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Usage of Silica Xerogel from African Sugarcane Leaves as a Catalyst in Biodiesel Production through Transesterification

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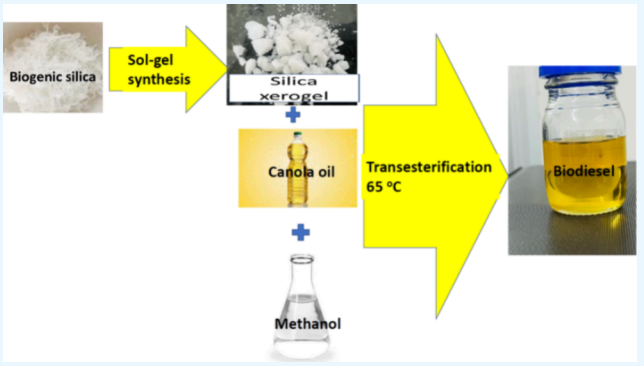
ABSTRACT: Biodiesel was produced through transesterification from canola oil and methanol in the presence of silica xerogel derived from sugar cane leaves as a solid catalyst. The transesterification reaction was carried out at 65 °C in a batch-type reactor where a three-neck round-bottom flask was used as a reaction vessel with a reflux setup. Reaction time, methanol to oil ratio, and weight percentage of the catalyst were varied to optimize the biodiesel yield. The xerogel catalyst was characterized by inductively coupled plasma-optical emission spectroscopy (ICP-OES), nitrogen physisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The produced biodiesel was characterized using gas chromatography-mass spectroscopy (GC-MS), Fourier transform infrared spectroscopy (FTIR), and a viscometer. The synthesized catalyst was found to operate as a true heterogeneous catalyst, since it preserved its solid nature and did not leach into the reaction medium. A biodiesel yield of 96.9% was achieved under optimal reaction conditions of 60 min reaction time, 6:1 methanol to oil ratio, and 3 wt % catalyst loading. The produced biodiesel was found to have a mixture of both saturated and unsaturated fatty acid methyl esters and had physical properties that met the ASTM and EN standards. The investigated catalyst was found to have a potential of being recycled up to 3 times, which positively affects the biodiesel production costs.



1. INTRODUCTION

Biodiesel is an alternative renewable fuel that can be derived from either animal fats or vegetable oils. Due to the inevitable depletion of fossil fuels and the environmental challenges they pose, biodiesel has the potential to replace petroleum-based/fossil diesel because it is renewable.[1] Among the existing biofuels, biodiesel is a formidable candidate to promote an eco-friendly environment and sustainability.[2] It is a mixture of different fatty acid alkyl esters, which can be obtained through the transesterification of triglycerides (usually animal fats and vegetable oils) with an alcohol (usually methanol or ethanol).[3]

For a successful reaction between a triglyceride and an alcohol, a catalyst needs to be used, which in turn helps speed up the reaction and also increases selectivity. Different types of catalysts have been used to facilitate transesterification, but the most popular catalysts are alkali hydroxides: sodium hydroxide and potassium hydroxide. These alkali hydroxides are very efficient basic catalysts for transesterification and have been the most used in the industrial production of biodiesel.[4] However, their drawback is that they are classified as homogeneous catalysts (catalysts in the same phase as the reactants and products), making it difficult to remove or separate them at the end of the reaction. In addition, using alkali hydroxides as catalysts results in large amounts of cleansing water that is contaminated since they are difficult to separate from the reaction for recycling,[5] which can successively lead to environmental concerns.[3] Other types of catalysts that have been extensively researched in the past decades are heterogeneous catalysts (where the catalyst is in a different phase than the reactants and products).[6] The most popular and investigated heterogeneous catalysts are in a solid form, and solid catalysts are reported to be convenient to work with since they are reported to provide high biodiesel yields[7] and they do not dissolve in the reactant mixture. Solid catalysts can be easily separated from the products, which implies a recycling/reusability potential.[8,9] They are usually not toxic or prone to cause reactor corrosion[10] and can be utilized in continuous processes.[8] Since most solid catalysts can be reused

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several times, this contributes to the reduction of biodiesel production costs and therefore makes them more desirable.[11]

Solid catalysts for triglycerides transesterification can be sourced from different materials, and recently, researchers have focused on catalysts that can be derived from waste,[1,6,10] thus providing an opportunity for additional waste valorisation. The biodiesel yield is greatly affected by the type of triglyceride used, the solid catalyst, the alcohol/oil ratio, the reaction time, the reaction temperature, and the catalyst weight percentage. One of the most used solid catalysts in the production of biodiesel is a calcium oxide-based solid catalyst that can be obtained from different waste materials. Alsaiari et al.,[12] Yaşar,[13] Jitjamnong et al.,[5] and Gaide et al.[14] used waste eggshells as a source of calcium oxide and reported biodiesel yields of 88.0, 95.1, 94.0, and 97.8%, respectively. Even though the same catalyst was used, the yields are significantly different due to different triglycerides used in these studies and other reaction conditions, which have been reported to affect the final yield as mentioned above. Puspitasari et al.[15] utilized scallop shell waste as a source of calcium oxide and reported a yield of 74.2%, while Adepoju et al.[16] obtained their calcium oxide from chicken feet bones and catfish bones and reported biodiesel yields of 93.6 and 92.5%, respectively. Other waste materials have also been used as catalyst sources for triglyceride transesterification: Coal fly ash was used by Kochaniec et al.,[17] where they obtained a yield of 97.2%, while Yusuff et al.[18] reported a biodiesel yield of 98.1% from using coal fly ash as a support for zinc oxide catalyst.

This work reports the use of an agricultural residue-derived catalyst for biodiesel production. Some work has been reported in the literature where agricultural residues were used to derive biodiesel catalysts. Banurea et al.[1] utilized a rice husk-based catalyst and reported a yield of 94.4% with palm oil as their feedstock. Jacinta et al.[19] also used rice husk as a catalyst source and waste cooking oil as a triglyceride in their production process and reported a yield of 86.3%. Hidayat et al.[20] used sugar cane bagasse biochar-based catalyst to convert palm oil industry waste residue and achieved a yield of 86.1%. The main focus of this study was to utilize waste from the sugar cane industry (sugar cane leaves) and produce a value-added material (high-purity amorphous biogenic silica xerogel), which was further investigated as a potential solid base catalyst in the production of biodiesel through transesterification. Sugar cane leaves are usually burnt preharvest, which has been reported to lead to some environmental and health concerns,[21−23] due to the presence of crystalline silica in the burnt ash. In the current study, sugar cane leaves were thermochemically treated with citric acid before controlled burning to produce biogenic silica. The obtained biogenic silica was used to synthesize silica xerogel via a sol−gel method, and the xerogel was used as a catalyst to produce biodiesel. The overall process was designed to be environmentally friendly by using the lowest possible organic acid concentration in the hydrolysis step and avoiding the use of energy-intensive distillation methods for biodiesel separation. Additionally, the catalyst's reusability was studied to minimize production costs. To the best of the authors' knowledge, this is the first reported use of silica xerogel derived from sugar cane leaves as a catalyst for biodiesel production.

