Synthesis and Evaluation of Catalytic Activity of Calcined Sodium Silicate for Transesterification of Waste Cooking Oil to Biodiesel

M.O. Daramola[‡], D. Nkazi, K. Mtshali

School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Wits 2050, Johannesburg, South Africa

(michael.daramola@wits.ac.za, Diakanua.Nkazi@wits.ac.za, mikkydara@gmail.com)

[‡] Corresponding Author; M.O. Daramola, School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Wits 2050, Johannesburg, South Africa, Tel: +27 11 717 7536, michael.daramola@wits.ac.za

Abstract- Biodiesel production from waste cooking oil (WCO) using heterogeneous sodium silicate catalyst is presented in this article. The conversion of WCO to biodiesel exploited the potential of the catalyst to convert high free fatty acid (FFA) content feedstock to biodiesel directly, thereby by-passing the esterification stage whereby FFA content of the feedstock is reduced prior to transesterification reaction. In the study, effect of reaction temperature and reaction time on the activity of the catalyst during transesterification of WCO to biodiesel was investigated. The transesterification reaction was conducted in a batch reactor with 2.51 g of the catalysts and at WCO to methanol ratio of 1:6. In addition, the reaction temperature was varied between 25°C to 63°C, and the reaction time was varied from 0 to 180 minutes at a 30 minute step increase. The fatty acid methyl ester (FAME) yield increased with reaction time and reaction temperature and the highest FAME yield of ~30% was obtained at 63°C after 180 minutes. However, further studies are required for in-depth understanding of the activity and kinetics of the catalyst for biodiesel production from WCO.

Keywords: Waste cooking oil; Biodiesel; Heterogeneous catalysis; Transesterification.

1. Introduction

The recent oil crises and growing public awareness of global climate change and greenhouse emissions are creating major technological, as well as social and political challenges worldwide. These challenges are related closely to energy generation and exploitation. The aforementioned problems have prompted the consideration of alternative and renewable types of energy. One of the expected key technologies for building sustainable societies and thus mitigating global global climate change due to CO_2 emission is the production of renewable fuels and chemicals from the conversion of biomass [1-3]. An alternative type of energy source that is highly favoured from an environmental perspective is biofuel of which biodiesel is a member. Biodiesel (mono-alkyl esters of long chain fatty acids derived from renewable feedstocks, such as vegetable oil or animal fats) is a promising alternative to conventional petroleum based diesel fuel. Biodiesel has a relatively high flash point (150°C) which makes it less volatile and safer to transport and handle than petroleum [4]. Biodiesel provides lubricating properties that can reduce engine wear and extend engine life [5]. Biodiesel has a number of other advantages, which include reduction in air pollutant emissions, reduction in carbon dioxide emissions, efficient resource and/or waste utilization, decrease of the volume of imported fossil fuel, biodegradability, non-toxicity, and essentially free of sulphur and aromatics. These attributes, when compared to fossil fuel diesel on a life cycle platform, makes biodiesel a more environmentally benign fuel. Several vegetable oils such as palm oil, soybean oil, sunflower oil, coconut oil, rapeseed oil and tung oil have been used as feedstock for the production

