Transesterification of Animal Fat to Biodiesel Over Calcined Solid Sodium Silicate Catalyst

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Abstract—**There is a great interest in biomass resources for fuel production as they are renewable, available in abundance and eco-friendly. Animal fat is associated with high free fatty acids content (FFA) that can reduce the quality and yield of biodiesel. As a result this catalyst selection is crucial to avoid soap formation during biodiesel production. Therefore this research evaluates the feasibility of transesterification of animal fat, (beef tallow) to biodiesel over sodium silicate catalyst in a batch reactor. Brunauer, Emmett and Teller (BET) analysis was used to determine the pore sizes, pore volume and the surface area of the catalyst. Scanning electron microscope (SEM) was used to determine the surface morphology of the catalyst and Fourier transform infrared (FTIR) was used to determine the chemical functionalities of the catalyst. The operating variables that were investigated in this study are: the effect of reaction time, reaction temperature and catalyst amount on the biodiesel yield. The catalyst activity and recovery were also investigated. Maximum catalyst recovery of 82% from catalyst amount of 1 g was achieved, from which a biodiesel yield of 15.5% was obtained compared to the 17.1% biodiesel yield obtained for 1 g catalyst amount. Therefore, sodium silicate catalyst is recyclable and can maintain its activity for a number of cycle.**

***Keywords*— Biodiesel, free fatty acids, sodium silicate catalyst, transesterification**

I. INTRODUCTION

There is a great interest in biomass resources for fuel production as they are renewable, available in abundance and are eco-friendly. The use of biomass can help sustain the world's growing population, industrial development and increasing energy demand. The need for alternative source of energy is also supported by the fact that fossil fuels are not only polluting the environment, but their reserves are finite.Several forms of edible and non-edible biomass exist, with special attention paid on the non-edible forms to avoid competition with food industries. As a result, animal fat is the biomass of interest in this investigation and was selected for fuel production amongst other sources such as vegetable oil, soybean and sugar cane. The use of animal fat helps conserve the land for agricultural purposes as it eliminates the need to dispose the fats into the environment, thereby reducing the number of landfill sites required for waste. On the other-hand, the usage of animal fat is associated with high free fatty acids content (FFA) which can reduce the quality and yield of biodiesel [1].As a result, catalyst selection is crucial to avoid soap formation during biodiesel production. Therefore this research evaluates the feasibility of transesterification of animal fat, beef tallow, to biodiesel over sodium silicate catalyst in a batch reactor. The biodiesel produced has advantages such as higher cetane number, non-toxicity, no aromaticsbiodegradability and higher combustion efficiency than petroleum diesel [1]. These properties are essential in reducing the carbon monoxide, hydrocarbons and particulate matter emissions in the exhaust gas [2].

Apart from transesterification, other methods that can be used to convert animal fat into biodiesel include blending, micro-emulsions and pyrolysis [3]. These methods has disadvantages such as; heavy carbon deposits production, incomplete combustion, an increase of lubricating oil viscosity and undesirable side products like alkanes, aromatic compounds and carboxylic acids [4]. On the other hand, transesterification has the ability to reduce the viscosity of oils [5], and therefore more attractive for biodiesel production than the other methods. Basically, the transesterification reaction involves replacing the fatty acid with an alcohol in the presence of a catalyst to form esters, the biodiesel [6]. A wide range of alcohols can be used to carry out transesterification reactions, but methanol was selected amongst others such as butanol and ethanol due to its abundance, cost effectiveness and better physic chemical properties [7].

In addition, the type of catalyst that can be used for transesterification can be either acidic or basic or rather in the category of homogeneous or heterogeneous. Homogenous catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) result in saponification reactions under feedstock with high FFA content (as it is the case with animal fat). These catalysts have higher and faster conversions, but are unattractive for transesterification due to their high corrosive nature, formation of carboxylic acids, high volumes of waste water production and separation difficulties from the product [8]. All these challenges can be overcome by the use of heterogeneous basic catalysts for transesterification of animal fat; hence special interest is on sodium silicate for this investigation. These type of catalysts is corrosion resistant, reusable and can be easily separated from the product [8]. At the current stage, no work has been reported on the conversion of animal to biodiesel fat via transesterification over sodium silicate catalyst, but rather the conversion of waste cooking oil (WCO) to biodiesel using the same catalyst by Daramola et al. [9]. Against this background, conversion of animal fat to biodiesel over sodium silicate is investigated and reported in this study.

