Current Journal of Applied Science and Technology

Volume 42, Issue 14, Page 24-33, 2023; Article no.CJAST.100759
ISSN: 2457-1024
(Past name: British Journal of Applied Science & Technology, Past ISSN: 2231-0843, NLM ID: 101664541)

Suitability Evaluation of Pumpkin Seed Oil Biodiesel as a Possible Diesel for Zambia

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CJAST/2023/v42i144118

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/100759

Original Research Article

Received: 25/03/2023
Accepted: 29/05/2023
Published: 07/06/2023

ABSTRACT

The global concern about ways through which fuels, are free from greenhouse gases and other environmental contaminants has been growing. The solution can be achieved by producing fuels from renewable feedstock such as biodiesel which is marked as a non-greenhouse emission energy source. Biodiesel can be derived from natural sources such as vegetable oils, which have gained significant attention as a promising substitute for conventional diesel fuel. Fuel produced from biodiesel has a higher flash point above 70℃, a high viscosity of 4.692, and relatively low contaminants of 15.3 mg/Kg and a low residue count of 1.8%. The parameters rate fairly as desirable for use.

Keywords: Pumpkin seed oil; biodiesel; high flash point; low residue.

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1. INTRODUCTION

Globally the demand for petroleum has been increasing and the supply has been dwindling due to many reasons among them, resource depletion in some parts, political conflicts and excessive demand for the commodity. Besides petroleum diesel emits greenhouse gasses, and its unavailability is compared to the demand, hence leading to escalating commodity prices globally hence affecting all economies of the globe. These factors make it necessary to find an alternative fuel to diesel [1, 2]. The alternatives to petroleum diesel have been biodiesel, ethanol, hydrogen, solar-powered cars, and electrically powered cars [3-9]. The economic standing of a particular country in most cases dictates the direction of innovation in the quest to replace diesel.

Zambia is a third-world country, with economic prospects by different rating systems showing not positive for most parts, implementation must follow what is workable [10,11]. Currently, Zambia is implementing a shift from high Sulphur to low Sulphur content diesel as a measure to contribute to the goal of greenhouse and other pollutants emissions from petroleum diesel. This comes as ZS 718:2020, Zambia Bureau of Standard (ZABS) working document implemented through the Energy Regulation Board (ERB). The ZS 718:2020 is an extract from ISO standards ISO: 21/17/13. These are regulatory benchmarks set by the Bureau of standards of Zambia. In their guidelines, they prescribe parameters such as: sulphur content, water content, cloud point, flash point, carbon residues, particulates, viscosity and boiling point range.

The ZS 718:2020 prescribes several parameters including low sulphur content (0.005% sulphur equivalent to 50 ppm) diesel, viscosity, cloud point, flash point, water content, carbon residue and a recommended recovery profile [12].

In this research, an attempt is made to extract pumpkin seeds' oil and its biodiesel synthesized, then chemical characterization especially transesterification process verification, then its parameter analysis to the set petroleum diesel standards according to ZS 718:2020 instrument. The rationale is that Pumpkin is scientifically called *Cucurbitaceae Pepo. L* is a tropical fruit. And they are readily grown in Zambia even at garbage heaps, with minimum or no attention to crop management like other edible (Sunflower, ground nuts, cocoa nuts and soya beans) or non-edible oils such as jantropa.

The pumpkin seed oil has two colours at the same time green and red (orange). The red colour comes from carotene and the green colour from chlorophyll. The refined pumpkin seed oil has a straw yellow colour. Pumpkin seed oil methyl ester (PSOME) was produced through a transesterification process using pumpkin seed oil. The oil content of the pumpkin seed varies from 42-54% and the composition of free fatty acids (FFA) is dependent on several factors (variety, area in which the plants are grown, climate, state of ripeness). The dominant FFA comprise palmitic acid (C18:0, 3.1-7%), oleic acid (C18:1, 21.0-46.9%) and linoleic acid (C18.2, 35.6- 60.8%) [1, 13-18]. Other contaminants produced into the environment by petroleum fuels are heavy metals which are toxic and pose a high health risk. Heavy metals constitute an important group of persistent toxic-pollutants occurring in ambient air and other media. One of the suspected sources of these metals in the atmosphere is the combustion of transport fuels in road vehicles. However, estimates of the emissions of these metals from road vehicles as reported in national emission inventories show very high variability in emission factors used [1].