of biodiesel [6-8]. Advantages of vegetable oils diesel fuel compared to diesels from fossil fuel include high heat contents; ready availability, liquid nature-portability, lower sulfur content, lower aromatic content, biodegradability and renewability [9]. Biodiesel is produced favourably via the transesterification reaction between a vegetable oil or an animal fat (which are complex mixtures of triglycerides) and a low molecular weight alcohol, such as methanol [9,10]. The transesterification reaction could be either a non-catalytic or a catalytic process. The non-catalytic transesterification process is slow and requires high pressures and temperatures for completion, which translates into high operating costs [11]. In the catalytic transesterification process, base catalysts, acid catalysts and enzymes have been studied. In the use of enzyme as catalyst for the production of biodiesel, formation of free fatty acid and water contents in the oil prevents soap formation, thereby making purification of biodiesel and glycerol an easy task [12,13]. However, enzymes are expensive and thus their use in commercial production of biodiesel is discouraged. Homogeneous acid and base catalysts have been extensively studied for the production of biodiesel [14-17]. For homogeneous acid-catalyzed production of biodiesel, sulphuric acid and hydrochloric acid have been studied (especially when the oil contains large amount of free fatty acids and water). This is because the catalysts can handle esterification and transesterification of triglyceride simultaneously. However, due to the corrosiveness and acidity of these catalysts to the environment, special equipment is required to withstand corrosion [17]. The process also requires a high alcohol to oil molar ratio and long reaction times [18]. In the case of homogeneously base-catalyzed biodiesel production, the use of sodium hydroxide and potassium hydroxide as homogeneous catalyst has been widely studied. The process occurs in a shorter reaction time at relatively moderate operating conditions when compared with the homogeneous acid-catalyzed biodiesel production process, however, competition between the saponification reaction and transesterification reaction is an issue [16, 19, 20]. Homogeneous catalysts cannot be reused or regenerated because the catalysts are consumed in part during the reaction. In addition, separation of the catalyst from products is difficult and requires additional equipment, which could result in higher production costs [18]. In addition, the process is not environmentally friendly because a large amount of wastewater is produced in the separation step [21]. Against this background, developing new solid catalysts seems to be an appropriate solution to overcome problems associated with the use of homogeneous catalysts. A few research efforts have been expended on the development of heterogeneous catalysts for biodiesel production [22-25]. For biodiesel production from WCO, recent concerted research efforts have investigated the use of solid-base catalysts

obtained from pyrolyzed rice husk [26] and silica sulfuric acid [27]. In addition, Guo et al. [23] has investigated the use of solid sodium silicate catalyst for biodiesel production from soybean oil. As far as could be ascertained, there is no report in the open literature on the conversion of WCO to biodiesel over calcined solid sodium silicate catalyst. As a contribution to the concerted research efforts in this area, this paper presents results of an investigation on the conversion of WCO to biodiesel over heterogeneous sodium silicate catalyst.

2. Experimental

2.1. Materials

Sodium hydroxide, methanol and silica powder (SiO_2) used in this study were of analytical grade and purchased from Sigma Aldrich. Waste cooking oil (WCO) was collected from a restaurant at the University of the Witwatersrand, South Africa, and its physical properties were analyzed.

2.2. Evaluation of the free fatty acid (FFA) content of the WCO

Free fatty acid (FFA) content of the WCO was evaluated according to the procedure described elsewhere [28]. The 1 ml of the WCO diluted with 10 ml of 99 % isopropyl alcohol was titrated against 0.025 M NaOH solution drop-wisely using phenolphthalein solution (0.05 g of phenolphthalein to 50 ml of 95 % pure ethanol and diluted to a 100 ml using distilled water) as the pH indicator. The percentage FFA was calculated according to Equation (1):

$$\% FFA = (V - b) \times N \times \frac{28.2}{w} \tag{1}$$

Where $\% FFA$ is the percentage free fatty acid (FFA) of the WCO; V, the titrant value (ml); b, the volume of the blank (ml); N, the concentration of the titration solution in mg/l, and w, the weight of the 1 ml sample of the WCO.

2.3. Catalyst preparation and characterization

Sodium silicate catalyst was prepared using 8 g NaOH, 6 g SiO_2 and 10 ml distilled water. During the synthesis of the catalyst, 10 ml of distilled water was poured inside a steel cup and placed on a heating mantle equipped with stirring device and heated to 41°C. Then 8 g of NaOH pellets was added and the mixture stirred with a magnetic stirrer until a homogeneous solution was obtained. Thereafter, 6 g of SiO_2 was added to the mixture. The mixture was stirred continuously at 41°C until all the solid content melted. Then the homogeneous mixture was left for another 20 minutes to ensure a complete reaction. After the reaction was

completed, the molten mixture was transferred into a crucible and calcined at 200°C for 5 hours to get rid of moisture and unreacted materials from the porous structure of the catalyst. After the calcination, the catalyst was crushed to fine particles (≤ 0.30 nm) using mortar and pestle. The purity of the catalyst was checked with FTIR, and the morphology of the catalyst was checked with scanning electron microscopy (SEM). TGA analysis was conducted as well, to understand the thermal stability of the catalyst.

