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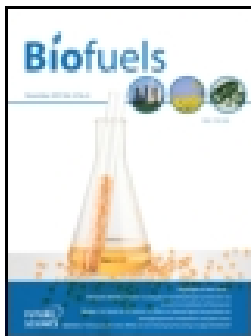
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ABSTRACT

This study investigates the effect of zeolite nano-catalyst on the yield of biodiesel and biochar formed from the pyrolysis of tallow (cow fat). Residual waste cow fat was pyrolyzed in a fixed-bed reactor of laboratory-scale volume $2200\,cm^3$, at operating temperatures of 450, 500, 530, and 580 °C and heating rates of 4, 5, and 6 °C/min. The molecular composition of cow fat was analyzed using a gas chromatography molecular spectrograph (GC-MS). It was observed that the biodiesel produced without a catalyst was mainly composed of aromatic carboxylic acids, esters, alkanes, alkenes, and alkanes, while the biodiesel produced with zeolite nano-catalyst consisted mainly of methyl esters, pentanoic acid, heptanoic acid, cyclo-olefins, 4,4-dimethylcyclohexene, butyl-cyclo-hexane, butyl-cyclopentane, and 1-pentylcyclopentene. A biodiesel yield of 58% was achieved when a 1% zeolite nano-catalyst was used to pyrolyze the tallow at an operating temperature of 530 °C and heating rate of 6 °C/min. When the tallow was pyrolyzed without a zeolitic catalyst, decarboxylation was promoted, and a higher biodiesel yield of 82.78 wt% was achieved. Results from this study revealed that although zeolite nano-catalyst did not show an incremental effect on the yield of biodiesel, it favors biogas production and biochar formation.

1. Introduction

The growing energy demand, population growth, and economic developments, worsened by the fast exhaustion of fossil fuel sources have necessitated a need to replenish energy sources with clean and renewable energy options to achieve sustainable development [1–4]. To achieve sustainable development in the environment, researchers have suggested biomass as an attractive supplement to fossil fuels because of its negligible Sulphur, nitrogen, and ash content, which leads to lower emissions of SO_2, NOx, and soot compared to conventional fossil fuels [5, 6]. Biomass is an important source of clean energy that can be converted directly into the liquid, gaseous, and solid fuels, usable for transport, heat, and power production [7]. Many plant-based biomass species such as almond shell, apple pulp, apricot stones, bagasse, beechwood, cellulose, corn–potato starch gel, corn stalk, cotton stalk, extracted oil palm fibers, filter pulp, grape, grass, groundnut shell, and maize have been pyrolyzed to produce several biofuels in the past [8, 9]. There is a need to consider other non-plant sources of biomass (for example cow fat) for the production of biodiesel.

Biodiesel is a fuel that comprises several mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats [10]. Biodiesel can be produced *via* the trans-esterification of vegetable oils, animal fats, or waste oil and methanol with a catalyst to produce Fatty Acid Methyl Ester (FAME). The major advantage of biodiesel as a fuel compared to conventional Petro-diesel fuel is its reduced exhaust emissions, high flash point, and renewable sources. Also, biodiesel has a higher oxygen content than Petro-diesel fuel; hence, when it is used in diesel engines, there is a reduction in particulate emissions, carbon monoxide (CO), sulfur, polyaromatic compound formation, smoke, and noise.

Animal fat is one of the sources of biomass for biodiesel production [11]. Other sources and uses of animal wastes that could be considered for biodiesel production are presented in Figure 1. Fats are found in living organisms, consisting essentially of fatty acid esters and glycerin mixtures, known as triacylglycerols or triglycerides [13]. These triacylglycerols have high viscosities, therefore they cannot be used directly as fuels in common diesel engines but will need to be refined to conform with diesel properties. Cow fat (tallow) is a mixture of triglycerides of which tristearin is a major component [14]. These saturated fatty acid components in tallow account for almost 50% of the total fatty acids. The higher palmitic and stearic acid contents of tallow also give it some unique properties such as high melting point and high viscosity [15]. The general molecular composition of animal fat used for the production of biodiesel in this study is presented in Table 1, and the properties of tallow (feedstock for this study) are presented in Table 2.

The main objective of this study is to investigate the effect of zeolite nano-catalyst (Zeolite- 96096) on the yield of biodiesel, biogas, and biochar formed during the pyrolysis of cow fat for biodiesel production. In the process, the effect of the catalyst on the yield of biodiesel produced, as well as its composition will also be determined. Most

