Rheological and Physicochemical Analysis of Nonedible Oils Used for Biodiesel Production

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ABSTRACT: Rheological and physicochemical characteristics of edible oils used for biodiesel production are well established; nonetheless, the rheological and physicochemical characteristics of nonedible oils are yet to be established. The present study therefore focuses on rheological and physicochemical characterization of nonedible vegetable oils that can be used as biodiesel feedstock. The selected vegetable oils studied include cashew nut shell liquid (CNSL), castor oil (CO), Croton megalocarpus oil (CMO), Podocarpus usambarensis oil (PUO), and Thevetia peruviana oil (TPO). Physicochemical parameters analyzed were free fatty acids, acid value, saponification value, peroxide value, iodine value, specific gravity, and moisture content using methods by the Association of Official Analytical Chemists (AOAC). Rheological properties were analyzed using a VT-550 Thermo Haake Viscotester operated by the Rheowin 3 Job Manager software. The preset parameters in the Viscotester were shear rate and temperature. The shear rate increased uniformly from 5 to 100 s$^{-1}$ at the temperature range of 30–60 °C. The experimental data were fitted into rheological models of Newton, Bingham, Ostwald–de Waele (power-law), and Herschel–Bulkley using Rheowin 3 Data Manager. The oil yield was 29–65%, highlighting the feedstock’s potential for commercial biodiesel production. At a constant temperature, all oil samples exhibited a Newtonian flow behavior. In contrast to edible oils, nonedible oils exhibited high shear stress, emphasizing the reconstruction of new appropriate designs of production systems. The rheological models appropriate to represent the flow behavior of the samples were the Newton and Ostwald–de Waele models, with a fit of $R^2 = 0.990–1.000$.

1. INTRODUCTION

Biodiesel is produced by the transesterification process that converts oils and fats into biodiesel (methyl esters) and glycerine.1 The characteristics of biodiesel produced are dependent on the physicochemical and rheological characteristics of the feedstock used during the manufacturing process.2 The performance and quality of biodiesel fundamentally depend on the chemical, structural, and flow properties of the vegetable feedstock oil used.3 Generally, biodiesel is characterized by higher density, higher viscosity, and lower volatility than mineral diesel, affecting steady fuel exhaustion.4 This preceding nature of biodiesel is based on the influence of the feedstock vegetable oils’ physical behavior and chemical composition.5 Vegetable oils are characterized by larger hydrocarbon chains of triglycerides (free fatty acids), and the fuel quality, stability, and conversion efficiency are compromised.5 Furthermore, free fatty acids influence the other physicochemical properties of the fuel including but not limited to the saponification value, iodine value, and peroxide value. Therefore, even though the biodiesel industry is fast-growing, the maintenance of fuel quality and stability remains an unsolved impediment.6 To address the challenge, physicochemical and thermophysical characteristics of the feedstock were studied for the designation of the process control systems and appropriate manufacturing facilities, storage facilities, and transportation facilities. A study7 emphasized the importance of analyzing the physicochemical and rheological characteristics of the raw materials of biodiesel.

Rheology is the study of the flow behavior of fluids and the effect of applied stress on the fluids.4 It provides the information to be used in the designation of the manufacturing facilities, storage facilities, and process control systems based on the flow behavior of the feedstock.4 A study by Silva et al.3 focused primarily on the rheology of the first-generation (edible vegetable oils) biodiesel feedstock at 35, 45, and 60 °C. To the best of the authors’ knowledge, there is no study that

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comprehensively reported the rheology behavior of non-vegetable oils as feedstock for biodiesel production. This study, therefore, aims to characterize second-generation feedstock (nonedible vegetable oils) that could be used as biodiesel feedstock. The flow behavior analysis of the selected vegetable oils was conducted at 30–60 °C. The selected nonedible oils used in this research were cashew nut shell liquid (CNSL), castor oil (CO), Croton megalocarpus oil (CMO), Podocarpus usambarensis oil (PUO), and Thevetia peruviana oil (TPO). The studied nonedible vegetable oils were selected based on the oil yield and the reproduction term (the life span) of the seed-bearing plant. The reported yield was 20–30% for CNSL, 35–45% for CMO, 28–59% for CO, and 50–67% oil yield for PUO and TPO. The average reproductive term starts after 6–18 months for CNSL, CO, and TPO; 4 years for CMO; and 15 years for PUO. The reproductive term for the seed-bearing plants lasted 45 years for PUO and CMO, 3 years for CO, 50 years for CNSL, and 75 years for TPO.

