REVIEW PAPER

Investigation of silicates as a catalyst in biodiesel production: A review

Hassan I. El Shimi[1], Nahed K. Attia[2,*,†], Guzine I. El Diwani[2] and Shakinaz T. El Sheltawy[1]

[1]Chemical Engineering Department, Cairo University, Giza, Egypt
[2]Chemical Engineering and Pilot Plant Department, National Research Center, Giza, Egypt

SUMMARY

Hiking of crude oil prices and diesel fuel shortage is incentive for the researchers to develop bioenergy sources. Biodiesel has environmental beneficial attributes, and its production processes are worthy of continued studies. Many biodiesel production processes are available but, most of them are not on a commercial scale. Biodiesel production using solid catalysts involved fewer unit operations compared with homogeneous catalyzed processes. Many heterogeneous catalysts have been extensively investigated in the recent years and well established. Researchers' focus is how to obtain active and more stable silicates catalyst that can be recycled for several times in the process. Silicates catalyst activity and stability are critically discussed in this work to assess their industrial application, as excessive purification steps could be avoided. This review provides a brief overview on semi-novel heterogeneous catalyst types 'silicates' used in the transesterification of vegetable oils for biodiesel production. Process conditions and leaching out of catalyst active sites are also highlighted. Product quality analysis is presented, in addition to concluded remarks regarding silicates as a selected catalyst. A preliminary economic assessment of biodiesel production catalyzed by the suggested catalyst 'silicates' compared with potassium hydroxide (KOH) and lime (CaO) is performed. Copyright © 2016 John Wiley & Sons, Ltd.

1. INTRODUCTION

Excessive diesel utilization in vehicle fuel stations is increasing the energy crisis worldwide [1,2]. Biodiesel as an ecological fuel can reduce the dependence on classic petrodiesel as it composed of alkyl esters of fatty acids derived from edible or non-edible vegetal oils [3]. Also, animal fats can be used as a feedstock for biofuel synthesis in some countries like France and Germany. Currently, biodiesel is produced by the conventional alkaline catalysts (KOH, NaOH or CH_3ONa) under relatively lower temperatures (50–70 °C) and atmospheric pressure [4]. In this case, neutralization and ultrafiltration steps for reaction mixture are necessaries, and excessive purification for biodiesel is also required, thus leading to use huge amounts of energy and water, and therefore, series of environmental problems are generated. These problems are incentives to search and develop a solid stable and environmental catalyst for alcoholysis process of biodiesel production [1].

Industrially, investigation of basic solid catalysts in biofuel synthesis has relevant limitations; owing to quick poisoning of their surface active sites when exposing the catalyst to atmosphere, because carbonates and hydroxyl groups are created because of the chemisorption of carbon dioxide and moisture, respectively [5,6]. Therefore, it is promising to find stable catalyst, which avoiding the direct exposure to normal atmosphere during its handling from the activation or storage unit into the reactor.

Calcium oxide (CaO) is the common heterogeneous alkaline catalyst experimented in biodiesel production under the same operating conditions employed for homogeneous basic catalysts. CaO has received attention in recent years worldwide as a catalyst for fatty acid methyl esters (FAME) synthesis because of its availability, low purchased cost, and ease preparation even in nanosize. It was used in alcoholysis of sunflower oil, where 94% biodiesel conversion is achieved using catalyst amount of 3%wt, and methanol-to-oil molar ratio of 13:1 at 60 °C for approximately 1.5 h [7]. CaO is pre-calcined at 700 °C for 2 h to desorb CO_2 prior

to transesterification, and hence enhance its catalytic activity. CaO as a heterogeneous catalyst was utilized in biodiesel production from *Jatropha curcas* oil because 93% conversion was obtained using 1.5%wt catalyst concentration and 9:1 alcohol-to-oil molar ratio at 70 °C for 2.5 h. The catalyst is treated with NH_4CO_3 solution followed by calcination at 900 °C to generate super CaO base catalyst; base strength (H−) of 26.5 [8].

However, CaO chemisorbs substantial quantities of H_2O and CO_2 from the atmosphere in few minutes [9,10]. To avoid catalyst deactivation when exposing to air during its storage, a paste of CaO-biodiesel has been recorded to protect CaO from direct contact with air [11,12]. Furthermore, calcium oxide is combined with the process's co-product, glycerol, forming calcium glyceroxide, which is an air exposure tolerant catalyst; however, the process efficiency is reduced because of its weak basicity than fresh CaO [13,14].

Many literatures investigate Li-impregnated CaO and MgO as catalysts in biodiesel synthesis [15–18]. Also, CaO impregnated with Li_2CO_3 was illustrated as an effective catalyst to yield 100% FAME from cottonseed oil using alcohol/oil molar ratio of 12:1 at 65 °C and 2.5 h, even in presence of 2%wt FFA and 5%wt H_2O [16]. Moreover, CaO impregnated with 1.75%wt Li was investigated in biodiesel production from Jatropha oil, as complete reaction was achieved in 2 h at 65 °C using 5% catalyst/oil mass ratio and 12:1 alcohol/oil molar ratio [15].

Many heterogeneous materials were suggested in biodiesel production from virgin or waste vegetable oils such as phosphate rock [19], sodium phosphate, Na_3PO_4 [20], and turkey bone, $Ca_3(PO_4)_2$ [21]. In this research, the author would like to give a detailed review on the investigations of silicates compounds like sodium metasilicate (Na_2SiO_3), calcium silicate ($CaSiO_3$), lithium orthosilicate (Li_4SiO_4), and waste cement concrete as catalysts in biodiesel industry. These catalysts are considered to be semi-novel and perfect materials in biodiesel synthesis. In addition, preliminary economic evaluation was performed for biodiesel production from spent cooking oils using sodium silicate (Na_2SiO_3) compared with potassium hydroxide (KOH) and calcium oxide (CaO).

2. CHARACTERISTICS AND USES OF SILICATES

As mentioned, silicate components are white powder and soluble in water, producing stable alkaline or neutral solutions. In acidic solutions, the silicate ion SiO_3^{2-} reacts with the hydrogen ions H^+ producing silicic acid, which on heating forms glassy hard substance, silica gel. Table I illustrates the physicochemical and thermodynamics characteristics of sodium silicates (Na_2SiO_3).

Silicates have many industrial applications as a metal source; binder and adhesive, corrosion control agent, and builder in detergents industry. Also, it is investigated in the paper and pulp industry to improve the efficiency and brightness of peroxide bleaching.