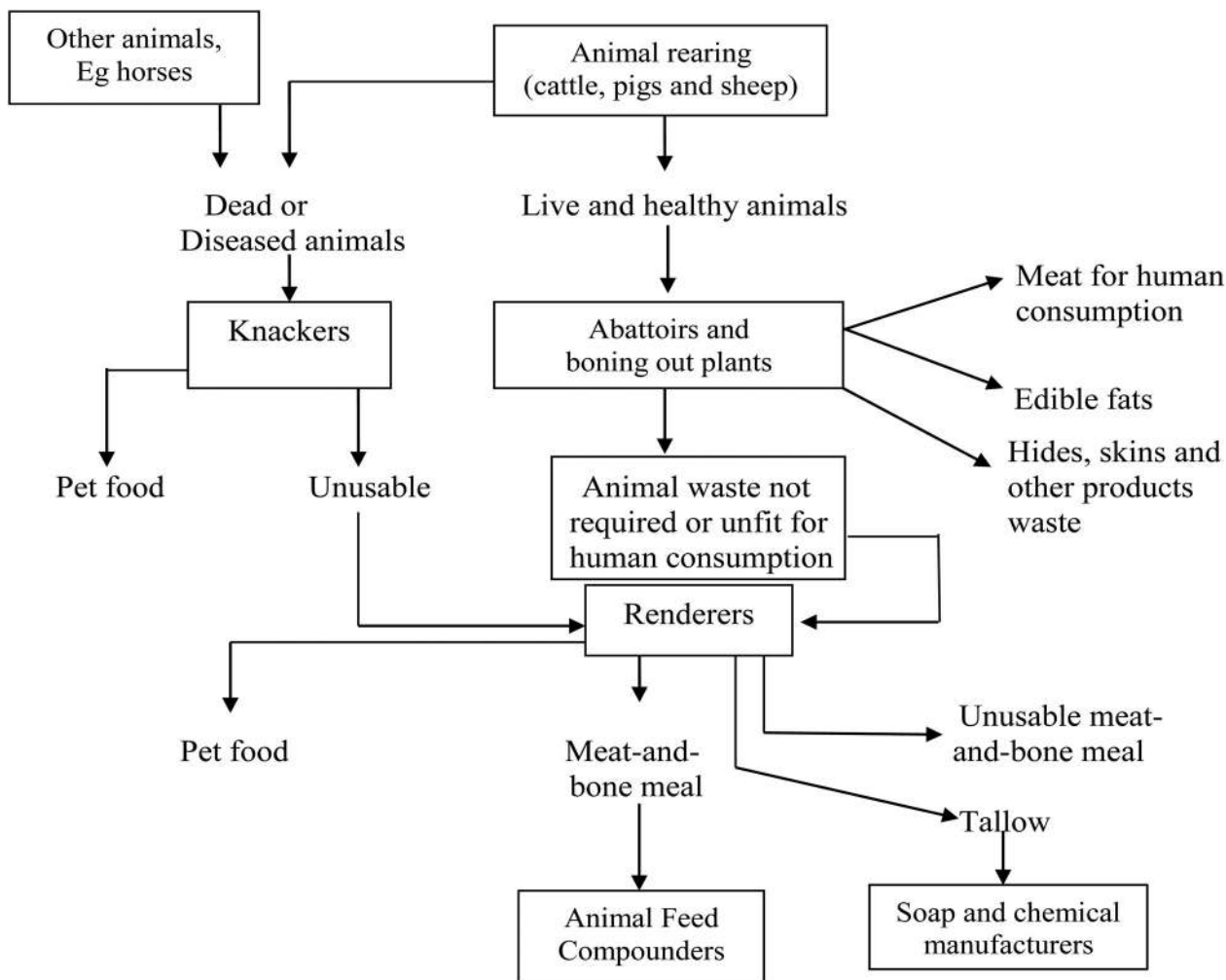**CONTACT** Kelvin O. Yoro ✉ kelvin.yoroo@gmail.com; koyoro@lbl.gov 🖂 School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Private Bag X3, Wits 2050, Johannesburg, South Africa

Figure 1. Sources and uses of wastes in red meat. Adapted and modified from Obidike [12].

Table 1. Molecular composition of the feedstock (Tallow).

Organic Acid	Content (%)
Linoleic acid	1.69
Linolenic acid	1.05
Myristic acid	1.01
Oleic acid	52.82
Palmitic acid	17.73
Stearic acid	11.58
Others	14.12

Table 2. Properties of the tallow.

Properties	Values
pH	5.72
Acid Value (mg KOH/g)	225.32
% Ash	6.33
% C	76.06
% H	11.72
% O	12.21
% N	–
% S	0.00
Density (g/cm^3)	0.63
Calorific Value (MJ/kg)	39.41

studies in the past that attempted to investigate the effect of catalysts on biodiesel yield did not consider investigating its effect on other properties such as biogas and biochar formation with different heating rates, which constitutes a major novelty in this study

Biochemical, thermochemical, physical, and chemical methods are the available technologies for recovering biodiesel from triglyceride-based materials. So far, thermochemical methods have been widely recommended for biodiesel production by different researchers in this field [16, 17]. Thermochemical methods for recovering biodiesel include gasification, pyrolysis, and combustion. Amongst these thermochemical technologies, pyrolysis is widely embraced because it is a simple and cost-effective technology [18]. Nonetheless, the effect of catalyst on the yield of biodiesel produced *via* the pyrolysis of cow fat (tallow) is an interesting area of research that is scarcely reported in the literature.

In response to fill the aforementioned research gap, this study will report the effect of zeolitic nano-catalyst on the yield of biodiesel produced during the pyrolysis of cow fat (tallow), as well as the effect of zeolite on the formation of biogas and biochar during the biodiesel production as earlier mentioned.

2. Energy security and the potential of producing biodiesel from animal wastes

Energy insecurity is one of the greatest threats facing humanity today, combined with human-induced climate change [19–21]. Different studies have established that oil reserves have fallen since the 1960s due to high demand and excessive consumption by developed countries [22, 23]. Global oil supplies have been estimated to be less than 10 gigatons a year since 2015, and with the current global energy consumption approaching 10 gigatons a year, the impending energy crisis needs to be avoided.

Hence, the need to conduct comprehensive waste management research to valorize waste animal fats to useful products like biodiesel which is a widely accepted alternative to fossil fuels. In addition, the recent work of Matušinec et al. [24] has established that waste animal fats have a promising potential in the upcoming years to allow for not only the production of biodiesel but also biodegradable polymers, thermal and electric energy.

Currently, more than 80% of the world's primary energy comes from fossil fuels, with crude oil up to 32.8%, coal, 27.2%, and natural gas, 20.9% [25–27]. The production of biodiesel is one of the most attractive and fast-expanding applications of clean, renewable, and sustainable energy sources in recent times [28, 29]. Also, the production of biodiesel guarantees better profitability of inedible animal by-products for sustainable energy development. Biodiesel consists of monoalkyl esters of long-chain fatty acids that produce oil or fat, and vegetable oil and waste cooking oil have been the main feedstocks used for biodiesel production so far. Although the aforementioned feedstocks for biodiesel production have yielded interesting results in the past, it is worth stating that the use of vegetable oil generates a high price for biodiesel, which has led to the use of animal fats as an interesting alternative [30]. In addition to its renewable nature, biodiesel also forms an interesting alternative to energy fuels due to its good lubricating properties, improved cetane number, flash point as well as its biodegradable and non-toxic nature. Biodiesel also contributes to environmental sustainability by reducing CO_2 footprints.

