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Assessment of Potential of *Croton gratissimus* Oil for Macroscale Production of Biodiesel Based on Thermophysical Properties

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ABSTRACT: Quantitative assessments of the potential of a novel non-edible feedstock for biodiesel production are crucial for two reasons in addition to the primary concern of food security. The first is to find alternative fuels as replacements for dwindling reserves of fossil fuels. The second is to ascertain whether biodiesel produced from oil extracted from *Croton gratissimus* has properties close to that for biodiesel from other feedstock. *C. gratissimus*, a non-food grain, native to Africa, was collected from the Democratic Republic of the Congo. Its oil was extracted and characterized for its fatty acid profile and its acid and saponification values. The efficiencies of homogeneous (sulfuric acid) and heterogeneous (sulfated zirconia oxide) acid catalysts were evaluated. Sulfated zirconia oxide gave a better biodiesel yield of 84.65 ± 0.45% based on the oil weight compared to a biodiesel yield of 80.35 ± 1.05% given by sulfuric acid. The synthesized biodiesel, from *C. gratissimus* oil, was tested for its thermophysical properties, such as density, specific gravity, and refractive index, at various temperatures. In addition, differential thermal analysis was also performed. In general, the data from these studies indicate that *C. gratissimus* oil has great potential as a non-edible feedstock for industrial-scale synthesis of high-quality biodiesel.

1. INTRODUCTION

On a global scale, the cost of energy is increasing at a rate that is negatively impacting the economies of many countries, irrespective of whether they are "developed" or "developing". In this context, the synthesis of biofuels has great appeal as a replacement for fossil fuels. Specifically, the synthesis and use of biodiesel is an attainable strategy. It is well-known[1−3] that the use of "food" biomass, as one of the starting materials, has been a major stumbling block to acceptance of this route. However, the use of non-food biomass[4] in the synthesis of biodiesel would find strong support from governments and the general populace of countries affected by fuel shortages. With regard to non-food biomass, some of them being used as sources of lipids are algae,[5] waste oil from frying establishments,[6] and non-food grains.[4] Of the sources listed above, it is relatively easier to grow and harvest non-food grains than the others. *Jatropha*[7,8] and *Croton*[9,10] plants are among those yielding non-food grains that have been used thus far as feedstock for biodiesel. No report on the use of *Croton gratissimus* was found in the ambit of the literature search performed for this project. In light of this, the potential of oil from this species was evaluated as a feedstock for biodiesel production. The choice of *C. gratissimus* was motivated by the fact that the species is abundant and found in many African countries. Pictures of *C. gratissimus* seed and tree are given in Figure 1. Because *C. gratissimus* oil is non-edible, its application as feedstock for biodiesel will not affect the food security.[11]

In addition to the availability of an inexpensive feedstock, the viability of biodiesel synthesis would be affected by cost of production of the biodiesel. In this regard, the yields of oils from the seeds as well as the efficiency of the steps for the conversion of the oil to biodiesel would be crucial. In the latter process, oils are converted to fatty acid alkyl esters (FAAEs) in the presence of a suitable catalyst and an acyl acceptor. The amount of free fatty acid (FFA) content, in the oil used as feedstock, determines the choice of catalyst.[12,13] In cases where the feedstock contains considerable amounts of FFA, acid catalysts need to be chosen to eliminate the formation of soaps.[14] Although the use of a conventional homogeneous acid catalyst results in faster reaction rates and higher yields, these advantages are negated by the difficulty of recovering the catalyst after the completion of reaction. This entails several washing and purification steps, which lead to generation of colossal amounts of wastewater. On the other hand, a heterogeneous solid acid catalyst can be easily separated from the final biodiesel product by simple steps, such as filtration or centrifugation. The reuse of the recovered catalyst helps in reducing the overall production cost of the biodiesel.[13,15]

The determination of the refractive index of biodiesel is simpler, faster, and less expensive as a characterization method, by comparison to, for instance, gas chromatography (GC). Santos et al.[16] and Chuck et al.[17] reported that each fatty acid methyl ester (FAME), present in biodiesel, possesses a characteristic refractive index. Hence, refractive index data can