3. PRODUCTION OF SILICATE COMPOUNDS

Silicate components are produced in solid or liquid phase reaction, where alkaline and quartz silica is investigated as raw materials.
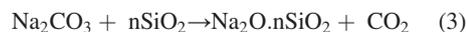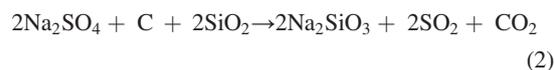
3.1. Liquid phase process

In general, alkali oxide (caustic soda NaOH or lime Ca (OH)$_2$), quartz sand, and water are mixed in a tank and introduced into a reactor, where steam is injected.

$$2NaOH + nSiO_2 \rightarrow Na_2O.nSiO_2 + H_2O \quad (1)$$
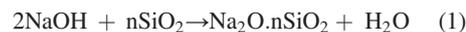
In this reaction, *n* is adjusted according to the specified product properties.

3.2. Solid phase or thermal process

As an example, sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3) are utilized for sodium silicate (Na_2SiO_3) preparation. Either is melted, and then silica (SiO_2) is added for reaction until homogeneous molten solution of sodium silicate is obtained, although the melting point of SiO_2 (>1600 °C) is far above that of Na_2SO_4 and Na_2CO_3 (<900 °C).

$$2Na_2SO_4 + C + 2SiO_2 \rightarrow 2Na_2SiO_3 + 2SO_2 + CO_2 \quad (2)$$

$$Na_2CO_3 + nSiO_2 \rightarrow Na_2O.nSiO_2 + CO_2 \quad (3)$$

In Eq. (3) if *n* = 1, the product is anhydrous sodium metasilicate, which is highly water soluble and highly hydroscopic. In the alcoholysis process of vegetal oils to synthesize biodiesel, this material as a catalyst, will dissolve in the reaction mixture to form NaOH, which enriching the biodiesel yield. Certain quantity of silicate compound will be

Table I. Properties of solid sodium silicate (Na_2SiO_3) compounds.

Property	Mean value
Specific gravity	2.61
Melting point	1088 °C
Solubility in water	22 g/100 ml at 25 °C
	160 g/100 ml at 80 °C
Solubility	Alcohol insoluble
Appearance	White to greenish crystals
Refractive index	1.52
Specific heat capacity, Cv	112 J/mol K
Standard molar entropy, S^o_{298}	114 J/mol K
Standard enthalpy of formation, ΔH^o_{298}	−1561 kJ/mol
Gibbs free energy, ΔG^o	−1427 kJ/mol

Source: https://en.wikipedia.org/wiki/Sodium_silicate. Accessed on January 2016.

lost in the products and moreover the catalyst activity will decreased. To avoid catalyst dissolution, it is promising to manufacture silicate compound wherein, silica-to-metal oxide mass ratio is greater than 3.4. It will be water insoluble and can be catalyze the transesterification process for biodiesel production with high catalytic activity where its alkalinity and stability are excellent [22]. Thereafter, sodium tetra-silicate ($Na_2O.4SiO_2$) is suggested to be a stable transesterification catalyst.

3.3. Manufacturing processes of sodium silicate in Egypt

Soda ash (Na_2CO_3) reacts with sand (SiO_2) in a rotary kiln at approximately 1400–1500 °C to produce sodium silicate in accordance with Eq. (3) as follows:

- Soda ash and silica are fed from storage silos to weighing units to adjust the correct/desired proportions.
- The materials are then discharged to a blender for mixing.
- A water spray is performed for dust control during feedstock's agitation.
- The raw materials are introduced to the rotary kiln for reaction, because the temperature is raised to 1500 °C producing molten solution of sodium silicate with CO_2 generation as a co-product. It is recommended to build algae farms there because CO_2 is required for algal strains cultivation [1].
- On the reaction, the moisture in raw materials or generated from spraying operation will be evaporated.

- Granular sodium silicate is yielded through quenching operation in which, the molten reaction product is discharged to a steel casting belt cooled from the blow with cooling water contact.
- At the end, sodium silicate pellets are stored in the specified storage area.

3.4. Process drawbacks

- Energy consumption inside the rotary kiln is excessive because of the high calcination temperature (1500 °C) required for reaction.
- Air pollution because of the dust, sulfur oxides and nitrogen oxides emissions.
- High maintenance expenses of kilns because of the attack possibility in the refractory materials by soda ash.

In general, soda ash (Na_2CO_3) is melted in the furnace at a temperature below 900 °C, but quartz sand is at 1600 °C, and the mixture is stirred continuously until molten solution is achieved. To ensure complete reaction, it is required to leave the homogenous mixture for another 15 min, and then the contents are passed through a spraying nozzle before quenching into cold water bath to obtain the required product particle size and shape; therefore, this product can be considered as a standard catalyst in biodiesel synthesis process with specified SiO_2-to-Na_2O weight ratio. The suggested industrial processes of sodium silicate plant are shown in Figure 1.
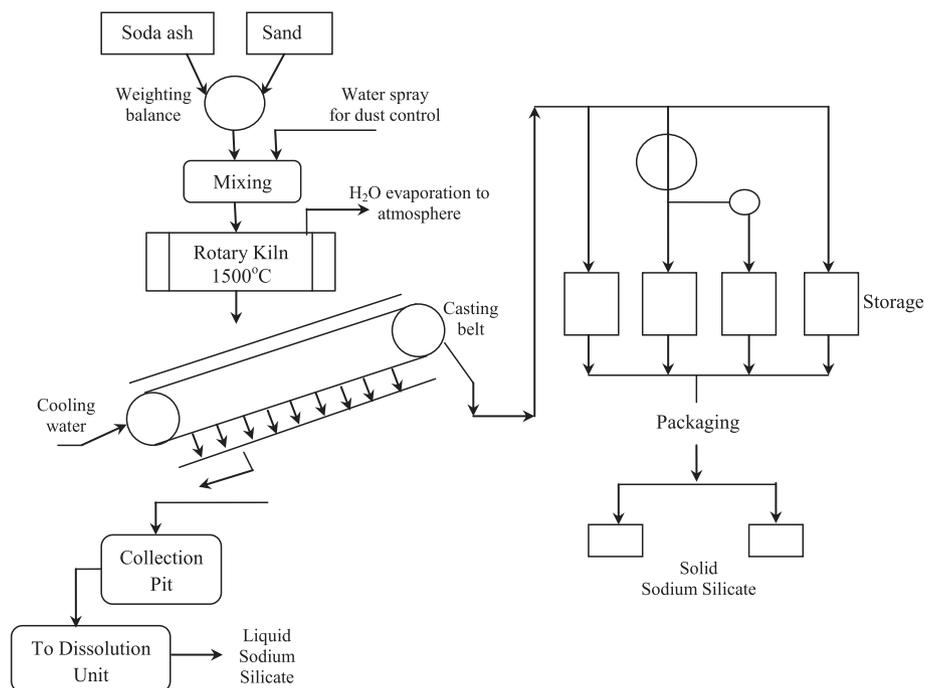

Figure 1. Suggested industrial processes for sodium silicate manufacturing.