2. LITERATURE REVIEW

2.1 Petroleum Diesel

Diesel is a combustible fuel which is a mixture of distillate fractions from crude oil and additives to improve its combustion character. Its evaluation indicates that it contains hydrocarbons with sixteen (16) to twenty-one carbons in the chains [19-21]. According to the ASTM D 975-21, diesel fuel is categorized into seven different types. The classification is based on the S xxx configurations. These are Grade No. 1-D S15; Grade No. 1-D S500; Grade No. 1-D S5000; Grade No. 2-D S15; Grade No. 2-D S500; Grade No. 2-D S5000; and Grade No. 4-D. Where the S is the sulphur rating instead of arbitrarily assigning words such as lower sulphur or medium sulphur [22]. The sulphur recommended in each of the grades is as shown below.

Table 1. The values of S xxx about the sulphur recommended by ASTM D 975-21 [23]

S/N	Description	Sulphur	Comment
1	Grade 1-D S15	15 ppm	The light middle distillate, high volatility
2	Grade 1-D S 500	500 ppm	
3	Grade 1-D S 5000	5000 ppm	
4	Grade 2-D S15	15 ppm	The middle distillate has lower volatility
5	Grade 2-D S500	500 ppm	than grades 1-D.
6	Grade 2-D S5000	5000 ppm	
7	Grade 4-D		The heavy distillate, low volatility

As already been alluded to, diesel is a wasting asset, demand has been increasing hence meeting the demand of the Globe by producing countries has been a great challenge. As such world fuel prices have been sky locating.

2.2 Biodiesel

Biodiesel is a biofuel, produced from oily plants and algae according to Britannia encyclopedia, meanwhile, the American Society for Testing and Measurement (ASTM) defines biodiesel as a fuel that comprises a mono-alkyl ester derived from vegetable oils or animal fats [19, 22]. The mono-alkyl derivatives may be of varying lengths from the fatty acids they are obtained from. The general reaction may involve alkaline, acidic, enzymatic, microwave-assisted, thermal and sonication esterification [23-28]. The general reaction scheme for transesterification can be understood as below.

The reaction mechanisms may proceed differently for each scheme with specific conditions, but overall trans-esterified fatty acid derivatives are obtained and Glycerol. Different vegetable and non-vegetable oils have been used to make diesel by several researchers [29-39].

The pumpkin seeds oil consists of several vegetable oils depending on the quality of plant management and the environmental conditions they are produced into. This also can be seen in the nutritional value of the final pumpkin fruits [1, 40,41]. The Table 2, shows some oils that can be extracted from pumpkin seed oil.

Several groups have vastly looked at the suitability of using biodiesels in motorized engines, compared the cetane value for biodiesel, emission of carbon dioxide and oxides of nitrogen and compared it to petroleum diesel, alternative feedstocks in the biodiesel production, evaluation of food supply concerning supply for biodiesel production and blending of the biodiesel for possible use in everyday machines [1-5, 7, 9, 13, 36]. It has been established that biodiesel has low emission of greenhouse gases especially since the feedstock is biomass, so no overall carbon is introduced to the globe, blends of various biodiesels produce comparatively similar performance output as petroleum diesel, different seeds with oil including non-edible ones are alternatives otherwise completion with food the biodiesel might influence food prices globally. The cetane values scores of biodiesel have been relatively high in the range of 56 to 78 [1, 2].

From that background, it seems vital that biodiesel is synthesized from pumpkin seed oil even if it is vegetable based oil, yet looking at Zambia's main food feedstock it may not impact adversely. And the best way to evaluate it is to compare the acceptable standards for the country, though the ZS 718: 2020 apply to neighbour countries too [12].

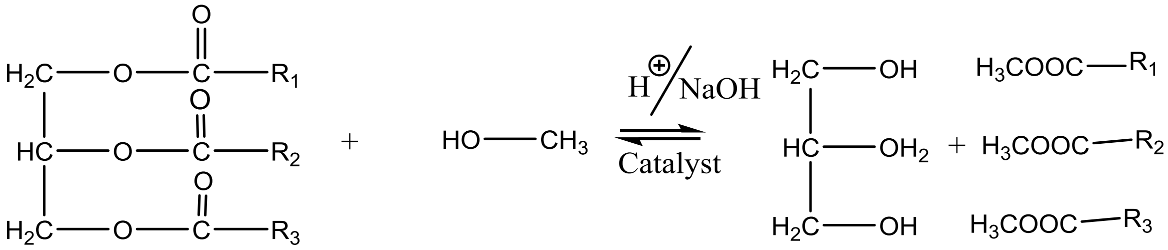

Fig. 1. Show the general acidic or basic or catalytic condition transesterification reaction

