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Development of CaO From Natural Calcite as a Heterogeneous Base Catalyst in the Formation of Biodiesel: Review

Nuni Widiarti[1], Yatim Lailun Ni'mah[1], Hasliza Bahruji[2] and Didik Prasetyoko[1,*]

[1]Department of Chemistry, Faculty of Sciences, Institute Technology Sepuluh Nopember Surabaya 60111, Indonesia Jl. Arief Rahman Hakim, Sukolilo, Surabaya 60111, Indonesia.

[2]Center of Advanced Materials and Energy Science, Universiti Brunei Darussalam, Negara Brunei Darussalam.

[*]Corresponding Author: Didik Prasetyoko. Email: didikp@chem.its.ac.id.

Abstract: Biodiesel is a fossil fuel that is in demand to be developed because it is bio-renewable, biodegradable and environmentally friendly. Biodiesel produced from the transesterification reaction of vege Tab. oil using a base catalyst. CaO is the most developed catalyst for the reaction of transesterification of oil into biodiesel because it is cheap, the process is easy and has a high level of alkalinity. CaO is a cheap catalyst because it is easily obtained from natural ingredients. The use of CaO catalysts in the reaction formation of biodiesel continues to develop through modification with various porous materials and different oxide materials. In this paper, we discuss the development of CaO, the modification of CaO with a porous material and metal oxide, the mechanism of reaction of CaO and the kinetics of reactions that occur in the reaction transesterification of oil to biodiesel.

Keywords: Biodiesel; CaO; modification; transesterification

1 Introduction

Biodiesel is a fuel substitute for fossil fuels that is very popular to be developed because of bio-renewable, biodegradable and environmentally friendly. Biodiesel is a mixture of alkyl esters from long chain fatty acids. [1]. Biodiesel is made from vegeTab. oils or animal fats containing triglycerides such as vegeTab. oils [2], soybean oil [3], animal fat, and used cooking oil [4], fish oil waste [5], palm oil [6] and alcohol (methanol or ethanol) through a transesterification reaction.

Transesterification reactions can be carried out by catalytic processes and non-catalytic processes. The catalyst used for this reaction is an acid catalyst, basic catalyst and catalyst enzyme [7]. In the transesterification reaction, the use of heterogeneous base catalysts is preferred because homogeneous base catalysts are corrosive, difficult to separate from the product so they can poison the biodiesel produced [8]. One of the cheap, easy to obtain and simple metal oxide catalysts to make an active base catalyst is CaO. CaO is a metal oxide obtained through a decomposition reaction of $CaCO_3$ at high temperatures between 600°C and 1000°C [1]. $CaCO_3$ is found in natural materials such as limestone [9], animal bones, fish bones [10], chicken egg shells [11], shellfish [12], snail shells, crab shells [12] were even found in chicken manure [13]. Besides being cheap and easy to obtain, the excess of CaO as an active base catalyst is non-toxic, has a high basic value and is not easily soluble in biodiesel products [1,14].

Production of biodiesel from oil with high FFA levels requires two reaction steps. Acid-base catalysts are very effective for the production of biodiesel from oil which has a high FFA value [15]. Acid catalysts are used to reduce the amount of free fatty acids (FFA) through etherification reactions, while triglycerides (TAG) as the main component of oil are catalyzed by active base catalysts through transesterification reactions [16]. However, the production of biodiesel in two steps are not much

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favoured because it requires the amount of methanol that is more, the amount of catalyst is more, the washing process repeated, the reaction time is longer, but the biodiesel produced less due to go wasted when washing [17]. Therefore a one-step transesterification reaction is an option for biodiesel production because it is easily separated from biodiesel product [18].

One-step transesterification reactions in low quality oils can be carried out using a CaO-bifunctional catalyst which has an active side of the acid as well as an active base. The active side of Lewis acid functions to convert carboxylic acid (FFA) to methyl ester while the conjugate base side converts triglycerides to FAME in one-pot reaction [19]. The CaO-bifunctional catalyst is a combination of CaO catalysts, with transition metal oxide or precious metals [20], through several methods such as impregnation, sol-gel method, coprecipitation and composites. The conjugation between CaO and metal oxides which have acidity sites and different basic sites can increase the basicity or provide an acid side and base side that can be used for direct transesterification reactions [19]. In general, the combination of CaO catalysts on the transesterification of oil into biodiesel can be described as shown in Fig. 1.

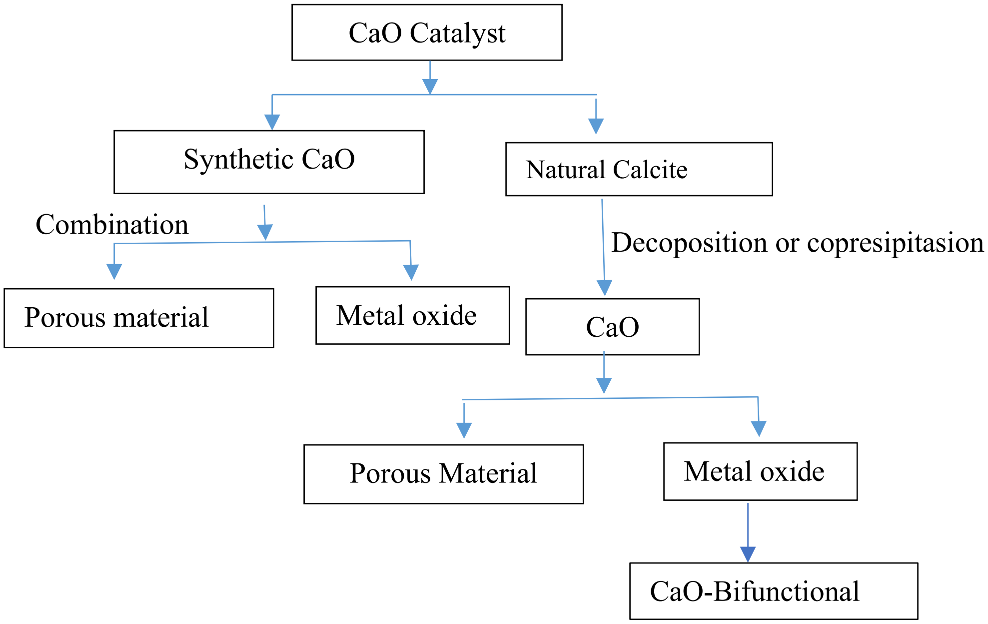


Figure 1: Chart of CaO catalyst combinations

In this paper, we will discuss the use of CaO-based catalysts derived from calcite for transesterification reactions, sources of CaO, modification of CaO with porous materials and transition metal oxides to form bifunctional catalysts, mechanisms and kinetics of transesterification reactions catalyzed by CaO-based catalysts. At the end of this paper, the prospect of mesoporous CaO as a transesterification catalyst on the future will be discussed and is expected to improve the performance of CaO in the oil transesterification reaction into biodiesel.

2 Raw Materials CaO as A Catalyst in Transesterification Reactions Oil into Biodiesel

Calcium oxide is generally made through thermal decomposition of calcite minerals containing calcium carbonate ($CaCO_3$) at high temperatures producing lime (CaO) and freeing carbon dioxide (CO_2) [1]. The process of obtaining CaO from different sources of raw material will produce CaO with different surface area and basicity. Some sources of CaO and the resulting CaO properties are shown in Tab. 1.

Table 1: Source of calcite, calcination temperature and CaO properties produced

No.	Source of $CaCO_3$	Initial CaO content (%)	Calcination Temperature (°C)	Post-calcination CaO content (%)	Physical and chemical properties of CaO		Reference
					Surface area (m^2/g)	Basicity µmol/mmol	
1	Mussel sells	59.7-60	800 -900	95-97	7.5-23.2	385-13157	[28,62-64,78]
2	Egg Sells	96.13	900	97.08	2.29-68	172.2	[11,65,66]
3	Buttom Ash	na	600-900	na	8.23-9.11	1.4-12	[23]
4	Chicken manure	14.9	850	74.1	10.8	12	[13]
5	Bone	na	900	na	43.8	0.757	[10,54]
6	Natural Lime	na	800	97.07	na	na	[9]
7	Hidrated Lime	na	800	75	15.0	326.4	[67]
8	Golden apple snail shell	na	800	na	0,9	207.8	[68]

Tab. 1 shows that the most CaO component is found in egg shells. The percentage of CaO obtained from the calcination of $CaCO_3$ from various precursors was 95-97%, except for CaO which was decomposed from chicken manure which was only 74.5 From several sources of raw materials that have been studied, it has been shown that CaO has a basicity level of 0.385-13.157 mmol/gram CO_2, and surface area of less than 15 m^2/g. Based on its surface area, CaO has a low surface area but has a high basicity value This high basicity enables CaO to have good activity on the oil transesterification reaction to biodiesel [14,1]. Based on several studies, CaO activity from natural calcite is good for oils that have low FFA values but are less active in oils with high FFA values [38].