4. TRANSESTERIFICATION PROCEDURE USING SILICATES CATALYSTS

In general, biodiesel manufacturing using solid catalysts involved fewer unit operations compared with KOH and H_2SO_4 catalyzed processes [23,24]. The feedstock oil is firstly filtered and heated to the specified temperature (e.g., 65 °C), and then reacts with the alcohol in presence of solid catalyst. After reaction completion, the catalyst was removed through settlers or hydro-cyclones to be used in the next batch. The products mixture is distilled under vacuum to recover the excess methanol, and then transferred into a decanter. Two distinct layers of biodiesel and glycerol are separated because of the densities difference of 0.86 and 1.22 g/ml, respectively. The glycerol (99% purity) is stored, while the FAMEs are treated before storage. Because minor part of silicate catalyst, alcohol, and glycerol traces may be dissolved in biodiesel, so it must get rid of these impurities. In the fuel treatment process, a fine hot water (55 °C) mist is sprayed over the fuel for two times. The fuel's residues are removed as the water settles to the bottom of the tank. The water layer is then decanted, and the biodiesel is dried before storing as shown in Figure 2 [25].

4.1. Sodium silicate (Na₂SiO₃)

Alcoholysis process of triglycerides is catalyzed previously by many solid materials such as alkali earth metal oxides [26,27], supported base catalysts [28–30], alkali metal phosphates [19,20], and waste materials [21,31,32]. Most of the solid catalysts are not FFAs or water tolerant, so soaps are not formed during the process especially in case of dirty feedstock. Perfect catalyst is that recycled to the

reaction several runs without activity decline, regardless the purity of raw material. Still, these catalysts are not available, and its preparation will be costly. Alkali metal carbonates (e.g., soda ash, Na_2CO_3) are also conducted for biodiesel production from feedstock of high moisture content that was eliminated by bicarbonate precipitation [33,34]. The catalysis of transesterification reaction by carbonates is not excessively illustrated in literatures because of their weak basic activity and the poor reaction kinetics.

Sodium silicate, Na_2SiO_3 was investigated in catalyzing the alcoholysis process of biodiesel production from rapeseed oil [35]. The authors precede the process with a maximum conversion of 99.6% using 3%wt sodium silicate, methanol/oil molar ratio 9/1, reaction time 60 min, reaction temperature 60 °C and stirring rate of 250 rpm, for six consecutive repetition times. Also, they used the same catalyst in lactic acid preparation from crude glycerol under alkaline hydrothermal conditions with a maximum yield of 80.5% [35].

Guo, F. *et al.* [36] were studied the biodiesel manufacturing from soybean oil as a feedstock using calcined sodium metasilicate (CSS). The catalyst is firstly calcined at 400 °C for 2 h to chemosorb CO_2 and then investigated in biodiesel synthesis. The transesterification process was yield approximately 100% of biodiesel under the best operating conditions: alcohol-to-oil molar ratio of 7.5/1, CSS of 3%wt, reaction temperature of 60 °C, process time of 1 h and agitation rate of 250 rpm.

Nanoparticles of Na_2SiO_3 were utilized as a catalyst for biodiesel production from waste cooking oils with acid index of 1.4%, where 30% of methyl esters is yielded using 8%wt catalyst concentration and 6/1 alcohol-to-oil molar ratio at 63 °C after 3 h [37]. This result is consistent with
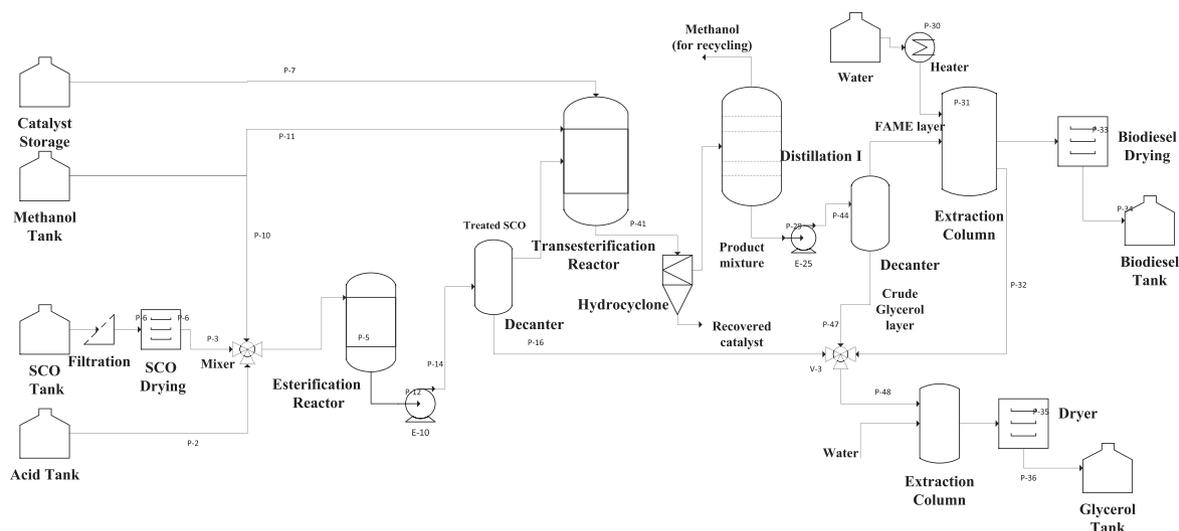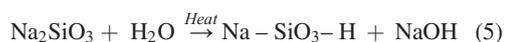

Figure 2. Heterogeneous processes of biodiesel production [25].

that reported by previous researchers on the use of CaO and La_2O_3-ZnO as catalysts for Jatropha biodiesel synthesis [30], and on the WCOs conversion to methyl esters over Ambertyst-15 solid catalyst [38]. However, increasing the reaction temperature will enhance the kinetics by increasing the breaking of reactants molecules bonds, producing in high precipitation of product bonds. In Na_2SiO_3 process, it is expected that temperature increase above 63 °C might precede the transesterification to conversion beyond 30%. In fact, Na_2SiO_3 combine with the moisture forming NaOH, which is the conventional homogenous base catalyst for biodiesel production, and hence it will catalyze the process, but still part of Na^+ ions was lost in the product, and therefore, the catalyst activity is decreased. This speculation is agreed with the process mechanism explained previously by Chang *et al.* [39]. In addition, the solid base catalysts are very sensitive to the low quality raw materials; so the catalyst activity and process kinetics are needed to modify in order to improve the bioester yield.