2. MATERIALS AND METHODS

2.1. Materials and Chemicals. The cashew nut shell liquid (CNSL) was obtained from Korosho Africa Limited, a local cashew nut processing factory in Tunduru district, Southern East Tanzania. Castor oil (CO) was obtained from the local small seed processing industry in Dodoma, central Tanzania. Croton megalocarpus oil (CMO), Podocarpus usambarensis oil (PUO), and Thevetia peruviana oil (TPO) were extracted from the seeds collected from various regions of the country. Croton megalocarpus and Podocarpus usambarensis seeds were purchased from Tanzania Forest Service Agency (TFSA). The seeds were collected from Usambara forests in Lushoto, Tanga, in the Northern East part of Tanzania. Thevetia peruviana seeds were collected from the outskirts of Arusha and Kilimanjaro regions in the northern part of Tanzania. Shown in Figure 1 are the seeds before the removal of the shells and the oil extraction process.

Reagents used as solvents for oil extraction were analytical-grade petroleum ether and chloroform. For physicochemical characterization of the samples, chemicals used were analytical-grade petroleum ether, ethanol, POP indicator, potassium hydroxide, hydrochloric acid, glacial acetic acid, chloroform, potassium iodide, starch indicator, sodium thiosulfate, carbon tetrachloride, and Wiji’s solution. The reagents were bought from Exodus Chemicals and Apparatus Trading (ECAT) in Arusha CBD.

2.2. Sample Preparation. The shells of the seeds were removed and separated from the kernels. The kernels were washed, sun dried for 12 h, and crushed to 2–5 mm particles. Except for the cashew nut shells, the oil samples were extracted from the kernels of the seeds.

2.3. Oil Extraction. Oil from CMO, PUO, and TPO was extracted from the crushed kernels of the seeds by employing the solvent extraction method. The petroleum ether was used to extract Croton megalocarpus oil and Podocarpus usambarensis oil from the seeds. Chloroform was used to extract Thevetia peruviana oil from the seeds. Solvent selection for oil extraction depends on the affinity of the solvent for a specific oil. All the sample oils from CNSL, CO, CMO, PUO, and TPO were used for physicochemical and rheological characterization with no further treatment.

2.4. Physicochemical Characterization of the Samples. The techniques followed in determining the physicochemical parameters are summarized in Table 1. Physicochemical parameters of the oil samples were studied using the methods by the Association of Official Analytical Chemists (AOAC).

| Parameter | Method | Principle |
|-----------|--------|-----------|
| oil yield | AOAC 940.28 | gravimetry |
| FFA | AOAC 940.28 | titrimetry |
| AV | AOAC 920.160 | titrimetry |
| SV | AOAC 965.33 | titrimetry |
| PV | AOAC 920.159 | Wiji’s titrimetry |
| SG | AOAC 920.212 | pycnometry |
| moisture content | AOAC 930.15 | gravimetry |

*FFA = free fatty acid, AV = acid value, SV = saponification value, PV = peroxide value, IV = iodine value, and SG = specific gravity.

2.5. Investigation of Rheological Characteristics of Oils. Flow properties of the samples were analyzed by a shear rheometer (Haake Viscotester, model VT 550, Karlsruhe, Germany). This research used a concentric cylinder measuring system (CC MS) employing Searle’s operating method for the experiments. The measuring system entailed a stationary outer cylinder mounted on the same axis as the rotating inner cylinder (sensor system).

The gap between the outer and inner cylinder was filled with the sample to be analyzed. To ensure a uniform stress distribution on the sample between the concentric cylinders, the degree of heterogeneity of stresses \( \left( \epsilon = \frac{R_R}{R_L^2} \right) \) for the setup was 1.084. The literature by Mezger and Schramm recommended that the ratio of the outer cylinder to that of the inner cylinder be at least a unit to get accurate measurements.