3 Method of Synthesis CaO Catalyst

$CaCO_3$ is a CaO source most commonly found in natural materials such as eggshell, oyster shell, bone, cement and limestone. The CaO preparation process is very influential on the character and activity of CaO in the oil transesterification reaction into biodiesel. The process for obtaining CaO from the source of natural calsite ($CaCO_3$).

3.1 Thermal Decomposition

Thermal decomposition is a chemical decomposition caused by heat. Decomposition reactions are endothermic reactions because they require heat to break down a chemical bond so that a compound can decompose into a simpler compound. Thermal decomposition of fresh raw materials, such as calcite, needs pre-processing at high temperatures to decipher raw materials and to improve the number of active sites on the surface of the catalyst [21]. Decomposition of Calcium carbonate ($CaCO_3$) at temperatures 600-1000°C produces CaO and CO_2 with a decomposition limit between the phases of $CaCO_3$ and CaO [22]. Thermal decomposition is generally used to obtain CaO from natural materials such as fish bones [10], bottom ash [23], eggshell [11], and other ingredients contains the main component of calcium. The decomposition temperature used to determine the optimal temperature of calcium material calcination was determined through the Thermal Graphimetry Analyzer-Deferesial Scanning Calorimetry (TGA-DSC) as shown in Fig. 2.

Fig. 2 shows that at 350°C there is a decomposition of crystalline water found in limestone, at a temperature of 450°C decomposition of hydroxide occurs, and at 798.50 the decomposition of carbonate groups into CO_2 [24]. The calcination temperature to obtain CaO is strongly influenced by the type of CaO and calcium salts which become precursors of CaO. Some results of research that show optimal calcination temperature in the decomposition of calcium to CaO salts are shown in Tab. 1.

Tab. 1 shows that the calcination temperature of 800-900°C is the optimal temperature for decomposition of $CaCO_3$ into maximum CaO. Calcination temperature below 800°C cause $CaCO_3$ component is not decomposed completely into CaO and CO_2, but the temperature above 900°C the CaO surface area decreases from 11.2 m^2/g to 10.0 m^2/g [13]. This decrease in surface area is due to the sintering process at high temperatures cause agglomeration of the catalyst material [13,25].

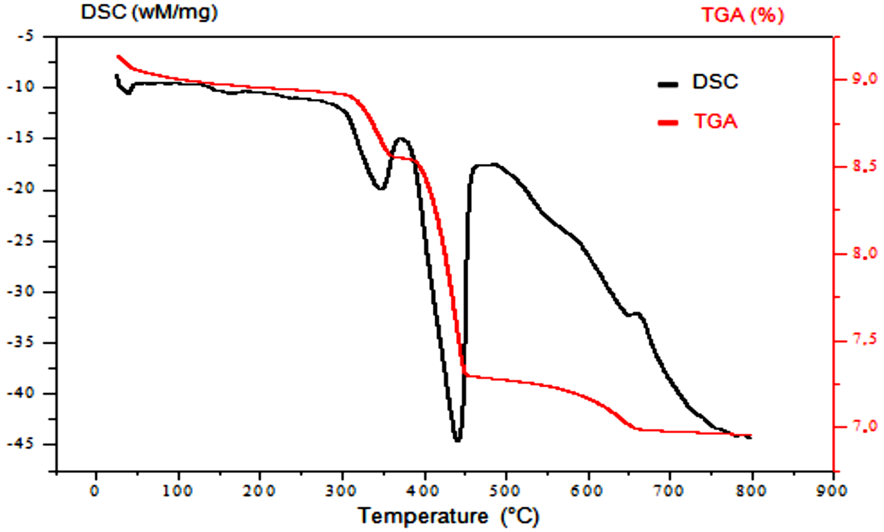


Figure 2: TGA-DSC curves of limestone at 30-800°C [9]

3.2 Coprecipitation

Coprecipitation is a method used to obtain solid material from its precipitate in the form of a solution [1]. The coprecipitation method is generally used to obtain a material with small particle sizes such as nanometers [26]. CaO obtained by coprecipitation may be from natural ingredients or derived from commercial calcium salts and other reagents through repeated dissolution and precipitation. The coprecipitation method is used for synthesis of catalysts with higher basicity [21]. Some CaO catalyst has been successfully synthesized by the coprecipitation method include CaO from limestone with HNO_3 solvent and precipitating agent NaOH followed by calcination at 800°C [9]. The CaO catalysts produced were used for the transesterification reaction of the Reutealis trisperma oil yielding yields of 37.74%. This result is greater than the results of the methanolysis reaction with CaO limestone catalyst from direct thermal decomposition that only 15.97% [9]. Yulianti et al. [26] synthesized CaO from Calcium acetate (Ca-Acetate) with oxalic acid as a precipitating agent to produce CaO with a particle size of 190 nm. Microsphere CaO was also successfully synthesized using $CaCl_2$ and Na_2CO_3 to produce CaO with a particle size of 100 nm and a surface area of 5.3 m^2/g [27].

4 Modification of CaO for Transesterification Reactions

4.1 Modification of CaO with Porous Material

Modification of CaO was carried out to increase the catalyst activity in the transesterification reaction. Increased activity of the catalyst is characterized by increasing concentration of FAME produced. The catalytic activity of CaO in transesterification reactions is influenced by several factors such as surface area and alkalinity of CaO catalysts [13,28-30]. The surface area of a CaO catalyst can be increased through a combination of CaO with porous materials such as Zeolite, silica, and other metal oxides which have a larger surface area. Loading of CaO in broad-surface materials such as silica, alumina, zeolit, SBA and zinc oxide is a good method to improve the dissolution stability of Ca^{2+} in methanol [31-33]. The larger surface area of the support to allows good metal oxide dispersion to increase the catalytically active surface.

Tab. 2 shows that porous material plays a major role in increasing CaO activity in transesterification reactions Doping of CaO in porous material with a type of molecular sieve provides a catalyst surface area between 100-960 m^2/gram. Based on the yield of biodiesel produced by CaO/SBA, CaO/Zeolite, CaO/Biochar, CaO/PVA and CaO/alumina, SBA are good material support to support CaO because this material has a large surface area so that it can increase the number of active sides of the catalyst. Based on the baseline analysis zeolite NaX is a CaO catalyst support which provides the highest base value with 94% biodiesel yield. Based on the analysis of the number of catalysts, reaction time, comparison of the amount of material oil: methanol, zeolite looks the most effective because in addition to the small mole ratio, the amount of catalyst is small, reaction time is short and reaction temperature used is middle reaction so the use of this support is feasible.

Table 2: Modification of CaO with porous material and the synthesis method used

No	The modified CaO catalyst used	Synthesis method	Feedstocks	Surface area m^2/g	Basicity (mmol/g)	Yield Biodiesel (%)	Reference
1	CaO/ silica mesopori	Impregnation	Soybeen oil	175	na	95.2	[69]
2	Ca/SBA-15	Impregnation	Sunflower seed oil	144	111	99.1	[70]
3	CaO/NaA	Impregnation	Oliv oil	na	na	94.5	[71]
4	CaO- MCM 41	Sol-gel	Palm oil	960	na	90	[72]
5	CaO-SiO_2	Sol- gel	Palm oil	15.47	na	80-90	[55]
6	CaO/ϒ Al_2O_3	Impregnation	Sunflower seed oil	112	9,87	94.3	[50]
7	CaO/Al_2O_3	mixed oksida	Algae oil	na	na	88.89	[47]
8	CaO/PVA	Impregnation	Coconut pulp	3.36	na	95	[73]
9	CaO/Na-ZSM5	Impregnation	Neem oil	370	na	95	[64]

4.2 Modification of CaO with Transition Metal Oxides to form CaO-Bifunctional Catalyst

Modification of CaO with metal oxides that have different acidity-basicity values aims to increase the basicity of the catalyst [19]. Addition of metal oxides can increase CaO based sites which are characterized by CO_2 adsorption at regions 400-700 with strong intensity [3,19,34,35]. When CaO is combined with other metal oxides, CaO can act as support as well as active side, CaO is supported on other oxides, or each combination has the same role. This depends on the ratio of the composition of each metal oxide and the method used in the combination. Modification of CaO with metal oxides aims to improve the performance of the catalyst in the reaction formation of biodiesel, especially from non-edible oils that have high FFA values. The incorporation of high acidity metal oxides with CaO will form a CaO-bifunctional catalyst with two active sides in one material [20].

