

Alkaline Earth Metal Oxide Supported on Zeolite as a Heterogenous Basic Catalyst for Clean Fuel (Biodiesel) Production: A Mini Review

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Abstract. The depletion of fossil fuel reserves, worsening greenhouse gas effects, and global warming issues have driven the development of renewable energy sources, such as biodiesel. Biodiesel is as an alternative fuel to petrodiesel, typically produced through a transesterification reaction of triglycerides and alcohol in the presence of a catalyst. Alkaline earth metal oxide supported on zeolite are heterogeneous basic catalysts that are widely used in biodiesel synthesis. The addition of alkaline earth metal oxide to zeolite enhances the distribution of active sites, leading to an increase in catalytic activity. Zeolite is widely used as catalyst support due to its high surface area, good thermal stability, shape selectivity, and porous structure. This article presents recent developments in the synthesis and application of alkaline earth metal oxide supported on zeolite for transesterification reaction. The challenges and prospects of catalyst development are also discussed. This article aims to provide information and inspire the development of alkaline earth metal oxide supported on zeolite as a basic catalyst for biodiesel synthesis.

1 Introduction

The depletion of fossil energy reserves, the increase in greenhouse gas emissions and global warming concerns have led to the exploration of renewable fuels such as biodiesel [1,2]. In contrast to petrodiesel, biodiesel exhibits greater sustainability, biodegradability, and enhanced combustion efficiently, resulting in lower emissions of CO₂, SO_x, NO_x, and CO [1]. The production of biodiesel involves the transesterification of vegetable oil such as castor oil [3], soybean oil [4], sunflower oil [5], animal fats [6], and waste cooking oil [7], using alcohol and a catalyst. However, the cost of biodiesel production is higher compared to petrodiesel production [8]. To address this economic challenge, researchers have been working on enhancing biodiesel production by developing high-performance catalysts that can improve efficiency [9].

Catalysts play an important role in biodiesel synthesis, specifically by reducing the reaction time, enhancing the biodiesel yield, and facilitating large-scale production [10]. Catalysts

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used in biodiesel synthesis can be categorized into three types: homogeneous catalysts [11,12], heterogeneous catalysts, and enzymatic catalysts [13]. Among these, homogeneous catalysts such as NaOH [14] and KOH [15] are more commonly used in biodiesel synthesis due to their high catalytic activity under mild conditions. However, these catalysts tend to be sensitive to free fatty acid content, more corrosive, easily dissolved in the reaction medium, and produce a high amount of wastewater [1,16]. Therefore, heterogeneous basic catalysts are believed to address the separation and purification challenges in biodiesel production [17].

Alkaline earth metal oxides such as MgO [18], CaO [19], SrO [20], and BaO [15], stand out as superior heterogeneous basic catalysts due to their high basicity, availability, and economic value [21]. However, the use of alkaline earth metal oxide catalysts is limited by their low porosity, low specific surface area, and a limited concentration of active sites. Alkaline earth metal oxides also tend to be inactive in the presence of air due to the chemical adsorption of carbon dioxide and water on their surfaces [22]. Therefore, the stability and catalytic activity of alkaline earth metal oxide catalysts can be enhanced by incorporating them into a support material like zeolite [9].

Zeolite is a porous crystalline aluminosilicate material extensively used as a catalyst support in transesterification reactions, due to its high thermal stability, large surface area, and shape selectivity attributed to its porous structure [23]. Adding alkaline earth metal oxides to zeolite can improve the distribution of basic active sites for transesterification reactions, thereby enhancing the catalytic activity [14]. Frequently used zeolite such as Faujasite (X and Y) [4,24,25], Mordenite [2,26,27], and MFI [16,28] stand out due to their high specific surface area and large pore diameter. Wu et al. (2013) reported that CaO/NaY catalyst prepared through microwave-assisted impregnation exhibited higher alkalinity and catalytic activity compared to a CaO catalyst without zeolite support in biodiesel synthesis from soybean oil. The improved catalytic activity was attributed to the increased surface area and alkalinity strength resulting from CaO dispersion on zeolite NaY [4].