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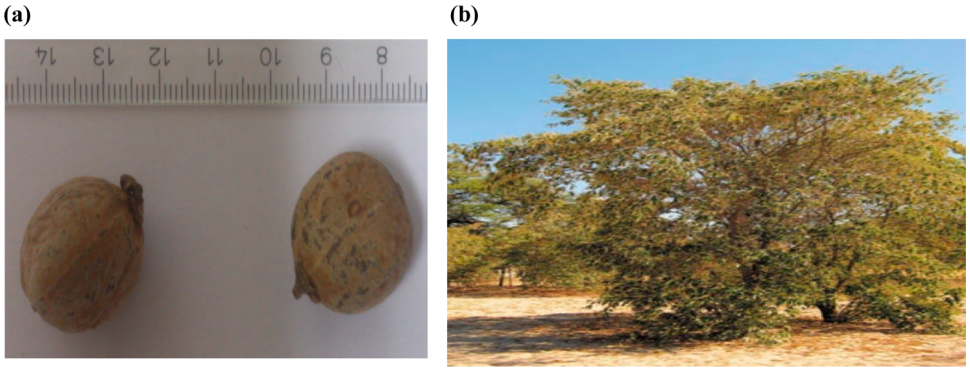

Figure 1. Pictures of *C. gratissimus* (a) seed and (b) tree.

be used to predict some important physical properties, such as density or viscosity for the biodiesel and its blend.[18] The refractive index data can also be used to test the applicability of predictive equations of refractive index for the systems containing biodiesel.[19] Santos et al.[16] monitored the progress of transesterification of oil, using the refractive index. These data could also be used to determine the methyl or ethyl ester content in biodiesel. The density of a fuel is also an important parameter. It influences the production, transportation, and distribution processes of biodiesel as well as the processes that it undergoes in the internal combustion engine.[20]

In the present study, a non-edible feedstock, *C. gratissimus* oil, was characterized and used for biodiesel synthesis. The performances of a homogeneous acid catalyst, namely, sulfuric acid, and a heterogeneous acid, namely, sulfated zirconia oxide (SO_4^{2-}/ZrO_2), for conversion of oil to biodiesel, were compared to a homogeneous catalyst with regard to the yield of biodiesel and reuse of the catalyst. The physical properties of the biodiesel, such as density, specific gravity, and refractive index, were measured at various temperatures.

2. EXPERIMENTAL SECTION

2.1. Materials. *C. gratissimus* grains used in this work were obtained from selected trees in Lubumbashi, the southeastern region of the Democratic Republic of the Congo. Immediately after collection, the grains were air-dried for 2 days at room temperature. They were ground using a laboratory mortar and pestle. The average diameter was found to be around 1.5 ± 0.05 mm. This was determined as the weighted arithmetical average from a granulometric analysis carried out on a series of sieves with decreasing meshes. The ISO method 665 was used to determine moisture and volatile matter contained in the ground grains. A sample (5 g) was dried in the oven at 103 ± 0.1 °C until a constant mass was reached within 0.005 g. The mass difference of the sample before and after drying, expressed as a percentage of the initial mass, was recorded as its moisture and volatile matter contents. Three different samples were tested, and the average value was reported. The moisture content of the ground grains was 9.20 ± 0.02% on a wet basis. Hexane, supplied by Fluka, with a purity of 99.0%, was used to extract oil from the *C. gratissimus* grains.

2.2. Procedure for Batchwise Extraction of Oil. Batchwise extraction of oil from *C. gratissimus* was carried out at 50 ± 0.1 °C with a solvent/feed ratio of 2.5 mL/g. *C. gratissimus* grains and *n*-hexane were loaded into a flask immersed in a thermostated water bath. The mixture was stirred at 400 revolutions per minute (rpm) by means of an impeller fitted to an electric motor.

For a typical extraction, 50 g of ground grains was placed in a round-bottomed flask. Hexane was added, and the mixture was stirred for 6 h. Vacuum filtration was used for the solid−liquid separation after extraction. Hexane was distilled off (using a rotary evaporator) to give *C. gratissimus* oil (16 g).