The transformation of animals into meat in a slaughterhouse produces a significant amount of wastes, comprising mainly of fats. Furthermore, cattle produce about 31 kg of solid wastes from their rumen content, manure, skins, horns, hooves, and bones [31]. Also, about 820 L/day of liquid wastes comprising blood, bile, urine, and water is usually discharged as animal wastes from abattoirs [32]. Most slaughterhouses in developing countries dispose off the aforementioned animal wastes using methods such as incineration, spraying, and burial which are environmentally unfriendly [33]. Some of these animal wastes find their way into nearby streams and lakes; thereby rendering such disposal methods unhygienic and dangerous to environmental health. The indiscriminate disposal of animal wastes into water bodies contributes to the high organic nutrient loads in streams, leading to eutrophication and the impairment of aquatic life [34]. Furthermore, some slaughterhouses have developed substandard ways to dispose off animal fats. For instance, some slaughterhouses pre-treat bulk animal wastes with sodium hydroxide in an inadvertent saponification process to produce a soap-like mass which is usually disposed into streams. This "soap-like" mass slowly dissolves in water bodies as it moves along and is harmful to aquatic life. Also, the sodium hydroxide used in pretreating these wastes is not cheap, and the costs of contracting a waste processing company is high, thereby making the total expenses for the disposal of these animal wastes unaffordable. Therefore, there is an urgent need to promote the development of green alternative fuels through the beneficiation and valorization of animal wastes to meet growing global energy demand as well as reduce CO_2 emissions. In response to this need, Obidike [12] studied

the Karan Beef abattoir in Johannesburg South Africa which slaughters about 1200 cattle per day. Waste fats (tallow) from these slaughtered cattle could produce about 1.6 MWh of electricity, and which could take care of 554.75 households monthly in Diepsloot which is a township in Johannesburg with a population of about 350,000 people and 87,500 households. About 158 abattoirs the size of Karan Beef would supply the electricity need of Diepsloot and this is feasible since there are 479 registered abattoirs in South Africa. Obidike [12] also established that it is possible to produce biodiesel on a large scale in South Africa. A process flow diagram describing the unit operations to produce biodiesel is presented in Figure 2.

3. Materials and methods

3.1. Materials

The materials used in this study consist of waste cow fat purchased from Karan Beef (Pty) Ltd in Johannesburg, South Africa. A freezer was used to store the cow fat at $-10\,°C$ in the course of the experiments, while commercially available nano-catalyst (zeolite powder) with product number 96096 manufactured by Sigma Aldrich South Africa, and molar composition: 0.6 K_2O: 4.0 Na_2O: 1 Al_2O_3: 2.0 "0.1 SiO_2: x H_2O and the particle size $<10\,\mu m$ was used to study the catalytic effect of zeolite on the yield of the biodiesel produced from the pyrolysis of tallow in this study.

3.2. Methods

3.2.1. Characterization of materials and products

Before the pyrolysis experiment was carried out, residual fats were lyophilized and analyzed by elemental analysis (CHNS-O). The CHNS content in the feedstock was determined using a Flash 2000 CHNS-O analyzer equipped with an automatic sampler manufactured by Thermo Scientific USA. About 2.0 mg sample was weighed in a tin capsule, the capsule was folded and weighed again. The sample was then placed on the Flash 2000 CHNS-O autosampler and the instrument was adjusted according to the following process conditions; O_2 pressure: 250 kPa, Oven temperature: 950 °C, Media flow 140 mL/min, Reference flow: 100 mL/min, Oxygen flow: 250 mL/min and column temperature: 65 °C.

To analytically determine the CHNS-O elements present in the feedstock, a sample was put into a quartz reactor filled with electrolytic copper. Oxygen was then introduced to aid the combustion of the sample while the carrier gas (Nitrogen) transports the sample through the reactor to the thermal conductivity detector (TCD) in an oven maintained at 65 °C. The results were processed and displayed. The oxygen determination was done using a TCD detector with inverted polarity, and the oxygen content was calculated based on the difference. Results obtained from the CHNS-O analysis are presented in Table 3.

3.2.2. Determination of acid value and ash content

5 g of the sample was placed in a 250 mL beaker containing a mixture of 30 mL of toluene, water, and propyl solvent. The proportion of the mixture was in the ratio of 100: 1: 100. The
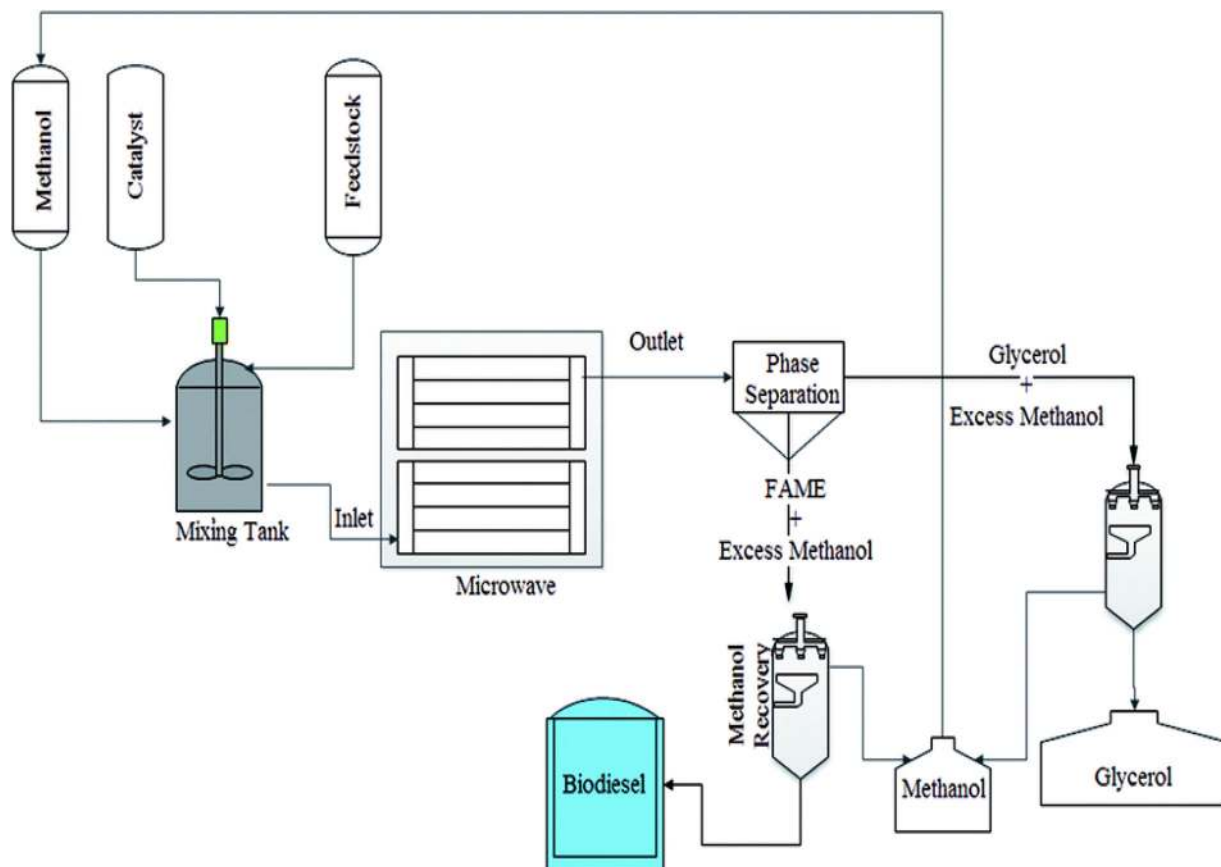
Figure 2. A microwave-supported biodiesel production process. Adapted from Ruhul et al. [35] with written copyright permission obtained from the original publishers.

