

Table 1
Temperature of formation of CaO depending on precursor and calcination condition.

Precursor	Calcination conditions (heating rate, atmosphere)	Formation temperature (K)	Reference
Calcium hydroxide	1.5 K/min, N ₂	693–923	[19]
Calcium hydroxide	10 K/min, 20 vol.% O ₂ /Ar	705–725	[20]
Calcium nitrate	1.5 K/min, N ₂	873	[19]
Calcium nitrate	10 K/min, 20 vol.% O ₂ /Ar	906	[20]
Limestone	–	990	[21]
Calcium carbonate	10 K/min, N ₂	914 or 1144 ^a	[22]
Calcium carbonate	Vacuum	934	[23]
Calcium carbonate	1.5 K/min, N ₂	~973	[19]
Calcium carbonate	10 K/min, 20 vol.% O ₂ /Ar	1058	[20]
Calcium acetate	< 20 K/min, air	973	[18]
Calcium acetate	20 K/min, air	1038	[18]
Calcium oxalate	10 K/min, 20 vol.% O ₂ /Ar	1000–1040	[20]
Calcite (Iceland spar)	2 K/min, air	1073–1123	[24]

^a Depending on decomposition time: 1144 K for 1 h and 914 K for 24 h.

Table 2
Physicochemical properties of the calcium oxide.^a

Characteristic	Description
Chemical name	Calcium oxide
Chemical formula	CaO
Common name	Lime, quicklime, caustic lime, calx, fluxing lime, burnt lime, unslaked lime
Molar mass (g/mol)	56.0774
Density (g/cm ³)	3.34
Odor	Odorless
Melting point (K)	2886
Boiling point (K)	3123
Heat of formation (kJ/mol)	635.55
Heat of hydration (kJ/mol)	63.18
Solubility in water (mg CaO/ml)	1.19 (298 K), 0.57 (373 K), exothermic reaction
Solubility in alcohols	
Methanol (mg CaO/ml) ^b	0.1–0.2 (298 K), 0.03–0.04 (333 K), exothermic reaction
Glycerol (mg CaO/ml) ^c	1.6 (0.5 h contact, 298 K), 5.7 (2 h contact, 298 K)
Glycerol+methanol (mg CaO/ml) ^b	~1 (333 K)
Solubility in biodiesel+methanol+glycerol (mg CaO/ml alcohol phase) ^b	0.4 (298 K), 0.6 (333 K)

^a [25].

^b [26].

^c [27].

and structural characteristics, depends on the activation procedure and the starting precursor used [20], as demonstrated by Table 3.

3. Reaction mechanism of transesterification with CaO

Biodiesel is commonly produced by transesterification of TAGs from vegetable oils and animal fats with methanol in the presence of a suitable catalyst to form fatty acid methyl esters (FAMES) and glycerol. The overall methanolysis reaction is presented by the stoichiometric equation shown in Fig. 1.

The main mechanism of heterogeneous catalysis follows principles similar to those of homogeneous catalysis. The important factor in homogeneous base-catalyzed reaction is to create nucleophilic alcoxides from alcohol that attack the electrophilic part of the carbonyl group of TAGs, while in acid catalysis the carbonyl group of TAGs is protonated and alcohol attacks the protonated carbon to create a tetrahedral intermediate [32]. The breakdown of TAGs requires three steps. The first step is to produce tetrahedral intermediate and the second step is the breakdown of the unstable tetrahedral intermediate to a diacylglycerol (DAG) ion and fatty acid ester. The last step is the recovery of the catalyst by proton transfer. These three steps are repeated for cleavage of each fatty acid ester and then finally three fatty acid esters and glycerol are formed [32].

In heterogeneous catalysis, adsorption of reactants and desorption of products take place on the surface of a solid catalyst. Two basic mechanisms, Eley–Rideal (ER) and Langmuir–Hinshelwood–Hougen–Watson (LHHW), represent the foundation of modern heterogeneous transesterification mechanisms. According to the ER mechanism, the reaction is performed by a direct pickup of species from the surface by a liquid phase molecule, whereas in the LHHW mechanism the reactants are first adsorbed on the catalyst surface and then react, followed by the product desorption. Dossin et al. [33] and Hattori et al. [34] give examples of applying ER and LHHW mechanisms, respectively.

The catalytic effect of CaO in transesterification reaction is due to the oxygen anion present on the CaO surface [17]. Chemically, CaO is an alkaline earth oxide with the ionic crystal structure. According to Lewis theory, because of its small electronegativity (1.00–Pauling scale [25]), the calcium cation is a very weak acid. Therefore, the conjugated oxygen anion displays a strong basic property [35]. The catalytic role of a basic site generated on the surface of CaO particles is to abstract a proton from the organic matter, thus initiating the base-catalyzed reaction.

One of the reaction mechanisms of the soybean oil transesterification catalyzed by the CaO/Al₂O₃ catalyst proposed by Pasupulety et al. [36] is presented in Figs. 2 and 3. The first stage includes the formation of intermediate compounds (A and B in Fig. 2) between CaO and methanol. The following parallel reactions occur: (a) the formation of the species A is preceded by proton binding from a Lewis basic site (oxygen anion) and (b) the species B is formed in the interaction between TAGs and some of the Lewis basic sites. As the FAME formation reaction progresses, these two species interact to form an intermediate compound, DAG, and to regenerate the catalyst. Similarly, at the start of the reaction, DAGs interact with the Lewis basic sites to form the intermediate species. This species reacts with A to give the next intermediate species monoacylglycerols (MAGs), along with FAME and regenerated CaO. Finally, MAGs interact with Lewis basic sites to form the intermediate D that reacts with the species A to produce FAME, regenerating the catalyst and glycerol. The second stage is the formation of calcium diglyceroxide, followed by its catalytic effect, as shown in Fig. 3. CaO reacts with glycerol and forms calcium diglyceroxide in the dehydroxilation process. Two adjacent OH groups in calcium diglyceroxide are favorable for abstracting protons from methanol and building an intermolecular hydrogen bond yielding the compounds E and F. At the end, the species F reacts with TAGs to form FAME and regenerated calcium diglyceroxide. The process itself is self-repeating and further accelerates the transesterification reaction.

As observed in the 1970s, water may increase the activity of alcohol when oxides of alkaline and alkaline earth metals are used as solid base catalysts, which is attributed to the activity of the basic OH⁻ species [28,37]. Liu et al. [38] found that the catalytic activity of CaO in the methanolysis of soybean oil was enhanced by the addition of a small amount of water into methanol, which was explained

Table 3
Structural and textural properties of calcium oxide [20].

Precursor	Crystal size (nm)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Basicity, CO ₂ desorbed (μmol/g)
Calcium carbonate	67	26	0.27	41	101
Calcium acetate	37	22	0.18	33	62
Calcium oxalate	47	26	0.24	38	63
Calcium nitrate	116	< 1	–	–	– ^a
Calcium hydroxide (obtained by precipitation from calcium acetate)	60	27	0.16	24	61
Calcium hydroxide (obtained by precipitation from calcium nitrate)	93	7	0.05	33	15
Limestone	56	13.2	–	–	270
Dolomite	46	14.6	–	–	221

All samples were activated under the same conditions (in situ air flow, 1073 K, 1 h).

^a No measurable amount of CO₂ was adsorbed.

