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REVIEW PAPER

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## CALCIUM OXIDE BASED CATALYSTS FOR BIODIESEL PRODUCTION: A REVIEW

### Article Highlights

- Various methods of CaO-based catalysts preparation were analyzed
- Categorization of Ca containing catalysts was proposed
- Activity of CaO containing catalysts in transesterification was analyzed
- Leaching and deactivation of CaO-based catalyst were reviewed

### Abstract

*Vegetable oils are mainly esters of fatty acids and glycerol, which can be converted to fatty acid methyl esters (FAME), also known as biodiesel, by the transesterification reaction with methanol. In order to attain environmental benignity, much attention has been focused in the last decades on utilizing heterogeneous catalysts for biodiesel production instead the homogeneously catalyzed transesterification of vegetable oil. The pure CaO or CaO mixed with some other metal oxide due to its low solubility in methanol, FAME and glycerol, low cost and availability, is one of the most promising among the proposed heterogeneous catalysts. Solid catalysts containing CaO usually fulfill a number of important requirements, such as high activity at mild temperature, marginal leaching of Ca cations, long life activity, reusability in transesterification of vegetable oil and easy recovery from the final products of transesterification (FAME and glycerol). This review is focused on the recent application of pure CaO or CaO in complex catalyst structure and their use as heterogeneous base catalysts for biodiesel synthesis and suitability for industrial application.*

*Keywords: biodiesel, heterogeneous catalysis, CaO, transesterification, leaching, kinetics.*

The use of biofuels is becoming increasingly common, mainly governed by environmental concerns, energy security and economic reasons. Biodiesel is a promising alternative for diesel fuel produced from crude oil due to its environmentally favorable properties such as non-toxicity, extremely low sulfur content and highly renewable character [1]. Also, the greenhouse gas emission benefits of biodiesel are especially significant because carbon is continuously cycled and reused for growing plants instead of being released into the atmosphere [2].

The most common way to produce biodiesel is the transesterification of vegetable oils or animal fats

with short chain alcohol such as methanol or ethanol to yield the fatty acid alkyl esters (biodiesel) and glycerol. The transesterification of triglycerides comprises of three consecutive and reversible reactions wherein triglycerides react with methanol to form diglycerides, monoglycerides, and finally glycerol and fatty acid methyl ester (FAME), as shown by the formal and summarized reaction in Figure 1. A catalyst (acids, bases or enzymes) is usually used to improve the reaction rate and the yield. A base-catalyzed transesterification is considerably faster than the acid-catalyzed one [3] and it is the most common and to-day applied commercial technology for biodiesel production mainly realized with different homogeneous catalysts [4]. Homogeneous-base transesterification processes have several drawbacks due to complexity in the purification step of biodiesel. Potentially severe problems can occur if soap is formed

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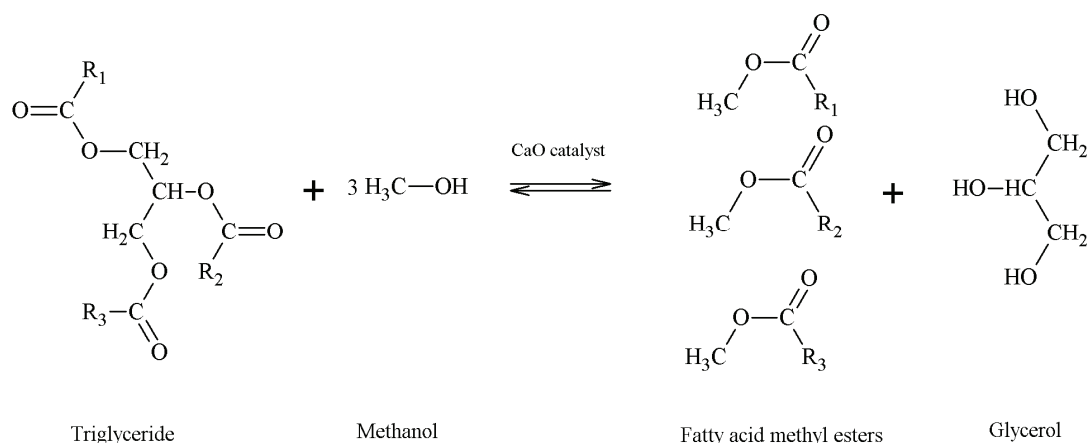


Figure 1. Transesterification reaction of triglyceride with methanol.

during transesterification caused by the presence of large amounts of free fatty acids in vegetable oil. For soap formation some amount of catalyst is consumed and therefore causes the reduction of catalytic efficiency. Furthermore, the large volume of wastewater is generated for removal of residual catalyst during the process of biodiesel purification or washing. Finally, used catalysts cannot be recovered and backed into the process of biodiesel synthesis [5].

In contrast to homogeneous catalysts, removal of heterogeneous catalysts from biodiesel is simple and does not produce wastewater. The use of heterogeneous catalysts could enable the design of an efficient, continuous process and improve the economy of biodiesel production [6]. However, the rate of transesterification process realized using heterogeneous catalysts is generally lower than that of the homogeneous catalysts because of diffusion problems of reactants to the active sites of solid catalyst, which is associated with the three-phase system (oil-methanol-solid catalyst) [7]. Also, active species of almost all the heterogeneous base catalysts leach out into the reaction mixture and produce soap if vegetable oil contains free fatty acids (FFAs). Dissolving of solid-base catalysts decreases a possibility of their reuse in subsequent batches or for longer use in continuous process. It is also important to be pointed out that solid-base catalysts are mainly active in the transesterification at the temperatures around boiling point of methanol [3]. Taking into account all above remarks, the current research and development of heterogeneously catalyzed biodiesel synthesis has been focused on improving the catalytic activity and stability of solid catalysts.

Heterogeneous catalysts comprehend a great variety of materials including both acidic and alkaline solids such as earth metal oxides (MgO and CaO) and other single metal oxides (SnO<sub>2</sub>, ZnO and CeO<sub>2</sub>),

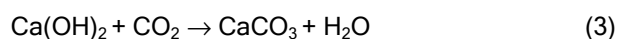
mixed metal oxides, zeolites, Al-Mg hydrotalcites, zirconium oxides, etc [7]. According to Kumar *et al.* [8] the basic heterogeneous catalysts are categorized into four categories: single component metal oxides, zeolites, supported alkali metal and clay minerals.

The most common heterogeneous base catalysts are single metal oxide, supported metal oxide, binary metal oxide (mixed oxide), hydrotalcite and natural waste shell base catalyst [9].

CaO catalyst is one of the most studied systems for biodiesel production due to high activity, availability and its low cost [10]. A large number of researches related to the application of CaO as a catalyst were reported in last decade [1-84] and, also, among them are three review articles by Kouzu *et al.* [11], Boey *et al.* [12] and Marinković *et al.* [13].

All these studies on transesterification reaction using CaO revealed the following [2,10]:

1) poisoning of CaO surface basic sites by the adsorption of H<sub>2</sub>O and CO<sub>2</sub>, after exposing CaO to air [14], as shown by the following equations:



2) formation of calcium glyceroxide during transesterification reaction and its role on the catalytic activity of CaO;

3) difficulties to complete CaO separation caused by its dissolution in methanol;

4) lower activity after applied reactivation of used CaO compared to the fresh CaO catalyst;

5) side reactions are possible together with methanolysis, such as saponification of glycerides and methyl esters and neutralization of free fatty acids by catalyst [15].

In this respect, some novel compounds containing Ca have recently provoked a considerable interest. A summary of the use of CaO-based heterogeneous catalysts in transesterification of vegetable oils is presented in Table 1 emphasizing the operating

conditions at which the experimental works were performed, used alcohol/oil molar ratio, catalyst amount, some other reaction conditions and obtained fatty acid methyl esters yield.