2.4. Evaluation of catalytic activity

The activity of the synthesized catalyst was evaluated through the conversion of WCO to biodiesel using the set-up depicted in Figure 1. Methanol to oil ratio of 6:1 was used in the evaluation following the report of Guo et al. [23]. Firstly, 2.51 g of Na_2SiO_3 catalyst, 214.29 ml of methanol, 35.71 ml of WCO were put into a 250 ml round bottom flask (see Figure 1), and the flask was connected to a Liebig condenser. The reaction mixture was stirred continuously with a magnetic stirrer to ensure uniform reaction, uniform distribution of heat and overcome mass transfer limitation during the reaction. The same amount of catalyst was used throughout the experiment and the temperature of the reaction mixture was measured with a mercury-in-glass thermometer. The level of the content in the 250 ml flask was below the level of water in the water-bath to ensure uniform distribution of heat in the reaction mixture. The reaction time was varied from 0 to 180 minutes at 30 minutes intervals and the reaction temperature was varied from 25°C to 63°C. At each temperature increase and at 30 minutes interval, 10 ml of the reaction mixture was withdrawn from the reaction vessel and analyzed for biodiesel following the procedure described elsewhere [23].
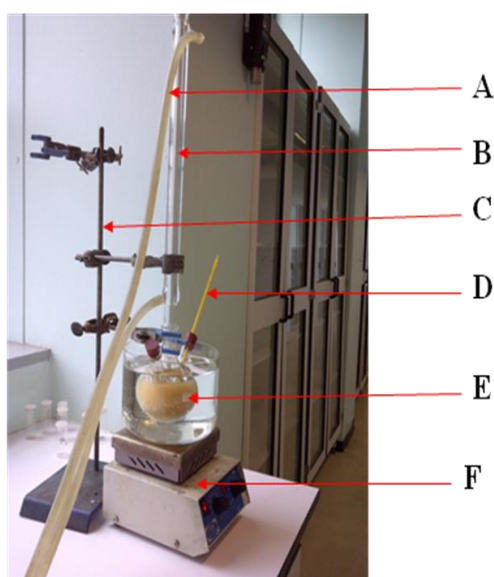
Fig. 1. Picture of the experimental set-up for the evaluation of the catalytic activity of Na_2SiO_3. A: Cold-water tubing connected to the condenser; B: condenser; C: Tripod stand

with clamp; D: Mercury-in-glass thermometer; E: round-bottom flask with reaction mixture; and F: Heating mantle equipped with magnetic.

3. Results and Discussion

3.1. Characterization of WCO and the catalyst

The physical properties of the WCO used in the study are presented in Table 1. The properties are consistent to the properties of WCO used by Awad et al. [29]. The FTIR and the SEM image of the synthesized sodium silicate catalyst are depicted in Figure 2 and Figure 3, respectively. In addition, the percentage FFA of the WCO was 1.4%. This value is >1%, indicating that the oil contains high FFA content, justifying the use of a heterogeneous catalyst to convert the WCO to biodiesel to eliminate the pretreatment stage via esterification reaction. The SEM image of the synthesized sodium silicate catalyst depicted in Figure 3 is the typical morphology of sodium silicate as reported by [23]. According to Guo et al. [23], structures that contain inter-particle space of 1-5 μm between agglomerates allow triglyceride and methanol to penetrate, exposing therefore the basic sites of the surface of the catalyst to transesterification. From Figure 3, it is evident that the inter-particle space is between 1-5 μm, promoting therefore an affinity transesterification reaction.