Table 3. Properties of the samples of the pyrolysis with zeolite catalyst.

Sample	pH	Acid Value mg KOH/g	Ash %	C %	H %	N %	S %	O %	Viscosity mm2/s	Density g/cm3	CV MJ/kg
C1	4.11	121.44	3.34	73.89	11.30	0.34	0	14.81	6.25	0.55	35.47
C2	4.08	121.86	3.36	74.07	11.31	0.36	0	14.23	6.33	0.55	35.40
C3	4.11	125.88	3.33	74.39	11.46	0.36	0	13.78	6.31	0.55	35.21

content of the beaker was then titrated with 0.1 mol/L KOH to determine the acid number, while 702 SM Titrino was used to determine the acid value of the samples. To determine the ash content for the sample in this study, 1 g of the sample was weighed in a porcelain crucible and transferred to an oven powered at 850 °C. The sample was left for 8 h in the oven until the ashing process was completed. The percentage of ash content was then calculated after cooling and weighing the sample using Equation 1.

$$\% \ Ash \ content = \frac{Weight \ of \ ash \ (g)}{Weight \ of \ original \ sample \ (g)} \ X \ 100$$

(1)

3.2.3. Determination of pH and calorific value

To determine the pH of the tallow, an Orion pH meter was calibrated using a set of solutions (with pH of 4, 7, and 9) while the sample was ground into a powder and made pasty. A pH electrode was then inserted into a beaker containing the pasty animal fat (tallow), and the readings were obtained from the pH meter.

Determination of calorific value of the biodiesel was done using a bomb calorimeter (Model: Supercal 2 Modular Calorimeter) and manufactured by Energy Instrumentation, South Africa. The sample was weighed and transferred to a calorie counter, and an ignition cable

was installed. The pump was closed tightly under gas pressure. The bomb was placed in the ignition calorimeter and the calorific value (CV) value was displayed on the device.

3.2.4. Determination of density, viscosity, and x-ray diffraction

The sample was mixed in a paste and poured into a measuring cylinder which was placed on an analytical chemical balance and weighed. The density was determined using the volume measured in the calibrated measuring cylinder according to Equation 2.

$$Density \ (g/L) = \frac{Mass \ of \ sample \ (g)}{Volume \ of \ liquid \ displaced \ (L)}$$

(2)

The viscosity of the biodiesel produced was determined using an Ubbelohde viscosity meter. The sample was mixed into a viscous paste and introduced into a capillary tube to determine its flow according to the Poiseuille equation presented in Equation 3.

$$Q = \frac{\pi P r^4}{8 \eta l}$$

(3)

where Q is the flow of the fluid, η is the viscosity of the fluid, P is the pressure gradient across the tubing, l is the length and r is the diameter of the tubing.
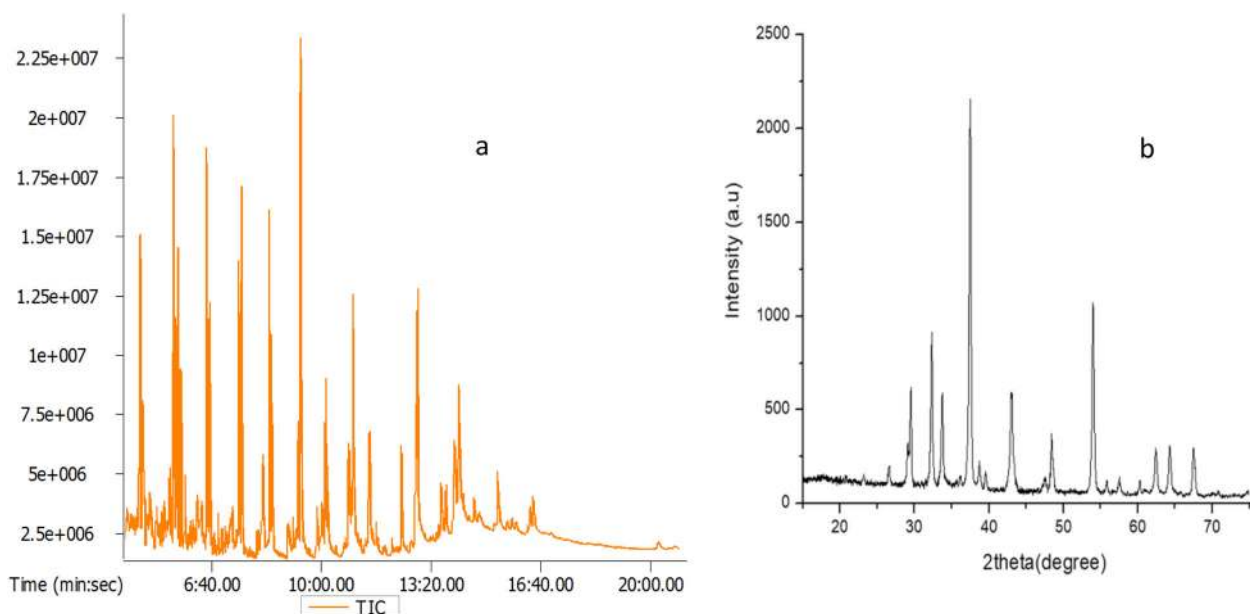
Figure 3. XRD analysis for catalyzed biodiesel production (3a) in this study versus (3b) without catalyst reported by Degfie et al. [37]. Figure 3b was adapted from Degfie et al. [37] with permission under a Creative Commons Attribution 4.0 International License. Creative Commons – Attribution 4.0 International – CC BY 4.0.

