Preparation and characterization of $CaSO_4$–SiO_2–CaO/SO_4^{2-} composite for biodiesel production

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Abstract: Biodiesel synthesis from waste frying oil (WFO), gained a huge industrial concern compared to the high priced virgin vegetable oils. The major catalysts used in biodiesel production are homogeneous catalysts, which are cheap. However, they have many drawbacks such as, serious separation problems, low biodiesel production yield and production of impure glycerol. This will lead to increase the produced biodiesel price. The latest trend in biodiesel production today is using heterogeneous catalysts that can address the homogeneous catalysts drawbacks. $CaSO_4$–SiO_2–CaO/SO_4^{2-} composites with various SiO_2 to CaO weight ratios were synthesized, characterized by XRD, SEM, EDX, and FTIR. In addition, the prepared composites were used for biodiesel production and for determining the optimum operating conditions using gas chromatograph (GC). The obtained results clearly indicate that $CaSO_4$–SiO_2–CaO/SO_4^{2-} can be used as stable and active catalyst for biodiesel production from WFO.

Keywords: Biodiesel, Heterogeneous Catalyst, Composite, Transesterification, Waste Frying Oil

1. Introduction

Biodiesel has attracted the global attention in recent years as a most notable alternative renewable biodegradable and sustainable source of energy. Biodiesel fuel, as defined by the American Society for Testing and Materials (ASTMs), consists of mono alkyl esters of long chain fatty acids [1-3]. Biodiesel can be produced from different feedstocks: (1) edible oils such as, soybean and sunflower oil (2) and inedible oils such as, jatropha, mango seed, jojoba oil and waste vegetable oils and fats. Biodiesel has many environmental benefits as it can be produced from waste frying oils and fats that are produced by huge quantities and lead to several environmental hazards. In addition, biodiesel contains virtually no sulfur or aromatics, and the use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, particulate matter and the other emissions compared to petro-diesel on its combustion in the diesel engine [4]. Microemulsions [5-7], transesterification and thermal cracking (pyrolysis) [8,9] are different techniques used in biodiesel production.

Transesterification is the most commonly used technique for biodiesel production due to its simplicity. It has been widely studied and industrially used to convert triglycerides which are the main component of the vegetable oil to biodiesel [6]. Today, most biodiesel is produced in presence of homogeneous catalysts like Sodium methoxide [10], potassium hydroxide [11] and sodium hydroxide [12,13]. Previous researches reported that homogeneous catalysts can transform vegetable oil to biodiesel completely in an hour. However, their disadvantages are the complicated processes of biodiesel and glycerol post treatments and pollution [14-17].

As a result of the previous homogeneous catalysts problems, the recent researches focused on finding alternative, suitable heterogeneous catalysts that can give higher yield in addition to its easy separation and avoid pollution [18]. Since the basic catalysts have higher activity than that of acidic catalysts, they have been widely studied. Many researches utilized several types of heterogeneous basic catalysts such as Alkaline earth metal oxides and derivatives such as Be, Mg, Ca, Sr, Ba and Ra oxides and loading aluminum and Al_2O_3 with various other metal oxides, halides, nitrates and alloys. Another researches

utilized carbon based catalyst such as asphalt and biochar, waste materials such as eggshell, mollusk shell, and bones and hydrotalcite metal oxides such as Mg–Al Hydrotalcite [19]. Although the heterogeneous catalysts have enormous advantages in pollution reduction, catalyst separation and glycerol pure production, most of them have some limitations in catalytic preparation method and preparation cost. Many researches mentioned that CaO is very efficient in biodiesel production with a low biodiesel production cost. However, using CaO alone as a heterogeneous catalyst leads to saponification reaction and many separation difficulties [20]. Hence, many researches tended to use CaO with other alkaline metal oxides to address the saponification problem [20-22]. Heterogeneous acidic catalyst $SO_4^{2-}/SnO_2–SiO_2$ was prepared and used in the transesterification of waste cooking oil with mixed methanol–ethanol to produce biodiesel [23].