Table 1. Summary of CaO-based catalysts, preparation methods and reaction conditions on the fatty acid methyl ester (FAME) yield/conversion

Catalyst	Catalyst preparation method and calcination temperature	Oils and fats	Reaction condition				Yield/conversion (Y/C in %)	Ref.
			<i>t</i> / °C	Methanol to oil mole ratio	Catalyst amount, wt.%	Reaction time, h		
CaO	Commercial CaO <i>T</i> <sub>calc.</sub> = 700 °C	Sunflower oil	60 (N <sub>2</sub> )	13:1	1	1.5	Y > 90	[14]
CaO	CaO <i>T</i> <sub>calc.</sub> = 550 °C	Sunflower oil	60	6:1	1	2	Y = 98	[15]
CaO	Dipping of CaO in ammonium carbonate solution <i>T</i> <sub>calc.</sub> = 850 °C, 1.5h	Jatropha curcas oil	70	9:1	1.5	2.5	C = 93	[20]
CaO	Various precursors of CaO <i>T</i> <sub>calc.</sub> = 800 °C, 2 h (N <sub>2</sub> )	Tributyrin	60	6:1	0.3	2	C = 95	[39]
CaO	Commercial CaO <i>T</i> <sub>calc.</sub> = 900 °C	Sunflower oil	80 (N <sub>2</sub> )	6:1	1	5.5	Y = 91	[40]
CaO	Calcination of pulverized lime stone, <i>T</i> <sub>calc.</sub> = 900 °C, 1.5 h (he)	Soybean oil (SBO) and waste cooking oil (WCO)	65	14:1	1	2	Y = 99	[41]
CaO	Purchased	Soybean oil	65	12:1	8	3	Y = 95	[44]
CaO	Purchased, nanocrystalline	Soybean oil (SBO) and poultry fat	23-25	27:1	1	24	C = 99	[45]
Li/CaO	Wet impregnation method <i>T</i> <sub>dry</sub> = 120 °C, overnight <i>T</i> <sub>calc.</sub> = 500 °C, 2 h	Sunflower oil	60	14:1	0.2	3	Y = 90	[46]
Li/CaO	Wet impregnation <i>T</i> <sub>calc.</sub> = 575 and 800 °C, 5 h	Semi-refined rapeseed oil	65	12:1	5	4	Y = 93	[24]
K-CaO	Wet impregnation method	WCO, KO and JO	65	12:1	7.5	1.25, 2.0 and 2.5 h	Y = 98±2	[23]
K <sub>2</sub> CO <sub>3</sub> /nano CaO	Incipient-wetness method (in ultrasonic water bath) <i>T</i> <sub>dry</sub> = 120 °C, 16 h <i>T</i> <sub>calc.</sub> = 500 °C, 3 h	Canola oil	65	9:1	3	8	Y = 97.7±1.7	[47]
CaO/MgO	Incipient wetness impregnation, <i>T</i> <sub>calc.</sub> = 700 °C under N <sub>2</sub> flow, 8 h	Rapeseed oil	64.5	18:1	2	6	C = 92	[48]
CaO/SBA-15	Incipient wetness method <i>T</i> <sub>dry</sub> = 60 °C <i>T</i> <sub>calc.</sub> = 600 °C, 6 h	Sunflower oil	60 (N <sub>2</sub> )	12:1	1	5	C = 95	[49]
CaO/SiO <sub>2</sub>	Sol-gel, <i>T</i> <sub>dry</sub> = 110 °C, 20 h <i>T</i> <sub>calc.</sub> = 650 °C, 3 h	Corn oil	60	16:1	6	8	C = 85.6	[25]
Ca(NO <sub>3</sub> ) <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <i>T</i> <sub>calc.</sub> = 450 °C, 3 h	Palm kernel oil (PKO) and coconut oil (CCO)	60	65:1	10 and 15-20	3	Y = 94	[22]
CaO/Al <sub>2</sub> O <sub>3</sub>	Impregnation method of aqueous solution of calcium acetate on alumina support <i>T</i> <sub>calc.</sub> = 718 °C, 5 h	Palm oil	65	12:1	3.5	5	Y = 95	[50]

Table 1. Continued

Catalyst	Catalyst preparation method and calcination temperature	Oils and fats	Reaction condition				Yield/conversion (Y/C in %)	Ref.
			<i>t</i> / °C	Methanol to oil mole ratio	Catalyst amount, wt. %	Reaction time, h		
CaO/Al <sub>2</sub> O <sub>3</sub>	Wet impregnation of CaO on acidic, basic and neutral Al <sub>2</sub> O <sub>3</sub> , <i>T</i> <sub>calc.</sub> = 550 °C, 6 h (N <sub>2</sub> )	Soybean oil	150	9:1	3	6	Y = 90	[51]
Al <sub>2</sub> O <sub>3</sub> supported CaO	Single step sol-gel method <i>T</i> <sub>dry</sub> = 120 °C, 18 h <i>T</i> <sub>calc.</sub> = 500 °C, 6 h	<i>Nannochloropsis oculata</i>	50	30:1	2	4	Y = 97.5	[26]
CaO/ZnO	Incipient wetness impregnation method <i>T</i> <sub>calc.</sub> = 600 °C, 6 h	Sunflower oil	60	12:1	1.3	2	Y > 90	[52]
CaO/mill fly ash	Incipient wetness impregnation method, <i>T</i> <sub>dry</sub> = 115 °C, 6 h, <i>T</i> <sub>calc.</sub> = 850 °C, 2 h	Crude palm oil (CPO)	45	12:1	6	3	Y = 79.76 C = 97.09	[53]
CaO/AC	Impregnation, <i>T</i> <sub>dry</sub> = 100 °C, 12 h, <i>T</i> <sub>calc.</sub> = 540 °C, 2 h	Palm oil	190	15:1	5.5	1.2	Y = 80.98	[54]
Zeolite supported CaO (CaO/NaY)	Microwave irradiation <i>T</i> <sub>calc.</sub> = 600 °C, 2 h	Soybean oil	65	9:1	3	3	Y = 95	[55]
CaO- La <sub>2</sub> O <sub>3</sub>	Coprecipitation method, <i>T</i> <sub>calc.</sub> = 750 °C, 8 h	Food-grade soybean oil, crude soybean oil, palm oil and waste cooking oil, oleic acid	58	20:1	5	1	Food-grade soybean, Y = 94.3 (other: 96 after 3 h)	[56]
CaO-La <sub>2</sub> O <sub>3</sub>	Co-precipitation method <i>T</i> <sub>dry</sub> = 100 °C, overnight <i>T</i> <sub>calc.</sub> = 950 °C, 6 h	Jatropha oil	160	25:1	3	3	Y = 98.76	[57]
CaO:ZnO Ca/Zn ratio of 0.25	Co-precipitation in the presence of Na <sub>2</sub> CO <sub>3</sub> , <i>T</i> <sub>calc.</sub> = 800 °C, 2 h	Palm kernel oil	60	30:1	10	1	Y > 94	[27]
CaO-ZnO	Ball milling - powder mixture of Ca(OH) <sub>2</sub> and ZnO, in the mole ratio of 1:2, with addition of water, <i>T</i> <sub>calc.</sub> = 700 °C, 3 h	Sunflower oil	60	10:1	2	4	Y = 97.5	[32]
Mixed metal oxide CaMgZn	Coprecipitation method, <i>T</i> <sub>calc.</sub> = 800 °C, 2 h	Palm kernel oil	60	20:1	6	3	Y = 97.5	[28]
Ca/Zr mixed oxide	Birch templated method, <i>T</i> <sub>dry</sub> = 100 °C, 1 h <i>T</i> <sub>calc.</sub> = 700 °C, 6 h	Rapeseed oil	120	72:1	8	6	Y = 92.6	[35]
CaO-NiO CaO-Nd <sub>2</sub> O <sub>3</sub>	Co-precipitation, <i>T</i> <sub>dry</sub> = 110 °C, overnight, <i>T</i> <sub>calc.</sub> = 900 °C, 6 h	<i>Jatropha curcas</i> oil	65	15:1	5	6	Y > 80%	[58]
CaMgO and CaZnO	Coprecipitation method <i>T</i> <sub>calc.</sub> = 800 and 900 °C, 6 h	<i>Jatropha curcas</i> oil	65	15:1	4	6	C > 80%	[59]
CaMgO/Al <sub>2</sub> O <sub>3</sub>	Homogeneous co-precipitation deposition method <i>T</i> <sub>calc.</sub> = 800 °C, 6 h	<i>Nannochloropsis oculata</i> oil	60	60:1	10	3	Y > 85.3	[60]