GC-MS analysis of the neutral biodiesel fraction was performed using a Pegasus 4 D GC x GC-MS low-resolution gas chromatograph machine. The injector was set at 250 °C and Nitrogen was used as the carrier gas. The Gas chromatograph (GC) oven temperature was kept at 40 °C for 2 min, then heated to 300 °C at a rate of 5 °C min^{-1} and finally maintained for 30 min at 300 °C. The identification of compounds was done using the NIST database as reported in a similar study by Farooq et al. [36] and Degfie et al. [37]. XRD analysis was used to identify the crystalline phases present in the sample (cow fat), as well as its chemical composition. For the analysis of X-ray diffraction of the sample, the animal fat sample was dried in a traditional oven at 110 °C and then ground to a fine powder. The ground sample of animal fat was mounted on a sample holder and inserted into the XRD machine where the measurement was performed. The XRD graph obtained for this study is presented in Figure 3a.

4. Experimental procedure for the pyrolysis of animal fat

All procedures and methodologies used in this study were adapted and modified from a dissertation [12] submitted to the University of Witwatersrand by the lead author of this study. The pyrolysis experiment was carried out in a laboratory bed reactor heated by an electric furnace which is controlled by a panel. The reactor was made of stainless steel but was protected by a plastic mesh covering the entire outline. The cylindrical tube (with silica inside the pyrolizer) has a height of 100 cm, an outer diameter of 60 cm, a volume of 2200 cm^3, and a total mass of 822 g. The control panel was adjusted to the desired temperature and heating speed for each trial run.

The silica tube containing animal fat samples within the reactor during the experiments is 60 cm in diameter and 100 cm in height. The inlet flow pipe of the carrier gas (nitrogen) and the pyrolysis vapor of the furnace were in the extended ends of the silicate tube. The temperature was controlled by submerging a thermocouple within the reactor. All pyrolysis experiments were carried out under atmospheric pressure and inert conditions. During the experiments, nitrogen gas was washed continuously while the reactor was held at 50 cm^3/min to reactor air, and all gases produced during pyrolysis were removed. The collections were sealed with Parafilm and Gel to prevent any type of gas leak.

In each experiment, 50 g of the sample with particle sizes between 0.6 − 0.85 μm was placed inside the reactor and heated from room temperature to the desired temperature at different heating rates. Heating was maintained at the final temperature for 15 min until no significant gas release was observed. A flow diagram describing the experimental set-up for the pyrolysis in this study is presented in Figure 4.

The gas and steam formed during pyrolysis flow from the top of the reactor through a capture system containing a condenser cooled with cold tap water. The original glass bottle which contains the biodiesel is kept in a container and the temperature is maintained at 20 °C. The biodiesel was composed of two phases; the primary phase where water is separated and the upper stage where rich organic compounds are formed. The result of the collected biodiesel, biochar, and biogas could be calculated using Equation 4;

$$Biodiesel\ collected = \frac{Mass\ of\ pyrolysed\ biomass}{Total\ size\ of\ feed\ material} \ x\ 100$$

(4)

The non-condensing vapor was passed through a starting line, while the amount of non-consolidated gases produced were determined by the difference in the mass balance.

5. Results and discussion

The calorific value (CV) of the residual animal fat (39.41 MJ/kg) in this study falls within the expected values, but its density of 0.63 g/cm^3 is slightly low. Increased yield of
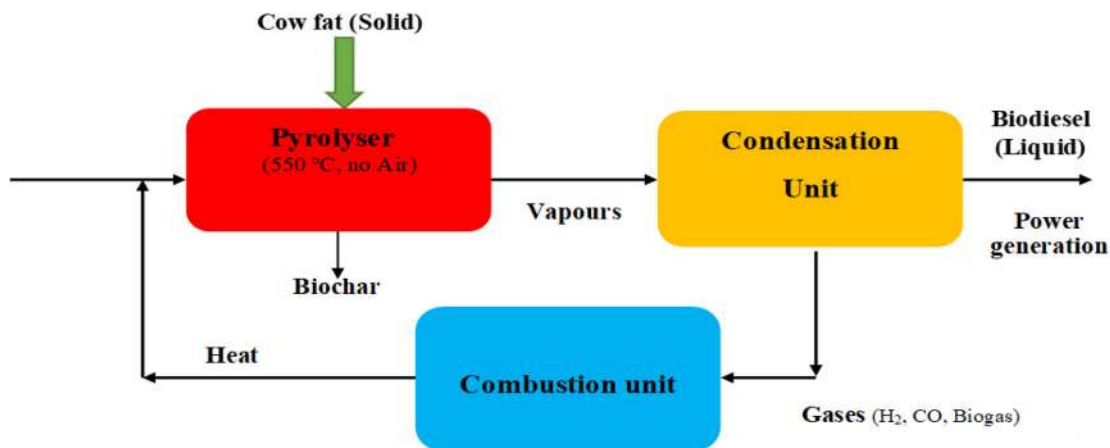
Figure 4. Schematic steps for the pyrolysis of cow fat.
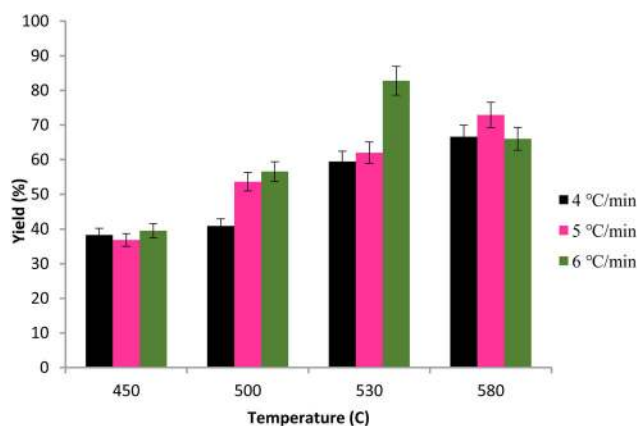