This mini review provides an overview of recent developments in synthesis, application, and characterization of alkaline earth metal oxide supported on zeolites as a heterogeneous basic catalyst in biodiesel production. The challenges and prospects associated with the use of impregnated alkaline earth metal oxide catalysts on zeolites are also discussed. The aim of this review is to contribute to the advancement of impregnated alkaline earth metal oxide catalyst in zeolites for biodiesel and other chemical productions.

2 Discussion

2.1 Alkaline Earth Metal Oxide Catalysts

Alkaline earth metal oxides catalysts, such as MgO, CaO, BaO, and SrO, play an important role in biodiesel synthesis due to their high basicity, ease of availability, and economical value [21]. The basicity of alkaline earth metal oxides comes from the presence of surface metal ions (M^{2+}), which act as Lewis acids (attracting electrons), and oxygen ions (O^{2-}), which act as Brønsted base sites (accepting protons) [15]. Yan et al. (2008) investigated the basicity of alkaline earth metal oxide using the Temperature-Programmed Desorption (TPD) of carbon dioxide analysis method. They reported that the number of basic sites was directly proportional to the increase in surface area and ionic radius, in the order of basicity $BaO > SrO > CaO > MgO$. Other studies also confirmed this pattern by measuring the basicity of BaO, SrO, CaO using the benzoic acid titration. They reported that BaO catalyst has the highest basicity (0.022 mmol/g), followed by SrO (0.018 mmol/g), and CaO (0.011 mmol/g) [29].

Increased catalyst basicity can enhance the efficiency of the transesterification reaction. For instance, Mootabadi et al. (2010) reported a biodiesel yield of 95.4% using a BaO catalyst, surpassing the yields obtained using SrO and CaO catalysts [30]. The mechanism of alkaline earth metal oxide catalysts begins with the withdrawal of protons by the Brønsted base site (O^{2-}) to form methoxide ions. Reactive methoxide ions will attack the carbonyl group on triglycerides to form diglycerides and 1 mole of fatty acid methyl esters. The attack of the carbonyl group by methoxide ions will continue until 3 moles of methyl ester (biodiesel) and glycerol are obtained [31].

Calcium oxide (CaO) is the most commonly used catalyst among other alkaline earth metal oxides due to its good basicity, low solubility in methanol, and economical value [11]. Calcium oxide can be derived from natural materials such as eggshells [7], animal shells [32], and limestone [33]. Maneerung, et al. (2016) successfully prepared the low-cost and efficient CaO catalyst by the calcination of chicken manure, exhibiting high basicity and catalytic activity with a fatty acid methyl ester (FAME) conversion up to 90% [34]. Similar studies also reported the superior catalytic activity of CaO synthesized from waste obtuse horn-shells by calcination at 800 °C. The palm oil conversion was 86.75% under optimum condition with a 5% catalyst [35]. To enhance the catalytic activity of CaO, the study of nanocatalyst alkaline earth metal oxides also gained significant attention for biodiesel production. Nanocatalysts promote high surface area, stability, as well as resistance to saponification reactions. Anbessi et al. (2019) reported the efficiency of CaO-nanocatalyst in transesterification reaction with a fatty acid methyl ester (FAME) conversion up to 96% [36]. Other applications of alkaline earth metal oxide catalysts can be seen in **Table 1**.

Table 1. Alkaline earth metal oxide catalyst used for biodiesel production

Feedstock	Catalyst	Reaction Condition				Yield (%)	Ref
		Catalyst (wt%)	Ratio MeOH:Oil	Temperature (°C)	Time (min)		
Waste cooking oil	CaO Nanocatalyst	1	1:8	50	10	95	[36]
Waste cooking oil	CaO	7.5	1:15	65	-	>90	[34]
Palm oil	CaO	5	1:12	n.d	360	87.75	[35]
Palm oil	SrO	5	1:12	80	180	98.2	[20]
Beef tallow	BaO	4	1:16	50	300	94.95	[15]
Used vegetable oil	BaO	0.75	1:6	n.d	2	91	[37]
Jatropha Curcas L.	CaO-MgO	7.5	1:18	n.d	10	92.39	[3]
Waste cooking oil	CaO/MgO	6	1:15	90	120	96.47	[38]

Although alkaline earth metal oxide has proven its superior catalytic activity in transesterification reactions, the application still faces challenges such as leaching with reaction mediums. Additionally, their interactions with moisture and air can weaken the active sites on the catalysts [22]. Their poor stability has also been reported by Ganbari et al. (2016) by reusing a BaO catalyst for biodiesel synthesis from beef tallow. They observed a gradual decline in the catalytic activity of the recovered catalyst after 5 cycles due to the deposition of products on the catalyst surface [15].

