% yield of the product while supercritical conditions provide ~100% of 'soybean methyl esters'.[21] Such studies prove that some catalysts are effective in oil transesterification processes exclusively in supercritical conditions.

Table 4 Comparison of optimal conditions for alkaline and supercritical processes.[46]

Parameters	Alkaline transesterification	Supercritical transesterification
MeOH to oil molar ratio	6 : 1	42 : 1
P/bar	1	200
T/°C	60	300
t/min	108	2–7
Catalyst	NaOH	None
Conversion (%)	95	97
Thermal power (kW_{th})	2407	888
Electrical power	N/A	25

Comparable data on the economic performance of the catalytic supercritical process are scarce. There is more focus on the optimal conditions for catalytic and non-catalytic supercritical transesterification processes. Yoo[22] performed comparative studies of catalytic supercritical transesterification and compared the results obtained with those obtained by Lim[47] who applied a non-catalytic supercritical process. The yield of methyl esters obtained during the catalytic process using ZnO was >95%, which was higher than the yield obtained during the non-catalytic process, and the reaction conditions are milder compared to the non-catalytic supercritical process. Optimal process temperature was 250 °C, pressure 105 bar, molar ratio of methanol to oil 40 : 1, duration 10 min. Given that the temperature and duration of the catalytic process are lower, it can be argued that the economic performance of the catalytic process is better.[22]

Similar results have been obtained by other researchers studying the non-catalytic and catalytic transesterification of coconut oil with supercritical methanol.[31] The non-catalytic supercritical method gave only 44% yield of 'coconut methyl esters' at 350 °C, 414 bar, molar ratio 42 : 1 and within 10 min. The use of CuO as the catalyst provided a yield of 75% of esters under milder process conditions: the process was carried out at 280 °C and 110 bar for 11 min and a molar ratio of methanol to oil of 30 : 1. Even better results (ester yield 98%) were obtained with the use of MnO_2 catalyst at 240 °C, 55.2 bar, a molar ratio of methanol to oil of 30 : 1 for 11 min.[31]

Studies have shown that heterogeneous catalysts not only accelerate the supercritical transesterification process, but result in higher ester yields under milder conditions.[22,31] In addition, the supercritical process is particularly suitable for the production of biodiesel from oils and fats with a high content of free fatty acids, as conventional alkaline transesterification requires additional free fatty acids esterification using acid catalysts. Supercritical process involves both esterification and transesterification simultaneously in one technological stage.[48]

Mazanov[37] investigated the transesterification of rapeseed oil with supercritical ethanol. Under the same process conditions (350 °C, molar ratio 12 : 1), the 78% yield of the esters was obtained without the use of catalyst. The ester yield of 91% was obtained using Al_2O_3 (2%) catalyst, yield of 91% was reported for ZnO/Al_2O_3 (5% ZnO) catalyst, and yield of 97% was achieved using SrO/Al_2O_3 (2% SrO) catalyst.

Although researchers point out that the price of raw materials has the greatest impact on the cost of biodiesel production, the price of energy and other necessary materials is no less important. Compared to the non-catalytic supercritical process, the economic performance of the catalytic process is affected by the cost of the catalyst, which can increase the cost of biodiesel production by using more expensive catalysts. It is therefore necessary to look for inexpensive catalysts from natural sources and their preparation. It is equally important that such catalysts to be regenerated and used for a longer period of time.

Conclusions

The synthesis of biodiesel from vegetable oil can be carried out under supercritical alcohol conditions: high temperature and pressure. This process is more efficient than the conventional

synthesis of biodiesel by transesterification of the oils with alcohols at their boiling points and using homogeneous catalysts. Supercritical transesterification occurs both with and without the use of catalysts. The quality of the raw materials influences the efficiency of the catalytic transesterification process and the yield of the resulting ester. Many scientists tested edible oils for catalytic biodiesel synthesis under supercritical conditions, but the results obtained are quite contradictory.