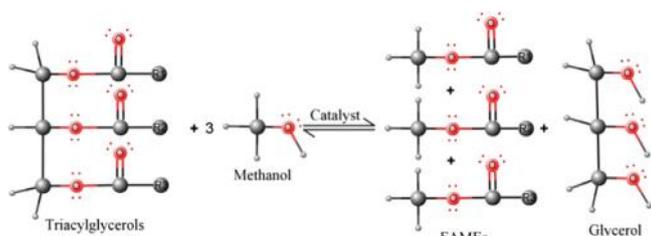


Fig. 1. Generalized schematic representation of transesterification reaction.

by the mechanism presented in Fig. 4. In step I, strongly basic and high catalytically active methoxide anions are formed directly and indirectly in two reactions: (a) O²⁻ from CaO can extract H⁺ from the hydroxyl group of methanol, and (b) O²⁻ from CaO extracts H⁺ from water to form OH⁻, which further extracts H⁺ from methanol to generate methoxide anion and water, respectively. In step II, the transesterification mechanism of acylglycerols takes place in the presence of methoxide anions. First, a methoxide anion attaches to a carbonyl carbon atom of the TAG molecule to form the tetrahedral intermediate. Second, this intermediate species picks up an H⁺ ion from CaO and reacts with methanol to produce methoxide anion. Finally, the reallocation of the tetrahedral intermediate results in the production of biodiesel and glycerol.

4. Kinetics of transesterification reaction catalyzed by CaO-based catalysts

Various models have been employed for describing the kinetics of methanolysis of different feedstocks over CaO-based catalysts (Table 4). These models are controversial regarding the overall or partial reaction orders with respect to TAG, methanol and FAME. The methanolysis reaction catalyzed by calcium compounds is reported to be the zeroth [40] or first [30,41–48] order with respect to TAG. Actually, because the increase of FAME concentration promotes miscibility of the reactants, the reaction order varies with progress of the methanolysis from the zeroth order to the first [30,49].

The methanolysis of vegetable oils over CaO-based catalysts can be controlled by either mass transfer or chemical reaction. Hence, some researchers usually split the kinetic data into two different regions with different dominant mechanisms, to further fit the data with two independent kinetic expressions [41]. More complex models include the mass transfer limitation and predict the reaction rate during the whole course of methanolysis with an acceptable accuracy [42,47–49]. Among them, the kinetic models of Lukić et al. [42] and Miladinović et al. [49] deserve a great attention as they have a capability to model the kinetics of methanolysis reactions over calcium-based catalysts [52,53].

5. Optimization of transesterification reaction catalyzed by CaO-based catalysts

The ester yield and the transesterification reaction rate are strongly influenced by the applied reaction conditions. Knowledge about the effects of the reaction conditions on the ester yield and the reaction rate as well as the determination of the optimal ones ensuring the highest ester yield are particularly important for increasing the process efficiency and reducing the production cost. As seen in Table 5, both statistical and experimental optimizations have been used so far to expand the knowledge on transesterification reactions, to determine the best reaction conditions and to develop more efficient and more cost-effective processes.

The conventional one-variable-at-a-time approach is to search for the optimal reaction conditions (factors) for biodiesel production by changing one factor at a time and keeping other factors constant. Although this approach is time-consuming and ignores the combined interactions among reaction conditions, it is frequently used in biodiesel synthesis optimization [61–64] because of its simple implementation and its usefulness in selecting important reaction conditions that affect the ester yield. Conversely, statistical methods like the response surface methodology (RSM) are useful tools for simultaneous study of the effect of several reaction conditions influencing the process of biodiesel synthesis by generating empirical models. This approach reduces the number of experiments required for biodiesel production optimization. So far, the RSM combined with central composite [54–57], Box–Behnken factorial [58,59] or factorial [60] design was used in the optimization of CaO-catalyzed transesterification. Using RSM, a model equation correlating the FAME yield with the reaction conditions is developed to be further used to determine the optimal reaction conditions ensuring the highest FAME yield.

According to a majority of the statistical optimization studies, the reaction temperature, the catalyst amount [54–56,58–60] and the reaction time [54,59,60] have the significant effect on FAME yield, while contradictory results are reported regarding the effects of alcohol-to-oil molar ratio on ester yield. Several research groups reported insignificant influence of the alcohol-to-oil molar ratio on the ester yield in methanolysis of various feedstocks like palm oil, jatropha oil and pork lard catalyzed by CaO/Al₂O₃ [57], calcium manganese oxide [56] and KOH-impregnated CaO catalyst [59], respectively. Other research groups observed significant effect of alcohol-to-oil molar ratio on the ester synthesis, for instance in methanolysis of soybean oil catalyzed by fly ash-supported CaO catalyst [55] and ethanolysis of cottonseed oil over CaO–MgO/Al₂O₃ [58]. Generally, an increase of the alcohol-to-oil molar ratio, the catalyst loading, the reaction temperature, the reaction time and the agitation intensity up to a certain value positively affects the FAME yield, while a further increase of the reaction parameters either does

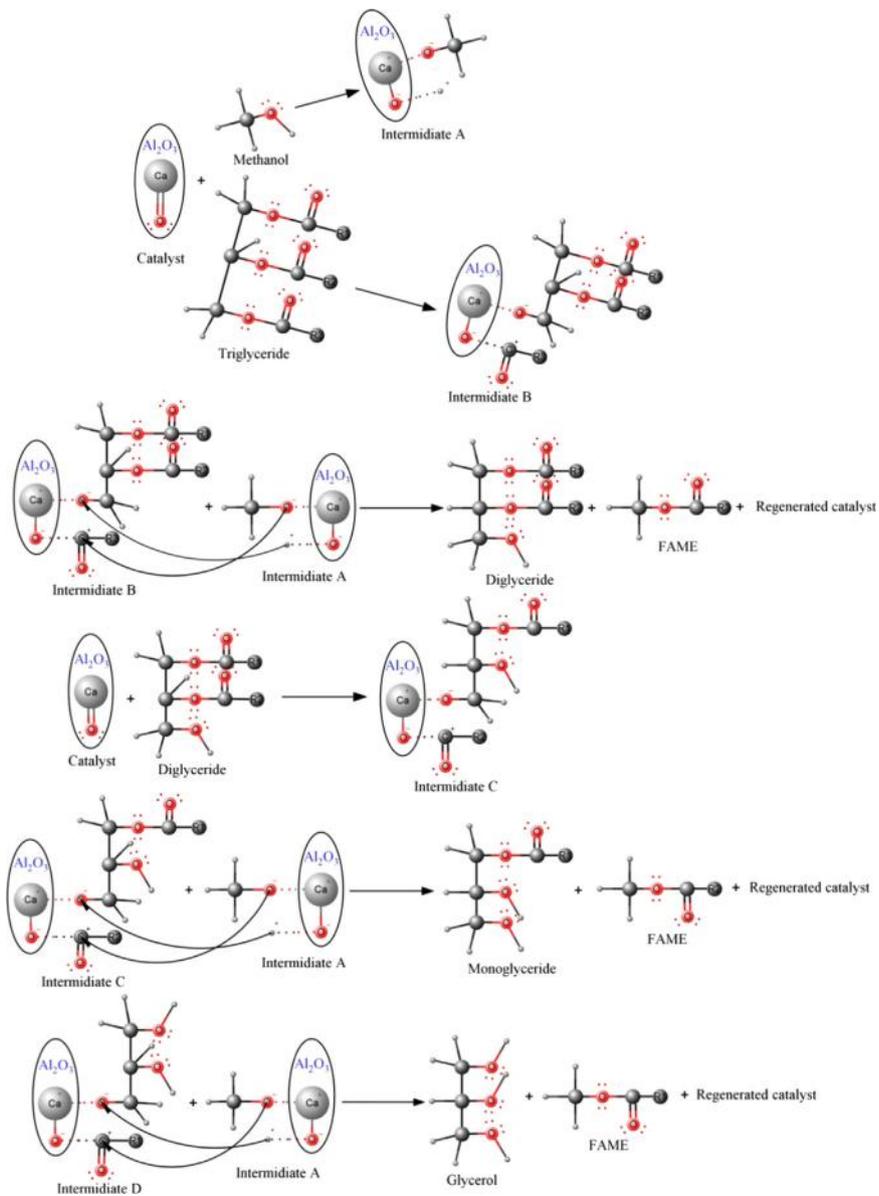


Fig. 2. Proposed reaction mechanism on CaO/Al₂O₃ catalyst for transesterification [36].