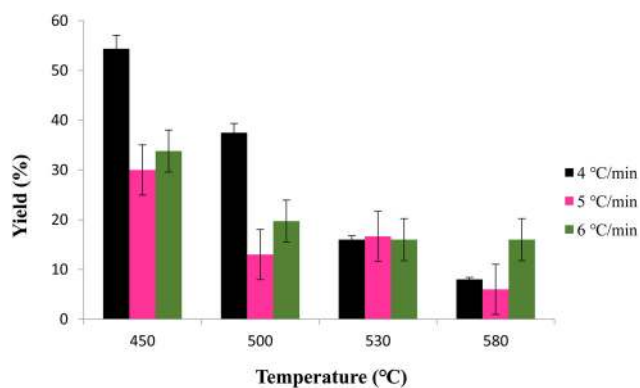**Figure 5.** Yield of biodiesel at 4, 5, and 6 °C/min heating rates.

Figure 6. Yield of biochar at 4, 5, and 6 °C/min heating rates.

biodiesel is expected after pyrolysis of the animal fats with zeolite due to the dehydrating nature of the process. However, this did not happen in this study; instead, an increased yield of biogas and biochar was observed.

Since there is no nitrogen in the tallow but only present as the carrier gas, any nitrogen oxide (NOx) contaminants formed during the process would have been formed during the high-temperature combustion. Atmospheric nitrogen gas entering the combustion zone as part of the combustion air also increases the nitrogen content of the fuel, although not all the nitrogen is infused into the fuel during combustion because some of the nitrogen escape the reaction chamber with the flue gas. The high ash content (6.33%) reported in this study is a huge cause for concern; this could be attributed to the aging and sedimentation of the oil produced. which could block the filter in an engine injection. The pH value of the biodiesel produced is almost neutral, but if we consider the dehydrating nature of the pyrolysis process, a drop in the acidic value is expected.

5.1. Pyrolysis experiments without the zeolitic nano-catalyst

5.1.1. Effect of temperature on yield and performance
At a heating rate of 6 °C/min, as shown in Figure 5, the yield of biodiesel increased from 56.56% to 82.78% as the final temperature was increased from 500 °C to 530 °C but dropped to 66% when it was increased to 580 °C. The resultant yield of 82.78% at a final temperature of 530 °C and a heating rate of 6 °C/min is the highest obtained for

this study. The yield of the biodiesel at a heating rate of 5 °C/min and final temperatures of 450 °C, 500 °C, 530 °C, and 580 °C is 36.86%, 53.62%, 62%, and 72.90% respectively, showing an obvious progressive trend. At a heating rate of 4 °C/min, the biofuel yield at final temperatures of 450 °C, 530 °C, and 580 °C was 38.32%, 59.44%, and 66.60% respectively which also show a progressive trend as presented in Figure 5.

At a heating rate of 5 °C/min, biochar production gradually decreased to 30%, 13%, 16.64%, and 6% at final temperatures of 450 °C, 500 °C, 530 °C, and 580 °C respectively as depicted in Figure 5. Similarly, the mass of gases (biogas) in Figure 6 decreased, resulting in yields of 33.14%, 33.38%, 21.36%, and 21.1% at operating temperatures of 450 °C, 500 °C, 530 °C, and 580 °C respectively.

Regarding the yield of biochar at 4 °C/min in Figure 6, a gradual decrease corresponding to 54%, 16%, and 8% were observed at final temperatures of 450 °C, 530 °C, and 580 °C respectively. Consequently, the yield of non-condensable gases depicted in Figure 7 reveals a gradual decrease. At operating temperatures of 450 °C, 530 °C, and 580 °C, the yields of non-condensable gases were 7.32%, 24.56%, and 25.40% respectively.

The results displayed in Figure 7 showed superiority compared to a yield of 58% wt reported by Hassen-Trabelsi et al. [38] for the pyrolysis of pork fat. Lower yields of biodiesel have also been reported for a comparable waste based on triglycerides. For example, Demirbas [15] reported 77.1 wt% yields with beef tallow at 500 °C, while about 73 wt% was obtained using fish oil waste at 525 °C. The
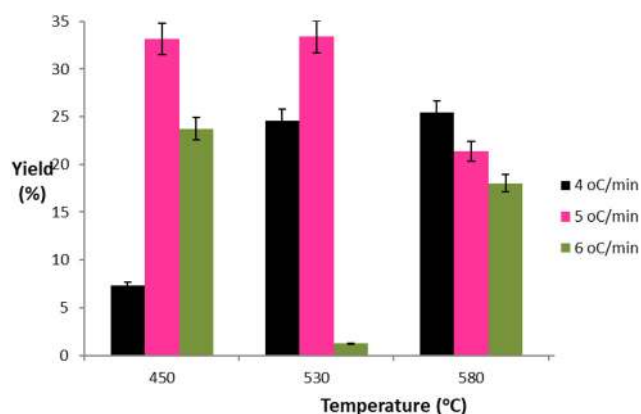
Figure 7. Yield of biogas at 4, 5, and 6 °C/min heating rates.

Figure 8. Biodiesel yield at selected heating rates and final temperatures.

yield reported in this study is also in agreement with the pyrolysis results from raw materials such as wood-biomass (60–75 wt%) reported by Papari and Hawboldt [39] and Veses et al. [40], Seaweed (38–47 wt%) reported by Bae et al. [41], Polyethylene-based materials (86.2 wt%) reported by Fekhar et al. [42] and Sewage sludge (27–54 wt%) reported by Karaca et al. [43] and Shahraki et al. [44].

5.1.2. Effect of heating rate on the yield of biodiesel

At final temperatures of 450, 500, 530 and 580 °C with alternation between heating rates of 4, 5 and 6 °C/min for each temperature, a gradual change in product yield occurred as depicted in Figure 8.

