Vol. 16(3), pp. 110-114, July-September, 2021
DOI: 10.5897/IJPS2021.4948
Article Number: EA40B1767758
ISSN 1992-1950
Copyright©2021
Author(s) retain the copyright of this article
http://www.academicjournals.org/IJPS

ACADEMIC JOURNALS
expand your knowledge

International Journal of Physical Sciences

Full Length Research Paper

Physical-chemical characterization of kanyu almond oil (*Sclerocarya birrea*) for use as biofuel

Alberto Julião Macamo*, Jardel Lourenço Macuácua and Lina Rafael Langa Macamo

Physics Department, Faculty of Sciences, Eduardo Mondlane University, Maputo, Mozambique.

Received 15 April, 2021; Accepted 26 May, 2021

Plant oil extracted from Kanyu almonds offers the potential to be an alternative to fossil fuel resources. This study aims to characterize the physico-chemical properties of kanyu almond oil, as safe indicators of the use of this biofuel for energy generators. Samples of the oils examined were density, kinematic viscosity, acid value, and oxidation stability. The experimental results showed that the oils had different sensitivities from the properties and indicate a clear deterioration of the kinematic viscosity and oxidation stability. These results were not in a condition to be used directly, such as fuels in diesel engines. Also, oil cannot be used immediately for feeding because it contains a high acid value. However, with the refining process, its kinematic viscosity and acid value can be improved, and can thus be used as biofuel and for other purposes.

Key words: Kinematic viscosity, Induction time, Acid value, and Kanyu (Marula).

INTRODUCTION

The Nkanyi is a plant of Savana origin, belongs to the Anacardiaceae family of Scientific name *Sclerocarya birrea*, in Mozambique known as Nkanyi, with green and pale yellow fruit when ripe, known as kanyu, similar to a plum, measuring between 3 to 4 cm in diameter and with a fleshy mucilaginous pulp (Mariod and Abdelwahad, 2012).

Kanyu (marula) has a hard brown seed known as nfula in southern Mozambique, which in turn contains an almond rich in oil and proteins, as shown in Figure 1.

Kanyu almond oil has a light, pale, yellow-brown color and a pleasant nutty aroma (Francis and Tahir, 2016). Biodiesel has attracted great attention due to its advantages, such as its renewability, non-toxicity, low emission of pollutants, and biodegradability (Liu et al., 2013). Kanyu oil is a potential raw material for the production of biodiesel due to its physical and chemical characteristics.

According to Bila and Vaz (2017) and Leewen et al. (2015), Mozambique has ideal climatic conditions for the production of kanyu, with sufficient capacity to open a kanyu almond oil processing company, as an example, the Chigubo district with a production capacity of about 13 345 kg of almond/year.

Kanyu is one of the fruits of Africa's drylands. It is rich in vitamin C, about five times more than citrus fruit. Oils

*Corresponding author. E-mail: arizona29.au@gmail.com.

Author(s) agree that this article remain permanently open access under the terms of the Creative Commons Attribution License 4.0 International License

Figure 1. (a) Kanyu, (b) kanyu seed (nfula) and (c) kanyu almond.

and fats are the largest sources of concentrated energy for human use. These can provide up to about 9 kCal/g of oil (Hundessa, 2014).

Kanyu is used for various purposes in rural areas where it is found. It is highly rich in vitamin C, can be consumed fresh, and can also be used to produce juice or alcohol when fermented. It has an almond rich in protein (28 - 31%), oil (56 - 61%), magnesium, phosphorus, and potassium (Muok et al., 2011).

Gandure and Ketlogetswe (2011) carried out an experimental study for the production of biofuels from kanyu almond oil and concluded that it is possible to produce it because it possess properties that allow it to function as fuel in variable compression diesel engines.

The physicochemical properties of vegetable oils produced by seeds vary according to regions and climatic conditions. There are no records of publications of scientific articles, studies on the extraction and physicochemical characterization of kanyu almond oil produced in Mozambique.

Kanyu oil can be classified as having high oleic acids (70 - 78%) with relatively low tocopherol content. It contains 67.2% oleic acids, 5.9% linoleic acids, and 14.1% palmitic acids (Mariod and Abdelwahab, 2012).

The final quality of vegetable oil depends on the steps involved in its production process. When oil seeds are stored in poor condition, problems can occur, such as heating the seeds, reaching carbonization, increased acidity, and darkening of the oil making the refining process arduous (Carvalho, 2017).

There are several parameters evaluated in the physical-chemical characterization of vegetable oils for different purposes, such as density, kinematic viscosity, acidity index, calorific value, saponification index, etc. However, among these, density, kinematic viscosity, acidity index, and induction time stand out in the literature.

The density of vegetable oils indicates the ratio of the mass of the sample to that of the water per unit volume of the same at a given temperature which applies to all oils and liquid fats. According to Machado (2014), the specific mass increases with the length of the alkyl ester carbon chain, being considered a property related to the quality of the fuel since it increases with the increase of the storage time.

According to Machado (2014), viscosity is a measure of the resistance to flow presented by a liquid due to the flow or displacement of the fluid over another portion of this same material. The lower the viscosity, the better the atomization of the engines when using oil as fuel.