Table 2. Showing the fatty acids that are found in pumpkin seed oil [1, 41]

S/N	Composition seed oil	Fatty acid %
1	Palmitic (16:0)	12.51
2	Stearic (18:0)	5.43
3	Oleic (18:1)	37.07
4	Linoleic (18:2)	43.72
5	Linolenic (18:3)	0.18
6	Lignoceric (24:0)	0.06
7	Others	1.03

3. METHODOLOGY

The methodology involved experimental work which involved the extraction of the pumpkin seed oil. It was followed by the transesterification of the oil. Then characterization of both the oil extract and biodiesel using spectroscopic evaluation for the presence of ester bonds, carbonyl groups and other peaks that signifies the formation of the biodiesel. Lastly chemical and physical properties characterization of biodiesel produced.

3.1 Extraction of the Oil from Pumpkin Seeds

Dried pumpkin seeds were blended and sieved for the extraction process. Using a Soxhlet extractor, 74g of grounded pumpkin seeds were used using n-hexane as a solvent. 250mls hexane was used for every 74g of the ground pumpkin seeds which produced 32.57mls of raw pumpkin seed oil. This extraction was repeated 7 times each producing a volume of oil ranging from 30mls to 35mls, which then produced a total volume of 228mls of raw pumpkin seed oil. Once the raw pumpkin seed oil was collected, the transesterification process then began. 120mls of the extracted pumpkin seed oil was poured into a 200mls beaker which was then placed on a hot plate and warmed up to 80 degrees Celsius. Then 28mls of methanol were added into a 50mls flask and placed on a stir plate at a minimum speed and 1g of sodium hydroxide pellets were slowly and carefully added. This was allowed to stir until the sodium hydroxide pellets were observed to have dissolved, which then formed sodium methoxide, a very strong and dangerous base and so precautious were followed. Then sodium methoxide was then slowly added to the warm pumpkin seed oil (off the hot plate). The reaction mixture was then stirred for 2 hours and transferred to a 250mls separating funnel, the solution was allowed to settle for 1 hour using a clamp and stand until the glycerol layer formed at the bottom. Once the glycerol had stopped forming it was drained into a measuring cylinder and its volume was recorded. The biodiesel formed was drained and its volume produced was recorded [1, 14].

The Fig. 2 shows the pumpkin seeds being processed at various stages.

The figure manipulation was followed by the chemical extraction of the oil from seeds using the Soxhlet extraction method. Hexane was used as the non-polar solvent. The Fig. 3 shows the various stages of extraction of the seed oil and other chemical modification of the oil.

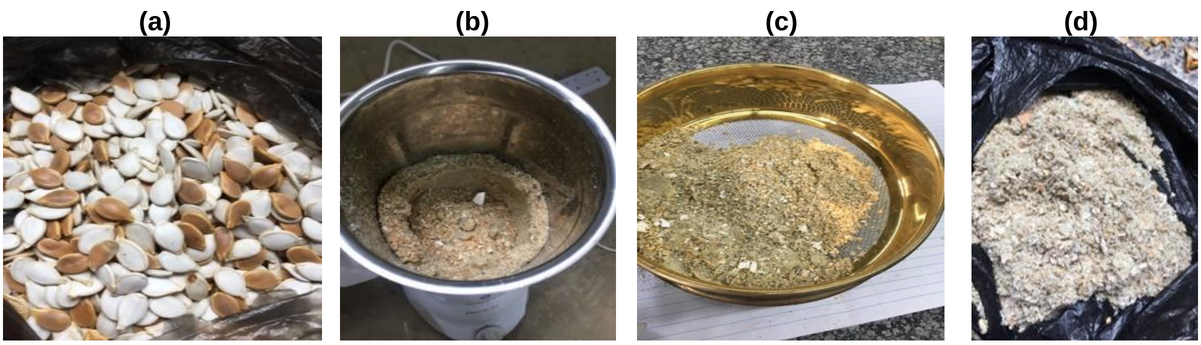

Fig. 2. Pumpkin seeds being processed (a) washed to remove b-carotene, (b) blend grinding of seeds (c) retrieving the grounded seeds and (d) powdered feedstock for oil extraction