As the inner cylinder was in rotation, adequate torque to subdue the sample’s viscosity, posing resistance to the induced motion, was measured. Rheological flow parameters that were analyzed in concurrence with the system fixtures and speed of inner cylinder (\( \omega \)) are expressed as shown:

![Figure 1](https://example.com/figure1.png)
3. RESULTS AND DISCUSSION

3.1. Proximate Analysis of the Seeds. As presented in Table 2, the proximate analysis of the selected seeds revealed

| Table 2. Proximate Composition of the Seedsa |
|------------------------------------------|
| constituents (%) | CNSL | CO | CMO | PUO | TPO |
| protein         | 3.8  | 28 | 41  | 17  | 26  |
| fat             | 32   | 51 | 29  | 65  | 63  |
| ash             | 10.6 | 9.4| 3.5 | 2.3 | 2.2 |
| carbohydrates   | 0.1  | 7.9| 19  | 11  | 5.5 |
| fiber           | 52   | 1.0| 4.5 | 3.0 | 1.9 |
| moisture        | 0.9  | 0.5| 0.3 | 0.1 | 0.4 |

aCNSL = cashew nut shell, CS = castor seeds, CM = Croton megalocarpus, PU = Podocarpus usambarensis, and TP = Thevetia peruviana.

that CS, CM, PU, and TP possessed a considerable amount of protein and fat compositions. However, in CNSL, there was a high fiber and oil composition. The moisture content in CNSL was also significant, which was attributed to the ability of the fiber to absorb moisture. The fat composition of the seeds was used as a key determinant of a good biodiesel feedstock in this study.

3.2. Physicochemical Characteristics of Oils. Physicochemical characteristics of selected nonedible oils are summarized in Table 3. The FFA profile of feedstock oils

| Table 3. Physicochemical Characteristics of the Selected Nonedible Oils |
|-----------------------------------------------------------------------|
| property                | unit         | CNSL | CO | CMO | PUO | TPO |
| FFA                     | %            | 6.6  | 0.9| 1.61| 1.2 | 0.96 |
| AV                      | mgKOH/g      | 13.2 | 1.8| 3.22| 2.4 | 1.92 |
| SV                      | mgKOH/g      | 66.8 | 183| 190.7| 190 | 120 |
| PV                      | mequiv/kg    | 43.1 | 3.7| 2.3 | 4.9 | 2.7 |
| IV                      | mgl/100 g    | 124.4| 82.8| 126.5| 96  | 83.1 |
| SG                      | g/s          | 935  | 910| 900 | 830 | 790 |
| moisture content        | %            | 5.53 | 0.05| 1.1 | 0.01| 0.03 |
| oil yield               | %            | 29   | 65 | 63  ||

determines the path taken in the biodiesel production process. The results showed that the FFA profile of CO, CMO, PUO, and TPO is <2%, suggesting that biodiesel synthesis from these oils can be achieved by a single-stage process. The low composition of FFA in the samples showed that the sample oils were still fresh and of high quality. Conversely, the CNSL FFA profile is >2%, suggesting that the route for the biodiesel manufacturing process should be achieved through a double-stage process. The double-stage process requires excess alkali to neutralize the oil's acidity and also function as a catalyst. Excess alkali increases the yield of biodiesel by inhibiting soap formation that is usually due to the high FFA composition in the feedstock. The high FFA composition in CNSL was due to the high moisture content in the sample oil. The results revealed that the FFA composition of the selected vegetable oils correlated to other studies conducted in East Africa. A study by Kivevele and Mbara and by Uwiragiye and Anyiam stated that the FFA profile of CO is 1.73 and 1.54%, respectively. Omari et al. reported that the FFA profiles in CO from different regions of Tanzania varied from 0.22 to 0.99%. Saponification values ranged from 66.8 to 190.7...
mgKOH/g. As depicted in Table 3, the saponification values of CMO and PUO were 190.7 and 190 mgKOH/g, respectively, indicating a relative similarity. The resemblance of saponification values suggests that incorporated oil samples of CMO and PUO in this study were composed of carbon--carbon chains with the same molecular weight and carried similar functional groups. The similarity in saponification values resulted from the direct linkage between the saponification value and the molecular weight of the triglyceride chains (fatty acid chains) present in the oil. While all the other sample oils possessed saponification values that agree with the commended saponification values reported in the literature (such as Chavan et al., 2018; Kyei et al., 2019; Omari et al., 2015), the observed value for PUO was slightly higher compared to the study by Minzangi et al. The study reported that the saponification value of PUO extracted from the seeds collected in Kivu, DRC, was 182.5 mgKOH/g, and the deviation could be attributed to the differences of ecological habitat features such as the soil’s primary nutrients, climatic conditions, and the altitude of the area where the plant was grown. The mentioned factors influence the plant’s nutrient uptake, causing minor variations in the properties of the oils. Also, the difference was possibly because of the chemical composition of impurities that were present in the sample oil. However, not enough amount of research based on PUO has been conducted.

