

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Oleochemicals from Palm Oil for the Petroleum Industry

Ademola Rabi, Samya Elias and
Oluwaseun Oyekola

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.76771>

Abstract

Waste vegetable oils as a sustainable, low-cost and low-toxicity feedstock are attracting more interests for the production of oleochemicals that are excellent substitutes for petroleum-based chemicals widely used in the petroleum industry. The compounds resulting from transesterification-epoxidation-sulfonation of waste vegetable oils have great potential as bio-based surface active agents with extensive application in the petroleum industry. The oleo-surfactant from vegetable oils is gaining increasing attention as alternative to the costlier and non-biodegradable petrochemical-based surfactants currently in use. This chapter reports on cost-effective processes to convert waste palm oil into high-grade surfactants aiming at its filed application in petroleum production to enhance recovery of crude oils from reservoir. The first section focused on the formulation of a high-performance bifunctional solid catalyst with basic and acidic sites that are able to mediate simultaneous esterification and transesterification reactions. In the second part, the methyl esters were epoxidized and then sulfonated to produce the anionic surfactant. The feedstock and the methyl ester produced were analyzed with gas chromatography-mass spectrophotometer (GC-MS) and the sulfonated functional group (S=O) was detected using Fourier-transform infrared spectroscopy (FTIR) analysis.

Keywords: oleochemicals, waste palm oil, surfactants, bifunctional catalyst, esterification, transesterification, epoxidation, sulfonation, enhanced oil recovery

1. Introduction

A cost-effective and sustainable supply of energy sources is of enormous importance to the economy and national security. Oleochemicals are chemicals derived from sustainable

resources that are majorly oils and fats of vegetable and animal origin [1]. These resources are widely available or can be easily cultivated (virgin vegetable oils) or cheaply sourced (waste vegetable oils and animal fat) in virtually all parts of the world. These ecological and economic advantages are responsible for the growing importance of oleochemicals as energy resources and intermediates for manufacturing of industrial chemicals [2, 3]. This is responsible for the renewed research interest in oleochemicals as one of the most cost-effective and widely available substitutes for a number of industrial chemicals and fuels currently derived from fossil fuels [2, 4].

Basic oleochemicals include fatty acids, methyl esters, fatty alcohols of these fatty acids and glycerol [1, 5] as well as fatty amines [6]. With a better understanding of oleochemistry, researchers now variously functionalize triglycerides in vegetable oils to manufacture different useful products [7]. The structure of oleochemicals with the presence of long-chain methylene sequences facilitates a ready functionalization into a wide range of products [8]. The approaches include epoxidation, acrylation of epoxies, transesterification reactions [7, 8] and amidation and amination to generate esters, amides and amines [1]. The sustained interest in the chemistry and conversion of fats and oils and the industrial applications of the bio-based or oleochemicals produced therefrom is being spurred by many factors. Prominent among the drivers is the fast depletion of the world fossil resources, the concern over extreme climatic conditions [7] leading to more stringent environmental standards and regulations and the growing demands for green fuels and cleaner technology with significantly reduced carbon and environmental footprints.

Also there is a growing surplus of fats and waste vegetable oils worldwide resulting in disposal and management challenges. Chhetri et al. [9] citing several sources reported that in 2008, the US produced about 100 million gallons of waste vegetable oil every day. The figures are 135,000 tons/year in Canada, 900,000 tons/year in EU countries while UK produced over 200,000 tons per annum. This is in addition to millions of tons of chicken fats being produced globally every year. The use of waste vegetable oils and non-edible oils in the production processes in place of refined vegetable oils has led to a significant improvement in the economics of oleochemical processes [5]. The conversion of the hitherto waste materials into industrial fuels and chemicals also significantly reduce the environmental impact of the production processes [5].

These have led to the growing awareness of the potentials of waste vegetable oils as sustainable and cost-effective feedstock [10] for the production of industrial chemicals and as energy carriers. Methyl esters produced from the transesterification of triglycerides molecules in the vegetable oils and animal fats with an alcohol [11] are used directly as green fuels (due to its lower emissions of particulate matter and greenhouse gasses) and as chemical intermediates due to its high functionality. Also aiding the extensive uses is the fact that vegetable oils are inherently biodegradable as well as its low toxicity [7]. Epoxidized methyl esters from vegetable oils are used as chemical intermediate to manufacture a variety of industrial chemicals that are ready substitute for petrochemicals [7].

Surfactants are employed in all stages of petroleum production and processing. Usual applications include the use of non-ionic surfactants as demulsifying agents [12], anionics as defoamers

and amphoteric and cationic as corrosion inhibitors and biocides [13]. Surfactants are also essential additives in drilling process operations [14] to reduce water loss and as additives in drilling, completion and fracking fluids to enhance lubricity (for better flow) and pumpability (to control foaming) [15]. It is also put into effective use in the clean-up of crude oil spillages serving as oil slick dispersants or spreader [16] or as oil herder for easy burning [17]. The world production of synthetic surfactants reaches 13 million tons annually, making it an economically important chemical [18].

However, commercial surfactants used in these processes are usually expensive and required in large quantities which limit the economics of the process [19]. Most of these petroleum-based surfactants are also toxic raising concern of their environmental impact [20]. Thus, a less hazardous and cost-effective but high performance surfactant formulation for an efficient oil recovery is required. These have led to interest in green and cost-effective processes for the manufacturing of commercial surfactants from sustainable feedstock [21]. Bio-based surfactants, due to their biodegradability and lower critical micelle concentration [22] are therefore becoming more attractive for the application in the petroleum industry [12]. It was reported that the global biosurfactant market value is expected to grow to around \$25 billion by 2018–2020 [23].

Surfactant is one of the oleochemicals that can be produced from epoxidized methyl esters from palm oil [1]. The sulfonation of the esters has been used to produce methyl ester sulfonate surfactants [15, 18]. The anionic surfactant possesses good surface-active properties [15], excellent detergency and is less sensitive to water hardness [24]. It is therefore projected that the global market for methyl ester sulfonates will experience significant growth as demand for biodegradable surfactants increases [18]. The first-generation feedstock employed to obtain the esters are coconut and soybean oils [25]. These edible oils still dominate the process accounting for more than 95% of biodiesel production [26]. Though easily cultivated and produced, these are relatively costly feedstock and have been the food materials that have ignited the food versus fuel issue [26]. Also, as the cost of edible oils rise due to growing demands, the cost of their derivative surfactants will increase as well [27].

This led to the interest in employing waste vegetable and non-edible oils as the preferred feedstock for commercial production of alternative surfactants [28]. However, a wider utilization of waste vegetable oils for bio-based chemicals production is still limited by the cost of pretreatment [2]. The poor quality of the waste vegetable oils due to high content of free fatty acids and water poses some challenges. Of equal interest is the heterogeneity of these cheap feedstocks in terms of compositions that necessitate pretreatment steps which led to increased cost of production and lower the competitiveness of the bio-products against petroleum-derived alternatives. This chapter presents cost-effective processes to produce a sulfonated surfactant from waste palm oil using heterogeneous bi-functional solid catalysts.

The goal is to synthesize a cheaper and less hazardous surfactant that will be both economical and effective for surface activity as well as reservoir rock wettability alteration to achieve a significant improvement in oil recovery.

2. Application of surfactants to enhance oil recovery

Surfactants are surface active polymeric molecules that contain amphiphilic molecules with hydrophilic part (that is, water soluble or polar) and a hydrophobic or lipophilic part (that is, oil soluble or nonpolar) [29]. These moieties will therefore partition preferentially at the interface of a immiscible fluid system with different degrees of polarity [29]. When introduced into a water-oil system for instance, the surfactant hydrophilic head interacts with water molecules and the hydrophobic tail interacts with the trapped oil [30]. Hence, they dissolve in both aqueous phase (water) and oleic phase (or organic solvents) resulting into reduced interfacial tensions between the phases. They as well alter the wettability of the reservoir rock surface by adsorbing to the liquid-rock interface, thus making the rock surface have a strong attraction toward one of the immiscible fluids, preferably water [31].

In petroleum production, crude recovery from matured fields are declining at a rate faster than the discovery and production of new fields needed to maintain or increase the production rate to meet the energy demand. Therefore, resources are being committed to maximize oil recovery from matured reservoirs and tight rock formations. More than half of the original oil in place (OOIP) remains trapped in the petroleum reservoirs, after conventional production operations. This is attributed to poor sweep efficiency and oil droplets trapped by capillary forces due to high interfacial tension (IFT) between oil and water. There is therefore the need to economically recover more of this residual (or tail end) crude in declining and abandoned wells [12].

More effective enhanced oil recovery (EOR) methods that ensure an economical production of the tail end (trapped oil) from these oil fields are being continuously researched. Such technologies include thermal flooding (steam injection, in-situ combustion), chemical (surfactants, polymers, solvents, alkali) flooding, miscible and immiscible gas displacement, and microbial EOR to produce the hard-to-recover oils in older fields [32–34]. Among these techniques, chemicals flooding techniques have emerged as one of the most effective techniques to improve crude oil recovery from maturing fields. Chemicals (also referred to as micellar) flooding is widely employed due to ease of application and availability of wide range of chemicals. It involves injections of surfactants, polymers and alkali, and their various combination into the reservoirs to mobilize the trapped oil and improve recovery [35].

The alkali-surfactant-polymer (ASP) flooding is the most cost-effective technique, so far having recorded as much as 68% improved recovery from abandoned and depleted oilfield, particularly field past its peak production stage. ASP flooding involves the injection of a mixture of alkali, surfactant, and polymer into the reservoir. It is an effective chemical EOR technique due to the fact that it employs the synergy of the three techniques [35]. It has been employed in the oil industry to, among others, allow for better sweeping of the reservoir by lowering the interfacial tension (IFT) between oil and water (by the surfactant), alter reservoir rock wettability from oil wet to water wet (using the alkali), and to increase the crude mobility ratio (with the polymer). The technique has resulted considerably to improve the recovery factors at additional cost estimated to be as low as US\$2.42 per additional barrel for an onshore field.

A microemulsion of hydrocarbons and water dosed with a large amount of surfactants was found to significantly improve crude recovery [36]. Surfactant flooding is widely employed to manipulate the phase behavior of the reservoir fluids to counteract the high capillary force trapping oil in the pores of the reservoir during enhanced oil recovery process [21, 37, 38]. Surfactant improves the microscopic displacement efficiency by lowering the interfacial tension between oil and water to form a highly stable water-in-oil emulsion as well as between crude oil and rock thus increasing the capillary number, which combines to facilitate greater mobilization of the oil droplets trapped in the reservoir rock [35, 39, 40]. The surface active chemical promotes the formation of microemulsions at the crude oil and the displacing fluid (mostly water) interface [41, 42] thus causing a significant lowering of the fluids' interfacial tension. This is required to efficiently mobilize a substantial percentage of the residual oil toward the production wells to enhance overall crude recovery [43]. Behind the oil bank, the surfactant prevents the mobilized oil from being re-trapped [44].