This study aims to prepare $CaSO_4–SiO_2–CaO/SO_4^{2-}$, heterogeneous three phases composite, by supporting bi-metal oxides (SiO_2, CaO) and metal sulfate ($CaSO_4$) on sulfated SiO_2 in order to improve the physicochemical properties and catalytic efficiency of the bulk CaO and address the operation and separation difficulties resulted in using CaO alone in biodiesel production. This catalyst catalyzed two reactions with two mechanisms. (1) Esterification reaction, which was catalyzed by SiO_2 and SO_4^{2-} group that have high acidic affinity and can convert the remaining Free Fatty Acids (FFA) in the esterified oil to biodiesel, leading to increase the biodiesel production yield. (2) Transesterification reaction, which is the main reaction in this process, was catalyzed by CaO. The reaction mechanism for CaO catalyzed transesterification is shown in Figure 1. (Step 1) The methoxide ion is attached to the catalyst surface. (Step 2) This group then attacks the carbonyl carbon of the triglyceride (TG) molecule and this results in the formation of a tetrahedral intermediate. (Step 3)Then the intermediate is rearranged to form a diglyceride anion and a mole of methyl ester. The charged-anion is then stabilized by a proton from the catalyst surface to form diglyceride and at the same time regenerates the catalyst. The cycle continues until all three carbonyl centers of the triglyceride have been attacked by the methoxide ions to give one mole of glycerol and three moles of methyl esters (biodiesel).
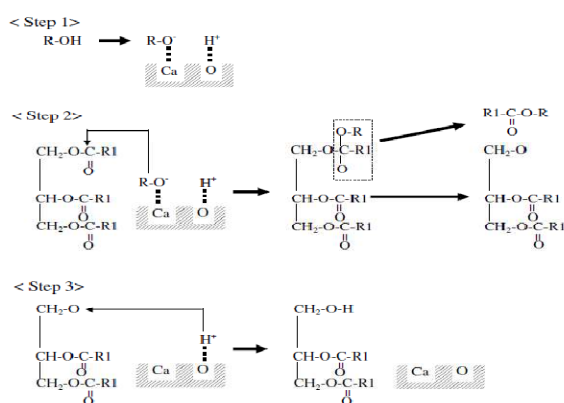

Figure 1. *Mechanism of triglyceride transesterification reaction*

In this study, the composites $CaSO_4–SiO_2–CaO/SO_4^{2-}$ with different SiO_2 to CaO weight ratios were prepared, characterized and utilized in biodiesel production in order to determine the optimum catalyst composition that can produce the highest biodiesel yield. This optimum catalyst was used to investigate the optimum operating conditions such as, time, methanol to oil molar ratio and catalyst loading.

2. Experimental

2.1. Materials

Waste frying oil WFO was supplied from Chipsy Company. The oil chemical composition is summarized in Table 1. Calcium oxide was supplied from Alexandria Company of iron and steel with a commercial grade. Silicon dioxide was supplied from Alfa Aesar A Johnson Matthey Company, sulphuric acid was supplied from ADWIC, El Nasr Pharmaceutical Product Company, assay 97-99% and anhydrous methanol was supplied from Sigma – Aldrich Company, assay > 99.8%.

Table 1. *Chemical composition of waste frying oil*

Fatty acid composition		wt. %
Palmitic	C 16:0	29.75
Stearic	C 18:0	3.08
Oleic	C 18:1	34.01
Linoleic	C 18:2	11.16
Linolenic	C 18:3	8.12
Arachidic	C 20:0	10.98
Behenic	C 22:0	2.06

2.2. Preparation of $CaSO_4–SiO_2–CaO/SO_4^{2-}$ Composite Catalysts

The catalyst had been prepared using impregnation method. Different weight ratios of SiO_2 to CaO were used to prepare calcium sulfate and calcium oxide supported on sulfated silica composite by ratios, 7:1, 5:1, 3:1, 1:1, 0.33:1, 0.2:1 and 0.14:1 SiO_2 to CaO weight ratio. For preparing $CaSO_4–SiO_2–CaO/SO_4^{2-}$ with 1:1 SiO_2 to CaO weight ratio, 20g CaO and 20g amorphous SiO_2 were slowly added to 300 ml of 2 molar (M) H_2SO_4 solutions. The mixture was stirred continuously for 6 h and 600 rpm at ambient temperature. The resulting solid precipitate was filtered and then calcined in muffle furnace at 300 °C for 3 h.

2.3. Catalyst Characterization

X-ray diffraction (XRD) analysis was carried out using (XRD 7000-Schimadzu, Japan), operating at 40 kV and 30 mA with CuKα radiation (λ = 1.5418 Å). The scan measurements were performed at 2θ range of 4-100° with a scan speed of 4°/min in sampling pitch of 0.02° to show the catalysts structure if crystalline or amorphous and to determine the crystals size.