5 The Synthesis Method of CaO Catalyst/Porous Material and CaO-Bifunctional

The combination of CaO with a porous material and CaO-bifunctional catalyst (acid-base) is a combination of a basic catalyst (basic oxide) with acid (acid oxide) catalyst in one material through several combination methods such as impregnation [36-38], Coprecipitation [19,26,39], Sol-gel [29] and composites (joint mixing) [40]. The choice of combination method is adjusted to the type and nature of metal precursors used. These three combination methods are chosen because, in addition to the simple process, they also do not involve complex procedures that require high costs [41].

5.1 Impregnation Method

The wet impregnation method is the easiest and simplest catalyst preparation method for the synthesis of supported catalysts. This system can evenly distribute the catalyst active site on the surface which is very well used in the esterification and transesterification reactions. The impregnation method is carried out by mixing solid support into a solution of metal acetate, sulfate or nitrate salts of metal oxides used. The mixture is stirred for 5 to 6 hours. After being shaped like slurry the solid is dried in an oven at 110°C for 24 hours [40,42]. Some combinations of CaO with transition metal oxides synthesized through the impregnation method are CaO/ZnO having a surface area of 12 m^2/g used for the castor esterification of castor oil [43], W-Mo/CaO has a surface area of 9.40 m^2/g for the transesterification reaction of used cooking oil [44], CaO/CeO has a surface area of 8.60 m^2/g for palm oil transesterification reactions [38].

5.2 Sol-Gel Method

The sol-gel method is known as one of the simple and easy nanoparticle synthesis methods. This method is one of the "wet methods" because the process involves the solution as a medium. In the sol-gel method, the solution undergoes a phase change into sol (colloid which has suspended solids in the solution), through a hydrolysis reaction and then becomes a gel (colloid but has a solid fraction greater than sol) through a condensation reaction [41]. The sols formed are then dried to obtain xerogel, the xerogel is then crushed to a certain size and calcined. Nano CaO-MgO synthesized by the sol-gel method can increase catalytic activity with the yield of biodiesel from used cooking oil by 99% [45]. [29] also synthesized CaO-SnO used in the transesterification reaction of babassu oil having a surface area of 7.80 m^2/g with a yield of 90%.

5.3 Coprecipitation Method

Coprecipitation method is a method of synthesis of catalysts by dissolving precursor salts into distilled water and stirring strongly. In the process of mixing added sedimentary agents which are generally alkaline such as Potassium carbonate (K_2CO_3), NaOH, KOH and NH_4OH and also acidic settling agents such as Oxalic acid. The coprecipitation method is generally used to make bimetal catalysts supported by CaO to increase the acidity or alkalinity of the synergistic effects of two or three metals involved [41].

In the coprecipitation process the solution is constantly stirred for 3 hours and pH 10, so that perfect precipitation occurs. The precipitate formed was then dried in an oven at 110°C for 12 hours and continued with calcination. The CaO-bifunctional combination successfully synthesized by the coprecipitation method was CaO-ZnO [26] for the transesterification of CPO, CaO-MgO reactions for the transesterification reaction of Elaeis guineensis oil [46].

5.4 A Mechanical Mixture of Metal Oxides

The metal oxide mixture is mechanically carried out by mixing two or more pure metal oxides (eg., CaO and ZnO) into ball milling. The mixture is then grinding until homogeneous. After the homogeneous mixture is put in aquades, stirred at a speed of 500 rpm for 5 hours, while being heated to a temperature of 60-80°C. After being shaped like slurry, the solid formed is dried at 110°C for 12 hours, then calcined at the appropriate temperature [40].

The combination of CaO and metal oxides synthesized through mechanical mixtures is CaO/Al_2O_3. This catalyst was then used for the transesterification of algae oil to produce biodiesel of 88.89% [47], CaO. ZnO synthesized with ball milling for the reaction of transesterification of sunflower oil has a surface area of 8.6 m^2/g, the mount base of 2.94 mol and biodiesel yield of 97% [30].

6 Effect of Metal Oxide on the Character of CaO-Bifunctional Catalyst

The performance of the catalyst is influenced by the basic property of the catalyst such as crystallinity, surface area, particle size, pore size and acidity or basicity of the catalyst. Combining CaO oxide with other metal oxides causes changes in the character of CaO surface area and catalyst basicity. Metal oxides supporting CaO are generally transition metal oxides that have different levels of basicity or acidity Among these transition metal oxides include CeO [36], ZnO [30], ZrO_2 [34], La_2O_3 [19] and W-Mo [44]. The presence of metal oxides in CaO causes changes in the character of CaO to be better so that it can be used for the reaction of non-edible oil transesterification in one reaction stage.

6.1 Effect of Metal Oxide Types on the Surface Area of CaO-bifunctional Catalysts

Surface area greatly influences the activity of the catalyst. Large surface area allows active sides more to distributed on the catalyst surface [1] so that the reaction between reactants on the active side will be more occurred. The surface area of the CaO-bifunctional catalyst is influenced by the type of metal oxide used, the large of the surface area of the metal oxide in its single form, then the greater the surface area of the CaO-bifunctional. The effect of metal oxide on the CaO-bifunctional surface area on the non-edible oil transesterification reaction can be seen in Fig. 3.

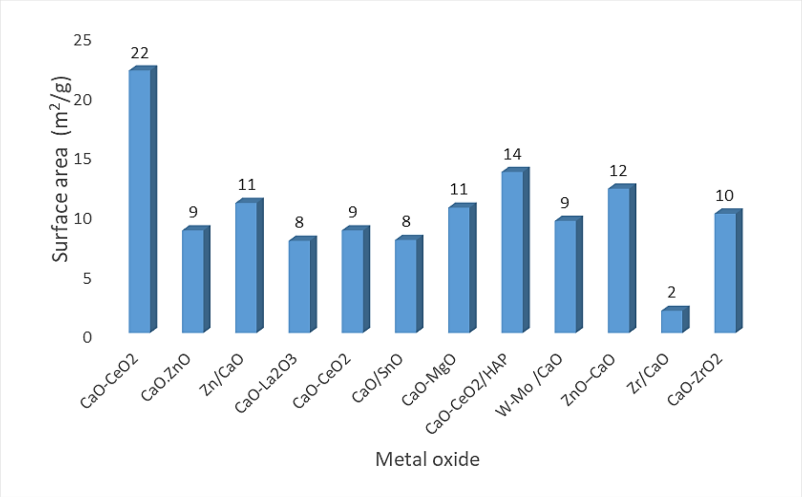


Figure 3: Effect of metal oxide types on the surface area of CaO-bifunctional catalyst

From Fig. 3, it can be seen that the mixture of CaO with other oxides produces a larger surface area than the CaO surface area in its single form. From the graph, it can be seen that the mixture of CaO with other oxides produces a larger surface area than the CaO surface area in its single form. The area of CaO in pure conditions is maximum of 4 m^2/gram while the area of CeO_2 is 57 m^2/gram. In the CaO-CeO_2 mixture, the surface area increases as the amount of CeO_2 is added, because CeO_2 has joined and distributed on the surface of the catalyst [36]. The different area of CaO-CeO_2 is shown by the results of the study of Wong et al. [38], the mixture of CaO-CeO_2 obtained in the study of Wong et al. [38] has an area in the range of 3.4-8.6 m^2/gram. The increase in the area obtained in the study is inversely proportional to the size of the Crystal obtained. The larger surface area of mixed-oxide the smaller the size of the crystal obtained [38]. The mixture-oxide CaO-CeO_2/HAP has the largest area of 27.076 m^2/gram, but the best catalytic activity is obtained on the mixed-oxide with an area of 13.501 m^2/gram. This very large surface area is influenced by the support of Heteropoli Acid (HAP), which has an area of 104.615 in its single state [48].

The incorporation of CaO with ZnO also greatly influences the surface area of the CuO-ZnO catalyst. Mixing ZnO with CaO can be through the impregnation method [37,43], coprecipitation [26] and sol-gel have a catalyst surface area with a range of 9-12 m^2/gram. The surface area of the catalyst mixture of metal oxides in addition to being influenced by the composition of metal oxides added is also influenced by the calcination temperature. The surface area of Zn/CaO catalyst increases with increasing calcination temperature from 150-550°C with a maximum area of 10.95 m^2/gram. The increase in the calcination temperature of 750-950°C causes a smaller surface area due to sintering of Zn/CaO particles which results in an increase in the size of the Crystal [37]. Besides the metal oxide composition and calcination temperature, the method of mixing metal oxides also affects surface area. According to Kesic et al. [30] CaO. ZnO synthesized through the ball milling method has a larger surface area than CaO. ZnO wich obtained by coprecipitation method which is 8.6 m^2/gram and 5.7 m^2/gram.