2. MATERIALS AND METHODS

2.1. Materials. Methanol (analytical grade) and sodium hydroxide were purchased from Reflecta Laboratory Supplies (South Africa). Citric acid was purchased from Merck (South Africa), Canola oil was purchased from a local grocery store, and sugar cane leaves were obtained from sugar cane farmers in Verulam (South Africa). All chemicals were used as purchased.

2.2. Methods. *2.2.1. Synthesis of Sugar Cane Leaves the Xerogel Catalyst and Characterization.* Biogenic silica was produced using a method reported by Maseko et al.[24] In a 3-neck round-bottom flask, 5 g of biogenic silica was mixed with 250 mL of 1 M NaOH, and the mixture was heated for 2 h at 80 °C. The resulting sodium silicate solution was cooled to room temperature and later filtered to remove any undigested matter present. In a 500 mL beaker, the sodium silicate solution was hydrolyzed with the addition of 3 M citric acid until the solution became turbid at a pH of around 8.7. The formation of silica gel took place according to the following reactions:

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

$$3Na_2SiO_3 + 2C_6H_8O_7 \rightarrow 3SiO_2 + 3H_2O + 2Na_3C_6H_5O_7$$

The solution was continuously stirred after it turned turbid for about 1 min more until it turned into a soft gel. The magnetic stirrer was then removed, and the gelled solution was covered with parafilm and left to age for 8 h at room temperature. After 8 h had lapsed, the gel was broken, washed with distilled water, and centrifuged three times to remove sodium citrate salt. Ethanol:water solution was then added into the washed gel in different ratios (1:3, 1:1, and 1:0) and was left overnight in each of the solution ratios to stimulate solvent exchange, where water molecules are slowly replaced by ethanol molecules. After solvent exchange, the gel was dried in an oven at 80 °C for 24 h. The sample was removed from the oven and kept in a desiccator for further usage.

2.2.2. Transesterification with the Silica Xerogel Catalyst. A reflux reaction setup was used with a heating mantle to conduct transesterification. In a 1000 mL round-bottom two-necked flask, 100 g of canola oil was added and heated up to 65 °C before the addition of 1, 3, 5, or 7 wt % of the silica xerogel catalyst and a 5:1, 6:1, 7:1, or 10:1 ratio of methanol to oil. The temperature was maintained at 65 °C until the desired reaction time was reached. Once a bright yellow solution was formed, the heating mantle was turned off, and the resulting liquid was poured into a beaker and kept in a fume hood to facilitate separation. Most (almost all) of the xerogel catalyst remained in the round-bottom flask, since it was in a solid form. After atmospheric evaporation of methanol, 2 layers separated within 20 h: the top biodiesel layer and bottom glycerol layer, as indicated in Supporting Information Figure S1.

After the layer separation, the resulting product was poured into a separation funnel, and the bottom glycerol layer was discarded while the biodiesel product was washed with hot water before it was placed in an oven to dry for 24 h. Since the catalyst was in a solid form, any of it that remained at the bottom of the beaker was combined with the catalyst left inside the round-bottom flask for further application. The catalyst could thus be recovered almost completely.

2.2.3. Characterization. The chemical composition of the xerogel catalyst was analyzed using an inductively coupled plasma-optical emission spectroscopy (ICP-OES) CETAC ASX-520 (Omaha, NE, USA) using HF digestion and according to the DIN EN ISO 16967;2015-07, DIN EN ISO 1 standard method. Nitrogen adsorption−desorption measure-

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ments were conducted to measure textural properties using an ASAP 2010, Micrometrics instrument (Norcross, GA, USA). All samples underwent pretreatment at 523 K in a vacuum for 8 h prior to analysis. The specific surface area was determined by utilizing the Brunauer–Emmett–Teller (BET) method, focusing on the relative pressure range (p/p_0) of the sorption isotherm from 0.05 to 0.25. Morphological characteristics and surface structure of the xerogel catalyst were determined through scanning electron microscopy (SEM) on a Zeiss Ultra Plus FEG SEM (Oberkochen, Germany) working at 5 keV. Transmission electron microscopy (TEM) images were obtained using JEOL 2100 (Tokyo, Japan) operating at an accelerating voltage of 200 kV. The phase identification was measured using a GE Seifert XRD 7 (Ahrensburg, Germany) that is equipped with Ni-filtered, Cu-Kα radiation and operating at an acceleration voltage of 40 kV and a beam current of 30 mA. The scanning range was set between 1.5° and 50° 2θ in the Bragg–Brentano configuration, utilizing a step width of 0.02° 2θ and a duration of 6 s per step. The phase analysis of the product was achieved by using the ICDD-PDF2 database, along with the DIFFRAC.SUITE EVAXRD software from Bruker Corporation and the Rietveld-based Seifert Auto Quan software. To determine the amorphous content, fluorite (20 wt %) was incorporated as an internal standard. A Nicolet Avatar 360 FTIR spectrometer (Madison, WI, USA) was used for the FTIR analysis to confirm the presence of characteristic absorption bands. 32 scans within the 4000–400 cm^{-1} spectral range were recorded. The biodiesel concentrations, expressed as the purity of the biodiesel product, were measured using a Shimadzu GC-MS-QP2010 SE (Tokyo, Japan). Helium was utilized as the carrier gas and set to a flow rate of 1.0 mL/min. The temperatures for both the injector and detector were fixed at 250 °C. The oven temperature started at 120 °C, then gradually rose to 230 °C, and finally reached 300 °C at a rate of 8 °C/min. An aliquot of 0.2 mL of dichloromethane (DCM) was injected using a split ratio of 1:50. The mass spectrometer was programmed to scan within the mass-to-charge ratio range of 40–700 m/z. An Anton Paar viscometer (Graz, Austria) was used to measure the viscosity and density.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Xerogel Catalyst.