Sodium silicate reacts with the feedstock moisture to form NaOH, which catalyze the biodiesel process hence, it is different from Na_2CO_3 as the latter produces alkali bicarbonate compounds that decrease the reaction rate. Moreover, Na_2SiO_3 is immiscible with the reaction components where, this immiscibility makes its catalytic activity excellent especially after calcinations [36]. Calcination reactions are usually take place below the melting point of compound or, in other words this process is done at or above the thermal decomposing temperature at which the Gibbs free energy is equal to zero. On calcination, the chemical structure of sodium silicate is changed and the calcined compound will have more regular crystalline nature. Additionally, Si-O-Si extensions were obtained between adjacent SiO_4^{-4} as illustrated Eq. (4) and Na^+ ions are agglomerate randomly around non-bridging oxygen [33,40].

$$Na_2SiO_3.9H_2O \xrightarrow{Heat} Na_2SiO_3 \xrightarrow{Heat} SiO_4^{2-}(calcined\ SS)$$

(4)
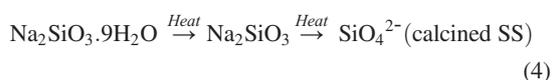
During the process, hydrolysis of Na_2SiO_3 is performed, in which Si-O-H and NaOH are produced Eq. (5) [41,42]. Sodium hydroxide is formed owing to the Na^+ and H^+ ion-exchange and it is greatly active catalyst for transesterification. Herein, soap formation is avoided by the catalyst hydrolysis Eq. (6), if the moisture content of triglycerides is below 4%wt [36].

$$Na_2SiO_3 + H_2O \xrightarrow{Heat} Na - SiO_3 - H + NaOH \quad (5)$$

$$RCOOCH_3 + Na_2SiO_3(Hydrolysis) \rightarrow No\ Soap \quad (6)$$

4.2. Lithium orthosilicate Li_4SiO_4

Catalysis of transesterification reaction by Li_4SiO_4 to produce biodiesel from soybean oil was mentioned previously in few literatures [32], where the molar ratio of

alcohol-to-feedstock (6:1–30:1) and mass ratio of catalyst-to-oil (2–10%) were optimized. The authors used the catalyst directly as it is, without pre-calcination, and they achieve 98.1% of biodiesel at catalyst-to-oil mass ratio of 8%, methanol-to-oil molar ratio of 18:1 and 65 °C for 2 h, and the catalyst was used for 10 cycles without activity loss.

To commercialize the catalyst, it is important to examine the catalytic activity of transesterification process especially in case of catalyst exposure to air. Initially, CaO exhibit high basic strength (15.0 < H− < 18.4), which converts 95.2% of triglycerides into methyl esters, but it deactivated rapidly after 3 min exposure to atmosphere (7.2 < H− < 9.8) because of hydration followed by carbonation reactions on the surface active sites because it produce 2.9% biodiesel after 24 h exposing to ambient air (temp. 28 °C and relative humidity of 52%). This CaO problem limited its industrial application as inert atmosphere is required to handle, store and charge the catalyst to the reactor [13].

In contrast, Li_4SiO_4 has relatively lower basic strength (12.2 < H− < 15.0) than CaO, but its catalytic activity is maintained constant, even after air exposing for 72 h. Hence, no recorded variations manifested in FAME conversion between the fresh Li_4SiO_4 (98.6%) and the air-exposed Li_4SiO_4 for 24 h (98.1%) and for 72 h (96.6%), which proved that the Li_4SiO_4 catalytic sites tolerated air moisture and carbon dioxide. Therefore, lithium orthosilicate is stable solid catalyst with benefit of tolerance to air-exposure, and then facilitated the catalytic process of biodiesel industry.

Capturing of CO_2 is widely studied in recent years because of the huge amounts of green house gases (GHGs) dispersed in atmosphere. Lithium orthosilicate had been investigated as a CO_2 absorbent [43], and the process reaction occurs as follows in Eq. (7) [44]:

$$Li_4SO_{4(s)} + CO_{2\ (g)} \leftrightarrow Li_2CO_{3(s)} + Li_2SiO_{3(s)} \quad (7)$$

Absorption rate of CO_2 by Li_4SiO_4 is slow; hence the latter did not clearly cracks to Li_2CO_3 and Li_2SiO_3 at ambient air temperature or even 65 °C (the maximum transesterification temperature recorded previously in many literatures), as it needs to approximately 720 °C as illustrated in Li_4SiO_4 X-ray diffraction (XRD) patterns [45]. Also, FTIR spectrum detected by Wang *et al.* [46] showing the dispersion of Li_2CO_3 traces on the Li_4SiO_4 surface; however, no clear degradation in the catalytic efficiency of biodiesel process is reported.

However, fresh Li_2CO_3 was investigated as a catalyst in biodiesel synthesis from soybean oil. The catalyst base strength (H−) is fixed in the range of 9.8–12.2, even after 72 h air-exposure, where no obvious difference in the feedstock conversion between the purchased Li_2CO_3 (95.5%) and the air-exposed Li_2CO_3 for 72 h (95.1%). Hence, Li_2CO_3 is more stable than CaO and can catalyze the alcoholysis process of FAME production.

In addition, Li_2SiO_3 similar as Na_2SiO_3 may be utilized in transesterification catalysis. Na_2SiO_3 was previously investigated in literatures as an optimum solid base catalyst for biodiesel manufacturing [36], although it is more hygroscopic and has not tolerance to air-exposure. In contrast, Li_4SiO_4 is a perfect anti-deliquescent compound to air as no further particles adhesion is showed in its SEM patterns, verifying the anti-deliquescent property in atmosphere for at least 24 h.