Mixing metal oxide La_2O_3 with CaO to form CaO-La_2O_3 has a smaller area compared to CaO-ZnO and CaO-CeO metal oxides. CaO-La_2O_3 has a surface area of 8 m^2/gram [19]. W-Mo/CaO and ZrO/CaO also have a smaller surface area compared to the surface area of the mixture of other metal oxides, however, both of these catalysts have good catalyst activity in some transesterification reactions of oil into biodiesel. The catalytic activity of W-Mo/CaO and ZrO/CaO is greatly influenced by the basicity of the catalyst, which is caused by transition metal oxides having different levels of alkalinity or acidity. The CaO-bifunctional catalyst produces two active sides of the catalyst that are acidic and basic so that they can be used for high-FFA oil transesterification reactions

6.2 Effect of Metal Oxide on Basicity of CaO-Bifunctional Catalyst

Transition metal oxides are acidic metal oxides. The combination of transition metal oxides in CaO to form a mixture of oxides will affect the nature of the catalyst base to be greater than the alkali nature of CaO in its single state The basicity strength of CaO in a single form when measured by the Hammet method obtained pH in the range 9.8-10.1 [37] whereas if measured using the CO_2TPD method it has a base mol number of 0.864 mmol/gram [38]. The CaO-bifunctional catalyst or a combination of CaO with transition metal oxides proved to have a greater base strength compared to the single CaO oxide. Basicity strength of some CaO-bifunctional catalysts can be seen in Tab. 3.

Tab. 3 shows that transition metal oxides have an influence on the base strength of CaO. The base strength found in some CaO mixed oxides with transition metal oxides depends on the acidity of each transition oxide. Besides adding base strength to the presence of transition metal oxides it can also provide acid strength in the CaO oxide mixture. Transition metals that provide both acidic and basic strength on the catalyst are La_2O_3, W, Mo and Zr. La_2O_3 is a super-acid metal oxide, which contributes to the formation of acidic and basic properties in the bifunctional catalyst system. Metal oxides contribute to the formation of base sides while metal ions contribute to the formation of the acid side. The synergistic interaction between La and Ca increase the strength of the acid and base CaO-La_2O_3 compared to each of the metal oxides [19].

Table 3: Basicity of several CaO mixed oxide catalysts with transition oxides

Catalyst	Basicity	Reference
CaO-CeO_2	na	[36]
CaO.ZnO	2.94	[30]
Zn/CaO	15 < pKbh < 18,4	[37]
CaO-La_2O_3	3.19874	[20]
CaO-CeO_2	1.783	[38]
CaO/SnO	Na	[29]
W-Mo/CaO	1.365	[44]
ZnO-CaO	15.0 < H_ < 17.3	[43]
Zr/CaO	20.21	[74]
CaO-ZrO_2	0.652	[75,34]

Base strength W-Mo/CaO catalyst is caused by a synergistic effect of interaction between the surface of the oxygen lattice and the induced Ca species, whereas Oxides from W^{3+} and Mo^{6+} are the preferred Lewis acid side in the esterification reaction [44]. Base strength is also influenced by the preparation proses of the CaO-bifunctional catalyst. The base strength of CaO.ZnO catalyst prepared by the ball milling reaction has a base strength of 2.94 mmol/gram while the one prepared through the coprecipitation method has a base strength of 1.31 mmol/gram [30]. The presence of transition oxides on binary CaO catalysts produces two acidic and alkaline active sides that are preferred in the reaction of the formation of biodiesel with high FFA values through the esterification and transesterification reactions in one reaction site.

6.3 Effect of Transition Metal Oxide on CaO-bifunctional Catalyst Activity

Combined CaO and CaO catalysts are heterogeneous base catalysts that are much in demand in the reaction of biodiesel formation because they are cheap, easy to obtain, stable and have a high basicity level [23]. CaO catalyst activity is strongly influenced by the nature of the catalyst such as the level of crystallinity, surface area, particle size, pore size and acidity or basicity of the catalyst. However, CaO has a small surface area, is easily soluble in methanol [49]. The transesterification reaction of non-edible oil with CaO catalyst is less effective because the high FFA and the amount of water in non-edible oil cause the formation of soap and $Ca(OH)_2$ [38] which can cause CaO performance to be less effective due to deactivation [41]. The low activity of CaO catalyst yield biodiesel approximately 37% [9].

Modification of CaO with metal oxides can increase the basicity strength of the catalyst so that it has better activity in the transesterification reaction of non-edible oil. Some catalysts that have better catalytic activity on the transesterification of non-edible oils include CaO. ZnO produces 97% biodiesel from sunflower oil [30], CaO-CeO_2 in P Chinese oil produces of 91% and CaO-La_2O_3 which produces 99% biodiesel from castor oil [19]. Among the three metals oxide of ZnO, CeO_2 and La_2O_3, metal oxide ZnO and La_2O_3 were able to increase the catalytic activity of CaO in castor oil transesterification reaction. Another advantage of other CaO-La_2O_3 catalysts compared to others is that they have good reusability because they are stable up to four times use, and biodiesel produced meets EN 14103 and ASTM D6751 standards [19]. Economically the CaO-La_2O_3 catalyst has a very good performance and is able to reduce the cost of biodiesel production, mainly seen from the raw materials of non-edible oil, shorter reaction times and reducing the need for methanol and washing biodieselTherefore the combination of CaO catalysts with transition oxides that have high acidity results in a bifunctional catalyst that is compatible with the transesterification reaction. Modification of CaO with transition metal oxides to form CaO-bifunctional catalyst is useful for increasing CaO catalyst activity in the reaction formation of biodiesel, especially non-edible oil which has a high FFA value. One-step transesterification reactions on non-edible oils can be carried out using metal oxide modified CaO catalysts that have different levels of basicity or acidity [19]. CaO supported by other oxides allows CaO to be distributed well throughout the support surface so that it will increase the number of active sides on the surface, increase catalyst stability and be resistant to FFA and water contained in the oil [50]. Thus the modified CaO catalyst activity on the oil transesterification reaction will be better than the single CaO catalyst. A complete review of the catalyst in the non-edible oil transesterification reaction is presented in Tab. 4. In Tab. 4, it can be seen that the CaO-bifunctional catalyst has good activity against the oil transesterification reaction. Biodiesel produced on the transesterification reaction of non-edible oil by the catalyst is above 90% and the condition of the transesterification reaction of non-edible oil can be achieved under moderate reaction conditions.

Table 4: Modification CaO with metal oxide and its activity in the transesterification reaction of oil to biodiesel

No.	Catalyst	Synthesis Method	Feedstocks	Reactan	Catalyst category (mesoporous/nano size)	Surface area	Basicity	Biodiesel Synthesis Method	Yield (%)	Reference
1	CaO-CeO2	Impregnation	P. chinesis oil	Methanol	Mesoporus	12	Na	Batch	91	[36]
2	CaO.ZnO	Mechanical preparation	Sunflower seed oil	Methanol	3,8 mikro	8.6	2.94 mmol/g	Batch	97	[30]
3	Zn/CaO	Impregnation	Non-edible oil	Methanol	23 nano	10.95	15<pKbh<18.4	Batch	99	[37]
4	CaO.ZnO	Copresipitation	Palm oil	Methanol	60 nm	Na	Na	Batch	93.57	[26]
5	CaO-ZrO2	Combustion of urea-nitrate with precursors Ca/Zr=4/6-9/1	Jiali plant oil (Cina)	Methanol	na	2.5	0.652	Batch	98	[34]
6	KBr/CaO	Impregnation	WCO	Methanol	na	Na	Na	Batch	83.6	[42]
7	CaO-La2O3	Copresipitation	Castor oil	Methanol	63-54 nm	7.73	Basicity = 3198,74 μmol/g Acidity = 287,05 μmol/g	Batch	98.76	[19]
8	Ca-La mixed oxide	Copresipitation	Castor oil	Methanol	56-73	7.8	4.71 mmol/g	Batch	80	[39]
9	CaO-CeO2	Impregnation	Palm oil	Methanol	58 nano	8.6	1783 μmol/g	Batch	95	[38]
10	Nano CaO-MgO	sol-gel	WCO	Methanol	69 nm	Na	Na	Batch	98.95	[45]
11	K2O/CaO-ZnO	Copresipitation	Soybean oil	Methanol	na	28	Na	Batch	81.08	[76]

		Wet impregnation								
12	CaO/ SnO	Sol-gel	Babasu oil	Methanol	1-5 µm	7.8	Na	Batch	89.58	[29]
13	MgFe2O3@CaO	Copresipitation	Soybean oil	Methanol	na	Na	Na	Batch	98.3	[3]
14	CaO-MgO	Copresipitation	Crude oil from Elaeis guineensis	Methanol	56.8 C 33.2 M	10,51	750µmol/g	Batch	99	[46]
15	CaO-MgO/Silika	Impregnation	Soybean oil	Ethanol	na	Na	Na	Batch	98	[77]
16	CaO-K2O/silika	Impregnation	Soybean oil	Ethanol	na	Na	Na	Batch	99	[77]
17	CaO-ZnO/silika	Impregnation	Soybean oil	Ethanol	na	Na	na	Batch	90.6	[77]
18	CaO-CeO2/HAP	Impregnation	Palm oil	Methanol	na	13.501	441,8	Batch	91.84	[48]
19	W-Mo /CaO	Impregnation	WCO	Methanol	52.225	9.4	1365 Acidity 3736	Batch	96.2	[44]
20	PA/CaO	Impregnation	Almont oil	Methanol	na	Na	9.3<H<15	Batch	88	[5]
22	PA/CaO	Impregnation	Waste fish oil	Methanol	na	Na	9.3<H<15	Batch	90	[5]

7 Optimization of Catalyst Performance in the Transesterification Reaction of Oil to Biodiesel

CaO catalyst activity is strongly influenced by the nature of the catalyst such as the level of crystallinity, surface area, particle size, pore size and acidity or basicity of the catalyst [44, 46]. However, the optimal condition of the reaction is also an important concern, because it also greatly affects the biodiesel produced [51]. Several factors that influence the transesterification reaction can be seen in Fig. 4. The determinants of the reaction must be in optimal condition to get the maximum yield. The optimal condition of each catalyst, both CaO and CaO-combined will differ depending on the precursor of CaO and the metal oxide used.