In the 2000s, oil fields subjected to surfactant-polymer and ASP flooding yielded higher oil recovery compared with those in the late 1970s and 1980s [25]. Improvement in the chemical functionality as a result of better insight into the process schemes is the principal reason for this accomplishment [21]. Since then, surfactants have been considered as an excellent enhanced oil recovery agents due to their ability to considerably reduce the interfacial tension and modify reservoir wetting characteristics. Depending on the nature of the hydrophilic group (head group), the surfactants are classified as anionic, cationic, zwitterionic or amphoteric or nonionic [45]. Typically in this field, anionic surfactants are used in sandstone rock matrices while for carbonate rocks, cationic amphiphiles are surfactants that are more effective. Nonionic surfactants are ideal for high salinity reservoirs, but are most often used as co-surfactants due to their lower surface activity ability [35, 45].

A major challenge with micellar flooding is the loss of surfactant through interaction with reservoir rock [46] and surfactant partitioning into the oil interface [47]. The high cost of production of surfactants makes this potential loss an issue. As previously mentioned, most of the commercial surfactants are petroleum-based and toxic raising concern of sustainability and environmental impact [20]. It is therefore imperative to find alternative, environmentally friendly, and cost-effective processes to produce surfactants on industrial scale from sustainable feedstock. Oleochemical surfactants aside from being biodegradable and less toxic possess other excellent properties suitable for several potential applications in the petroleum industry and a good substitute for the petroleum-based commercial surfactants. These include functionality under extreme conditions and the inherent high specificity [48].

3. Production of methyl esters from waste palm oil

Fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE) are produced from transesterification of glycerides with methanol and ethanol, respectively. The triglycerides which serve as the starting material for the alkyl esters production are found in all vegetable oils, and other edible oils [49] and animal fats. Conventional feedstocks for the alkyl esters production

are vegetable oils from palm, sunflower, groundnut, soybean, cotton, coconut, rapeseed, palm kernel, olive and nonedible oils (for instance, oil from *Jatropha*, sesame, rubber seed, tobacco seed, rice bran, camelina, and karanja) [50]. Other renewable resources such as oils from plant carbohydrates, sucrose, glucose, sorbitol, starches, animal fats and so on, have also been reported for FAME production [51].

Triglycerides (also referred to as phospholipids or triacylglycerols) are triesters of fatty acids [52] comprising of three fatty acid units attached to a three-carbon backbone [53]. A fatty acid is a carboxylic acid containing a long unbranched aliphatic chain of an even number of carbon atoms, from 4 to 2, which can be either saturated or unsaturated [54]. If all carbon atoms of the fatty acid are attached to single bonds, they are considered saturated. Fatty acid molecules are further grouped as monosaturated if the fatty acid molecules have one double bond and polysaturated if it contains more than one double bond (as shown in **Figure 1**). The fatty acid composition of a specific oil sample has a major influence on its reactivity as well as on the physical and performance properties of the esters obtainable therefrom [54]. When the fatty acid molecule is attached to other fragments, it is referred to as free fatty acid (FFA).

Palm oil is a triacylglycerol obtained from the oil palm *Elaeis guineensis* [6]. The fact that palm oil predominantly consist of short-chain (C_8 - C_{10}) and medium-chain (C_{12} - C_{14}) fatty acids (as shown in **Table 1**) therefore makes it a valuable feedstock for the manufacturing of oleochemicals [55]. In fact, close to 60% of the palm kernel oil and about 5% of the palm oil were used for the manufacture of oleochemicals [56]. The rapid increase in production in the last decade has made palm oil the most consumed vegetable oil in the world [57, 58]. Global consumption of vegetable oils in 2016 was reported to be around 184 million tons, of which palm oil accounted for 38.7% while soybean oil, rapeseed oil, and sunflower oil accounted for 28.9, 15, and 8.5%, respectively [59]. An estimated 58 million metric tons of palm oil was reportedly produced in 2016 [60].

Waste or used vegetable oils are cheap source of triglycerides and are widely available in large quantities worldwide. About 29 million tons of waste cooking oil are generated every year [29],

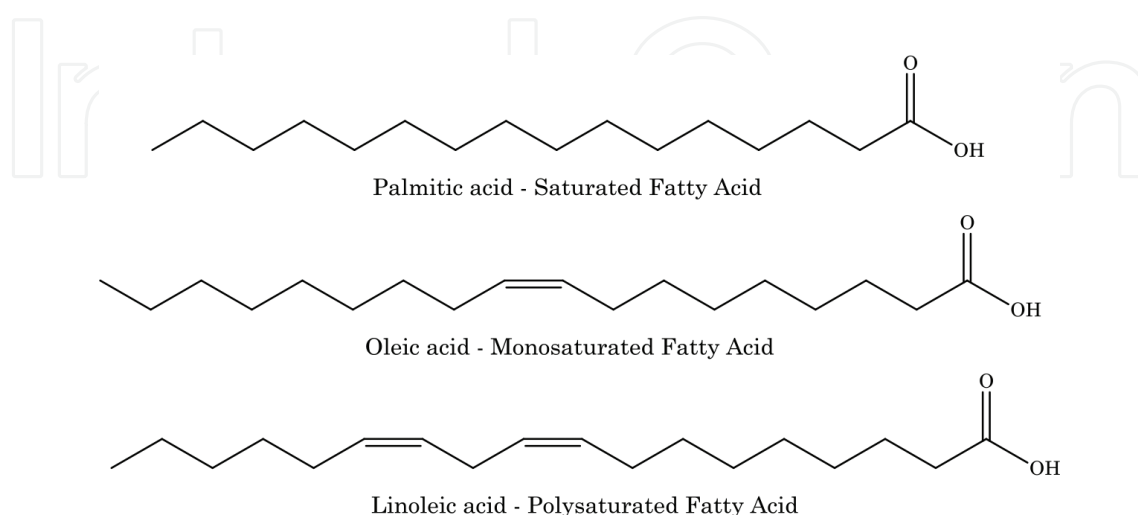


Figure 1. Classification triglyceride molecules.

Fat/oil	Carbon chain (%)										
	8	10	12	14	16	18	18:01	18:02	18:03	20:01	22:01
Tallow				4	30	20	40	5	1		
Palm				2	42	5	41	10			
Soya					8	5	28	53	6		
Palm kernel	4	5	51	15	7	1	15	2			
Coconut	8	7	48	17	9	1	7	2	1		

Table 1. Fatty acids distribution of common oils and fat.

a figure that is expected to increase rapidly as a result of growth in human population and increase in food consumption [61]. Some of waste vegetable oil is utilized in soap making, but the larger volumes are dumped into rivers and landfills with its attendant environmental pollution [62]. The use of waste cooking oil to produce oleochemicals will assist in the reduction of this environmental issue [9] and, at the same time, lower the cost of production. However, the high FFA contents, solids and water impurities in waste vegetable oils will impact on the yield, product quality, and the economic feasibility of the process [63]. A relatively high FFA content in the feedstock will promote saponification of triglycerides forming by-products such as soap and water as illustrated in **Figure 2** [64].

This has resulted in poor yield as well as need for products purification [63, 65]. Waste cooking oils also contain water, which if not removed will promote hydrolysis of triglyceride to form more FFA [66]. The choice of the catalyst is a key factor when producing biodiesel via catalytic transesterification, which is also dependent on the FFA existent in the oil [67]. For virgin vegetable and other oils with a lower FFAs content, base-catalyzed reaction gives a significant conversion in a reasonably short time whereas for oils containing higher FFAs stock, acid-catalyzed esterification followed by transesterification is the best option [68] to prevent hydrolysis of the esters product.

In this work, the goal is to use the fatty acid esters from waste vegetable oils to produce bio-based surfactants. The processes involved simultaneous esterification and transesterification of waste palm oil over bifunctional heterogeneous catalyst to produce alkyl esters (majorly methyl or ethyl esters) and glycerol. The catalyst esterified the FFA into methyl esters in a one-step process and hence eliminated the pretreatment step. The first section of this study focused on formulation of a high performance bifunctional solid catalyst, $\text{CaO}/\text{Al}_2\text{O}_3$, with basic and acidic sites that are able to mediate simultaneous esterification and

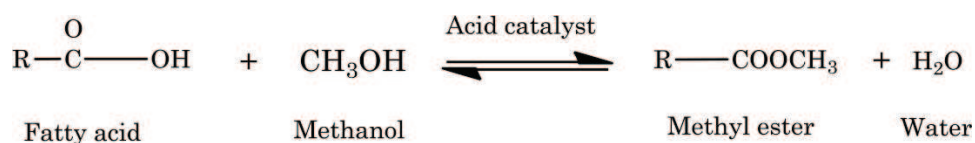


Figure 2. Esterification of free fatty acid reaction.

transesterification reactions for the production of methyl esters from waste vegetable oils. This is necessitated by the high FFA content of waste palm oil. The acidic oxide eliminated the need for the removal of the FFA by converting it to esters via the esterification reaction. The esterification step facilitated by the acidic oxide eliminate acid pretreatment step which is required to remove the FFA and hence costly and as well required disposal of the fatty acid (wastes). The reaction with methanol was investigated over the catalyst in a well stirred batch reactor at an optimum reaction condition.

3.1. Catalysts preparation and characterization

Due to difficulties encountered during homogeneous transesterification, attention was shifted to heterogeneous catalyzed transesterification for methyl ester production [69–74]. The most studied solid heterogeneous catalysts are metal oxides of alkaline earth metals (Mg, Ca, Be, Ba, Sr), mixed oxides, zeolites, γ -alumina as well as hydrotalcites [11, 75]. CaO is mostly utilized due to its cheap price, high activity (due to a relatively high basic strength), long catalyst life as well as moderate reaction conditions [76]. Presently, most of the industrial processes for the production of methyl esters involve the reaction between edible oils and methanol in the presence of an alkaline catalyst [11]. But as mentioned earlier, waste and other cheap oils contain high amounts of FFA and water and are therefore not suitable for the process using an alkali (or even acidic) catalyst owing to simultaneous saponification reaction which lowers yield of the esters.