Table 1. Continued

Catalyst	Catalyst preparation method and calcination temperature	Oils and fats	Reaction condition				Yield/conversion (Y/C in %)	Ref.
			<i>t</i> / °C	Methanol to oil mole ratio	Catalyst amount, wt. %	Reaction time, h		
Ca/Al composite oxide	NaAlO <sub>2</sub> solution and the Ca(OH) <sub>2</sub> solution were mixed for 3 h at 80 °C, contains <i>T</i> <sub>calc.</sub> = 600 °C, 8 h	Rapeseed oil	65	15:1	6	3	Y > 94	[21]
Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> and CaO								
CaTiO <sub>3</sub> , CaMnO <sub>3</sub> , Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub> , CaZrO <sub>3</sub> , and CaO-CeO <sub>2</sub>	Conventional solid-state reaction, <i>T</i> <sub>calc.</sub> = 1050 °C, 4 h	Rapeseed oil	60	6:1	10	10	Y = 79-92	[29]
CaO	Eggshell, <i>T</i> <sub>dry</sub> = 100 °C, 24 h <i>T</i> <sub>calc.</sub> = 1000 °C, 2 h	Soybean oil	65	9:1	3	3	Y > 95	[64]
CaO	Waste shells of egg and two types of waste mollusk shells - golden apple snail and <i>Meretrix venus</i> , <i>T</i> <sub>calc.</sub> = 800 °C, 4 h	Palm olein oil	60	18:1	10	2	Y > 90	[65]
CaO	Palm kernel shell biochar <i>T</i> <sub>calc.</sub> = 800 °C, 2 h	Sunflower oil	65	9:1	3	5	Y = 99	[66]
CaO/biochar	Wet impregnation method <i>T</i> <sub>calc.</sub> = 600 °C	<i>Mesuaferreal</i> . Oil	65	12:1	3	6	Y = 96	[67]
CaO-MgO-Fe <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	Waste water scale <i>T</i> <sub>dry</sub> = 105 °C, 24 h <i>T</i> <sub>calc.</sub> = 1000 °C, 2.5 h	Soybean oil	70	12:1	1	5	Y = 93	[68]
CaO	Hydration-dehydration, clams ( <i>meretrix meretrix</i> ), <i>T</i> <sub>dry</sub> = 100 °C, 24 h <i>T</i> <sub>calc.</sub> = 600 °C, 3 h	Palm olein	65	9:1	1	2	Y = 98	[69]
Calcium methoxide	Directed reaction of calcium with methanol in a slurry reactor at 65 °C for 4 h	Soybean oil	65	1:1 (volume ratio)	2	2	Y = 98	[70]
Ca(OCH <sub>3</sub> ) <sub>2</sub>	Ca(OCH <sub>3</sub> ) <sub>2</sub> was prepared by heating calcium oxide in an excess dehydrated methanol under 65 °C at 8 h with N <sub>2</sub> flow. <i>T</i> <sub>dry</sub> = 105 °C, 1 h	Jatropha curcas oil	65	15:1	2	1.5	Y = 95	[71]
Calcium glyceroxide	CaO was poured into a flask containing a mixture of MeOH and glycerol, heated at 50 °C	Sunflower oil	60	14:1	0.7	2	Y > 90	[72]
Commercial CaO samples	Calcination of commercial CaO, <i>T</i> <sub>calc.</sub> = 1000 °C, 2 h	Refined sunflower oil	60	12:1	2	2	99 C = 83.4 29.9	[1]
Ca-glyceroxide	CaO mixed with glycerol and methanol, <i>T</i> <sub>dry</sub> = 60 °C, overnight. A mixture of Ca(OH) <sub>2</sub> and glycerol							
calcium glycerolate	<i>T</i> <sub>dry</sub> = 60 °C, overnight							
calcium di-glyceroxide (CaDG)	Ball milling - CaO powder and glycerol in the mole ratio of 1:5, <i>T</i> <sub>dry</sub> = 60 °C, 24 h	Sunflower oil	60	10:1	0.5	2.5	C = 97.7	[73]
CaO	Purchased	Sunflower oil	252	41:1	3	0.1	Y = 100	[74]
CaO	Purchased	Rapeseed oil	200-220	40:0	1	0.17	Y = 96	[75]

Table 1. Continued

Catalyst	Catalyst preparation method and calcination temperature	Oils and fats	Reaction condition				Yield/conversion (Y/C in %)	Ref.
			<i>t</i> / °C	Methanol to oil mole ratio	Catalyst amount, wt. %	Reaction time, h		
CaLaO mixed oxide	Co-precipitation method <i>T</i> <sub>calc.</sub> = 800 °C, 6 h	<i>Jatropha curcas</i> oil	240	21:1	1	0.17	Y = 93	[76]

### Mechanism of CaO catalyzed reaction

Many different studies reported the reaction mechanism of CaO-catalyzed transesterification, as for example articles of Boey *et al.* [12], Marinković *et al.* [13], Kawashima *et al.* [16] and Lam *et al.* [17]. The proposed mechanism is shown in Figure 2.

As shown in Figure 2, the reaction begins with the attack of a methoxide ion, attached to the catalyst surface, to the carbonyl carbon of the triglyceride molecule to form a tetrahedral intermediate. In the second step, the unstable tetrahedral intermediate is rearranged and broken down to diglyceride anion and fatty acid methyl ester. The diglyceride anion is then stabilized by a proton from the catalyst surface to form diglyceride and at the same time the active site at the catalyst surface is regenerated. Then, the methoxide anion attacks on another carbonyl carbon atom in diglyceride, forming another mole of methyl ester and monoglyceride. These three steps are repeated until all three carbonyl centers of the triglyceride have been attacked by the methoxide ions to give one mole of glycerol and three moles of methyl esters.

According to results of different investigations reported in literature the first and second step of complex process (reaction of triglyceride and methanol and formation of diglycerides and FAME, as well as, reaction of diglycerides with methanol in which mono-

glycerides and FAMES are formed) are always much faster than reaction of monoglycerides and methanol producing the final amount of FAME and glycerol.

### Catalyst preparation

Catalyst synthesis is an important and vital segment of catalysis research. It is widely accepted that the catalytic activity of alkaline earth oxide catalysts is very sensitive to their preparation and activation procedure [18].

Different methods of catalyst synthesis have been reported in literature including thermal pretreatment [14,15,19,39-43,64-66,68], precipitation (co-precipitation) [27,28,31,56-60,76], impregnation [22-24,46-48,50-54,67], sol-gel [25,26,50], mechanochemistry [32,61,73,83]. Several reported papers were focused to find the optimal temperature for CaO calcination and activation. There is disagreement in the literature regarding the optimal pretreatment temperature of CaO. As already mentioned, the surfaces of calcium oxide can be covered with carbon dioxide and water as it is handled in air. In order to have maximum basic sites on the surface of CaO catalyst, pretreatment at high temperatures is required. According to Granados *et al.* [14] CaO calcined at 700 °C has the best catalytic activity. Other data indicated, on the basis of kinetic investigation of sunflower oil meth-

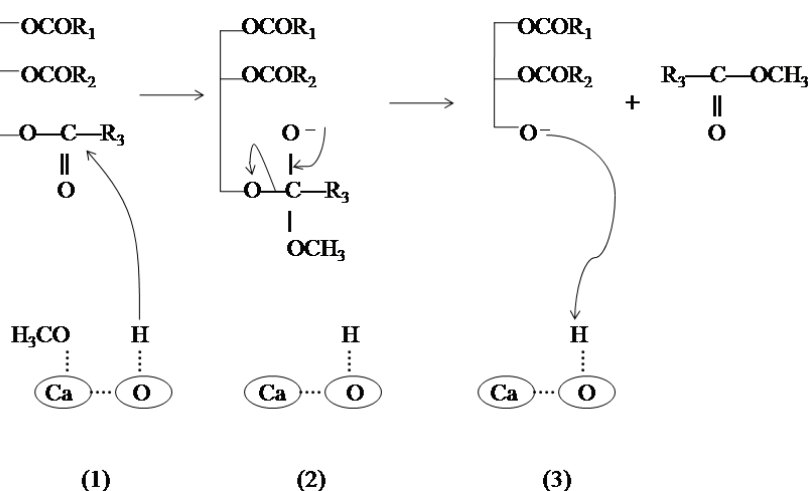


Figure 2. Mechanism of CaO-catalyzed transesterification [12].

analysis catalyzed by CaO calcined in air for 2 h at different temperatures (300, 500, 550, 600, 700 and 900 °C), as reported by Veljković *et al.* [15], that optimal calcination temperature is 550 °C. Mičić *et al.* [19] also performed calcination of CaO at different temperatures to activate basic sites on its surface and showed that activity of CaO catalyst for biodiesel synthesis is a complex function of nature of active sites and textural properties, both induced by activation temperature. Thermal treatment at 800 °C, resulted in the best CaO crystallinity and preferable pore structure, which were beneficial for catalytic activity. Solid super base of CaO was obtained by dipping CaO in ammonium carbonate solution, followed by calcinations at 900 °C [20]. The effect of the calcination temperature ranging from 120 to 1000 °C on the catalytic activity of the Ca/Al composite oxide which contained  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  and CaO was also investigated [21].

Loading active components on a porous support is a common way to obtain the desired physical properties and a high catalytic activity of a solid catalyst. Impregnation is one of the most used techniques to synthesize supported catalysts.  $\text{Al}_2\text{O}_3$ -supported calcium oxide prepared through the conventional impregnation method was used for transesterification of palm kernel oil and coconut oil [22]. CaO/ $\text{Al}_2\text{O}_3$  catalyst was prepared according to the conventional incipient-wetness impregnation of aqueous solution of the  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  precursor on an aluminum oxide support and it was calcined at 450 °C for 2 h before being used. In order to promote the basicity of calcium oxide Kumar *et al.* [23] prepared potassium ion impregnated calcium oxide in nanoparticle form as a solid base catalyst for the production of biodiesel. The nanocrystalline K-CaO was synthesized using the wet impregnation method. Li/CaO catalyst was prepared using the same technique, followed by calcinations at 575 and 800 °C and used for the transesterification of soybean oil. [24]

In the study by Moradi *et al.* [25], CaO/ $\text{SiO}_2$  was used as a catalyst of biodiesel production process. This catalyst was synthesized by the sol-gel method. Umdu *et al.* [26] prepared CaO on alumina,  $\text{Al}_2\text{O}_3$ , by using a modified single step sol-gel method. They used the required amounts of aluminum isopropoxide (AIP), water and  $\text{HNO}_3$  and mixed them at 85 °C under total reflux for 1 h. Then, calcium nitrate tetrahydrate was added. Finally, excess water was removed with slow evaporation to obtain the mixed oxide gel. The gels were first dried at 120 °C for 18 h, and then calcined at 500 °C for 6 h.