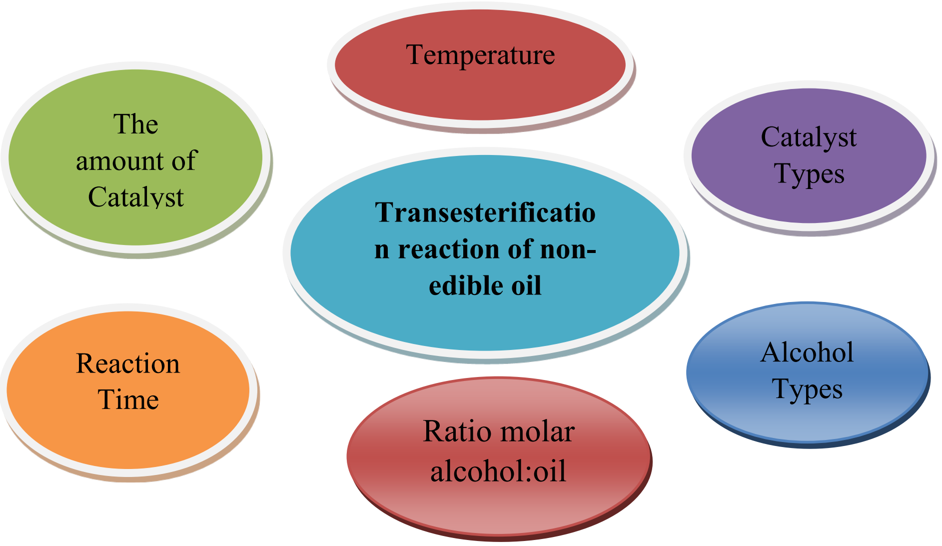


Figure 4: Factors that influence the transesterification reaction of oil to Biodiesel

7.1 CaO catalyst

CaO is very active for some transesterification reactions because it has high alkalinity with varies _H between 9.8 < pKbh H < 18. 8 [49,52]. The CaO catalyst activity in the transesterification reaction is strongly influenced by several important factors including reaction temperature, a number of catalysts, reaction time, stirring speed, and a molar ratio of methanol: oil [12,53]. The optimal condition of the oil transesterification reaction catalyzed by CaO from various $CaCO_3$ raw materials can be seen in Tab. 5.

Table 5: Optimation of CaO catalyst from various sources of raw materials in oil transesterification reactions

		Feedstocks	Reaction conditions					Reference
No.	Source of CaO		Temperature (T)	Amount of catalyst (b/v)	Ratio of Methanol: Oil	Time (t)	Yield (%)	
1	Duck eggshell	Soybean oil	80°C	10%	10 : 1	80 minit	94.6	[66]
2	Commercial	Soybean oil	65°C	8 %	12 : 1	3 h	95	[3]
3	Chicken bones	Soybean oil	65°C	5%	15 : 1	4 h	89.33	[54]
4	Chicken eggshell	Used cooking oil	60°C	1.5%	12 : 1	90 minit	96.07	[61]
5	Chicken manure	Used cooking oil	65°C	7.5%	15 : 1	4 h	90	[13]
6	Abalone Shell	VegeTab. oil	65°C	7%	10 : 1	2.5 h	96.2	[28]
7	Freshwater shells	Palm oil	70°C	5%	12 : 1	1.5 h	90	[78]
8	Fishbone	Chinese fat oil	65°C	4%	3 : 1	6 h	93	[10]
9	Limestone	Reutealis trisperma	60°C	1%	1 : 1	2 h	37.74	[9]
10	Crabs and shells 1: 1	Used cooking oil	-	5%	13 : 1	3 h	98	[12]

Tab. 5 shows that the use of CaO as a catalyst has produced high biodiesel for several transesterification reactions. The transesterification reaction catalyzed by CaO takes an average of 3 hours, the molar ratio of methanol: oil between 10: 1 to 15: 1, the number of catalysts is between 3-7%, a reaction temperature is 65-70°C. Time of 3 hours is the optimal time for some oil transesterification reactions using CaO catalyst. Addition of the number of catalysts, molar ratio of methanol: oil, and the temperature of the catalyst above the optimal conditions are not effective against the addition of biodiesel yield.

The maximum CaO catalyst performance is obtained from calcined CaO at a temperature of 800°C-900°C because at this temperature $CaCO_3$ has been completely decomposed into CaO and CO_2, while temperatures above 900°C CaO undergo sintering which results in small surface area [13]. The reaction temperature of 65-70°C is the optimal temperature of the transesterification reaction using a CaO catalyst. At temperatures of 65-70°C mass transfer between oil-methanol-water occur optimally at 65-70°C, but the reaction temperature above 70°C causes methanol evaporates and remains in the vapour phase, so the concentration of methanol that reacted with oil becomes small [13,54]. Methanol: oil ratio is an important factor in the reaction of transesterification of oil into biodiesel. At the transesterification reaction oil to biodiesel using CaO catalyst, the optimal ratio of methanol: Oil is achieved at 10:1 to 15:1. Excesses methanol in the transesterification reaction causes a decrease in yield of FAME. This decrease in FAME is caused by the solubility of glycerol in methanol and FAME, and insoluble of methanol in oil [41]. The excess methanol in the mixture causes the reaction equilibrium to shift towards the reactants so that yield FAME becomes small [13].

7.2 CaO Catalyst in the Porous Material

CaO catalyst activity in the porous material is strongly influenced by the type of support used. The greater of the surface area of the support material used, the greater of a surface area of CaO catalyst. However, the increased surface area does not have a significant effect on catalyst activity. Chen et al. [55] combined $CaO-SiO_2$ with the biometric silicification method with various concentrations of SiO_2. In studies Chen et al. [55], the more the amount of CaO added in porous materials causes the smaller the surface area, but the activity increases. The more amount of SiO_2 added (0Si5Ca, 1Si5Ca, 2Si5Ca, 3Si5Ca, 5Si5Ca) the catalytic activity $CaO.SiO_2$ decreased from 90.2% to 87.7%, 80.1%, 40.7% and 13.5%. The optimization of CaO catalyst work on porous material is also influenced by the amount of loading, amount of catalyst, reaction time, and reaction temperature. Some optimal conditions of catalyst CaO/porous material on transesterification reactions are presented in Tab. 6.

Table 6: Optimation of CaO catalyst/porous material on the oil transesterification reaction

No.	Catalyst	Feedstock	Optimal reaction conditions				Yield (%)	Reference
			Tempe -rature (T)	Amount of catalyst (b/v)	Ratio Meth : oil	Time (t)		
1	CaO supported on bimodal meso-macroporous silica	Palm oil	60	5	12:1	5 h	94.15	[79]
2	Mesopororous Calcium Titanat	Waste cooking oil	65	0,2	3:1	1 h	80.0	[80]
3	$CaO-MoO_3-SBA-15$	Soyben oil	65	6	50:1	50 m	83.2	[34]
4	Ca/SBA-15	sunflower oil	200	5	9:1	8 h	99.1	[70]

Based on Tab. 6 it can be seen that the optimal condition of the transesterification reaction of oil to biodiesel depends on the support material of CaO. Based on the concentration of biodiesel produced, MCM-41 and ZSM-5 are supported which provide small catalytic activity on CaO. While SBA-15 produces large biodiesel, it requires a high reaction temperature of 200°C [70]. Impregnation of CaO in porous material does not increase the base strength of CaO but increases the reusability of the catalyst to several times the reaction without re-activation [79].