Teng et al. [77] reported that the presence of water at 4 wt% in rapeseed oil lowered the conversion to 86% from 98%. This is attributed to hydrolysis of the triglycerides in the presence of water. This also causes serious separation and emulsification problems. Consequently, a two-stage process [78] where the feedstock is first pretreated to reduce the content of FFA was developed. It is achieved by the use of catalysts such as ferric sulfate or iron sulfate and sulfuric acid (to remove the FFA), followed by the use of a basic catalyst to produce methyl esters [79]. Patil et al. [80] also reported a two-step process to convert waste cooking oil to methyl esters. The process included esterification reaction for the conversion of FFA to esters using iron sulfate, followed by transesterification of the triglycerides using KOH. However, the two-stage process still faced the issue of catalyst removal in both steps. It was suggested that in the first step, the catalyst removal issue can be prevented by acid catalyst neutralization and by using high quantities of alkaline catalyst in the second step [81]. But the use of extra amount of catalyst will not only add additional costs to methyl ester production, the catalysts must still be removed from the product stream.

Bimetallic solid oxide catalysts with acidic and basic oxide sites are able to efficiently convert high FFA oils into esters due to their ability to facilitate simultaneous esterification and transesterification reactions. These catalysts are also more tolerant of the water in the feedstock while given better esters yield in shorter reaction time [82]. Processing cheap oils with these catalysts requires no neutralization step (to remove the FFA contents) and since they do not dissolve in the reaction mixture, simple products purification steps are required. The catalysts being recyclable give a more sustainable resource management as well.

CaO/Al₂O₃ catalysts with different oxide ratios were studied in the production of methyl esters from waste palm oil. Alumina (Al₂O₃) was chosen as the acidic oxide due to its exceptionally thermal and mechanical stability, large pore size and pore volume, and high specific surface area [83]. The catalyst was produced via the co-precipitation method and characterized using thermal gravimetric analysis (TGA), X-ray diffraction (XRD), Brunner-Emmett-Teller (BET) analysis, scanning electron microscopy with energy dispersive X-ray (SEM-EDX), and transmission electron microscopy (TEM) techniques. All chemicals utilized for the catalyst synthesis were of analytical reagent grade and were used without prior purification. Calcium and aluminum nitrates were used as the basic and acidic oxide precursor salts, while sodium hydroxide was used as the precipitating agent.

A 80% CaO/20% Al₂O₃ (by weight) catalyst is prepared using NaOH to co-precipitate the respective oxyhydroxides from a solution containing the calculated amount of the respective metal nitrates. The required amount of Al(NO₃)₃·9H₂O (Kimix, 98%) and Ca(NO₃)₂·4H₂O (Merck, 99%) were introduced into a 2 L flask. Just enough deionized water to dissolve the salts but to avoid splashing of the solutions during the vigorous stirring was added. The solution was heated to boiling over a Heidolph MR 3001 K hot plate fitted with a thermocouple (Heidolph EKT 3001). The flask and the hot plate are arranged under a Dragon Lab OS20-S overhead stirrer setup. The required amount of NaOH pellets (Merck, 98%) is dissolved in deionized water and brought to boiling as well and added to the boiling nitrate solutions. The solution is maintained at 90°C and stirred vigorously for about 15 min to promote the nucleation-dissolution processes. The stirrer speed was initially set at 1000 rpm, but increased gradually to 2200 rpm as the solution viscosity due to nucleation rises using the high power overhead stirrer.

The solution was allowed to cool for about 20 min and then filtered in a Buckner filter setup fitted with a vacuum pump. The precipitate was washed several times with warm distilled water until the filtrates were free of nitrate confirmed with the silver brown ring test. The precipitates were placed in a convective oven and dried overnight at a temperature of 120°C, to decompose the oxyhydroxides into the desired hydroxides (and possibly oxides). The above procedure was repeated to synthesize other test catalysts but with different basic to acidic oxides ratios, 70% CaO/30% Al₂O₃ and 60% CaO/40% Al₂O₃. A higher ratio of basic (CaO) oxide was used in all cases due to the prevalence of triglycerides in the waste oils.

Prior to reaction, the catalyst powder was calcined to decomposes the hydroxides, activate and stabilize the crystalline structure. First, the calcination temperature required was determined using TGA. The dried precipitate was calcined in a well-defined pattern (**Figure 3**).

This is done with an induction furnace (Kiln Contracts) fitted with Gefran P800 programmable temperature controller with ramping capacity, in flowing air set at the flow rate to fluidized the powder in a fluidized bed reactor. The calcination step involves thermal decomposition, crystallization, and recrystallization processes and some degree of sintering. This step will remove interstitial water in the sample and other volatiles from the solid catalyst precursor. It also helps to convert and stabilize the particles in the crystallite form.

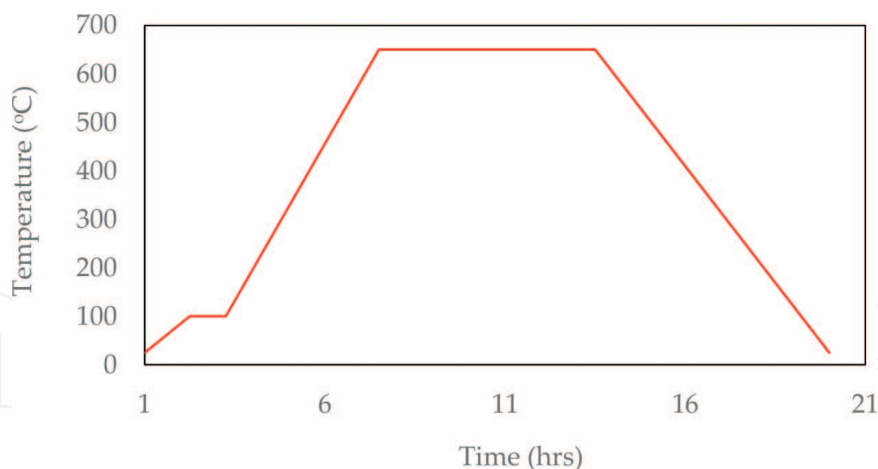
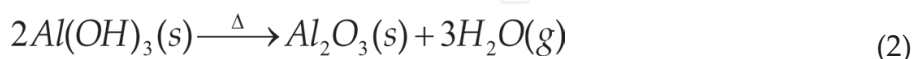
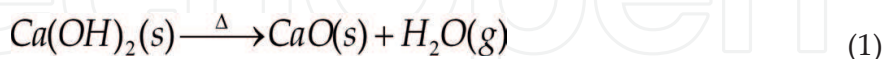


Figure 3. Catalyst calcination pattern.

Samples of the catalyst were characterized to determine among others the thermal behavior, the morphological properties, and elemental compositions. The BET, SEM-EDX, and TEM analyses were used to determine the surface area, particle size, particle size distribution, pore size, the pore volume distribution, elemental composition, and distribution. The bulk phases present were studied using XRD, whereas the reducibility and the maximum degree of reduction of the metal oxides were studied by means of the TGA method.

3.1.1. Thermal stability

Thermogravimetry analysis (TGA) continuously measures the mass and the rate of change in the weight of a sample subjected to a steady increase in temperature in a controlled atmosphere. The TGA profile will typically exhibit weight loss corresponding to various stages in the degradation of the substance. The thermal degradation behavior of the catalyst was performed on the dried sample to obtain the optimum calcination temperature and hence before the calcination step above. This was carried out with a Perkin Elmer TGA7 bench model thermogravimeter analyzer. The dried sample (20 g) was heated from room temperature to 900°C with high flow of nitrogen (100 ml/min) at a heating rate of 20°C/min. The weight change presented in **Figure 4** corresponds to water removal, possible carbon burning, and metals oxidation (Eqs. (1) and (2)) stages.



There was a sharp weight loss at 300°C and then at 600°C to around 750°C. These reduction are as a result of the decomposition of the respective hydroxides to the oxides. Using the thermal profile, 750°C is selected as the calcination temperature for this study.

3.1.2. Scanning electron microscopy analysis

After calcination, the morphology of the catalyst was studied with SEM as shown in **Figure 5**. The figure shows aggregated (interconnected) particles.

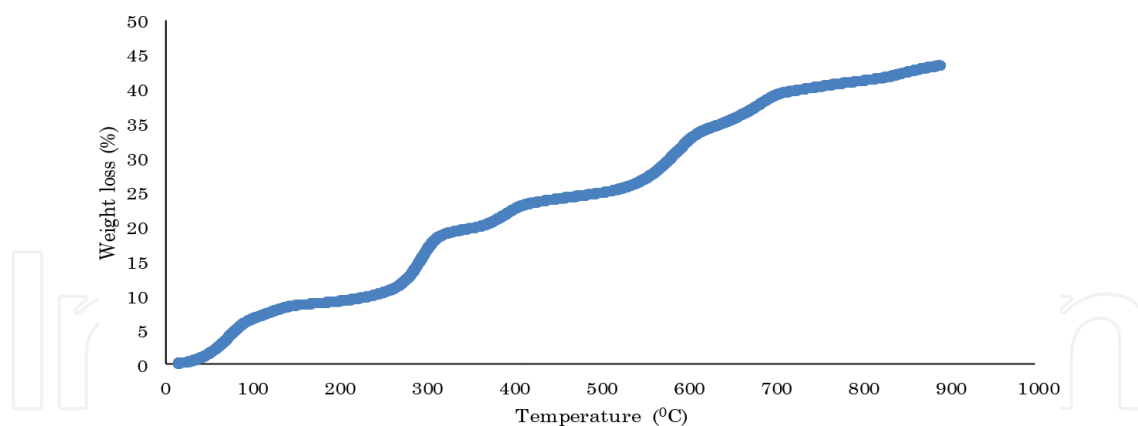


Figure 4. TGA curve for 80% CaO/20% alumina catalyst before calcination.