**Table 1.** Physical properties of the WCO

Moisture content (%)	High heating value (MJ/kg)	Melting point (°C)	Specific gravity
<0.05	40	30	0.87

The structure of the synthesized sodium silicate catalyst after calcination was analyzed with FT-IR (Fig. 2). The Si–O–Si stretching is indicated at 712 cm^{-1} and the Si–O–H absorption at 898 cm^{-1}. The Si–O–Na absorption stretch is indicated at 964 cm-1; the Si–O bending at 1033 - 1037 cm^{-1} and the OH absorption: 3404 cm^{-1}. This is consistent with the report of Guo et al. [23].
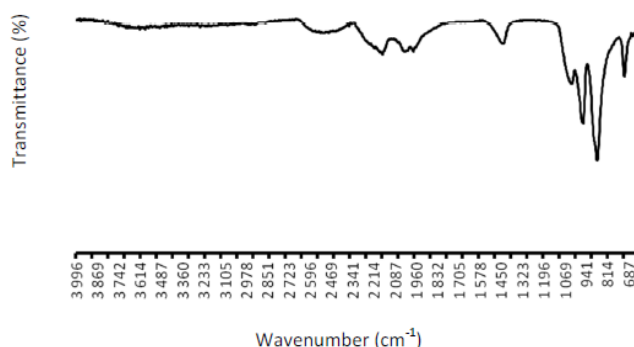

Fig. 2. Fourier-tansformed infrared (FTIR) of the synthesized sodium silicate catalyst after calcination
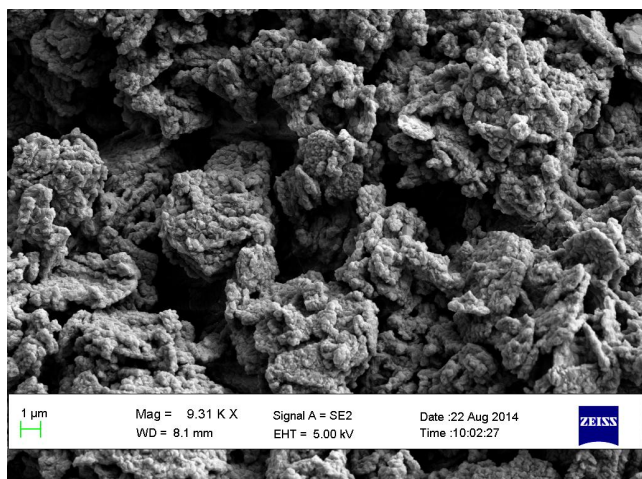
Fig. 3. SEM image of the synthesized sodium silicate catalyst after calcination.

Result of the TGA analysis is presented in Figure 4. Thermo gravimetric analysis (TGA) of the synthesized sodium silicate catalyst was carried out to understand its thermal stability. Figure 4 depicts the percentage weight loss as a function of temperature. In the first 100°C, a weight loss of about 5% was observed. The weight loss could be attributed to the evaporation of water content and some organic matters. Then the catalyst was thermally stable until 300°C after which about 0.2% weight loss was observed. Since the maximum reaction temperature during the transesterification reaction in this study was 63°C, and presence of water could affect the conversion and the yield of biodiesel [11], complete removal of water content and other organic matters from the catalyst was done by heating the catalyst in an oven to 200°C and keeping it at this temperature for 1 hour. This procedure was carried out before every transesterification reaction.
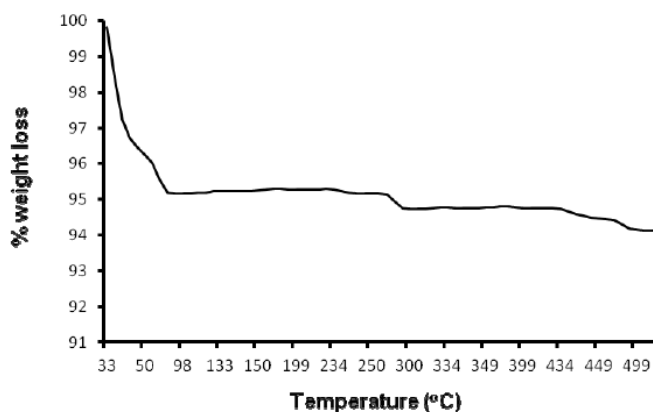