2.3. Characterization of Oil from *C. gratissimus*. The extracted oil was characterized to determine its fatty acid profile as well as its saponification and acid values. Saponification and acid values were determined by standard ASTM D5558-95 and D664-07 titration methods, respectively. The latter was performed using an automatic titrator (TIM 855 Titration Manager, Radiometer Analytical, Titralab, France). Molecular weight was determined from saponification and acid values using the formula: $M = 168300/(SV - AV)$, where M is the molecular weight, SV is the saponification value, and AV is the acid value.[21] For fatty acid profiling, the extracted oil was transesterified using sulfuric acid and methanol to obtain FAMEs. The fatty acid composition of *C. gratissimus* was determined using GC (Shimadzu GC-2014, Japan) equipped with a flame ionization detector (FID). A capillary column (SP2380, Supelco Analytical) was used for separation. The oven temperature was programmed to start at 60 °C with a hold time of 2 min and then initially increased to 160 °C at a rate of 10 °C min^{-1} and further to 240 °C (with a holding time of 1 min) at a rate of 7 °C min^{-1}. The injector and detector were maintained at a temperature of 250 °C. Nitrogen was used as the carrier gas.

2.4. Conversion of *C. gratissimus* Oil to Biodiesel. Biodiesel synthesis from *C. gratissimus* oil was carried out using sulfuric acid and sulfated zirconia oxide as catalysts. Methanol was selected as an acyl acceptor for the FAME synthesis, and *n*-hexane was used as the reaction solvent. Reactions for conversion into FAMEs were carried out in screw-capped vials. Reaction conditions were 10% catalyst (amount based on the weight of oil), reaction temperature of 60 °C, 1 mL of *n*-hexane, and a methanol/oil molar ratio of 30:1. All of the reactions were carried out in an orbital shaker incubator at 200 rpm for 4 h.[22] After completion of the reaction, the ester layer was extracted from the reaction mixture. Hexane (4 mL) and water (2 mL) were added to the reaction mixture and centrifuged for 5 min at 4000 rpm. The upper layer, containing FAMEs, was collected in a preweighed vial. Further, 2 mL of hexane was added to re-extract the remaining FAMEs from the reaction mixture. The yield of FAME was determined gravimetrically. Conversion to FAME was checked by GC−FID analysis. A 37-component FAME was chosen as an external standard, and methyl heptadecanoic acid ester was used as an internal standard.

2.5. Thermophysical Properties of Biodiesel. *2.5.1. Density and Specific Gravity Measurements of Biodiesel.* The density and specific gravity of biodiesel were measured at 15, 20, 25, and 30 °C and at atmospheric pressure. The densities were measured using an Anton Paar DMA 5000 vibrating U-tube densimeter. Ultrapure water supplied by SH Calibration Service GmbH Graz, and dried air was used for the calibration of the densimeter at each temperature. The temperature maintenance and control were performed using a built-in thermostat controller with a temperature uncertainty of ±0.1 °C. The uncertainty in density was ±0.000 05 g cm^{-3}.

2.5.2. Refractive Index Measurements of Biodiesel. The refractive index (n) of biodiesel was determined at 15, 20, 25, and 30 °C and at atmospheric pressure. The refractive indices were measured using a digital automatic refractometer (ATAGO, model RX-7000a, Japan) with an accuracy of ±0.03 °C in temperature. The calibration for the RX-7000a was performed by measuring the refractive index of

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Table 1. Oil Characterization of *C. gratissimus* and Some Other Non-food Biomass

parameter	unit	*C. gratissimus*	*C. megalocarpus*	*Schleichera triguga*	*Jatropha* seeds
saponification value	mg of KOH g^{-1}	158.49 ± 1.65	194.9[2]		180.6[7]
acid value	mg of KOH g^{-1}	12.29 ± 1.14	4.8[2]	21.30[3]	14.6[7]