At a final temperature set at 500 °C in this study (see Figure 8), the yield increased from 53.62% to 56.56% with an increase in heating rate from 5 °C/min to 6 °C/min. At a temperature of 530 °C, the trend continued with yields of 59.44%, 62%, and 82.78% at corresponding heating rates of 4, 5, and 6 °C/min. This is similar to the results reported in the work of Hassen-Trabelsi et al. [38] using lard pyrolysis, where an increase in pyrolysis temperature from 400 °C to 500 °C led to an increase from 54 wt% biodiesel to 76 wt%. Incidentally, the yield was reduced to 580 °C, leaving 82.78% as the maximum yield obtained in the pyrolysis experiments. This also corresponds to the results in the work of Hassen-Trabelsi et al. [38], where the biodiesel yield did not increase significantly when the temperature was raised from 500 °C to 550 °C.

5.2. Effect of zeolite nano-catalyst on the pyrolysis experiment

The pyrolysis experiments reported herein were performed with 1% and 2% zeolitic-nano catalyst at a heating rate of 6 °C/min, and a temperature of 500 °C and 530 °C, respectively. An initial 1% zeolite Nano-catalyst was used in the pyrolysis experiment at a maximum temperature of 500 °C resulting in a yield of 56% as shown in Figure 9.

Furthermore, as the final temperature was raised to 530 °C and the zeolite nano-catalyst was kept at 1%, a yield of 58% was obtained. When the amount of zeolite nano-catalyst was increased to 2%, the yield reduced to 54%. It was observed that instead of improving the yield of bio-diesel, the zeolite in the nano-catalyst inhibited yield increase for biodiesel, with a high degree of coke and gas formation. This agrees with the work of Rehan et al. [45]
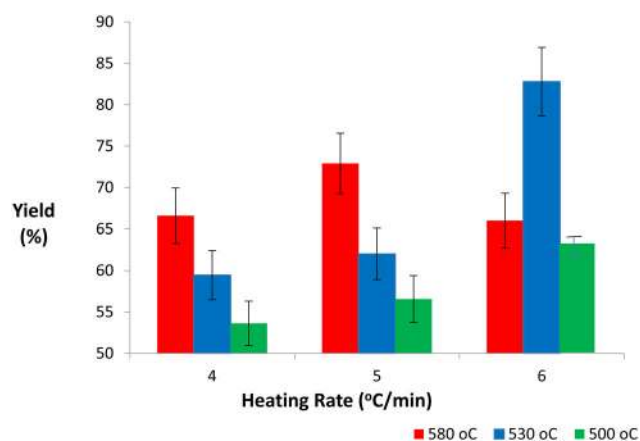
on thermal pyrolysis of polystyrene (PS) plastic waste where they produced a maximum liquid oil of 80.8% with gases of 13% and char of 6.2%, but the catalytic pyrolysis using zeolite decreased the liquid oil yield (52%), increased the gases yield (17.7%) and char (30.1%).

This confirms the speculation in the works of Ingle et al. [46] and Romero et al. [47], which states that irrespective of the feedstock pyrolyzed to produce biodiesel, the addition of zeolite nano-catalyst does not improve the yield of biodiesel produced but aids the formation of biogas. It was also observed in this study that increased operating temperatures do not show any incremental effect on the yield of biodiesel.

The effect of zeolitic nano-catalyst on the yield of biochar during the pyrolysis of cow fat (tallow) was investigated and presented in Figure 10. It was observed that the yield of biochar also dropped when the feedstock was increased with 1 and 2% zeolite content. Also, the increased operating temperature did not show any incremental effect on the yield of biochar with or without zeolite, and there was no significant change in mass-produced biochar and undesirable gases.

The reduced yield and improved quality of the bio-oil through catalysis could be ascribed to the high BET surface area (4.3 m^2/g), pore size (18.7 Å), and volume (0.02 cc/g) of natural zeolite [45, 48]. This microporous nature of zeolite adsorbs selective larger hydrocarbon chain molecules and other impurities to produce improved quality bio-oil with an increase in char and biogas production in the reactions that facilitate thermal cracking [49–51]. According to (52), catalysts with higher acidity, like zeolite, increase the cracking process and also increases biogas production and decrease liquid oil yields.