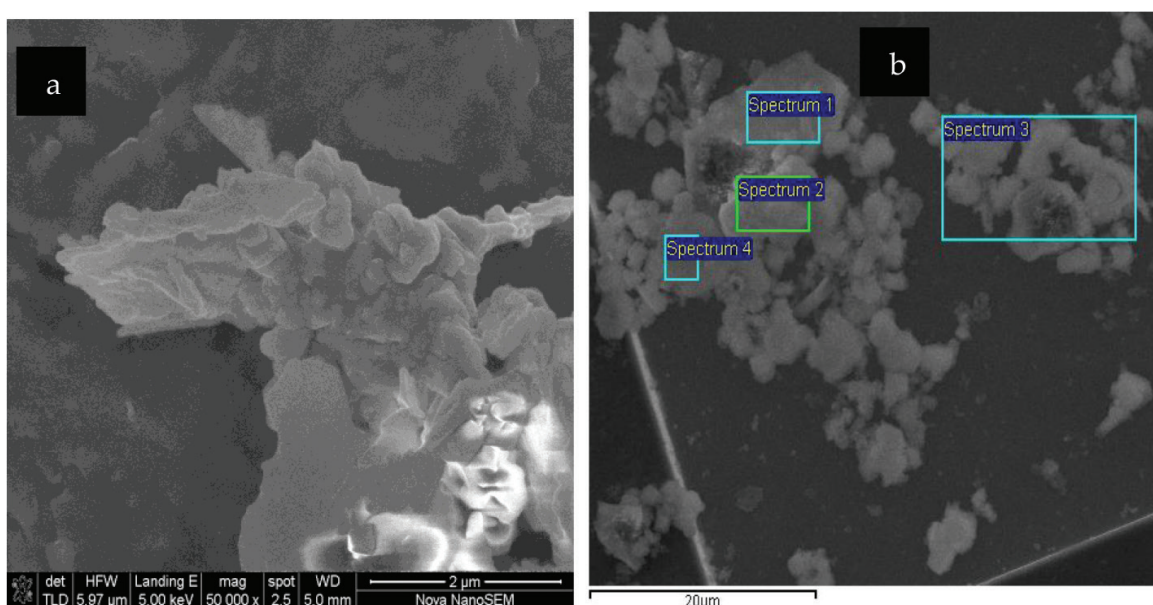


Figure 5. SEM-EDX micrograph of (a) the 80% CaO and (b) showing the areas chosen for EDX analysis at different magnifications.

Figure 6 shows the elemental composition of areas examined (determined by 4 replicates of EDX) for the catalyst sample. The SEM-EDX analysis of the catalyst confirmed the presence of Ca(CaO) and Al(Al_2O_3).

The SEM image also shows that Ca particles were well distributed on Al regardless of the 4.6:1 ratio obtained instead of the expected 4:1 which could have been caused by the impurities in the salts. It also showed a significant homogeneity of the $\text{CaO}/\text{Al}_2\text{O}_3$ catalyst which was visible in the value of Al and Ca acquired from the EDX analysis.

3.1.3. Transmission electron microscopy analysis

The morphology of the particles of the 80% CaO catalyst was studied with the transmission electron microscopy (TEM). **Figure 7** shows the micrograph of the catalyst particles. Most of

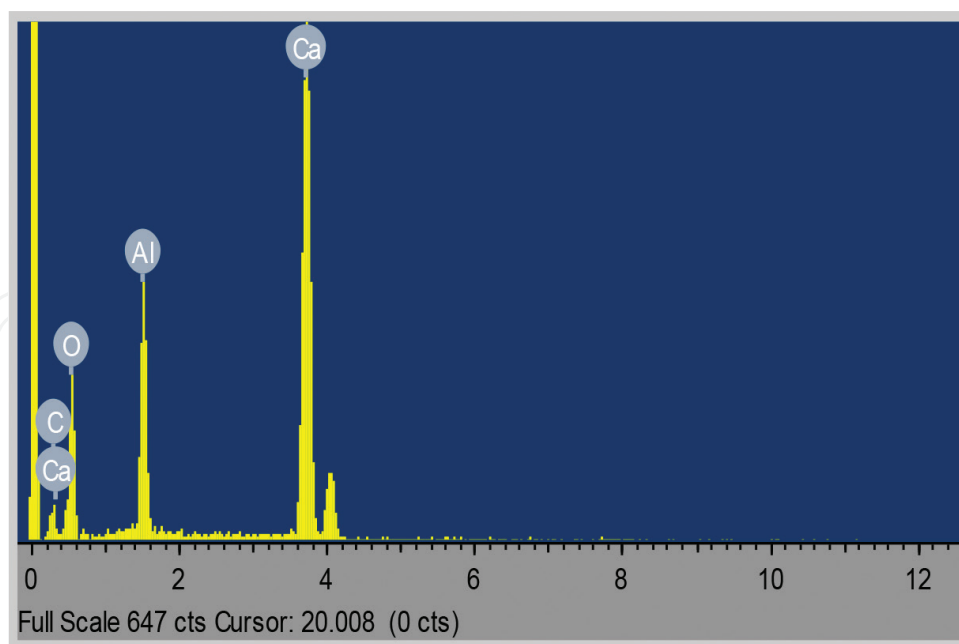


Figure 6. EDX spectrum for 80% CaO/Al₂O₃ catalyst.

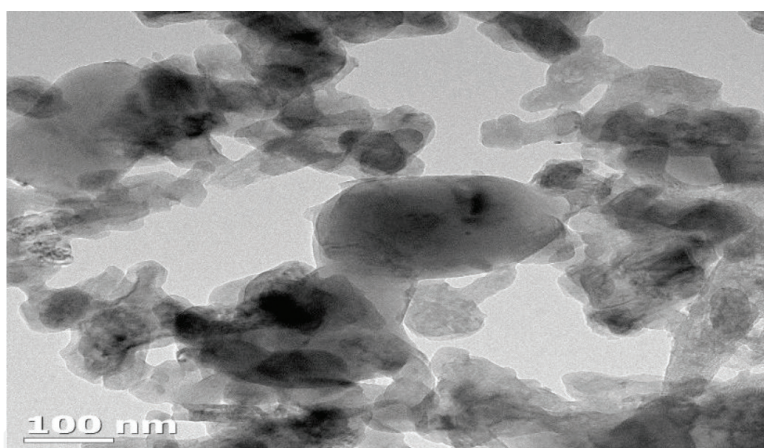


Figure 7. TEM images of the catalyst.

the particles were in the range of 10–100 nm. The porosity of the catalyst particles was confirmed by the TEM image and most of the crystal particles were in rectangular shape.

3.1.4. Bulk phase of catalyst

The qualitative and quantitative X-ray diffraction spectra XRD patterns of the 60, 70, and 80% CaO on Al₂O₃ used in this study are shown in **Figure 8**. The XRD of the catalysts showed expected peaks. A broad reflection of the CaO crystalline phases was clearly observed at 2θ range of 20.0–40.0° for 60, 70, and 80% CaO/Al₂O₃ which supports the presence of highly dispersed CaO particles in all CaO on Al₂O₃ catalysts.

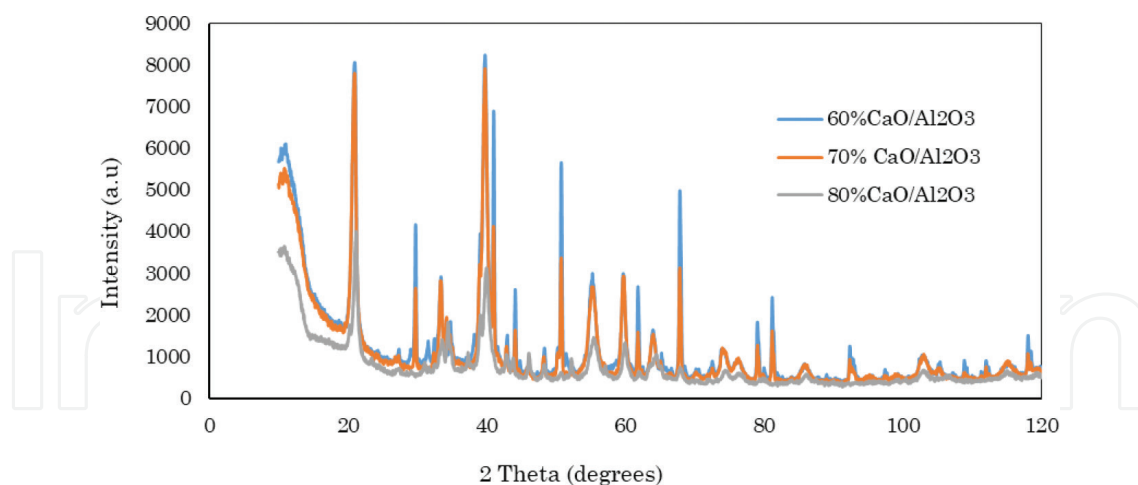


Figure 8. XRD pattern of 60, 70, and 80% CaO wt% catalysts.

There were also some diffraction peaks detected at ~ 51 and $68^\circ 2\theta$ angles which did not correspond to CaO crystalline phases but were identified as hydrated calcium aluminate and alumina crystalline phases. The formation of these phases is expected due to the adsorption of water and CO_2 from air which must have occurred during the XRD analysis [84].

3.2. Methyl esters production

Waste sunflower and waste palm oil were used in this study. The samples FFA contents were found via titration to be 0.3825 and 76.96 mg/g, respectively. These oils were transesterified with a methanol at methanol/oil molar ratio of 9:1 and reaction temperature 65°C for 4 h. The optimum catalyst loading selected for the transesterification of both waste oils was 4 wt% based on previous studies [85, 86]. The effect of basic/acidic oxides ratio on the yield of FAME was investigated by varying the catalyst CaO ratio as 60, 70, and 80%. The yields of the esters are presented in **Figure 9**.

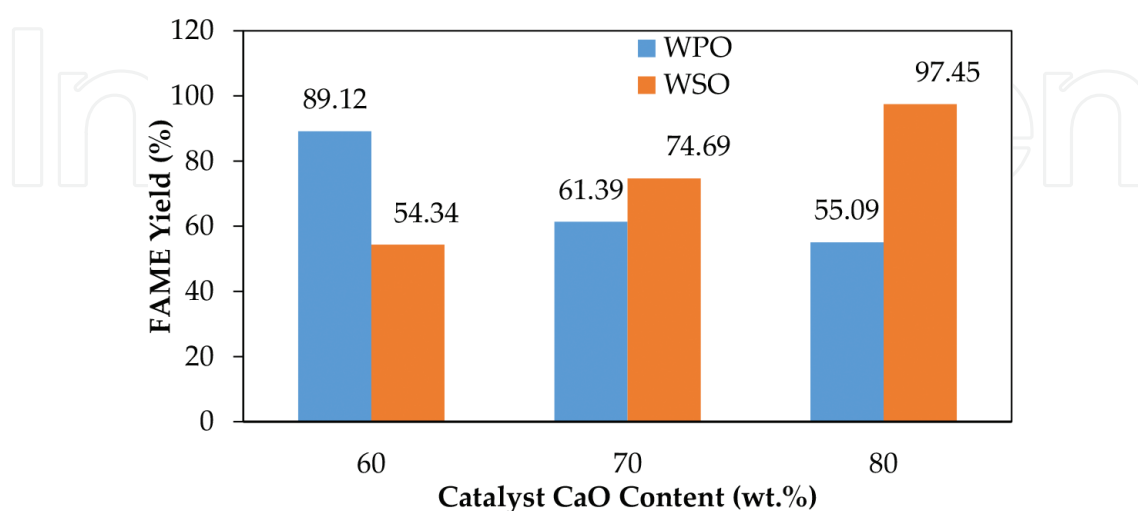


Figure 9. Methyl ester yield versus catalyst CaO content.

