

Review

## A Review of Supercritical Technologies for Lipid-Based Biofuels Production: The Glycerol-free Processes

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**Abstract.** Supercritical transesterification of lipid-based biomasses, a recent technique to produce biofuel without a catalyst, is discussed. This review focused on a glycerol-free process. The supercritical reactants include dimethyl carbonate, diethyl carbonate, methyl acetate, ethyl acetate (ETA), and methyl *tert*-butyl ether. The by-products from the glycerol-free process can improve both the quantity and quality of the resultant biofuel. This review suggests that supercritical transesterification of lipid-based biomasses using ETA as a co-reactant can provide the most valuable advantages, as involves inexpensive and renewable resources, which are important for biofuel production and sustainability.

**Keywords:** Supercritical fluids, biofuel, biomass, oxygenated fuel, glycerol.

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## 1. Introduction

There are global challenges associated with the increasing utilization of energy and the depletion of fossil fuels and diminishing petroleum resources. For the transportation and agricultural sectors, diesel fuel is one of the resources in tremendous demand, resulting in its shortage and increased cost. In the last few decades, there has been a large amount of research into developing and producing liquid fuels with properties similar to diesel from alternative energy sources.

As an early alternative to diesel fuel, pure plant oil was directly used to power diesel engines. The high molar masses and unsaturated fatty acids of the oil cause high viscosity, which leads to incomplete combustion and carbon deposition on the injector parts [1]. To resolve these problems, many processes such as dilution by blending or dilution with diesel [2], catalytic transesterification of vegetable oils with alcohols [3], enzymatic transesterification [4], catalytic pyrolysis [5], and non-catalytic transesterification [6] have been investigated to improve the properties of pure plant oils for use in diesel engines without modification.

From these alternatives, chemical transesterification of plant oil and alcohol to ester compounds has been an attractive process because of its ability to produce a product with identical properties to petroleum diesel [7]. Furthermore, this process can use renewable raw materials from sustainable biological sources. However, in the transesterification of lipid-based biomasses and alcohols, the presence of unwanted glycerol as a by-product [8] has to be eliminated from the resultant biodiesel, which must be treated before use [9]. Therefore, this review focuses on a transesterification reaction for clean biofuel production without glycerol contamination. The methods that were discussed are enzymatic transesterification and non-catalytic supercritical reactions.

The non-catalytic transesterification of triglycerides (TGs) with short-chain alcohols to produce fatty acid alkyl esters (FAAEs) and glycerol as a by-product presents the advantages of high yield and clean production in a short reaction time. In earlier studies of supercritical transesterification methods, edible or non-edible vegetable oils were utilized to produce biodiesel in supercritical alcohols [6]. Short-chain alcohols, such as methanol and ethanol, are effective for transesterification of TGs to FAAEs and are utilized as supercritical reactants because an alcohol molecule directly attacks the carbonyl groups of the TGs at high pressure, producing FAAEs and glycerol [10]. In the supercritical state, depending on pressure and temperature, the intermolecular hydrogen bonding in the alcohol molecule will be significantly decreased by the severe conditions [11]. However, the alcohols utilized as supercritical reactants in transesterification require treatment after the complete reaction to separate the purified ester products and the glycerol by-product.

An organic compound with alkyl groups in its structure is considered as a reactant in supercritical

conditions because these groups can substitute the alkyl groups of fatty acids in TGs during by-product formation [12]; this is therefore an essential step in the reaction. Prospective studies of reactants have been conducted to improve heterogeneous systems, since the solubility parameter, which is a key factor in the transesterification reaction, controls the kinetic parameters of the reaction [13].

This review suggests supercritical methods to produce biofuel without glycerol as a by-product and presents potential reactants for substitution of the short-chain alcohols in the transesterification of vegetable oils to biofuel. The by-product formation from individual reactants in supercritical conditions is examined qualitatively and quantitatively for the achieved production. It should be noted that the biofuel is produced concurrently with the by-product during the reaction. Therefore, in this review, the combination of products will be identified as biofuel [14].

## 2. Chronology of Research and Development of the Supercritical Glycerol-free Process

Non-catalytic supercritical biofuel production is universally carried out through transesterification reactions between TGs and short-chain alcohols (typically methanol or ethanol). The products are a mixture of FAAEs or biodiesel, with glycerol as a by-product. However, the problem of crude glycerol surplus has led to the exploration and development of glycerol-free processes using supercritical technologies. In this respect, alternative solvents such as dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl acetate (MTA), ethyl acetate (ETA), and methyl *tert*-butyl ether (MTBE) have been adapted to replace conventional alcohols. These solvents produce lipid-based biofuels without generating glycerol as a by-product and simultaneously convert glycerol to oxygenated biofuel.