7.3 CaO-bifunctional Catalyst

7.3.1 Influence of Metal Oxide Loading on Biodiesel Yield

The percentage of metal oxide addition on CaO catalyst greatly influenced the character and activity of bifunctional CaO catalyst in the transesterification reaction. In $CaO-CeO_2$ catalyst, the biodiesel yield is obtained at a maximum at 50% Ca/Ce ratio. Biodiesel yield increases with the increase in the number of CeO added to reach a ratio of 1:1 with an increase in yield between 6%-95%. The amount of CaO which is greater than CeO_2 causes higher CaO leaching in reactants so the biodiesel produced decreases [38]. The increase of biodiesel yield is also influenced by the higher basicity of the catalyst, but too much addition of CeO_2 to CaO causes the catalyst basicity to decrease so that the yield produced is also small [38,48]. In addition, the composition of excessive CeO_2 on $CaO-CeO_2$ causes the emulsion to form during the transesterification reaction so that the reaction does not run optimally and the resulting biodiesel is smaller [48].

At La_2O_3-CaO catalyst it was found that the increase in La_2O_3 which was greater caused a large surface area, but decreased the number of moles of basicity and basicity strength, while the increase in CaO which was too large caused the formation of CaO phase agglomerations which caused pore closure resulting in decreased surface area Teo et al. [39]. The same statement was expressed by [34,37,44] which states that biodiesel yield is achieved on catalysts which have high base strength and a surface area large, with a ratio of optimal loading of CaO: metal oxide.

7.3.2 Influence of Percent Catalyst (B/B) on Biodiesel Yield

A catalyst is a substance that can speed up the reaction and can be recovered after the reaction is complete. The conversion of triglycerides to biodiesel depends on the amount of catalyst used. Optimization of the number of catalysts starts with the smallest amount of catalyst until the optimal amount of catalyst is obtained so that maximum conversion is obtained [41]. The addition of the amount of catalyst is usually stopped when the conversion obtained starts to go down or constant. Tab. 4 shows that the optimal amount of catalyst used by CaO-CeO_2 catalyst is 9% with 91% yield [36], CaO. ZnO catalyst 2% b/b with 97% yield [30], 5% Zn/CaO with 99% yield [37], 3% CaO-La_2O_3 with 99% yield [19], 2% W-Mo/CaO with 96% yield [44]. In Tab. 4 it also shows that the optimal amount of catalyst achieved in a similar catalyst (CaO-CeO_2 and Zn/CaO) is not the same for different types of oil. Similarly, the yield produced is also not the same. The need for the amount of catalyst and the yield obtained depends on the oil feedstock used. The amount of catalyst needed in feedstock with high FFA is more than the feedstock with a low FFA value. After getting the optimal amount of catalyst, adding the amount of catalyst does not increase the yield, it can even reduce the yield of biodiesel. The amount of catalyst that is too much causes the agglomeration of the active site and the formation of soap resulting in the reactants becoming thick or the viscosity of the reactants increasing, thus inhibiting the transesterification reaction [39].

7.3.3 Influence of Reaction Time on Biodiesel Yield

Optimization of reaction time is used to find the optimal reaction time for the conversion of oil into biodiesel. In some time optimization catalysts begin in reactions for one hour to 6 hours. Based on Tab. 4, it can be seen that the reaction time for the formation of biodiesel from non-edible oil occurs between 1 hour and 6 hours, with an average reaction time of 3 hours For bifunctional CaO catalysts from a mixture of super acidic metal oxides such as ZrO_2, La_2O_3, ZnO, W-Mo the time needed to form optimal biodiesel is only 1-2 hours. This time is faster than a mixture of CaO metal oxides with other metal oxides that are alkaline or weak acids. However, the addition of time after reaching the optimal time is not effective against the transesterification reaction because it is not followed by changes in the yield of the biodiesel produced. Biodiesel yield that is not significant with an increase in reaction time is due to an equilibrium reaction between reactants and products [48].

7.3.4 Influence of Mole Ratio of Oil: Methanol to Biodiesel Yield

The Comparison of moles of oil with methanol is one parameter that plays an important role in the reaction of oil transesterification in biodiesel [41]. In the transesterification reaction of oil with a high FFA value, excess methanol is needed to accelerate the reaction and produce biodiesel, because the transesterification reaction of triglycerides to biodiesel is an equilibrium reaction [56]. At Tab. 4, it can be seen that the maximum biodiesel yield achieved in the transesterification reaction of oil to biodiesel was obtained at the mole ratio of oil: methanol between 1:9 to 1:30. The difference in the mole ratio of oil: methanol in each reaction depends on the type of oil and the catalyst used The addition of the amount of methanol after achieving the optimal ratio is not effective against the biodiesel yield. This occurs because too much methanol will flood the active side of the catalyst so that it inhibits protonated TG in the carbonyl group [19,41]. Besides that the excess methanol in the transesterification reaction causes greater energy requirements in the heating process, separating the resulting methanol and glycerol, which can lead to greater production costs [39,48].

8 Mechanism of Oil Transesterification Reaction into Biodiesel Using a Cao-Catalyst and a Modified CaO

Biodiesel is produced from the transesterification of triglycerides (TAGs) from vegeTab. oil, animal fat with methanol assisted by suiTab. catalysts into fatty acid methyl esters (FAME) and glycerol in general, the oil transesterification reaction into biodiesel is presented in Fig. 5.

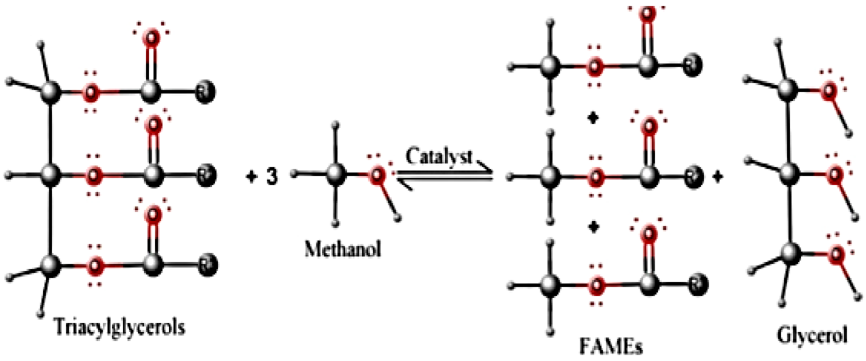


Figure 5: The general mechanism of oil transestrification reaction to FAME and glycerol [1]

Fig. 5 is the mechanism of the overall transesterification reaction. But the reaction consists of 3 stages of the reaction, namely the reaction of triglycerides with methanol to form diglycerides and 1 methyl ester, then the formation of monoglycerides and 2 methyl esters and the third stage is the formation of 3 methyl esters and glycerol [57]. The mechanism of transesterification of oil into biodiesel with heterogeneous base catalysts follows the mechanism of the transesterification reaction with a homogeneous catalyst [1]. In a homogeneous catalyst, the Bronsted base situs mixed with alcohol forms a nucleophilic alkoxide which then attacks the electrophilic group (carbonyl atom) of the triglyceride molecule [58], whereas in the acid catalyst, carbonyl triglyceride group undergoes protonation, and alcohol attack protonated carbon to form tetrahedral intermediates, so that this reaction runs with three reaction stages [59].

8.1 The Mechanism of Transesterification Reaction Using Cao Catalyst

Modified CaO and CaO solids are compatible heterogeneous base catalysts for the reaction of transesterification of oil into biodiesel. The mechanism of the reaction that occurs in the oil transesterification reaction with CaO catalyst consists of two reaction stages, namely the adsorption of the reactants by the surface of the catalyst followed by the reaction between the reactants, then the desorption of the product The catalytic activity of CaO in the transesterification reaction is influenced by the presence of conjugated oxygen anions on the CaO surface [60], which is a strong base [1]. This mechanism is based on the existence of a base degenerate site on the surface of CaO which attacks protons inorganic compounds.

The mechanism of the oil transesterification reaction using CaO Catalyst proposed by Kouzu et al., [49] can be seen in Fig. 6. According to [49] the transesterification reaction begins with the transfer of protons from methanol by the base side to form an anion of methoxide. Anion methoxide then attacks the carbonyl group of triglycerides to form an intermediate of carbonyl alkoxy. At this stage, one FAME and one anionic diglyceride molecule will be formed. In the next stage, the attack of methoxide anion against carbonyl diglyceride group forms one FAME and one anionic monoglyceride molecule. In step 3 the carbonyl group attacks the carbonyl group again from monoglyceride to form FAME and glycerol. Of the three reaction stages, 3 FAME and glycerol were obtained as by-products [49].

