Contents lists available at ScienceDirect



# Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



# Calcium oxide as a promising heterogeneous catalyst for biodiesel production: Current state and perspectives



Dalibor M. Marinković<sup>a</sup>, Miroslav V. Stanković<sup>a</sup>, Ana V. Veličković<sup>b</sup>, Jelena M. Avramović<sup>b</sup>, Marija R. Miladinović<sup>b</sup>, Olivera O. Stamenković<sup>b</sup>, Vlada B. Veljković<sup>b,\*</sup>, Dušan M. Jovanović<sup>a</sup>

<sup>a</sup> University of Belgrade, Institute for Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia
 <sup>b</sup> University of Niš, Faculty of Technology, Bulevar oslobođenja 124, 16000 Leskovac, Serbia

#### ARTICLE INFO

Article history: Received 28 February 2015 Received in revised form 15 August 2015 Accepted 10 December 2015 Available online 30 December 2015

Keywords: Biodiesel Calcium oxide Heterogeneous catalysis Leaching Purification Transesterification

## ABSTRACT

The present paper is an overview of the recent progress in the development of various CaO-based catalysts suitable for biodiesel production. The mechanism, kinetics and optimization of transesterification reaction over these catalysts are first considered. Then, the practical application of CaO-based catalysts is discussed with a special stress on leaching and reusability of these catalysts. Also, various continuous reactor systems currently in use for biodiesel production are appraised. In addition to it, purification of crude biodiesel and the ecological aspects of using CaO-based catalysts are considered. Finally, the potentials of CaO-based catalysts for heterogeneous catalysis for biodiesel production are emphasized to assess the future perspectives of their use. This review might help in selecting suitable CaO-based catalysts and the optimum reaction conditions for biodiesel production.

© 2015 Elsevier Ltd. All rights reserved.

#### Contents

1.	Introduction	1388
2.	Properties of CaO-based catalysts	1388
3.	Reaction mechanism of transesterification with CaO.	1389
4.	Kinetics of transesterification reaction catalyzed by CaO-based catalysts.	1390
5.	Optimization of transesterification reaction catalyzed by CaO-based catalysts	1390
6.	The use of CaO-based catalysts	1395
	6.1. Pure CaO catalyst	1395
	6.2. Doped CaO catalysts	1397
	6.3. Loaded CaO catalysts	1397
	6.4. Mixed oxides catalysts containing CaO	1399
	6.5. Other calcium-based catalysts	1402
7.	Comparative performance of CaO-based catalysts with different oily feedstocks	1402
8.	CaO leaching	1403
9.	Reactors in use	1403
10.	Purification of crude biodiesel	1404
11.	Ecological aspects of the use of CaO-based catalysts	1404

*Abbreviations:* CA, calcium acetate monohydrate; CC, calcium carbonate; CH, calcium hydrate; CN, calcium nitrate tetrahydrate; CO, calcium oxalate monohydrate; CO<sub>2</sub>-TPD, temperature-programmed desorption of CO<sub>2</sub>; CSMO, calcium containing silicate mixed oxide; DAG, diacylglycerol; ER, Eley–Rideal; FAME, fatty acid methyl ester; FFA, free fatty acid; LHHW, Langmuir–Hinshelwood–Hougen–Watson; MAG, monoacylglycerol; PMCS, phosphoric acid monoester-directed mesoporous calcium containing silicate; TAG, triacylglycerol; TEOS, tetraethyl orthosilicate

\* Corresponding author. Tel.: +381 16 247203; fax: +381 16 242859.

E-mail address: veljkovicvb@yahoo.com (V.B. Veljković).

12.	Future perspective	1405
Ackr	nowledgment	1405
Refe	erences	1405

#### 1. Introduction

Finding alternatives to fossil fuels has attracted a worldwide interest in recent years due to limited reserves of traditional fossil fuels, the instabilities of the crude oil price and the concerns over greenhouse gas emissions. An alternative is biodiesel, a biodegradable and biorenewable fuel, chemically a mixture of alkyl esters of long-chain fatty acids. It is typically made from biological resources containing triacylglycerols (TAGs) such as vegetable oils, animal fats, algal oils, waste vegetable oils, used cooking oils and waste fats, and alcohols like methanol and ethanol out of which a new ester and glycerol are formed through transesterification reactions. Biodiesel offers many advantages such as a high flash point, high cetane number, low viscosity, high lubricity, biodegradability and environmentally friendly use because of lower carbon monoxide emissions and improved emission profiles compared to conventional fossil fuels [1]. Although the biodiesel properties vary with the oily feedstock and the alcohol used, it can be utilized as a direct substitute for traditional diesel fuel [2] providing that the standard specifications are satisfied.

Transesterification reaction can be carried out by either a catalytic or a non-catalytic process. Base catalysts, acid catalysts and enzymes have been commonly used in biodiesel production at all scales. Acid- or base-catalyzed transesterification is the most commonly used technique since it is the most cost-effective process [1,3]. Acid catalysts are especially suitable if the oil contains high amount of FFAs and water since these catalysts are capable of coping with esterification of FFAs and transesterification of TAGs simultaneously [2]. However, the process requires a high alcoholto-oil molar ratio, high acid catalyst concentration and a long reaction time [2,4–6]. In addition to it, it causes problems related with the corrosive action of acid catalysts [2]. Alkali hydroxides and methoxides are most often used in industrial biodiesel production [7] since transesterification is performed during shorter reaction times and under relatively modest operating conditions [6,8,9]. The fact that homogeneous catalysts cannot be reused or regenerated is one of their major disadvantages. The separation of a homogeneous catalyst from products is difficult, requires more equipment and results in a higher production cost [8]. In addition, large amounts of wastewater are produced in the purification step [10]. Moreover, crude biodiesel produced by alkali-catalyzed transesterification must be refined to fulfill the biodiesel standard specifications for commercial use [11].

Novel, promising technologies that overcome problems associated with homogeneous catalysts are based on the use of heterogeneous (solid) catalysts in the transesterification process. Solid catalysts can be acidic or basic. The acidic catalysts include sulfated metal oxides, sulfonic ion-exchange resin, heteropolyacids, zeolites, VOPO<sub>4</sub>, etc. The basic catalysts are hydroxides, dolomites, hydrotalcites, neat metals, mixed oxides, loaded and supported alkaline and alkaline earth elements and oxides. Solid catalysts are environmentally advantageous, can be used in continuous processes and might be reused with or without regeneration. Since heterogeneous catalysis does not require water washing, the purification of the products is simplified and a very high ester yield is obtained, close to the theoretical value [3]. Glycerol is directly produced with high purity levels (at least 98%) and is devoid of any salt contaminants [12]. However, heterogeneously-catalyzed transesterification generally requires more severe operating conditions (relatively elevated temperatures and pressures and higher alcohol-to-oil molar ratio), and the performance of heterogeneous catalysts is generally lower compared to homogeneously catalyzed transesterification [3]. Commonly, heterogeneous transesterification reactions are conducted at higher alcohol-to-oil molar ratios (6:1 to 40:1, most frequently 12:1) in the presence of solid catalyst compared to the homogeneous ones (usually 6:1). Moreover, one of the main problems with heterogeneous catalysts is their deactivation with time owing to many possible phenomena, such as poisoning and leaching [3]. The problem with poisoning is particularly evident when the process involves used cooking oils [13]. More dramatic is catalyst leaching, which increases the operational cost due to the need for the catalyst replacement and leads to product contamination. Because of the above-mentioned drawbacks, heterogeneous catalysts are nowadays used only in a few commercial biodiesel production facilities [14,15]. Among the base solid catalysts, calcium compounds in various forms (oxide, hydroxide, carbonate, alcoxides and diglyceroxides) have widely been tested in transesterification reactions. Of these compounds, CaO-based catalysts have most frequently been used in the form of neat, supported, loaded and mixed CaO [16,17].

This paper considers CaO-based catalysts used in transesterification reactions of TAGs from biorenewable sources. The important properties of CaO-based catalysts are first emphasized. Then, the mechanism and kinetics of transesterification reaction catalyzed by CaO-based catalysts are considered. Also, the practical application of CaO-based catalysts is discussed with special reference to their leaching and reusability and various continuous reactor systems for their use. Moreover, purification of crude biodiesel is examined, as well as the ecological aspects of using CaO-based catalysts. Finally, potentials of CaO-based catalysts are discussed to evaluate the future perspectives of their use.

## 2. Properties of CaO-based catalysts

Calcium oxide is usually made by thermal decomposition of minerals such as limestone and calcite or from natural sources such as sea- and eggshells which contain calcium carbonate (CaCO<sub>3</sub>). This is achieved by calcination of CaCO<sub>3</sub>-containing raw materials at high temperatures in order to liberate a molecule of carbon dioxide leaving quicklime. Different raw materials require different temperatures of calcination in order to obtain CaO, as seen in Table 1. Experimental results suggest that heating rate significantly affects the temperature of formation of CaO [18]. Quicklime is not stable and will spontaneously react with CO<sub>2</sub> and water from the air to form CaCO<sub>3</sub> and Ca(OH)<sub>2</sub>. The main physical and chemical properties of CaO are listed in Table 2.

The catalytic activity of CaO in transesterification is based on the existence of basic sites and their spatial dispersion defining their availability. During the 1970s the basicity of CaO was found to be 0.57 mmole g<sup>-1</sup> (titration method) at calcination in air at approximately 773 K [28]. The basic sites on the surface of CaO quickly react with the ambient H<sub>2</sub>O and CO<sub>2</sub>. Therefore, the basic strength of CaO varies from the minimum value of  $9.8 < H_{-} < 12.2$  [29] for commercial inactivated CaO, via  $15.0 < H_{-} < 18.4$  [30] for CaO that probably was in contact with air, up to  $H_{-} > 26.5$  [31]. It has recently been concluded that the basicity of CaO, as well as its other textural

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

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

<sup>a</sup> Depending on decomposition time: 1144 K for 1 h and 914 K for 24 h.

#### Table 2

Physicochemical properties of the calcium oxide.<sup>a</sup>

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 <sup>3</sup> )	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) <sup>b</sup>	0.1-0.2 (298 K), 0.03-0.04
	(333 K), exothermic
	reaction
Glycerol (mg CaO/ml) <sup>c</sup>	1.6 (0.5 h contact, 298 K),
	5.7 (2 h contact, 298 K)
Glycerol+methanol (mg CaO/ml) <sup>b</sup>	~1 (333 K)
Solubility in biodiesel+methanol+glycerol (mg	0.4 (298 K), 0.6 (333 K)
CaO/ml alcohol phase) <sup>b</sup>	

<sup>&</sup>lt;sup>a</sup> [25]. <sup>b</sup> [26].

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 basics 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/Al<sub>2</sub>O<sub>3</sub> 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

<sup>&</sup>lt;sup>c</sup> [27]

Structural and textural properties of calcium oxide [20].

Precursor	Crystal size (nm)	Surface area (m²/g)	Pore volume (cm <sup>3</sup> / g)	Pore diameter (nm)	Basicity, CO <sub>2</sub> 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).

<sup>a</sup> No measurable amount of CO<sub>2</sub> 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)  $O^{2-}$  from CaO can extract  $H^+$  from the hydroxyl group of methanol, and (b)  $O^{2-}$  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 CaObased 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/Al<sub>2</sub>O<sub>3</sub> [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/Al<sub>2</sub>O<sub>3</sub> [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/Al<sub>2</sub>O<sub>3</sub> catalyst for transesterification [36].



Fig. 3. The mechanism of formation of calcium diglyceroxide and its catalytic effect in transesterification reaction when using CaO/Al<sub>2</sub>O<sub>3</sub> as catalyst [36].