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II. MATERIALS AND METHODS

Methanol and commercialized sodium silicate were obtained from the University of the Witwatersrand. Animal fat, beef tallow, was obtained from an open butchery market in Germiston, Johannesburg South Africa. Potassium hydroxide, isopropanol, phenolphthalein, sulfuric acid, phenolphthalein indicator and ethanol were of analytical grade.

The acid value of the animal fat was determined using a titration method [10]. Initially, a titrant was prepared by dissolving 1 g of KOH in a litre of distilled water to make a KOH solution. A phenolphthalein indicator was prepared by mixing 0.05 g of phenolphthalein and 50 ml of ethanol. Then 1 ml of liquid fat was mixed with 10 ml of isopropanol in a beaker that was placed on a hot plate magnetic stirrer set at 60ºC to avoid solidification of the fat. In order to carry out titration, a few drops of phenolphthalein solution was added to the liquid –fat isopropanol, and the titrant (KOH solution), was added to the mixture until a pinkish colour change was observed. In the process, the volume of KOH solution required to neutralize the sample was recorded and used to estimate the free fatty acid content of the animal fat using the equation (i):

$$\%FFA = \frac{V \times M \times W}{m} \times 100 \qquad \text{(i)}$$

where, V and M are the volume (ml) and molarity (mol/1000 ml) of the KOH solution respectively. W is the molecular weight (g/mol) of fatty acid component in the animal fat and m is the mass (g) of the sample taken for analysis.

Saponification value is a measure of the free fatty acid and saponifiable ester groups. It is expressed as milligrams of KOH required to neutralize free acids and saponify the esters contained in one gramme of the material. For evaluating the saponification value of the free acid in the animal fat firstly, 1 g of animal fat was weighed into a 250 ml Erlenmeyer flask. Then 20 ml of 0.5 ethanol-KOH was added to the flask with fat and another flask that was blank. The flasks were placed on a hot plate and the solutions were allowed to reflux for an hour. Added to the flasks prior to titration, were a few drops of phenolphthalein indicator. Then sulphuric acid which is a titrant in this case, was added to both the flasks until the pinkish colour of the mixtures disappeared. The volume of sulphuric acid used for each sample (the blank solution and the mixture of animal fat and ethanol-KOH solution) was recorded.

Equation (ii) was used to estimate the saponification value of the free acid in the animal fat:

$$Saponification\ Vale = \frac{(ml\ blank - ml\ sample) \times NH_2SO_4 \times 56.1}{g\ sample} \qquad \text{(ii)}$$

Biodiesel was produced via the transesterification reaction. The experimental procedure was modified from Guo, et al. [11]. Initially, extraction of oil from the beef tallow was conducted at 200˚C. The water filled in the water bath was allowed to stabilize at the set temperature for 30-45 minutes until the temperature reading on the thermometer was constant. Then the 250 mL three-necked round-bottomed flask, which acted as the batch reactor was charged with 30 g of animal fat. This quantity of fat was measured to be 34.5 ml in volume. The reactor was equipped with a reflux condenser which allows for the condensation of the methanol that evaporated from the reaction mixture. There was also an insulation tape that was fitted between the reactor and the condenser in order to avoid methanol loss, thus maintaining mass conservation. A methanol to oil ratio of 8:1 was kept constant throughout the investigation. Therefore, a calculated volume of 261 ml of methanol was charged to the reactor and this was done in reference to the proposed ratio. In accordance with Guo [11], a catalyst weight of 2% of animal fat was preferable; and was used as a basis. Therefore, the catalyst amount that was calculated at this weight % was found to be 0.6 g and used to carry out transesterification.

In order to investigate the operating variables of time, temperature and catalyst amount, certain parameters were kept constant. These were the methanol to oil ratio of 8:1, animal fat of 30 g and the hot plate magnetic speed of 5. In order to investigate the effect of time on the biodiesel yield, time variations were made between 30 and 300 minutes with increment of 30 minutes at constant catalyst amount and reaction temperature of 0.6 and 64˚C respectively. In order to study the effect of reaction temperature, variations were made between 34˚C and 64˚C at constant catalyst amount of 0.6 g and reaction time of 5 hours. The catalyst amounts were varied between 0.5 and 3 g with an increment of 0.5 g. The variations in catalyst amount were made at constant reaction temperature of 64˚C and reaction time of 3 hours.