On the other hand, SrO catalyst tends to absorb water vapor to form $Sr(OH)_2$ and absorb CO_2 to form $SrCO_3$. Regenerating SrO is also quite challenging because it requires a high calcination temperature (above 1200 °C) [39]. Similarly, CaO catalysts still face challenges in catalysis as they tend to form a suspensions in methanol-oil mixtures [15]. To address these

challenges, enhancing the catalytic activity of alkaline earth metal oxides can be achieved by incorporating them to a supporting material such as zeolite. The porous structure of zeolite provide shape selectivity, high porosity, and a large surface area, thus enhancing the catalytic activity of alkaline earth metal oxides [15,40]

2.2 Alkaline Earth Metal Oxide Supported on Zeolite Catalysts

Zeolite is a porous crystalline aluminosilicate composed of tetrahedral silica (SiO_4^{4-}) and tetrahedral alumina (AlO_4^{5-}) which are connected through interlinkage of oxygen atoms [41]. The incorporation of Al^{3+} ions into the SiO_4^{4-} framework generates a negative charge in the zeolite framework. The negative charge of the framework can be balanced by metal cations or other protons bound to the zeolite lattice through coulombic interactions [42].

Zeolite finds extensive application as a basic catalyst in transesterification reactions due to its selectivity, high thermal stability, ion-exchange ability, and its capacity to entrap metal ions or their oxides within its micropores [41]. The introduction of alkaline earth metal oxides into zeolites results in superior basic heterogeneous catalysts due to the increased distribution of active sites of metal oxide on the surface and within the pores of zeolite. This process also augments the density and partial negative charge of oxygen atoms in the zeolite framework [42], acting as Lewis bases and exhibiting better ability to attract protons from compounds [2,43].

Wu, et al. (2013) conducted a study investigating the catalytic activity of CaO/NaY catalysts compared with CaO catalysts, as mentioned earlier. The experimental results revealed an increase in the basicity and catalytic activity of CaO after its impregnation into zeolite. This improvement can be attributed to the large porosity and high surface area of NaY zeolite, facilitating the effective dispersion of CaO on NaY surface and within its pores and also increasing the number of active basic sites [4]. Moreover, Taslim, et.al (2017) observed the effects of adding CaO derived from chicken eggshells into natural zeolite. They reported superior catalytic activity of $\text{CaO}/\text{Zeolite}$ compared to pure CaO , demonstrating an increase in biodiesel yield from 51.17% to 87.40% [7].

Additionally, the incorporation of alkaline earth metal oxides into zeolite has been reported to enhance the stability of the catalyst for the transesterification reaction. Pavlović et al. (2020) reported that CaO impregnated into zeolite derived from rice husk exhibited high catalyst stability, allowing for reuse as a catalyst for 5 cycles without a significant decrease in catalytic activity. The biodiesel yield only decreased from 99.2% in the first cycle to 97.6% in the fifth cycle [44]. Other studies have reported similar findings on $\text{MgO}/\text{ZSM-5}$ catalysts utilized in the biodiesel synthesis from *Spirulina platensis*. They observed a reduction in biodiesel yield from 92.1% (highest) to 85.3% (lowest) over 5 transesterification cycles, suggesting the catalyst's sustained stability [16].

Recently, there has been a focus on exploring the application of magnetic heterogeneous alkaline earth metal oxide supported into zeolite catalyst for biodiesel production. This is interest attributed to their convenient recovery through an external magnet, presenting a more practical approach compared to traditional catalyst separation methods like centrifugation and filtration. A study by Firouzjaee et al. (2017) reported that the use of $\text{CaO}/\text{NaY-Fe}_3\text{O}_4$ catalysts with 30% CaO loading on the zeolite exhibited superior catalytic activity, achieving a maximum biodiesel yield of 95.37% [45].