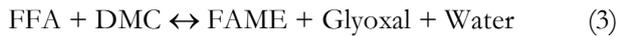
### 2.1. Dimethyl and Diethyl Carbonate

DMC and DEC are multipurpose alkylating agents, and they are non-toxic and biodegradable because of a green preparation process [15]. They have a high oxygen content and can be blended with diesel for improved delivery and spray in diesel fuel engines [16]. Using DMC and DEC could mitigate the glycerol excess problem by converting TGs to fatty acid methyl esters (FAMEs) with glycerol carbonate (GC) as a by-product. The global reaction steps via a reversible reaction process are shown in Eq. (1). The development of biofuel production in both DMC and DEC supercritical processes is reviewed in the next sections.



### 2.1.1. The state of the art

The glycerol-free process in supercritical DMC was first introduced for biofuel production by Ilham and Saka [17]. They selected DMC as a supercritical reactant for one-step conversion of transesterified rapeseed oil to biofuel in a batch-type system with an oil-to-DMC molar ratio of 1:42. The operating pressure and temperature were investigated up to 200 MPa and 550 °C, respectively, which were monitored in real-time. At the optimal conditions of 350 °C and 20 MPa, 94 wt% of FAMEs was obtained after 12 min of reaction time. After evaporation of the excess DMC, the by-products of GC and citramalic acid (CA) were automatically separated from the FAMEs in the lower portion. Furthermore, free fatty acids (FFAs) can be converted by supercritical DMC via an esterification reaction to produce FAMEs, glyoxal, and water. All the quantities of the by-products were much higher than the amount of glycerol produced by the conventional process. All reactions in this study and a schematic of the experiment are shown in Eqs. (2)–(3) and Fig. 1, respectively.



Ilham and Saka [18] proposed a two-step method of water hydrolysis and transesterification of *Jatropha curcas* oil

and supercritical DMC under milder conditions. First, hydrolysis of TGs was conducted at 270 °C and 27 MPa for 25 min, producing FAs and glycerol. Second, transesterification of the hydrolyzed product was performed with supercritical DMC at 300 °C and 9 MPa for 15 min to obtain 97 wt% of FAMEs and glyoxal as a by-product. The glyoxal was separated and purified for use as a raw material for production of glycolic acid and glyoxalic acid in the pharmaceutical industry [19]. The process flow diagram is shown in Fig. 2.

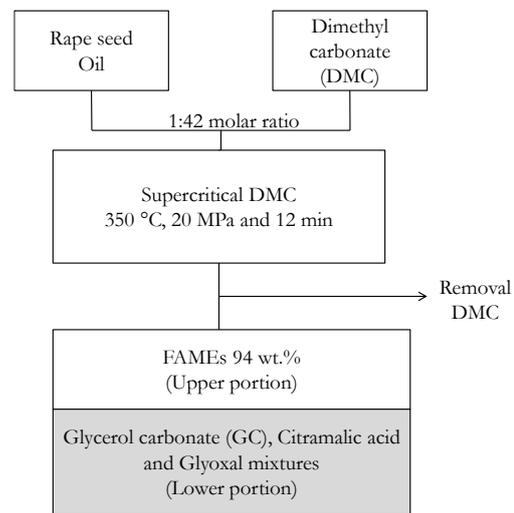


Fig. 1. A schematic diagram of the process for single-step biofuel production by supercritical DMC treatment.

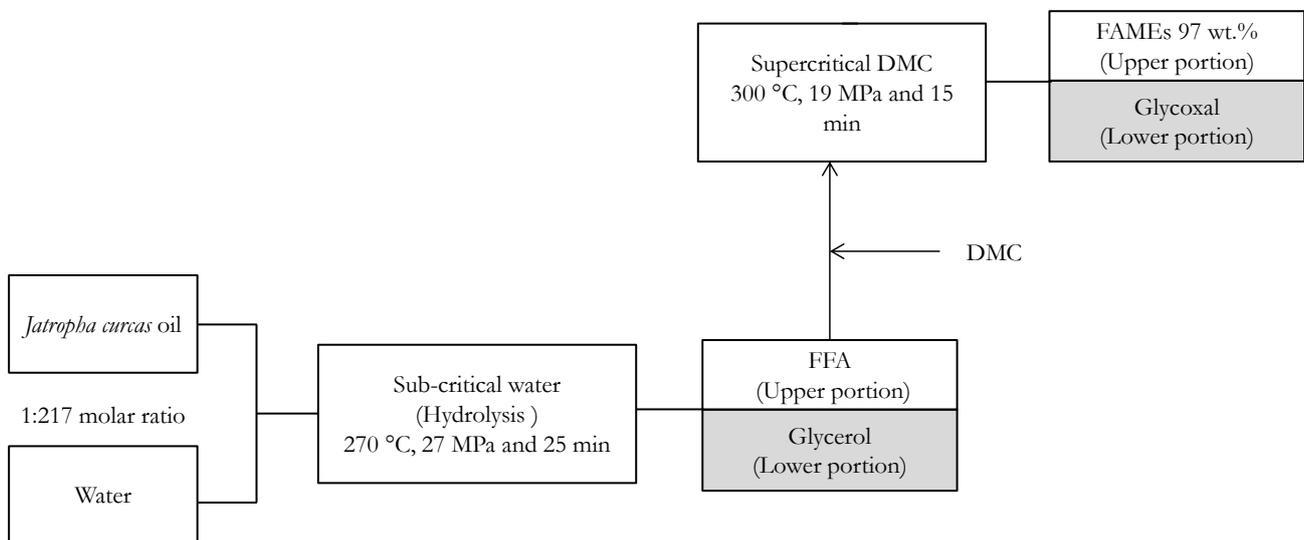


Fig. 2. Schematic of biodiesel production process by the non-catalytic two-step supercritical DMC method.