A 60% CaO/40% Al₂O₃ catalyst was found to be optimum for waste palm oil, whereas the optimum catalyst ratio for the waste sunflower oil was 80% CaO/20% Al₂O₃ at the same reaction conditions. This is due to the fact that waste palm oil contains higher amount of FFAs, and hence requires more acidic sites on the catalyst to esterify the FFA to FAME. The high yield of FAME obtained despite the low quality of the oils used demonstrated that the use of a bifunctional catalyst will provide an opportunity to lower the cost of production as well as assist in disposal of the waste vegetable oils.

4. Surfactants productions from the methyl esters

Currently, increasing research efforts are going into formulating cheaper, biodegradable, and nontoxic surfactants, because the existing commercial surfactants are mostly slow-degrading compounds produced from petrochemicals [13]. In many instances, the products from their degradation are detrimental to the environment or to humans [87]. The high cost of commercial surfactants imposes additional challenges and limits their widespread application in the petroleum industry. Therefore, to cut down on the surfactant production cost and to satisfy the intended specifications, increasing attention is being giving to agriculturally and waste resources [13] as substitutive feedstock to petroleum for surfactants manufacturing.

Waste and nonedible vegetable oils for the production of surfactant are of interest because utilizing these waste materials will result in low material and processing costs, thus making biosurfactants attractive in large scale applications. It is also biodegradable [18] and the relatively high interfacial tension reduction potential or surface active properties are comparable to synthetic surfactants [15]. Most of ionic and nonionic surfactants are derived from C₁₂ and C₁₄ fatty acids which are abundant in palm kernel and palm oil [1]. The longer chain fatty acids exhibit a high hydrophobicity making it unsuitable for micelle formation and, hence, are used only after necessary modification to increase their polarity [1]. The esters produced in the preceding step were further subjected to epoxidation reaction to reduce the mono- and polyunsaturated esters content and obtain more stable epoxides. Finally, the sulfonated surfactant is produced using sulfonating agents such as sulfuric acid, oleum or chlorosulfonic acid. The fatty acid composition of the methyl esters produced used is analyzed using a GC-MS. The spectra are as shown in **Figure 10**.

The GC-MS confirmed the fatty acids distribution as, saturated fatty acids: palmitic acid (16:0), stearic acid (18:0), arachidic acid (20:0), heneicosylic acid (21:0), behenic acid (22:0), and palmitoleic acid (16:1). The monounsaturated groups are gadoleic acid (20:1) and oleic acid (18:1) while the polyunsaturated fatty acids are linoleic acid (18:2) and linolenic (18:3). The saturated fatty acids content was found to be 19.95%, which is considered to be quite high.

To reduce the saturated fatty acids contents and to epoxidize the unsaturated fatty acids, investigations regarding the effects of solvent-free and solvent in the epoxidation reaction at 25, 30, and 50°C using formic acid were conducted. Formic acid was utilized in this study owing to the fact that the performic acid formation rate is superior in comparison to that of peracetic acid and the formic acid method is well-known to progress at a faster rate [88, 89].

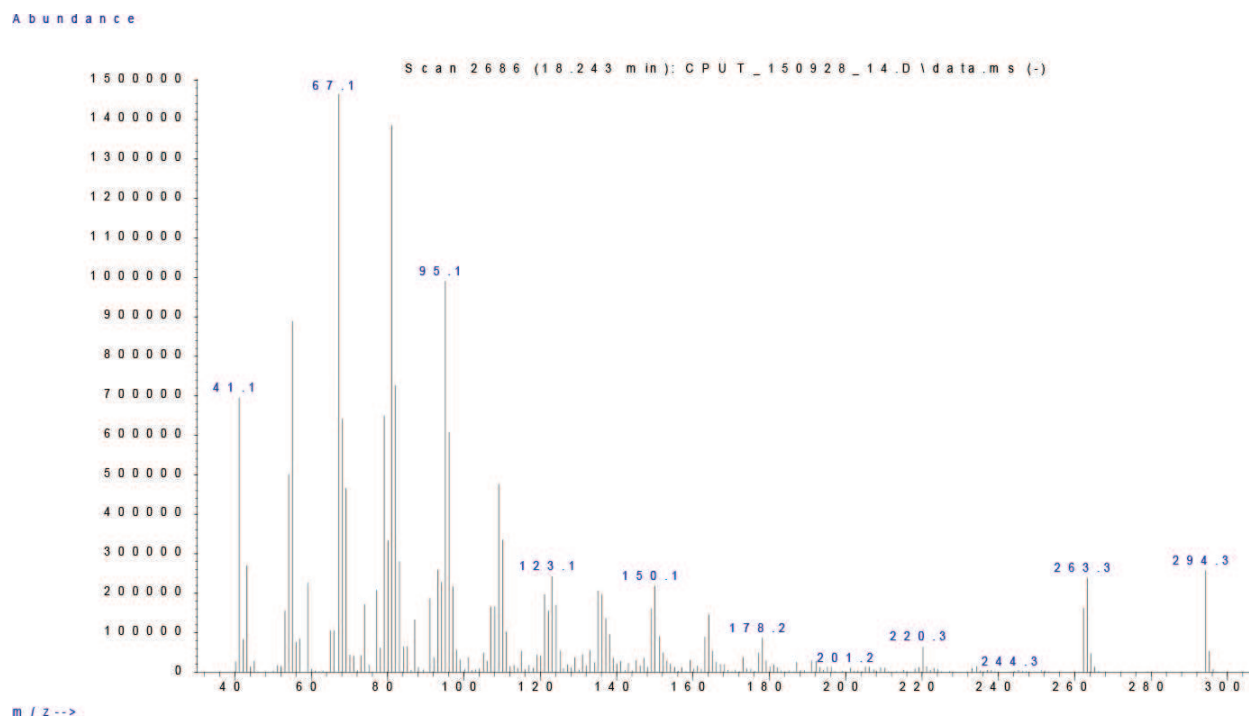


Figure 10. Chromatogram of the palm oil methyl esters.

Moreover, to generate peracetic acid in high concentrations, the use of a catalyst is required [89]. The chemicals utilized for the epoxidation of methyl esters are formic acid (99.81% CH_2O_2), sodium bicarbonate (7.5% aqueous NaHCO_3), sodium chloride (ACS reagent, $\geq 99.0\%$ NaCl), hydrogen peroxide (30% aqueous H_2O_2), diethyl ether ($\geq 99.0\%$ $\text{CH}_3(\text{CH}_2)_2\text{O}$), toluene (anhydrous, 99.8% C_7H_8), n-hexane (anhydrous, 95% C_6H_{14}), and propan-2-ol (anhydrous, 99.5% $\text{CH}_3\text{CHOHCH}_3$). These were purchased from Sigma Aldrich.

4.1. Epoxidation with no solvent

The epoxidation reaction was performed in a temperature controlled batch reactor. About 10.7 g of CH_2O_2 and 100 g of FAME is added to the reaction vessel. The vessel is connected to a condenser and placed in a water bath maintained at 25°C . 58.8 g of H_2O_2 was added dropwise to the vessel through the top of the condenser which then formed peroxyformic acid by reacting with the formic acid (Eq. (3)) and allowed to stand for 4 h. The principal product is epoxidized methyl ester (EFAME) with oxirane rings at the position of double bonds. Possible by-products include keto compounds due to the redistribution of oxirane group or vicinal dihydroxy because of oxirane hydrolysis.



Epoxidized FAME purification step was carried out to remove the unreacted H_2O_2 and the excess acid. About 20 ml of diethyl ether (Sigma Aldrich, 99.9%) is added to the EFAME in a 250 ml separation funnel and stirred well. First, the EFAME/ether solution is washed thrice with deionized water to get rid of the excess acid. Then, the product was washed again with

about 10 ml of aqueous sodium bicarbonate solution (5 g NaHCO_3 /100 g H_2O) which neutralized the residual acid and peroxide. As the bicarbonate solution was added to react with the rest of the acid and slowly agitated, the stopper of the separating funnel was pointed away and into the fume hood and occasionally opened to allow produced gasses to be discharged safely from the funnel. This was repeated until pH paper indicated that it was neutral, showing that the only components remaining in the organic layer was the epoxidized methyl esters. If the solution was too basic, it was rinsed again with water, and if it was too acidic, it was rinsed again with NaHCO_3 solution.

Then, about 10 ml of sodium chloride solution (5 g NaCl /100 g H_2O) is added to remove the remaining H_2O from the organic phase. The aqueous layer was decanted from the reaction system and disposed of. The organic layer was vacuum distilled in a rotary evaporator (Buchi Rotavapor Model R-205) for 30 min at 80°C to evaporate both the ether and any residual H_2O from the organic phase.

4.2. Epoxidation with solvent

Carrying out epoxidation reaction at lower temperatures and in the presence of organic solvents will minimize oxirane degradation and by-products formation [53, 90, 91]. The presence of organic solvents also has some stabilizing effect on the oxirane formed during the peroxyformic or peroxyacids epoxidation of oils and FAMEs [91]. Moreover, solvent can control the reaction temperature thus reducing the adverse temperature effects [92]. Solvent use also offers good solubilization for all inorganic and organic substances thus promoting good mass transfer.

The epoxidation reactions were conducted with toluene at 25, 30, and 50°C . The approach of Akintayo et al. [90] was used. 100 g of FAME was dissolved in 50 ml of toluene and 4 mol of CH_2O_2 was added at temperature of 25°C with stirring. Hydrogen peroxide (100 ml) was then added while keeping the temperature constant. Afterward the reaction was allowed to continue for 4 h. Reaction mixture was then allowed to settle and the aqueous layer removed using a separating funnel. The organic layer was repeatedly rinsed with warm H_2O until free of acid. The residual toluene and H_2O were removed under reduced pressure in the Buchi rotary evaporator. The same procedure was repeated at 30 and 50°C .

The produced epoxy fatty acid methyl esters are analyzed using a GC-MS to detect and determine the different epoxy acids present. From the results, it is noted that performing epoxidation reactions at 30 and 50°C and in presence of the organic solvents minimized side- and by-products formation and ring-opening reactions especially to hydroxyl compounds. Deshpande [93] argued that the presence of an inert solvent-like toluene stabilizes the epoxide product and reduced the adjacent reactions. Reaction at lower temperature of 25°C showed lower rate of epoxidation and high rate of hydrolysis of the product to various by-products.