In another study by Saaidah et al. (2022), the impact of adding Fe_3O_4 to $\text{CaO}/\text{ZSM-5}$ catalysts on its catalytic activity was investigated. They reported biodiesel yields obtained using CaO , CaO-ZSM-5 , $\text{CaO-ZSM-5}/\text{Fe}_3\text{O}_4$ catalysts were approximately 65%, 96%, and 91%. Magnetic catalysts exhibited lower biodiesel yields compared to CaO-ZSM-5 catalysts, likely due to a reduction in surface area leading to a decrease in active sites. However, the addition of Fe_3O_4 was considered beneficial for separating catalyst from product mixture based on

their magnetic properties. The application of alkaline earth metal oxides to zeolites as catalysts in transesterification reactions can be seen in **Table 2**.

The catalytic activity of zeolite is influenced by various factors such as chemical composition, structure, pore size, surface area, and the purity of the zeolite [41,46]. By its composition, zeolites are categorized into low silica (Si/Al < 2; highly polar), medium silica (Si/Al: 2 – 5; medium polarity), and high silica (Si/Al > 5) [40]. A higher Si/Al ratio in the zeolite results in superior thermal stability. However, a higher Si/Al ratio leads to a reduction on the acidity of the zeolite due to the loss of aluminum from the zeolite framework [47].

In a study conducted by Mieczyzynski, et. al (2021), a 10% MgO/ZSM-5 catalyst, with a Si/Al ratio of 50, exhibited higher catalytic activity, resulting in 88.9% biodiesel yield, higher than 10% MgO/ZSM-5 catalyst with Si/Al ratio of 23 (achieved a 86.2% biodiesel yield) [27]. This report highlights the significant impact of the Si/Al ratio on the catalytic activity of zeolite as a supporting catalyst. Moreover, similar studies also demonstrated that MgO/ZSM-5 catalysts with higher Si/Al ratio (Si/Al = 50) exhibit superior catalytic activity with a triglycerides conversion of 94.6%, higher than MgO/ZSM-5 catalysts with lower Si/Al ratio (Si/Al = 23) with 88.9% triglycerides conversion [1].

Wu et al. (2013), investigated the effect of zeolite types as supporting materials for CaO catalysts. Their findings revealed that the catalytic activity of CaO/NaY outperformed other catalysts in the following order: CaO/NaY > CaO > NaZSM-5 > KL. This superior performance is attributed to differences in the specific surface area of the zeolite used, following order: NaY > NaZSM-5 > KL. The specific surface area influences the distribution of CaO on the surface and frameworks of the zeolite, impacting overall catalytic activity efficiency [4].

The utilization of zeolite as a support for alkaline earth metal oxide encounters some challenges related to its micropore size. This limitation affects molecular diffusion within zeolite and is also correlated with their ability to trap alkaline earth metal oxide within zeolite pores [48,49]. To overcome this challenge, several studies have focused on developing mesoporous zeolite framework. Mesoporous zeolite offer longer catalyst life and superior catalytic activity compared to microporous zeolite [50]. Purnamasari et al. (2017) reported that the addition of CaO to mesoporous H-ZSM-5 zeolite was found to cause pore clogging and filling, leading to an increased number of alkaline active sites on the catalyst and consequently improving its catalytic activity [51].

Table 2. Alkaline earth metal oxide catalyst used for biodiesel production

Feedstock	Catalyst	Reaction Condition				Yield (%)	Ref
		Catalyst (%wt)	Ratio MeOH:Oil	Temp (°C)	Time (min)		
Sunflower oil	CaO/FA-ZM	6	1:6	60	180	99.2	[44]
Sunflower oil	CaO Nano/NaX	10	1:6	60	360	95	[52]
Treated waste cooking oil	CaO/Natural Zeolite	8	1:12	65	180	87.40	[7]
Waste Lard	CaO/ZSM-5	8	1:30	65	70	90.98	[6]
Used cooking oil	CaO-ZSM-5/Fe ₃ O ₄	3	1:5	65	240	91	[53]
Canola oil	CaO/NaY-Fe ₃ O ₄	n.d	-	65	60	95.37	[45]
Rapeseed oil	MgO/ZSM-5	10	1:9	220	180	94.6	[1]
Spirulina plantesis	MgO/ZSM-5	3	1:15	75	60	92.1	[16]
Rubber seed	MgO/Zeolite A	12.5	1:10	70	360	89	[18]
Jatropha Curcas L.	BaO/ Zeolite Y	2	1:9	65	120	94	[54]
Vegetable oil	MgO/NZ	n.d	1:9	220	120	94	[27]
	SrO/NZ					93.2	
	CaO/NZ					98.5	
Soybean Oil	CaO/NaY	3	n.d	65	180	95	[4]