دائلو دکننده مقالات علمي freepaper.me paper 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/	Reaction condition			Kinetic model	$R^2$	Ref.
	amount (%)	Reactor/stirring (mL/ rpm)	Methanol-to-oil molar ratio	Temperature (K)			
<i>Camelina sativa</i> Soybean Canola	CaO/0.5 CaO/0.5 Mixed CaO- MgO/0 5-6	250/1000 130/- 250/-	15:1 - 3:1-12:1	373 488 298–340.5	$\frac{dx_{A}}{dt} = k \cdot (\theta_{B} - 3 \cdot x_{A})$ $-\frac{dc_{A}}{dt} = 3.9579 \cdot 10^{-3} c_{A} \cdot c_{B}^{-1/2}$	0.332 0.490 0.918	[50] [40] [45]
Soybean	CaO/2	100/900	12:1	313-338	$-\frac{d(1-Y_C)}{dt} = \frac{1/\phi_{oil}}{\frac{1}{a \cdot k_{d,a}} + \frac{1}{a_C \cdot m_A \cdot k_{C,a}} + \frac{1}{a_C \cdot m_A \cdot k_{hotorn}}} \cdot (1-Y_C)$	-	[51]
Soybean, waste frying Soybean Soybean, virgin/waste cot- ton seed, castor, karanja	CaO/2 CaO/1.2 K-CaO/7.5	500/- 500/- 100/600	6.03:1 12:1 12:1	333 - 308-338	$-\frac{dc_A}{dt} = k_{app} \cdot c_A$	-	[43] [30] [46]
Sunflower	CaO/1-10	250/900	6:1	333	$\frac{dx_A}{dt} = \frac{k_{mtA} \cdot k_2}{k_{mtA} + k_2} \cdot (1 - x_A)$	0.920- 0 981	[41]
Sunflower	Quicklime/1-10	250/900	6:1-18:1	333	$\frac{dx_A}{dt} = k_m \frac{(1 - x_A) \cdot (c_{R0} + 3 \cdot c_{A0} \cdot x_A)}{K + c_{A0} \cdot (1 - x_A)}$	0.968- 0.998	[49]
Sunflower (refined, used)	CaO · ZnO/2	300/300	10:1	333–369	$\frac{d\mathbf{x}_{A}}{dt} = \frac{k \cdot (k_{mtA})_{0} \cdot [1 + \alpha \cdot \mathbf{x}_{A}^{\beta}]}{k + (k_{mtA})_{0} \cdot [1 + \alpha \cdot \mathbf{x}_{A}^{\beta}]} \cdot (1 - \mathbf{x}_{A})$	0.960- 0.994	[42]
Sunflower Jojoba	CaO·ZnO/0.5–2 Mussel shell CaO/6–10	300, 1000/300 250/-	6:1, 10:1 6:1–12:1	333 318-338		-	[47] [48]

# دانلو دکننده مقالات علمی freepaper.me paper

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

Feedstock	Reactor	Applied reaction cond	litions			Optimal reaction co	onditions			Optimization	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)	method	
Waste cooking oil	Batch, stirred (500 rpm)	CaO <sup>b</sup> /0.9–5.1	15:1	b.p. <sup>c</sup>	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 <sup>d</sup> /fly ash/1–5	5.5-6.9	b.p.	74–97/300	3 (1% of 30% loa- ded 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 <sub>2</sub> O <sub>3</sub> /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 <sup>e</sup> /Al <sub>2</sub> O <sub>3</sub> /5- 25	3:1-14:1 <sup>f</sup>	353-383	38.8-92.5/180	14.4% of CaO–MgO loaded on Al <sub>2</sub> O <sub>3</sub>	12.24:1 <sup>f</sup>	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 <sup>g</sup> /5.86-34.14	6:1	b.p.	1.6–99.6/70– 410	25	6:1	b.p.	70.8 <sup>h</sup> /300	FD	[60]
Soybean oil, raw	Batch, stirred (600 rpm)	CaO-KF/cinder <sup>i</sup> /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 <sup>i</sup> /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 Rapeseed oil	Batch, stirred Batch, stirred (60– 360 rpm)	Li/CaO <sup>k</sup> /1-8 Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub> -CaO <sup>l</sup> /2- 8	3:1-18:1 9:1-18:1	308–348 303–338	- < 90/60- 3600	5 6	12:1 <sup>f</sup> 15:1	338 338	98/150 90/180	Experimental Experimental	[63] [64]

<sup>a</sup> CCD - central composite design; BBD - Box-Behnken design; FCCD - faced central composite design; FD - factorial design.

<sup>b</sup> Sourced from boiler ash.

<sup>c</sup> b.p. – boiling point.

<sup>d</sup> Sourced from egg shells, CaO loaded on ash: 10–30 wt%.

<sup>e</sup> CaO/MgO mass ratios 8:2.

<sup>f</sup> Ethanol.

<sup>g</sup> Powdered oyster shell combusted at 973 K.

<sup>h</sup> Purity 98.4%.

<sup>i</sup> Calcination: 773 K, 5 h.

<sup>j</sup> NaY, KL and NaZSM-5 zeolites; CaO loading on zeolite: 5-50 wt%; activation prior to use: 873 K, 2 h.

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

<sup>1</sup> Calcination: 1273 K, 8 h.

The review of neat CaO catalyzed transesterification

Feedstock	Catalyst preparation	Optimal reaction	on condition			Yield (conversion) (%)/	Leaching (ppm)	Ref.
		Stirring rate (rpm)	Methanol-to-oil molar ratio	Catalyst loading (wt% to the oil)	Tempe- rature (K)	- ne pap		
Sunflower oil	Microcrystalline CaO: boiled in distilled water overnight	1200	4:1	1.5	348	93/2	-	[70]
Rapeseed oil	under vigorous stirring; the filter cake (from slurry) dried					90/2		
Soybean oil	(393 K) and heated (773 K, 10 h) under vacuum; activation prior the reaction: 873 K under Ar for 2 h					89/2		
Palm oil	Nano-CaO: prepared by thermal-decomposition method	Stirred	15:1	2.5	338	94/2.5	-	[71]
	Bulk CaO: prepared by calcination of CaCO <sub>3</sub> (973 K, 2 h)					90/2.5		
Sunflower oil Rapeseed oil	Commercial CaO: activation prior the reaction: 873 K under Ar for 2 h	1200	4:1	1.5	348	76/2 78/2	-	[70]
Soybean oil	CoO not positivation prior the reaction, 1172 K for 15 h	600	11 00.1	2 5 2	220	77/2 (OC) (astarification by famia		[70]
oil (27–31% FFA)	CaO p.a., activation prior the reaction: 11/3 K for 1.5 h	600	11.69:1	2.52	338	(96) (esterification by ferric sulfate)/2.45		[72]
Waste frying oil	Commercial CaO: dried overnight (393 K)	Stirred	12:1	5	333	87/4	-	[73]
Acidified rape oil with oleic acid (0.5–10%; AC <sub>05</sub> –AC <sub>10</sub> )						97/4 95 (AC <sub>05</sub> ), 93 (Ac <sub>075</sub> ), 94 (AC <sub>1</sub> ), 86 (AC <sub>2</sub> ), 77 (AC <sub>5</sub> ) and 37 (AC <sub>10</sub> )/4		
Refined sunflower oil	Commercial CaO, p.a., calcined (1273 K, 2 h)	Stirred	12:1	2	333	(99)/2	-	[74]
Tributyrin	CaO from calcined precursors (2 h in $N_2$ flow at optimum temperature): CA (1073 K)	200	6:1	0.1	333	68/2	100 (CA), 160 (CC), 150 (CH), 30 (CN), 120 (CO)	[19]
	CC (1173 K)					38/2		
	CH (973 K)					82/2		
	CN (873 K)					< 1/2		
Comfloring all	CO(10/3  K)	1000	14.1	0.2	222	(60)/2		[20]
Sumower on	flow, 1 h) of CC, CA, CO and CH	1000	14:1	0.2	323	≈ 90/3 (CC, CA, CO, CH)		[20]
Southaan oil	UN Commercial pape gruggalling CaO	Vigorouchu	27.1	1.25	Boom	Almost inactive		[75]
Soybean on	commercial nano-crystanne CaO	stirred	27:1	1.25	(296–298)	(>99)/12	-	[/5]
Soybean oil		800	12:1	8	338	95/3	107	[38]
Soydean oll Rapassad oil	Calcined CaCO <sub>3</sub> (11/3 K, He flow, 1.5 fl) CaO activated with methanel (200 K 1 h under ctirring)	Yes	12:1	0.85	222	93/1	187	[30]
latropha curcas oil	Commercial CaO, dipped into ammonium carbonate	ies	10.8.1 Q·1	0.7	3/3	90/5 (93)/2 5	- 12 mg/ml	[09]
	solution (30 min) and calcined (1173 K, 1.5 h)	-	5.1	1.5	545	(33)/2.3	1.2 mg/m	[51]
Rapeseed oil	CaO p.a.	Intense	30:1	0.85	338	92/2.5	-	[67]
Sunflower oll, renned	CaU p.a., calcined (9/3 K, 2 n) Chielen agentalla gurrad grinded and calcined (1072 K	1000	13:1	1	333	94/1.5	0.6 mg/mi	[26,68]
Karanja oli (nign FFA)	2 h)	600	8:1	2.5	338	2.5 (esterification by $H_2SO_4$ )/	-	[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), $\Theta = 0$ and $KC$ and drived (452 K 12 b)	1000	-	-	333	95.5/2	-	[77]
	auteu to $ca(100_3)_2 \cdot 9\pi_20$ allu KCI allu ulleu (453 K, 12 ll)							

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

#### 6. The use of CaO-based catalysts

Alkaline earth oxides, as solid bases, have potential for transesterification processes. The basic sites in alkaline earth oxides are generated by the presence of  $M^{2+}$  and  $O^{2-}$  ion pairs in different co-ordination environments. It is known that the basic strength of group II oxides and hydroxides increase in the order Mg < Ca < Sr < Ba, which is confirmed experimentally by the CO<sub>2</sub>-TPD [65]. Among the oxides, the catalytic activity is in the sequence of CaO < SrO < BaO [66]. However, leaching of barium from BaO-based catalysts in the ester phase is too high [65]. SrO shows a high activity but is fully dissolved in the reaction mixture. so the catalysis is not considered heterogeneous. Another alkaline earth oxide, MgO, shows no catalytic activity [67]. Despite its lower catalytic activity than that of SrO and BaO, CaO is most frequently applied for transesterification processes because of its low price, low solubility in methanol, minor toxicity, high availability from both natural and waste sources, easy preparation, mild reaction condition and high ester yield.

According to the form of their use in transesterification, CaObased catalysts can be classified into four groups: (a) neat, (b) doped, (c) loaded and (d) mixed CaO. Commercial pure CaO is most frequently used after thermal activation, though nano-sized CaO has become also very attractive in recent years. The catalytic activity of neat CaO can be improved not only by enlarging the surface area (i.e. by reducing the catalyst particle size) but also by increasing the number of the basic sites by doping CaO particles by alkaline compounds - the obtained catalyst is denoted here as the doped CaO. The catalytic activity is also increased by incorporation of CaO into various carriers like alumina, silica, MgO and others. These catalysts are described as the supported CaO. In the case of mixed CaO, the catalytic ability of CaO is enhanced by mixing it with metal oxides like zinc. lanthanum and cerium oxides. Besides CaO-based catalysts, some other calcium-based catalysts like calcium methoxide, diglyceroxide and glycerolate have also been tested in transesterification reactions.

#### 6.1. Pure CaO catalyst

An overview of the use of neat CaO, with a short description of the preparation procedures and the reaction conditions, is shown in Table 6. CaO shows high catalytic activity at temperatures close to the boiling point of methanol at atmospheric pressure [26]. Its catalytic activity is mainly due to strong basic sites (stronger than  $H_{-}=26.5$  [38]). Unlike many other solid catalysts, catalytically active CaO is prepared without much preparation effort. Moreover, its catalytic activity can be improved by employing thermal activation treatment (calcination) [68], methanol washing [69] and dipping in ammonium carbonate, followed by calcination [31].

The catalytic ability of CaO depends not only on the calcination temperature but also on the precursor salt used for obtaining CaO. In testing catalysts prepared from different salts [19,20], the lowest ester yield was obtained using the catalyst prepared from calcium nitrate tetrahydrate (CN), which was almost inactive, while catalysts obtained from other salts like calcium acetate monohydrate (CA), calcium carbonate (CC), calcium hydroxide (CH) and calcium oxalate monohydrate (CO), showed significantly higher and quite uniform yields. The use of CaO should be thoughtful because its surface active sites can be poisoned by the adsorption of CO<sub>2</sub> and H<sub>2</sub>O from the air [68]. CaO is rapidly hydrated and carbonated in the contact with room air, even a few minutes are sufficient to chemisorb significant amounts of H<sub>2</sub>O and CO<sub>2</sub>. It is worth mentioning that CO<sub>2</sub> is the main poisoning agent, whereas the negative effect of water is less important. In addition, it is possible to revert the CO<sub>2</sub> poisoning and reactivate the catalyst by outgassing at temperatures above 973 K [68].