3.1.1. Chemical Analysis. The chemical composition of the xerogel catalyst was determined using ICP-OES. It can be observed from Table 1 that silica was the most dominant element in the xerogel product. The second dominant element was sodium oxide, since the catalyst synthesized was a base catalyst. During the study, it was observed that the composition of sodium oxide can be controlled and managed through the number of gel washes: the more the gel is washed, the less the amount of sodium oxide is present in the gel. As a result, it was discovered that washing the gel more than 3 times reduced the composition of sodium oxide to less than 5 wt % and this made the xerogel not effective as a catalyst because the reaction times were observed to be longer and the yield was low. Potassium oxide (K_2O) and calcium oxide (CaO) were also present as contaminants, as shown in Table 1.

Table 1. Chemical Composition of Silica Xerogel Catalyst from Sugarcane Leaves Determined by ICP-OES Analysis

element	silica xerogel (wt%)
SiO_2	93.66
K_2O	0.02
CaO	0.01
Na_2O	6.31

3.1.2. Textural Properties. The textural properties of the xerogel catalyst were determined by using nitrogen physisorption. Adsorption–desorption isotherm of silica xerogel catalyst from sugar cane leaves is displayed in Figure 1. The obtained isotherm has a closed hysteresis loop and consists of a knee at p/p_0 = 0.5, and this is followed by a continuous nitrogen uptake until high relative pressure values are reached.[24] According to IUPAC classification, this type of adsorption–desorption isotherm belongs to type IV. Schlumberger and Thommes[25] reported that type IV isotherms are typical for mesoporous materials (materials with a pore diameter between 2 and 50 nm). The hysteresis loop in the isotherm indicates the presence of larger mesopores.[25] The shape of the hysteresis loop indicates the possibility of additional macropores that are not completely filled with the pore condensate.[26,27] The nitrogen adsorption intake displayed no saturation at relative pressure ratios close to unity, which indicates the presence of pores in the macroporous region. This means that the synthesized xerogel catalyst had both meso and macropores with a broad size distribution.[27]

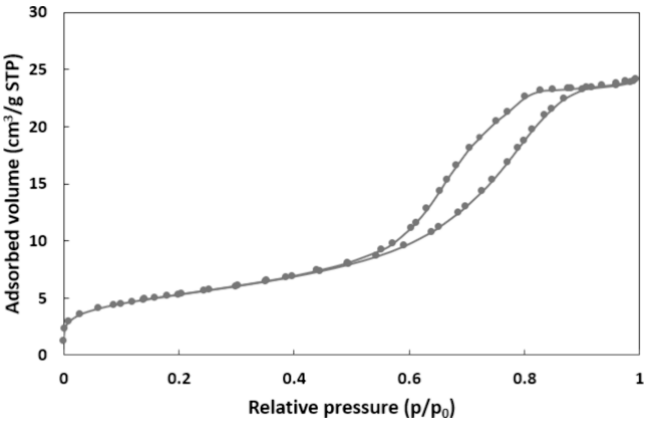

Figure 1. Nitrogen adsorption–desorption isotherm of a silica xerogel from sugar cane leaves.

Textural properties such as BET surface area, pore diameter, and pore volume were also attained. The BET surface area of the gel was 498 $m^2\ g^{-1}$, while the pore diameter and the pore volume were 7.1 nm and 0.88 $cm^3\ g^{-1}$, respectively. The obtained specific surface area is lower than the one reported in the previous work by Maseko et al.;[28] however, it is still higher than most BET surface areas reported in the literature with similar sodium compositions.[29−31] For sample preparation, a solvent exchange method was used where ethanol molecules gradually replaced water molecules within the gel as reported by Maseko et al.[28] This indicates the effectiveness of the employed ethanol–water solvent exchange method, which has been reported to produce a silica xerogel product with a high specific surface area even in the absence of a surfactant.[28] The reason for the reduced surface area is suspected to be due to the presence of sodium oxide species that have filled some of the mesopores.

3.1.3. Phase Identification. Crystallinity of the xerogel catalyst was assessed by XRD as displayed in Figure 2. There is

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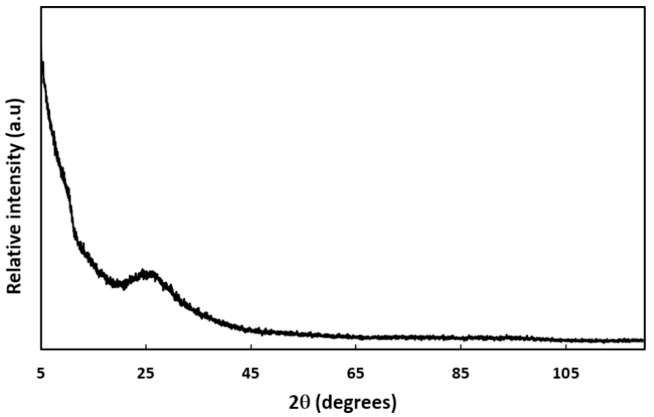

Figure 2. XRD pattern of a silica xerogel catalyst from sugar cane leaves.

an observed broad single reflex with a corresponding Bragg angle of 2θ = 21.9 °. This peak is an indication of the xerogel catalyst being completely amorphous, with no crystalline silica detected. Only amorphous silica was expected to be present in the xerogel catalyst since crystalline silica is reported by Boyles et al.[32] to start forming at temperatures above 1000 °C, and the maximum temperature used in this study was 80 °C. Several authors in the literature worked at temperatures below 1000 °C and also obtained amorphous biogenic silica. Banurea et al.[1] utilized a rice husk-derived catalyst that was calcined at 500 °C to produce biodiesel and reported a silica xerogel with an amorphous structure. Akinfalabi et al.[6] used a nanocatalyst from sugar cane bagasse waste in the production of biodiesel. This catalyst was calcined at 500 °C and was also reported by these authors to have an amorphous nature. Prempheh et al.[31] burnt rice husk at 600 °C and obtained amorphous silica with no traces of crystalline silica.