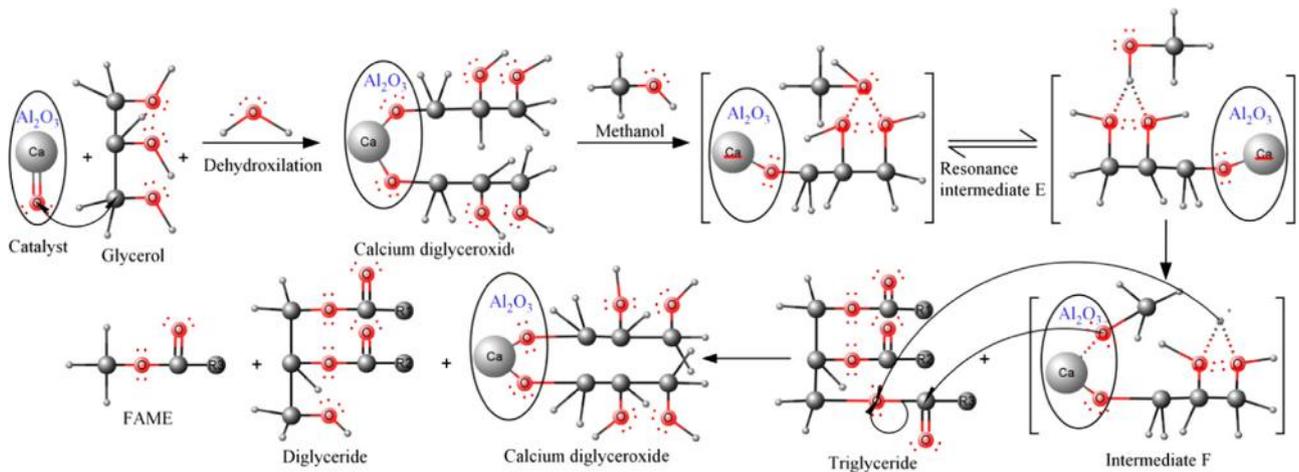


Fig. 3. The mechanism of formation of calcium diglyceroxide and its catalytic effect in transesterification reaction when using CaO/Al₂O₃ as catalyst [36].

not affect the FAME yield or even decreases it. Optimization studies confirm that CaO-based catalysts are highly efficient for oil and fat transesterification at moderate optimal reaction conditions.

Generally, the highest FAME yields are achieved for alcohol-to-oil molar ratios of up to 15:1, catalyst amounts up to 5% and close to the boiling point of methanol.

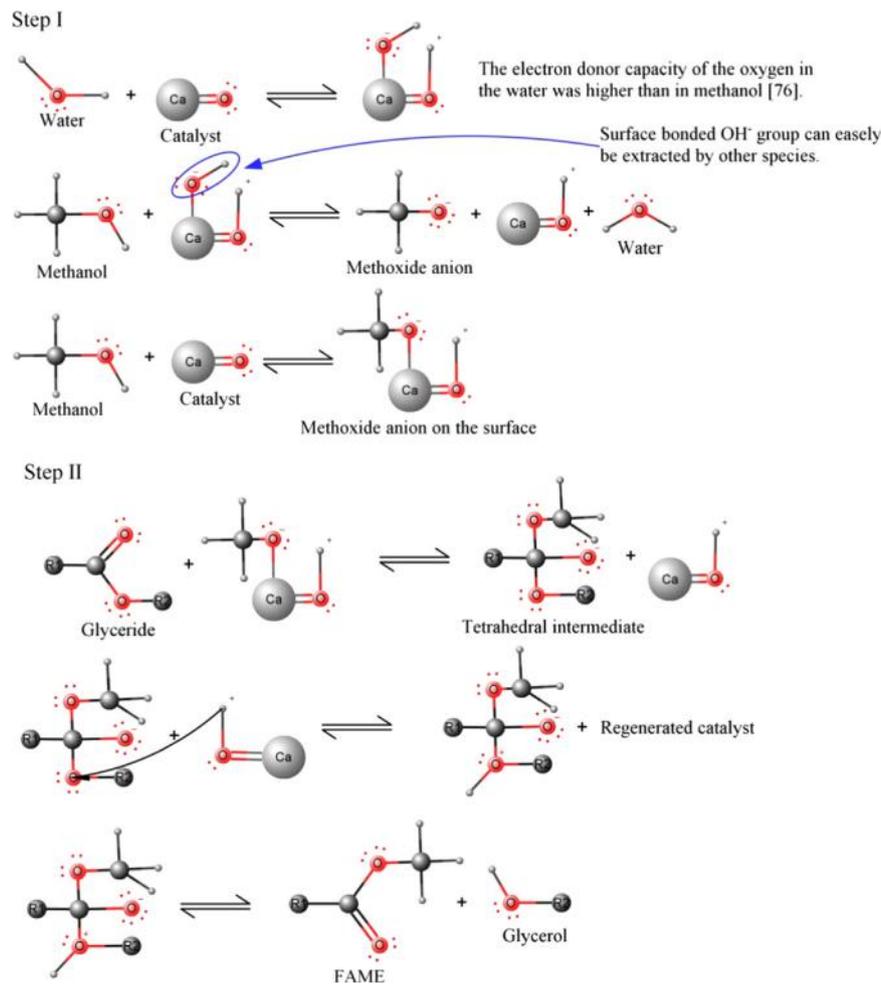


Fig. 4. Mechanism of transesterification reaction on calcium oxide in the presence of a small amount of water [38,39].

Table 4
Modeling the kinetics of methanolysis reactions over CaO-based catalysts.

Oil	Catalyst/ amount (%)	Reaction condition			Kinetic model	R ²	Ref.
		Reactor/stirring (mL/ rpm)	Methanol-to-oil molar ratio	Temperature (K)			
Camelina sativa	CaO/0.5	250/1000	15:1	373	$\frac{dx_A}{dt} = k \cdot (\theta_B - 3 \cdot x_A)$	0.332	[50]
Soybean	CaO/0.5	130/-	-	488		0.490	[40]
Canola	Mixed CaO- MgO/0.5-6	250/-	3:1-12:1	298-340.5	$-\frac{dc_A}{dt} = 3.9579 \cdot 10^{-3} C_A \cdot C_B^{-1/2}$	0.918	[45]
Soybean	CaO/2	100/900	12:1	313-338	$-\frac{d(1-Y_C)}{dt} = \frac{1/\phi_{oil}}{\alpha \cdot k_{dA} + \alpha_S \cdot m_A \cdot k_{SA} + \alpha_S \cdot m_A \cdot k_{hetero}} \cdot (1-Y_C)$	-	[51]
Soybean, waste frying	CaO/2	500/-	6.03:1	333	$-\frac{dc_A}{dt} = k_{app} \cdot C_A$	-	[43]
Soybean	CaO/1.2	500/-	12:1	-		-	[30]
Soybean, virgin/waste cotton seed, castor, karanja and jatropa	K-CaO/7.5	100/600	12:1	308-338		-	[46]
Sunflower	CaO/1-10	250/900	6:1	333	$\frac{dx_A}{dt} = \frac{k_{mA} \cdot k_2}{k_{mA} + k_2} \cdot (1-x_A)$	0.920- 0.981	[41]
Sunflower	Quicklime/1-10	250/900	6:1-18:1	333	$\frac{dx_A}{dt} = K_m \frac{(1-x_A) \cdot (c_{80} + 3 \cdot c_{40} \cdot x_A)}{K + c_{40} \cdot (1-x_A)}$	0.968- 0.998	[49]
Sunflower (refined, used)	CaO-ZnO/2	300/300	10:1	333-369	$\frac{dx_A}{dt} = \frac{k \cdot (k_{mA})_0 \cdot [1 + \alpha \cdot x_A^2]}{k + (k_{mA})_0 \cdot [1 + \alpha \cdot x_A^2]} \cdot (1-x_A)$	0.960- 0.994	[42]
Sunflower	CaO-ZnO/0.5-2	300, 1000/300	6:1, 10:1	333		-	[47]
Jojoba	Mussel shell CaO/6-10	250/-	6:1-12:1	318-338		-	[48]