The effects of other important parameters for esters and value-added GC production from a supercritical DMC process in a batch-type system were studied by Tan et al. [20]. The parameters included reaction temperature, molar ratio, and reaction time, which were optimized using response surface methodology analysis. The main finding of this work is the developed mathematical model; it is statistically significant and adequate to predict the optimum yield. The optimum conditions were 380 °C, a

1:39 molar ratio of oil to DMC, and a 30 min reaction time. A FAME yield of 91 wt% was reported. Moreover, Ilham and Saka [21] noted that additional important key parameters such as thermal decomposition, degree of denaturation, tocopherol content, and oxidation stability should be examined for high-quality biodiesel production. They found that FAMEs from the optimal conditions (300 °C, 20 MPa, 20 min, and 1:42 molar ratio) meet all

the specification standards for biodiesel except oxidation stability.

The development of a supercritical DMC method for biodiesel production from coconut oil was investigated in a continuous-flow system under ambient pressure by Kwon et al. [22]. In this study, activated alumina was packed into the reactor to enhance the conversion. They found that the FAME yield was 98 wt% at temperatures of 360–450 °C within 1–2 min. Recently, a subcritical DMC process for biofuel production was successfully investigated in a novel microwave processing by Ong et al. [23]. The advantages of this method were its simplicity, fewer production steps, and low energy consumption. The reaction temperature of 167 °C provided a maximum biodiesel yield of 86% after 2.5 h without using any catalyst.

The supercritical DEC method was introduced to produce biodiesel from non-edible oils such as *Jatropha* and *Pongamia* oils as feedstock [24]. In a supercritical condition, TGs can be reacted with DEC to produce fatty acid ethyl esters (FAEEs) and GC as a by-product (Eq. (4)). The nearly complete conversion was observed after 45 min at 325 °C and 150 bar. Furthermore, the fuel properties from both feedstocks met the specific standards ASTM D6751, EN 14214, and IS 15607 for biodiesel.



## 2.1.2. Applications of value-added by-products

The supercritical DMC and DEC transesterification processes improve biofuel production and obtain valuable by-products, i.e., GC, glyoxal, and CA, instead of glycerol, as summarized in Table 1.

GC is a chemical component used in membrane separation, as a surfactant, in coatings, and in the detergent industry. It is commonly utilized as a polar monomer for synthesis of new functionalized polymers and is also employed as a substitution for petrol-derivative compounds [25]. Currently, GC shows great potential for use as a solvent for pretreatment of biomass, e.g., sugarcane bagasse [26] and rice husk [27]. As GC is a non-toxic compound, it has been used as an ingredient in cosmetic products such as gel nail lacquer removers and as an emulsifier, a plasticizer, or a humectant [28].

Glyoxal is an accredited chemical substance in the production of paper using a foam baking process [29] and shows good potential as a solubilizer and crosslinking agent for many types of biopolymer such as collagen, cellulose, and chitosan [30, 31]. One of the other by-products is CA, and this can be used in clinical applications and for fruit juice quality control [32]. It also serves as a precursor for the production of methacrylic acid. Polymethyl methacrylate is a polyester that is widely used in transparent thermoplastics in construction, furniture, medical materials, and display technologies [33].

Table 1. Summary of literature-reported experimental data using the supercritical DMC and DEC processes.

Process type	Oil types	Solvents	T (°C)	P (MPa)	Molar ratio	t (min)	EC/FC (%)	By-product	Ref
Batch	Rapeseed	DMC	350	20	1:42	12	94% EC	GC and CA	[17]
Batch	Rapeseed	DMC	300	20	1:42	20	97.4% EC	GC and CA	[21]
Batch	palm	DMC	380	39	1:30	30	91% EC	GC	[20]
Batch (microwave Reactor)	palm	Sub-DMC	167	~5 bar	1:9.5	120	86% EC	GC	[23]
Continuous (packed bed reactor)	coconut	DMC	360–450	ambient	1:42	1–2	98% EC	GC	[22]
Batch	<i>Jatropha</i> and <i>Pongamia</i>	DMC/DEC	325	150	1:40	45	96.5–98.6% EC	GC	[24]
Two-step batch	<i>Jatropha curcas</i>	Sub-Water	270	27	1:217	25	>80% FC	glycerol	[18]
		DMC	300	9	1:14	15	97% EC	glyoxal	

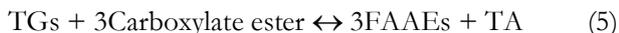
EC: % Ester content, FC: % Fatty acid content. The significant digits are the same as in the original sources.