Fig. 4. Thermal stability of synthesized sodium silicate from TGA analysis

3.2. Evaluation of the catalytic activity

A qualitative analysis of the biodiesel produced was done using FT-IR spectroscopy. Fourier infrared transformation is being employed as a modern analytical technique for the detection of biodiesel due to its rapid detection method [30]. The analysis was conducted using a commercial biodiesel standard purchased from Sigma Aldrich as a reference. The spectra for the biodiesel from the commercial biodiesel and WCO are depicted in Figure 5 (a) and Figure 5 (b), respectively.


(a)

(b)
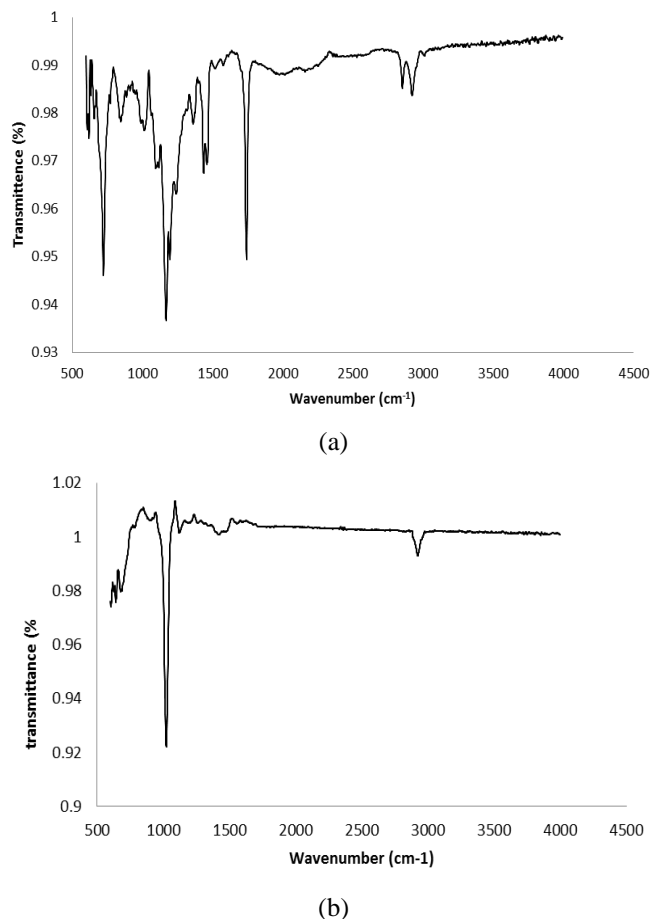
Fig. 5. Qualitative analysis of biodiesel using FTIR. Reference biodiesel (a); Biodiesel from WCO (b)

The most characteristic peak on a biodiesel IR spectrum is one at 1200 cm^{-1} which is related to O-CH$_3$ vibrations [31]. Comparing Figure 5 (a) to Figure 5 (b) shows that the peak characterized by O-CH$_3$ vibrations is prominent in both spectra. The peak gives an indication of the attachment of the alkyl group of the alcohol to the fatty acid group in the triglyceride, thus forming an ester. In addition, there are bands appearing between 1170-1200 cm^{-1} attributed to ester peaks with a (C-O) vibration [30]. The presence of the (CH$_2$)$_n$ group vibrations band appears at about 700 cm^{-1} [30]. The ester carbonyl (C=O) group stretching vibration is found between 1500-1700 cm^{-1}.