With the exception of CNSL, peroxide values of oils observed were <10 mequiv/kg, verifying that the samples used were still fresh. It also showed that it would take some time before the samples deteriorated. The peroxide value of CNSL was 43.1 mequiv/kg, relatively higher, which could be attributed to the oxidation reaction occurring during the oil extraction process, which involved roasting the shells. Also, the high moisture content contributed to the oxidation of the liquid and resulted to a high peroxide value. The peroxide values of CO, CMO, PUO, and TPO were in sync with those reported in other literature. The iodine values recorded in this study were between 82.8 and 126.5 mgI$_2$/100 g. It was observed that CNSL and CMO had the highest iodine values of 124.4 and 126.5 mgI$_2$/100 g, respectively. The values suggested that the oil samples possessed a considerable amount of unsaturated fatty acids and had low oxidative stability characteristics. A study by Shalaby stated that nonedible oils were characterized by high iodine values and hence have low oxidative stability. Also, the iodine values of CNSL and CMO were comparatively similar, which could be accredited to an approximately equal number of unsaturated carbon–carbon bonds in the fatty acids. However, the value of CMO observed in this study was less than that observed by Kumar et al., which was 139.2 mgI$_2$/100 g. Similarly, the observed iodine value of CNSL was lower than the reported standard value of 250 mgI$_2$/100 g. The difference could be accounted for by thermo-oxidative alteration during the extraction process that caused the unsaturated carbon bonds of fatty acids to break.

Figure 2. Flow curves of sample oils at the temperatures of 30, 40, 50, and 60 °C. (A) Cashew nut shell liquid, (B) castor oil, (C) Croton megalocarpus oil, (D) Podocarpus usambarensis oil, and (E) Thevetia peruviana oil.
As reported on Table 3, the specific gravity values of oils were between 800 and 960. Specific gravity values of CNSL and CO samples were within the set standard range, which is 950−970 and 968−975.7 for the oils, respectively. The moisture content in CO, CMO, PUO, and TPO was within the accepted standard range that was ≤0.05% for maintenance of the oil quality. However, the moisture content in CNSL was 5.53%, which was extremely high considering the recommended standard value. The high moisture content in CNSL increased the rate of degradation of the oil. The studies show that moisture content in biodiesel feedstock compromised the quality of the feedstock. Also, it affected the production efficiency of the oil because of soap formation during the process. To resolve the drawbacks caused by the high moisture content of the feedstock, it is recommended for the oils to be dried to a moisture content of ≤0.05%. After extraction, the yield of vegetable oils was between 29 and 65%. CSMO had the lowest yield of only 29%, below the average range of 30−32% reported by Aliyu et al. and Wu et al. However, the yield was above the satisfactory range for biodiesel feedstock, which was at least 20% oil yield from the seeds.

### 3.3. The Variation of Shear Stress and Dynamic Viscosity with Shear Rate

The internal resistance to flow offered by the selected raw materials that are used in the manufacturing process of biodiesel predetermines the flow behavior that is to be exhibited by the produced biodiesel. Therefore, carrying out a thermophysical analysis of the feedstock in advance determines the suitable production processes and facilities designs. Figure 2 presents the computed flow curves that show the shear rate−shear stress relationship of each oil sample at 30, 40, 50, and 60 °C. As shown in Figure 2, for all the samples analyzed, a uniform linear correlation of shear stress as a function of shear rate is revealed. For CNSL, CO, CMO, PUO, and TPO, the shear stress−shear rate flow relationship observed in this study was that of an ideal liquid that exhibits a Newtonian flow behavior. The results revealed that at zero shear rate, there was no minimum shear stress (γ-intercept = 0 Pa) required to break the interactive bonds among the particles of the sample to start the flow of the sample oils. The shear rate applied to the samples was directly proportional to the shear stress exhibited by the samples for overcoming the viscous resistance offered. Because the rheograms illustrate that the sample oils possessed a Newtonian flow behavior, it implies that for each of the samples analyzed, the viscosity remained constant regardless of the increase in the shear rate applied. To further confirm the observed nature of the flow exhibited by the samples in the study, a linear fit on a power model was carried out to determine the behavior index of the samples.