The prepared catalysts were investigated with scanning electron microscope (SEM - JEOL JSM 6360LA, Japan). SEM analysis was carried out at room temperature with accelerating voltage of 20 kV to characterize the sample

morphology and homogeneity of the catalysts. The SEM system equipped with an energy dispersive X-ray spectroscopy (EDX) detector to determine and ensure the elemental composition of the prepared catalysts.

Fourier transforms infrared spectrometer (FTIR) studies was carried out using an (Spectrum BX 11 spectrometer FTIR LX 18-5255 Perkin Elmer). Measurements were conducted in wave number range of 4000–350 cm^{-1}, with 4 cm^{-1} resolution to determine the functional groups that may affect the transesterification reaction and to ensure the preparation of the catalysts.

2.4. Transesterification Reaction and Product Analysis

Esterification and transesterification of WFO was performed in a 250 mL three-neck round bottom flask equipped with a water-cooled reflux condenser and a magnetic stirrer. The system was temperature controlled by a water bath to adjust the reaction temperature. Chipsy waste frying oil was esterified by 6:1 methanol to oil molar ratio in presence of 0.25 % (w H_2SO_4 /w Oil) at 50 °C and 300 rpm for 120 min reaction time. After the esterification process, the oil was washed with water for several times till getting clear oil layer. The oil was then taken for the transesterification reaction that was carried out using $CaSO_4$–SiO_2–CaO/SO_4^{2-} composite catalyst with different SiO_2 to CaO weight ratios to determine the optimum catalyst composition. 40 g of the esterified WFO was added to the three-neck flask and heated to 55°C, then the required volume of methanol (from 3:1 to 15:1 methanol to oil molar ratio) was added to the preheated oil. The optimum prepared catalyst was used with different amounts (from 1 to 7% w Catalyst /w Oil), at adjusted temperature with continuous stirring of 300 rpm in order to achieve uniform temperature and suspension of the entire content of the reaction mixture. After running the reaction time (from 30 to 180 min), the mixture is filtered to separate the catalyst. The biodiesel was then washed with distilled water at 50º C for 2-3 times for removing formed glycerol and excess methanol. Then, biodiesel was heated to 100°C with stirring speed of 150 rpm for 15 to 30 min to remove the water and methanol present in the prepared biodiesel.

2.5. Biodiesel Analysis Method

The conversion of the oil triglycerides to fatty acid methyl esters (FAMEs or biodiesel) yields was determined using a gas chromatograph (GC). The GC device was HP (Hewlett Packard) 6890 GC, (Agilent Technologies / Hewlett Packard Company. U.S.A.). The carrier gas was Nitrogen, with flow 1 ml/min, using FID (Flame Ionization Detector) at temperature 250 °C. The injector temperature was 220°C, injection volume 2 μl, splitlessmode. The temperature program of the GC was as follows: 2 min isothermal at 150ºC, 150-200ºC with 10ºC/min, 9 min held at 200ºC, 200–250ºC with 5ºC/min. The used column was HP-5 (5% diphenyl, 95% dimethyl polysiloxane), 30 m, 0.32 mm ID, and 0.25 μm film thickness at temperature 200–250 ºC with 5 ºC/min. The produced biodiesel yield was determined using the following equation:

$$\% \text{ GC conversion} = \text{Summation area of fatty acid methyl esters/ Total area of all fatty acid methyl esters} \quad (1)$$