It is evident that CaO needs thermal activation before use, but there is no agreement among researchers about the optimum temperature of calcination, since many factors affect it. Although the reported calcination temperature is usually above 1000 K, different approaches have been applied. For instance, commercial CaO was heated up to 773 K in vacuum for 10 h, followed by pretreatment in an ultrasonic bath with methanol for 1 h at room temperature prior to the reaction [70]. The prepared catalyst showed a strong catalytic activity under mild reaction conditions. On the other side, the catalysts activated at 623, 788 and 873 K under argon for 2 h showed a worse performance under the same reaction conditions. Besides thermal activation. CaO was also activated by pretreatment with methanol for 1.5 h at room temperature [69]. The reaction with the methanol-activated catalyst resulted in the 90% yield of methyl esters within 3 h at 333 K, in contrast to the 5% yield in the reaction over the non-activated catalyst under the same conditions. The activation is attributed to the formation of calcium methoxide that acts as an initiating catalyst and forms calcium diglyceroxide by the reaction of CaO with glycerol that functions as the main catalyst in the later reaction stages [69]. Also, an efficient method for CaO activation is dipping it in an ammonium carbonate solution followed by calcination at 1073 K [31]. The obtained catalyst, denoted as super base CaO (having base strength  $H_2 > 26.5$ ), was successfully used in methanolysis of jatropha oil with a high FFAs content, reaching a 93% conversion under the common reaction conditions.

The addition of a small amount of water also has a positive effect on the FAME yield in CaO-catalyzed methanolysis. For instance, in the methanolysis of refined soybean oil, a biodiesel yield higher than 95% was obtained within 3 h while it was only 80% when *pro-analysi* (p.a.) grade CaO was used [38]. However, a higher water amount ( > 2.8% by methanol weight) favors the hydrolysis of FAMEs into FFAs that can react with the catalyst to form soap. On the other side, CaO is unable to catalyze the reaction successfully when oily feedstocks, such as low-cost, non-edible vegetable oils, animal fats and waste oils, contain high amounts of FFAs. This is caused by the inactivation of catalytically active sites at the surface of the catalyst particles [72,73]. Two-step processes consisting of acid-catalyzed esterification and CaO-catalyzed transesterification are used to overcome this problem [30,72,76].

Nano-crystallized CaO is also an efficient catalyst for the transesterification reaction due to its large surface area associated with small crystallite sizes and low number of defects. Nanocrystalline CaO was active in methanolysis of soybean oil at room temperature within 12 h while the activity of amorphous CaO used without any pretreatment before the reaction was ignorable [75]. In another study, the nano-CaO produced by the thermaldecomposition method showed a slightly better ester yield (94%) in methanolysis of palm oil than the bulk CaO prepared by calcination of CaCO<sub>3</sub> (90%) [71]. The shape-controlled growth of CaO nanoparticles appears to be an important factor to enhance its catalytic properties. Using a controlled hydrothermal growth of flower-like CaO, Liu and Zhang [77] produced a unique CaO morphology with predominant catalytic active  $O^{2-}$  on favorable planes. Also, a simple and flexible method involving hydrationdehydration of calcined natural calcites resulted in CaO with less crystallinity, larger surface area and larger amount of basic sites compared to CaO generated by the decomposition of calcite [29]. With these characteristics, CaO exhibited higher catalytic activity than the decomposed calcite as observed from the palm oil methanolysis in which a FAME content of 93.9% was obtained, while only a 75.5% ester content was achieved by the calcined calcite.

A new approach to use neat CaO as a heterogeneous catalyst for biodiesel production was demonstrated by Calero et al. [78], who performed partial sunflower oil methanolysis to produce one mole

دائلر دکنده مقالات علمي freepaper.me paper

## Table 7

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

Feedstock	Catalyst preparation	Optimal rea	action conditions		Yield (conversion)	Leaching (ppm)	Ref.	
		Stirring (rpm)	Methanol-to-oil molar ratio	Catalyst loading (wt% to the oil)	Tempe- rature (K)	(%)/time (ff)		
Rapeseed oil	LiNO <sub>3</sub> /CaO, NaNO <sub>3</sub> /CaO, KNO <sub>3</sub> /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. Calcina- tion 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 tributyrate	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 iatropha oil	Nanocrystalline-K/CaO: prepared by wet impregnation method. K <sup>+</sup> 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 ojl	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 bromoctane/ 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]

1396

of MAG, two moles of FAMEs and no glycerol. This blend is a new type of biofuel (the so-called Ecodiesel) with improved pour point, cold filter plugging point, viscosity and lubricity. A 98% selectivity at 100% conversion was achieved within 1 h of sunflower oil methanolysis catalyzed by calcined CaO under modest reaction conditions (6:1 molar ratio of methanol-to-oil, 0.3% water content respect to oil, 7 wt% of catalyst, and 338 K reaction temperature). Also, an excellent reusability of the catalyst was observed. After being used for 20 cycles, without any pretreatment between the successive cycles, CaO did not lose its activity. In addition to this, a minimal water amount present in methanol promoted the activation of CaO surface.

#### 6.2. Doped CaO catalysts

Many attempts have been made to promote the activity of CaO by increasing the number of basic sites. A possible approach is to dope CaO that serves as both a catalyst and a carrier with an active ingredient. Both alkali and organic compounds can be used as doping materials. As it can be concluded from Table 7, where a systematic survey of studies using catalysts prepared by loading a compound onto CaO is given, a high FAME yield is obtained in transesterification of different oily feedstocks over doped CaO.

A clear correlation between the base strength and the activity is found for alkali-doped CaO catalysts, such as LiNO<sub>3</sub>/CaO, NaNO<sub>3</sub>/ CaO and KNO<sub>3</sub>/CaO. Catalysts with alkali metal loading of 5% were prepared by the incipient wetness method, followed by drying and calcination of the resulting paste [79]. All catalysts reached conversion higher than 99% within 3 h in rapeseed transesterification. Among the same catalysts prepared with 1.25% metal loading without calcination, the highest catalytic activity was observed for Li/CaO (94.9% FAME yield in 8 h) [83]. The performance of this catalyst was slightly affected by the presence of FFAs, since a small FAME yield reduction (from 94.9% to 90.3%) is observed with increasing the FFA content from 0.48% to 5.75%. Also, Li/CaO catalyst has the best catalytic performance among alkali-doped CaO catalysts in the methanolysis of canola oil whereby the FAME yield of 70.7% is achieved under mild reaction conditions [65]. The transesterification reaction was also studied in the presence of Li/ CaO catalyst prepared by the wet impregnation method with and without thermal activation. For calcined catalysts, Alonso et al. [82] concluded that Li amounts higher than 3.6% increased the catalytic activity, especially at the beginning of the reaction. Among non-calcined catalysts, the most active catalyst contained 1.23% Li, but higher Li loadings reduced the catalytic activity dramatically [81]. The optimal activation temperature for calcined catalysts is from 773 K to 973 K, but the catalytic activity does not increase significantly with increasing temperature above 773 K [82]. Among MgO/CaO catalysts with Mg/Ca molar ratio between 3 and 15, prepared by the coprecipitation method, the catalyst with Mg/Ca molar ratio of 3 is the most active one in transesterification of ethyl butyrate, achieving conversion close to 60% within 3 h, whereas pure MgO is inactive [80].

K- and Zn-doped CaO are successful catalysts in transesterification of various non-edible and waste oils with a high FFA content without any pretreatment [46,84]. The former is in the form of nanoparticles, while the latter is in the nanocrystalline form. A simple wet impregnation method was used, followed by calcination. The optimum amounts of deposited K and Zn onto CaO are 3.5% and 1.5%. The complete conversion of used oils is achieved with both catalysts under similar reaction conditions within different reaction times depending on the FFA content in the oily feedstock. K/CaO and Zn/CaO show a high tolerance to variations of FFA and moisture contents. Additionally, examining the effect of various transition-metal ions on the catalytic activity of calcined catalysts with 1.5% of transition metal in CaO, Kumar et al. [84] observed an increase of FAME yield in the following order: Co/ CaO < neat CaO < Cu/CaO < Mn/CaO < Fe/CaO (all with yields  $\leq 20\%$ ) < Cd/CaO < Ni/CaO (80% yield) < Zn/CaO (98% yield).

KF/CaO prepared by the impregnation method is highly efficient in the production of FAME from raw materials with a high FFA amount. In transesterification of the Chinese tallow seed oil containing 40–70% FFAs over KF/CaO with 25% of KF to CaO and under mild reaction condition, the obtained ester yield was higher than 96% within 2.5 h [85]. The catalyst is active and stable through 16 successive cycles, whereas the ester yield in the last cycle is above 91%. Taking into account the high FFA content of the oil, these results are very significant.

One of the most recent methods to enhance the catalytic performance of CaO is the loading of organic compounds. An example is bromooctane loaded onto the surface of CaO [86]. The catalyst is prepared chemically in a simple way by adding commercial CaO into a bromooctane/hexane solution, keeping it at room temperature for 24 h and drying under vacuum. The catalyst treated with 1 mg/g bromooctane gives the highest conversion (over 99%) within 3 h, which is significantly higher than the yield obtained by commercial CaO (35.4%). The modified CaO is water tolerant as the FAME yield is higher than 99% in the presence of water up to 2% and is maintained at over 90% even if 5% of water is presented in the reaction system. The possible explanation may be the hydrophobicity of alkyl groups of bromooctane, which prevents the contact of water molecules with the catalyst surface.

## 6.3. Loaded CaO catalysts

The catalytic abilities of CaO can be improved by its incorporation into various carriers. The most frequently used carriers are various metal oxides, alumina and silica. The standard fabrication method includes the deposition of CaO from precursor salts onto the carrier by precipitation, coprecipitation or wet impregnation, followed by thermal treatment (calcination) of the CaOloaded carrier. The general opinion is that loaded CaO shows a superior catalytic performance over neat CaO due to the positive effects of the chemical and textural properties of the carrier on the dispersion of CaO particles. Additionally, because of the created bonding, the stability of CaO-loaded catalysts is improved against leaching and water and FFA effects. In this case, the catalytically active species of the solid catalyst is CaO, while the carrier stabilizes the active species on its surface. Various oxygen anions with low coordination number are mainly responsible for the catalytic activity of CaO. By changing coordination of  $Ca^{2+}$  and  $O^{2-}$  on the catalyst surface, the amount and strength of basic sites are changed, thereby affecting the catalytic performance significantly. The amount of surface oxygen is affected by the calcination temperature. For easier separation from the reaction mixture, CaO-loaded catalysts are commonly shaped into particles. A comparative view on CaO-loaded catalysts and the key parameters of the transesterification reaction are given in Table 8.

Xie et al. [94] incorporated CaO onto the surface of an acidic  $SnO_2$  support, leading to an improved stability of the CaO-loaded catalyst due to interactions between the two metal oxides. Regarding the amount of CaO loaded onto the support, there was a trend of increasing the FAME yield with increasing the amount of CaO up to 6%, above which the FAME yield decreased. Using the catalyst calcined at the optimal temperature of 973 K, a conversion degree of 89.3% was obtained. The catalyst calcined at a temperature higher than 973 K showed a reduced catalytic activity, probably due to "sintering of fine crystals and cluster agglomeration" [94]. The calcination temperature exerted a greater influence on the FAME yield than the calcination duration. The increase in calcination temperature exerts a much greater influence on the CO<sub>2</sub> dissociation rate, compared to the calcination duration [95].