	CaO/KL						95
	CaO/ZSM-5						95
Kapok Seed Oil	CaO:BaO/Active Natural Mordenite	n.d	n.d	65	15	73.6	[55]

2.3 Synthesis and Characterization of the Basicity of Alkaline Earth Metal Oxide Supported on Zeolite

The addition of alkaline earth metal oxides into zeolites can be done by using the impregnation method [1,4,51]. This technique involves combining zeolites with solutions containing alkaline earth metal oxides, in the form of their hydroxide, carbonate, or nitrate, followed by thermal decomposition (calcination) to produce their oxide [40,46,56]. Alternatively, the impregnation method can be done by mixing the solid phase of alkaline earth metal oxides into zeolite, followed by physical treatments such as grinding to ensure well-distributed active sites and higher surface area, finished by thermal decomposition [4]. The thermal decomposition of the precursor plays a significant role in the impregnation process. For instance, magnesium hydroxide, $Mg(OH)_2$, will decompose to MgO when heated at $377\text{ }^\circ\text{C}$, while magnesium carbonate, $MgCO_3$ will decompose at $547\text{ }^\circ\text{C}$. Similarly, calcium hydroxide, $Ca(OH)_2$, transform into CaO at $512\text{ }^\circ\text{C}$, while strontium nitrate ($SrNO_3$) and strontium carbonate ($SrCO_3$) decompose into SrO at temperatures above $600\text{ }^\circ\text{C}$ and $1000\text{ }^\circ\text{C}$, respectively. Barium hydroxide, $Ba(OH)_2$, decomposes into BaO at $800\text{ }^\circ\text{C}$ [57]. At lower decomposition temperatures, alkaline earth metal oxides might not fully form completely, leaving precursor salts on the zeolite surface. As reported by Mierczynski et al. (2021) XRD analysis of SrO/ANZ synthesized through the wet impregnation method with calcination at $400\text{ }^\circ\text{C}$ revealed the presence of $SrNO_3$ that did not decompose into SrO due to the lower calcination temperature compared with $SrNO_3$ decomposition temperature [27]. Although the impregnation of alkaline earth metal oxide offers superior catalytic activity, their addition might lead to particle agglomeration, resulting in a decrease in catalytic activity. To address these challenges, researchers have recently developed microwave and ultrasonic-assisted impregnation methods. Microwave radiation provides higher energy efficiency, reduces drying time, and enhances the distribution of active sites within the zeolite framework. Additionally, microwave radiation helps minimize agglomeration by inducing an electric field that polarizes the charges in the material. A study by Wu et al. (2013) showed that CaO/NaY catalysts prepared using microwave radiation exhibited high basicity, with a basic strength (H_-) above 27 and total basicity of 3.798 mmol/gram , indicating a high basicity [4]. Another study by Qu et al. (2020) also reported that ultrasonic treatment of $MgO/ZSM-5$ catalysts improves the distribution of MgO active sites on zeolites and minimizes the occurrence of agglomeration [16]. Recent preparation methods for synthesizing alkaline earth metal oxides impregnated on zeolite can be seen in **Table 3**.

Table 3. Recent impregnation of alkaline earth to zeolite methods

Catalyst	Synthesis Methods			Total Basicity (mmol/g)	Yield (%)	Ref
	Methods	Treatment	Calcination			
MgO/ ZSM-5	Mixing $Mg(NO_3)$ solution with zeolite for 24 hours	-	$500\text{ }^\circ\text{C}$ (4 hours)	0.49	92.9	[1]
MgO/ ZSM-5	Mixing $Mg(CH_3COO)_2$ with zeolite for 24 hours	Ultrasonic for 30 min	$650\text{ }^\circ\text{C}$ (4 hours)	0.873	92.1	[16]