Table 2. Lipid Profile of *C. gratissimus* Oil (Percentage Composition) and Some Other Non-food Biomass

fatty acid	*C. gratissimus*	*C. megalocarpus*	*S. triguga*	*Jatropha* seeds
C16:0 (palmitic acid)	36.47	6.5[2]	10.35[3]	1.4[7]
C16:1 (palmitoleic acid)	0.32	0.1[2]		0.1[7]
C18:0 (stearic acid)	32.12	3.8[2]	11.11[3]	21[7]
C18:1 (oleic acid)	8.91	11.6[2]	27.08[3]	24.3[7]
C18:2 (linoleic acid)	9.63	72.7[2]	6.14[3]	22.5[7]
C18:3 (linolenic acid)	4.13	3.5[2]		3.8[7]
C20:0 (arachidic acid)	2.34		15.79[3]	
SFA[a]	75.29		53.11[3]	
MUFA[b]	9.23			
PUFA[c]	14.40			
others	1.08			

[a]SFA = saturated fatty acids. [b]MUFA = monounsaturated fatty acids. [c]PUFA = polyunsaturated fatty acids.

ultrapure water at experimental temperatures. The estimated error in the refractive index was less than ±0.000 05.

2.5.3. Water Content of Biodiesel. The water content of biodiesel was determined using a Karl Fischer coulometer (Metrohm 756) and was found to be less than 0.05%.

2.5.4. Isobaric Expansivity Coefficient. The isobaric expansivity coefficient at a constant pressure (α_p) of biodiesel is defined as

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\delta\rho}{\delta T}\right)_p \quad (1)$$

The isobaric expansivities were estimated from the measured data.

2.6. Correlation of Density, Specific Gravity, and Refractive Index Data. Density, specific gravity, and refractive index data measured in this work were correlated using a linear temperature dependency optimization algorithm based on the least-squares method using Origin software, version 7.1

$$Y = a + bT \quad (°C) \quad (2)$$

where Y refers to the experimental density, specific gravity, or refractive index and a and b are the fitting parameters. It is noted that this approach was also used previously.[23,24]

2.7. Differential Thermal Analysis (DTA) Measurement of Biodiesel. The thermal behavior of the biodiesel was investigated by DTA, using a Modulated SDT Q 600. The DTA cell was purged with nitrogen at a flow rate of 50 mL/min. DTA of the samples were performed at 50−300 °C. The melting point was taken as the value of the temperature at the tip of the endothermic peak, which formed upon heating.

3. RESULTS AND DISCUSSION

3.1. Extraction of Oil from *C. gratissimus*. The method used to extract oil from *C. gratissimus* grains is similar to that used in industry. The successful extraction using this method is an indication that the scaling up of the process and, hence, its industrial implementation would not be too challenging. The choice of hexane as the extraction solvent in this project was based on the fact that *n*-hexane is the most frequently used extraction solvent in the chemical industry for obtaining non-edible oil from biomass, while the search for "greener" solvents is being driven by environmental concerns. *C. gratissimus* grains yielded 23.5% oil based on dry biomass weight. Extractions were performed in triplicate, and the reproducibility of the yield was within ±0.5% of the reported value. Because one of the main objectives of this project was to check whether extraction could be achieved under conditions that are close to those prevailing in industry, no optimization experiments were carried out.

3.2. Characterization of Extracted *C. gratissimus* Oil. *C. gratissimus* oil was characterized to check its suitability for its use as a feedstock for biodiesel synthesis. Moreover, data such as acid value and fatty acid composition determine the nature of downstream processing of oil to produce biodiesel. The saponification value of *C. gratissimus* oil was determined to be 158.49 ± 1.65 mg of KOH g^{-1}. A high saponification value indicates the presence of sufficient saponifiable content, which can be converted to biodiesel by esterification and/or transesterification. The acid value was determined to be 12.29 ± 1.14 mg of KOH g^{-1}. This indicates that the oil contains significant amounts of free fatty acids. The presence of free fatty acids in *C. gratissimus* necessitated the use of an acid catalyst for conversion to FAMEs, to obviate a considerable amount of saponification if a base catalyst was used for conversion of such oils. Table 1 lists the chemical characteristics of oil extracted from *C. gratissimus* grains and those of similar feedstock oils. The fatty acid profile and the percentage composition of *C. gratissimus* oil and similar feedstock oils are shown in Table 2. Palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3) were the major contributors to the total fatty acid profile.