## 2.2. Carboxylate Esters

The carboxylate esters, namely, MTA and ETA, are intensively involved in the conversion of TGs into FAAEs and triacetin (TA) as a by-product. The global reversible reaction of interesterification is shown in Eq. (5). TA is a fuel additive, is completely soluble in biofuel, and can

improve its cold-flow properties [34]. Both MTA and ETA have a characteristically pleasant smell and low toxicity. They can be used as a solvent with weakly polar bonds and are classified as lipophilic compounds. Both MTA and ETA dissolve in fats, oils, lipids, and non-polar solvents [35]. MTA has the potential to provide the highest yield in supercritical biofuel production [36],

whereas ETA has advantages in terms of being renewable and economically viable. ETA can be manufactured from low-cost agricultural waste materials through ethanol fermentation [37].



### 2.2.1. The state of the art

The earliest application of MTA as a supercritical reactant was proposed by Saka and Isayama [38]. The supercritical non-catalytic method was employed to transform rapeseed oil into FAMES and TA at an oil-to-MTA molar ratio of 1:42. A FAME yield of 97% was obtained at the optimal conditions of 350 °C, 20 MPa, and 45 min. As TA and FAMES are completely miscible, the theoretical weight of the product mixture (FAMES + TA) is 125 wt%, whereas supercritical methanol transesterification results in only 100 wt% of FAMES. In this study, 105 wt% of biofuel was obtained. The schematic of the flow system is shown in Fig. 3. In addition, they studied the effect of TA on fuel properties by mixing TA with methyl oleate in a molar ratio of 1:3. The fuel characteristics, including kinematic viscosity, pour point, cold filter plugging point, and oxidation stability, were observed to follow the Kyoto, JASO, EU, and USA biodiesel standards. However, the cetane number should be improved by adding some kind of fuel modifier.

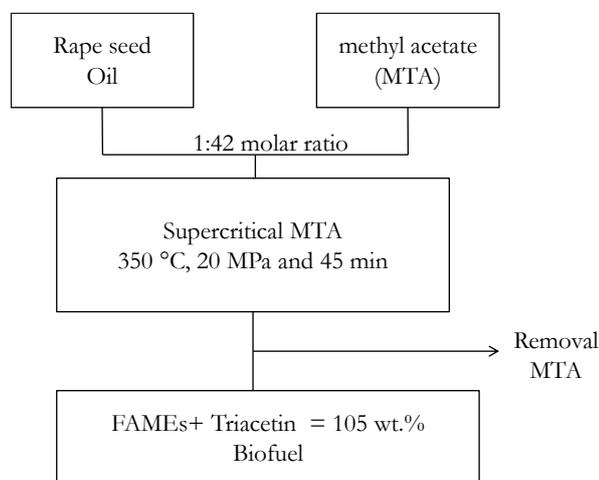


Fig. 3. A schematic diagram of the process for biofuel production from rapeseed oil and supercritical methyl acetate.

Response surface methodology analysis has been utilized in optimization studies of palm biodiesel production in supercritical MTA [39]. A biodiesel yield of 97.6% was achieved at an optimum temperature of 399 °C, a reaction time of 59 min, and an MTA-to-oil molar ratio of 30:1. Goembira and Saka also studied the effects of the MTA-to-oil molar ratio, reaction pressure, reaction temperature, and reaction time on biodiesel yield and degree of thermal decomposition [40]. They found

that a 42:1 molar ratio, 350 °C, 20 MPa, and 45 min provided the maximum yield of 96.7 wt% FAMES and 8.8 wt% TA. With the high temperature, the thermal decomposition of the products and tocopherols was observed in their study.

The thermal stability of FAMES and TA was studied by Niza et al. [41]. They found that the obtained biodiesel yield was only 71.9% because of thermal decomposition at the reaction temperature of 400 °C [42]. Thus, decomposition in supercritical MTA was investigated between 330 °C and 420 °C by using methyl oleate and methyl linoleate as the model FAMES. The methyl oleate decomposed at 390 °C and above, whereas polyunsaturated methyl esters (methyl linoleate) dramatically decreased with increasing temperature from 330 °C to 420 °C. Moreover, a similar phenomenon was also demonstrated with TA; a TA yield of only 4.52% was obtained at a temperature of 360 °C.

The influence of impurities in feedstocks on biodiesel synthesis in supercritical MTA was then investigated by Niza et al. [43] and Tan et al. [44]. Both studies reported that the presence of water and FFAs did not show a significant effect on the biodiesel yield. They noted that TGs could be hydrolyzed with water into FFA and glycerol under supercritical conditions. Subsequently, FFAs were reacted with MTA to generate FAMES and acetic acid. Finally, glycerol was then acetylated with acetic acid into TA and water. The overall reactions are shown in Eqs. (6)–(8).