Table 5
 A literature survey on optimization of transesterification reaction over CaO-based catalysts.

Feedstock	Reactor	Applied reaction conditions				Optimal reaction conditions				Optimization method ^a	Ref.
		Catalyst/loading (wt%)	Methanol-to-oil molar ratio	Temperature (K)	Yield (%) / time (min)	Loading (wt%)	Methanol-to-oil molar ratio	Temperature (K)	Yield (%) / time (min)		
Waste cooking oil	Batch, stirred (500 rpm)	CaO ^b /0.9–5.1	15:1	b.p. ^c	20.0–99.5/24–66	3.39	15:1	b.p.	99.5/32.1	CCD	[54]
Soybean oil	Batch, stirred (500 rpm)	CaO ^d /fly ash/1–5	5.5–6.9	b.p.	74–97/300	3 (1% of 30% loaded CaO)	6.9:1	b.p.	96.97/300	FCCD	[55]
Pork lard	Batch, stirred	Calcium manganese oxide/1–5	9:1–27:1	313–333	43.7–95.8/480	1	21:1	333	99.6/480	CCD	[56]
Palm oil	Batch, stirred (1000 rpm)	CaO/Al ₂ O ₃ /1–8	6:1–24:1	328–338	29–91/300	6.0	12.1:1	337.4	97.9/300	CCD	[57]
Cottonseed oil	Batch, stirred	CaO–MgO ^e /Al ₂ O ₃ /5–25	3:1–14:1 ^f	353–383	38.8–92.5/180	14.4% of CaO–MgO loaded on Al ₂ O ₃	12.24:1 ^f	367.77	97.6/180	BBD	[58]
Jatropha oil	Batch, stirred (600 rpm), microwave	KOH/CaO/2–4	6:1–10:1	333	86.4–97.0/45–75	3.17	8.42:1	333	97.6/67.9	BBD	[59]
Soybean oil	Batch, stirred	CaO ^g /5.86–34.14	6:1	b.p.	1.6–99.6/70–410	25	6:1	b.p.	70.8 ^h /300	FD	[60]
Soybean oil, raw	Batch, stirred (600 rpm)	CaO–KF/cinder ⁱ /1.0–10.9	4:1–14:1	338	80–99/20	2.1	12:1	338	99.9/20	Experimental	[61]
Soybean oil	Batch, stirred (300 rpm)	CaO/zeolites ^j /0.5–5.0	3:1–18:1	323–343	40.5–94.6/300	3 (30% CaO loading)	9:1	338	95/180	Experimental	[62]
Cottonseed oil	Batch, stirred	Li/CaO ^k /1–8	3:1–18:1	308–348	–	5	12:1 ^f	338	98/150	Experimental	[63]
Rapeseed oil	Batch, stirred (60–360 rpm)	Ca ₁₂ Al ₁₄ O ₃₃ –CaO ^l /2–8	9:1–18:1	303–338	< 90/60–3600	6	15:1	338	90/180	Experimental	[64]

^a CCD – central composite design; BBD – Box–Behnken design; FCCD – faced central composite design; FD – factorial design.

^b Sourced from boiler ash.

^c b.p. – boiling point.

^d Sourced from egg shells, CaO loaded on ash: 10–30 wt%.

^e CaO/MgO mass ratios 8:2.

^f Ethanol.

^g Powdered oyster shell combusted at 973 K.

^h Purity 98.4%.

ⁱ Calcination: 773 K, 5 h.

^j NaY, KL and NaZSM–5 zeolites; CaO loading on zeolite: 5–50 wt%; activation prior to use: 873 K, 2 h.

^k Li (0.5–5.0%) impregnated in CaO by wet chemical method; drying: 393 K, 24 h.

^l Calcination: 1273 K, 8 h.

Table 6
The review of neat CaO catalyzed transesterification.

Feedstock	Catalyst preparation	Optimal reaction condition				Yield (conversion) (%)	Time (h)	Leaching (ppm)	Ref.
		Stirring rate (rpm)	Methanol-to-oil molar ratio	Catalyst loading (wt% to the oil)	Temperature (K)				
Sunflower oil Rapeseed oil Soybean oil	Microcrystalline CaO: boiled in distilled water overnight under vigorous stirring; the filter cake (from slurry) dried (393 K) and heated (773 K, 10 h) under vacuum; activation prior the reaction: 873 K under Ar for 2 h	1200	4:1	1.5	348	93/2 90/2 89/2	–	[70]	
Palm oil	Nano-CaO: prepared by thermal-decomposition method Bulk CaO: prepared by calcination of CaCO ₃ (973 K, 2 h)	Stirred	15:1	2.5	338	94/2.5 90/2.5	–	[71]	
Sunflower oil Rapeseed oil Soybean oil	Commercial CaO: activation prior the reaction: 873 K under Ar for 2 h	1200	4:1	1.5	348	76/2 78/2 77/2	–	[70]	
<i>Zanthoxyl umbungeoanum</i> seed oil (27–31% FFA)	CaO p.a., activation prior the reaction: 1173 K for 1.5 h	600	11.69:1	2.52	338	(96) (esterification by ferric sulfate)/2.45	–	[72]	
Waste frying oil Neat semi-refined rape oil Acidified rape oil with oleic acid (0.5–10%; AC ₀₅ –AC ₁₀)	Commercial CaO: dried overnight (393 K)	Stirred	12:1	5	333	87/4 97/4 95 (AC ₀₅), 93 (AC ₀₇₅), 94 (AC ₁), 86 (AC ₂), 77 (AC ₅) and 37 (AC ₁₀)/4	–	[73]	
Refined sunflower oil Tributyrin	Commercial CaO, p.a., calcined (1273 K, 2 h) CaO from calcined precursors (2 h in N ₂ flow at optimum temperature): CA (1073 K)	Stirred 200	12:1 6:1	2 0.1	333 333	(99)/2 68/2	– 100 (CA), 160 (CC), 150 (CH), 30 (CN), 120 (CO)	[74] [19]	
Sunflower oil	CC (1173 K) CH (973 K) CN (873 K) CO (1073 K) CaO, prepared by thermal decomposition (1073 K, O ₂ /Ar flow, 1 h) of CC, CA, CO and CH	1000	14:1	0.2	323	38/2 82/2 < 1/2 (60)/2 ≈ 90/3 (CC, CA, CO, CH)	–	[20]	
Soybean oil	Commercial nano-crystalline CaO	Vigorously stirred	27:1	1.25	Room (296–298)	Almost inactive (> 99)/12	–	[75]	
Soybean oil	CaO p.a.	800	12:1	8	338	95/3	–	[38]	
Soybean oil	Calcined CaCO ₃ (1173 K, He flow, 1.5 h)	Yes	12:1	0.85	333	93/1	187	[30]	
Rapeseed oil	CaO activated with methanol (298 K, 1 h under stirring)	Yes	10.8:1	0.7	333	90/3	–	[69]	
<i>Jatropha curcas</i> oil	Commercial CaO, dipped into ammonium carbonate solution (30 min) and calcined (1173 K, 1.5 h)	–	9:1	1.5	343	(93)/2.5	1.2 mg/ml	[31]	
Rapeseed oil	CaO p.a.	Intense	30:1	0.85	338	92/2.5	–	[67]	
Sunflower oil, refined	CaO p.a., calcined (973 K, 2 h)	1000	13:1	1	333	94/1.5	0.6 mg/ml	[26,68]	
Karanja oil (high FFA)	Chicken eggshells, purged, grinded and calcined (1073 K, 2 h)	600	8:1	2.5	338	95 (esterification by H ₂ SO ₄)/2.5	–	[76]	
Palm oil	Commercial calcite, thermally decomposed (1073 K, 3 h), refluxed in water (333 K, 6 h), filtered, heated overnight (393 K) and calcined prior to use (873 K, 3 h)	500	15:1	7	333	95.7/1	–	[29]	
Soybean oil	Flower-like CaO: solution of NaOH in deionized water was added to Ca(NO ₃) ₂ · 9H ₂ O and KCl and dried (453 K, 12 h)	1000	–	–	333	95.5/2	–	[77]	
Sunflower oil	Commercial CaO, calcined (873 K, 6 h)	500	6:1	7	338	(100) ^a	–	[78]	