3.3. Biodiesel Synthesis from *C. gratissimus* Oil. As noted above, the high FFA content of *C. gratissimus* oil necessitated the use of an acid catalyst to avoid the loss of product because of saponification. However, the acid catalyst could be homogeneous or heterogeneous. To compare the yields on conversion, homogeneous (sulfuric acid) and heterogeneous (sulfated zirconia oxide) acid catalysts were used for synthesis of biodiesel from *C. gratissimus* oil. When reaction conditions were kept the same, the heterogeneous acid catalyst, SO_4^{2-}/ZrO_2, gave a yield of 84.65 ± 0.45% biodiesel (on the basis of oil weight) and FAME content of 72.26%. With the homogeneous acid catalyst (H_2SO_4), the biodiesel yield obtained was 80.35 ± 1.05% and a FAME content of 69.77%. Hexane was used as the reaction solvent to provide efficient mass transfer. With the heterogeneous catalyst, SO_4^{2-}/ZrO_2,

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the biodiesel yield was found to be higher than that from the homogeneous catalyst (H_2SO_4) at a moderate temperature of 60 °C and is depicted in Figure 2. A yield of 95% biodiesel was

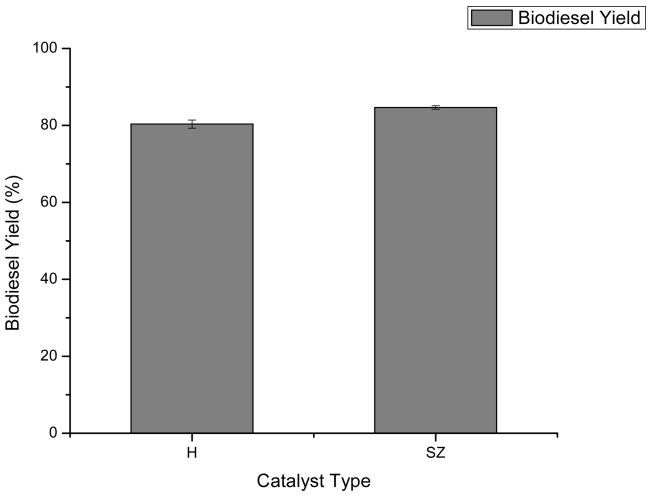

Figure 2. Biodiesel yield from *C. gratissimus* oil, where H is sulfuric acid (homogeneous catalyst) and SZ is sulfated zirconia (heterogeneous catalyst).

reported by Kafuku et al.[25] when sulfated tin oxide was used for conversion of *Croton megalocarpus* oil to biodiesel. Reaction conditions used in this study were: catalyst concentration, 3 wt %; temperature, 180 °C; reaction time, 2 h; and a methanol/oil molar ratio, 15:1. To achieve a higher yield, reaction parameters used in this study would need further optimization. The heterogeneous acid catalyst is preferred because it can be reused after separation. Homogeneous catalysts form a monophasic mixture with the products and, thus, require separation, purification, and washing steps. Moreover, sulfuric acid used as a homogeneous catalyst is corrosive in nature and can cause damage to the reactor and piping. Thus, for conversion of high acid value feedstock, such as *C. gratissimus* oil, a heterogeneous acid catalyst could be a better option at commercial-scale biodiesel production.

3.4. Thermophysical Properties of Biodiesel (Density, Specific Gravity, and Refractive Index). Density, specific gravity, and refractive index data at different temperatures and cloud and pour points for biodiesel synthesized from *C. gratissimus* oil are given in Table 3. The experimental data show that the density, specific gravity, and refractive index of biodiesel decrease with an increase in the temperature. This is expected and is in line with data reported in the literature for pure biodiesel.[26] Fuel density or specific gravity affect engine performance because fuel injection pumps meter fuel by volume and not by mass. Thus, the mass of fuel injected depends upon its density or specific gravity, and also, the air–fuel ratio and energy content within the combustion chamber are evidently influenced by the fuel density or specific gravity. In view of this, the measurements of density and specific gravity of biodiesel are very important properties of biodiesel.[27]

It was found (in the present project) that there is a linear correlation between the concentration of the FAAEs and refractive index of biodiesel. The values of R^2 were 0.9997 and 0.9996 for the methyl ester of *Croton* oil and ethyl ester of soybean oil, respectively. Further, it was found that the value of the refractive index decreased with the increase in transesterification (i.e., formation of FAAE) and that the refractive index of biodiesel was lower than that of *C. gratissimus* oil, as shown in Table 4.