When the temperature was increased from 30 to 50°C , a change in the composition of the fatty acid methyl esters to epoxy esters and a decrease in side reactions were observed. The results obtained at 50°C with the use of a solvent suggest simultaneous decrease in the side reactions

that open the epoxy ring and minimization of the rate of hydrolysis (oxirane cleavage) of the product. This is in agreement with Ahmad et al. [92]. At 50°C and in the presence of a solvent, the epoxidized FAME showed a very low or no hydroxyl formation compared to the solvent-free epoxidation and at 25°C. Furthermore, increasing temperature demonstrated a favorable influence on the formation of performic acid. The results further showed substantial reduction in the percentage composition of saturated and unsaturated fatty acids in product composition for epoxidation reactions carried at higher temperatures. It can be concluded, therefore, that moderate temperature of 30°C were most suitable for epoxidation of oleic acid with PFA (performic acid generated *in-situ* for optimum oxirane levels and minimal hydrolysis rate).

4.3. Production of epoxidized methyl ester sulfonate

A number of methods for the preparation of sulfonated fatty acid esters from oleochemicals can be found in literatures. The sulfonation reaction of fatty acid methyl esters using SO_3 was studied in detail by Stein and Baumann [94], and products with distinct carbon chains which have excellent properties for surfactant formulation were obtained. Triglycerides with the required number of carbon chains can be found in coconut oil (~48% C_{12} , 17% C_{14}), palm oil (~46% C_{16}), palm kernel oil (~50% C_{12} , 17% C_{14}), and tallow (~26% C_{16} , 23% C_{18}) as mentioned earlier. In general, unsaturated esters contained in vegetable oils and tallow (comprising approximately 43% oleic acid) result in the bad color of the ester sulfonates. Thus, the esters must be hydrogenated or distilled before sulfonation so that their iodine number is less than 0.5.

For surfactant synthesis, chlorosulfonic acid (97% HSO_3Cl), pyridine (99.5% $\text{C}_5\text{H}_5\text{N}$), sodium carbonate (99.5% Na_2CO_3), sodium bicarbonate (7.5% aqueous solution of NaHCO_3), n-butanol (99.5% $\text{C}_4\text{H}_9\text{OH}$), and diethyl ether [$(\text{C}_2\text{H}_5)_2\text{O}$] were purchased from Sigma Aldrich. About 2.63 g of chlorosulfonic acid (HSO_3Cl) was added very slowly while stirring (at 800 ppm) to 15 ml of pyridine ($\text{C}_5\text{H}_5\text{N}$) in a 500 ml round bottom flask placed in ice-cooled water bath for 15 min. 2.60 g of the epoxidized fatty acid methyl ester solution obtained above was introduced slowly to the round bottom flask with continuous stirring, for another 30 min. The reactor and its contents were afterward heated to a temperature of 65°C in a water bath until the solution turned clear. For the second step, the reaction was quenched and the solution is poured into an ice-cooled 500 ml flask containing 33 g in 300 ml solution of sodium carbonate (Na_2CO_3) and enough (approximately 30 g) solid sodium bicarbonate (NaHCO_3) to keep the solution saturated with inorganic sodium salts.

The sulfonated product was extracted into 40 ml of n-butanol ($\text{C}_4\text{H}_9\text{OH}$) using a separating funnel. The solvent was removed from the crude product via drying with a rotary evaporator. The powder obtained is redissolved in 200 ml of water. Then, the organic impurities were eliminated from the aqueous solution of sodium epoxidized methyl ester sulfonate (SEMES) via extraction with 50 ml of diethyl ether. The crude product is concentrated and dried under vacuum for 24 h. Since $\text{C}_4\text{H}_9\text{OH}$ and Na_2CO_3 are typically utilized in CEOR as co-solvent and alkali, the sulfonated esters produced were analyzed without further purification so as to reduce the cost of surfactant manufacturing [25].

A FTIR spectrophotometer was utilized to analyze the composition and the chemical functional group present in the synthesized surfactants. The synthesized (SEMES) powder was grinded and mixed with potassium bromide (KBr) to obtain a fine powder. The powder was then compressed into a thin pallet for analysis. About 15 mg of this pallet in each case was put on the Attenuated Total Reflectance (ATR) sample holder of a Perkin Elmer spectrum 100 FTIR spectrometer (model JASCO FT/IR-4100). The sample was recorded in the range of $4000\text{--}500\text{ cm}^{-1}$, baseline was corrected, and the spectra smoothed.

FTIR spectra in the range of $500\text{--}4000\text{ cm}^{-1}$ of SEMES are shown in **Figure 11**. All the IR absorption bands were investigated with respect to the spectrometric identification of organic compounds by Silverstein et al. [95].

The peak at 1450 cm^{-1} is typically assigned to the disproportion stretching vibration band of methyl group (C—H). Elraies et al. [25] obtained a similar peak for epoxidized methyl ester sulfonate from jatropha oil. The symmetric and asymmetric C—H stretching vibration of the —CH_3 group appears at 2497 and 2926 cm^{-1} . Analogous peaks between 2473 and 2955 cm^{-1} were reported by Babu et al. [96] for sulfonated methyl esters synthesized from castor oil and the ricinoleic acid methyl ester was sulfonated without the epoxidation step. The peak at 3679 cm^{-1} in the SEMES is attributed to the OH stretching of the sorbed water. This sorbed water vibration band suggests that the surface property of SEMES changed from hydrophobic to hydrophilic [96]. The existence of the epoxy ring in the SEMES was shown by the presence of C—O stretching absorption band in the area of $988\text{--}830\text{ cm}^{-1}$.

The strong vibration (absorbance) peak at 1614 cm^{-1} corresponds to the existence of sulfonate group due to S=O stretching which is also an indication of the presence of esters [95, 97]. These results clearly indicate that the substance synthesized is a sodium epoxidized methyl ester sulfonate. For better understanding the structural arrangement of the surfactants investigated in this study, commercial anionic, SDS, and cationic, CTAB surfactants were also characterized using the same procedure. The FTIR spectra of pure SDS showed similar pattern with the synthesized SEMES, but the percentage of transmission were different as a

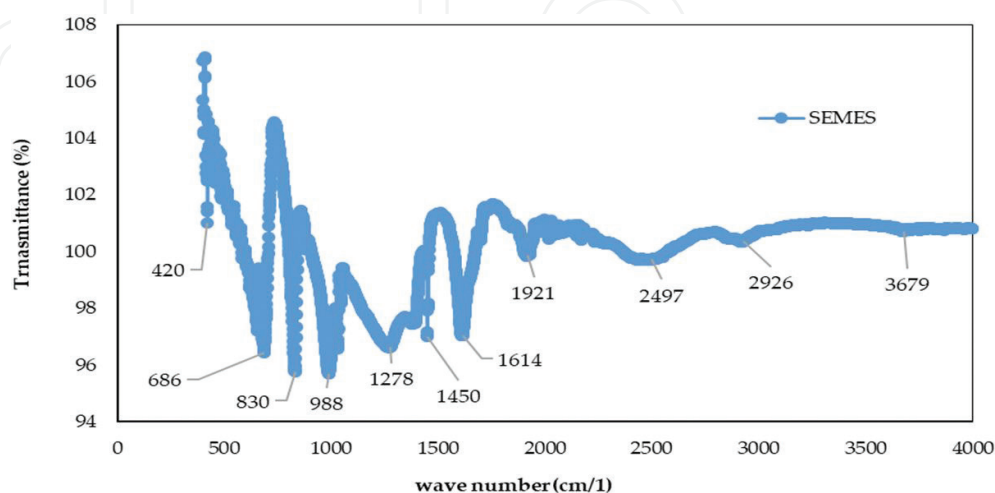


Figure 11. FTIR spectrum of SEMES.

result of the discrepancy in their relative molecular mass. This clearly indicates that the formulated surfactant SEMES is an anionic surfactant.

5. Conclusion

The $\text{CaO}/\text{Al}_2\text{O}_3$ employed as the catalyst to produce methyl esters used from the waste oil performed as expected, despite the presence of free fatty acids. The catalysts synthesized by the co-precipitation method exhibited high dispersion of the Ca and Al particles. The optimum reaction conditions for the production of methyl esters via simultaneous esterification and transesterification reaction of the waste pal oil were found to be: a reaction time of 4h at 65°C with a methanol:oil ratio of 9:1 and 4 wt% catalyst amount. A 60% $\text{CaO}/40\% \text{Al}_2\text{O}_3$ ratio was found to be optimum for waste palm oil. The high esters yield obtained despite the low quality of the oils used demonstrated that the use of a bifunctional catalyst will provide an opportunity to lower the cost of production of the esters. Furthermore, the catalyst showed substantial chemical stability and could be used again for at least 8 times with minor losses in its catalytic activity.

It is evident that the saturated fatty acid contents of the methyl esters subjected to epoxidation reaction in the presence and absence of a solvent at 25, 30, and 50°C were reduced while promoting the desired conversion of the unsaturated fatty acid methyl esters to epoxy esters (with oxirane groups). A temperature of 30°C was found to be suitable for epoxidation of oleic acid with PFA (performic) for optimum oxirane levels and hydrolysis rate diminishment. The EFAME was consequently sulfonated to produce the sodium epoxidized methyl ester sulfonate (SEMES) surfactant, which was then compared with the synthetic SDS and CTAB surfactants. The identified FTIR spectrum of SEMES was similar to that of SDS which indicated that the formulated SEMES is an anionic surfactant. The same result has been reported [98]. The sulfonated surfactant has been evaluated in a separate study for performance in petroleum reservoir [15]. It was found to exhibit excellent characteristics comparable to commercial petroleum-based anionic surfactant.

Acknowledgements

The study was made possible by the generous fund provided by South Africa Technology Innovation Agency (TIA).