A mixed oxide of Ca and Zn was prepared by Ngamcharussrivichai *et al.* [27] according to the con-

ventional co-precipitation of a mixed aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with  $\text{Na}_2\text{CO}_3$  or  $(\text{NH}_4)_2\text{CO}_3$  as a precipitant. The same group of authors prepared a series of mixed oxides of Ca, Mg and Zn for the synthesis of methyl esters *via* the transesterification of palm kernel oil with methanol [28]. The mixed oxides with different elemental compositions were prepared via the pH-controlled co-precipitation using  $\text{Na}_2\text{CO}_3$  as a precipitant and the effects of the precipitation conditions on the physico-chemical and catalytic properties were studied.

Kawashima *et al.* [29] prepared different kinds of mixed metal oxide catalysts using a simple physical mixing method, followed by calcination at high temperatures, while Ngamcharussrivichai *et al.* [30] synthesized a series of catalysts through a wet mixing of ground limestone with different divalent and trivalent metal precursors, as binders, followed by drying and calcination.

Yan *et al.* [31] studied the effects of preparative parameters on the surface basicity, composition, and activities in transesterification reaction of several Ca-La metal oxide catalysts. They used four different preparation methods: ammonia-ethanol-carbon dioxide precipitation, physical mixing, impregnation and co-precipitation, and showed that catalyst surface composition and basicity are a function of calcination temperature, precipitants, pH, molar ratio of Ca to La in precursor solution, and storage conditions.

The synthesis of  $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$  by mechanochemical treatment of  $\text{Ca}(\text{OH})_2$  and ZnO powders in water medium followed by calcination at 700 °C with the goal to obtain CaO·ZnO mixed oxide as a catalyst for transesterification reaction was reported by Kesić *et al.* [32]. Powder mixture of  $\text{Ca}(\text{OH})_2$  and ZnO, in the mole ratio of 1:2 with stoichiometrically required addition of water, were used as starting materials for mechanochemical treatment. Mechanochemical treatment was carried out in the planetary ball mill, which consists of zirconia vials charged with zirconia balls in air atmosphere.

Nualpeng *et al.* [33] synthesized CaO catalyst for biodiesel production by gel-combustion technique with  $\text{Ca}(\text{NO}_3)_2$  as a calcium precursor and citric acid as fuel and gelling agent. The Ca-complex gel was heated at 420 °C until the fine powder was obtained and calcined at 800 °C for 4 h before being used as a catalyst in methanolysis reaction.

The urea-nitrate combustion method was demonstrated to be a simple, fast and effective method for the preparation of CaO- $\text{ZrO}_2$  solid base catalysts without a further high temperature and longtime calcination step [34].

Liu *et al.* [35] prepared Ca/Zr mixed oxide catalysts *via* a birch-template pathway. A birch template method was found to improve the pore structure and dispersion of basic sites.

CaO-SiO<sub>2</sub> catalysts, used for transesterification of palm oil, were successfully synthesized through a biomimetic silicification approach by using eggshell and Na<sub>2</sub>SiO<sub>3</sub> as raw materials [36].

### Activity of CaO containing catalysts in transesterification reaction

#### *Neat CaO*

The results of Lopez Granados *et al.* [14] revealed that calcination temperature and duration significantly affected the transesterification activity of CaO. Transesterification of sunflower oil, with CaO, activated by calcination at 700 °C, gave FAME yield larger than 90% at 60 °C and 13:1 methanol to oil mole ratio after 1.5 h. The catalyst could be reused up to eight times. Authors evaluated the role of H<sub>2</sub>O and CO<sub>2</sub> in the deterioration of the catalytic activity of CaO by exposing it to air. The formed carbonate groups were established as the main catalyst surface poisoning species. Granados *et al.* [37] have also studied in details the leaching aspects of CaO. They found that 0.134 mg of CaO was dissolved per 1 mL of methanol after 1 h of their contact. However, a larger amount of dissolved calcium was observed when glycerol is present in reaction mixture. The same authors have also shown that the presence of a small amount of biodiesel in the initial methanol-triglyceride mixture (3 wt.% based on oil) significantly increased the rate of triglyceride methanolysis carried out in a batch reactor [38].

Transesterification of sunflower oil with 6:1 mole ratio of methanol to oil and 1 wt.% of CaO based on oil weight, activated at 550 °C, showed that 98% conversion is achieved at 60 °C after 2 h reaction in batch process. The average particle size of activated catalyst was 2.8 µm [15].

A high catalytic activity of heterogeneous solid super base CaO catalyst in the production of biodiesel from *Jatropha curcas* oil was also reported [20]. That investigation resulted in 93% conversion of triglycerides after 2.5 h of transesterification at 70 °C, using methanol to oil mole ratio of 9:1 and 1.5 wt.% of catalyst based on oil.

A series of calcium oxide catalysts obtained by calcination of various precursors (calcium acetate monohydrate, calcium carbonate, calcium hydroxide, calcium nitrate tetrahydrate, calcium oxalate monohydrate) were synthesized and tested in transesterification of tributyrin with methanol [39]. The calcium

oxide obtained by calcination of calcium hydroxide at 600–800 °C showed the highest activity in the transesterification among the prepared catalysts. The basicity of the prepared calcium oxide catalysts also varied according to the precursors, and the relationship between the basicity of the prepared CaO catalysts and conversion was established.

Calcium oxide as a heterogeneous catalyst was activated at 900 °C and its effect on the biodiesel synthesis from refined sunflower oil was investigated at higher temperatures which are above the boiling point of methanol [40]. At temperatures of 100 and 80 °C, biodiesel yields of 91% were achieved after 1.5 and 5.5 h reaction time, respectively. The catalyst activation in air at high temperature is leading to the formation of strong basic sites, which are responsible for higher catalytic activity.

Transesterification of edible soybean oil with methanol was carried out in the presence of calcium oxide, as well as calcium hydroxide and calcium carbonate, for comparison [41]. After 1 h reaction time, the yield of FAME was 93% for CaO and only 12% for Ca(OH)<sub>2</sub>. To obtain 93% yield of FAME, with Ca(OH)<sub>2</sub> a longer time (3.5 h) was necessary while CaCO<sub>3</sub> catalyst was fully inactive for transesterification under the same condition [6].

Similar results were obtained by other investigation [42]. It was reported that calcium carbonate does not accelerate the transesterification of soybean oil and that calcium hydroxide also exhibits much lower catalytic activity. In the presence of the freshly prepared Ca(OH)<sub>2</sub> the FAME yield was less than 10% even after 5 h of the reaction.

Kouzu *et al.* [41] reported that FAME yield decreased from 93% to 10% at 1 h of the reaction time if CaO was exposed to air for 30 min, showing that even a 3 min exposure of CaO to air can deactivate the catalyst. Showing that CaO obtained by calcinations of pulverized stone was active catalyst in transesterification of soybean oil as well as for waste cooking oil at the reflux of methanol [41], Kouzu *et al.* in further investigation found out that calcium oxide was the active phase only in the beginning of the reaction [43].

Liu *et al.* [44] studied transesterification of soybean oil to biodiesel using CaO as a solid catalyst. A biodiesel yield of 95% can be obtained under suitable reaction condition using methanol to oil mole ratio of 12:1, 8 wt.% catalyst at 65 °C after 3 h. Liu *et al.* found that a catalytic activity of CaO in the transesterification of soybean oil to biodiesel is enhanced with the addition of a small amount of water into methanol. However, if too much water is added, the FAME will



hydrolyze to generate fatty acids, which react with CaO forming the soaps.

Commonly, calcium oxide catalysts are synthesized from various calcium precursors by direct calcination method [39]. Nualpaeng *et al.* [33] prepared calcium-based catalyst for methanolysis of palm oil *via* gel-combustion synthesis. The calcium oxide catalysts from simple calcinations of Ca nitrate and carbonate precursors were also studied for comparison. The gel-combusted CaO catalyst showed improved surface area, porosity, and basic site and higher catalytic performance in methanolysis of palm oil.

Performance of CaO in transesterification can be improved by using nanocrystalline calcium oxides. Nanocrystalline CaO exhibited a higher activity than laboratory-grade CaO due to its high surface area associated with nano crystallite sizes. The mean particle size and BET surface area of used nanocrystalline CaO were 20 nm and 90 m<sup>2</sup>/g, respectively. However, the rate of reaction was quite slow under room temperature and it took 6–24 h to obtain high conversion. It was also reported that the deactivation of catalyst after eight cycles for soybean oil methanolysis and after three cycles for biodiesel synthesis from poultry fat occurred [45].