Table 4. Fitting Parameters, *a* and *b*, and Standard Deviations, *σ*, Obtained for the Biodiesel Using Equation 1

property	*a*	*b*	*σ*
ρ (g cm^{-3})	1.06955	−0.00069	0.00000
SG	1.00630	−0.00047	0.00016
n	1.58904	−0.00036	0.00000

The isobaric expansivities estimated for the biodiesel are shown in Table 3. The values of α_p increase with an increase in the temperature. These values are similar to those for other biodiesel fuels and for pure FAMEs previously reported in the literature.[23,24,26] *C. gratissimus* oil showed commendable cold flow properties.

The refractive indexes of *C. gratissimus* oil at various temperatures are given in Table 5. It can be seen, from Tables 3 and 5, that the refractive index of the biodiesel reaction mixture decreased from 1.474 519 (refractive index of the oil) to 1.455 41 (after transesterification of the oil) at 288.15 K. The percent conversion of croton oil to biodiesel was calculated to be 84.65 ± 0.45%. The refractive index of biodiesel obtained in the present study is close to that determined by other

Table 5. Refractive Index (*n*) of *C. gratissimus* Oil at Different Temperatures

T (°C)	*n*
15	1.47451
20	1.47252
25	1.47064
30	1.46895

Table 3. Density (ρ), Specific Gravity (*SG*), Refractive Index (*n*), and Isobaric Expansivity Coefficient (α_p) of Synthesised Biodiesel at Different Temperatures

	T (°C)	ρ (g cm^{-3})	cloud point (°C)	pour point (°C)	*SG*	*n*	α_p (×10^3, K^{-1})
CGB[a]	15	0.87058			0.87145	1.45541	0.8041
CGB[a]	20	0.86713			0.86887	1.45351	0.8073
CGB[a]	25	0.86367			0.86654	1.45164	0.8105
CGB[a]	30	0.86022			0.86442	1.44975	0.8137
CGB[a]			−4.5	−7.3			
ASTM D6751		0.82–0.9 (20 °C)			0.87–0.9		
EN 14214		0.86–0.9 (15 °C)					

[a]CGB = *C. gratissimus* biodiesel.

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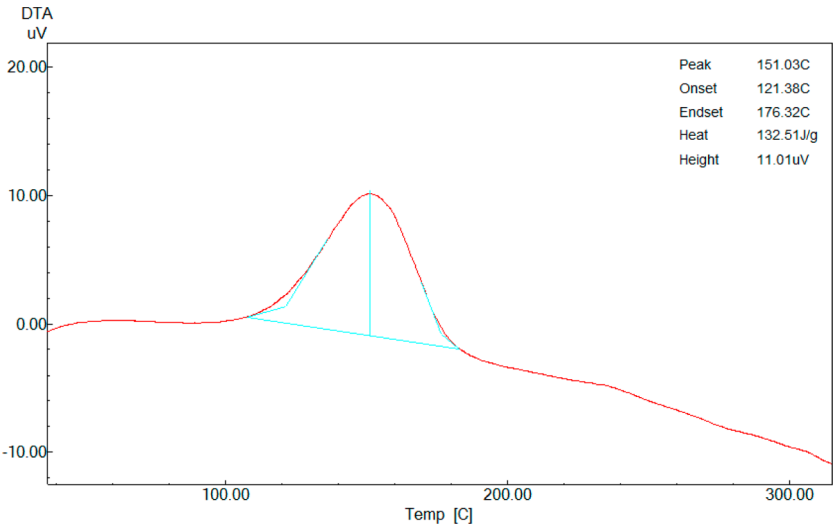