# 1398

#### Table 8

<b>Table 8</b> The review of CaO-I	ble 8 e review of CaO-loaded catalysts used in transesterification reactions.								
Feedstock	Catalyst preparation	Optimal reaction	n condition			Yield (conversion) (%)/time	Leaching (ppm)	Ref.	
		Stirring (rpm)	Methanol-to-oil molar ratio	Catalyst loading (wt% to the oil)	Temperature (K)	(h)			
Palm oil	$CaO/\gamma$ - $Al_2O_3$ : 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 <sub>2</sub> O <sub>3</sub> (acidic, neutral and basic): prepared by wet impregnation method (aging time for 2 h). The precursor was calcined in N <sub>2</sub> 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 <sub>2</sub> O <sub>3</sub> : prepared by incipient-wetness impregnation method. The precursor was calcined at 723 K for 4 h (Al <sub>2</sub> O <sub>3</sub> support was calcined at 723 K for 2 h before used). Metal loading was 20 mmol $\frac{1}{2}$	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 <sub>3</sub> . Prior to use, CaCO <sub>3</sub> 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 impregna- tion method. The precursor was calcined in air (1073 K, 3 h). Ca loading of 15 wt%. (Mesoporous silica synthesis – Pluronic 123, HCl and tetraetoxysilane was mixed and stirred for $2 \times 4$ 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 cat- alyst 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 <sub>2</sub> O <sub>3</sub> , CaO/SiO <sub>2</sub> : 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 pre- cursor was calcined in N <sub>2</sub> gas flow (973 K, 8 h).	950	18:1	2	337.5	(92) (CaO/MgO), (60) (CaO/ SIO <sub>2</sub> ), (36) (CaO/Al <sub>2</sub> O <sub>3</sub> )/6	-	[92]	
Rapeseed oil	Magnetic CaO hollow fiber (CaO/ $\alpha$ -Fe): produced by organic gel- thermal decomposition. The samples were annealed at 1273 K under reducing atmosphere. Ca <sup>2+</sup> :Fe <sup>3+</sup> = 1:2.	600	12:1	5	333	95.7/2	56 (FAME), 1048 (glycerol)	[93]	
Soybean oil	CaO/SnO <sub>2</sub> : 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<sub>3</sub>, 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. CaO/Al<sub>2</sub>O<sub>3</sub> showed the highest activity among catalysts consisting of CaO loaded onto several carriers (MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and zeolite HY) [92]. The calcination temperature influenced the catalytic activity of CaO/Al<sub>2</sub>O<sub>3</sub> 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 ( $\alpha$ -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 Ca<sup>2+</sup>:Fe<sup>3+</sup> 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 CaO/  $\alpha$ -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 el. [99] prepared CaO  $\cdot$  La<sub>2</sub>O<sub>3</sub> catalysts with different Ca: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 <sub>2</sub>	338-393	Inner and outer crystal water	[96,97]
	665-691	CaCO <sub>3</sub> , CO <sub>2</sub> , H <sub>2</sub> O	
	853-878	CaO, CO <sub>2</sub>	
Oxidizing/air, or mix- ture O <sub>2</sub> and N <sub>2</sub> (v/v	418–521	Inner and outer crystal water	[18,98]
1:4)	595–793 923–1038	CaCO <sub>3</sub> , C <sub>3</sub> H <sub>6</sub> O CaO, CO <sub>2</sub>	

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 Ce: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 CaO · 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 CaO 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 CaO · ZnO catalyst. A CaO · ZnO catalyst prepared with Na<sub>2</sub>CO<sub>3</sub> as the precipitant proved itself more active than those prepared with  $(NH_4)_2CO_3$  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 CaO · 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 Ca–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%

The review of mixed oxide with CaO catalyzed transesterification.

Feedstock	Catalyst preparation	Optimal reaction	condition		Yield (conversion) (%)/time	Leaching	Ref.	
		Stirring (rpm)	Methanol-to-oil molar ratio	Catalyst loading (wt% to the oil)	Temperature (K)	(h) aper.me	(ppm)	
Food-grade soybean, crude soybean, palm and waste cooking oil	CaO-La <sub>2</sub> O <sub>3</sub> 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 <sub>2</sub> flow. Molar ratios Ca:La=3:1.	450	7:1	5	331	94.3/1	-	[99]
Jatropha curcus oil	CaO-La <sub>2</sub> O <sub>3</sub> 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]
Pistacia chinensis oil	CaO-CeO <sub>2</sub> was prepared by incipient wetness impregnation method. Ce/Ca molar ratio of 0.15. Samples were calcined at 973 K in He/O <sub>2</sub> (9/1 v/v) gas flow.	1500	30:1	9	373	93/6	33	[101]
Palm oil	CaO-CeO <sub>2</sub> was prepared by coprecipitation method. The pre- cursor was calcined at 923 K for 8 h. Ca/Ce molar ratio of 1.09.	1200	20:1	5	358	95/3	$\approx 100$	[102]
Waste cooking oil	CaO–ZrO <sub>2</sub> was prepared by coprecipitation method. Ca/Zr molar ratio of 0.5.	500	30:1	10	338	92.1/2		[103]
Palm oil	Ca <sub>3.5x</sub> Zr <sub>0.5y</sub> Al <sub>x</sub> O <sub>3</sub> (0.1 $\le$ x $\le$ 0.5, 0.5 $\le$ y $\le$ 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 $H_2O$ , 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 $H_2O$ , 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]
Jatropha curcus 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	$\geq 20$	[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 sun- flower 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 pre- cursor (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 <sup>a</sup> , non-edible <sup>b</sup> and used cooking oils (sun- flower o.).	CaAl2-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	<ul> <li>&gt; 91 (for all oils except</li> <li><i>Castor</i> 70 and <i>Marotti oil</i></li> <li>62)/5</li> </ul>	1.5%	[111]
Jatropha curcas 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]

<sup>a</sup> Sunflower, ground nut, palmolein, gingelly, mustard, soybean, cottonseed, corn and ricebran oil. <sup>b</sup> Jatropha, Pungai, Pinnai, Karingatta, Neem, Castor and Marotti oil.

Table 11
----------

Table 11         The review of other calcium-based catalysts used in transesterification reactions.							داللر دکنده مقالات علمي FR		
Feedstock	Catalyst preparation <sup>a</sup>	Optimal reaction condition				and (conver-	Leaching	Ref.	
		Stirring (rpm)	Methanol-to- oil molar ratio	Catalyst loading (wt% to the oil)	Temperature (K)	- sion) (%)/time (h)	(ppm)		
Soybean oil	Ca(C <sub>3</sub> H <sub>7</sub> O <sub>3</sub> ) <sub>2</sub> /n-Al <sub>2</sub> O <sub>3</sub> : 20% CaO/n-Al <sub>2</sub> O <sub>3</sub> , 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	$C_{a}(C_{3}H_{7}O_{3})_{2}$ 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 <sup>b</sup>	-	[114]	
Soybean oil	$Ca(C_3H_7O_3)_2$ : CaO, obtained from limestone in He flow (1173 K, 1.5 h), was immersed in glycerol (333 K, N <sub>2</sub> flow).	500	12:1	3.5	-	~70/1	-	[115]	
Sunflower oil	$Ca(C_3H_7O_3)_2$ : CaO, obtained from CaCO <sub>3</sub> , was poured into methanol and glycerol, heated (323 K, N <sub>2</sub> atmosphere) and left under agitation overnight.	1000	14:1	0.7	333	90/3	-	[120]	
Sunflower oil, refined	$Ca(C_3H_7O_3)_2$ : 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	Insigni- ficant	[74]	
Sunflower oil, refined	$Ca(C_3H_6O_3)$ : $Ca(OH)_2$ 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	-	$\sim 25/1$	-	[114]	
Soybean oil	Ca(OCH <sub>3</sub> ) <sub>2</sub> , commercial (min. 90%), grounded.	1000	9:1	1	338	> 90/1.5		[44]	
Tributyrin	Ca(OCH <sub>3</sub> ) <sub>2</sub> , commercial.	-	6:1	2	333	$\sim 90/4$	-	[121]	
Sunflower oil,	$Ca(OCH_3)_2$ : 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 <sup>c</sup>	[116]	
Sunflower	Ca(OH) <sub>2</sub> ; commercial, grounded.	900	6:1	5	333	~97/2	-	[122]	

<sup>a</sup>  $Ca(C_3H_7O_3)_2$  – calcium diglyceroxide,  $Ca(C_3H_6O_3)$  – calcium glycerolate and  $Ca(OCH_3)_2$  – calcium methoxide. <sup>b</sup> Reaction is conducted with reflux od methanol.

<sup>c</sup> Catalyst was reused for 20 cycles.

CaO, 31.2% MgO, 298 ppm Fe<sub>2</sub>O<sub>3</sub> and 198 ppm SrO. In the methanolysis of palm kernel oil over this catalyst the FAME yield of 98% was achieved within 2 h. Despite a loss of activity because of methanol leaching (110 ppm of Ca+Mg), the FAME yield higher than 90% was maintained within seven repeated cycles. Also, hydrotalcite-like materials are good precursors for the preparation of heterogeneous transesterification catalysts [64,110–112]. Metal oxides with a high surface area and with strong Lewis base sites are derived from these materials by thermal decomposition. The catalytic activity of these catalysts depends on calcination temperature. The optimum calcination temperature is between 873 K and 1023 K [110–112]. Under relatively mild reaction conditions (methanol-to-oil molar ratio  $\leq$  15:1, catalyst amount  $\leq$  6%, and  $\leq$  338 K), the ester yield higher than 90% was obtained using catalysts with different molar ratios of calcium and aluminum [110–112]. Calcium containing silicate mixed oxide (CSMO) materials are used to develop non-porous and anionic-surfactanttemplated catalysts [105]. The synthesis of CSMO and phosphoric acid monoester-directed mesoporous calcium containing silicate (PMCS) by the co-condensation method is critically affected by the amounts of cetyltrimethylammonium bromide, water and Ca(OH)<sub>2</sub> as well as by pH. The CSMO catalyst is prepared by the reaction of tetraethylorthosilicate (TEOS) and dry CaO powder in the presence of water at a pH of 9.2. After 2 h of aging, the product is filtered hot and the filter cake is washed with water and methanol and then dried by lyophilization. With this catalyst the ester yield of 100% was achieved in 4.5 h [105]. The PMCS catalyst is prepared from a solution of phosphoric acid monoester surfactant and water at a pH higher than 11.5 to which TEOS and solid CH are added. After 24 h aging, the product is washed with water and methanol and then calcined at 873 K for 6 h. This catalyst showed even better results than CSMO in the transesterification of soybean oil where the 100% conversion was achieved in 2 h. In addition, the CSMO catalyst was tried in the reaction with poultry fat (having about 10% FFAs) and the complete conversion was achieved in 8.7 h. The catalyst activity of this catalyst is in correlation with Ca/Si ratio. The CSMO catalyst was recycled 9 and 3 times in transesterification of soybean oil and poultry fat, respectively, without a decrease in its activity, while the PMCS catalyst was reused 8 times after recalcination. The Ca/Si ratio of the CSMO catalyst decreased from 5.3 to 2.9 after 9 cycles, which reduced the catalyst activity by 30%.

The biodiesel synthesis from edible oils can be enhanced using the modified mixed oxides of CaO, for instance KF-modified CaO·MgO [113]. This catalyst gave much better result than CaO·MgO under the same methanolysis conditions (97.9% and 63.6%, respectively). The better catalytic performance is attributed to the formation of an active KCaF<sub>3</sub> crystal sandwich that improves saponification resistance [85]. Namely, since the electronegativity of fluorine is greater than that of oxygen, Ca<sup>2+</sup> in KCaF<sub>3</sub> is a stronger Lewis acid with a stronger attraction for CH<sub>3</sub>O<sup>-</sup> and F<sup>-</sup> is a stronger Lewis base with stronger attraction to H<sup>+</sup>, which enables easier conversion of CH<sub>3</sub>OH to CH<sub>3</sub>O<sup>-</sup> by KCaF<sub>3</sub> than by CaO.

#### 6.5. Other calcium-based catalysts

Concerning methanolysis of vegetable oils over CaO, some researchers believe that calcium methoxide functions as the substantial solid active species under the reacting condition [44,69,114– 116], but some others think that CaO is combined not only with methanol but also with by-produced glycerol, depending on the methanolysis reaction phase [3,36,49,74,114,115,117–120]. Based on this, calcium methoxide [44,114,116,121], diglyceroxide [36,74, 114,117,120] and glycerolate [74] have been tested as solid catalysts in transesterification reactions. The performances of calcium-based catalysts excluding CaO are compared in Table 11.