Results of the evaluation of the catalytic activity of the synthesized catalyst during production of fatty acid methyl esters (FAME) from WCO to biodiesel are presented in Figure 6. The yield of FAME during the reaction increased with time and a highest FAME yield of about 30% was

obtained after 180 minutes and at reaction temperature of 63°C. The increase in FAME yield at increasing reaction time is consistent with results from previous research efforts on the use of a homogeneous catalyst (NaOH) for the conversion of Jatropha Curcas oil seeds and palm oil to biodiesel [14-16] and on the conversion of WCO to biodiesel over RHC-SO3H and Ambertyst-15 catalysts [26]. Increase in the yield of FAME at increasing reaction time, and reaction temperature could be attributed to the kinetics of the reaction.
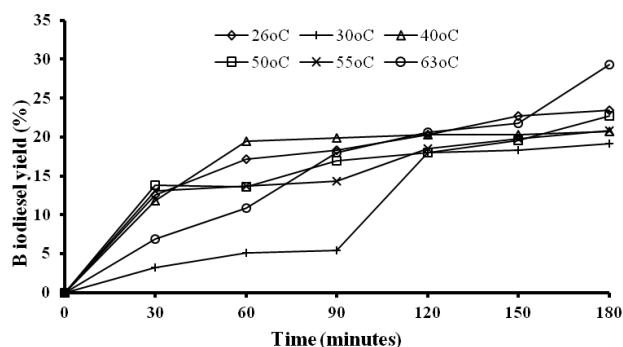
Fig. 6. Biodiesel yield as a function of reaction temperature and reaction time.

Generally, it is known that higher temperature in chemical reactions enhances breaking of bonds, thereby resulting in more radicals/atoms/molecules to participate in the formation of new bonds. In addition, research report has shown that during the biodiesel production over the sodium silicate catalyst, sodium silicate react with water to form sodium hydroxide, which eventually catalyzes the transformation of the WCO to biodiesel [25]. The mechanism of the reaction could be explained according to the speculation of Chang et al. [25], where the sodium silicate reacts with water in the reaction mixture to form sodium hydroxide that catalyzed the transesterification of the waste cooking oil to FAME.

Our results compared with literature are presented in Table 2. In spite of the difference in the methanol-to-oil ratio and the temperature at which the transesterification reaction was conducted, our results still compare very well with literature. On the same reaction time scale, the yield of FAME obtained in this study was about 5% higher that the FAME yield obtained for Ambertyst-15 catalyst. However, the performance of our catalyst in terms of the yield of FAME is lower than that of RHC-SO3H catalyst by about 12%. It could be speculated that the lower reaction temperature and lower methanol-to-oil ratio at which transesterification was conducted in this study resulted in the difference. Since reaction rate increases with increasing temperature, it is expected that increase in reaction temperature beyond 63°C in this study might enhance the yield of FAME beyond 30% while keeping the time and the methanol-to-oil ratio the same.

Table 2. Results compared with literature

Catalyst	Nature	Reaction temperature (°C)	Reaction time (hours)	Methanol/oil ratio	Biodiesel yield (%)	Reference
Ambertyst-15	acid	110	3	20:1	~25	[26]
RHC-SO3H	acid	110	3	20:1	42	[26]
Na2SiO3	base	63	3	6:1	30	This study

4. Conclusions

In this study, heterogeneous solid sodium silicate catalyst was synthesized and its catalytic activity evaluated for biodiesel synthesis from WCO. Results of the investigation reveal that the calcined as-prepared catalyst is able to convert WCO to biodiesel at mild temperature. At 63°C, methanol-to-oil ratio of 6:1 and reaction time of 180 minutes, the yield of FAME was about 30%. In addition, the results agree with reported results from literature. As far as could be ascertained, this is the first report on the conversion WCO to biodiesel over calcined heterogeneous solid sodium silicate catalyst. However, more in-depth study on the activity of the catalyst and the kinetics in transforming WCO to biodiesel is required to improve the yield of FAME. At the same time, improvement of the synthesis protocol of the catalyst via optimization study is essential to improving the activity of the catalyst. Evaluation of performance stability and optimization of the transesterification operating conditions are essential to achieving optimized process.

Acknowledgements

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