\[
\tau = \gamma^n \quad \tau = K \gamma^0
\]

\[
\ln \tau = n \ln \gamma + \ln K
\]

\[
K = n R^2
\]

\[
\eta = \frac{K n R^2}{K n R^2}
\]
for substances that exhibit Newtonian flow, which is \( n = 1 \). Moreover, upon fitting the computed data in the respective model, the calculated correlation coefficient \( R^2 \) values for all the samples were greater than 0.99. This verified that the linearity of the flow curves and Newtonian flow behavior exhibited by the sample oils of the samples were appropriately represented by the power-law. A report by Wang et al.\(^{44}\) that studied the rheological characteristics of CO observed a similar behavior. However, no rheological studies have been conducted for other selected vegetable oils used in this research. High values of shear stress were observed during the analysis of CNSL and CO samples because of the oils' high viscous resistance. The high viscosity of these samples is associated with strong intermolecular cohesive forces that resist the motion of the molecules. As a result, high torque is required to overcome the intermolecular force resistance for the flow to occur. The average viscosity of CNSL, CO, and TPO observed in this study was higher than the average viscosity of edible oils reported by Silva et al.\(^{39}\) The average viscosity of CMO and PUO was equivalent at \( p \leq 0.05 \) to the average viscosity of canola oil, which was observed to have the highest viscosity among the other edible oils assessed in the study. A study by Sahasrabudhe et al.\(^{45}\) reported the average viscosity of canola oil to be lower than that of CMO and PUO. The high viscosity of the assessed oils in this study results from the high FFA composition in nonedible oils compared to edible oils.

### 3.4. The Influence of Temperature on Shear Stress and Viscosity

The influence of temperature on shear stress as a function of shear rate was analyzed at the temperatures of 30, 40, 50, and 60 °C. As expected, the results in Figure 3 revealed that, with an increase in temperature, the shear stress values exhibited by the samples decreased. The shear stress values of CNSL, CO, CMO, PUO, and TPO at the temperature of 30 °C and shear rate 100 s\(^{-1}\) were 16.95, 31.06, 3.76, 2.13, and 5.42 Pa, respectively. At 60 °C, the maximum shear stress values observed for CNSL, CO, CMO, PUO, and TPO were 4.25, 7.32, 1.20, 0.52, and 2.13 Pa, respectively. At the shear rate of 100 s\(^{-1}\), the decrease in the shear stress from 30 to 60 °C was 74.5% for CNSL and CO, 31.9% for CMO, 24.4% for PUO, and 39.3% for TPO. Also, the viscosity of all the samples analyzed decreased as the temperature increased. The decrease in viscosity resulted in the low torque required to overcome the viscous resistance offered by the sample. This describes the decrease in shear stress, which resulted from the decrease of dynamic viscosity in the samples as the temperature increased. Figure 3 shows the effect of temperature on the dynamic viscosity of the samples. Drastic alterations of dynamic viscosity in CNSL and CO samples were observed as the temperature increased because the samples had carbon–carbon chains with a high unsaturation degree of FFA.\(^{45}\) Unsaturated bonds were deformed under heat (temperature), bringing about drastic changes in the viscosity of the samples. Contrarily, the viscosity of CMO, PUO, and TPO steadily decreased, which implied that FFA bonds in the oil were not substantially deformed with the temperature increment. The results show that, regardless of the temperature variations, all samples maintained a constant linear flow behavior, with a constant viscosity resulting in a flow behavior index of approximately equal to 1 at 30, 40, 50, and 60 °C.

Since the viscosity of the samples was maintained at uniform temperatures, it is possible that the molecular structure and the molecular arrangement of the molecules were maintained as well throughout the experiments.\(^{46}\) Newtonian fluids possess isotropic molecules that have a symmetrical shape, and the molecules are not oriented by the shear rate applied in the samples, therefore not causing any changes in the flow properties of the oils.\(^{46}\) If the molecules are oriented by the force applied into the sample, dilatant or pseudoplastic flow of the samples would be observed. The molecules’ orientation changes the direction of the molecular flow, resulting in the deviation of the direction of the shear stress. However, a comprehensive study on the microstructural changes resulting from shearing and temperature variations is recommended to examine their impacts on the sample’s quality and the produced fuel.