In the supercritical synthesis of biodiesel, heterogeneous catalysts are most commonly used, which are easier to separate from the reaction mixture for the reuse. Among them, oxides of various metals have high catalytic efficiency. The optimum amount of catalyst to achieve a biodiesel yield of more than 95% is 1–5% depending on the nature of the catalyst. Mixtures of metal oxides simultaneously catalyze esterification and transesterification processes and can therefore be used for the production of biodiesel from poor quality feedstocks with high contents of free fatty acids. Nanomagnetic catalysts, which can be used in the synthesis of biodiesel under supercritical conditions, also have considerable prospects. The results obtained by many researchers show that the yield of methyl and ethyl esters of more than 90% is achieved at a molar ratio of alcohol to oil of about 20 : 1, but some researchers suggest that a high yield of esters requires a significantly higher excess of alcohol.

The results of transesterification studies of waste cooking oil, sunflower oil, rapeseed oil, soybean oil reveal that the optimal molar ratio of methanol to oil is 40 : 1–41 : 1, which gives an ester yield of more than 97%. Raising the process temperature increases the yield of esters. Some scientists claim that 220 °C provides a yield of methyl esters of more than 95%, but most scientists recommend 240–250 °C as the optimal temperature. The duration of the process is one of the independent variables determining the yield of esters. In most cases the average process time is found to be about 60 min, some authors indicate that 90% of the yield of methyl esters is reached in 2 min and 97% of the ethyl esters take 6 min to achieve. Transesterification with ethanol is slower. The rate of the esterification process of free fatty acids is higher, the optimal set process time is from 0.5 to 1 min.

In summary, the optimal conditions for catalytic supercritical transesterification found by different investigators differ significantly from each other, which is due to the interaction of four variables that affect the yield of esters. The process also depends on the type of catalyst used. With more efficient catalysts, the process can be carried out at lower temperatures and high ester yields can be obtained in shorter times. However, the use of more expensive catalysts increases the cost of biodiesel; therefore, the possibilities of catalyst reuse are being examined. The results show that heterogeneous catalysts can be used for 17 cycles without further treatment, or the process can be carried out for up to 260 h.

Although biodiesel synthesis under supercritical conditions can use lower quality feedstocks with high biodiesel outputs, the main problems hindering the commercialization of this process are the higher material and energy costs of the process compared to conventional biodiesel production. High process temperature and pressure increase the cost of the product, making biodiesel uncompetitive with mineral diesel. The cost of the catalyst also has a significant effect on the cost of biodiesel. The price of synthetic heterogeneous catalysts is related to the chemicals used in the synthesis and the processes used, and the price of natural catalysts is affected by the cost of their extraction and preparation. Researchers who have studied the supercritical process suggest that it could compete with the conventional alkali transesterification process in the case of using cheaper raw materials with particularly suitable fatty wastes. The cost of the product decreases with increasing yield, which also depends on the type of catalyst used, so it is necessary to explore the usage of new types of low-cost catalysts, focusing on natural catalysts and their preparation efficiency and energy costs.

Some of the more promising and innovative are nanocatalysts, whose contribution into the efficiency of biodiesel synthesis should be expanded. The impact of the catalyst on the cost of biodiesel would involve the reuse of catalysts without any further treatment. Although the reuse of heterogeneous catalysts directly or after regeneration is being explored, it is still not possible to reuse catalysts without any further treatment by more than several times. It is therefore appropriate to develop new methods for regeneration of catalysts that require less energy and less material inputs.

Given the significantly higher excess of alcohol used for the synthesis of biodiesel under supercritical conditions, it is necessary to investigate measures to efficiently regenerate and recycle unused alcohol, as well as to reduce the amount of alcohol used by replacing with other solvents or using supercritical methyl acetate, methyl *tert*-butyl ether, dimethyl carbonate for transesetreification of oil. In these processes, other valuable products would be obtained together with biodiesel. Only a complex solution of the above-mentioned problems will enable wider application of catalytic transesterification under supercritical conditions.

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