For each cycle, the catalyst was recovered in order to evaluate if sodium silicate catalyst was recyclable and can be easily separated from the product. A separating funnel, flask and suction pump were used to conduct the recovery. A pipe was connected between the suction pump and the flask. The product from the reactor was charged into the funnel after every cycle to allow for solid-liquid separation. The pump was then switched on so that it could suck all the liquid products from the reactor onto the flask. A catalyst amount of 1 g was recycled and used for a new transesterification run under conditions described above, in order to evaluate if the catalyst maintain its activity under a number of cycles.

The catalysts were characterized using Brunauer, Emmett and Teller (BET) analysis to determine the pore sizes, pore volume and the specific surface area of the catalyst. Scanning electron microscope (SEM) was used to determine the surface morphology of the catalyst and Fourier transform infrared (FTIR) was used to determine the chemical functionalities of the catalyst.

III. RESULTS AND DISCUSSION

Table I shows the BET analysis results of the catalyst (sodium silicate). The result shows the specific surface area, pore volume and pore sizes of the catalyst. Since the catalyst weight needs to be maintained during the transesterification process, the values obtained in Table I can be used to calculate the catalyst weight. This is because weight can be calculated from the pore volume and pore sizes.

TABLE I
BET ANALYSIS OF THE CATALYST (SODIUM SILICATE)

Parameter	**Value**
Surface area (m^2/g)	0.3862
Pore volume (cm^3/g)	0.006242
Pore size (nm)	59.18

The BET evaluation is important because the pore volume and size have a tendency to decrease when the metal ion (Na^+) penetrates the silica.

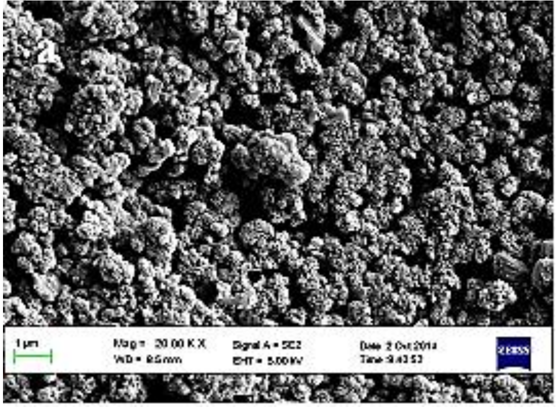

Fig. 1. SEM image of sodium silicate

Fig. 1 showed the SEM image of sodium silicate. This characterization technique is important since the re-use of the catalyst after a number of cycles tends to make the catalyst agglomerate to large blocks which may lead to activity loss due to reduced contact area between the catalyst and the reactants. Therefore, after every cycle, the catalyst needs to be washed and characterized using SEM to evaluate if the catalyst structures have not formed coarse accumulation of large blocks that can affect its activity.

Fig. 2 shows the chemical functionality of the catalyst (sodium silicate). The spectra band around 650-700 cm^{-1} represent O-Si-O. The weak peak at 3300 is an hydroxyl bond (O-H). C-H bond is detected at around 2800 cm^{-1}, and Si-O-Si at spectrum band of around 1000 cm^{-1}