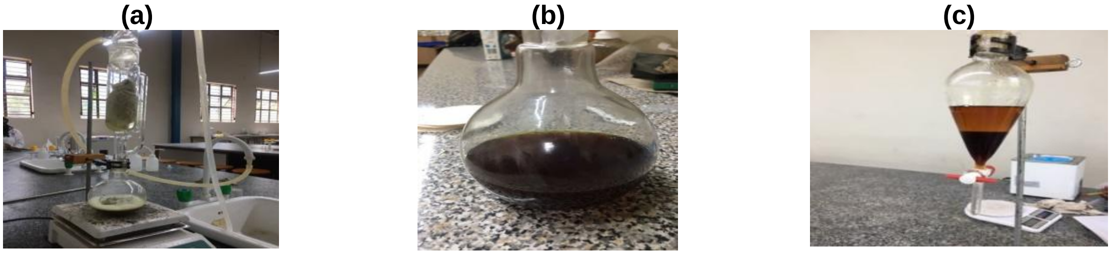

Fig. 3. Shows various stages of biotransformation (a) Soxhlet extraction of oil from pumpkin (b) Crude trans-esterified mix of pumpkin seed oil and (c) Separated crude trans-esterified seed oil

3.2 Chemical Characterization of Pumpkin Seed Oil and Trans-esterified Oil

In this section, the spectroscopic evaluation of chemical modification to the oil was evaluated using the FT IR spectrometer TJ 270-30A Dual Beam from Chine, It was set to scanning range from 4000cm^{-1} to 450cm^{-1}, with the scan rate of 4 cycles per minute in transmittance mode. The biodiesel characterization was done using parameters such as distillation profile (B.P), density, viscosity, water content, free water, sulphur content, contaminations, cleanliness, and colour done on the commercial machine used for petroleum diesel and other petroleum products.

4. RESULTS

4.1 FT-IR Spectral Analysis of Raw Pumpkin Seed Oil

The pumpkin seed oils' FT-IR spectra were evaluated, and as already mentioned that the oil has a mixture of products, indeed the spectra show several peaks suggest the same [1]. Nevertheless, it was observed that the following absorption peaks were present as depicted in Fig. 4.

Absorption bands in the region of 3000 and 2800cm^{-1}, which in this case are the peaks at 2034cm^{-1}, 2124cm^{-1}, 2278cm^{-1}, and 2986cm^{-1}, indicate the correspondence to C-H stretching vibrations. These bands arise from the aliphatic chains present in fatty acids and triglycerides, which are the major components of pumpkin seed oil. The intensity and pattern of these C-H stretching vibrations provide information about the degree of unsaturation and the length of the carbon chains in the oil.

O-H bonds are observed at the peaks formed at 3236cm^{-1}, 3414cm^{-1}, and 3568cm^{-1}, these indicate the presence of hydroxyl (O-H) groups. These bands can arise from compounds such as free fatty acids or minor components with hydroxyl groups. A peak at 1654cm^{-1} is observed, this peak is related to C=C double bonds (alkenes). The peaks are also consistent with those of Morrison and Boyd 2002 [4].

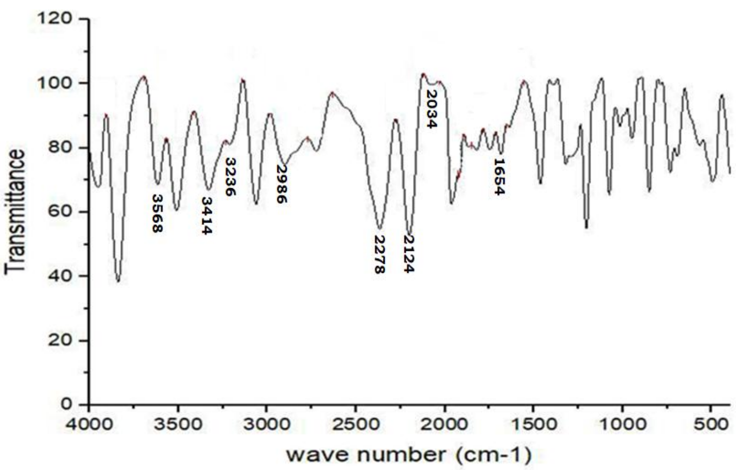

Fig. 4. Shows the FT-IR spectra of the pumpkin seed oil extract

4.2 Biodiesel of pumpkin Seed Oil Evaluation

The FT-IR spectra for the trans-esterified pumpkin seed oil were obtained, this was done to check for the transesterification process so that it could be seen that indeed the biodiesel was formed. Fig. 5 shows the spectra for trans-esterified pumpkin seed oil.