However, as shown in Figure 4, the viscosity of PUO was comparatively similar to that of CMO. Likewise, as the temperature varied, the dynamic viscosity values comparison were still maintained. The Tukey test confirmed the resemblance in mean dynamic viscosity values at \( p \leq 0.05 \), as shown in Figure 4. The results suggested that the samples had equal internal resistance to flow, which could be contributed by the resemblance of the morphology of CMO.
and PUO. The similarities in morphology could include but are not limited to the inner structure, shape, arrangement, and size of the particles in the samples. Thus, the torque required to start the flow in CMO was equivalent to that of PUO. As a result, there was no significant difference in the shear stress exhibited at the respective shear rate for both CMO and PUO.

Moreover, according to power-law, the consistency index \( K \), which describes the ease of flow for each sample, decreased as dynamic viscosity reduced. The computed data revealed that the consistency index fluctuated with the temperature increase, which decreased with an increase in temperature. Low consistency index values were observed at high temperatures, which suggested that the samples flow readily at high temperatures and vice versa. The computed consistency index values for each sample at 30, 40, 50, and 60 °C are presented in Tables 4–7.

### 3.5. Determination of the Appropriate Rheological Predictive Model for the Oils

Rheological models that could describe the flow behavior of the selected nonedible vegetable oils were assessed by fitting the experimental data into four rheological models selected. The models were the Newton, Bingham, Ostwald–de Waele (power-law), and Herschel–Bulkley rheological models. The selection of the models was on account of the time-independent behavior that was portrayed by the rheograms of the samples. The predictive models represented the shear stress–shear rate relationship by employing the introduction of flow predictive parameters in each model. The predictive flow parameters that were used for modeling are described in Tables 3–6.

In Newton’s rheological model, the determinant predictive parameter was the apparent viscosity \( \eta \) (Pa·s). For all the samples, it was observed that the apparent viscosity was decreasing with the increase in temperature. As a result, it affected the shear stress (the study’s dependent variable). The correlation coefficient calculated by the experimental data fitting into this rheological model was \( R^2 \geq 0.987 \). In Bingham’s rheological model, the predictive parameters introduced in the shear rate–shear stress relationship were yield stress \( \tau_0 \) (Pa) and Bingham’s plastic viscosity \( \eta_p \) (Pa·s). Bingham’s rheological model focused on the apparent viscosity of the samples at very low shear rates. The yield stress values exhibited by all the selected samples were \( \tau_0 < 0 \), which were not in correlation to the accepted values for the Bingham’s fluids. The latter require yield stress greater than 0 (\( \tau_0 > 0 \)) to initiate flow of the samples at the shear rate of 0 s\(^{-1}\). The Bingham’s plastic values for the samples were less than 0.5 Pa·s, resulting in negative yield stress values calculated. The correlation fit of the experimental data into this rheological model was \( R^2 \geq 0.956 \).

In Ostwald–de Waele’s rheological model, the predictive parameters were consistency index \( K \) (Pa·s\(^{n}\)) and flow behavior index \( n \). Irrespective of the characterization temperature, \( n = 1 \) and \( K > 0 \) for all the samples. The decrease of the consistency index with the increase in temperature revealed that the viscous resistance was weakened, resulting in oil thinning; hence, the pumping ability of the oils was increased. This observation would also be reflected in the manufactured biodiesel, which would mean that the quality of fuel atomization would be achieved at high temperatures. The computed predictive parameter values were correlated to the expected parameter values for the Ostwald–de Waele model, and a positive correlation was revealed. The experimental data fit in this model showed a correlation of \( R^2 \geq 0.990 \). The predictive parameters in the Herschel–Bulkley flow model were yield stress \( \tau_0 \) (Pa), consistency index \( K \) (Pa·s\(^{n}\)), and flow behavior index \( n \). The calculated yield stress values at 0 s\(^{-1}\) were \(-0.7259 \leq \tau_0 \leq 0.0728\), which showed that the computed values were out of the expected range of \( \tau_0 > 0 \) for Herschel–Bulkley fluids. However, computed values for \( n \) and \( K \) were within the expected range for Herschel–Bulkley fluids, i.e., \( 0 < n < \infty \) and \( K > 0 \). The correlation of the fit in the Herschel–Bulkley model was \( R^2 \geq 0.929 \), which is not the most appropriate fit among the selected flow behavior predictive models.