3. Results and Discussion

3.1. Catalyst Characterization

3.1.1. X-Ray Diffraction Results (XRD)

X-ray diffraction patterns of $CaSO_4$–SiO_2–CaO/SO_4^{2-} catalyst with various SiO_2 to CaO weight ratios, SiO_2 and CaO are shown in Figure (2a-i). As may be observed from Figure (2a), the structure of SiO_2 is amorphous [24], while CaO is semi crystalline with diffraction peaks at 2θ = 18.03, 34.19, 37.46, 47.25, 50.91 and 54.03 ° as shown in Figure (2i). By supporting CaO and $CaSO_4$ on sulfated SiO_2, new existential state is formed for the composite of $CaSO_4$–SiO_2–CaO/SO_4^{2-} with the all SiO_2 to CaO weight ratios. The amorphous structure of SiO_2 and some peaks of the semi crystalline structure of CaO are vanished as shown in Figure (2b-h) and new crystals of the composite $CaSO_4$–SiO_2–CaO/SO_4^{2-} are formed with new six well distinguished diffraction peaks at 2θ = 25.5, 31.5, 36.34, 38.72, 40.92, 43.42. The small three peaks at 2θ = 48.78, 52.32 and 55.82º are appeared at the semi crystalline structure of CaO Figure (2i) with small shifting and more sharpening according to the more organizing and more crystallization of CaO in the composite than CaO alone. The peaks at 2θ= 25.5, 31.5, 36.34, 38.72, 40.92 and 43.42 ° are attributed to $CaSO_4$ (according to the PDF Card paper - 00-001-0578, the International Centre for Diffraction Data ICDD 2014). Moreover, these peaks are related to strong interaction between SO_4^{2-} group and the metal oxides surface due to the electron infinity of the sulfate preserved the textual properties of the metal oxides [23]. There is no peak associated with SiO_2 in the XRD pattern, suggesting that SiO_2 is highly dispersed in $CaSO_4$ / CaO. Figure 2 shows that, by decreasing the SiO_2 weight ratio against CaO, the degree crystallinity of the catalyst have been proven to increase with higher intensities for the all formed peaks [20]. $CaSO_4$–SiO_2–CaO/SO_4^{2-} composite with 1:1 and 0.33:1 SiO_2 to CaO weight ratio have the most crystalline structure and highest intensities. By decreasing the SiO_2 content in the catalyst and increasing the CaO content the $CaSO_4$ peaks intensities are increased. These phenomena may be related to presence of high amount of CaO which has alkaline affinity to react and attach with SO_4^{2-} group to the surface forming $CaSO_4$. By increasing CaO weight ratio than 0.33:1 SiO_2 to CaO, the degree crystallinity of the catalyst and the peaks intensities have been decreased. It is suggested that the spontaneous dispersion capacity of the CaO phase on the mixture occurred because of the continuous increment of the Ca^{2+} content [20]. Hence, the catalyst structure tend to return to the semi crystalline structure of CaO and some peaks of CaO tend to appear again like the peak at 2θ = 31.96º which presents in $CaSO_4$–SiO_2–CaO/SO_4^{2-} with 0.14:1 SiO_2 to CaO weight ratio.
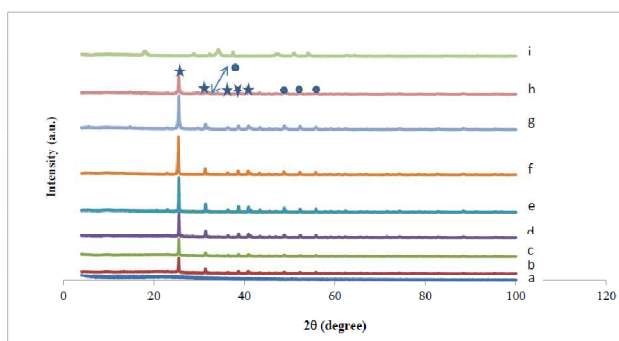
Figure 2. *XRD pattern of (a) SiO₂, (b) 7:1, (c) 5:1, (d) 3:1, (e) 1:1, (f) 0.33:1, (g) 0.2:1, (h) 0.14:1, SiO₂: CaO weight ratio and (i) CaO*

CaSO₄ ★   CaO ●

3.1.2. Crystallite Size
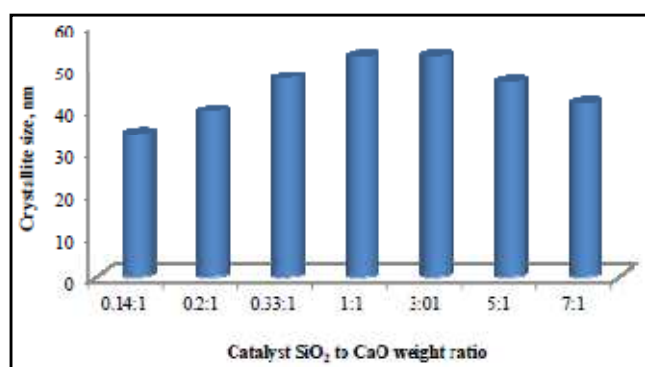
Figure 3. *Crystallite size of the produced catalyst with different SiO₂ to Cao weight ratios*

Crystallite size of $CaSO_4$–SiO_2–CaO/SO_4^{2-} composite particles with all SiO_2 to CaO weight ratios catalyst can be calculated using Debye–Scherer's equation [25]. Figure 3 shows that, by increasing the SiO_2 weight ratio in the produced composite, the crystallite size is increased until 1:1 and 3:1 SiO_2 to CaO weight ratios that have the highest crystallite size. At the higher SiO_2 weight ratios, the crystallite size tends to increase again.