During the years 2010–2019, the development of biofuel production with supercritical MTA was focused on feedstock flexibility. Several types of oil, namely, soybean oil, sunflower seed oil, *J. curcas* oil, Crambe oil, *Pongamia pinnata* oil, algal lipids, and waste cooking oils, were employed as feedstocks [45–48]. Campanelli et al. [45] compared edible and non-edible oils and waste cooking oil, which have different fatty acid compositions. The results indicated that biofuel yield was not negatively affected by the feedstock composition. The conversions of all feedstocks reached 100% after 50 min at 345 °C, 20 MPa, and a 42:1 molar ratio of MTA to oil. *Pongamia pinnata* oil, which is a non-edible oil and has a high FFA content, has the potential to produce biodiesel in supercritical MTA [47]. At the operating conditions of 300 °C, 20 MPa, 45 min, and a 42:1 molar ratio of MTA to oil, the highest yields of FAMES and TA were obtained as 96.6 wt% and 11.5 wt%, respectively. Lastly, algal lipid biodiesel has been successfully generated by a supercritical MTA process. At an operating temperature of 310 °C, the MTA process provided the highest FAMES yield, at 72%, and a total biodiesel fuel yield of 80%.

Various carboxylate esters, such as methyl, ethyl, propyl, and butyl carboxylates, were first compared in supercritical biodiesel production by Goembira et al. [36]. They found that TGs could be converted with various carboxylate esters to produce FAAEs and TA under supercritical conditions without any catalysts. Among all carboxylate esters, supercritical MTA provided the highest yield of 97.7 wt% at 350 °C and 17.8 MPa. Komintarachat et al. investigated biofuel synthesis from palm oil in supercritical ETA using both batch [49] and tubular continuous reactors [50]. In a continuous system, the highest yield was 90.9 wt%, which was a mixture of FAAEs, TA, and diacetin, was obtained at 380 °C, 16 MPa, and a 1:30 molar ratio of oil to ETA. They also

reported that the addition of water significantly enhances the reaction products (FAEEs and TA) at the optimum conditions. Additionally, acetic acid from TGs and ETA hydrolysis protected the products from thermal decomposition. The yield of FAAEs was increased by transesterification of ethanol and TGs, and the TA yield was increased by esterification of glycerol and acetic acid. These complex reactions were proposed as shown in Fig. 4. Recently, supercritical carboxylate esters in novel reactors, i.e., micro-reactors and fixed-bed reactors [51–55], as well as a two-step method [46], have been proposed as ways to increase the efficiency and quality of biofuel production.

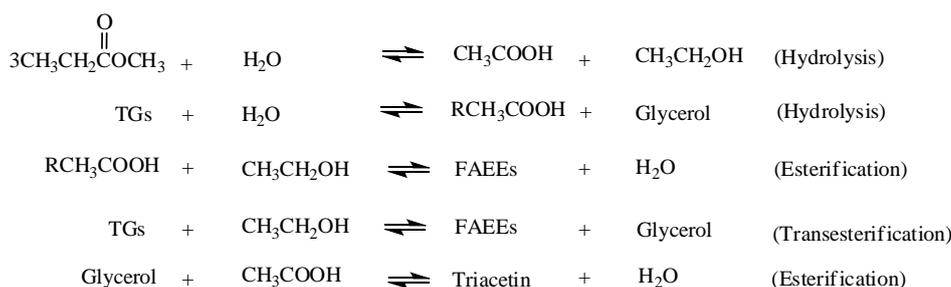


Fig. 4. The reactions of palm oil in supercritical ETA during water addition.

### 2.2.2. Applications of triacetin and its effect on biofuel properties

TA is an oxygenated additive that is used to supplement fuels in an appropriate proportion for cleaner burning, higher combustion efficiency, more stable fuel mixtures, protecting the engine from abrasion and wax deposition, and reducing greenhouse gas emissions through complete combustion [56–58]. In general, TA is synthesized by acetylation of glycerol with acetic acid in the presence of catalysts [59]. There have been several studies into the influence of TA on engine performance [14, 36, 56, 60, 61]. It has been reported that 10 wt% of TA is a value that shows encouraging results. Table 2 shows a comparison of the properties of biofuels with the European (EN 14214) and American (ASTM D6751) biodiesel-specific standards. The combination of FAAEs and TA are in the range 72–96 wt% and 3–20 wt%, respectively.

The density of biodiesel is limited by the EN 14214 standard to 860–900 kg/m<sup>3</sup>. The density directly affects the efficiency of fuel consumption and atomization, as well as the output engine power [62]. The blending of TA into biodiesel increases the density of the mixture because of the density of TA being 1183 kg/m<sup>3</sup>, which is higher than that of FAMEs (~879 kg/m<sup>3</sup>) and FAAEs (~868 kg/m<sup>3</sup>). In the studies of Patil et al. [11] and Akkarawatkhoosith et al. [51], the density of the biofuel was below the EN 14214 guidelines, whereas other studies have shown that densities were slightly high because of an excess of TA over 10 wt%. A similar result was reported in the intensive study by Goembira et al. [36]; the

maximum amount of 10 wt% TA was required to maintain the biofuel density within the EN 14214 regulations.