According to the correlation coefficient \( (R^2) \) values computed by fitting the experimental data into the rheological models, the Newtonian, Ostwald–de Waele, and Bingham rheological models show an appropriate fit to describe the flow behavior of the samples. However, Herschel–Bulkley’s model showed a weak correlation to the data. Also, some \( \tau_0 \) values in Herschel–Bulkley’s model were negative, which contrast with the expected yield stress of Herschel–Bulkley’s model, \( \tau_0 > 0 \). Similarly, the computed yield stress values in the Bingham model were negative, meaning that none of the oils required externally applied stress to start flowing. Hence, Bingham’s and Herschel–Bulkley’s rheological models were not appropriate for presenting the flow behavior of the selected sample oils. The results of this study showed a resemblance to those of Paul et al.,\(^{43} \) a study that analyzed the rheological characteristics of CO and methyl ester. Furthermore, the study reported that at low shear rates of 5–100 s\(^{-1}\), CO and the manufactured methyl ester portrayed a non-Newtonian flow behavior. However, in this study, non-Newtonian flow behavior was not portrayed by any of the selected vegetable oils at the same shear rate. Additionally, a study by Abdelraziq and Nierat\(^{47} \) showed that CO had a depicted Newtonian flow behavior irrespective of the shear rate and temperature at which the rheometer was operated. Therefore, all sample oils portrayed a Newtonian flow behavior, which was appropriately represented by Newton’s and Ostwald–de Waele’s rheological models. Research by Silva et al.\(^{4} \) and Sahasrabudhe et al.\(^{45} \) described that a similar flow behavior was exhibited by edible oils where the flow behavior index maintained was equal to 1 at elevated temperatures from 20 °C. The studies concluded that Newton’s and Ostwald–de Waele’s rheological models were...
appropriate to present the flow behavior of the analyzed edible oils.

4. CONCLUSIONS

All the selected vegetable oils in this study had an oil yield of 29–65% from the seeds. The high oil yield shows that all the studied nonedible vegetable oils can be used to produce biodiesel commercially. However, the results revealed a significant difference in nonedible physical and chemical properties, solidifying the emphasis on the optimization of suitable designs of production facilities. Suitable designs should withstand the high viscous resistance offered by nonedible oils during the mixing process of raw materials. Rheological characterization revealed that, at a constant temperature, all selected nonedible vegetable oils exhibited a Newtonian flow behavior $n = 1$. All the sample oils used in this study maintained the same behavior at 30–60 °C. CNSL and CO had high viscosity among all the selected sample oils. In correspondence to their high viscosity nature, the produced biodiesel from CNSL and CO will perform poorly in cold climates. The high viscosity of CNSL and CO results in the increased cloud and pour points, which compromise the quality of fuel atomization. Though in-tank fuel heaters can resolve this issue, the method consumes enormous energy, which restricts the biodiesel's affordability aspect. A blend of CMO and PUO did not show any significant difference at the probability of $p \leq 0.05$. The rheological characteristics of the selected samples were appropriately represented by the Newtonian and Ostwald–de Waele rheological models. The rheological models showed a strong correlation to the fit of the experimental data ($R^2 = 0.990–1.000$). Therefore, for optimizing the biodiesel manufacturing process from nonedible oils, the average temperature for high-viscosity oils such as CSNL and CO should be maintained at 30–45 °C to avoid the irreversible deformation of the molecular structure of the produced biodiesel resulting in the compromise of the fuel’s quality. However, for low-viscosity nonedible oils, there were no observed effects that could compromise the fuel’s quality at the elevated temperatures. Correspondingly, the shear rate does not affect the oil’s viscosity, ensuring the preservation of the fuel’s quality through the production process. However, since the shear rate was directly proportional to the shear stress exhibited by the oils, the agitation speed to not exceed 800 rpm, to avert the damage on the manufacturing facilities from the exerted pressure. Manufacturing systems that can contain the high shear stress exerted by nonedible oils should as well be designed. Since this study focused solely on the flow behavior of the samples in relation to the production process, a further study on the microstructural interaction of the samples occurring because of the temperature and shear rate variations is recommended.

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Notes

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NOMENCLATURE

CNSL & #x2212; cashew nut shell liquid CO & #x2212; castor oil CMO & #x2212; Croton megalocarpus oil PUO & #x2212; Podocarpus usambarensis oil TPO & #x2212; Thvetina peroviana oil $n$ & #x2212; viscosity $n$ & #x2212; behavior index

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