Li_4SiO_4 hydration was studied using TGA method by Ortiz *et al.* [43], as only 0.045%wt of moisture was absorbed on the compound surface at 26 °C and 60%RH. As mentioned before, traces of Li_2CO_3 were formed over Li_4SiO_4 surface during reaction of LiOH (presented according to hydration) with CO_2 (carbonation process). However, Li_4SiO_4 catalytic activity is maintained stable because Li_2CO_3 was reported as an efficient solid catalyst in biodiesel process. In contrast to CaO, which is fast to chemisorb the air moisture, hence $Ca(OH)_2$ is generated.

TGA analysis of fresh Li_4SiO_4 prepared by solid state method, verified some of weight losses as follows:

- The 1st weight loss is produced at approximately 65 °C; owing to evaporation of residual alcohol
- The 2nd weight loss is attributed to catalyst dehydration in range of 130–250 °C
- The large mass reduction was achieved in range of 490–750 °C because of some complicated reactions between Li compounds (e.g., Li_2CO_3) and Si compounds (like SiO_2) according to the next two steps [47,48]

$$Li_2CO_3 + SiO_2 \rightarrow Li_2SiO_3 + CO_2 \qquad T : 515\text{-}565^oC \tag{8}$$

$$Li_2CO_3 + SiO_2 \rightarrow Li_2SiO_3 + CO_2 \qquad T : 565\text{-}730^oC \tag{9}$$

$$\text{Finally, } Li_2CO_3 + Li_2SiO_3 \rightarrow Li_4SiO_4 + CO_2 \tag{10}$$
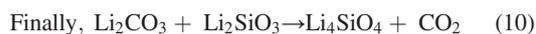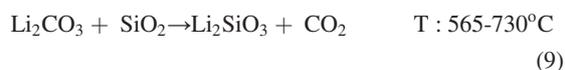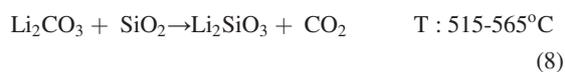
X-ray diffraction patterns estimated by Wang *et al.* [32] did not indicate the presence of Li_2CO_3 impurities on Li_4SiO_4 active sites, but these traces might be created by carbonation reaction of catalyst in air. In general, silicates are detected in the analyses if their concentration is above 3% with crystal size bigger than 3 nm [49]. Differential thermal analysis of catalyst indicate that, the phase transition is performed at 670–710 °C [50]. Thereafter, the mass is decreased continuously in slow rate with an endothermic signal as Li_2O vaporization takes place [51].

4.3. Calcium Silicates (CaSiO₃)

Calcium silicate ($CaSiO_3$) has been used in manufacture of ceramic insulators and as host of phosphors, but its investigation in biodiesel synthesis is not widely appreciable [52–54]). Generally, it is prepared by solid state method,

in which limestone ($CaCO_3$) or CaO reacts with quartz (SiO_2) at approximately 1150–1200 °C for 10 [52,53]. In addition, $CaSiO_3$ could be produced via chemical techniques such as sol–gel, combustion and co-precipitation routes followed by thermal treatment [55,56]. Industrial application of these methods is limited because of some drawbacks like excessive heat consumption, low purity of product, long processing residence time and also inherent hazardous to environment and health.

Calcium silicate ($CaSiO_3$) was used to catalyze transesterification reaction of palm oil; where 86% FAME is performed using 3% catalyst/oil mass ratio, 1:9 oil/alcohol molar ratio and 70 °C for at least 3 h reaction time [57]. The investigated catalyst was prepared by wet sol–gel method using spent CaO (from *Tegillarca granosa* shell) and SiO_2 (from rice husk ash), and the catalyst was activated prior to process by calcination at 400 °C for 6 h in muffle kiln. The authors recommended that, $CaSiO_3$ is a novel catalyst to build continuous biodiesel reactor and produce high quality biofuel and glycerol.

Recently, preparation of $CaSiO_3$ in nanosize has received much attention [58] because of their unique properties. Mechanochemical method of nanoparticles synthesis opens up a brilliant page in the nanotechnology; especially in the field of renewable fuels. This methodology is ease, cheap, energy saving, commercial, and can be used to prepare homogeneous nanosized particles in range of 1–100 nm [59–62]. In contrast to chemical methods, mechnochemical route is solvent-free, waste-free and friendly to environment, and furthermore it carried out at ambient air temperature.

Nanoparticles of $CaSiO_3$ by mechanochemical technique at room temperature without thermal treatment, is a novel process and was not widely illustrated in literatures. Practically, it consumed excessive energy because of the too much processes involved such as mixing, deformation, comminuting and welding the reactant particles in ball mill [63–66]. High purity $CaCO_3$ and dehydrated silica gel (SiO_2) were used to synthesize $CaSiO_3$ at approximately 27 °C by the mechanochemical solid state method in high energy planetary ball mill. The process is summarized in Figure 3.

4.4. Waste Concrete

Today, heavy consumption of natural resources maximized the need to renewable energy sources. Vegetable oils, biomass and spent materials gaining international interest in biofuel industry. Biodiesel is a green alternative fuel to petrodiesel, which is produced by transesterification of triglycerides with methanol in presence of a catalyst. Investigation of homogeneous catalyst in biodiesel production has some serious drawbacks [67], so impetus to develop a stable heterogeneous catalyst has been increased to esterify FFA and transesterify TGs into FAMEs [68–71].

Ordinary Portland cement is abundant worldwide to be used as a binder in construction sector [72]. Egypt had the 5th ranked of cement exporters in 2007 according to the
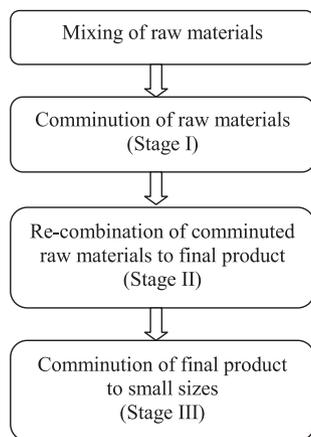
Figure 3. Mechanochemical route of nanosize synthesis [58].

statistics of Foreign Trade Ministry of Egypt. Waste concrete (WC) is composed of cement and chemical admixtures, which is generated from construction sector and has a bad effect to environment. Landfill is the common used method for WC management as there is no economical way to utilize it. Currently, serious law regulations were implemented in developed countries; in order to limit WC dumping sites [73]. Catalysis of biodiesel process using cement concrete not only minimizes the total production cost, but also environmental friendly management plan of WC recycling.