#### *Loaded CaO*

A series of Li-doped CaO catalysts which are effective in the transesterification of sunflower oil with methanol were prepared to study the promoter effect [46]. The activation process of these samples was also necessary to obtain an active catalyst. However, the leaching of alkali promoters in these doped systems was observed. For such catalyst calcined at 500 °C, its activity is mainly attributed to the heterogeneous process due to the presence of solid CaO promoted with LiNO<sub>3</sub>, while homogeneous contribution due to the presence of Li<sub>2</sub>O is significant for sample calcined at 700 °C.

In order to increase CaO basicity, Puna *et al.* [24] impregnated commercial CaO with aqueous solution of lithium nitrate (Li/Ca = 0.3 atomic ratio), and to remove nitrate ions before reaction, prepared samples were calcined at 575 and 800 °C, for 5 h. For each transesterification tests realized at temperatures close to the boiling temperature of methanol, 5 wt.% (oil basis) of catalyst and a mole ratio of methanol to oil of 12:1 were used. Such working conditions and duration of transesterification of 4 h always performed with fresh catalysts resulted in similar biodiesel yields (FAME > 93%). However, the Li-doped CaO catalyst showed a faster deactivation than the pure CaO. These results revealed a negative effect on the catalyst stability of Li/CaO probably due to the enhanced

formation of calcium diglyceride caused by the presence of Li.

Preparation of nanoparticles of CaO impregnated by potassium ion and its activity for the biodiesel synthesis from a variety of feedstocks, namely waste cotton seed oil - WCO, karanja oil - KO and jatropha oil - JO, was analyzed at 65 °C with 12:1 mole ratio of methanol to oil and 7.5 wt.% amount of catalyst based on oil [23]. A high yield of FAME (98±2%) was detected after 70 min of transesterification. K-CaO was found to be an effective catalyst for the transesterification of a variety of feedstocks showing a high tolerance to the free fatty acid and moisture contents present in oil compared to pure CaO. Also, the analysis of biodiesel quality showed minimal concentrations of K and Ca in FAMEs, most of the leached metal ions were settled in glycerol layer.

The nanoparticles of CaO were also functionalized with the high-temperature decomposition products of K<sub>2</sub>CO<sub>3</sub> to increase the basicity of the catalyst surface. This was achieved by the impregnation of the CaO nanoparticles with different loadings of K<sub>2</sub>CO<sub>3</sub> followed by calcination at 500 °C [47]. The transesterification reaction of canola oil with methanol was carried out in a batch reactor with such functionalized CaO nanoparticles catalyst under systematically varied sets of reaction conditions. Activity of nano CaO was significantly increased by the impregnation with K<sub>2</sub>CO<sub>3</sub>. The functionalized CaO enabled the methyl ester yield to reach 97.7±1.7% after 8 h of reaction performed in batch reactor at 65 °C and with alcohol/oil mole ratio of 9:1.

#### *Supported CaO*

Another important group of heterogeneous base catalysts used in biodiesel production through transesterification of triglycerides is supported metal oxides [22,25,26,48–55]. Different supports were tested: MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, various types of zeolite HY, NaY, KL and ZSM-5 [22,25,26,48,50,51,55]; mesoporous silica (SBA-15 and MCM-41) [49]; ZnO [52]; ash [53] and activated carbon [54], and among them the mostly applied support was Al<sub>2</sub>O<sub>3</sub> [22,26,50,51].

Investigation showed that CaO supported on different carriers: MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and zeolite HY, is active in the transesterification reaction for biodiesel production [48]. These samples were prepared by incipient wetness impregnation method and results of these investigations showed that CaO/MgO had the highest activity, which was higher than that of unsupported CaO. With the CaO/MgO catalyst, the conversion of rapeseed oil reached 92% at 64.5 °C. The supporting CaO onto MgO increased both the specific area and the strength of basic sites, and therefore it

showed a higher catalytic activity than either CaO or MgO alone used for biodiesel synthesis.

Silica was very often tested as suitable support for CaO. Albuquerque *et al.* [49] tested the catalytic activity of mesoporous silica (SBA-15 and MCM-41)-supported CaO for the transesterification of sunflower oil with methanol. SBA-15, as compared to MCM-41, was proven to be thermally more resistant and to interact more strongly with supported calcium species. Under optimum condition, 95% conversion of triglycerides was achieved at 60 °C after 5 h, and methanol/oil mole ratio of 12:1 with 1 wt.% of the most active catalyst (14 wt.% CaO/SBA-15). The strong interaction between CaO and SBA-15 effectively prevented the leaching of active calcium species. The authors estimated that the catalytic activity of CaO/SBA-15 was better than that of homogeneous NaOH when the catalytic activity was expressed per gram of active phase (CaO compared to NaOH). The SBA-15 silica is favored over MCM-41 as support material of catalysts due to existence of large pore diameter.

Prepared CaO/SiO<sub>2</sub> catalyst [25] was used as heterogeneous catalyst for biodiesel production from corn oil. The experiments were conducted in a two-necked flask using corn oil, methanol (mole ratio of methanol to oil was 16:1) and 6 wt.% of catalyst (based on oil) at 60 °C during 8 h.

It was shown that catalytic activity of Al<sub>2</sub>O<sub>3</sub>-supported alkali and alkali earth metal oxides for transesterification of palm kernel oil and coconut oil into biodiesel varies based on the types of the loading active component [22]. Ca(NO<sub>3</sub>)<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> calcined at 450 °C was the most suitable catalyst giving 94.3% conversion of triglycerides after 3 h of transesterification at 60 °C when 10 wt.% catalyst and a methanol/oil mole ratio of 65:1 was used.

In a study of palm oil transesterification with methanol conducted with CaO/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from calcium acetate precursor and alumina, response surface methodology (RSM) in conjunction with central composite design (CCD) was used to optimize the activity of prepared catalyst samples containing different amounts of CaO [50]. With 3.5% of the optimal catalyst based on oil and with methanol to oil mole ratio of 12:1, a 95% FAME yield was obtained at 65 °C after 5 h of transesterification. These investigations showed that both the calcination temperature and the amount of calcium oxide loaded on the support had significant positive effects on the biodiesel yield and that the leaching of the CaO active species into the reaction media can be significantly reduced by anchoring it onto a catalyst support.

Alumina loaded with CaO as solid base catalyst was synthesized using wet impregnation of CaO on acidic, basic and neutral Al<sub>2</sub>O<sub>3</sub> and tested for the transesterification of soybean oil [51]. CaO supported on neutral Al<sub>2</sub>O<sub>3</sub> exhibited the highest FAME yield at 150 °C with oil to methanol ratio of 9:1 and catalyst amount of 3 wt.% based on oil. The appropriate CaO loading on *n*-Al<sub>2</sub>O<sub>3</sub> for transesterification of soybean oil was considered to be around 20 wt.%. The results of this investigation showed that the nature of Al<sub>2</sub>O<sub>3</sub> support played an important role on the catalytic activity.

The activities of Al<sub>2</sub>O<sub>3</sub> supported CaO and MgO catalysts in the transesterification of lipids of yellow green *Nannochloropsis oculata* microalgae was analyzed and the results showed that unsupported CaO and MgO had negligible activity, whereas CaO/Al<sub>2</sub>O<sub>3</sub> system due to higher basic sites concentration and basic strengths yields the most promising activity [26].

ZnO loaded with 16 wt.% CaO was used as a solid base catalyst for the transesterification of sunflower oil with methanol [52]. With methanol to oil mole ratio of 12:1 at 60 °C with 1.3 wt.% of catalyst based on oil, biodiesel yield higher than 90% was achieved in 2 h. Calcium oxide is stabilized by filling the mesoporous ZnO, avoiding the lixiviation of the active phase in the reaction medium.

A palm oil mill fly ash supported calcium oxide was developed to be used as a heterogeneous base catalyst for biodiesel synthesis using crude palm oil [53]. Transesterification performed with 6 wt.% catalyst loading, 12:1 methanol to oil mole ratio, at 45 °C and 3 h reaction time were used for testing catalytic activity of synthesized catalysts. Under these conditions, 75.7% of biodiesel yield was obtained.

The process optimization of used palm oil transesterification with activated carbon supported calcium oxide (CaO/AC) was realized according to response surface methodology (RSM) [54]. Activated carbon was chosen as support due to its high porous structure as well as lower cost compared to conventional ones such as alumina and silica.

A series of supported CaO catalysts with zeolites (NaY, KL and ZSM-5) were prepared by microwave irradiation [55]. The activities of synthesized catalysts were investigated in transesterification of soybean oil with methanol and compared to pure CaO. CaO/NaY exhibited the best performance among prepared catalysts.

#### *CaO-based mixed oxides*

Different binary or more complex mixtures of Ca and other metals were investigated as potential catalysts for biodiesel synthesis. Among them, some

mixed systems with two alkaline metals or Ca and other metals, like Ca-La [56,57], Ca and Mg [59,60], or mixed oxide of Ca and Zn [27,32,59], Ca-Al [21], Ca-Zr [35], Ca-Ni [58], Ca-Nd [58] or mixed oxide Ca-Mg-Zn [28] and compounds which contain Ca ( $\text{CaTiO}_3$ ,  $\text{CaMnO}_3$ ,  $\text{Ca}_2\text{Fe}_2\text{O}_5$ ,  $\text{CaZrO}_3$ ) [29, 61] were analyzed.