The effect of the zeolite nano-catalyst on the yield of biogas was further studied and presented in Figure 11. It was observed that at both temperatures (500 and 530 °C), the presence of zeolite improved the yield of biogas. This means that the zeolitic nano-catalyst has a favorable effect on the yield of biogas (not biodiesel) during the pyrolysis of cow fat than pig fat reported by Hassen-Trabelsi et al. [38]. However, when more zeolite nano-catalyst was introduced into the biodiesel production process, the yield of biogas began to slightly decline. Since the bio-oil of thermal pyrolysis is a complex mixture of oxygenated hydrocarbons and water [38] which is often unstable, low-grade, acid-corrosive, tarry, and discoloured [53, 54]. Conversely, the high concentration of methyl esters has high stability,
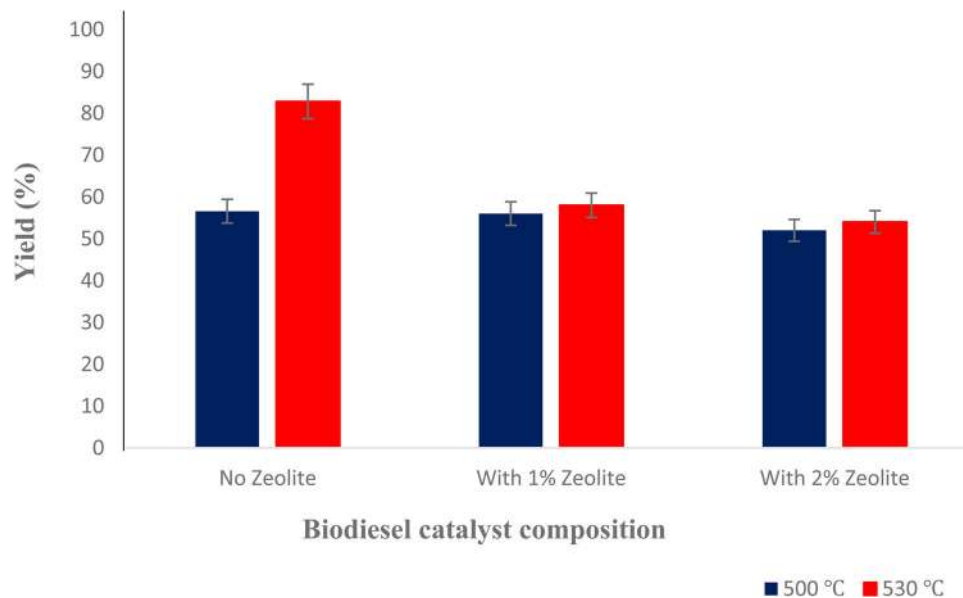
Figure 9. Comparison of biodiesel yields with and without zeolite at 500 °C and 530 °C.
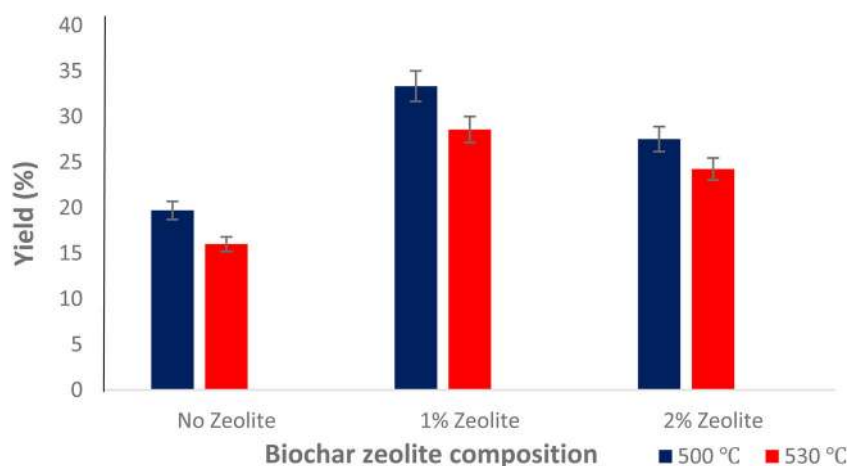

Figure 10. Comparison of biochar yields with and without zeolite at 500 °C and 530 °C.

Table 4. Methyl esters of significant concentration in biodiesel produced with zeolite nano-catalyst.

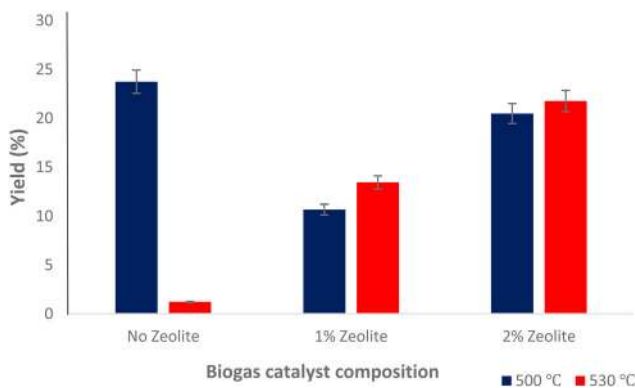| Name	Mol. Wt. (g/mol)	Formula	CV (MJ/kg)
5,8,11,14,17-Eicosapentaenoic acid, methyl ester	316	$C_{21}H_{32}O_2$	–
7-Hexadecenoic acid, methyl ester, (Z)-	268	$C_{17}H_{32}O_2$	–
Heptanoic acid, methyl ester	130	$C_6H_{10}O_3$	31.89
Pentanoic acid, 5-oxo-, methyl ester	130	$C_6H_{10}O_3$	21.83

Figure 11. Comparison of biogas yields with and without zeolite at 500 °C and 530 °C.

which inhibits their further cracking or hydrogenation into paraffin and olefins, thus decreasing the formation of biogas and biochar [55].

This means that although zeolite is needed for more biogas formation, higher quantities of zeolite could be counterproductive because of an increased concentration of methyl esters in the biodiesel produced when zeolitic catalysts are introduced as shown in Table 4.

Information provided in Table 4 describes the methyl esters present in the sample with their calorific value (CV). In addition, a group of cyclo-olefin such as; 4, 4-dimethylcyclohexene, butyl cyclohexane, butyl cyclopentane, 1-pentyl-cyclopentene could also be formed during the cyclization of the C=C bonds present in the unsaturated acids produced.

6. Conclusions and future prospects

The production of biodiesel from waste cow fats (tallow) was studied *via* a catalyzed pyrolytic process (thermal cracking). It was observed that the yield of the biodiesel

produced increased as the temperature improved up to an optimal value before decreasing again. The maximum yield of 82.78% was achieved at 530 °C and a heating rate of 6 °C. The performance efficiency also increased by increasing the heating rate to a value for each final temperature. The zeolite nano-catalyst (Zeolite 96096) did not show significant improvement in the yield, reducing it from 82.78% to 58% and 54% when a 1% and 2% respectively of zeolite nano-catalyst were used. It also did not show an improved yield of the biochar. Biochar yield slightly decreased from 56.56% (at 0% nano-zeolite) to 56% and 52% respectively when 1% and 2% of nano-zeolite was added. The biogas yield increased from 16% without nano-zeolite to 28.57% and 24.24% respectively with 1% and 2% of added nano-zeolite. Some of the properties of the biodiesel produced were compared with the SIN 342-2006 specification of South African diesel gasoline: Carbon, hydrogen, Sulphur, oxygen, density and calorific value, and were found to comply with the specification. Therefore, it can be inferred that the biodiesel investigated in this study has acceptable values and could be used as a transport fuel. However, the pH, acid number, ash content, nitrogen percentage, and density were not perfectly within specifications and need to be improved in future studies. Furthermore, this study suggests that to ensure a cost-effective biodiesel production process in future research, the chemistry of other heterogeneous catalysts needs to be thoroughly explored, developed, and tested for biodiesel production. Finally, if the goal is on improving the biodiesel yield during biodiesel production via pyrolysis of tallow, future studies may consider using non-zeolitic catalysts like palladium supported activated carbon (Pd/C), hydrochloric acid, sulfonic acid, and sulfuric acid as catalysts.

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