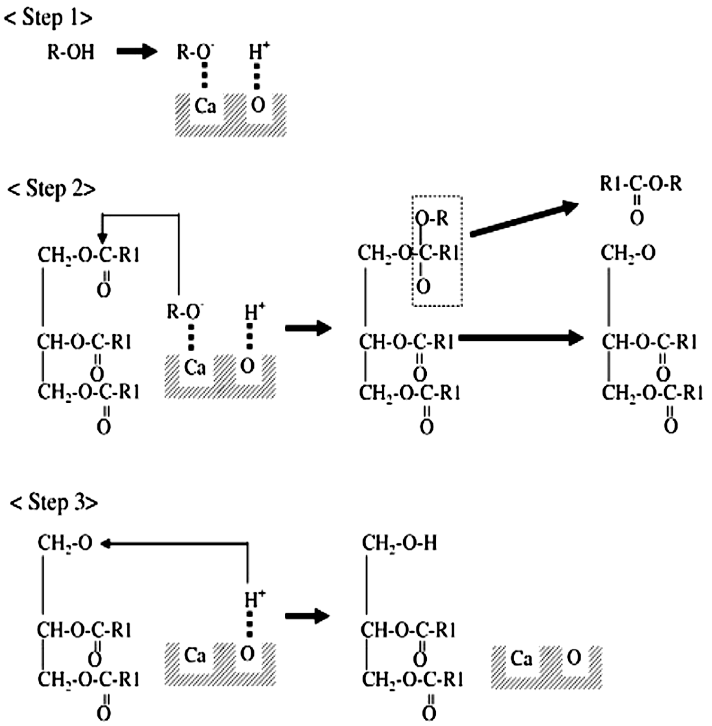


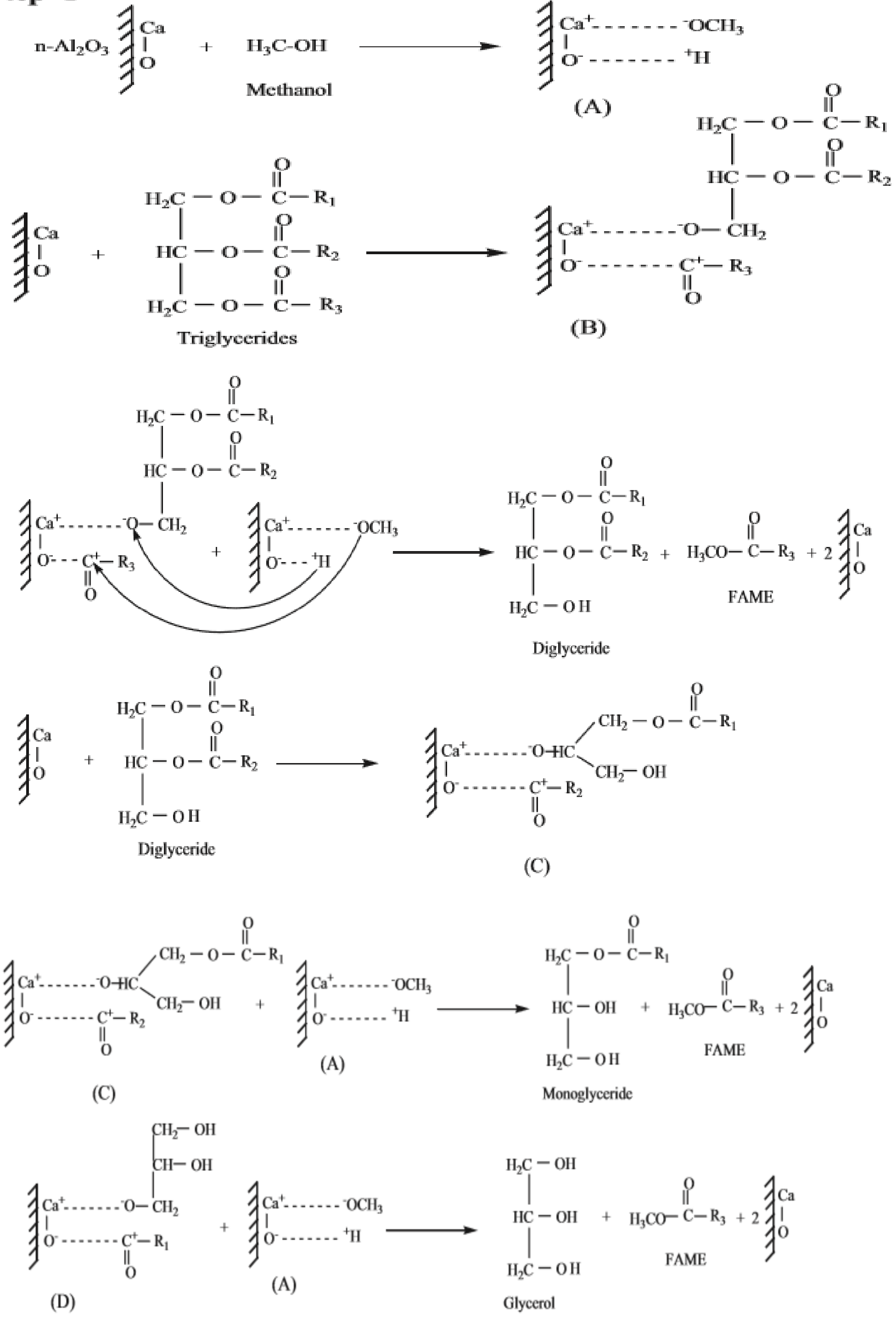
Figure 6: The mechanism of transesterification reaction using CaO catalyst [49]

8.2 The Mechanism of Transesterification Reaction Using Cao/Al_2o_3 Catalyst

The mechanism of the soybean oil transesterification reaction proposed using the CaO/Al_2O_3 catalyst proposed by [60] can be seen in Fig. 7.

In Fig. 7, it is explained that the reaction mechanism consists of two stages. In Stage 1, intermediates A and B are formed between methanol and CaO. The formation of compound A is preceded by a proton bond from oxygen anion which is a Lewis base site, while compound B is formed due to the interaction between Triglyceride TAG and several sites of Lewis base. Formation of FAME occurs because the interaction of the two compounds A and B forms intermediate compounds, DAG and the formation of the catalyst again. DAG interacts to form intermediate compounds C. Compound C reacts with A to form mono glycerol intermediates. Monoglycerol reacts with A to form glycerol and methyl ester accompanied by the formation of the catalyst again. In Stage 2 when glycerol meets CaO it will form calcium glyceroxide with the release of water (H_2O). Two OH groups adjacent to calcium glyceroxide will attack protons from methanol forming hydrogen molecular bonds in compounds E and F. Species F will react with triglycerides to form FAME and degenerate calcium glyceroxide [60].

Step -I


n-Al2O3
Ca
O
H3C-OH
Methanol
(A)
Triglycerides
(B)
Diglyceride
FAME
(C)
Monoglyceride
(D)
Glycerol

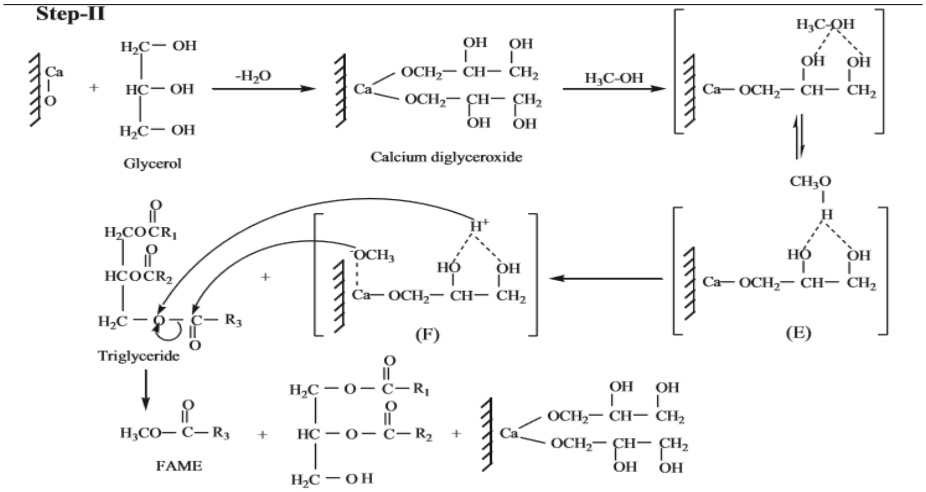


Figure 7: The reaction mechanism proposed in the transesterification reaction of soybean oil with CaO/ Al_2O_3 catalyst [60]

8.3 The Mechanism of the Transesterification Reaction Uses a CaO-Bifunctional Catalyst

The CaO-bifunctional catalyst activity in the oil transesterification reaction is influenced by the acid side and the base of the catalyst. The acidic side of a positively charged bifunctional catalyst functions to absorb fatty acids, while the base side is an active site with a negative charge which functions to adsorb methanol. In heterogeneous base catalyst, the intermediate tetrahedral compound is formed by the reaction between alkoxide ion and alkyl triglyceride group, which is followed by reaction with alcohol. At the next stage is the rearrangement of intermediates to form FAME and glycerol [81]. The description of the mechanism of transesterification of oil using bifunctional catalyst can be seen in Fig. 8. In heterogeneous acid catalysts, carbocation is formed because the attack of alcoholic nucleophiles produces tetrahedral intermediates, which do not include glycerol and form new esters which regenerate catalysts [51].