Contradictory results are reported regarding the catalytic activity of calcium methoxide. Low conversion of soybean oil over calcium methoxide is obtained by immersion of CaO in refluxing methanol (the obtained FAME yield was about 25% within 1 h) [114]. However, the ester yield higher than 90% is observed in sovbean oil transesterification over commercial calcium methoxide under ultrasonic irradiation in 1.5 h reaction time [44]. The enhanced rate of transesterification reaction is mainly attributed to the positive effects of ultrasonic cavitation on the mass transfer process. Calcium methoxide prepared by a directed reaction of calcium with methanol has strong basicity and high catalytic activity, achieving 98% FAME vield within 2 h of reaction under mild reaction conditions [116]. Also, an almost complete conversion of tributyrin over commercial calcium methoxide is achieved at longer reaction time [121]. As a conclusion, the catalytic activity of calcium methoxide might depend on the method of its preparation, type of feedstock and reaction conditions.

Calcium diglyceroxide is slightly less active in the transesterification than CaO [114]. Its lower catalytic performance is attributed to the formation of another calcium compound, CH<sub>3</sub>O–Ca–O (OH)<sub>2</sub>C<sub>3</sub>H<sub>5</sub>, denoted as Ca-X, in the reaction of calcium diglyceroxide and methanol, which has a lower basic strength than CaO [117]. Under the same reaction conditions, FAME yields within 2 h over Ca-X and calcium diglyceroxide are 89% and 83%, respectively [117]. The catalytic activity of calcium diglyceroxide is higher if thermally activated CaO is used in its synthesis. Being contaminated with calcium carbonates and hydroxides, non-calcined CaO is incompletely converted into calcium diglyceroxide [74]. The activity of calcium diglyceroxide supported on neutral alumina is almost the same as that of the 20% CaO/n-Al<sub>2</sub>O<sub>3</sub> catalyst [36].

Calcium glycerolate is less catalytically active than calcium diglyceroxide because of a lower basic strength, basicity and specific surface area [74]. In sunflower oil transesterification, calcium glycerolate gives nearly 95% conversion within 8 h, while an almost complete conversion is achieved with calcium diglyceroxide in a 6 h reaction. An important characteristic of Ca-glycerolate is its resistance to poisoning by ambient  $CO_2$  and  $H_2O$  [74].

#### 7. Comparative performance of CaO-based catalysts with different oily feedstocks

The performance of CaO-based catalysts has been tested in biodiesel production from various low-cost oily feedstocks like waste cooking and non-edible oils in order to evaluate the effects of FFA and moisture that are commonly present in these feedstocks. The main goals of these studies were to estimate and to improve the resistance of CaO-based catalysts to the negative effects of high FFAs and moisture levels. This is of great practical importance because the use of low-cost (and usually low-quality) oily feedstocks and solid base catalysts reduces the biodiesel production cost. The use of solid base catalysts is generally recommended for methanolysis of these feedstocks as they are more effective than homogeneous base catalysts.

Commercial CaO loses its catalytic activity in the methanolysis of oily feedstock with increasing the acidity because of neutralization of catalyst basic sites by FFAs [30], promoting catalyst loss in the form of soap. Soares Dias et al. [73] demonstrated that the ester yield linearly decreases from 95% to 37% with increasing the acidity of acidified rapeseed oil from 0.5% to 10%. In the case of the most acidic oil, the catalyst was completely converted to soap. Much research work has been done to increase the resistance of neat CaO toward FFAs. For this purpose, neat CaO can be doped by alkaline compounds, loaded onto carriers and mixed with other oxides.

Nanocrystalline K/CaO (3.5% of K) [46] and Zn/CaO (1.5% of Zn) [84] are used in the methanolysis of mutton fat and soybean,

cottonseed (both virgin and waste), castor, karanja and jatropha oils with FFA and moisture levels up to 8.5% and 10.3%, respectively. For both catalysts the reaction time needed for a complete conversion increased with increasing the FFA content of the feedstock, which was attributed to partial deactivation of the catalyst by FFAs and soaps formed from FFAs. K/CaO was also able to complete the methanolysis of waste cotton oil containing 10.3% moisture in 3.5 h. Zn/CaO was more sensitive to moisture content since the complete conversion was achieved only with the oil having up to 4.3% of moisture. Deactivation of catalysts at higher moisture content is attributed to the change of stronger Lewis basic sites (-O-) into weaker Brønsted basic sites (-OH) in the reaction between water and catalyst [123]. Having a good moisture and FFA resistance, K/CaO is a promising catalyst for biodiesel synthesis from low-quality feedstocks in a single step without any pretreatment. The same result is observed with CaO/Al<sub>2</sub>O<sub>3</sub>, which is more active with palm oil having an acid value of 2.49 mg KOH/g oil than with more acidic coconut oil (acid value of 11.59 mg KOH/g oil) [88]. At the same reaction conditions, the FAME yield from palm oil was higher than that from coconut oil (94.3% versus 85%), which was attributed to a stronger deactivation effect of the higher FFA content of coconut oil.

It seems that the same ester yield can be obtained from feedstocks having different FFA contents if the optimized reaction conditions or prolonged reaction times are applied for transesterification reaction. A good example is the use of CaAl2-LDH (hydrocalumite) in methanolysis of edible, non-edible and used cooking oils with acid value in the range from 0.47 to 30.82 mg KOH/g [111]. A FAME yield higher than 95% was obtained from all oils without any pretreatment but under different optimal reaction conditions. Exceptionally, relatively low yields from marotti and castor oils (62% and 70%, respectively) were attributed to the presence of cyclic fatty acids and ricinoleic acid, respectively. Therefore, this catalyst is promising not only for simplifying biodiesel synthesis and purification but also for reducing the biodiesel production cost due to a wide range of usable raw materials. Another example is CaO-La<sub>2</sub>O<sub>3</sub> used in methyl ester synthesis from soybean (food-grade and crude), crude palm and waste cooking oils [99]. The FAME yield of 94.3% was reached from wellrefined soybean oil having low water and FFA content (0.02%) in 60 min, while other oily feedstocks containing high amount of water (0.04–0.27%) and FFA (0.24–3.78%) gave the 96% FAME yield within 3 h. Also, a similar FAME yield (>94%) was obtained for CaO · ZnO-catalyzed methanolysis of refined palm, refined sunflower, palm olein and soybean oils [107]. In addition, ultrasoundassisted methanolysis of sunflower, rapeseed and soybean oils over thermally and ultrasonically activated CaO occurred with similar conversions (89–93%) and yields (76–78%) [70].

All of the above-mentioned examples confirm that the nature of vegetable oils can influence the catalytic performance of a CaObased catalyst, but it may be expected that the catalyst will contribute to an effective conversion of feedstocks with similar composition into corresponding biodiesel.

## 8. CaO leaching

The leaching of active catalyst sites into the reaction medium is one of the most important issues when considering the use of solid catalysts. The level of leaching of a catalyst is inversely associated to the ability of the catalyst for reuse. CaO has a considerably low solubility in methanol. For instance, solubility levels of CaO in methanol, biodiesel–glycerol–methanol (v/v ratio 50:18:72) and glycerol–methanol mixture at 333 K are 0.04 mg/ml, 0.6 mg/ml and 1 mg/ml of alcohol, respectively [26]. Larger amounts of leached species were observed when glycerol was present because the reaction between CaO and glycerol formed calcium diglyceroxide, which is a more soluble compound than CaO. Yoosuk et al. [29] revealed that the amount of catalyst (neat CaO) dissolved into the biodiesel phase was 0.456 mg CaO/ml, while the amount of calcium in the glycerol-methanol phase was equivalent to 0.975 mg CaO/ml of the final alcoholic phase. Verziu et al. [70] found that leaching of calcium from microcrystalline CaO was 325 ppm of Ca<sup>2+</sup> after the second cycle and 825 ppm after the third cycle. The increase of the number of leached calcium ions in repeated cycles coincided with the decrease of both the conversion and the yield of the reaction. However, the yield reduction was explained by the effect of blocking a part of catalytic sites with organic molecules from the reaction mixture. The contribution of homogeneous catalysis arising from leached species from CaO-based catalysts can be considered negligible [26].

Leaching of CaO into the reaction medium can be significantly reduced by anchoring the catalyst onto a support [1,110] or using its mixed oxides [106]. Zabeti et al. [87] revealed that the level of calcium leached from  $CaO/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst into the reaction medium was only 31 ppm. Using a very similar catalyst for methanolysis of soybean oil, Pasupulety et al. [36] found that an essentially insignificant amount of active species was leached into the reaction solution. Campos-Molina et al. [110] did not observe leaching of the mixture of CaO and mayenite (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) used in sunflower oil methanolysis. In the case of mixed oxide CaO/ZnO, Kesic et al. [106] determined a lower concentration of calcium ion in methanol (8.9 mg/l), compared to the solubility of neat CaO (96 mg/l) [26]. Taufiq-Yap et al. [108] did not found significant leaching of mixed oxide catalyst CaO-La<sub>2</sub>O<sub>3</sub> into the reaction medium during three repeated runs (about 1.5 ppm in every run). A slight decrease in activity was attributed to the deposition of organic compounds on the active sites of the catalyst.

#### 9. Reactors in use

A majority of the studies on CaO-catalyzed methanolysis use batch stirred reactors. Batch processes are simpler, but require a larger reactor volume, which increases capital investments. Continuous processes allow achieving a desired TAG conversion using a smaller reactor volume. In addition to a lower production cost, continuous processes ensure more uniform quality of the biodiesel produced. The most commonly used type of reactor in continuous heterogeneously-catalyzed methanolysis is the packed-bed (fixedbed) reactor [124–127]. Other types of reactors, such as slurry [128], tower spray [128], trickle-bed [129], packed-bed membrane [130] and down-stream plug-flow [131] reactor, have also been investigated.

Packed-bed reactors are used in biodiesel synthesis from different oily feedstocks over various catalysts such as shell-core Ca (C<sub>3</sub>H<sub>7</sub>O<sub>3</sub>)<sub>2</sub>/CaCO<sub>3</sub> [125], activated limestone [132], calcined quicklime [127], porous zirconia, titania and alumina [126], as well as anion-exchange [133,134] and cation-exchange [124,135] resins. The advantages of this reactor are flexibility and simple operation, prolonged use of catalysts, easy product separation from catalyst and continuous reaction mixture discharge from the reactor. Calcium-based catalysts were used in packed-bed reactors in a few studies. Good ester yields were obtained in a simple packed-bed reactor filled with activated limestone-based catalysts (atomic ratio Ca:Mg:Al=4:3:1) using different oily feedstocks (bleached deodorized palm, food grade palm olein and waste cooking oils) and alcohols (methanol and ethanol) [132]. Continuous methanolysis of sunflower oil in a packed-bed tubular reactor with activated quicklime bits under optimal reaction conditions (methanol-to-oil molar ratio of 13.75:1, 333 K, residence time of 2 h) resulted in a yield of  $98.6 \pm 1.1\%$  within 30 h [127].

دائلو دکننده مقالات علم reepaper.me

Paper

Usually transesterification reactions in classical packed-bed reactors proceed at relatively slow rates because of diffusion limitations in the three-phase system (oil-methanol-solid catalyst). For achieving high FAME yields the reaction should be carried out (depending on other applied reaction conditions) at higher methanol-to-oil molar ratios (in range 8:1-30:1), higher temperatures (333-623 K) and during longer residence times (up to 240 min). In order to enhance mass-transfer rates, packed bed reactors are modified in various ways like stirring or rotating the packed beds or circulating reactants through the packed bed. In the case of reactors with stirred packed beds [136], solid catalyst  $(Ca(C_3H_7O_3)_2/CaO)$  in the form of pellets is placed in static columns with hollow walls that are fixed in the stirred reactor filled with reactants. Circular motion in the reactor reduced the masstransfer resistance in the system by thickening the boundary layer. The highest biodiesel yield of 96.75% was achieved at a methanolto-oil molar ratio of 20:1, a reaction temperature of 333 K, a residence time of 123 min and a stirring speed of 200 rpm. Also, a rotating packed-bed reactor (RPB) can be applied to increase mixing efficiency by applying great centrifugal force, which leads to an enhanced mass transfer rate in the reaction system [137]. The use of this reactor type allows high FAME yields within shorter residence times and a great production capacity at lower methanol-to-oil molar ratios.