Various calcium-lanthanum mixed oxide catalysts having different Ca/La mole ratio were prepared and their catalytic activities for the transesterification of food-grade soybean oil, crude soybean oil, palm oil and waste cooking oil with methanol for synthesis of biodiesel were compared [56]. Mixed oxides catalyst showed a superior transesterification activity over pure calcium or pure lanthanum oxide catalysts. The most active catalyst had the highest basic site concentration and it was obtained when a 1:3 mole ratio of  $\text{La}(\text{NO}_3)_3$ : $\text{Ca}(\text{Ac})_2$  mixture was co-precipitated using ammonia solution with bubbling  $\text{CO}_2$  to form carbonate precipitate. Such formed precipitate was for 1 h calcined at  $750^\circ\text{C}$  in inert atmosphere ( $\text{N}_2$ ). The catalyst showed high activity in transesterification with a 94.3% yield of FAME after 1 h of transesterification.

Investigation of different Ca/La compositions on the surface area, its acidity-basicity and their activity for transesterification of crude *J. curcas* oil with methanol were performed [57] with the goal to determine the correlation between these characteristics and catalytic activity. Among the series of  $\text{CaO-La}_2\text{O}_3$  catalysts, the Ca:La prepared with 8:1 atomic ratio showed the best catalytic properties. The highest biodiesel yield (98.8%) was achieved at  $160^\circ\text{C}$ , after 3 h of transesterification performed with 25:1 methanol to oil mole ratio and 3 wt.% catalyst based on oil.

$\text{CaO-ZnO}$  was considered by several researchers [27,32]. Transesterification of palm kernel oil with Ca and Zn mixed oxides with 30:1 methanol to oil mole ratio at  $60^\circ\text{C}$  was shown to produce 94% of FAME in 1 h [27]. A mixed oxide was prepared according to the conventional co-precipitation of a mixed aqueous solution of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with  $\text{Na}_2\text{CO}_3$  or  $(\text{NH}_4)_2\text{CO}_3$  as a precipitant. The authors reported that the combination of Ca and Zn reduces the calcination temperature required for decomposition of  $\text{CaCO}_3$  to the active CaO phase. The mixed oxide can be also applied in transesterification of palm, soybean and sunflower oil.

The influence of the preparation method on the activity of this catalyst was also studied [32]. Different samples of  $\text{CaO-ZnO}$  mixtures were prepared by ball milling of  $\text{Ca}(\text{OH})_2$  and ZnO powders with or without the addition of water: for comparison with the mechanochemical synthesis, samples were also prepared

by co-precipitation of ZnO and  $\text{Ca}(\text{OH})_2$  added into 20% KOH solution, followed by calcination at  $700^\circ\text{C}$ . Activated catalyst obtained by ball milling was more active compared to the catalyst prepared by co-precipitation at the same reaction conditions.

Dependence of the FAME yield on time in the transesterification over different CaMgZn mixed oxides prepared with the different Ca:Mg:Zn mole ratios was investigated [28]. The FAME yield of 97.5 wt.% was achieved over the CaMgZn mixed oxide, prepared with the Ca:Mg:Zn ratio of 3:1:1 using the following reaction conditions: the methanol/oil mole ratio of 20:1, catalyst amount of 6 wt.% and temperature of  $60^\circ\text{C}$ .

Ca/Zr mixed oxide catalysts were prepared using three different methods (impregnation, co-precipitation and a birch-templating pathway) and were tested in the transesterification of rapeseed oil with methanol for biodiesel production [35]. A cost effective, simple templating route for the preparation of a mixed oxide catalyst for biodiesel production was found to improve the pore structure and dispersion of basic sites.

Calcium based  $\text{CaO-NiO}$  and  $\text{CaO-Nd}_2\text{O}_3$  mixed oxides exhibited a high activity; both catalysts were easily separated from the product [58]. The reusability study showed that catalysts could be recycled for six successive runs without significant loss in their activity.

Among different calcium-based mixed oxides catalysts ( $\text{CaO-ZnO}$  and  $\text{CaO-MgO}$ ) the  $\text{CaO-MgO}$  showed a superior catalytic activity due to its high base strength for the conversion of *Jatropha curcas* oil (JCO) into biodiesel [59] compared to pure calcium oxide, magnesium oxide or zinc oxide catalysts. In this study, the JCO conversion of more than 80% can be achieved over  $\text{CaO-MgO}$  and  $\text{CaO-ZnO}$  catalysts within 6 h at  $65^\circ\text{C}$  with a methanol to oil mole ratio of 15:1 and a catalyst loading of 4 wt.% of catalyst based on oil. The research suggested that such mixed  $\text{CaO-MgO}$  systems also possesses improved resistance to deactivation by  $\text{CO}_2$  when compared to CaO alone [18].

Calcium magnesium ( $\text{CaO-MgO}$ ) and  $\text{CaO-MgO}$  supported on alumina ( $\text{Al}_2\text{O}_3$ ) were prepared via pH-controlled co-precipitation [60]. Prepared catalysts were used for transesterification of crude *Nannochloropsis oculata* algal oil with methanol. The supported  $\text{CaO-MgO}$  mixed oxide catalyst gave a higher FAME yield at same reaction conditions due to high content of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  precipitated on  $\text{Al}_2\text{O}_3$  support. That catalyst showed increased total basicity providing more active sites for transesterification reaction.

The Ca/Al composite oxide was prepared and used as an environmentally benign solid catalyst in the transesterification of rapeseed oil with methanol. The generation of crystalline  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  improved the catalytic activity due to its synergistic effect with CaO [21].

Different kinds of A-B-O type metal oxides (where: A is a Ca and B is a transition metal) were tested for transesterification of rapeseed oil in a batch-type reactor at 60 °C. These catalysts belong to the perovskite structure -  $\text{CaTiO}_3$ ,  $\text{CaMnO}_3$ ,  $\text{Ca}_2\text{Fe}_2\text{O}_5$ ,  $\text{CaZrO}_3$  and  $\text{CaO-CeO}_2$  and were signed as good catalysts for transesterification process and biodiesel synthesis even at lower temperature according to article by Kawashima *et al.* [29]. A high durability of catalytic activity was found for the catalyst samples of  $\text{CaZrO}_3$  and  $\text{CaO-CeO}_2$ , which were able to provide methyl ester yields greater than 80% after several times reuse. However, recently reported examination of such perovskites [61] showed that pure perovskites containing Ca ( $\text{CaTiO}_3$ ,  $\text{CaMnO}_3$ ,  $\text{Ca}_2\text{Fe}_2\text{O}_5$  and  $\text{CaZrO}_3$ ) could be effective catalysts for transesterification of vegetable oil but only at temperatures above 140 °C. It was explained by the difference of applied procedure of perovskite synthesis. Namely, Kawashima *et al.* [29] did not observe that prepared perovskites contained a small amount of CaO. This artifact was recently explained after synthesis of pure perovskites [61] (data shown in Figure 3).

#### CaO from natural and waste sources

Utilization of natural calcium sources from waste materials as alternative way to synthesize CaO has been considered as a new trend for preparation of

catalysts that could be active for biodiesel synthesis [62]. The calcination step is crucial for the decomposition of different raw materials used as sources of  $\text{CaCO}_3$  and formation CaO. The basic heterogeneous catalysts obtained from waste sources can be categorized into four categories: shells, ashes, rocks and clay bones [63]. Catalysts produced from renewable sources have high potential for being applied as catalysts in commercial biodiesel production. The advantages of using these catalysts are availability, low cost, large number of resources, suitable catalytic activity and renewability.

Calcined egg shells were tested as catalyst in the methanolysis of soybean oil [64]. The effect of calcination temperature was investigated to determine the change of the activity of the eggshell-derived catalyst. It was found that a 9:1 mole ratio of methanol to oil and a temperature of 65 °C for 3 h with a catalyst amount of 3 wt.% resulted in biodiesel yield over 95% when eggshell-derived catalysts, calcined at 1000 °C, was used for soybean oil transesterification.

In another study, the solid oxide catalysts derived from waste shells of egg and two types of waste mollusk shells - golden apple snail and meretrix venus were employed to produce biodiesel from transesterification of palm oil [65]. After calcination at 800 °C for 4 h, all shell-derived catalysts mainly consisted of CaO phase. All the catalyst samples exhibited the high FAME yield greater than 90% after reaction time of 2 h.