^a Second generation biodiesel (molar ratio MAG:FAME=1:2/1).

Table 7

The review of CaO-supported catalysts used in transesterification reactions.

Feedstock	Catalyst preparation	Optimal reaction conditions				Yield (conversion) (%) / time (h)	Leaching (ppm)	Ref.
		Stirring (rpm)	Methanol-to-oil molar ratio	Catalyst loading (wt% to the oil)	Temperature (K)			
Rapeseed oil	LiNO ₃ /CaO, NaNO ₃ /CaO, KNO ₃ /CaO: prepared by the incipient wetness method. Alkaline metal loading 5 wt%. Calcination at 873 K for 5 h.	600	6:1	5	333	(100)/3	200–600	[79]
Ethyl butyrate	MgO/CaO: prepared by the coprecipitation method. Calcination at 1073 K for 1 h in He gas flow. Molar ratio Mg:Ca=3:1.	1250	4:1	–	333	(60)/3	Not observed	[80]
Glyceryl tributyrates	Li/CaO: prepared by wet impregnation method. Li content of 1.23 wt%.	–	310:1	27.7	333	(100)/3	–	[81]
Food grade sunflower oil	Li/CaO: prepared by wet impregnation method. Li content of 4.5 wt%. Activation at 773 K in inert gas flow.	1000	14:1	0.2	333	90/1.5	–	[82]
Karanja oil (<i>Pongamia pinnata</i>) oil (5.75% FFA)	Li/CaO, Na/CaO, K/CaO: prepared by wet impregnation. Metal content of 2 wt%.	600	12:1	2	338	90.3/8	–	[83]
Canola oil	Li/CaO, Na/CaO, K/CaO: prepared by the wet impregnation method. Metal content of 1.25 wt%. The catalyst was preheated at 373 K prior the reaction.	600	6:1	2	323	70.7 (Li), 6.0 (Na), 6.5 (K)/4	–	[65]
Mutton fat, virgin cotton seed, waste cotton seed, soybean, castor, karanja and jatropha oil	Nanocrystalline-K/CaO: prepared by wet impregnation method. K ⁺ content was 3.5%.	Stirred	12:1	7.5	338	98/2.5	4.5 (in FAME), 40 (in glycerol)	[46]
Mutton fat, virgin cotton seed, waste cotton seed, soybean, castor, karanja and jatropha oil	Nanocrystalline-Zn/CaO: prepared by using wet impregnation method. Calcination at 823 K for 12 h in air. Zn ²⁺ content was 1.5 wt%.	500	9:1	5	338	99/0.75	–	[84]
Chinese tallow seed oil	KF/CaO: prepared by using impregnation method. Calcination in air at 873 K for 4 h. KF content: 25% w/w.	Stirred	12:1	4	338	96.8/2.5	31.6 mg/L	[85]
Refined soybean oil, refined rapeseed oil	Bromooctane/CaO: commercial CaO added into bromooctane/hexane solution (1 mg/g CaO). After 24 h of activation under stirring, the catalyst was vacuum dried.	–	15:1	5	338	99.2/3	26	[86]

Table 8

The review of CaO-loaded catalysts used in transesterification reactions.

Feedstock	Catalyst preparation	Optimal reaction condition				Yield (conversion) (%) / time (h)	Leaching (ppm)	Ref.
		Stirring (rpm)	Methanol-to-oil molar ratio	Catalyst loading (wt% to the oil)	Temperature (K)			
Palm oil	CaO/ γ -Al ₂ O ₃ : prepared using an impregnation method of aqueous solution of CA on alumina support (mass ratio CA to alumina was 1:1). The precursor was calcined in air (991 K, 5 h).	1000	12:1	6	338	98/5	31 (I cycle), 12 (II cycle)	[57,87]
Soybean oil	CaO/Al ₂ O ₃ (acidic, neutral and basic): prepared by wet impregnation method (aging time for 2 h). The precursor was calcined in N ₂ flow (823 K, 6 h). CaO loading was 20 wt%.	500	9:1	3	423	90 (neutral), 82 (basic), 72 (acidic)/6	–	[36]
Palm oil Coconut oil	CaO/Al ₂ O ₃ : prepared by incipient-wetness impregnation method. The precursor was calcined at 723 K for 4 h (Al ₂ O ₃ support was calcined at 723 K for 2 h before used). Metal loading was 20 mmol _{metal} /g _{support} .	Vigorously stirred	65:1	10 15	333	94.3/3 94/3	–	[88]
Crude palm oil	CaO/palm oil mill fly ash: prepared by wet impregnation method. Precursor composition of 45 wt% CaCO ₃ . Prior to use, CaCO ₃ was calcined at 1073 K for 1.5 h. The sample was aged for 18 h. The solid was calcined in air (1123 K, 2 h).	700	12:1	6	333	75.73 (98.3)/3	–	[89]
Soybean oil	CaO/mesoporous silica: prepared by incipient-wetness impregnation method. The precursor was calcined in air (1073 K, 3 h). Ca loading of 15 wt%. (Mesoporous silica synthesis – Pluronic 123, HCl and tetraethoxysilane was mixed and stirred for 2 × 4 h before hydrothermal treatment was applied. The solid was calcined at 873 K for 3 h)	Vigorously stirred	16:1	5	333	95.2/8	–	[90]
Sunflower oil	CaO/SBA-15: prepared by incipient-wetness impregnation method. The precursor was calcined at 873 K for 4 h. (SBA-15 synthesis – pluronic 123 and other chemicals was aged at room temp. for 5 days. The solid was calcined at 823 K for 6 h.) Prior the reaction the catalyst was activated in He flow (1073 K, 1 h). CaO loading was 14 wt%.	1025	12:1	1	333	95/5	Not detected	[91]
Refined rapeseed oil	CaO/MgO, CaO/Al ₂ O ₃ , CaO/SiO ₂ : prepared by incipient wetness impregnation method. (The carrier (MgO) was first calcined at 773 K.) Impregnation solution of lime acetate had concentration of 22.6% (For CaO/MgO catalyst CaO loading was 16.5 wt%). The precursor was calcined in N ₂ gas flow (973 K, 8 h).	950	18:1	2	337.5	(92) (CaO/MgO), (60) (CaO/SiO ₂), (36) (CaO/Al ₂ O ₃)/6	–	[92]
Rapeseed oil	Magnetic CaO hollow fiber (CaO/ α -Fe): produced by organic gel-thermal decomposition. The samples were annealed at 1273 K under reducing atmosphere. Ca ²⁺ :Fe ³⁺ = 1:2.	600	12:1	5	333	95.7/2	56 (FAME), 1048 (glycerol)	[93]
Soybean oil	CaO/SnO ₂ : prepared by incipient wetness impregnation method. The precursor was calcined in air (973 K, 6 h) before it was used in the reaction. Ca/Sn ratio was of 4:1.	600	4:1	8	338	89.3/6	29	[94]