3.1.4. Structural Properties. Different surface morphologies of the xerogel catalyst were studied using scanning electron microscopy. The results are displayed in Figure 3, where Figure 3A,B show high and low magnification, respectively. Both of the obtained SEM images show aggregation, which is caused by the presence of nanoparticles in the xerogel catalyst, as reported in nitrogen sorption.[28] Agglomerated particles with different shapes and sizes are observed in these SEM images. Figure 4B further demonstrates xerogel with a rough and

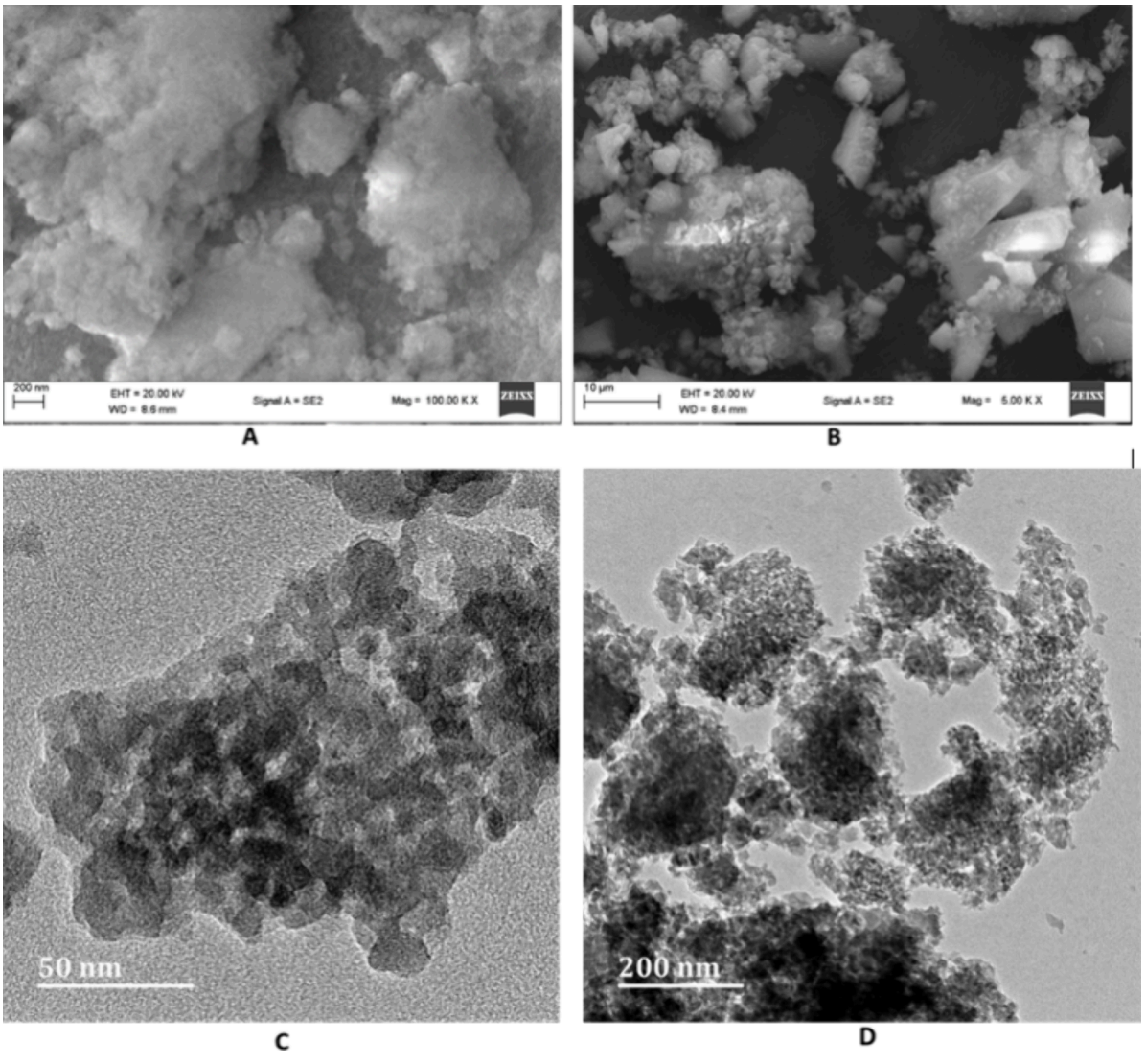

Figure 3. SEM images (A and B) and TEM images (C and D) of a xerogel catalyst from sugar cane leaves.

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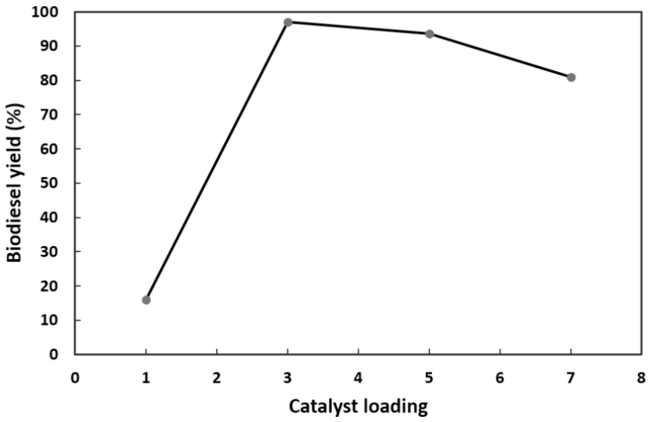

Figure 4. Effect of catalyst loading on the yield of biodiesel in the presence of a silica xerogel catalyst derived from sugar cane leaves.

amorphous surface, which is represented by the brighter surfaces, while the darker surfaces indicate pore cavities.[33] Dhaneswara et al.[34] reported this type of silica to be a heterogeneous mesopore silica. This confirms the results obtained through nitrogen adsorption−desorption, where the presence of mesoporous silica was detected.

TEM images are displayed in Figure 3C,D. Both images show agglomeration, and the particles lack a defined shape. The XRD detected an amorphous phase, so it is expected that the produced xerogel catalyst to have no regular geometry. The formed small nanoparticles seem to have agglomerated to form mesopores. This observation agrees with nitrogen adsorption−desorption findings.

3.2. Optimization of the Transesterification Reaction. All reactions were conducted at a constant temperature of 65 °C, which is the boiling point of methanol. Different parameters were varied in order to obtain ideal conditions for the optimum biodiesel yield. During transesterification, the organic group "R" of an ester is exchanged with the organic group 'R' of an alcohol.[8,35] At optimal conditions, the reaction stops when there are no available group "R" to be replaced by the group "R".[35] In the current study, this was when the entire product had turned yellow and all the canola oil in the bottom of the round-bottom two-necked flask had disappeared, as shown in Supporting Information Figure S1.

The following equation was used to calculate the biodiesel yield:

$$\text{yield of biodiesel} = \frac{\text{mass of obtained biodiesel}}{\text{mass of oil used}} \times 100\%$$

3.2.1. Effect of Catalyst Loading. Catalyst weight percentages of 1, 3, 5, and 7 wt % were all investigated in this study. To investigate the effect of catalyst loading, all other parameters had to be kept constant, so temperature, time, and methanol to oil ratio were kept at 65 °C, 60 min, and 6:1, respectively. It was noticed that 1 wt % of catalyst gave a very low yield of 16%, but increasing the amount of catalyst to 3 wt % increased the yield to 96.9%, which is an 81% increase. This phenomenon has also been reported by Jitjamnong et al.[5] as a reflection of an increment in the available catalyst's basic sites for interaction with the reactants. However, increasing the catalyst loading further to 5 wt % slightly decreased the yield to 93.6%, and 7 wt % of catalyst had a drastic negative effect, since a yield of 81% was obtained, which is a 13% further decrease. Figure 4 shows the effect of catalyst loading, which was investigated in this study.