Another way to promote mass transfer is to combine a packed bed of catalyst bits and a stirred tank placed in a loop through which the reaction mixture is circulated. The reactants are thermostated and mixed in the stirred vessel, while the reaction occurs in the column reactor. This system was used for rapeseed oil methanolysis catalyzed by calcined crushed limestone [138]. Under the optimal reaction conditions (temperature of 333 K, methanol-to-oil volume ratio 0.78:1 and residence time of 2 h) a FAME yield of 96.5% was obtained.

Trickle-bed reactors (TBRs) are suitable for biodiesel synthesis since vaporized methanol and the reaction products are continuously separated without the use of an additional evaporation unit, which is a setup that can reduce the production cost. A high FAME yield (98%) was achieved in this reactor type in methanolysis of sunflower oil over CaO particles under moderate reaction conditions (a reaction temperature of 373 K, liquid methanol and oil flow rates 3.8 and 4.1 ml/h, respectively) [139]. The rapeseed oil methanolysis over Ca/Al oxide-based catalyst (mixture of Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> and CaO) was also investigated in conventional and modified TBRs [112]. The TBR is modified by dividing the catalystbed into three equal sections separated by stainless steel wire to ensure the redistribution of the reaction phases. This design reduces the volume of the packed bed by 35% compared to the conventional reactor. Under the same reaction conditions (temperature 338 K, methanol-to-oil molar ratio 3:1 and rapeseed oil flow rate range from 0.5 to 1 ml/min) the FAME yield was higher in the modified TBR (over 94.5%) than in the conventional reactor (about 80%) [112].

Hu et al. [140] developed a novel integrated continuous process for biodiesel production with gas–liquid countercurrent contact, on-line separation of glycerol and automatic reuse of excess methanol. Their system consisted of three fluidic modules filled with KF/CaO catalyst. Under optimum reaction conditions for rapeseed oil methanolysis (18 ml/min flow rate of oil and methanol, 354.5 K reaction temperature, 105.98 kPa reaction pressure and 51.7 cm fill height of catalyst), a FAME yield of 93.7% was maintained during 114 h of continuous reaction. The developed reactor type is economically favorable since 90% of glycerin is recovered and there is no methanol escape from the system.

High quality biodiesel can be produced in packed-bed membrane reactors where methanolysis and separation of TAGs are simultaneously performed. Methanol, biodiesel and glycerol pass through a membrane ensuring their separation from TAGs. A methanol recovery unit based on continuous distillation is also integrated in the production system. A tubular ceramic  $(TiO_2/Al_2O_3)$  membrane reactor packed with KOH supported on activated carbon as catalyst was employed for palm oil methanolysis [130]. A FAME yield of 94% was achieved at 343 K, methanol-to-oil volume ratio 1:1, cross flow circulation velocity of 0.21 cm/s (corresponding to a residence time of 3.2 min) and catalyst mass per unit volume of reactor of 157 mg/ml.

#### 10. Purification of crude biodiesel

Leaching of calcium into the reaction mixture occurs during transesterification of vegetable oils over CaO-based catalysts, thus contaminating the reaction products. Calcium concentration in crude biodiesel from both batch and continuous production processes is usually higher than the EN 14214 standard limit of maximal 5 ppm [27,70,138]. Therefore, crude biodiesel must be further purified in order to lower the calcium level below the specified limit.

Since recently, special attention has been paid to eliminating the leached calcium from the crude biodiesel in a separate purification stage. The methods for purification of crude biodiesel can be classified in several groups [141]: wet washing, dry washing, membrane extraction, precipitation, complexation and simultaneous biodiesel synthesis and purification. So far, no systematic investigation has been performed on influencing the combination of the purification method and the type of oily feedstock on the biodiesel properties. Only a few investigations compare various purification methods regarding to the efficiency of crude biodiesel decalcification [31,142-144]. These studies show (a) the decalcification efficiency is dependent on the type of oily feedstock and (b) wet washing methods are unsuitable for decalcifying crude biodiesel. Better results with purification are obtained by combining membrane extraction, dry washing with a resin or ionexchange-based precipitation and water washing [143]. Also, citric acid is successful in decalcification of crude biodiesel by precipitation [31]. In addition, dry washing with sulfonic acid, followed by water washing, reduces the calcium level efficiently, but the acid value of the refined biodiesel is above the biodiesel standard specification [142]. Treating crude biodiesel with a boiling methanol-sodium carbonate mixture, followed by water washing results in effective calcium removal below the level specified by biodiesel quality regulations [142]. Also, simultaneous biodiesel synthesis and purification has recently been suggested as a method for successful decalcification, but further studies should be undertaken to optimize the amounts of methanol and sodium carbonate required for the simultaneous removal of calcium from the ester phase [142].

#### 11. Ecological aspects of the use of CaO-based catalysts

Although the heterogeneous biodiesel production processes are considered to be environmentally friendly compared to homogeneous catalysis, different types of waste are generated by them. They can be classified into (a) wastes from separation and purification of biodiesel product and (b) wastes from catalyst regeneration [11]. The first group includes used catalyst, wastewater, spent dry washing agents (adsorptive materials, cation-exchange resins), ceramic membranes, insoluble compounds formed by precipitation or ion exchange and the aqueous phase obtained by complexation of calcium ions with EDTA, and the second one involves organic solvents, alcohols and water.

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 CaCO<sub>3</sub> 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 CO<sub>2</sub> and H<sub>2</sub>O 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  $CO_2$  and  $H_2O$ . 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. Pelleting 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 CaObased 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.

#### References

- Zabeti M, Daud WMAW, Aroua MK. Activity of solid catalysts for biodiesel production: a review. Fuel Process Technol 2009;90:770–7.
- [2] Canakci M, Van Gerpen J. Biodiesel production from oils and fats with high free fatty acids. Am Soc Agric Eng 2002;44:1429–36.
- [3] Refaat AA. Biodiesel production using solid metal oxide catalysts. Int J Environ Sci Technol 2011;8:203–21.
- [4] Serio MD, Tesser R, Dimiccoli M, Cammarota F, Nastasi M, Santacesaria E. Synthesis of biodiesel via homogeneous Lewis acid catalyst. J Mol Catal A: Chem 2005;239:111–5.
- [5] Kiss AA, Dimian AC, Rothenberg G. Solid acid catalysts for biodiesel production n – towards sustainable energy. Adv Synth Catal 2006;348:75–81.
- [6] Vicente G, Martinez M, Aracil J. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. Bioresour Technol 2004;92:297–305.

- [7] Boey PL, Maniam GP, Hamid SA. Biodiesel production via transesterification of palm olein using waste mud crab (*Scylla serrata*) chell as a heterogeneous catalyst. Bioresour Technol 2009;100:6362–8.
- [8] Lopez DE, Goodwin Jr. JG, Bruce DA, Lotero E. Transesterification of triacetin with methanol on solid acid and base catalysts. Appl Catal A 2005;295:97– 105.
- [9] Demirbas A. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. Energy Convers Manag 2008;49:125– 30.
- [10] Vicente G, Martinez M, Aracil J. Optimization of integrated biodiesel production, part I. A study of the biodiesel purity and yields. Bioresour Technol 2007;97:1724–33.
- [11] Stojković IJ, Stamenković OS, Povrenović DS, Veljković VB. Purification technologies for crude biodiesel obtained by alkali-catalyzed transesterification. Renew Sustain Energy Rev 2014;32:1–15.
- [12] Melero JA, Iglesias J, Morales G. Heterogeneous acid catalysts for biodiesel production: current status and future challenges. Green Chem 2009;11:1285–308.
- [13] Lam MK, Lee KT, Mohamed AR. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. Biotechnol Adv 2010;28:500–18.
- [14] Hillion G, Delfort B, le Pennec D, Bournay L, Chodorge JA. Biodiesel production by continouos process using a heterogeneous catalyst. Prepr Pap – Am Chem Soc, Div Fuel Chem 2003;48:636–8.
- [15] Menlo Energy LLC. Tecnology-Proprietary catalyst driven process. [cited 2014]. Available from: (http://www.menloenergyllc.com/technology.php).
- [16] Boey PL, Maniam GP, Hamid SA. Performance of calcium oxide as a heterogeneous catalys in biodiesel production: a review. Chem Eng J 2011;168:15– 22.
- [17] Kouzu M, Hidaka J-s. Transesterification of vegetable oil into biodiesel catalyzed by CaO: a review. Fuel 2012;93:1–12.
- [18] Bilton M, Brown AP, Milne SJ. Investigating the optimum conditions for the formation of calcium oxide, used for CO<sub>2</sub> sequestration, by thermal decomposition of calcium acetate. J Phys: Conf Ser 2012:012075.
- [19] Cho YB, Seo G, Chang DR. Transesterification of tributyrin with methanol over calcium oxide catalysts prepared from wariuos precursors. Fuel Process Technol 2009;90:1252–8.
- [20] Alonso DM, Vila F, Mariscal R, Ojeda M, Granados ML, Santamaria-Gonzalez J. Relevance of the physicochemical properties of CaO catalysts for the methanolysis of triglycerides to obtain biodiesel. Catal Today 2010;158:114–20.
- [21] Moriyasu H, Koshi K, Sato A, Suzuki T, Nakagaito A, Kouzu M. Preparation of CaO catalyst from calcined limestone by mechanical grinding for biodiesel production. J Jpn Inst Energy 2012;91:495–502.
- [22] Galan I, Glasser FP, Andrade C. Calcium carbonate decomposition. J Therm Anal Calorim 2013;111:1197–202.
- [23] L'vov BV. Mechanism and kinetics of thermal decomposition of carbonates. Thermochim Acta 2002;386:1–16.
- [24] Rodriguez-Navarro C, Ruiz-Agudo E, Luque A, Rodriguez-Navarro AB, Ortega-Huertas M. Thermal decomposition of calcite: mechanisms of formation and textural evolution of CaO nanocrystals. Am Miner 2009;94:578–93.
- [25] Hammond CR. Section 4: properties of the elements and inorganic compounds. In: Lide DR, editor. CRC handbook of chemistry and physics. Boca Raton, US: CRC Press; 2005.
- [26] Granados ML, Alonso DM, Sadaba I, Mariscal R, Ocon P. Leaching and homogeneous contribution in liquid phase reaction catalysed by solids: the case of triglycerides methanolysis using CaO. Appl Catal B 2009;89:265–72.
- [27] Kouzu M, Yamanaka S, Hidaka J, Tsunomori M. Heterogeneous catalysis of calcium oxide used for transesterification of soybean oil with refluxing methanol. Appl Catal A 2009;355:94–9.
- [28] Iizuka T, Hattori H, Ohno Y, Sohma J, Tanabe K. Basic sites and reducing sites of calcium oxide and their catalytic activities. J Catal 1971;22:130–9.
- [29] Yoosuk B, Udomsap P, Puttasawat B, Krasae P. Modification of calcite by hydration-dehydration method for heterogeneous biodiesel production process: the effects of water on properties and activity. Chem Eng J 2010;162:135-41.
- [30] Kouzu M, Kasuno T, Tajika M, Sugimoto Y, Yamanaka S, Hidaka J. Calcium oxide as a solid base catalyst for transesterification of soyabean oil and its application to biodiesel production. Fuel 2008;87:2798–806.
- [31] Zhu H, Wu Z, Chen Y, Zhang P, Duan S, Liu X, et al. Preparation of biodiesel catalyzed by solid super base of calcium oxide and its refining process. Chin J Catal 2006;27:391–6.
- [32] Endalew AK, Kiros Y, Zanzi R. Heterogeneous catalysis for biodiesel production from *Jatropha curcas* oil (JCO). Energy 2011;36:2693–700.
- [33] Dossin TF, Reyniers MF, Marin GB. Kinetics of heterogeneously MgOcatalyzed transesterification. Appl Catal B 2006;61:35–45.
- [34] Hattori H, Shima M, Kabashima H. Alcoholysis of ester and epoxide catalyzed by solid bases. Stud Surf Sci Catal 2000;130:3507–12.
- [35] Chambers C, Holliday AK. Acids and bases: oxidation and reduction. In Modern inorganic chemistry. Chichester: Butterworth & Co; 1975. p. 84–111.
  [36] Pasupulety N, Gunda K, Liu Y, Rempel GL, Ng FTT. Production of biodiesel
- [36] Pasupulety N, Gunda K, Liu Y, Rempel GL, Ng FIT. Production of biodiesel from soybean oil on CaO/Al<sub>2</sub>O<sub>3</sub> solid base catalysts. Appl Catal A 2013:452:189–202.
- [37] Zhang G, Hattori H, Tanabe K. Aldol adition of acetone, catalyzed by solid base catalysts: magnesium oxide, calcium oxide, strontium oxide, barium oxide, lanthanum (III) oxide and zirconium oxide. Appl Catal 1988;36:189–97.