Since the dissociation of CO_2 progresses from the outer surface into the particle, a CO_2 film is formed at the surface leading to the recarbonation of CaO to CaCO_3 , which adversely affects the performance of the catalyst.

Several research groups utilized wet impregnation of CaO on some form of alumina carrier using CN [36,88] or CA [57,87] as precursor salts. The amount of CaO loaded on the carrier was 20% [36], > 50% [88] and 35.5% [57,87]. The optimum calcination temperature observed in these studies ranged from 723 to 991 K, depending on salt precursor and type of oil. Ester yields higher than 90% were achieved in less than 5 h in transesterification reactions over all of the used catalysts. At the same reaction conditions during rapeseed oil methanolysis, $\text{CaO}/\text{Al}_2\text{O}_3$ showed the highest activity among catalysts consisting of CaO loaded onto several carriers (MgO , SiO_2 , Al_2O_3 and zeolite HY) [92]. The calcination temperature influenced the catalytic activity of $\text{CaO}/\text{Al}_2\text{O}_3$ since the catalyst calcined at 991 K [92] showed significantly lower activity than the catalyst calcined at 973 K [87], the ester yield being 36% versus 94.5%, respectively. The huge difference in the two catalysts can be explained by the smaller catalyst amount (2% versus 5%) and different types of calcination atmosphere (inert versus oxidizing). CA follows different thermal decomposition paths in different atmospheres as shown by thermogravimetric analysis (Table 9).

Some researchers have recently focused on loading of CaO on mesoporous silica carriers. In their studies [90,91], a triblock copolymer (Pluronic 123) was hydrothermally treated and aged at room temperature in order to get a mesoporous silica carrier. Then, the impregnation method was employed to dope the carrier with CA . Finally, the CaO -loaded catalyst was calcined applying an appropriate temperature regime. The catalysts showed great effectiveness of edible oil transesterification in mild reaction conditions with about 95% conversion.

Most recently, magnetic (α -Fe) recycled CaO hollow fibers have been used as a heterogeneous catalyst for biodiesel production [93]. The catalyst was obtained through the organic gel thermal decomposition method, followed by annealing in reducing atmosphere at 1273 K. The optimum loading of the active compound (CaO) is the $\text{Ca}^{2+}:\text{Fe}^{3+}$ molar ratio of 1:2. This magnetic material has a high mechanical and chemical stability and enables easy separation of the reaction products. The great stability of the $\text{CaO}/\alpha\text{-Fe}$ hollow fibers catalyst is reflected onto a high ester yield over 20 repeated cycles with washing of the catalyst between cycles. The greatest benefit of this catalyst is the short reaction time (2 h) needed to achieve the ester yield over 95% at moderate reaction conditions.

6.4. Mixed oxides catalysts containing CaO

Mixed oxides comprising CaO are applied in transesterification of edible oil for the purpose of biodiesel production because of their stronger alkalinity compared to that of pure constituents. The performances of various mixed oxides containing CaO as catalysts for biodiesel production are compared in Table 10.

Many authors have tried to enhance the catalytic ability of CaO by mixing it with metal oxides from the lanthanide group, lanthanum [99,100] and cerium [101,102] oxides being the most commonly used. Besides their increased basic strength, these catalysts are highly tolerant to water and FFAs and can be used with unrefined or waste oils. Taufiq-Yap et al. [100] and Yan et al. [99] prepared $\text{CaO}\cdot\text{La}_2\text{O}_3$ catalysts with different $\text{Ca}:\text{La}$ ratios using similar coprecipitation methods and performing calcination in different temperature regimes. Transesterification reactions in the two studies were conducted under similar reaction conditions (methanol-to-oil molar ratio of 20–24:1, catalysts of 4–5% refer to oil and 331–338 K). The ester yield of about 95% was obtained in

Table 9

Thermal decomposition characteristics of calcium acetate conducted in different atmospheres.

Reacting atmosphere/ gas	Temperature range (K)	Decomposed compounds	Reference
Inert/ N_2	338–393	Inner and outer crystal water	[96,97]
	665–691	CaCO_3 , CO_2 , H_2O	
	853–878	CaO , CO_2	
Oxidizing/air, or mix- ture O_2 and N_2 (v/v 1:4)	418–521	Inner and outer crystal water	[18,98]
	595–793	CaCO_3 , $\text{C}_3\text{H}_6\text{O}$	
	923–1038	CaO , CO_2	

the soybean oil methanolysis within only 1 h, which was similar to that obtained with NaOH [99]. It was also observed that the presence of water had almost no influence on the ester yield, while FFAs showed a noticeable negative effect. The reaction was only slightly slower even in the presence of 10% of water. The critical amount of FFAs was 3.6% and above it the complete conversion could not be achieved. With crude *Jatropha curcas* oil having a high FFA level (6.8%), the ester yield of about 87% was reached in 6 h [100]. In this study, no leaching of calcium to the reaction mixture was observed in several consecutive runs. Thitsartarn et al. [102] and Yu et al. [101] prepared stable mixed oxides containing cerium using coprecipitation and incipient wetness impregnation, respectively, followed by calcination. Using different feedstocks with a low FFA level, they determined different optimum $\text{Ce}:\text{Ca}$ molar ratios (1 and 0.15, respectively). Both catalysts showed high activity and durability in several consecutive runs, with the 6 h reaction yields higher than 90%.

Some transition metals and their oxides like zirconium [103,104], zinc [47,106–108] and manganese [32,108] have also attracted the interest of many researchers. Basic ZnO with weakly hydrogenating character, which is particularly useful when feedstocks have a high FFA content, improves the transesterification activity of CaO . Mixed $\text{CaO}\cdot\text{ZnO}$ catalyst (a molar ratio of 1:2) can be synthesized by coprecipitation and mechanochemical processing [106]. The catalyst synthesized mechanochemically gave much better conversion than that obtained by coprecipitation (97.5% versus 80% in 4 h) under the same reaction conditions, which could be attributed to smaller particle size of the former catalyst [106]. The additional benefit of $\text{CaO}\cdot\text{ZnO}$ is its good stability and a decreased rate of CaO leaching that is attributed to the strong interaction of CaO with less soluble ZnO . A proper selection of the precipitant for coprecipitation is important for the catalytic activity of $\text{CaO}\cdot\text{ZnO}$ catalyst. A $\text{CaO}\cdot\text{ZnO}$ catalyst prepared with Na_2CO_3 as the precipitant proved itself more active than those prepared with $(\text{NH}_4)_2\text{CO}_3$ using urea hydrolysis, since the three methods of precipitation resulted in ester yields of 93.5%, 73.9% and 27.6%, respectively [107]. The repeated use of $\text{CaO}\cdot\text{ZnO}$ catalyst is limited because of its deactivation by deposition of organic matter on the active surface. After washing with methanol and calcination, the catalytic activity of the washed mixed oxide was successfully recovered. Although CaZnO and CaMgO catalysts gave conversion yields higher than 80% within 6 h in the *jatropha* oil methanolysis, the latter was more active because of higher total basicity and better basic site distribution [108]. Compared to pure CaO , these mixed oxides showed weaker activity but better reusability.