Author details

Ademola Rabiou*, Samya Elias and Oluwaseun Oyekola

*Address all correspondence to: rabiua@cput.ac.za

Cape Peninsula University of Technology, Cape Town, South Africa

References

- [1] Noor Armylisas AH, Siti Hazirah MF, Yeong SK, Hazimah AH. Modification of olefinic double bonds of unsaturated fatty acids and other vegetable oil derivatives via epoxidation: A review. *Grasas y Aceites*. 2017;**68**(1). <http://grasasyaceites.revistas.csic.es/index.php/grasasyaceites/rt/captureCite/1640/2040/ApaCitationPlugin>
- [2] Fiorentino G, Ripa M, Ulgiati S. Chemicals from biomass: Technological versus environmental feasibility. A review. *Biofuels, Bioproducts and Biorefining*. 2017;**11**(1):195-214
- [3] Biermann U, Bornscheuer U, Meier MAR, Metzger JO, Schäfer HJ. Oils and fats as renewable raw materials in chemistry. *Angewandte Chemie (International Ed. in English)*. 2011;**50**:3854-3871
- [4] Zhou YJ, Buijs NA, Zhu Z, Qin J, Siewers V, Nielsen J. Production of fatty acid-derived oleochemicals and biofuels by synthetic yeast cell factories. *Nature Communications*. 2016;**7**:11709
- [5] Werth K, Kaupenjohann P, Skiborowski M. The potential of organic solvent nanofiltration processes for oleochemical industry. *Separation and Purification Technology*. 2017;**182**:185-196
- [6] Rupilius W, Ahmad S. Palm oil and palm kernel oil as raw materials for basic oleochemicals and biodiesel. *European Journal of Lipid Science and Technology*. 2007;**109**(4):433-439
- [7] Tan SG, Chow WS. Biobased epoxidized vegetable oils and its greener epoxy blends: A review. *Polymer-Plastics Technology and Engineering*. 2010;**49**(15):1581-1590
- [8] Vanbésien T, Le Nôtre J, Monflier E, Hapiot F. Hydroaminomethylation of oleochemicals: A comprehensive overview. *European Journal of Lipid Science and Technology*. 2018;**120**(1):1700190
- [9] Chhetri AB, Watts KC, Islam MR. Waste cooking oil as an alternate feedstock for biodiesel production. *Energies*. 2008;**1**(1):3-18
- [10] Peralta-Yahya PP, Zhang F, del Cardayre SB, Keasling JD. Microbial engineering for the production of advanced biofuels. *Nature*. 2012;**488**:320-328
- [11] Lee HV, Juan JC, Binti Abdullah NF, Nizah Mf R, Taufiq-Yap YH. Heterogeneous base catalysts for edible palm and non-edible *Jatropha*-based biodiesel production. *Chemistry Central Journal*. 2014;**8**(1):30
- [12] Geetha S, Banat IM, Joshi SJ. Biosurfactants: Production and potential applications in microbial enhanced oil recovery (MEOR). *Biocatalysis and Agricultural Biotechnology*. 2018;**14**:23-32
- [13] Permadi P, Fitria R, Hambali E. Palm oil based surfactant products for petroleum industry. *IOP Conference Series: Earth and Environmental Science*. 2017;**65**(1):012034
- [14] Rust D, Wildes S. A Market Opportunity Study Update. Midland, MI: OmniTech International Ltd.; 2008

- [15] Rabiou AM, Elias S, Oyekola O. Evaluation of surfactant synthesized from waste vegetable oil to enhance oil recovery from petroleum reservoirs. *Energy Procedia*. 2016;**100**:188-192
- [16] Marti M, Colonna W, Patra P, Zhang H, Green C, Reznik G, et al. Production and characterization of microbial biosurfactants for potential use in oil-spill remediation. *Enzyme and Microbial Technology*. 2014;**55**:31-39
- [17] Buist I, Potter S, Nedwed T, Mullin J. Herding surfactants to contract and thicken oil spills in pack ice for in situ burning. *Cold Regions Science and Technology*. 2011;**67**(1-2):3-23
- [18] Ishak SA, Ghazali R, Abd Maurad Z, Zolkarnain N. Ecotoxicology study of various homologues of methyl ester sulfonates (MES) derived from palm oil. *Journal of Surfactants and Detergents*. 2017;**20**(6):1467-1473
- [19] Elias SD, Rabiou AM, Oyekola O, Seima B. Adsorption characteristics of surfactants on different petroleum reservoir materials. *Online Journal of Science and Technology*. 2016;**6**(4):6-16
- [20] Lechuga M, Fernández-Serrano M, Jurado E, Núñez-Olea J, Ríos F. Acute toxicity of anionic and non-ionic surfactants to aquatic organisms. *Ecotoxicology and Environmental Safety*. 2016;**125**:1-8
- [21] Babu K, Maurya NK, Mandal A, Saxena VK. Synthesis and characterization of sodium methyl ester sulfonate for chemically-enhanced oil recovery. *Brazilian Journal of Chemical Engineering*. 2015;**32**(03):795-803
- [22] Al-Sulaimani H, Joshi S, Al-Wahaibi Y, Al-Bahry S, Elshafie A, Al-Bemani A. Microbial biotechnology for enhancing oil recovery: Current developments and future prospects. *Biotechnology, Bioinformatics and Bioengineering*. 2011;**1**(2):147-158
- [23] Rahman P, Joshi S, Makkar R. Recent developments in Biosurfactants. *Frontiers in Microbiology*, Published online. July 2017
- [24] Zulina AM, Razmah G, Parthiban S, Zahariah I, Salmiah A. Alpha-sulfonated methyl ester as an active ingredient in palm-based powder detergents. *Journal of Surfactants Detergent*. 2006;**9**:161-167
- [25] Elraies KA, Isa MT, Saaid I. Synthesis and performance of a new surfactant for enhanced oil recovery. *International Journal of Petroleum Science and Technology*. 2009;**3**(1):1-9
- [26] Roschat W, Siritanon T, Yoosuk B, Sudyoardsuk T, Promarak V. Rubber seed oil as potential non-edible feedstock for biodiesel production using heterogeneous catalyst in Thailand. *Renewable Energy*. 2017;**101**:937-944
- [27] Mba OI, Dumont M-J, Ngadi M. Palm oil: Processing, characterization and utilization in the food industry – A review. *Food Bioscience*. 2015;**10**:26-41
- [28] Bhuiya MMK, Rasul MG, Khan MMK, Ashwath N, Azad AK. Prospects of 2nd generation biodiesel as a sustainable fuel—Part: 1 selection of feedstocks, oil extraction techniques and conversion technologies. *Renewable and Sustainable Energy Reviews*. 2016;**55**:1109-1128

- [29] Maddikeri GL, Gogate PR, Pandit AB. Improved synthesis of sophorolipids from waste cooking oil using fed batch approach in the presence of ultrasound. *Chemical Engineering Journal*. 2015;**263**:479-487
- [30] Pashley RM, Karaman ME. *Applied Colloid and Surface Chemistry*. England: John Wiley & Sons; 2004
- [31] Elraies KA, Tan I, Fathaddin M, Abo-Jabal A. Development of a new polymeric surfactant for chemical enhanced oil recovery. *Petroleum Science and Technology*. 2011;**29**(14):1521-1528
- [32] Joshi SJ, Abed RM. Biodegradation of polyacrylamide and its derivatives. *Environmental Processes*. 2017;**4**(2):463-476
- [33] Mohsenzadeh A, Al-Wahaibi Y, Al-Hajri R, Jibril B, Mosavat N. Sequential deep eutectic solvent and steam injection for enhanced heavy oil recovery and in-situ upgrading. *Fuel*. 2017;**187**:417-428
- [34] Rudyk S, Spirov P, Samuel P, Joshi SJ. Vaporization of crude oil by supercritical CO₂ at different temperatures and pressures: Example from Gorm field in the Danish North Sea. *Energy & Fuels*. 2017;**31**(6):6274-6283
- [35] Blesic M, Dichiarante V, Milani R, Linder M, Metrangolo P. Evaluating the potential of natural surfactants in the petroleum industry: The case of hydrophobins. *Pure and Applied Chemistry*. 2018;**90**:305
- [36] Bera A, Mandal A. Microemulsions: A novel approach to enhanced oil recovery: A review. *Journal of Petroleum Exploration and Production Technology*. 2015;**5**(3):255-268
- [37] Zargartalebi MKR, Barati N. Enhancement of surfactant flooding performance by the use of silica nanoparticles. *Fuel*. 2015;**143**:21-27
- [38] Kamari ASMMAH, Ramjugernath D. Reliable method for the determination of surfactant retention in porous media during chemical flooding oil recovery. *Fuel*. 2015;**158**: 122-128
- [39] Zolfaghari R, Fakhru'l-Razi A, Abdullah LC, Elnashaie SSEH, Pendashteh A. Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry. *Separation and Purification Technology*. 2016;**170**:377-407
- [40] Koh A, Wong A, Quinteros A, Desplat C, Gross R. Influence of sophorolipid structure on interfacial properties of aqueous-Arabian light crude and related constituent emulsions. *Journal of the American Oil Chemists' Society*. 2017;**94**(1):107-119
- [41] Ahmadi MA, Shadizadeh SR. Experimental investigation of a natural surfactant adsorption on shale-sandstone reservoir rocks: Static and dynamic conditions. *Fuel*. 2015;**159**: 15-26
- [42] Spildo KSLDK, Skauge A. A strategy for low cost, effective surfactant injection. *Journal of Petroleum Science and Engineering*. 2014;**117**:8-14

- [43] Lu J, Goudarzi A, Chen P, Kim DH, Delshad M, Mohanty KK, Sepehrnoori K, Weerasooriya UP, Pope GA. Enhanced oil recovery from high-temperature, high-salinity naturally fractured carbonate reservoirs by surfactant flood. *Journal of Petroleum Science and Engineering*. 2014;**124**:122-131
- [44] Berger PD, Lee CH. Improved ASP process using organic alkali. In: *SPE/DOE Symposium on Improved Oil Recovery*. Society of Petroleum Engineers; 2006
- [45] Gupta R, Mohanty KK. Temperature effects on surfactant-aided imbibition into fractured carbonates. *SPE Journal*. 2010;**15**(3):588-597
- [46] RVF P, Carvalho MS, Alvarado V. Oil recovery modeling of macro-emulsion flooding at low capillary number. *Journal of Petroleum Science and Engineering*. 2014;**119**:112-122
- [47] Bera A, Kumar T, Ojha K, Mandal A. Adsorption of surfactants on sand surface in enhanced oil recovery: Isotherms, kinetics and thermodynamic studies. *Applied Surface Science*. 2013;**284**:87-99
- [48] De Almeida DG, Soares Da Silva RdCF, Luna JM, Rufino RD, Santos VA, Banat IM, et al. Biosurfactants: Promising molecules for petroleum biotechnology advances. *Frontiers in Microbiology* 2016;**7**:1718
- [49] Demirbas A. Studies on cottonseed oil biodiesel prepared in non-catalytic SCF conditions. *Bio/Technology*. 2008;**99**:1125-1130
- [50] Jacobson KGRMLC, Dalai AK. Solid acid catalyzed biodiesel production from waste cooking oil. *Applied Catalysis B: Environmental*. 2008;**85**:86-91
- [51] Balat M. Potential alternatives to edible oils for biodiesel production—A review of current work. *Energy Conversion and Management*. 2011;**52**(2):1479-1492
- [52] Ferreira ML, Tonetto GM. *Enzymatic Synthesis of Structured Triglycerides: From Laboratory to Industry*. Cham, Switzerland: Springer International Publishing; 2017
- [53] Goud VV, Patwardhan AV, Pradha NC. Kinetics of in-situ epoxidation of natural triglycerides catalyzed by acidic ion exchange resin. *Industrial and Engineering Chemistry Research*. 2007;**46**:3078-3085
- [54] Babajide OO. *Optimisation of Biodiesel Production Via Different*. Department of Chemistry. MSc. Cape Town: University of the Western cape; 2011
- [55] Ali O, Yusaf T, Mamat R, Abdullah N, Abdullah A. Influence of chemical blends on palm oil methyl esters' cold flow properties and fuel characteristics. *Energies*. 2014;**7**(7):4364
- [56] Yasin MHM, Mamat R, Najafi G, Ali OM, Yusop AF, Ali MH. Potentials of palm oil as new feedstock oil for a global alternative fuel: A review. *Renewable and Sustainable Energy Reviews*. 2017;**79**:1034-1049
- [57] Hansen SB, Padfield R, Syayuti K, Evers S, Zakariah Z, Mastura S. Trends in global palm oil sustainability research. *Journal of Cleaner Production*. 2015;**100**:140-149