- [38] Liu X, He H, Wang Y, Zhu S, Piao X. Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. Fuel 2008;87:216–21.
- [39] Stoffel W, Chu F, Ahrens Jr. EH. Analysis of long-chain fatty acids by gasliquid cromatography. Anal Chem 1959;31:307–8.
- [40] Singh AK, Fernando SD. Reaction kinetics of soybean oil transesterification using heterogeneous metal oxide catalysts. Chem Eng Technol 2007;12:1716– 20.
- [41] Veljković VB, Stamenković OS, Todorović ZB, Lazić ML, Skala DU. Kinetics of sunflower oil methanolysis catalyzed by calcium oxide. Fuel 2009;88:1554– 62.
- [42] Lukić I, Kesić Ž, Maksimović S, Zdujić M, Liu H, Krstić J, et al. Kinetics of sunflower and used vegetable oil methanolysis catalyzed by CaO\*ZnO. Fuel 2013;113:367–78.
- [43] Birla A, Singh B, Upadhyay SN, Sharma YC. Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell. Bioresour Technol 2012;106:95–100.
- [44] Deshmane VG, Adewuyi YG. Synthesis and kinetics of biodiesel formation via calcium methoxide base catalyzed transesterification reaction in the absence and presence of ultrasound. Fuel 2013;107:474–82.
- [45] Ilgen O. Reaction kinetics of dolomite catalyzed transesterification of canola oil and methanol. Fuel Process Technol 2012;95:62–6.
- [46] Kumar D, Ali A. Nanocrystalline K–CaO for the transesterification of a variety of feedstocks: structure, kinetics and catalytic properties. Biomass Bioenergy 2012;46:459–68.
- [47] Lukić I, Kesić Ž, Maksimović S, Zdujić M, Krstić J, Skala D. Kinetics of heterogeneous methanolysis of sunflower oil with CaO-ZnO catalyst: influence of different hydrodynamic conditions. Chem Ind Chem Eng Q 2014;20:425– 39.
- [48] Sanchez M, Marchetti JM, El Boulifi N, Aracil J, Martinez M. Kinetics of Jojoba oil methanolysis using a waste from fish industry as catalyst. Chem Eng J 2015;262:640–7.
- [49] Miladinović MR, Krstić JB, Tasić MB, Stamenković OS, Veljković VB. A kinetic study of quicklime-catalyzed sunflower oil methanolysis. Chem Eng Res Des 2014;92:1740–52.
- [50] Patil P, Gude VG, Pinappu S, Deng S. Transesterification kinetics of *Camelina sativa* oil on metal oxide catalysts under conventional and microwave heating conditions. Chem Eng J 2011;168:1296–300.
- [51] Liu X, Piao X, Wang Y, Zhu S. Model study on transesterification of soybean oil to biodiesel with methanol using solid base catalyst. J Phys Chem A 2010;114:3750–5.
- [52] Tasić MB, Miladinović MR, Stamenković OS, Veljković VB, Skala DU. Kinetic modeling of sunflower oil methanolysis catalyzed by calcium-based catalysts. Chem Eng Technol 2015;38:1550–6.
- [53] Miladinović MR, Tasić MB, Stamenković OS, Veljković VB, Skala DU. Further study on kinetic modeling of sunflower oil methanolysis catalyzed by calcium-based catalysts. Chem Ind Chem Eng Q 2015. <u>http://dx.doi.org/</u> 10.2298/CICEQ150618027M.
- [54] Boey PL, Ganesan S, Maniam GP, Khairuddean M. Catalysis derived from waste sources in the production of biodiesel using waste cooking oil. Catal Today 2012;190:117–21.
- [55] Chakraborty R, Bepari S, Benerjee A. Transesterification of soybean oil catalyzed by fly ash and egg shell derived solid catalysts. Chem Eng J 2010;165:798–805.
- [56] Dias JM, Alvim-Ferraz MCM, Almeida MF, Diaz JDM, Polo MS, Utrilla JR. Selection of heterogeneous catalysts for biodiesel production from animal fat. Fuel 2012;94:418–25.
- [57] Zabeti M, Daud WMAW, Aroua MK. Biodiesel production using aluminasupported calcium oxide: an optimization study. Fuel Process Technol 2010;91:243–8.
- [58] Mahdavi V, Monajemi A. Optimization of operational conditions for biodiesel production from cottonseed oil on CaO-MgO/Al<sub>2</sub>O<sub>3</sub> solid base catalysts. J Taiwan Inst Chem Eng 2014;45:2286–92.
- [59] Liao CC, Chung TW. Optimization of process conditions using response surface methodology for the microwave-assisted transesterification of Jatropha oil with KOH impregnated CaO as catalyst. Chem Eng Res Des 2013;91:2457– 64.
- [60] Nakatani N, Takamori H, Takeda K, Sakugawa H. Transesterification of soybean oil using combusted oyster shell waste as a catalyst. Bioresour Technol 2009;100:1510–3.
- [61] Liu H, Su L, Shao Y, Zou L. Biodiesel production catalyzed by cinder supported CaO/KF particle catalyst. Fuel 2012;97:651–7.
- [62] Wu H, Zhang J, Wei Q, Zheng J, Zhang J. Transesterification of soybean oil to biodiesel using zeolite supported CaO as strong base catalysts. Fuel Process Technol 2013;109:13–8.
- [63] Kaur M, Ali A. Ethanolysis of waste cottonseed oil over lithium impregnated calcium oxide: kinetics and reusability studies. Renew Energy 2014;63:272– 9.
- [64] Wang B, Li S, Tian S, Feng R, Meng Y. A new solid base catalyst for the transesterification of rapeseed oil to biodiesel with methanol. Fuel 2013;104:698–703.
- [65] D'Cruz A, Kulkarni MG, Meher LC, Dalai AK. Synthesis of biodiesel from canola oil using heterogeneous base catalyst. J Am Chem Soc 2007;84:937– 43.
- [66] Mootabadi H, Salamatinia B, Bhatia S, Abdullah AZ. Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts. Fuel 2010;89:1818–25.

- [67] Gryglewicz S. Rapeseed oil methyl esters preparation using heterogeneous catalysts. Bioresour Technol 1999;70:249–53.
- [68] Granados ML, Poves MDZ, Alonso DM, Mariscal R, Galisteo FC, Moreno-Tost R, et al. Biodiesel from sunflower oil by using activated calcium oxide. Appl Catal B 2007;73:317–26.
- [69] Kawashima A, Matsubara K, Honda K. Acceleration of catalytic activity of calcium oxide for biodiesel production. Bioresour Technol 2009;100:696– 700.
- [70] Verziu M, Coman SM, Richards R, Parvulescu VI. Transesterification of vegetable oils over CaO catalysts. Catal Today 2011;167:64–70.
- [71] Isahak WNRW, Ismail M, Jahim JM, Salimon J, Yarmo MA. Characterisation and performance of three promising heterogeneous catalysts in transesterification of palm oil. Chem Pap 2012;66:178–97.
- [72] Zhang J, Chen S, Yang R, Yan Y. Biodiesel production from vegetable oil using heterogenous acid and alkali catalyst. Fuel 2010;89:2939–44.
- [73] Soares Dias AP, Puna J, Neiva Correia MJ, Nogueira I, Gomes J, Bordado J. Effect of the oil acidity on the methanolysis performances of lime catalyst biodiesel from waste frying oils (WFO). Fuel Process Technol 2013;116:94– 100.
- [74] Reyero I, Arzamendi G, Gandia LM. Heterogenization of the biodiesel synthesis catalysis: CaO and novel calcium compounds as transesterification catalysts. Chem Eng Res Des 2014;92:1519–30.
- [75] Reddy C, Reddy V, Oshel R, Verkade JG. Room-temperature conversion of soybean oil and poultry fat to biodiesel catalyzed by nanocrystalline calcium oxides. Energy Fuels 2006;20:1310–4.
- [76] Sharma YC, Singh B, Korstad J. Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from pongamia pinnata oil. Energy Fuels 2010;24:3223–31.
- [77] Liu F, Zhang Y. Hydrothermal growth of flower-like CaO for biodiesel production. Ceram Int 2012;38:3473–82.
- [78] Calero J, Luna D, Sancho ED, Luna C, Bautista FM, Romero AA, et al. Development of a new biodiesel that integrates glycerol, by using CaO as heterogeneous catalyst, in the partial methanolysis of sunflower oil. Fuel 2014;122:94–102.
- [79] MacLeod CS, Harvey AP, Lee AF, Wilson K. Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. Chem Eng J 2008;135:63–70.
- [80] Albuquerque MCG, Azevedo DCS, Cavalcante Jr. CL, Santamaria-Gonzalez J, Merida-Robles JM, Moreno-Tost R, et al. Transesterification of ethyl butyrate with methanol using MgO/CaO catalysts. J Mol Catal A: Chem 2009;300:19– 24.
- [81] Watkins RS, Lee AF, Wilson K. Li–CaO catalysed triglyceride transesterification for biodiesel applications. Green Chem 2004;6:335–40.
- [82] Alonso DM, Mariscal R, Granados ML, Maireles-Tores P. Biodiesel preparation using Li/CaO catalysts: activation process and homogeneous contribution. Catal Today 2009;143:167–71.
- [83] Meher LC, Kulkarni MG, Dalai AK, Naik SN. Transesterification of karanja (*Pongamia pinnata*) oil by solid basic catalysts. Eur J Lipid Sci Technol 2006;108:389–97.
- [84] Kumar D, Ali A. Transesterification of low-quality triglycerides over a Zn/CaO heterogeneous catalyst: kinetics and reusability studies. Energy Fuels 2013;27:3758–68.
- [85] Wen L, Wang Y, Lu D, Hu S, Han H. Preparation of KF/CaO nanocatalyst and its application in biodiesel production from Chinese tallow seed oil. Fuel 2010;89:2267–71.
- [86] Tang Y, Xu J, Zhang J, Lu Y. Biodiesel production from vegetable oil by using modified CaO as solid basic catalysts. J Clean Prod 2013;42:198–203.
- [87] Zabeti M, Daud WMAW, Aroua MK. Optimization of the activity of CaO/Al<sub>2</sub>O<sub>3</sub> catalyst for biodiesel production using response surface methodology. Appl Catal A 2009;366:154–9.
- [88] Benjapornkulaphong S, Ngamcharussrivichai C, Bunyakiat K. Al<sub>2</sub>O<sub>3</sub>-supported alkali and alkali earth metal oxides for transesterification of palm kernel oil and coconut oil. Chem Eng J 2009;145:468–74.
- [89] Ho WWS, Ng HK, Gan S, Tan SH. Evaluation of palm oil mill fly ash supported calcium oxide as a heterogeneous base catalyst in biodiesel synthesis from crude palm oil. Energy Convers Manag 2014;88:1167–78.
- [90] Samart C, Chaiya C, Reubroycharoen P. Biodiesel production by methanolysis of soybean oil using calcium supported on mesoporous silica catalyst. Energy Convers Manag 2010;51:1428–31.
- [91] Albuquerque MCG, Jimenez-Urbistondo I, Santamaria-Gonzalez J, Merida-Robles JM, Moreno-Tost R, Rodriguez-Castellon E, et al. CaO supported on mesoporous silicas as basic catalysts for transesterification reactions. Appl Catal A 2008;334:35–43.
- [92] Yan S, Lu H, Liang B. Supported CaO catalysts used in the transesterification of rapeseed oil for the purpose of biodiesel production. Energy Fuels 2008;22:646–51.
- [93] Lin L, Vittayapadung S, Li X, Jiang W, Shen X. Syntesis of magnetic calcium oxide hollow fiber catalyst for the production of biodiesel 2013;32:1255–62.
- [94] Xie W, Zhao L. Production of biodiesel by transesterification of soybean oil using calcium supported tin oxides as heterogeneous catalysts. Energy Convers Manag 2013;76:55–62.
- [95] Ngamcharussrivichai C, Nunthasant P, Tanachai S, Bunyakia K. Biodiesel production through transesterification over natural calciums. Fuel Process Technol 2010;91:1409–15.