3.1.2. Energy Dispersive X-Ray Spectroscopy (EDX)

The elemental composition of the synthesized $CaSO_4$–SiO_2–CaO/SO_4^{2-} composite catalysts is determined by EDX spectrometer. Several typical points on the surface of each catalyst are selected for the test. EDX results show that the catalysts are consisted of Si, S and Ca elements. Table 2 shows that, the detected actual Si/Ca weight ratios in the composite are very close to the theoretical weight ratios. It is clear that, by decreasing the Si percentage content from 79.9 to 7.1% and increasing Ca percentage content from 11.8 to 52.7% in the composite, the sulfur content is increased from 8.3 to 40.2%. The reason for the sulfur increase may be due to the Si decrease that has acidic properties and Ca increase that has alkaline properties permit S to attach with it.

Table 2. *Elemental composition of the prepared catalysts*

Detected Element	% wt.			Actual
Theoretical Si/Ca weight ratios	Si	Ca	S	Si/Ca weight ratios
7:1	79.9	11.8	8.3	6.77:1
5:1	75.9	15.4	8.7	4.93:1
3:1	63.1	20.5	16.4	3.08:1
1:1	33.9	35.5	30.6	0.96:1
0.33:1	13	48.1	38.9	0.27:1
0.2:1	9.9	51.3	38.8	0.19:1
0.14:1	7.1	52.7	40.2	0.14:1

3.1.3. Fourier Transforms Infrared Spectrometer (FT-IR)

FT-IR spectroscopy, as an effective tool for a semi-quantitative estimation of structural information in complex solids [26], is used to investigate the functional groups in the catalyst. Figure (4a-g) show that, FTIR spectrums for the $CaSO_4$–SiO_2–CaO/SO_4^{2-} composite with various SiO_2 to CaO weight ratios are nearly identical in their % transmittance and their distinguished peaks. FTIR spectrums are recorded in between the region 350 and 4400 cm^{-1}. Strong and broad band detected in the region of 3400–3600 cm^{-1} indicates the presence of physisorbed and coordinated water molecules (–OH bond) in the catalyst. Park et al. reported that the formation of –OH bonds on the surface of solid acid catalyst are essential to enhance its catalytic activities [27]. BrØnsted acid sites referring to sulfuric acid appears as the strong band at wave numbers of 1620 cm^{-1} [28]. Bands at 1156 is related to SO [29]. Bands at 1638 and 1159 cm^{-1} are related to calcium sulfate [30]. The bands at 674 and 597 cm^{-1} represents the Ca-O bonds [31, 32] these bands appear stronger and sharper by increasing the CaO weight ratio. On the other hand, the IR band at 1120 is related to SiO_2 [24] that appear strongly in the high SiO_2 weight ratio. The IR peaks in the region of 380– 400 cm^{-1} are associated with Si-O-Si bending vibration [33]. The decreasing adsorption intensity of the peak in this region between the peak of 400 and the band of 597 cm^{-1} is mainly due to the stretching vibration of S=O and interaction of SiO_2 on the surface of CaO resulted to a weaker bonding of Ca–O [34].
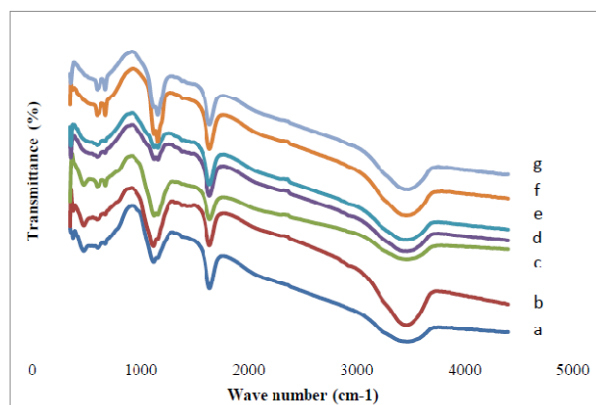

Figure 4. *FTIR image of (a) 7:1, (b) 5:1, (c) 3:1, (d) 1:1, (e) 0.33:1, (f) 0.2:1, (g) 0.14:1 SiO₂: CaO weight ratio.*