Kinematic viscosity has an important impact when using biofuel as an alternative fuel for a transport engine. High viscosity leads to problems with fuel injection and combustion [63]. In EN 14214 and ASTM D6751, the safety ranges are set as 3.5–5.0 and 1.9–6.0 mm<sup>2</sup>/s, respectively. In previous studies, the kinematic viscosity was observed to increase slightly with 20 wt% of TG in biofuel [14, 38]. On the basis of Table 3, the kinematic viscosity of modified biofuels, except the study of Sakdasri et al. [55], satisfied the requirements of both the EU and USA standards. Sakdasri et al. [55] reported that the higher viscosity was a result of polymerizing products. These were generated via the Diels–Alder reaction during the supercritical condition of 400 °C and long reaction duration of 10 min [55].

The pour point, cloud point, and cold filter plugging point of biofuels are not regulated in either EN 14214 or ASTM D6751, but they are important indices for the utilization of biofuel in cold climates. In extensive studies [14, 36, 38], the additional TG in biofuel encouraged the reduction of the pour point and the cloud point. For example, reductions in the pour point of approximately 2 °C [38] and 9 °C [14] were reported for proportions of 20 wt% TA in methyl oleate and rapeseed biodiesel, respectively. The presence of TA reduced the cold filter plugging point depending on the composition of FAAEs in biodiesel [64]. It was reduced by up to 2.7 °C with the addition of 20 wt% TA. The effect of TA on the cold filter plugging point was also investigated for different types of biodiesels, i.e., palm, soybean, sunflower, and high-oleic sunflower biodiesels, by Casas et al. [14]. They found that

the presence of TA had an effect only in palm biodiesel: a reduction of 2 °C was reported with the addition of 20 wt% TA. However, the direct influence of TA was reported in Saka and Isayama's [38] study. A slight reduction in the cold filter plugging point was observed from -16 °C to -17 °C with the blending of 20 wt% TA in methyl oleate [38].

Flash point values of all obtained biofuels are above the minimum requirements set by the European and American biodiesel standards. As TA is a highly volatile substance, it slightly reduces the flash point of biofuel. In the study of Melero et al. [56], a reduction of about 5 °C

was reported by blending 25 wt% of TA into pure biodiesel.

The main aim of glycerol conversion in biofuel production is to transform the glycerol into other substances during the reaction process. In this respect, TA can be used as an additive in biodiesel. This additive is remarkable in its reduction of the pour point, cloud point, cold filter plugging point, and flash point; however, it slightly influences the density and kinematic viscosity. The recommended amount of TA to meet the EN 14214 quality requirements is 10% by mass [14].

Table 2. Summary of literature-reported fuel properties of biofuel using the supercritical carboxylate ester process.

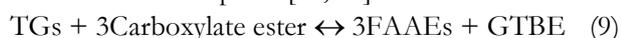
Properties	References						Biodiesel Specification			
	[38]	[47]	[14]	[48]	[51]	[55]	EN 14214	AST M D6751		
FAAEs content (wt%)	80.30	96.6	90	80	72	98.5 ± 0.3	76.5 ± 0.3	72.3 ± 0.5	≥96.5	-
Triacetin content (wt%)	19.70	11.5	10	20	8	3	12%	12%	-	-
Density at 15 °C (kg/m <sup>3</sup> )	920	940	885 to 900	912 to 920	840 to 860	850 ± 3.0	920.3 ± 0.5	921.5 ± 0.4	860–900	-
Kinematic viscosity at 40 °C (mm <sup>2</sup> /s)	4.5	4.9	4.2 to 4.5	4.2 to 4.5	4.5 to 4.8	4.7 ± 0.1	6.1 ± 0.01	6.9 ± 0.02	3.5–5.0	1.9–6.0
Pour point (°C)	-18.0	-10.0	-18 to 20	-20 to 10	-11 to -8	2.3 ± 1.0	N/A	N/A	-	-
Cloud point (°C)	N/A	-10.0	14 to -6	14 to -7	N/A	8.6 ± 1.0	12 ± 2	6.5 ± 2	-	-
Cold filter plugging point (°C)	-17.0	-10.0	-8 to 12	-7 to 12	N/A	N/A	12 ± 2	6.5 ± 2	-	-
Flash point (°C)	154.5	163	160	155	N/A	N/A	135 ± 2	124 ± 5	≥101	≥93

\*Calculated from 10 wt% sample.

N/A: Not available, N/D: Not detected.

### 2.3. Methyl *tert*-butyl ether

Oxygenated additives such as ethanol, diethyl ether, MTBE, and ethyl *tert*-butyl ether (ETBE) are usually employed as gasoline additives for enhancing the octane number [65]. In contrast to diesel or biodiesel, these oxygenated compounds are additives for improving some properties of the fuel. The global reaction of biofuel production with supercritical MTBE is shown in Eq. (9). By this reversible reaction, FAMES and glycerol *tert*-butyl ether (GTBE) are obtained. Adding GTBE to diesel fuel has a positive impact on fuel properties. For example, it helps to reduce the production of particulate matter (PM) and carbon monoxide (CO), improves the cetane number, and reduces the cloud point [66, 67].