Methanolysis of soybean oil using cement concrete as a heterogeneous catalyst to yield FAME, was experimented in a batch reactor at 65 °C for 3 h with continuous stirring at 900 rpm under various alcohol/oil molar ratio (6/1–24/1), catalyst calcination temperature (150–950 °C) and catalyst/oil weight ratio (1–4%). The conversion yield of FAME could reach 97.6% at 65 °C for 3 h, alcohol/oil molar ratio of 24/1 and 32.8%wt catalyst quantity (cement and aggregate) calcined at 650 °C for 3 h [74]. The authors indicated the efficiency of thermal decomposition in catalyst activation to remove coarse aggregate, and therefore, it can be utilized in industrial biodiesel manufacturing.

Waste cement concrete (WCC) is composed of calcium hydroxide (CH), calcium silicate hydrate (CSH) and calcium aluminates hydrate (CAH) due to reaction of ordinary cement components (C_3S, C_2S, C_3A and C_4AF) with H_2O. Complexity of cement concrete may be explained by XRD curves as Alite (C_3S), Belite (C_2S), $Ca(OH)_2$, CaO and $CaCO_3$ are appeared when the catalyst was calcined in the range of 250–650 °C. The phase change of components is performed on calcination; most of diffraction peaks related to $Ca(OH)_2$ are observed at 250 °C while peaks of CaO were illustrated at 450–650 °C [46]. As reported in many literatures, CaO is active solid catalyst for transesterification process more than $Ca(OH)_2$. The high base strength (H− = 15–18.4) of WCC makes it an active catalyst for FAME synthesis if calcined above 450 °C. Morphology and particle size distribution of waste concrete and cement are identical.

Waste cement concrete was thermally assessed where the moisture is completely evaporated at 120 °C, while gypsum starts to decompose at temperatures above 110 °C. Dehydration of CSH and CAH take place between 175 and 300 °C, and $CaCO_3$ decomposition is achieved beyond 700 °C [75,76].

Fresh cement is tested as a heterogeneous catalyst for methanolysis of soybean oil and the results indicated that about 96.1–98.8% of biodiesel was achieved, when the catalyst is calcined at temperature above 450 °C as below this point, FAME yield is maintained <16%; therefore, dehydroxylation reaction of $Ca(OH)_2$ is suggested to be the reason of catalyst reactivity. Of course, as catalyst amount increased the biodiesel conversion increased, and between 4 and 5%wt, the yield reached to a plateau value. Transesterification reaction requires 3 mol of alcohol for each mole of feedstock, but due to the reversibility of the process, excess alcohol is utilized to shift the equilibrium towards the biodiesel formation.

# 5. STABILITY OF SILICATES IN TRANSESTERIFICATION PROCESS

To improve the biodiesel business using alkali silicate as a catalyst, its stability and reaction mechanism must be firstly studied. Additionally, the catalyst must be standard and recycled for several times in the process without excessive regeneration. Furthermore, solubility of solid catalyst in reaction mixture is of interest to assess its industrial application because excessive products refining processes will be necessary if the utilized catalyst is partly dissolved, hence the fabrication process will become complex.

Testing of catalyst stability can be carried out on laboratory scale in 250 ml three-necked flask fitted with reflux condenser and magnetic stirrer supported by hot plate. Fresh catalyst with an anhydrous alcohol is fed in the reactor at specified temperature (e.g., 60 °C) and agitates the mixture for 1 h. Decantation of suspended mixture is performed using filter paper and the filtrate is further centrifuged at 2000 rpm for 30 min to recycle the fine particles. The recovered solid catalyst is then dried using solar beds for 4 h or in dryer at 110 °C for 2 h to eliminate the absorbed alcohol, and thereafter the catalyst is utilized for the next batch process. The catalyst basicity is then measured using Hammett indicator-titration method [77] where the extracted basic sites of alkali-silicate into alcohol is evaluated as the difference between the fresh and recycled solids, and finally the recovered catalyst is characterized by FT-IR. Some of catalyst species will be leached out in the methanol, and this is the responsible for decreasing of biodiesel conversion.

Guo *et al.* [33] was test the stability of calcined sodium silicate (CSS), and the authors reported that the total basicity of SS is approximately 16 mmol/g. Evaluation of catalyst basicity after washing process that mentioned before, indicating the presence of basic species in the alcohol solution. The leached Na + quantity decreased when the

batches number of washing is increase; therefore, some alkali species of Na_2SiO_3 were soluble in methanol. To investigate the influence of $Na+$ lose on the catalytic activity, the washed SS must be tested in the alcoholysis process of crude oil. Guo *et al.* [33] was proved that calcined SS is still of high activity after five cycles washing with methanol. In addition, the recycled alcohol is high active catalytic specie owing $Na+$, so it can be catalyze the process. But, the biofuel conversion decline as the washing runs rose. Improvement of reaction rate and FAME yield can be achieved by pre-mixture of SS and CH_3OH.

Structural changes of calcined catalyst during the stability test (or washing process) was proved the hydration of Si-O-Na and Si-O-Si, wherein Si-O-Si bridging units were formed by the adjacent SiO_4^{-4} (silicon-oxygen tetrahedral structure) on calcination at $400\,°C$ for $2\,h$ as a best conditions. As a result, CH_3O^- is formed, which is named the active specie required to start the reaction Eq. (11). In other words, sodium methoxide is produced from the hydration reaction Eq. (11) that makes the recycled methanol is of catalytic activity.

$$Na_2SiO_3 + H_3C\text{-}OH \rightarrow SiO_3H^- + Na^+ + H_3C\text{-}O^- \tag{11}$$
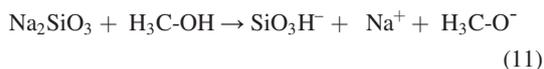
6. TRANSESTERIFICATION MECHANISM PROCEEDED BY ALKALI SILICATE

First of all, alcohol is absorbed on the catalyst surface to start the transesterification of vegetable oil; wherein the mass transfer rate is extremely high. Then, ion exchange between metal ions (e.g., Na^+) and H^+ is performed to yield the active species (CH_3O^-) as illustrated in Eq. (7). Nucleophilic attack of methoxide anion (CH_3O^-) will form tetrahedral unstable compound on the carbonyl carbon atom of oil triglycerides and rearrangement produced the methyl esters. Thereafter, diglycerides are formed by protons transfer into diglycerides anions, and this protons-transfer indicate that metal–silicate (e.g., Na_2SiO_3) is various from a lot of solid alkaline catalysts. The mechanism procedure of process reaction catalyzed by sodium silicate to yield clean biofuel is elucidated in Figure 4.