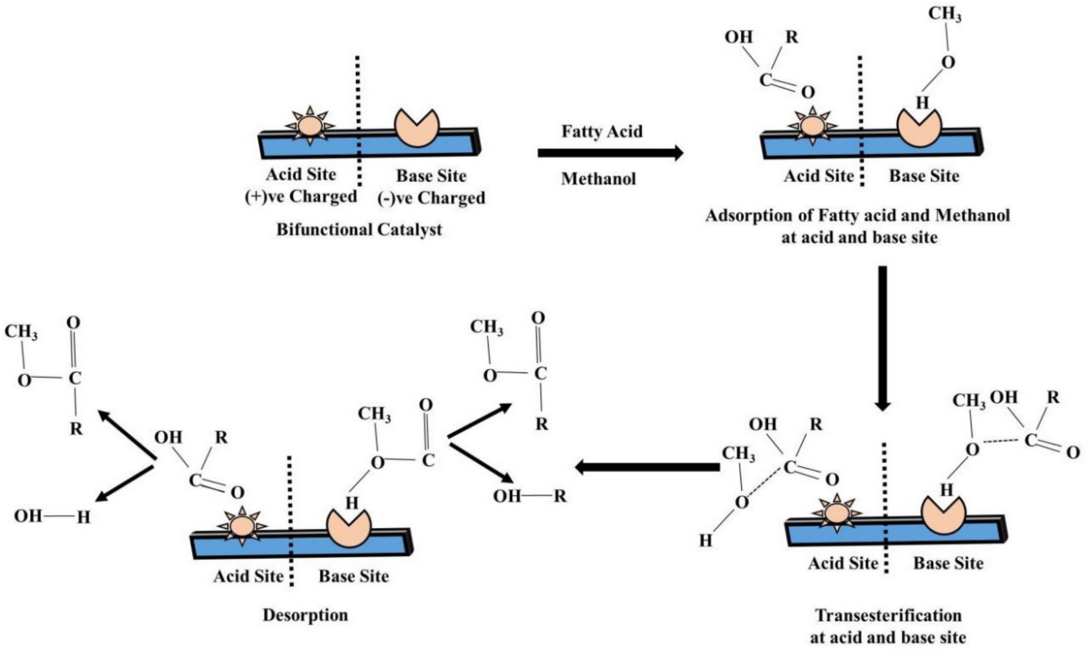


Figure 8: Oil transesterification reaction mechanism using a heterogeneous Bifunctional Acid-base catalyst [81]

9 Reaction Kinetics of Transesterification Reactions with CaO Catalyst

The reaction kinetics takes place. In the transesterification reaction, 1 mole of triglycerides reacts with 3 moles of methanol to produce 3 moles of FAME and 1 mole of glycerol and can be described as follows:

$$\text{TG} + 3\ \text{MeOH} \rightleftarrows 3\ \text{FAME} + \text{glycerol} \tag{1}$$

In general, the reaction rate formula is

$$(-r_A) = -\frac{d[TG]}{dt} = k'.[TG'.MeOH]^3 \tag{2}$$

where [TG] and [MeOH] are concentrations (mol/L) of triglycerides and methanol and k is the reaction rate constant. Transesterification reaction is a reversible reaction so that the addition of excess MeOH will cause a change in balance towards the product. So this transesterification reaction follows the reaction of order 1.

$$-r_A = -\frac{d[TG]}{dt} = k\,.TG' \tag{3}$$

k = k'.[MeOH]^3. The integration of Eq. (3) from the concentration [TG0] at t = 0 becomes the concentration of [TGt] when t = t then

$$\text{Ln}\ [TG_0] - \text{Ln}\ [TG_t] = k.t \tag{4}$$

Eq. (4) is converted to

$$-\text{Ln}\ (1\text{-}X) = k.t \tag{5}$$

Thus the activation energy Ea can be determined from the Arrhenius equation

$$kA\,.\exp(-\frac{Ea}{RT}) \tag{6}$$

where A is the exponential factor, T is the temperature (^{o}K) and R is the gas constant (8.314 j/molK) [61].

Based on Eq. (6) can be seen that the activation energy affects the speed of reaction. The greater the price of Ea, the smaller the reaction speed, because the value of k is inversely proportional to Ea. The results of research Khaur & Ali's [74] in 2014 have shown that the presence of ZrO in CaO catalyst produces activation energy of 29.8 kJ/mol in the castor oil transesterification reaction. This activation energy is smaller when compared to the use of CaO catalyst in the transesterification reaction of vegeTab. oil at 81.09 kJ/mol. Thus the transesterification reaction time with ZrO/CaO catalyst is shorter than using CaO catalyst in the same reaction.

Some models of reaction kinetics in the transesterification reaction from oil sources that are different from methanol using CaO catalyst are shown in Tab. 7. Based on Tab. 7, in general, the transesterification reaction of oil with methanol produces reaction kinetics which follows order 0 or order 1 where the reaction rate is affected by the concentration of triglycerides [1].

Table 7: The kinetic model of several methanolysis reactions with CaO catalysts

Oil	Catalyst	Kinetics Model
Camelina sativa	CaO/0.5	$\frac{dx_A}{dt} = k.(\theta_B - 3.X_A)$
Canola	Mixed CaO-MgO/0.5-6	$-\frac{dC_A}{dt} = 3.9579\ x\ 10^{-3} C_A.{C_B}^{-1/2}$
Soybean	CaO/2	$-\frac{d(1-\gamma_C)}{dt} = \frac{\frac{1}{\emptyset_{oil}}}{\frac{1}{a.k_{DA}} + \frac{1}{a_s.m_A.k_{sA}} + \frac{1}{a_s.m_A.k_{hetero}}}.(1 - Y_C)$
Sunflower	CaO/1–10	$\frac{dx_A}{dt} = \frac{k_{mtA}.k_2}{k_{mtA} + k_2 2} x(1 - X_A)$
Sunflower	Quicklime/1–10	$\frac{dx_A}{dt} = k_m \frac{(1 - x_A).(Cr0 + 3.C_{A0}.x_A}{K + C_{A0}.(1 - x_A)}$
Sunflower (refined, used)	CaO-ZnO/2	$\frac{dx_A}{dt} = \frac{k.(k_{mtA})_0.[1 + \alpha.X_A^{\beta}]}{k + (k_{mtA})_0.[1 + \alpha.X_A^{\beta}]}.(1 - X_A)$

Reference [1]

10 Search Opportunities for Mesopore CaO in the Transesterification Reaction Oil into Biodiesel

CaO is a good catalyst in the oil transesterification reaction into biodiesel because it has a high basicity. CaO is very active in oil transesterification reactions with low FFA, but for oils that have high FFA values, CaO is less effective because it can react with FFA to form soap. To avoid the formation of soap, CaO needs to be combined either through modification with porous material or other metal oxides which can increase the base properties and surface area of the CaO catalyst. However, research on modification of CaO pore as a catalyst has not been done. Therefore the research on the synthesis of mesoporous CaO has a great opportunity to be developed to improve the performance of CaO catalysts because triglycerides are a large material. Addition of surfactants such as CTAB, Ethylene glycol, Polyethylene glycol in CaO material is one way to increase CaO activity through the formation of mesoporous structures between particles. With large pores, it is expected that triglycerides can react easily on the active side of the catalyst. A natural surfactant that has the same activity as CTAB also allows it to be used to form a good mesopore CaO catalyst on the reaction formation of biodiesel. The use of modified CaO catalyst can shorten the reaction time, reduce the need for methanol, the catalyst has a high and sTab. reusability up to 5 times of used. Besides that, it can reduce the cost of procuring basic materials for making biodiesel because it can use non-edible oil which does not compete with food needs and the price is much cheaper than edible oil.

11 Conclusion

Based on the results of the discussion it can be drawn the conclusion that CaO is a heterogeneous base catalyst which is active in the reaction of transesterification of oil into biodiesel because it is influenced by the high alkalinity. CaO catalyst activity can be increased by increasing surface area and increasing the number of base sides through modification of CaO with porous materials such as zeolite, MCM-41 and alumina and CaO composites with other metal oxides which have different acidity and basicity forming a bifunctional catalyst. The mechanism of reaction of CaO as a heterogeneous base catalyst is influenced by the side of the Lewis base on the surface of CaO which will react with methanol to form alkoxide Ca which is followed by reaction of alkoxide Ca with triglyceride to form FAME and glycerol. The kinetics model of the oil transesterification reaction into Biodiesel follows order 0 or order 1 where the reaction rate is affected by the concentration of triglycerides.

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