#### 2.3.1. The state of the art

This review focuses on producing biofuel without glycerol as a by-product using alternative supercritical reactants with their various alkyl groups. Following this

concept, Farobie et al. [68] examined using the *tert*-butyl group in MTBE to produce biofuel in supercritical conditions. They investigated biofuel production from canola oil in supercritical MTBE using a flow-reactor system. The canola oil was reacted with MTBE to generate FAMES and GTBE without glycerol as a by-product. Parameters such as temperature, pressure, and reaction time were investigated. The optimal conditions were attained at 400 °C and 10 MPa for 12 min with an oil-to-MTBE molar ratio of 1:40, which achieved 95.36 wt% of total FAMES. The schematic diagram of the flow system is shown in Fig. 5. The by-product GTBE is an advantageous oxygenating additive for diesel and biodiesel [69].

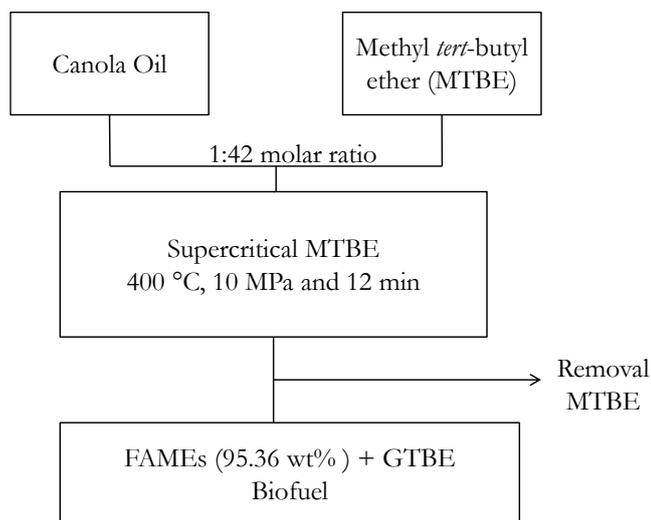


Fig. 5. A schematic diagram of the process for biofuel production from canola oil and supercritical *tert*-butyl ether.

Farobie et al. also proposed biofuel synthesis in supercritical MTBE using a spiral reactor. This reactor was effective in terms of heat recovery [70]. In comparison with a conventional reactor, the spiral reactor has a more energetically efficient process [71]. They found that the energy requirement for biofuel production was reduced from 0.7344 to 0.1071 MJ/d. In the spiral reactor, the conversion of canola oil was complete, achieving 1.00 mol/mol of FAME yield at 385 °C after 20 min [70].

Supercritical MTBE has been employed in the synthesis of biodiesel using inedible vegetable oils (neem and mahua oils) as feedstock [72]. The effects of temperature, pressure, reaction time, and molar ratio on the triglyceride conversion were investigated in an 11-ml stainless steel (SS-316) batch reactor. Conversions of 46% and 59% were obtained after 15 min at 450 °C for neem and mahua oils, respectively. These authors reported that supercritical MTBE appeared to be a more promising process than did the conventional acid-catalytic process because of the higher conversion that was achieved with shorter reaction times.

For supercritical MTBE, ETBE is one of the alternative reactants that can be recommended for use in biofuel production [65]. However, ETBE is deleterious to health because of its carcinogenicity, high solubility in water, and difficulty in biodegradation [73]. However, a study investigating the effects of ETBE addition to diesel and biodiesel [74] showed that the addition of 10% ETBE by volume to diesel can significantly reduce PM emissions and smoke. These authors concluded that ETBE addition could lower the surface tension and improve fuel atomization, thereby increasing thermal efficiency and reducing exhaust emissions.

### 2.3.2. Applications of glycerol *tert*-butyl ether and its effect on biofuel properties

GTBE is an oxygenated compound that is also used as a cetane booster and combustion enhancer in fuels [75].

The effects of adding GTBE to diesel fuel have been reported by Lovstead and Bruno [76]. Three types of GTBEs, namely, mono-, di-, and tri-GTBE, were compared. A slight change in the initial boiling behavior was observed in the blending of di- and tri-GTBE, but this was not significantly affected by mono-GTBE. The addition of mono- and di-GTBE resulted in displacement to a lower distillation curve temperature. Bozkurt et al. [77] also reported the effects of GTBE on the properties of gasoline. The addition of 3.45 vol% GTBE reduced the viscosity of the fuel from 57 to 55 kPa·s and improved the octane number from 95 to 96.

The influence of additional GTBE on biodiesel performance has been reported elsewhere [78]. Modified injection pressure reduces NO<sub>x</sub> emissions by 10.5% in combustion with 2.5% GTBE addition. In addition, a maximum of 20% cut in CO emissions was observed with the modified injection pressure of 240 bar and 5% GTBE addition. However, there have not yet been any studies examining the effect GTBE on the properties of supercritical biofuels.