As well, the diglyceride anions are greatly diffused in the liquid phase and eventually contact to alcohol where hydroxyl can donate proton. Hence, if SS catalyzing the transesterification, two different means of proton-transfer are presented. But, based on molecular calculation recorded by Guo *et al.* [33] SS donate proton easier than hydroxyl group of alcohol. However, continuous exchange of Na^+ in Si-O-Na with H^+ proton in CH_3OH is proceed as the reaction started, because the catalyst active $Na+$ species decreased with repetition of catalyst cycles and the biodiesel yield is also dropped. Methoxide anions (CH_3O^-) are the catalytic efficient species for the biodiesel manufacturing process and their formation depend on the type of solid base catalyst. For example, in case of process catalysis using CaO; the basic site of CaO is O^{2-} surface that leaching H^+ from the feedstock moisture (H_2O) to form OH^-, and then OH^- extracts H^+ proton from alcohol to produce CH_3O^- species [78]. The surface area of CaO is small, and once the glycerol is produced, it is packed or caked that hindering the contact nature between the catalyst basic sites and the alcohol, although CaO generates more if the feedstock moisture is limited by 2.8%wt and prevents the soap formation [69]. Finally, silicate components are of perfect catalytic activity in comparison with other solid base catalysts.
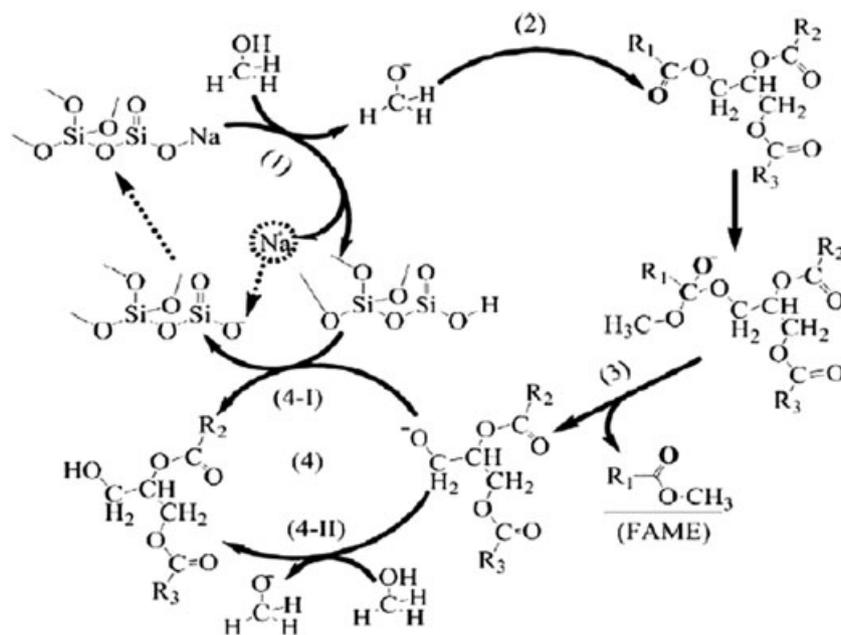

Figure 4. Alcoholysis process mechanism catalyzed by Na_2SiO_3 [33].

7. REUSABILITY OF ALKALI SILICATE CATALYSTS

Successful biodiesel processes may be achieved using solid base catalysts whose recycled by simple filtration or centrifugation, and investigated for the process catalysis several times with cheap reactivation methods. However, the active sites of solid alkaline catalysts are leached out in the product resulting in poor biofuel quality and conversion [79,80].

Long *et al.* [35] achieve 99.6% of biodiesel yield using oil-to-alcohol molar ratio of 1:9 and catalyst amount of 3% wt for only 1 h at 60 °C and 250 rpm from rapeseed oil, but the biofuel conversion was reduced to 92% after five recycling times. This result is in convenient with that reported by Guo *et al.* [33] The decline of catalyst activity is due to the Na + lost by totally 0.2%wt where, ion-exchange between Na + and H+ was performed; therefore, it is the responsible for the decline in methyl esters yield. Moreover, water absorption by sodium silicate followed by alkaline groups loses and explosion of Si-O-Si bonds are also responsible [36].

The activity of sodium silicate may be regenerated by reaction with sodium hydroxide, NaOH at the optimum calcinations temperature (400 °C) as illustrated in Eq. (12) because the hydrolysis process is reversible. This method was reported previously by Guo *et al.* [33]) and the regenerated catalyst was tested in soybean biodiesel synthesis with high performance as 96.5% is yielded in the first time and 85% of biodiesel is achieved after the regenerated sodium silicate was recycled for five runs.

$$\equiv Si - O - H \xrightarrow{400 \circ C} \equiv Si - O - Na + H2O \quad (12)$$
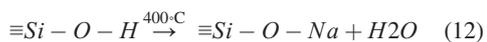
In this manner, the Li_4SiO_4 activity is maintained stable after recovered by centrifugation because 96.1% of biodiesel conversion is obtained after six repetition cycles in transesterification. Also, the product purity is slightly decreased to $94.6 \pm 0.5\%$ when the catalyst is reused 7 to 10 times because of the lower catalyst amount investigated in the next batch than that in the initial run; therefore, the FAME purity is reduced [81]. During the process, Li_4SiO_4 surface is coated with glycerol that generated as a co-product, and it is considered another reason for loss of catalytic activity and declining of biodiesel yield. To make a better comparison, the feedstock and alcohol amounts are minimized to fulfill a constant feedstock/Li_4SiO_4 weight ratio in each successive cycle. Additionally, the catalyst activity can be regenerated by washing with anhydrous methanol and drying at 80 °C in water bath for approximately 1 h because 96.3% of FAME conversion is achieved for at least eight successive cycles.

Lithium orthosilicate is more stable heterogeneous catalyst for recycling in biodiesel industry, in contrast to sodium metasilicate (Na_2SiO_3) and lithium metasilicate (Li_2SiO_3) as they degrade before eight repetition cycles [36,81]. CaO is one of the alkali-earth oxides that demonstrate excellent initial activity in transesterification, but it inter-reacted with the released glycerin forming calcium glyceroxide, and its regeneration is more serious [7,12]. Therefore, Li_4SiO_4 stability is better than that of CaO and Li_2SiO_3 in alcoholysis process of FAME synthesis because its crystalline phase maintained unchanged, and the active sites can be recovered by simple regeneration process.