This decrease in the yield as the catalyst loading increases has been reported by several researchers in the literature. According to Jitjamnong et al.[5] and Mardhiah et al.,[36] the decrease in the yield might be due to mass transfer restricted efficiency between the two phases (solid catalyst and liquid reactants). In addition, this might be due to some mandatory washing cycles of the produced biodiesel, since the obtained product was a bit turbid and slightly more viscous than the other ones. As a result, several (roughly 4) extra washing cycles were needed in order to obtain clear biodiesel, and the addition of water caused the sample to be slightly cloudy, even though it later settled. Unfortunately, each additional washing step posed a threat to yield reduction, as some biodiesel might have been lost during washing. Ngaini et al.[37] conducted a study on the conversion of palm fatty acid distillate to biodiesel using rice husk ash as a catalyst. These researchers reported obtaining a viscous, almost jelly-like product when 5 wt % of catalyst loading was employed, and their resulting product turned cloudy upon the addition of water during the separation/purifying process. Ali et al.[38] used goat bone as their source of calcium oxide catalyst, and they also reported that their biodiesel yield significantly decreased when more than 6 wt % catalyst loading was employed. Buasria et al.[39] used calcium oxide catalyst from dolomitic rock in their study, reported obtaining biodiesel which was in a slurry foam when using catalyst loading above 4 wt %. The same findings were reported by Hidayat et al.,[20] who used sugar cane bagasse biochar as a catalyst in the conversion of palm oil industry waste residue to biodiesel. They reported a decrease in yield when the amount of catalyst used was above 5 wt %. In this study, 3 wt % catalyst loading produced the highest biodiesel yield.

3.2.2. Effect of Reaction Time. Additionally, the effect of the reaction time on the biodiesel yield was investigated. Reaction temperature, catalyst loading, and methanol to oil ratio were all kept constant at 65 °C, 3 wt % and 6:1, respectively. The yield of biodiesel increased steadily as time progressed, until it reached equilibrium. After 20 min, the biodiesel yield was only 42%; it further increased to 74% as time reached 30 min. At 40 min reaction time, the yield had increased to 87% and finally reached its optimum yield of 96.9% after 60 min, as indicated in Figure 5. When the catalyst amount was increased to 5 wt % and leaving all the other parameters as stated above, the reaction proceeded at a faster rate, reaching its maximum yield of 94.8% after 40 min reaction time, and as the reaction time reached 60 min, the biodiesel yield dropped to 93.6% as demonstrated in Figure 5.

This occurrence of yield reduction might be due to the possibility of a reversible reaction, since the transesterification reaction is reversible.[8] Ngaini et al.[37] and Bazhdan et al.[40] reported that longer reaction times beyond the optimum obtainable yield trigger the reverse reaction, thereby reducing the biodiesel yield. Saputro et al.[41] studied the effect of reaction time when waste cooking oil was used as a triglyceride in biodiesel production. These researchers also reported a decrease in the biodiesel yield when the reaction time went above the time at which equilibrium had been reached.

3.2.3. Effect of the Methanol-to-Oil Ratio. Determining the ratio of methanol to oil in a transesterification reaction has a vital effect on both the quality of the produced biodiesel fuel and the completeness of the reaction.[13] In a transesterification

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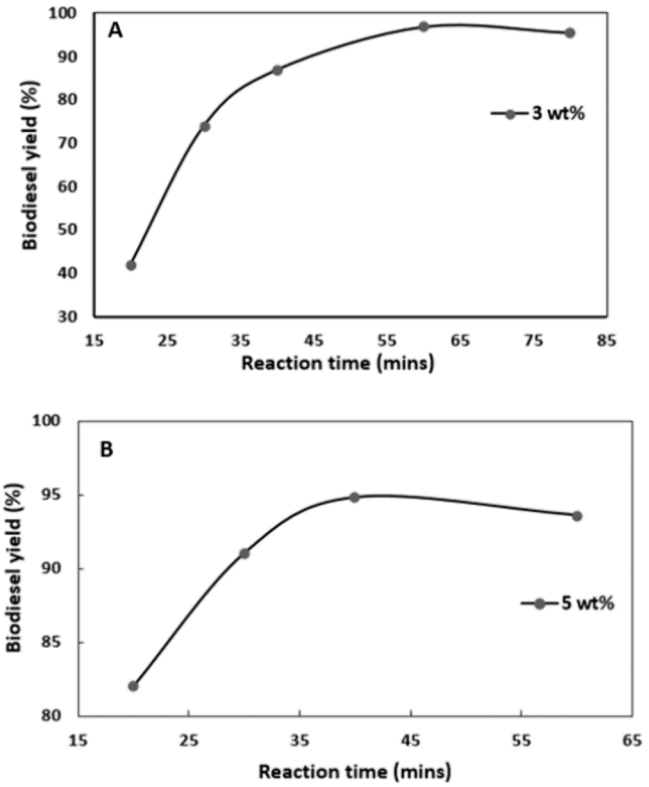

Figure 5. Effect of reaction time on the yield of biodiesel in the presence 3 wt % (A) and 5 wt % (B) silica xerogel catalyst loading.

reaction, 1 mol of a triglyceride (canola oil was used in this study) reacts with 3 mol of an alcohol (methanol was used in this study) to produce 1 mol of glycerol and 3 mol of biodiesel in the presence of a catalyst. Since a transesterification reaction is a reversible reaction, it is always advisable to use methanol in that it is greater than the stoichiometric amount in order to encourage the reaction to shift toward the right.[42−45] In heterogeneous catalysis, reactant adsorption and mass transfer are important.[46−48] The amount of methanol used is indeed directly related to the product cost, so it is of the utmost importance to determine the lowest molar alcohol amount that will result in the maximum yield. This study aimed at investigating different methanol to oil ratios: 5:1, 6:1, 7:1, and 10:1 at a constant temperature of 65 °C, fixed catalyst loading of 3 wt % and 60 min reaction time.