## 2.4. Perspectives on Synthetic Biofuel as a Renewable Energy Source

The potential of non-catalytic supercritical transesterification of fluids for glycerol-free processes has been highlighted herein. Supercritical technologies have the benefit of saving on the operational cost of raw materials, for instance, through the use of inedible oils, used cooking oil, and animal fat. A value-added by-product, which forms simultaneously with the ester yield, can be classified as an oxygenated additive for improving gaseous exhaust emissions and the release of PM. In the economic analysis, it is notable that the cost of equipment can be reduced because of the absence of a glycerol-recovering and purifying unit [79]. However, the extreme molar ratio proportion of oil to reactants that is required, combined with the price of the reactants, is still the main drawback of supercritical processes. The effects of these factors on supercritical glycerol-free processes are now discussed.

### 2.4.1. Oil-to-reactants molar ratio

The molar ratio of the oil to the reactants strongly affects transesterification reactions in the supercritical condition. As the reactions are reversible, an excess of reactants is necessary to drive the reaction forward. Furthermore, the high oil-to-reactants molar ratio also reduces the critical temperature of the mixture, which enables the easier formation of a homogeneous supercritical phase in milder conditions. In Table 3, the molar ratios employed in supercritical conditions are in the range 1:25 to 1:50. It can be observed that lower molar ratios reduce the yield for all systems. The alternative supercritical reactants use molar ratios between 1:30 and 1:50, showing optimistic yields of esters, and the by-products simultaneously formed during the reaction. The

thermal decomposition and reversible reactions from a high proportion of co-reactant in supercritical conditions leads to lower yields of FAAEs [39, 53].

Table 3. Supercritical transesterification in different systems and conditions for biofuel production.

Systems	Molar ratio (Oil:Reactant)	Temp./Pressure/time (°C /MPa/min)	% Fuel yield*	By-product	Process
Soybean oil–MTA [39]	1:25	345/20/50	50.0	TA	Batch
Soybean oil–MTA [39]	1:42	345/20/50	104.0	TA	Batch
Macauba oil–MTA [53]	1:50	325/20/45	83.0	TA	Continuous
Rapeseed oil–MTA [40]	1:42	350/20/45	105.5	TA	Continuous
Palm oil–ETA [50]	1:30	380/16/49	90.9	TA, DA	Continuous
Canola oil–MTBE [68]	1:40	400/8/12	95.4	GTBE	Continuous

\* Based on weight of lipid-based feedstock alone.

Although a relatively high oil-to-reactants molar ratio provides a high yield of fuel, it also presents the following problems. First, a large energy consumption is required for recycling and recovering the excess reactants. As reported in the biofuel production by a supercritical methanol process at a 1:42 molar ratio, the energy was mainly consumed by the methanol recovery unit [80]. In comparison with the low-molar ratio process (1:12), the energy consumption was observed to be 2.36-fold higher. Second, the equipment costs are increased because of greater volumetric throughput and the corresponding increase in heat consumption for the complete conversion [80].

#### 2.4.2. Price of reactants

In many previous reports relating to supercritical biofuel production [80–84], the price of the raw materials played an important role in the production cost. Although supercritical fluid transesterification for glycerol-free processes is more flexible with feedstocks, especially having the ability to use inexpensive raw materials, the high cost of the reactants should be considered. Table 4 illustrates the price of alternative reactants. Although the costs are quoted for laboratory-grade reagents, they could be representative of industrial-grade reagents. As shown in the table, DEC is the most expensive reactant, followed by MTA, DMC, MTBE, and ETA. Their costs are approximately 1.6- to 4.98-fold higher than that of methanol.

In summary, supercritical biofuel production with a glycerol-free process still faces some limitations, such as the requirement for a high molar ratio of oil to reactants and the high price of reactants. From the perspective of utilizing synthetic biofuel as a form of renewable energy, the energy consumption and the economical assessment need to be determined and optimized.

Table 4. Costs of alternative supercritical reagents.

Item	Specification	Price (USD/liter) <sup>a</sup>
Methanol	ACS reagent, ≥99.8%	51.4
Ethanol	anhydrous, ≥99.5%	123.0
DMC	anhydrous, ≥99%	101.0
DEC	anhydrous, ≥99%	254.0
MTA	≥99.8%	140.0
ETA	anhydrous, 99.8%	82.8
MTBE	anhydrous, 99.8%	95.2

<sup>a</sup> 2019 selling price from Sigma-Aldrich, Inc., © 2019 Merck KGaA, Darmstadt, Germany.

### 3. Conclusion

This paper has reviewed the production of lipid-based biofuels by supercritical technologies focusing on glycerol-free processes. Supercritical DMC and DEC were demonstrated as alternative reactants to generate high-value by-products (GC and CA) in a single-step process. Furthermore, supercritical DMC and DEC could be applied to a two-step process with subcritical water hydrolysis in the first step. Using carboxylate esters as reactants simultaneously enables the solution of phase transfer limitations and the synthesis of value-added by-products in a one-step reaction. By-products such as TA improve the quantity and quality of the biofuel. The supercritical MTBE and ETBE processes generate GTBE as a by-product. However, GTBE is an octane enhancer for gasoline. The toxic nature of MTBE and ETBE is a disadvantage of these processes. From an economics perspective, the oil-to-reactant molar ratio and the cost of the reactants have to be considered for sustainability and energy security in the future.

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