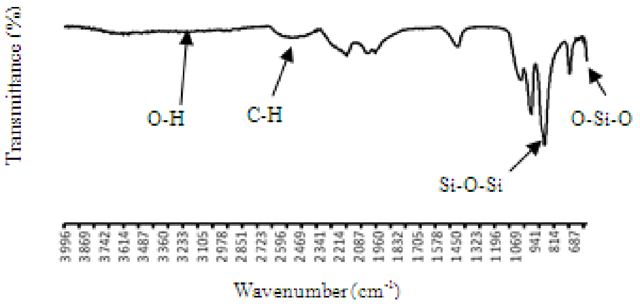

Fig. 2. FTIR spectra of sodium silicate catalyst

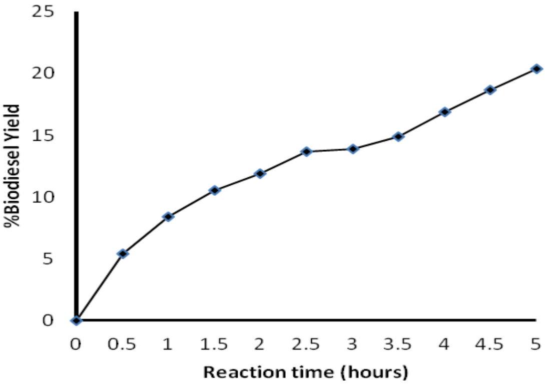

Fig. 3. Effect of reaction time on biodiesel yield

Fig. 3 represents the result of biodiesel yield. Biodiesel yield increased with an increase in time. It is also expected that the biodiesel yield should increase linearly with time until equilibrium is reached. Observed in Fig. 3 is an almost linear trend and it can be concluded that at higher reaction time (5 hours), the yield is expected to be higher because the longer the period of contact between the reactants, the higher the conversion and therefore increased yield.

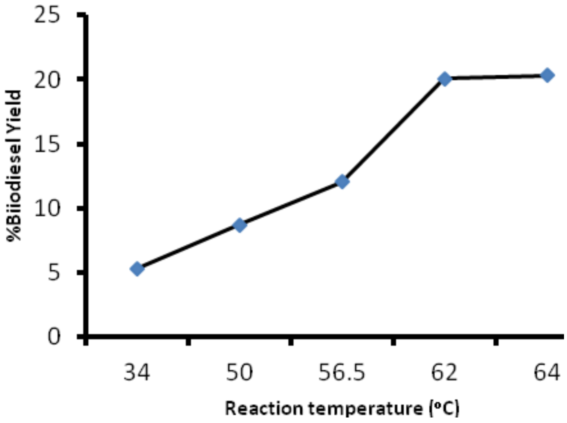

Fig. 4: Effect of reaction temperature on biodiesel yield.

In Fig. 4, the effect of temperature on the biodiesel yield is shown. Biodiesel yield increased with an increase in reaction temperature. The effect of temperature on yield is more pronounced above 50˚C, which is indicated by the higher slope of the curve after 50˚C. Similar results were observed by Daramola et al. [9]. The observed trend can further be explained by the Arrhenius equation, where the reaction constant K, increases as temperature increases. In elaboration, increasing temperature causes effective collisions between the reacting molecules, thus increasing conversion of the animal fat to biodiesel, hence higher biodiesel yields are obtained at higher temperatures.

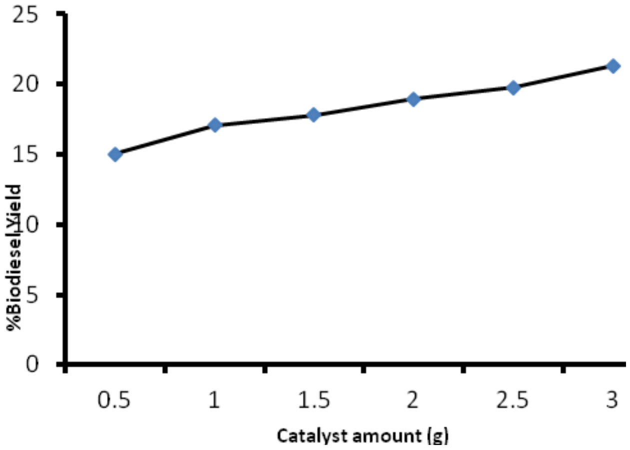

Fig. 5. Effect of the amount of catalyst on biodiesel yield

Fig. 5 shows the effect of concentration of catalyst on biodiesel yield. Biodiesel yield increased with an increase in amount of catalyst. The observed trend can be attributed to the fact that the higher the catalyst amount, the more the active sides of the catalyst hence increased biodiesel yield. However, the impact of increasing catalyst amount is not as significant as with the influence of the other two operating variables (Figs. 3 and 4). This is because with heterogeneous catalysts, there are a mass transfer limitation that causes solid catalysts to not impact greatly on conversion, thereby influencing an increase in amount of catalyst to slightly affect biodiesel yield compared to the effect of temperature and reaction time.

IV. CONCLUSIONS

The production of biodiesel from animal fat is feasible over sodium silicate catalyst. Biodiesel yield increased with an increase in reaction time, reaction temperature and amount of catalyst. The results agreed well with literatures. The yield achieved in this work was relatively lower compared to previous works by other researchers. This is because with heterogeneous catalysts, the amount of catalyst did not have much effect on conversion but the surface area did, unlike homogenous catalysts. This was a result of mass transfer limitations that were more pronounced in heterogeneous catalysts than homogenous catalysts.

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