Figure 6 indicates that the biodiesel yield increased by 2.5% when increasing the methanol-to-oil ratio from 5:1 to 6:1. Boro et al.,[49] Sivakumar et al.,[45] and Sanchez et al.[50] also observed that increasing the methanol-to-oil ratio positively affected the biodiesel yield until the optimum yield was achieved. This effect was attributed to methoxy species being formed on the surface of the catalyst, which are reported by Boro et al.[49] to shift the reaction toward the forward direction. However, a significant yield reduction of 3.8% was observed when the methanol to oil ratio was increased to 10:1, as can be observed in Figure 6. Since transesterification is reversible, too much methanol being present promotes the formation of maximum glycerol, which in turn triggers the reverse reaction and thereby reduces the biodiesel yield.[51] Ali et al.[38] reported that excessive methanol usage causes deactivation of the catalyst, which would automatically result in yield decrease. It can be concluded that in this study, the methanol to oil ratio of 6:1 gave the optimum yield, and 10:1 resulted in the lowest yield.

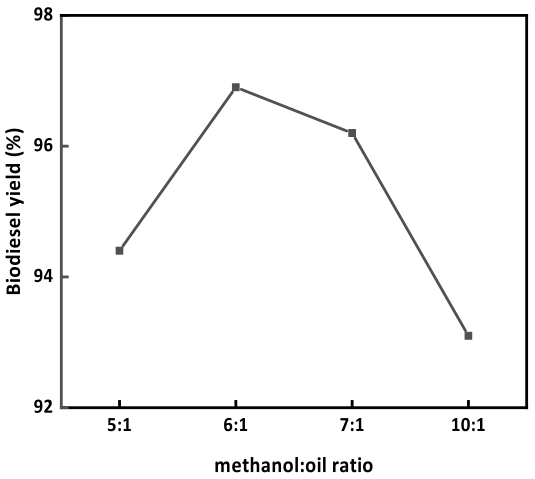

Figure 6. Effect of methanol to oil molar ratio on the yield of biodiesel in the presence of silica xerogel catalyst derived from sugar cane leaves.

This shows that elevated methanol-to-oil ratios do not necessarily result in higher biodiesel yields but rather could negatively affect the yield. In addition, several disadvantages, such as higher cost of production and increased glycerol solubility in methyl ester, which could lead to a complicated separation process, are associated with excessive methanol usage in transesterification.[52]

3.2.4. Effect of Catalyst Nature. As already mentioned, the type of catalyst is one of the factors that affect the yield of biodiesel. Table 2 is used to compare the catalyst synthesized in this study with other catalysts used in the literature, where the same triglyceride as canola oil, was used to produce biodiesel through transesterification. Chong et al.[53] used a catalyst that is a mixture of ZnO with CaO synthesized from shells of chicken eggs, mussels, oysters, and lobsters. These researchers used microwave-assisted transesterification and reported a biodiesel yield of 92.2%. Tavizón-Pozos et al.[54] used a catalyst where potassium and strontium are supported on calcium oxide that had been obtained from egg shells. They reported a biodiesel yield of 92.5%, and the yield reported by these authors is lower than the one obtained in this study, despite the usage of more methanol and the greater catalyst content they used. Khatibi et al.[55] used a CaO/Na−K doped CaO catalyst where the CaO was derived from egg shells. These researchers reported a biodiesel yield of 97.6%, which is 0.7% more than the yield reported in this study. They used 180 min to conduct their experiment and a 9:1 methanol to oil ratio instead of 60 min and a 6:1 methanol to oil ratio used in this study, respectively. Alsharifi and Znad[56] used a Lithium−Zinc system that had been supported on CaO, which was obtained from chicken bones. They reported a biodiesel yield of 98% from using an 18:1 methanol-to-oil ratio, 4 wt % and a reaction time of 300 min. The yield reported by these researchers is higher than the one obtained in this study; however, longer reaction times are time and energy-consuming, and high methanol-to-oil ratios are not budget-friendly. Other researchers who used canola oil to produce biodiesel through transesterification were Abdulkareem and Nasir;[57] they used titanium dioxide/calcium oxide (TiO_2/CaO) as a catalyst. They reported a biodiesel yield of 96.9% where a 16:1 methanol to oil ratio and 300 min reaction time were used as indicated in Table 2. This yield is the same as the

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Table 2. Comparison of Silica Xerogel Catalyst with Other Catalysts Used in the Production of Biodiesel Using Canola Oil

catalyst	methanol:oil ratio	reaction time (min)	temperature (°C)	catalyst content (wt %)	biodiesel yield (%)	ref
CaO/ZnO	9:1	10	microwave	1	92.2	Chong et al.[53]
SrK/CaO	12.5:1	60	70	7	92.5	Tavizón-Pozos et al.[54]
CaO/Na−K	9:1	180	50	3	97.6	Khatibi et al.[55]
Li−Zn/CaO	18:1	210	60	4	98.0	Alsharifi and Znad[56]
TiO_2/CaO	16:1	300	65	1.5	96.9	Abdulkareem and Nasir[57]
NaOH/sepiolite	9:1	180	60	6	80.9	Aslan et al.[58]
SiO_2/Au nanoparticles	6:1	40	65	3	99.2	Maseko et al.[59]
SiO_2	6:1	60	65	3	96.9	present study

one reported in this study, but these authors used a longer reaction time and a lot of methanol to obtain the reported yield. Aslan et al.[58] obtained a biodiesel yield of 80.9% through the usage of NaOH/sepiolite catalyst. Even though they used a 9:1 methanol to oil ratio and carried out their transesterification reaction for 180 min, their yield is quite low compared with the one reported in this study. Maseko et al.[59] used gold nanoparticles deposited on a silica xerogel support from sugar cane leaves to produce biodiesel. These authors reported a biodiesel yield of 99.2%, which is 2.3% higher than the yield reported in this study. This higher yield was explained to have been enhanced by the addition of gold nanoparticles.

3.2.5. Catalyst Reusability. One of the most important advantages of a heterogeneous catalyst over a homogeneous catalyst is its ability to be recycled, thereby reducing production costs. The synthesized silica xerogel catalyst from sugar cane leaves was investigated for reusability potential using the optimized conditions: reaction temperature of 65 °C, 3 wt % catalyst loading, 60 min reaction time, and 6:1 methanol to oil ratio. The reported yield that was obtained from the optimum conditions is 96.9%. After the first use of the silica xerogel catalyst, it was separated from the reaction and washed with methanol before being dried in the oven overnight at 80 °C. When the catalyst was used for the second time, its yield dropped to 92.3%, which is a 4.6% decrease. The catalyst was used again for the third and fourth time after being subjected to methanol rinsing and drying, and a yield of 80.4 and 69%, respectively, was obtained. Figure 7 represents the results that were attained with the synthesized catalyst's reusability potential.