As a view point, catalyst solubility is critical issue to assessment its industrial application because presence of metals in the reaction mixture requires additional neutralization and purification steps that increase the product manufacturing cost. When Li_4SiO_4 was used for the 1st time, quality control analysis indicate presence of 0.4 ppm of Li in biodiesel and 147 ppm in glycerol; however, the catalyst stability is remained constant because after 3 repetition cycles, the FAME yield was $97.1 \pm 0.4\%$ and also, exposure to atmosphere report the yield at $97.2 \pm 0.3\%$, which demonstrated existence of free Li^+ traces in the biodiesel. In overall, lithium orthosilicate is stable to be applied in biodiesel business.

In contrast, WCC was investigated for 5 cycles; however, catalytic activity is decreased because of calcium diglyceroxide formation by reaction of CaO and glycerol, and therefore, WCC lifetime should be prolonged to be practical in biodiesel commercialization.

8. QUALITY ASSESSMENT OF BIODIESEL

To be utilized as a standard fuel and enhance its commercialization, quality analysis of biodiesel fuel must be performed under the optimal engineering conditions as shown in Table II. The measurements revealed that, the product fulfilled the most important criteria assigned by EN 14214 and ASTM D-6751 and illustrated in Table III [32].

9. BIODIESEL ECONOMICS

Preliminary economic evaluation of biodiesel production from spent cooking oils (SCO) at the optimum conditions reported for transesterification process by KOH, CaO and Na_2SiO_3 has been done and depicted in Table IV. Economic assessment is presented based on the following assumptions and according to the procedure illustrated in [82]. The annual feedstock capacity is assumed to be 600 kt with cost of $380/t, and biodiesel price is $500/t. Glycerol as a co-product will help in minimizing the total biodiesel production cost and its price is suggested to be $200/t. About 80% of used methanol is assumed to be recovered. Operating hours based on three shifts (8 h) per day and 300 working days per year. The storage capacity is suggested to be only one week for raw materials and products.

Table II. Optimum conditions of biodiesel process using alkali-silicates as catalysts.

Component	Catalyst			
	Na_2SiO_3	Li_4SiO_4	$CaSiO_3$	Waste concrete
Raw oil	Rapeseed	Soybean	Palm	Soybean
Reaction time (h)	1	2	3	3
Reaction temperature (°C)	60	65	70	65
Alcohol:oil molar ratio (x:1)	7.5	18	9	24
Catalyst loading (%wt/wt oil)	3	8	3	4
Pressure (atm)	1	1	1	1
Stirring rate (rpm)	250	250	300	300
Biodiesel conversion (%)	99.7	98.1	86	97.6
Recyclability (times)	6	10	1	4
Reference	[36]	[31]	[57]	[46]

Table III. Quality assessment of biodiesel synthesized by Li_4SiO_4 [32].

Property	Unit	Value	EN 14214	ASTM D-6751
Esters content	%wt	98.1	>96.5	—
Free glycerol	%wt	0.008	—	<0.02
Relative density at 15 °C		0.889	0.86–0.9	—
Kinematic viscosity at 40 °C	cSt	4.1	3.5–5.0	1.9–6.0
Flash point	°C	161	>120	>130
Cloud point	°C	—	—	—
Pour point	°C	—	—	—
Cetane no.		54	>51	>47
Iodine no.	g I_2/100 g	115	<120	—
Acid value	mg KOH/g oil	0.1	—	<0.5
Saponification value	mg KOH/g oil	—	—	—
Calorific value	kJ/kg	—	—	—
Sulfur content	mg/kg	2.4	10	15

Table IV. Economic indicators for biodiesel industry using KOH, CaO and Na_2SiO_3 [25].

Item	Catalyst		
	KOH	CaO	Na_2SiO_3
Raw materials, $/year	2.57E + 08	2.72E + 08	2.53E + 08
Annual revenues, $/year	3.14E + 08	3.01E + 08	3.19E + 08
Equipment cost (EC), $	7487000	8350000	6652000
Capital investment (CI), $	29468832	32865600	26182272
Total production cost (TPC), $/year	2.66E + 08	2.86E + 08	2.66E + 08
Net profit, $/year	47599878	15205441	53700928
% rate of return (ROR)	161	46	205
Payback period, year	0.5	1.74	0.4

Electricity cost is using straight line method for 15 years span life. Working capital investment represents 20% of fixed investment as the products are already marketed. Taxes expenses are accounted to be 10% of gross earnings. According to Table IV, biodiesel production from SCO using Na_2SiO_3 as a catalyst could be a good alternative to fossil fuel, leading to savings in foreign exchange for importing and generating employment [25].

10. CONCLUSIONS

This research concluded that for efficient heterogeneous catalyzed biodiesel processes, catalyst activity, stability and its regeneration are important issues. CaO has received attention in recent years worldwide as a catalyst for FAME synthesis because of its availability, cheap price, and ease preparation even in nano-size. However, it chemisorb a substantial quantities of H_2O and CO_2 from the

atmosphere in few minutes during transferring and storing the activated catalyst and combined also with the process co-product, glycerol forming calcium glyceroxide, which is an air exposure tolerant catalyst; however, the process efficiency is reduced. Sodium Silicate (SS) is suggested to be a golden heterogeneous catalyst for biodiesel synthesis because of its excellent water-resistant as in presence of water, hydrolysis taking place forming NaOH and the catalyst is still active. And in contact with alcohol, it is hydrated producing active species CH_3O^- that initiate the reaction, or forming CH_3ONa that catalyze the reaction and also the hydrated SS is still active, in addition, the reused methanol has highly catalytic efficiency. Moreover, the losing active base sites of SS catalyst can be recycled by simple reaction and used again in the catalysis process with excellent efficiency. Therefore, the unique catalytic properties of SS, availability, reproducibility, and its low price could enhance the marketing of biodiesel business in Egypt and worldwide. Lithium ortho-silicate (Li_4SiO_4) is also appeared to be an optimum catalyst in biodiesel manufacturing to replace traditional homogenous alkaline and other heterogeneous catalysts as the reaction time is low enough to commercialize the industry. Moreover, the Li_4SiO_4 is air-insensitive, highly active and available as its preparation is neither costly nor difficult. Additionally, it can be recycled several times in the process. From economic point of view, catalyst is not the controlling factor of biodiesel industry; however, biodiesel production from SCO using Na_2SiO_3 as a catalyst could be a good alternative to fossil fuel with net profit of approximately \$54m and short payback period of 6 months based on 600 kt of feedstock per year and biodiesel price of \$500 per ton, leading to savings in foreign exchange.

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