3.1.4. Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) micrograph of nano crystalline $CaSO_4$–SiO_2–CaO/SO_4^{2-} catalyst with various SiO_2 to CaO weight ratios are compared to SiO_2 and CaO as shown in Figure (5a-i). SEM images show the surface morphology and the physical features of each catalyst. The SEM images of the catalysts are uneven. SEM of CaO has been measured with two levels of magnification as in Figure (5a) and (6a). These figures show that, the particles are adjacent, hence the CaO particles seem to be compacted and form bulks with a rugged particles surface. The absence of separated particles and the bulk morphology of the CaO may be the reason for the separation difficulties occurred when processing CaO in biodiesel production. There are some separated cavities due to the CO_2 departure during CaO preparation from the limestone [34]. For SiO_2 as shown in Figure (5b), the particles are defined and their shapes are irregular [24]. Figure (5c) shows the SEM of the composite $CaSO_4$–CaO–SiO_2/SO_4^{2-} catalyst of 1:1 SiO_2 to CaO weight ratio. It shows that, mixing by this equal weight ratio leads to CaO bulk particles separation and the particles are well defined with some particles elongation is occurred. The SEM analysis in Figure (5d-f) show that, by decreasing the SiO_2 ratios from 0.33:1 in Figure (5d) to 0.14:1 in Figure (5f) the particles tended to form sheets layers of long plane sheets that seem to be as rods. In case of 0.33:1 SiO_2 to CaO the particles started forming some long wide sheet layers. As the particles content of SiO_2 is decreased the formed sheets tended to lower their width as shown in Figure (5e). The composite of the composition 0.14:1 SiO_2 to CaO shown in Figure (5f) has the lowest SiO_2 content, the lowest particles width and the densest. In this figure, the particles tended to be like needles. The formed sheets and needles consisted of accumulated layers above each other, their appearance is like wood and this morphology is shown clearly with the higher magnification level in Figure (6b). SEM analysis in Figure (5g-i) and (6c) show that, by increasing the SiO_2 weight ratio, the catalyst particles become significantly different and show absence of the rod and needle shaped particles. It is observed that, merging and embedding of CaO with SiO_2 lead to form new shaped particles of the mixture and the spacing between the particles is increased.
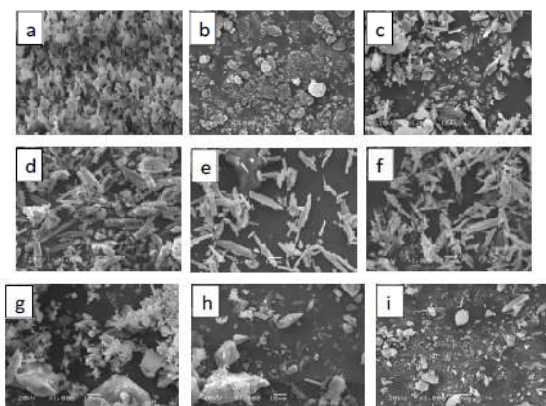
Figure 5. SEM image of (a) CaO, (b) SiO_2, (c) 1:1, (d) 0.33:1, (e) 0.2:1, (f) 0.14:1, (g) 3:1, (h) 5:1, (i) 7:1 SiO_2: CaO weight ratio with magnification factor 1000.
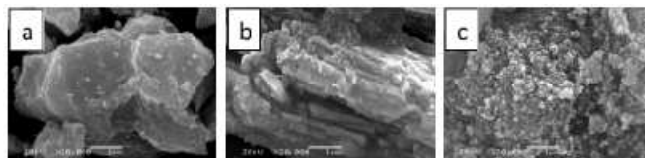
**Figure 6.** SEM image of (a) CaO, (b) 0.33:1, (c) 7:1 SiO_2: CaO weight ratio with magnification factor 20000.