The low-cost CaO basic catalyst derived from palm kernel shell gasification residues was also tested for transesterification reaction [66]. The optimum reaction conditions were found to be: catalyst loading

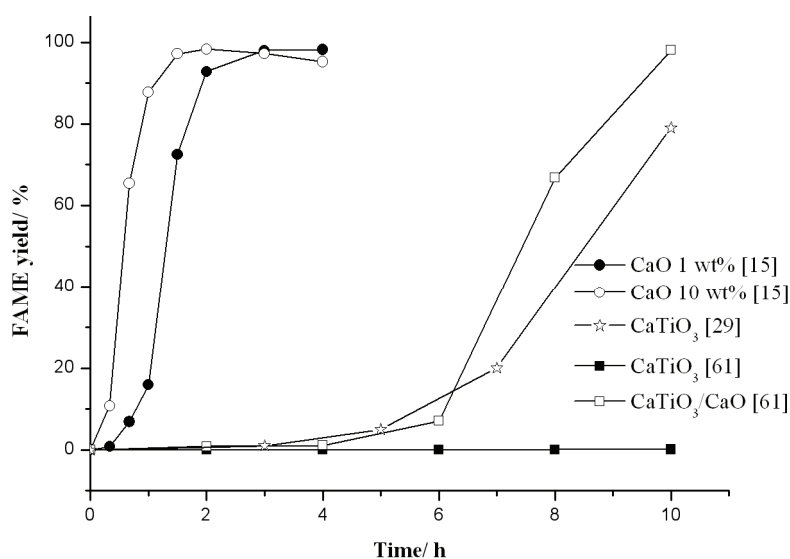


Figure 3. FAME yield as a function of reaction time at  $T = 60$  °C, methanol:oil = 6:1 using pure  $\text{CaTiO}_3$  perovskite (10 wt.% of catalyst, [61]);  $\text{CaTiO}_3/\text{CaO}$  composite (10 wt.% of catalyst, [61]); pure CaO (1 and 10 wt.% of catalyst [15]) and  $\text{CaTiO}_3$  (10 wt.% of catalyst [29]).

of 3 wt.%, temperature of 65 °C and methanol to oil mole ratio of 9:1 which gave 99% of FAME yield. However, the main disadvantage of the prepared catalyst was proved to be the leaching of calcium into the biodiesel product.

The biochar supported CaO was reported as an environmentally benign heterogeneous catalyst that could be used for biodiesel synthesis [67]. Both the active part as well as catalyst support reported in this work has been derived from waste materials.

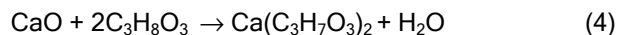
A novel waste water scale-derived catalyst was prepared [68] using calcination of the waste water scale. After calcination, a complex CaO-MgO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> solid material with high catalytic activity was formed and used for the production of biodiesel via transesterification reaction of soybean oil with methanol. The catalyst calcined at 1000 °C resulted in biodiesel yield of about 93% at reaction conditions as follows: methanol to soybean oil molar ratio of 12:1, amount of catalyst 1 wt.%, reaction temperature 70 °C and reaction time 5 h.

The modified CaO catalyst was prepared applying hydration-dehydration treatment of waste clamshell (*Meretrix meretrix*) [69]. Such treatment of clamshell improved the following characteristics of the catalyst: textural properties, basicity, transesterification activity and catalyst reusability. The triglyceride conversion was over 98% after transesterification under reflux conditions of methanol, with methanol to oil mole ratio of 9:1, with 1 wt.% of catalyst based on oil and 2 h reaction time.

#### *Calcium methoxide, calcium glyceroxide and calcium glycerolate*

During transesterification with CaO on the surface of CaO, calcium methoxide is formed, and it was supposed to represent, in fact, the real catalyst for the reaction. The results of different studies [70,71] showed that calcium methoxide has strong basicity and high catalytic activity as a solid base catalyst. A 98% biodiesel yield within 2 h was obtained using this catalyst [70] or 95% after 90 min in case of transesterification of non-edible *J. curcas* oil using 2 wt.% of Ca(OCH<sub>3</sub>)<sub>2</sub> as catalyst and methanol to oil mole ratio of 15:1 [71]. The order of reactivity among different calcium based catalysts was defined as: Ca(OH)<sub>2</sub> < CaO < Ca(CH<sub>3</sub>O)<sub>2</sub>. Moreover, the recycling experiment results showed it had a long catalyst lifetime and could maintain activity even after being reused for 20 cycles [70].

Kouzu *et al.* [43] reported the chemical change of bulk calcium oxide with glycerol during transesterification into calcium diglyceroxide (CaDG):



They found that glycerol was more reactive with CaO compared to methanol. Calcium diglyceroxide was the active phase in the catalytic reaction and this catalyst had the advantage of tolerance to air-exposure.

In a study by León-Reina *et al.* [72] calcium glyceroxide (prepared by mixing of CaO with methanol and glycerol) was much more active than CaO, achieving a biodiesel yield above 80 wt.% after 2 h of reaction time whereas that for CaO was 20% for the same working conditions.

Reyero *et al.* [1] also investigated the role played by CaO-glycerol compounds on the catalytic performance as methanolysis catalysts. Moreover, they showed that two calcium compounds could be synthesized in reaction between calcium and glycerol - calcium glyceroxide and calcium glycerolate. The activity of synthesized samples was compared with the materials obtained from commercial samples.

In recently published research [73], calcium diglyceroxide (CaDG) was synthesized by mechanochemical treatment of CaO dispersed in glycerol, and tested as a catalyst in the methanolysis of sunflower oil under different working conditions. A high yield of FAME was obtained, as shown in Figure 4. The main advantage of CaDG used as a catalyst in methanolysis compared to CaO catalyst is related to the initial rate of methanolysis.

#### **Transesterification under supercritical and subcritical conditions of methanol with CaO as catalyst**

The studies of synthesis of biodiesel under supercritical conditions of lower alcohols (methanol, ethanol) in the presence of heterogeneous catalysts are of great interest as well. The heterogeneous catalysis and transesterification of triacylglycerols under subcritical condition of methanol (higher temperature and pressure; 120-200 °C and 5-35 MPa) has some advantages in biodiesel production compared to heterogeneous transesterification performed near the boiling temperature of methanol (60-70 °C, 0.1-0.2 MPa). Under these conditions it is possible to use a lower amount of catalyst. Furthermore, comparing to supercritical and non-catalyzed synthesis of biodiesel the use of solid catalyst enables the decrease of reaction temperature, which makes the process more energy efficient.

The role of CaO in the supercritical transesterification of sunflower oil to biodiesel was investigated [74] and performed in an autoclave in the presence of 3 wt.% CaO as a catalyst at 252 °C showing that

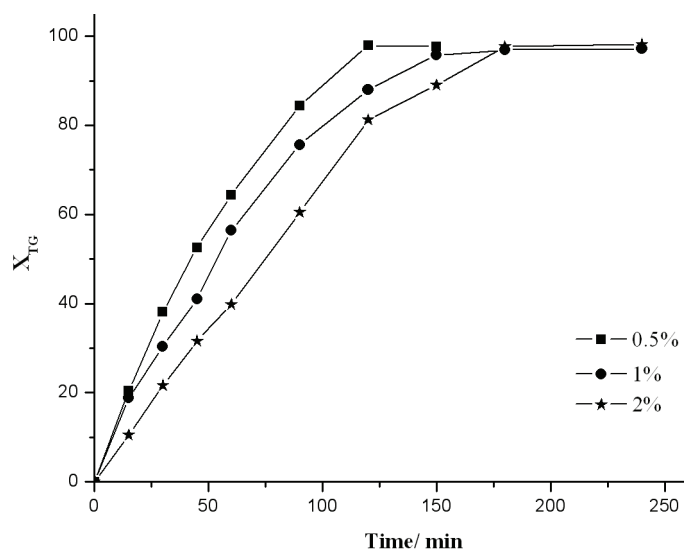


Figure 4. Influence of calcium diglyceride (CaDG) amount as catalyst on triglyceride conversion at 60 °C, methanol:oil mole ratio 10:1, agitation speed 1000 rpm [73].

faster transesterification process under supercritical condition could be obtained.

Influence of CaO as catalyst for transesterification under subcritical or supercritical conditions of methanol was also investigated [75] and compared with different metal oxides (SrO, ZnO, TiO<sub>2</sub> and ZrO<sub>2</sub>). A high yield of FAMES was obtained with CaO, which has a high basic strength, at relatively low temperatures ranging from 200 to 220 °C.

Experiments performed with Ca/La mixed oxide showed its good catalytic activity for biodiesel synthesis from *Jatropha curcas* oil (JCO) at subcritical and supercritical methanol condition [76]. Transesterification of crude JCO was carried out in a temperature range of 200–280 °C, and pressure range of 3–16 MPa, using mole ratio of methanol to oil from 14 to 42, reaction time from 300 to 1500 s and catalyst loading from 0 to 2.5 wt.% based on oil. The optimum reaction conditions which enabled 93% of FAME yield were near critical point of methanol: 240 °C and 8.2 MPa, using mole ratio of methanol to oil of 21:1 and reaction time of 10 min in the presence of 1 wt.% Ca/La mixed oxide catalyst. The presence of Ca/La mixed oxide catalyst in the reaction system reduced reaction temperature, time and pressure of supercritical transesterification.