Natural resources like dolomite, hydrotalcite-like materials (layered $\text{Ca}\text{--}\text{Al}$ double hydroxides) and silicates are preferred for preparation of solid catalysts for transesterification. A catalyst with high activity is obtained from dolomite at the proper calcination temperature of 1073 K [95]. The active catalyst consists of 16.6%

Table 10
The review of mixed oxide with CaO catalyzed transesterification.

Feedstock	Catalyst preparation	Optimal reaction condition				Yield (conversion) (%) / time (h)	Leaching (ppm)	Ref.
		Stirring (rpm)	Methanol-to-oil molar ratio	Catalyst loading (wt% to the oil)	Temperature (K)			
Food-grade soybean, crude soybean, palm and waste cooking oil	CaO–La ₂ O ₃ was prepared by coprecipitation method, and then was calcined at 703 K for 1 h and at 1023 K for another 8 h. Prior the reaction was activated at 1023 K for 1 h in pure N ₂ flow. Molar ratios Ca:La=3:1.	450	7:1	5	331	94.3/1	–	[99]
<i>Jatropha curcus</i> oil	CaO–La ₂ O ₃ was prepared by coprecipitation method. Samples were calcined at 1073 K for 6 h. Ca/La atomic ratios of 4.0%.	–	24:1	4	338	86.51/6	24.9	[100]
<i>Pistacia chinensis</i> oil	CaO–CeO ₂ was prepared by incipient wetness impregnation method. Ce/Ca molar ratio of 0.15. Samples were calcined at 973 K in He/O ₂ (9/1 v/v) gas flow.	1500	30:1	9	373	93/6	33	[101]
Palm oil	CaO–CeO ₂ was prepared by coprecipitation method. The precursor was calcined at 923 K for 8 h. Ca/Ce molar ratio of 1.09.	1200	20:1	5	358	95/3	≈ 100	[102]
Waste cooking oil	CaO–ZrO ₂ was prepared by coprecipitation method. Ca/Zr molar ratio of 0.5.	500	30:1	10	338	92.1/2	–	[103]
Palm oil	Ca _{3.5x} Zr _{0.5y} Al _x O ₃ (0.1 ≤ x ≤ 0.5, 0.5 ≤ y ≤ 2.5) was synthesized through the coprecipitation of metal hydroxides (aging at 353 K for 5 h). Sample was calcined at 773 K for 5 h. Ca:Zr ratio of 7:1.	500	12:1	2.5	423	87/5	–	[104]
Degummed soybean oil, poultry fat	CSMO was prepared by co-condensation reaction of TEOS in water (480 ml H ₂ O, 5 ml TEOS, pH=9.2). Ca/Si ratio was 5.3. PMCS preparation: Ca/Si ratio was 2.15. pH=11.5, 100 ml H ₂ O, 1 ml TEOS. Aged at 363 K for 24 h and calcined at 873 K for 6 h.	–	≈ 175:1	20	337.7	88 (CSMO)/4 100 (PMCS)/2	–	[105]
Edible sunflower oil	CaO·ZnO was synthesized from corresponding powder by ball mill and subsequent calcination at 973 K in air atmosphere.	300	10:1	2	333	92/2, 97.5/4	8.9 mg/L	[106]
Refined palm kernel, refined sunflower, palm olein, and soybean oil	CaO·ZnO was prepared by coprecipitation method. Atomic Ca/Zn ratio was 0.25. Catalyst was calcined at 1073 K for 2 h prior the reaction.	–	30:1	10	333	> 94 (for all oils)/3	–	[107]
<i>Jatropha curcus</i> oil	CaMgO and CaZnO were prepared by coprecipitation method. The precursors were calcined at 1073 K (CaMgO) and 1173 K (CaZnO) for 6 h. Molar ratio Ca/Mg of 0.3 and Ca/Zn of 0.22.	Vigorously stirred	15:1	4	338	(83) CaMgO, (81) CaZnO/6	≥ 20	[108]
Ethyl butyrate and sunflower oil	Mg/Ca oxide was prepared by coprecipitation method. Sample was calcined at 1073 K for 6 h. Mg:Ca molar ratio of 3.8.	1250	12:1	2.5	333	(45) ethyl b./1; 92.4 sunflower o./3	–	[109]
Palm kernel oil	Dolomite (mainly CaMg(CO ₃) ₂) was calcined at 1073 K for 2 h in air.	Stirred	30:1	6	333	98.6/3	–	[95]
Rapeseed oil	Ca ₁₂ Al ₁₄ O ₃₃ was prepared by chemical synthesis method (prepared emulsion were Ca:Al molar ratio of 3:2). The precursor (hydrated tricalcium aluminate) was calcined at 873 K for 8 h in air.	270	15:1	6	338	94.34/3	Negligible	[6,64]
Sunflower oil	Hydrocalumite was transformed by thermal activated at 1023 K for 13 h into mixture CaO and Ca ₁₂ Al ₁₄ O ₃₃ . Prior the reaction the catalyst was activated at 773 K in He flow for 1 h. Ca:Al molar ratio of 2:1.	1000	12:1	1	333	98/3	–	[110]
Various edible ^a , non-edible ^b and used cooking oils (sunflower o.)	CaAl ₂ -LDH (hydrocalumite) was prepared by coprecipitation (slurry was aged at 338 K for 18 h). Ca/Al atomic ratio was 3.0. The precursor was calcined at 973 K for 5 h in air.	Vigorously stirred	5.6:1	5	338	> 91 (for all oils except <i>Castor</i> 70 and <i>Marotti</i> oil 62)/5	1.5%	[111]
<i>Jatropha curcus</i> oil	La _{0.1} Ca _{0.9} MnO ₃ (La loaded on perovskite) was prepared by the precipitation method and was calcined at 923 K.	300	6:1	5	333	10/3	–	[32]

^a Sunflower, ground nut, palmolein, gingelly, mustard, soybean, cottonseed, corn and ricebran oil.

^b *Jatropha*, Pungai, Pinnai, Karingatta, Neem, Castor and Marotti oil.

Table 11
The review of other calcium-based catalysts used in transesterification reactions.