3.2. Studying Factors Affecting Biodiesel Production Yield

3.2.1. Effect of Catalysts Type on Biodiesel Yield

Figure 7 shows a comparison between CaO (the most common heterogeneous catalyst in the researches), SiO_2 and the composite $CaSO_4$–CaO–SiO_2 /SO_4^{2-} with various SiO_2 to CaO weight ratios in biodiesel production yield. The experimental results show that CaO has the highest production yield but it has many operation and separation difficulties. Utilizing SiO_2 as a catalyst for biodiesel production gives the lowest biodiesel production yield, which was expected due to its acidic properties. Transesterification occurs approximately 4000 times slower in the presence of an acidic catalyst than those catalyzed by the same amount of alkaline catalyst [8]. Mixing SiO_2 with CaO in presence of 2M H_2SO_4 improve the biodiesel yield that produced from using SiO_2 alone, and avoid the CaO usage problems. Catalyst composite with 7:1 SiO_2 to CaO weight ratio has a lower biodiesel yield than the other composites. The basicity of CaO is high and between 15 to 18.4 values [35]. Hence, increasing CaO weight ratio increases the composite basicity. Since the transesterification activity depends upon the number of basic sites present in the catalyst as well as their strength, decreasing SiO_2 and increasing the CaO up to 1:1 weight ratio increases the biodiesel production yield. Further increment of Ca content from 1:1 to 0.14:1 SiO_2 to CaO weight ratio increases the Ca presence in the composite surface and reduces the average pore diameter [21]. Hence, $CaSO_4$–CaO–SiO_2/SO_4^{2-} with 1:1 SiO_2 to CaO weight ratio could be considered as the optimum catalyst for the transesterification process and biodiesel production yield.
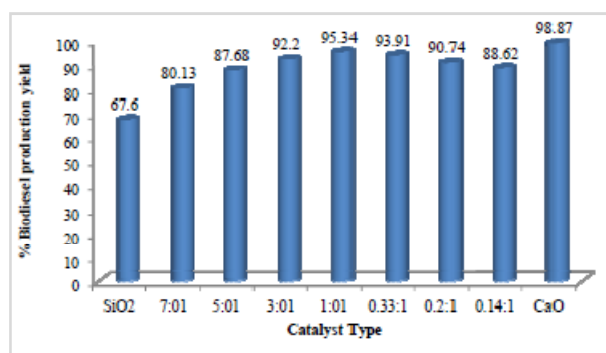
Figure 7. Effect of using SiO_2, $CaSO_4$–CaO–SiO_2/SO_4^{-2} with different SiO_2 to CaO weight ratios and CaO on % biodiesel production yield (during transesterification process in the conditions of 9 : 1 methanol to oil molar ratio at 55 °C and 300 rpm with 3% catalyst loading for 60 min).

3.2.2. Effect of Reaction Time

Figure 8 shows the effect of reaction time on the biodiesel

production yield over the catalyst composite with 1:1 SiO$_2$ to CaO weight ratio. The reaction time is varied from 30 to 180 min. this figure investigates the biodiesel production yield increases slightly from 94.26 to 97.21% during this period. However, with further increase in the reaction time, the biodiesel production yield remains almost constant as a result of near equilibrium conditions. These results agree with Liu et al., [26], Ramachandran et al., [36] and M. Su et al., [37]. Trans-esterification reaction is carried out efficiently after 30 min and there are no remarkable difference of biodiesel yield in the reaction time in the range from 30 to 180 min is recorded.
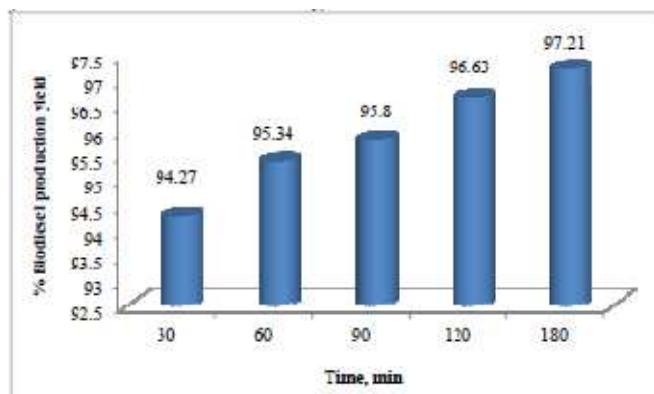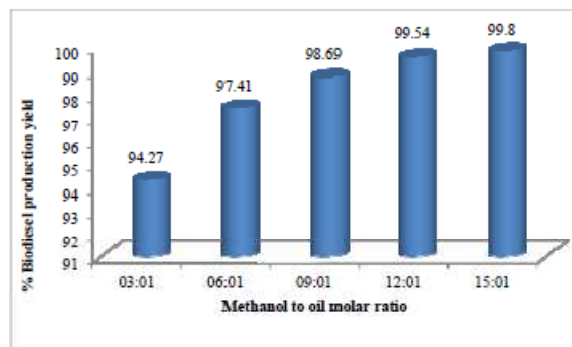

Figure 8. *Effect of transesterification reaction time on % biodiesel yield (during transesterification process in the conditions of 9 : 1 methanol to oil molar ratio at 55 °C and 300 rpm with 3% of 1:1 SiO$_2$: CaO weight ratio catalyst loading).*