- [96] Masumeci AW, Frost RL, Waclawik ER. A spectroscopic study of the mineral paceite (calcium acetate). Spectrochim Acta A Mol Biomol Spectrosc 2007;67:649–61.
- [97] Han DH, Sohn HY. Calcined calcium magnesium acetate as a superior sorbent: I. Thermal decomposition. AIChE J 2002;48:2971–7.
- [98] Niu S, Han K, Lu C, Sun R. Thermogravimetric analysis of the relationship among calcium magnesium acetate, calcium acetate and magnesium acetate. Appl Energy 2010;87:2237–42.
- [99] Yan S, Kim M, Salley SO, Simon Ng KY. Oil transesterification over calcium oxides modified with lanthanum. Appl Catal A 2009;360:163–70.
- [100] Taufiq-Yap YH, Teo SH, Rashid U, Islam A, Hussien MZ, Lee KT. Transesterification of Jatropha curcas crude oil to biodiesel on calcium lanthanum mixed oxide catalyst: effect of stoichiometric composition. Energy Convers Manag 2014;88:1290–6.
- [101] Yu X, Wen Z, Li H, Tu ST, Yan J. Transesterification of *Pistacia chinensis* oil for biodiesel catalyzed by CaO-CeO<sub>2</sub> mixed oxides. Fuel 2011;90:1868–74.
- [102] Thitsartarn W, Kawi S. An active and stable CaO-CeO<sub>2</sub> catalyst for transesterification of oil to biodiesel. Green Chem 2011;13:3423-30.
- [103] Dehkordi AM, Ghasemi M. Transesterification of waste cooking oil to biodiesel using Ca and Zr mixed oxides as heterogeneous base catalysts. Fuel Process Technol 2012;97:45–51.
- [104] Amani H, Ahmad Z, Hameed BH. Synthesis of fatty acid methyl esters via the methanolysis of palm oil over Ca<sub>3.5x</sub>Zr<sub>0.5y</sub>Al<sub>x</sub>O<sub>3</sub> mixed oxide catalyst. Renew Energy 2014;66:680–5.
- [105] Hsin TM, Chen S, Guo E, Tsai CH, Pruski M, Lin VSY. Calcium containing silicate mixed oxide-based heterogeneous catalysts for biodiesel production. Top Catal 2010;53:746–54.
- [106] Kesić Ž, Lukić I, Brkić D, Rogan J, Zdujić M, Liu H, et al. Mechanochemical preparation and characterization of CaO-ZnO used as catalyst for biodiesel synthesis. Appl Catal A 2012;427–428:58–65.
- [107] Ngamcharussrivichai C, Totarat P, Bunyakia K. Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil. Appl Catal A 2008;341:77–85.
- [108] Taufiq-Yap YH, Lee HV, Hussein MZ, Yunus R. Calcium-based mixed oxide catalysts for methanolysis of *Jatropha curcas* oil to biodiesel. Biomass Bioenergy 2011;35:827–34.
- [109] Albuquerque MCG, Santamaria-Gonzalez J, Merida-Robles JM, Moreno-Tost R, Rodriguez-Castellon E, Jimenez-Lopez A, et al. MgM (M=Al and Ca) oxides as basic catalysts in transesterification processe. Appl Catal A 2008;347:162– 8.
- [110] Campos-Molina MJ, Santamaria-Gonzales J, Merida-Robles J, Moreno-Tost R, Albuquerque MCG, Bruque-Gamez S, et al. Base catalysts derived from hydrocalumite for the transesterification of sunflower oil. Energ Fuel 2010;24:979–84.
- [111] Sankaranarayanan S, Antonyra CA, Kannan S. Transesterification of edible, non-edible and used cooking oils for biodiesel production using calcined layered double hydroxides as reusable base catalysts. Bioresour Technol 2012;109:57–62.
- [112] Meng YL, Wang BY, Li SF, Tian SJ, Zhang MH. Effect of calcination temperature on the activity of solid Ca/Al composite oxide-based alkaline catalyst for biodiesel production. Bioresour Technol 2013;128:305–9.
- [113] Fan M, Zhang P, Ma Q. Enhancement of biodiesel synthesis from soybean oil by potassium fluoride modification of a calcium magnesium oxides catalyst. Bioresour Technol 2012;104:447–50.
- [114] Kouzu M, Kasuno T, Tajika M, Yamanaka S, Hidaka J. Active phase of calcium oxide used as solid base catalyst for transesterification of soyabean oil with refluxing methanol. Appl Catal A 2008;334:357–65.
- [115] Kouzu M, Tsunomori M, Yamanaka S, Hidaka J. Solid base catalysis of calcium oxide for a reaction to convert vegetable oil into biodiesel. Adv Powder Technol 2010;21:488–94.
- [116] Liu X, Piao X, Wang Y, Zhu S, He H. Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol. Fuel 2008;87:1076–82.
- [117] Kouzu M, Hidaka Js, Wakabayashi K, Tsunomori M. Solid base catalysis of calcium glyceroxide for a reaction to convert vegetable oil into its methyl esters. Appl Catal A 2010;390:11–8.
- [118] Granados ML, Alba-Rubio AC, Vila F, Alonso DM, Mariscal R. Surface chemical promotion of Ca oxide catalysts in biodiesel production reaction by the addition of monoglycerides, diglycerides and glycerol. J Catal 2010;276:229–36.
- [119] Urasaki K, Takagi S, Mukoyama T, Cristopher J, Urasaki K, Kato S, et al. Effect of the kinds of alcohols on the structure and stability of calcium oxide catalyst in triolein transesterification reaction. Appl Catal A 2012;411–412:44–50.
- [120] Leon-Reina L, Cabeza A, Rius J, Maireles-Torres P, Alba-Rubio AC, Granados ML. Structural and surface study of calcium glyceroxide, an active phase for biodiesel production under heterogeneous catalysis. J Catal 2013;300:30–6.
- [121] Martyanov IN, Sayari A. Comparative study of triglyceride transesterification in the presence of catalytic amounts of sodium, magnesium and calcium methoxides. Appl Catal A 2008;339:45–52.
- [122] Stamenković OS, Veljković VB, Todorović ZB, Lazić ML, Banković-Ilić IB, Skala DU. Modeling the kinetics of calcium hydroxide catalyzed methanolysis of sunflower oil. Bioresour Technol 2010;101:4423–30.
- [123] Henrich VE, Cox PA. In the surface science of metal oxides. Cambridge, UK: Camridge University Press; 1996.
- [124] Feng Y, Zhang A, Li J, He B. A continuous process for biodiesel production in a fixed bed reactor packed with cation-exchange resin as heterogeneous catalyst. Bioresour Technol 2011;102:3607–9.

- [125] Xiao Y, Gao L, Xiao G, Fu B, Niu L. Experimental and modeling study of continuous catalytic transesterification to biodiesel in a bench-scale fixedbed reactor. Ind Eng Chem Res 2012;51:11860–5.
- [126] McNeff CV, McNeff LC, Yan B, Nowlan DT, Rasmussen M, Gyberg AE, et al. A continuous catalytic system for biodiesel production. Appl Catal A 2008;343:39–48.
- [127] Miladinović MR. Qiuck-lime catalyzed methanolysis of sunflower oil [PhD dissertation]. Leskovac, Serbia: University of Nis, Faculty of Technology in Leskovac; 2013.
- [128] Santacesaria E, Tesser R, Di Serio M, Guida M, Gaetano D, Garcia Agreda A, et al. Comparison of different reactor configurations for the reduction of free acidity in raw materials for biodiesel production. Ind Eng Chem Res. 2007;46:8355–62.
- [129] Meng YL, Tian SJ, Li SF, Wang BY, Zhang MH. Transesterification of rapeseed oil for biodiesel production in tricle-bed reactors packed with heterogeneous Ca/Al composite oxide-based alkaline catalyst. Bioresour Technol 2013;136:730–4.
- [130] Baroutian S, Aroua MK, Raman AAA, Sulaiman NMN. A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst. Bioresour Technol 2011;102:1095–102.
- [131] Lu P, Yuan Z, Li L, Wang Z, Luo W. Biodiesel from different oil using fixed-bed and plug-flow reactors. Renew Energy 2010;35:283–7.
- [132] Ngamcharussrivichai C, Meechan W, Ketcong A. Preparation of heterogeneous catalysts from limestone for transesterification of vegetable oils effects of binder addition. J Ind Eng Chem 2011;17:587–95.
- [133] Ren Y, He B, Yan F, Wang H, Cheng Y, Lin L, et al. Continuous biodiesel production in a fixed bed reactor packed with anion-exchange resin as heterogeneous catalyst. Bioresour Technol 2012;113:19–22.
- [134] Lianhua L, Pengmei L, Wen L, Zhongming W, Zhenhong Y. Esterification of high FFA tung oil with solid acid catalyst in fixed bed reactor. Biomass Bioenergy 2010;34:496–9.
- [135] Liu Y, Wang L. Biodiesel production from rapeseed deodorizer distillate in a packed column reactor. Chem Eng Process 2009;48:1152–6.
- [136] Li ZH, Lin PH, Wu JCS, Huang YT, Lin KS, Wu KCW. A stirring packed-bed reactor to enhance the esterification-transesterification in biodiesel production by lower mass-transfer resistance. Chem Eng J 2013;234:9–15.

- [137] Chen YH, Huang YH, Lin RH, Shang NC, Chang CY, Chang CC, et al. Biodiesel production in a rotating packed bed using K/γ-Al<sub>2</sub>O<sub>3</sub> solid catalyst. J Taiwan Inst Chem E 2011;42:937–44.
- [138] Kouzu M, Hidaka Js, Komichi Y, Nakano H, Yamamoto M. A process to transesterify vegetable oil with methanol in the presence of quick lime bit functioning as solid base catalyst. Fuel 2009;88:1983–90.
- [139] Son SM, Kusakabe K. Transesterification of sunflower oil in a countercurrent tricle-bed reactor packed with a CaO catalyst. Chem Eng Process 2011;50:650–4.
- [140] Hu S, Wen L, Wang Y, Zheng X, Han H. Gas-liquid countercurrent integration process for continuous biodiesel production using a microporous solid base KF/CaO as catalyst. Bioresour Technol 2012;123:413–8.
- [141] Veljković VB, Banković-Ilić IB, Stamenković OS. Purification of crude biodiesel obtained by heterogeneously-catalyzed transesterification. Renew Sustain Energy Rev 2015;49:500–16.
- [142] Alba-Rubio AC, Alonso Castillo ML, Albuquerque MCG, Mariscal R, Cavalcante Jr. CL, Granados ML. A new and efficient procedure for removing calcium soaps in biodiesel obtained using CaO as a heterogeneous catalyst. Fuel 2012;95:464–70.
- [143] Ferrero GO, Almeida MF, Alvim-Ferraz MCM, Dias JM. Water-free process for eco-friendly purification of biodiesel obtained using a heterogeneous Cabased catalyst. Fuel Process Technol 2014;121:114–8.
- [144] Kouzu M, Hidaka J. Purification to remove leached CaO catalyst from biodiesel with the help of cation-exchange resin. Fuel 2013;105:318–24.
- [145] Wei Z, Xu C, Li B. Application of waste eggshell as low-cost solid catalyst for biodiesel production. Bioresour Technol 2009;100:2883–5.
- [146] Berrios M, Skelton RL. Comparison of purification methods for biodiesel. Chem Eng J 2008;144:459–65.
- [147] Veljković VB, Stamenković OS, Tasić MB. The wastewater treatment in the biodiesel production with alkali-catalyzed transesterification. Renew Sustain Energy Rev 2014;32:40–60.
- [148] Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. Membrane biodiesel production and refining technology: a critical review. Renew Sustain Energy Rev 2011;15:5051–62.