- [58] Choong YY, Chou KW, Norli I. Strategies for improving biogas production of palm oil mill effluent (POME) anaerobic digestion: A critical review. *Renewable and Sustainable Energy Reviews*. 2018;**82**:2993-3006
- [59] Kadarusman YB, Herabadi AG. Improving Sustainable Development within Indonesian Palm Oil: The Importance of the Reward System. *Sustainable Development* 2018. Published online in Wiley Online Library. DOI: 10.1002/sd.1715
- [60] Indonesia Investments. Palm Oil. 2017. <https://www.indonesia-investments.com/business/commodities/palm-oil/item166?> [Accessed: 3 March 2018]
- [61] Yaakob ZMMAMAZ, Sopian K. Overview of the production of biodiesel from waste cooking oil. *Renewable and Sustainable Energy Reviews*. 2013;**18**:186-191
- [62] Yang H, Chien S, Lo M, Lan JC, Lu W, Ku Y. Effects of biodiesel on emissions of regulated air pollutants and polycyclic aromatic hydrocarbons under engine durability testing. *Atmospheric Environment*. 2007;**41**(34):7232-7240
- [63] Eze VC, Phan AN, Harvey AP. Intensified one-step biodiesel production from high water and free fatty acid waste cooking oils. *Fuel*. 2018;**220**:567-574
- [64] Amoah J, Quayson E, Hama S, Yoshida A, Hasunuma T, Ogino C, et al. Simultaneous conversion of free fatty acids and triglycerides to biodiesel by immobilized *Aspergillus oryzae* expressing *Fusarium heterosporum* lipase. *Biotechnology Journal* 2017;**12**(3):1600400
- [65] Demirbas A. Progress and recent trends in biodiesel fuels. *Energy Conversion and Management*. 2009;**50**(1):14-34
- [66] Photaworn S, Tongurai C, Kungsanunt S. Process development of two-step esterification plus catalyst solution recycling on waste vegetable oil possessing high free fatty acid. *Chemical Engineering and Processing: Process Intensification*. 2017;**118**:1-8
- [67] Helwani Z, Othman MR, Aziz N, WJN F, Kim J. Technologies for production of biodiesel focusing on green catalytic techniques: A review. *Fuel Processing Technology*. 2009;**90**:1502-1514
- [68] Schuchardt USR, Vargas RM. Transesterification of vegetable oils: A review. *Journal of Brazilian Chemical Society*. 1998;**9**(1):199-210
- [69] Arzamendi G, Campoa I, Arguinarena E, Sanchez M, Montes M, Gandia LM. Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: Comparison with homogeneous NaOH. *Chemical Engineering Journal*. 2007;**134**:123-130
- [70] Di Serio M, Tesser R, Pengmei L, Santacesaria E. Heterogeneous catalysts for biodiesel production. *Energy & Fuels*. 2008;**22**:207-217
- [71] Hara M. Environmentally benign production of biodiesel using heterogeneous catalysts. *Chemical Engineering Communications*. 2009;**2**(2):129-135
- [72] Lopez-Granados M, Alba-Rubio AC, Vila F, Martín AD, Marisacl R. Surface chemical promotion of calcium oxide catalyst in biodiesel production reaction by the addition of monoglycerides, diglycerides and glycerol. *Journal of Catalysis*. 2010;**276**:229-236

- [73] Janaun J, Ellis N. Perspectives on biodiesel as a sustainable fuel. *Renewable and Sustainable Energy Reviews*. 2010;**14**:1312-1320
- [74] Zabeti M, Wan Daud MAW, Aroua MK. Biodiesel production using alumina-supported calcium oxide: An optimization study. *Fuel Processing Technology*. 2010;**91**(2):243-248
- [75] Wen Z, Yu X, Tu ST, Yan J, Dahlquist E. Biodiesel production from waste cooking oil catalyzed by TiO₂-MgO mixed oxides. *Bioresource Technology*. 2010;**101**:9570-9576
- [76] Math MC, Kumar SP, Chetty SV. Technologies for biodiesel production from used cooking oil—A review. *Energy for Sustainable Development*. 2010;**14**:339-345
- [77] Teng G, Gao L, Xiao G, Liu H. Transesterification of soybean oil to biodiesel over heterogeneous solid base catalyst. *Energy & Fuels*. 2009;**23**:4630-4634
- [78] Hayyan A, Alam M, Mirghani M, Kabbashi N, Hakimi N, Siran Y, et al. Sludge palm oil as a renewable raw material for biodiesel production by two-step processes. *Bioresource Technology*. 2010;**101**:7804-7811
- [79] Hayyan A, Alam M, Mirghani M, Kabbashi N, Hakimi N, Siran Y, et al. Production of biodiesel from sludge palm oil by esterification process. *Journal of Energy and Power Engineering*. 2010;**4**:13-14
- [80] Patil P, Deng S, Rhodes JL, Lammers PJ. Conversion of waste cooking oil to biodiesel using ferric sulfate and supercritical methanol processes. *Fuel*. 2010;**89**:360-364
- [81] Liu X, He H, Wang Y, Zhu S. Transesterification of soybean oil to biodiesel as a solid base catalyst. *Catalysis Communication*. 2007;**8**:1107-1111
- [82] Lotero E, Liu Y, Lopez DE, Suwannakarn K, Bruce DA, Goodwin JG. Synthesis of biodiesel via acid catalysis. *Industrial & Engineering Chemistry Research*. 2005;**44**:5353-5363
- [83] Pasupulety N, Gunda K, Liu Y, Rempel GL, Ng FTT. Production of biodiesel from soybean oil on CaO/Al₂O₃ solid base catalysts. *Applied Catalysis A: General*. 2013;**452**:189-202
- [84] Balakrishnan K, Olutoye MA, Hameed BH. Synthesis of methyl esters from waste cooking oil using construction waste material as solid base catalyst. *Bioresource Technology*. 2013;**128**:788-791
- [85] Farooqa M, Ramlib A, Subbaraoa D. Biodiesel production from waste cooking oil using bifunctional heterogeneous solid catalysts. *Journal of Cleaner Production*. 2013;**59**: 131-140
- [86] Saifuddin M, Goh PE, Ho WS, Moneruzzaman KM, Fatima A. Biodiesel production from waste cooking palm oil and environmental impact analysis. *Bulgarian Journal of Agricultural Science*. 2014;**20**(1):186-192
- [87] Gervajio GC. Fatty Acids and Derivatives from Coconut Oil. In: Shahidi F, editor. *Bailey's Industrial Oil and Fat Products*. 6th ed. New Jersey: John Wiley and Sons, Inc.; 2005. DOI: DOI: 10.1002/047167849X.bio039

- [88] Scala J, Wool RP. Effect of FA composition on epoxidation kinetics of TAG. *Journal of American Oil Chemistry Society*. 2002;**79**:373-378
- [89] Campanella A, Baltanas MA, Fontanini C. High yield epoxidation of fatty methyl esters with performic acid generated in-situ. *Chemical Engineering Journal*. 2008;**118**:141-152
- [90] Akintayo E, Ziegler T, Onipede A. Gas chromatographic and spectroscopic analysis of epoxidised canola oil. *Bulletin of the Chemical Society of Ethiopia*. 2006;**20**(1):75-81
- [91] Espinoza Perez JD, Haagenson DM, Pryor SW, Ulven CA, Wiesenborn DP. Production and characterization of epoxidized canola oil. *American Society of Agricultural and Biological Engineers*. 2009;**52**(4):1289-1297
- [92] Ahmad M, Khan MA, Zafar M, Sultana S. Biodiesel from Non Edible Oil Seeds: a Renewable Source of Bioenergy. In: Marco Aurelio Dos Santos Bernardes, editor. *Economic Effects of Biofuel Production*. Rijeka, Croatia: InTech; 2011. ISBN: 978-953-307-178-7. <http://www.intechopen.com/books/economic-effects-of-biofuel-production/biodiesel-from-non-edible-oil-seeds-a-renewable-source-of-bioenerg>
- [93] Deshpande PS. Chapter 3 Epoxidation of oleic acid and vegetable oils: Synthesis, characterization and utilization as biolubricants and additives for plastics. *Journal of Cleaner Production*. 2013;**59**:89-152
- [94] Stein W, Baumann H. α -Sulfonated fatty acids and esters: Manufacturing process, properties, and applications. *Journal of the American Oil Chemists Society*. 1975;**52**(9):323-329
- [95] Silverstein RM, Webster FX, Kiemle DJ. John Wiley & Sons, Inc; 2005
- [96] Babu K, Pal N, Bera A, Saxena VK, Mandal A. Studies on interfacial tension and contact angle of synthesized surfactant and polymeric from castor oil for enhanced oil recovery. *Applied Surface Science*. 2015;**353**:1126-1136
- [97] Awang M, Seng GM. Sulfonation of phenols extracted from the pyrolysis oil of oil palm shells for enhanced oil recovery. *ChemSusChem*. 2008;**1**(3):210-214
- [98] Elraies KA, Tan IM. The Application of a New Polymeric Surfactant for Chemical EOR. In: Romero-Zerón L, editor. *Introduction to Enhanced Oil Recovery (EOR) Processes and Bioremediation of Oil-Contaminated Sites*. Rijeka, Croatia: InTech; 2012. ISBN: 978-953-51-0629-6. Available from: <http://www.intechopen.com/books/introduction-to-enhanced-oil-recovery-eor-processes-and-bioremediationof-oil-contaminated-sites/the-application-of-a-new-polymeric-surfactant-for-chemical-eor>