The presence of the peak at 2648cm^{-1} in the spectrum suggests the presence of a stretching vibration of an aliphatic carbon-hydrogen (C-H) bond. The peak corresponds to the C-H stretching vibrations in the methylene (CH_2) groups present in the fatty acid chains of the oil. A peak at 2284 cm^{-1} could suggest a presence of an ester bond in the biodiesel that was produced. A peak appearing at 1730 cm^{-1} could also suggest the presence of a C=O bond which is a carbonyl group which is likely to be found in the biodiesel as well. 1787cm^{-1}, 1716cm^{-1}, for the C=O, the alpha carbon for both saturated and unsaturated, and the 1300-1000cm^{-1} for the C-O bond. The peaks are consistent with the data in organic chemistry standard charts [40].

4.3 Pumpkin Seeds oil Biodiesel Characterization

4.3.1 Chemical and physical properties characterization

In this section, a sample of trans-esterified pumpkin seed oil was subjected to the evaluation of the same tests the other petroleum diesel samples are analyzed. Then various parameters were checked.

4.3.2 The distillation profile

The diesel distillation helps to determine the boiling point range and the various fractions obtained after the evaluation. It was noted that the various fractions boiled from 182^{O}C to 345^{O}C. Table 3 shows the recovery at different temperatures.

Fig. 6 is the distillation profile and the percentage of recovered, residue and lost materials.

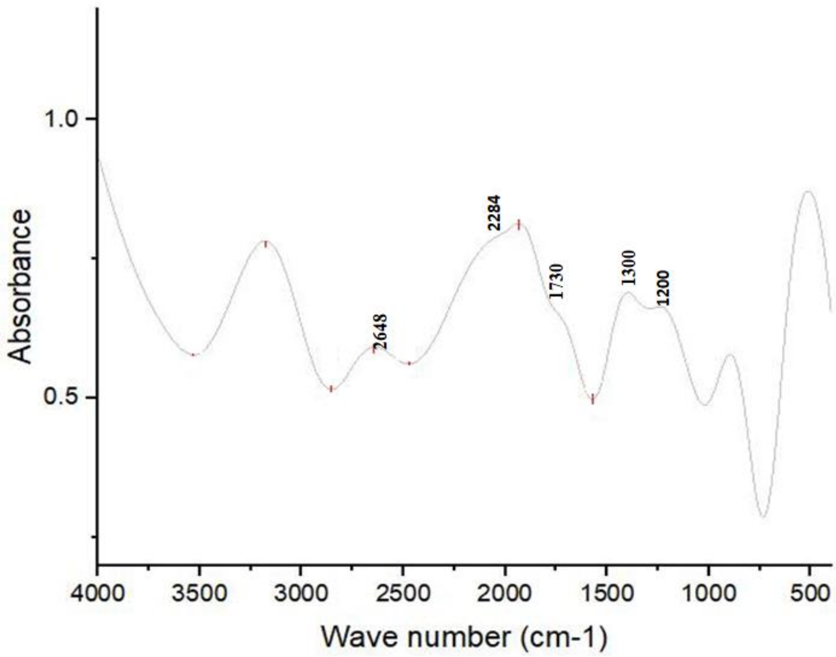

Fig. 5. Shows the trans-esterified pumpkin seed oil

Table 3. The temperature and recovery percentage from the distillation process

Recovery %	IBP	10	20	30	40	50	60	70	80	90	FBP
Temp ^{O}C	182	210	230	249	264	279	293	308	324	345	370