#### Leaching and deactivation

Leaching represents the loss of active species from the solid phase or catalyst that are transferred into the liquid medium (biodiesel, methanol and glycerol), causing catalyst deactivation after its reuse or even complex homogenous-heterogenous catalytic activity during its use [77]. It is the main problem of

solid catalysts and major drawback to their implementation in a larger scale.

In the study reported by Lopez Granados *et al.* [37] amount of CaO dissolved in methanol was 0.134 mg/mL of methanol after 1 h of contact time, but it is increased to 0.169 mg/mL after 3 h. Moreover, after 6 h of contact time the solubility was 0.532 mg/mL of methanol. The solubility of CaO in methanol, as well as in methanol-glycerol solution and methanol-glycerol-biodiesel mixtures was investigated, and showed that CaO was more soluble in glycerol-methanol and biodiesel-glycerol-methanol mixtures compared to that in methanol.

When calcium oxide was employed for the transesterification reaction of soybean oil at methanol reflux, the calcium concentrations of the produced biodiesel-rich and glycerol-rich phases were 139 and 4602 ppm, respectively, showing that the amount of the soluble substance corresponded to 10.5 wt.% of the employed catalyst [78].

In order to clarify the contribution of leached Ca<sup>2+</sup> to the overall biodiesel yield, the following test was performed: the fresh CaO-La<sub>2</sub>O<sub>3</sub> catalyst (Ca:La atomic ratio of 8:1) was first stirred with certain amount of methanol at usual transesterification condition and after that the catalyst was filtered out and the methanol filtrate was reacted with fresh *jatropha* oil under the same reaction condition [57]. They reported that 8% of FAME yield was obtained which means that 8% from total of 98.8% of the FAME yield was contributed by the homogeneously catalyzed reaction with leached Ca<sup>2+</sup>.

Some of the species present in the reaction medium can accelerate the leaching process by

reacting with the catalyst. In the case of transesterification of oils with high free fatty acid content, using solid basic catalyst, the acids can react with the base catalyst and form soaps, causing a deactivation by leaching.

#### **Transesterification realized by microwave heating and ultrasonication**

The introduction of ultrasound and microwave irradiation in biodiesel production allows the reaction to reach completion in a shorter time.

Ultrasonication has recently received attention as a novel tool for process intensification in many research areas. It can help overcome the problem of mass transfer resistance, which is obviously present in triglycerides transesterification, by formation of finely emulsion in the case of liquids that are poorly miscible [79].

The ultrasonic-assisted transesterification of palm oil in the presence of CaO, SrO and BaO catalysts was investigated in a batch process assisted by 20 kHz ultrasonic cavitation at different operating conditions [80]. The catalytic activity was in the sequence of CaO < SrO < BaO which was related to their basic strength. The FAME yields obtained after 60 min of reaction time increased from 5.5 to 77.3% (CaO), 48.2 to 95.2% (SrO) and 67.3 to 95.2% (BaO).

Ultrasound-assisted heterogeneous solid catalyzed (CaO) synthesis of biodiesel from crude *Jatropha curcas* oil showed that ultrasound induced micro-mixing was capable of producing finer emulsion than mechanical stirring [81]. Such transformation of methanol-oil dispersion into fine emulsion increases the rate of transesterification and TG conversion. The intense micro-convection induced by ultrasound enhances the mass transfer characteristics of the system with 20% reduction in activation energy of transesterification process, compared to mechanically agitated systems. The optimum values of reaction parameters were defined: alcohol to oil mole ratio 11:1, catalyst concentration 5.5 wt.% and temperature 64 °C.

Microwave assisted transesterification is another alternative tool which can be used for the biodiesel synthesis. Hsiao *et al.* [82] examined the effect of CaO in the form of powder and nano-particles on the transesterification of soybean oil assisted by microwave irradiation using methanol to oil mole ratio of 6:1, 1 wt.% of catalyst based on oil at 60 °C. Almost complete triglycerides conversion was obtained after 30 min of transesterification.

#### **Kinetics of transesterification process with heterogeneous catalyst based on CaO**

Transesterification is an equilibrium reaction in which a higher mole ratio of methanol to oil than the stoichiometrically required (3:1) has been usually applied for improving the rate of FAME formation. Due to the presence of excessive methanol in the reaction media, it can be assumed that transformation of intermediates (diglyceride and monoglyceride) to methyl ester of fatty acids occurs very fast. Therefore, the most of the kinetic studies on the methanolysis of vegetable oils are based on the overall reaction represented by one summary stoichiometric equation in which triglycerides react with methanol resulting in formation of FAME and glycerol. From studies on kinetics of vegetable oils methanolysis it can be seen that these processes are described with models considering different kinetic orders [15,25,40,41,51,66,83,84].

The kinetics of the methanolysis of sunflower oil, over CaO catalyst, was studied in a batch reactor for low reaction temperature (60 °C) [15] and it was found that triglyceride (TG) conversion versus time is in the form of the S-shape curves with induction period. It was explained by the initial TG mass transfer controlled phase of complex transesterification process, which is after that shorter period of time, followed by the chemical reaction controlled region.

Other authors also investigated the kinetics of the transesterification reaction using solid catalyst at lower temperatures. Many of them use kinetic of pseudo-first order rate equation for prediction the results of oil transesterification [25,51] like in investigation of the kinetics of the transesterification reaction of corn oil in the presence of CaO/SiO<sub>2</sub> catalyst [25]. According to Kouzu *et al.* [41], order of reaction kinetics changed with progress of the transesterification from the zero order to the first with respect to triglycerides.

For the methanolysis of sunflower oil, catalyzed by low-cost CaO basic catalyst derived from palm kernel shell gasification residues, the kinetic model that combines the changing- and first-order reaction rate laws with respect to triacylglycerols and FAMEs, respectively, was proposed [66]. It is reported, in the same study, that for the methanolysis of vegetable oils over various CaO-based catalysts including neat, doped, supported and mixed CaO, the activation energy of transesterification process is within the range 29–136 kJ/mol.

There are also attempts to make correlations that can define both resistances which obviously determine the heterogeneous transesterification [83]. Two correlations (for mass transfer- and reaction rate-

controlled stage) have been combined into a single one that predicts the reaction rate during the whole course of methanolysis of refined and used sunflower oil with CaO-ZnO used as catalyst. In recently reported study [84] it was shown that this model could be recommended for modeling the kinetics of sunflower oil methanolysis over calcium-based catalysts over a wide range of reaction conditions.

## CONCLUSION

Numerous data reported in the literature in the past decade indicated that CaO as a solid catalyst is able to increase the rate of transesterification of triglycerides and formation of fatty acid methyl esters and glycerol. The catalytic activity of the pure CaO or CaO in combination with other metal oxide was reviewed in this study demonstrating characteristics and possibility for their use in biodiesel synthesis. Experimental conditions such as mole ratio of methanol and oil, reaction temperature and catalyst amount were evaluated and optimal conditions for achieving the higher yields were evaluated, as well as catalyst synthesis procedure and optimal activation procedure (calcination temperature and duration). It was shown that catalytic activity of calcium oxide based catalysts is very sensitive to their preparation.

The utilization of waste materials suitable for CaO catalysts preparation has recently been of interest in the search for a more sustainable process of biodiesel synthesis. The environmental advantages of the use of natural and waste materials as catalyst precursors in a heterogeneously catalyzed transesterification are complemented by the fact that CaO precursors are inexpensive and available worldwide.

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PREGLEDNI RAD

## KATALIZATORI NA BAZI OKSIDA KALCIJUMA U PROCESIMA SINTEZE BIODIZELA: PRESEK STANJA

*Metil estri masnih kiselina (MEMK ili biodizel) se dobijaju reakcijom transesterifikacije biljnih ulja (triacilglicerola tj, estara masnih kiselina i glicerola) sa metanolom. Trenutno se najveći broj komercijalnih procesa sinteze biodizela zasniva na primeni homogenih katalizatora, kojima se zagađuje čovekova okolina, zato je sve veća istraživačka aktivnost usmerena ka njihovoj zameni sa heterogenim katalizatorima. Čist CaO ili CaO u mešovitim oksidima, zbog male rastvorljivost u metanolu, biodizelu i glicerolu, niske cene i dostupnosti predstavlja jedan od najperspektivnijih heterogenih katalizatora. Heterogeni katalizatori na bazi CaO zadovoljavaju niz značajnih zahteva u reakciji transesterifikacije biljnih ulja kao što su: visoka katalitička aktivnost na umerenim temperaturama, neznatno izluživanje, mogućnost ponovnog korišćenja, kao i lako odvajanje od proizvoda reakcije. Ovaj pregledni rad je usmeren na analizu efekata primene čistog CaO ili CaO u složenoj smeši sa drugim oksidima ili metalnim solima kao katalizatorima u reakciji sinteze biodizela.*

*Ključne reči: biodizel, heterogena kataliza, CaO, transesterifikacija, izluživanje, kinetika.*