CaO/ ZSM-5	Mixing Ca(CH ₃ COO) ₂ with zeolite for 24 hours	-	700 °C (3 hours)	n.d	90.89	[6]
CaO/ Zeolite Y	Grinding CaO with zeolite for 20 min	Microwave for 20 min	600 °C (2 hours)	3.798	95	[4]
SrO/Natural Zeolite	Mixing Sr(NO ₃) ₂ with active natural zeolite	-	400 °C (2 hours)	1.29	93.2	[27]
BaO/ Zeolite Y	Mixing (BaNO ₃) ₂ solution with zeolite Y	-	550 °C (4 hours)	n.d	94	[54]

The basicity of alkaline earth metal oxide catalysts impregnated on zeolite can be evaluated through using various methods, such as CO₂-TPD [27], Hammett indicator [4,52], and benzoic acid titration [52,58]. The TPD-CO₂ method is a commonly used technique for measuring the quantity and the strength of basic sites on catalysts, with the desorption temperature and peak area in the TPD plot serving as indicators. Additionally, the total basicity can be determined using a Thermal-Conductivity Detector (TCD) [59].

The desorption peaks observed in the range of 100 °C – 300 °C, 300 °C – 450 °C, and 450 °C – 600 °C, signify weak, moderate, and strong basicity, respectively [1]. In a study by Martinez et al. (2011) MgO/ZSM-5 catalysts exhibited superior basicity, as indicated by their CO₂-TPD plots. The profile revealed desorption peaks at around 100 °C, indicating weak base interaction with CO₂ on the surface of the catalyst. Another desorption peak at 200 °C – 400 °C signified a high oxygen density in the catalyst lattice. The total basicity of the catalyst was quantified from the TPD plot, resulting in an alkalinity intensity of 0.873 mmol/g, reflecting its high basicity [52].

The basicity of alkaline earth metal oxide supported on zeolite can also be determined using the Hammett indicator and benzoic acid titration. The Hammett indicator is a compound used to determine the basic strength of the catalyst, relying on the neutralization principle of basic sites in a nonpolar solution. This is indicated by the color change of the indicator, as shown in **Table 4**. [60]. Determining basic strength using Hammett indicator involves mixing 0.1 g sample with 4.5 mL Hammett indicator in methanol and allowing it to reach equilibrium for 2 hours with periodic shaking until no color change occurs [1]. The Hammett indicator method is typically combined with carboxylic acid titration to determine the total basicity of the catalyst expressed in mmol/gram. The total basicity is measured by titrating the catalyst in anhydrous ethanol suspension with benzoic acid (2 mmol/L) [4,44]. The number of basic sites can be calculated by observing the color change when a certain amount of acid added has been added, sufficient to neutralize the basic sites on the catalyst [52].

Table 4. Hammett's Indicator for Determining the Basic Strength of a Catalyst

Indicator	Real Color	Basic Color	Basic Strength (H ₊)
Bromothymol blue	Colorless	Blue	7.2
m-Cresol purple	Yellow	Purple	8.3
Phenolphthalein	Colorless	Red	9.3
Alizarin yellow R	Yellow	Red	11.0
2,3,4-Trinitroaniline	Yellow	Reddish-orange	12.2
2,4-Dinitroaniline	Yellow	Violet	15.0
4-chloro-2-nitroaniline	Yellow	Orange	17.2
4-Nitroaniline	Yellow	Yellow-orange	18.4
Benzidine	Colorless	Purple	22.5
4-Chloroaniline	Colorless	Peach	26.5
Aniline	Colorless	Mauve	26.5
Triphenylmethane	Colorless	Red	35.0
Xylene	Colorless	Yellow	39.0
Toluene	Colorless	Olivine	41.0

Source: [60]

3 Conclusion

Alkaline earth metal oxides such as MgO, CaO, SrO, BaO, are superior heterogeneous basic catalysts due to their high basicity, ease of separation, and also can be derived from economically raw materials. The catalytic activity of alkaline earth metal oxide can be enhanced by incorporating it into a porous material such as zeolite. Zeolite possesses high porosity, large surface area, and good thermal stability. The addition of alkaline earth metal oxides to zeolite can improve the distribution of active base sites and enhance catalyst stability, allowing for repeated use without a drastic reduction in catalytic activity. Further analysis of key factors influencing zeolite catalytic activity, including pore size, Si/Al ratio, crystallinity, and the maximum metal oxides still requires additional exploration. Investigating these aspects could significantly contribute to the future advancement of catalyst development in biodiesel synthesis.

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