Feedstock	Catalyst preparation ^a	Optimal reaction condition				Yield (conversion) (%) / time (h)	Leaching (ppm)	Ref.
		Stirring (rpm)	Methanol-to-oil molar ratio	Catalyst loading (wt% to the oil)	Temperature (K)			
Soybean oil	Ca(C ₃ H ₇ O ₃) ₂ /n-Al ₂ O ₃ : 20% CaO/n-Al ₂ O ₃ , methanol and glycerol were charged to a vessel and mixture was refluxed at 423 K with stirring for 4 h.	500	9:1	3	423	82/6	Insignificant	[36]
Soybean oil	Ca(C ₃ H ₇ O ₃) ₂ prepared from CaO under reflux of methanol in the presence of glycerol (50 vol%) for 2 h.	500	12:1	1.5-3.5	-	88/2 ^b	-	[114]
Soybean oil	Ca(C ₃ H ₇ O ₃) ₂ : CaO, obtained from limestone in He flow (1173 K, 1.5 h), was immersed in glycerol (333 K, N ₂ flow).	500	12:1	3.5	-	~70/1	-	[115]
Sunflower oil	Ca(C ₃ H ₇ O ₃) ₂ : CaO, obtained from CaCO ₃ , was poured into methanol and glycerol, heated (323 K, N ₂ atmosphere) and left under agitation overnight.	1000	14:1	0.7	333	90/3	-	[120]
Sunflower oil, refined	Ca(C ₃ H ₇ O ₃) ₂ : CaO was mixed with glycerol and methanol (mass ratio of 1:4.4) at 333 K and left under agitation for 3 h.	Stirred	12:1	2	333	(~99)/6	Insignificant	[74]
Sunflower oil, refined	Ca(C ₃ H ₆ O ₃): Ca(OH) ₂ was mixed with glycerol (mass ratio of 1:10; 453 K, 2 h), the solid was recovered and washed twice with ethanol and dried overnight at 333 K under vacuum.	Stirred	12:1	2	333	(~95)/8		[74]
Soybean oil	Ca(OCH ₃) ₂ : prepared by immersion of CaO in methanol (2 h).	500	12:1	1.5-3.5	-	~25/1	-	[114]
Soybean oil	Ca(OCH ₃) ₂ , commercial (min. 90%), grounded.	1000	9:1	1	338	> 90/1.5	-	[44]
Tributyrin	Ca(OCH ₃) ₂ , commercial.	-	6:1	2	333	~90/4	-	[121]
Sunflower oil, refined	Ca(OCH ₃) ₂ : synthesized by reaction of calcium with methanol (338 K, 4 h), dried (378 K, 1 h).	900	~7.5:1	4	338	98/2	Almost none ^c	[116]
Sunflower oil	Ca(OH) ₂ ; commercial, grounded.	900	6:1	5	333	~97/2	-	[122]

^a Ca(C₃H₇O₃)₂ – calcium diglyceroxide, Ca(C₃H₆O₃) – calcium glycerolate and Ca(OCH₃)₂ – calcium methoxide.

^b Reaction is conducted with reflux of methanol.

^c Catalyst was reused for 20 cycles.

No reports deal with handling of used catalysts and treating of wastewater generated during water washing of crude biodiesel. However, the amount of used catalyst can be minimized by its reuse. Depending on the resource type, CaO can be reused either with [7] or without [145] regeneration of catalytic activity. Also, the amount of the used catalyst can be reduced by its appropriate modification in order to improve its catalytic stability and allow its long-term usage. Almost the same methods, albeit with certain modifications, can be used for treating wastewaters generated by homogeneous and by heterogeneous biodiesel production processes. Solid catalyst particles used in stirred reactors are removed from the reaction mixture through an additional stage of separation by filtration or centrifugation. Dry washing agents are used as a packed bed or suspended in crude biodiesel. In the latter case, suspended particles of the dry washing agent are removed by filtration. The spent adsorbent is usually disposed of to a landfill, although other uses might be invented [146]. Some resins exhausted ionically, after several regeneration cycles by methanol washing, can be returned to manufacturer for ionic regeneration [147]. Being non-hazardous, spent resins can be disposed of in a landfill or incinerated. Although no method of membrane cleaning has been reported, it should include washing with appropriate solvents to remove compounds collected by the membrane [148]. The precipitate formed by the reaction of calcium ions with a precipitating agent (citric acid) or an ion-exchanging compound (sodium carbonate) is removed by filtration. There are no reported studies on how to treat or use the obtained calcium salts. Calcium citrate may be converted to citric acid and calcium sulfate using dilute sulfuric acid, while CaCO₃ can be utilized as a building material or an ingredient of cement. A relevant identified use of the calcium–EDTA complex is as fertilizer.

A catalyst can be repeatedly used without or after its treatment by organic solvents like hexane, petroleum ether, acetone and methanol [147]. After catalyst separation by filtration, the hazardous waste filtrate can be subjected to evaporation or distillation in order to recover the washing agent.

12. Future perspective

A large number of studies prove that CaO-based catalysts have a potential as heterogeneous catalysts for biodiesel production in the future. CaO shows a high basic strength and causes a low environmental impact because of its low solubility in methanol and cheap natural or waste sources from which it can be obtained. However, reusability and the application of the catalyst in successive cycles are still questionable. The main reason for a doubtful reusability is the reduction of its catalyst activity caused by deposition of organic matter on the active surface, poisoning the catalyst active sites by ambient CO₂ and H₂O and CaO leaching into the reaction medium. Reports indicate that CaO does not leach into the reaction medium in large amounts, especially when bonded with carriers or other species. However, the calcium concentration in crude biodiesel is usually above the EN 14214 standard limit, which requires an additional purification step in the overall process of biodiesel production.

A well-known disadvantage of CaO is its sensitivity to the ambient conditions even during a short exposure of 5–10 min. Hence, finding materials that will be stable under ambient conditions is one of the primary goals in focus of many researchers. A possible solution might be the use of calcium diglyceroxide and glycerolate as transesterification catalysts because they are resistant to the atmospheric poisoning. Moreover, modifications of CaO to organometallic compounds like calcium methoxide or diglyceroxide are very effective with respect to reusability. Also, the addition of a small amount of biodiesel (3% referred to oil) to the

activated CaO can protect the catalyst from poisoning by ambient CO₂ and H₂O. Mixing biodiesel with the catalyst prior to the reaction not only protects CaO but also results in an increase of the TAG methanolysis rate as biodiesel acts as cosolvent.

Looking for the optimum calcination temperature regime for CaO-containing raw or waste materials will be a task for the researchers working on the improvement of the overall biodiesel production process. However, the increase of the catalytic performance of neat CaO will not be significant in the future. Therefore, researchers should focus onto enhancing the catalytic performance of CaO by mixing it with appropriate oxides through either loading or supporting. In addition, using low-cost waste materials can contribute significantly to the reduction of the overall process costs. For instance, promising catalytic performance and good reusability of biomass-based ashes as CaO-based catalysts or supports for CaO are demonstrated by several research groups.

Since the loss of catalyst amount because of leaching can be neglected, the chances for extending reusability of CaO are substantial. Pelletizing CaO or loading it onto a suitable carrier is another area that researchers can explore to simplify the catalysts recovery and to extend the number of cycles in which the catalyst can be used. Also, cost-effective and efficient methods for CaO-based catalyst regeneration like washing with a mixture of methanol and ammonium solution should replace commonly used thermal calcination. Moreover, the integration of a byproduct (glycerol) in the final biodiesel product is an undisputed success in the fields of energy production and environmental protection. Partial methanolysis of sunflower oil over CaO powder produces a new type of biofuel (Ecodiesel) that is fully applicable in diesel engines.

The main challenge for using CaO as catalyst will be how to prepare raw feedstocks with a high FFA content for transesterification. In this respect, the raw material must be pre-treated in order to reduce the amount of FFAs below a preferred level. In addition, researchers have increasingly been occupied by continuous biodiesel production processes. Based on the current encouraging results, it should be expected that more emphasis will be given to these methods in the future.

Despite many difficulties that remain to be solved, the number and variety of research areas in studying of CaO confirm its promising potential as a heterogeneous catalyst for biodiesel production at the industrial level.

Acknowledgment

The project is financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia through the Project no. III 45001.

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