It was noticed that after each usage of the catalyst, it became more off white since the initial color of the catalyst was white. From Figure 7, it can be concluded that the catalyst activity decreased as the catalyst was being reused, and the decrease was fairly significant after the fourth run. The decrease in the biodiesel yield is reported to be due to the result of active species leaching from the surface of the active catalyst as the reaction takes place.[20,60] Miyuranga et al.[61] reported that the deactivation of the used catalyst sites could be the result of their poisoning by involved metal glyceroxides with some absorbed intermediates such as glycerine, monoglyceride, diglyceride, and also possible contaminations by CO_2, H_2O, and O_2 present in the air. It can be deduced that silica xerogel produced from sugar cane leaves, when employed as a catalyst in the production of biodiesel, can be reused up to 3 times and still obtain a biodiesel yield greater than 60%.

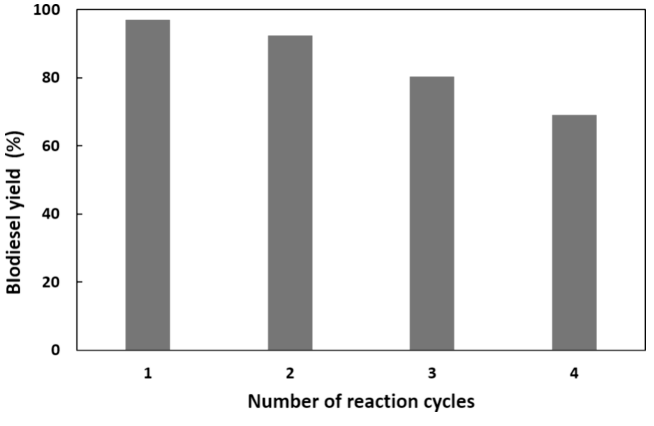

Figure 7. Reusability of sugar cane leaf-derived xerogel catalyst.

3.3. Biodiesel Characterization. *3.3.1. FTIR Analysis.* An FTIR analysis of biodiesel produced at optimum conditions: 3 wt % catalyst loading, 60 min reaction time, 6:1 methanol to oil ratio, is displayed in Figure 8. The small band at 3006 cm^{-1}

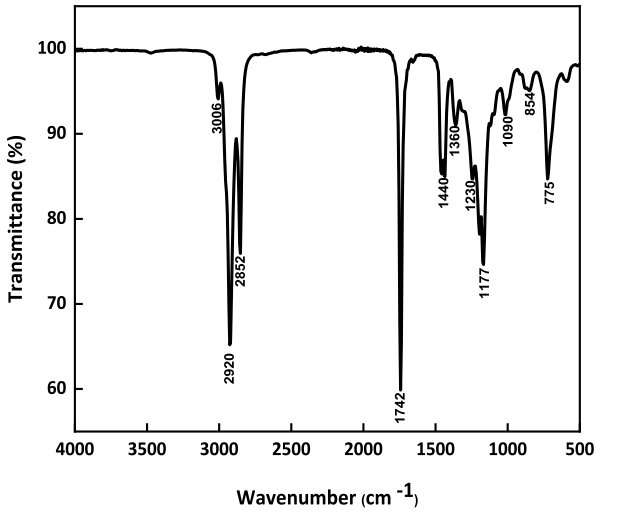

Figure 8. FTIR spectra of biodiesel produced from a sugar cane leaf-derived silica xerogel catalyst.

is reported by Qiu et al.[62] to be due to =C−H stretching.[62] The IR bands observed at 2920 and 2852 cm^{-1} indicate the symmetric and antisymmetric stretching vibrations of CH in CH_2 and CH_3 groups, respectively.[38] The strongest band at 1742 cm^{-1} is due to the presence of C=O stretching vibrations of carbonyl groups, which are present in esters and triglycerides.[63] The peak located at 1440 cm^{-1} is due to shear-type vibrations of CH_2 in the aliphatic groups.[62] The band at 1360 cm^{-1} is due to the bending vibrations of CH_3, while the band at 1230 cm^{-1} represents the stretching vibrations of C-0 ester.[38] The reasonably strong IR band at

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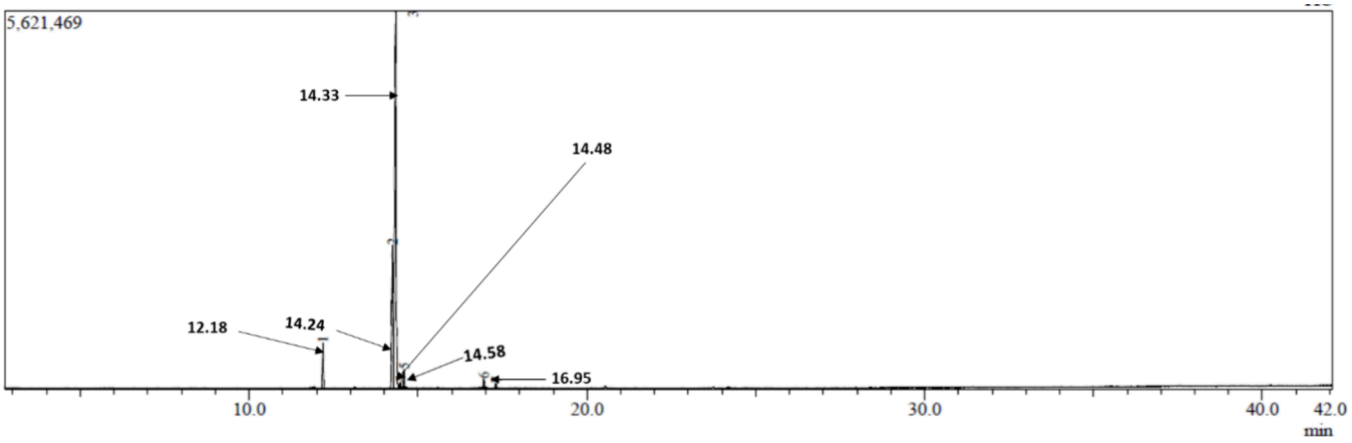

Figure 9. GC-MS chromatogram of biodiesel produced from methanol and canola oil in the presence of sugar cane leaves-derived silica xerogel catalyst.

1177 cm^{-1} is due to the symmetric stretching vibration of C−O−C.[62] The IR band at 1090 cm^{-1} is due to the C−O−C antisymmetric stretching vibration,[63] while the band at 775 cm^{-1} is due to the plane rocking vibration of CH_2.[62] The produced biodiesel only included the biodiesel functional groups reported in literature, which implies that canola oil was converted to long-chain fatty acid methyl esters. No peaks corresponding to unreacted canola oil were detected, which means that the produced biodiesel had a high purity.