Figure 3. Typical DTA thermogram of pure biodiesel.

researchers. Ghanei et al.[28] reported that both specific gravity and refractive index decrease linearly with the advancement in the transesterification reaction and the subsequent production of biodiesel. It was reported that specific gravity decreased from 0.922 to 0.883, whereas the refractive index decreased from 1.4668 to 1.4490 when the conversion was 0 and 95.2%, respectively. With regard to refractive index values, Chisti[29] reported the refractive index of biodiesel to be in the range from 1.46 to 1.47. Possetti et al.[30] determined the refractive index of pure biodiesel to be 1.454 40 ± 0.000 13 and that of oil to be 1.471 90 ± 0.000 13. The refractive index of biodiesel changes with the temperature because of the thermo-optic effect. Biodiesel has been reported to show a negative thermo-optic coefficient, implying that an increase in the temperature will cause a decrease in the refractive index. Wazilewski et al.[31] studied the refractive index of biodiesel to evaluate the oxidation stability of biodiesel derived from *Crambe abyssinica* Hochst. While the biodiesel contaminated with iron showed little alteration in the refractive index, the change in refractive index was significant in biodiesel (from *C. abyssinica* Hochst. and soybean) contaminated with bronze.

Xie and Li[32] also observed that the refractive index could give an indication of the extent of conversion of triglyceride to biodiesel. They found the refractive index to be 1.4704 when the conversion was 0% (i.e., the constituents being only triglycerides) and 1.4515 when the conversion was 100% (i.e., FAME) at 30 °C. The monitoring of the conversion of oil to biodiesel using the refractive index was reported by Xie and Li[32] to correlate well with proton nuclear magnetic resonance (^{1}H NMR) as the monitoring technique. Thus, the refractive index of biodiesel could provide a simple and quick determination of the FAME constituent in biodiesel. The density of biodiesel observed was in the range of 0.8640−0.8715 at the temperature ranging from 30 to 15 °C, as shown in Table 3. Ávila and Sodré[33] reported that the density of biodiesel could also be used as an indicator of the extent of contamination of biodiesel. The density of biodiesel reported by Ávila and Sodré[33] was 877 kg/m^3 at 20 °C. The EN 14214 limits for the density of biodiesel are from 860 to 900 kg m^{-3},[34] Thus, the biodiesel synthesized in the present work fulfils the EN norms. "Pour point" and "cloud point" values determined for the synthesized biodiesel were −7.3 ± 0.2 °C and −4.5 ± 0.2 °C, respectively. These values indicate that the biodiesel from *C. gratissimus* oil could be used even during cold conditions.

3.5. DTA of Biodiesel. The results for DTA analysis of the biodiesel are shown graphically in Figure 3. The data from the graph can be used to assess the thermal stability of the biodiesel in the temperature range of 50−300 °C. The boiling point and enthalpy of fusion were obtained from the DTA curve and were found to be 151.03 °C and 132.51 J/g. respectively. Although the boiling points of diesel and biodiesel may be similar, the distillation behavior of biodiesel is different from that of diesel. It is noteworthy that all of the values for the properties obtained for the biodiesel produced from the grains of *C. gratissimus* are well within those reported in the literature for biodiesel from biomass samples similar to *C. gratissimus*.[35,36]

4. CONCLUSION

The percentage content and characteristics of the oil from *C. gratissimus* have shown that it can be used as a promising feedstock for large-scale biodiesel production. Because it is a non-food grain feedstock, the use of the oil from *C. gratissimus* does not impact the food security issues, which are a major concern for Africa. Because *C. gratissimus* grows well in the wild, it should be economical to cultivate and use by small, medium, and micro-sized enterprises (SMMEs). The latter will have the potential to create employment in rural areas. The thermophysical properties, such as density, specific gravity, refractive index, and pour and cloud points, obtained for the biodiesel produced from the grains of *C. gratissimus* are well within those reported in the literature. In the light of results obtained from characterization measurements, it is concluded that the grains, from *C. gratissimus*, have a high potential to be used as a biomass source for viable production of high-quality biodiesel.

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Notes

The authors declare no competing financial interest.

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