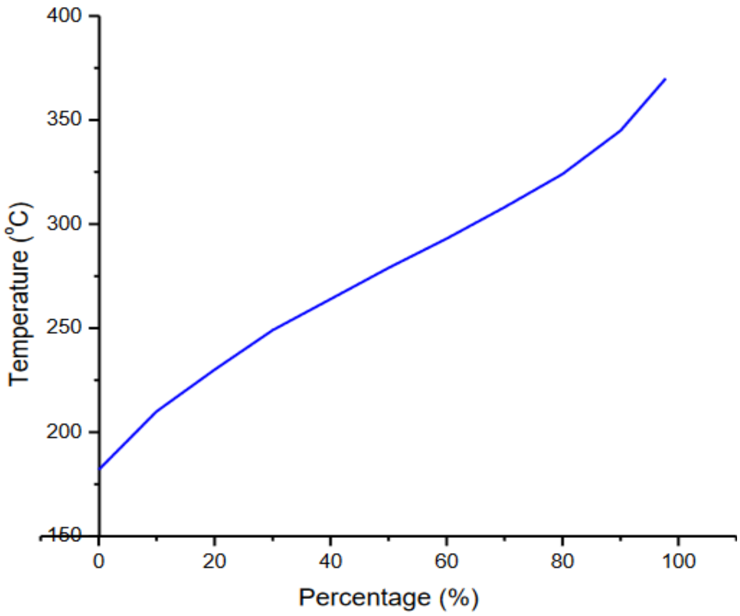

Fig. 6. Shows the distillation profile for the pumpkin seed oil biodiesel

The distillation profile too indicates that the constituents of the pumpkin biodiesel are a mixture of various trans-esterified fatty acid molecules as they can be seen from the distillation profile where the initial boiling point is set at 182°C to 345°C. This is comparable to the reported literature value of 163 to 357 °C [39,42,43]. The recovery data indicates 97.8%, 1.8% residue carbon and a loss of 0.4%.

From the results tabulated below, it was found that three parameters; total contamination, viscosity, and also flash point were within the limits set by wear check Zambia to issue a certificate to the fuels that are used by different engines within Zambia and outside. The flash point was found to be above 70℃ which is in line with the required flash point for biodiesel. The viscosity was found to be 4.692 cSt which is also in line with the required standards. In comparison with the ASTM standard for diesel fuel which ranges from 0.9 –4.1 (ASTM D2 / 2 /5) standard test valve) the results are acceptable.

The moisture content, sulfur, and density are out of the acceptable limits set by ZS 718:2020 Specifications. Contamination of sulphur in the biodiesel could have happened during the distillation profile test as sodium sulphate was used to remove moisture. Other parameters could have been affected by the purification of the biodiesel that was produced.

Table 4. Chemical and physical characterization of biodiesel from pumpkin seed oil vs specification

Biodiesel			**Specifications** ZS 718:2020 @WEAR CHECK ZM	
Parameter Description	**quantity**		**Parameter Description**	**quantity**
Density (kg/L) @ ambient	0.8889	vs	Density (kg/L) @ ambient	0.820 - 0.880
Flashpoint (℃)	>70℃	Vs	Flashpoint (℃)	60, minimum
Viscosity @ 40℃ (cSt)	4.692	vs	Viscosity @ 40℃ (cSt)	2.00 – 5.50
Water content (%)	1.5	Vs	Water content (%)	0.05, max
Total contamination (mg/kg)	15.3	Vs	Total contamination (mg/kg)	24.0, max
Sulphur content (ppm)	76	Vs	Sulphur content (ppm)	50, max
90% recovery temperature	345	Vs	90% recovery temperature	360, max
% Residuals	1.6	Vs	% Residuals	Nill
Colour of biodiesel	Golden straw yellow			

5. CONCLUSION

This study showed that biodiesel from pumpkin seed oil can be blended and viscosity adjusted for possible use as an alternative fuel. It was found that a flash point above $70^{O}C$, viscosity of 4.692, Boiling point range of 182 to 345 ^{O}C and residue carbon of 1.8% were standards by both ZS 718:2020 and also ASTM standard for diesel fuels. The density was found to be $0.8889g/cm^3$. All the parameters compared are with range of the guideline of ZABS, Even density that seems slightly higher than tabulated still with blending the parameter can just come within the set boundaries. The parameters in some parameters rate fairly well compared even to ASTM stipulated quantities. It can be noted therefore that indeed pumpkin based biodiesel when blended can work as diesel for the nation Zambia.

ACKNOWLEDGEMENTS

We wish to acknowledge Mr Nyirenda P, for the non-spectra analysis, M.U tech staff for the cooperation in lab work. Mr Nondo J for the FT-IR characterization, M. U management for support and continued encouragement on the research.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/100759