3.3.2. Gas Chromatography-Mass Spectroscopy. Gas chromatography-mass spectrometry (GC-MS) was used to determine the chemical composition of the produced biodiesel. Six peaks were observed from the GC-MS chromatogram of the biodiesel sample as shown in Figure 9 below.

The observed major peaks shown in the chromatogram were identified by a comparison with reported data and profiles found from NIST and Wiley GC-MS libraries. The identified FAMES were methyl palmitate (RT = 12.18), methyl linoleate (RT = 14.24), methyl oleate (RT = 14.33), methyl linolenate (RT = 14.48), methyl stearate (RT = 14.58) and methyl gondoate (RT = 16.95) as indicated in Table 3 together with their compositions.

This indicates that saturated FAME (methyl palmitate and methyl stearate) were the least present in the produced biodiesel with a total percentage of 7.4 wt %, followed by polyunsaturated FAME (methyl linoleate and methyl linolenate) with a total composition of 20.0 wt %, while monounsaturated FAME (methyl oleate and methyl gondoate) were the most abundant FAMEs with a total composition of 72.6 wt % and methyl oleate was the most dominant FAME with a composition of 71.3 wt % as indicated in Table 3. According to the report published by the US Department of Energy, the perfect biodiesel would contain monounsaturated fatty acid methyl esters,[64] and if at all present, saturated and polyunsaturated fatty acids should be at low compositions.[65] The produced biodiesel falls within the "ideal" biodiesel composition since polyunsaturated and saturated fatty acid methyl esters are the least dominant, with saturated FAME being less than 8 wt %.

Table 3. Composition of Fatty Acid Methyl Esters Produced from the Transesterification of Canola Oil with Methanol Using Sugarcane Leaves-Derived Silica Xerogel Catalyst

peak number	composition (%)	fatty acid methyl ester	corresponding acid
1	4.95	hexadecenoic acid (methyl palmitate)	palmitic acid
2	19.07	methyl 10-*trans* 12-*cis*-octadecadienoate (methyl linoleate)	linoleic acid
3	71.28	9,9-octadecenoic acid methyl ester (methyl oleate)	oleic acid
4	0.95	9,12,15-octadecatrienoic acid (methyl linolenate)	linolenic acid
5	2.42	methyl stearate	stearic acid
6	1.33	11-eicosenoic acid methyl ester (methyl gondoate)	gondoic acid

3.3.3. Physical Properties of Biodiesel. The physical properties of biodiesel produced under the optimum conditions were investigated. The physical properties that were analyzed are density, kinematic viscosity, cloud point, pour point, and flash point. Table 4 shows the obtained results.

Table 4. Physical Properties of Biodiesel Produced From Sugarcane Leaves-Derived Silica Xerogel Catalyst

physical property	biodiesel	ASTM D 6751	EN 14214
density (kg/m^3)	877 ± 2	870−900	860−900
kinematic viscosity (mm^2/s)	4.4 ± 0.06	1.9−6.0	3.5−5.0
cloud point (°C)	−1 ± 1	−3 to 15	[a]
pour point (°C)	−6 ± 1	−15 to 10	[a]
flash point (°C)	166 ± 0.8	>130	>120

[a]Not specified.

The kinematic viscosity, density, and flashpoint of the produced biodiesel were found to be 4.4 mm^2/s, 877 kg/m^3, and 166 °C, respectively. These values are within the American and European standards of biodiesel, as reflected in Table 4. The produced biodiesel remained as a liquid in temperatures above zero and only started to be cloudy at temperatures around −1 °C, thereby reaching its cloud point, which can be described as the minimum temperature at which solid crystals start forming within the biodiesel fuel and causing it to be cloudy. Biodiesel reached its pour point at −6 °C, where it was observed to gel and thereby resist flow. This means that the produced biodiesel can be successfully used at temperatures above −6 °C without the need to blend it with fossil diesel. The flash point indicates the biodiesel's potential flammability and helps to determine the level of safety precautions needed

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when working with the fuel. The measured flash point of the biodiesel produced in this study was found to be 166 °C, which indicates a lower possibility of the produced biodiesel accidentally igniting.[66]

4. CONCLUSIONS

The application of sugar cane leaf-derived silica xerogel catalyst was investigated in the production of biodiesel through transesterification, where methanol and canola oil were used as an alcohol and triglyceride, respectively. Different parameters, such as reaction time, catalyst weight percent, and methanol to oil ratio, were studied to obtain the optimum yield. Increasing all these parameters had a positive effect on the catalyst up to a certain extent, and their further increase caused the yield to decrease. It was discovered that transesterification conducted at 65 °C, 3 wt % catalyst loading, 60 min reaction time, and 6:1 methanol to oil ratio resulted in the highest yield of 96.9%. The investigated catalyst was also discovered to have a recycling potential and is reported to produce biodiesel yields above 60% after four runs. The produced biodiesel was found to have physical properties within the accepted ASTM and EN standards with a cloud point of −1 °C, a pour point of −6 °C, and a flash point of 166 °C. Kinematic viscosity and density were also found to be 4.4 mm^2/s and 877 kg/m^3, respectively. The produced biodiesel consisted of a mixture of both saturated and unsaturated FAME, with methyl oleate (a monounsaturated FAME) having an amount of 71 wt % and therefore being the most dominant fatty acid methyl ester. Based on the results obtained, it can be concluded that xerogel from sugar cane leaves is an effective, environmentally friendly, and economical catalyst for the production of biodiesel with high application potential.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.5c01971.

> Biodiesel separation process after transesterification, the biodiesel separating after 5 h and completely separated after 20 h; transesterification using silica xerogel from sugar cane leaves as a catalyst, at the beginning of the reaction, liquid being cloudy and the reaction considered complete when all the canola oil at the bottom of the flask had reacted and the solution had turned bright yellow (PDF)

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Conceptualization: N.N.M.; methodology: N.N.M.; validation: N.N.M., D.E., and P.A.O.; formal analysis: N.N.M., D.E., and P.A.O., investigation: N.N.M.; data curation: N.N.M.; writing—original draft preparation: N.N.M.; writing—review and editing: S.A.I., P.A.O., D.E., O.S.O., and J.P.; visualization: N.N.M., S.A.I., and D.E.; supervision, J.P., S.A.I., and O.S.O. All authors have read and agreed to the published version of the manuscript.

Notes

The authors declare no competing financial interest.

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