3.2.3. Effect of Methanol to Oil Molar Ratio

Another important variable affecting the biodiesel yield is the molar ratio of alcohol to oil. The stoichiometric ratio for the trans-esterification requires three moles of alcohol and one mole of oil to yield three moles of fatty acid alkyl ester and one mole of glycerol. However, trans-esterification is an equilibrium reaction in which excess alcohol is required to drive the reaction to the right. However, too high molar ratio of alcohol to vegetable oil causes an increase in the solubility of glycerol in methyl ester layer, which makes the separation process difficult. When glycerol remains in solution, it helps drive the equilibrium back to the left, lowering the yield of esters. [38]
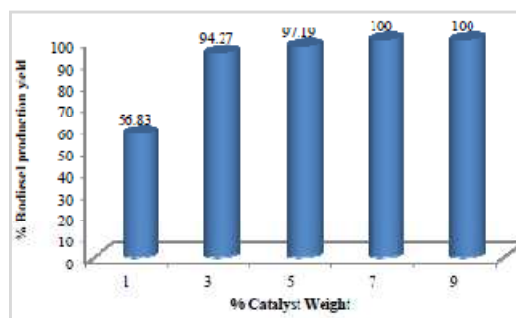
Variations on the methanol to oil molar ratio have been examined in the range (3:1, 6:1, 9:1, 12:1 and 15:1) to study their effect upon the biodiesel production yield. Figure 9 shows that, increasing methanol to oil molar ratio, increases the biodiesel production yield. The % biodiesel production yield is increased from 94.27 to 99.8 % by increasing methanol to oil molar ratio from 3:1 to 15:1. Hence, 3:1 methanol to oil molar ratio can be utilized for biodiesel production from the economical wise. These results agree with Dehkordi and Ghasemi [21] and Xu et al., [39] who found the same trend.

Figure 9. *Effect of Methanol to oil molar ratio on % biodiesel yield (during transesterification process in the conditions of 55 °C and 300 rpm with 3% of 1:1 SiO$_2$: CaO weight ratio catalyst loading for 30 min).*

3.2.4. Effect of Catalyst Loading

Effects of varying the catalyst loading have been studied at the range from 1 to 7 % (w Catalyst /w Oil). The results are displayed in Figure 10, which shows that the biodiesel production yield depends on the amount of catalyst. The catalyst amount of 1% produces the lowest biodiesel yield. By increasing the amount of catalyst, the biodiesel production yield is increased. This is because with more catalyst addition, the total number of available active sites increased resulted in faster reaction rate to reach reaction equilibrium [40]. Using 5, 7 and 9 % (w Catalyst /w Oil), increased the % biodiesel production yield from 97.19 to 100%. Hence, from the economical point of view, 5% (w Catalyst /w Oil) can be considered as the optimum catalyst amount of the composite with 1:1 SiO$_2$ to CaO weight ratio. Further increase in catalyst loading beyond 5% (w Catalyst /w Oil) will have negligible increase in biodiesel production yield. This might be due to the immiscibility of waste cooking oil and methanol, which causes the reaction to be the rate limiting step at the beginning of the reaction. However, as catalyst is introduced in the reaction mixture, it provides an external contact surface area that facilitates the formation of biodiesel. Subsequently, the reaction rate is being controlled by the diffusion of the reactants to the active sites, instead of catalyst loading. Hence, increasing the dosage of catalyst in the reaction mixture will have an insignificant effect on the biodiesel production yield [34]. These results agreed with Kondamudi et al., 2011 [28], Ramachandran et al., [36].

Figure 10. *Effect of 1:1 SiO$_2$: CaO weight ratio catalyst loading on % biodiesel yield (during transesterification process in the conditions of 3:1 methanol to oil molar ratio at 55 °C and 300 rpm for 30 min reaction time).*

4. Conclusion

In conclusion, the composite of CaSO$_4$–SiO$_2$–CaO/SO$_4^{2-}$ with various SiO$_2$ to CaO weight ratios were successfully synthesized. XRD proved that the material is crystalline, SEM helped determining the surface morphology, FTIR detected the existing functional groups and EDX insured the right preparation of the composites. The catalyst showed excellent performance in biodiesel production. The advantages of these composites are that, they could address the CaO operating problems and give higher yield than utilizing SiO$_2$ alone. The experimental results showed that the composite with 1:1 SiO$_2$ to CaO weight ratios has the highest biodiesel production yield. The optimum conditions were a 3:1 methanol to oil molar ratio, 5 wt% (w Catalyst /w Oil) catalysts loading at 55ºC, 300 rpm stirring speed for 30 min reaction time. The simple operation, processing and separation of this catalyst, its low preparation cost and its high efficiency make this composite catalyst a strong candidate for large-scale operation.

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