According to Rei (2007), Bressan (2018), and Souza (2016), viscosity is an extremely important parameter in the evaluation of oils for uses as fuel, as well as cosmetics, since as fuel, its high value can damage the engine's injection pump, increasing the maximum fuel inlet pressure, thus causing a decrease in the fuel flow, incorrect spraying on the injectors and the cylinder.

According to Nadaletti et al. (2014), vegetable oils and fats are subject to lipid oxidation when stored for long periods and by exposure to heat and air; thus causing the deterioration of vegetable oil or fat. Oils and fats can be oxidized in different ways, namely: auto-oxidation, photo-oxidation, enzymatic oxidation, and hydrolytic reactions.

The induction period is characterized using the Rancimat method, approved by the entities responsible for normalizing the use and consumption of vegetable oils and fats. This parameter is related to the quality of the oil and its state of conservation. Therefore, the measurement of the induction period is very important to characterize the state of conservation and quality of the oil, to preserve food safety and biodiesel quality.

This study aims to characterize the physic-chemical properties of kanyu almond oil, as safe indicators of the use of this biofuel for energy generation. For this purpose, the following specific activities have been proposed: Collecting and storing of kanyu almonds; extraction of kanyu almond oil using a hydraulic press, and determining the physicochemical properties of the oil (volumetric density, kinematic viscosity, acid value, and induction time).

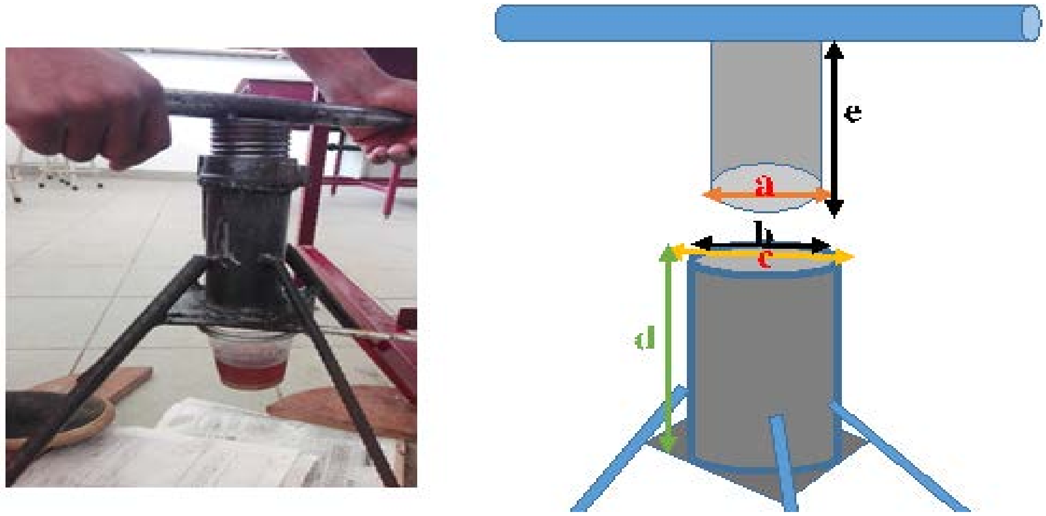

Figure 2. Prototype hydraulic press (a-closing diameter 5.7cm, b –internal diameter 6.1 cm, c-external diameter 6.8 cm, d-depth 17.37 cm, and e-closing height 19.0 cm).

MATERIALS AND METHODS

For this study, the laboratory of the Chemistry Department of the Faculty of Sciences was used for oil extraction and determination of the acid value, and the laboratory of the Chemistry Department of Engineering of the Faculty of Engineering was used for the determination of the kinematic viscosity, density, and induction time.

The almonds were processed in 52 kg of kanyu seeds using pliers, stones, needles, and hammers and placed in closed containers for conservation.

The oils are extracted using the hydraulic press in Figure 2, which operates under a rotating motion similar to an endless screw. As the piston descends, the pressure on the almonds increases, thus expelling the oil that is collected in an open container as a beaker.

The adapted hydraulic press is made of a precarious metallic material as the threads part of a plumb and pieces of iron is used for the press support.

After oil extraction, the density is determined by the pycnometer method, measuring the mass of the empty pycnometer and then the pycnometer with the oil recording the values as m_1 and m_2 respectively. Using Equation 1, the density value was calculated.

$$\rho = \frac{\mathrm{m_2 - m_1}}{\mathrm{V}} \tag{1}$$

The acid value was determined by the titration method initially with the preparation of potassium hydroxide solution (85% KOH).

A 250-ml glass is placed on the scale and its mass value is recorded; thereafter the scale was zeroed, and approximately 1.32 g of 85% KOH, with ethyl alcohol, is measured, with the aid of a stick dissolving 85% KOH with ethyl alcohol. Finally, the solution was transferred to a 200-ml volumetric flask and the volume was made up until meniscus and homogenizing mix was attained. The actual concentration of the solution is determined according to Equation 2.

$$\mathrm{C_{Real}} = \frac{\mathrm{m_0 \times 85\%}}{\mathrm{56.11 \times V}} \tag{2}$$

Where m_o is the mass of the solution (g), V is the volume of the solution, and C_{Real} is concentration (N). Once prepared, the solution is determined by the acid value.

The weight of the Erlenmeyer was measured on the scale and the value of its mass was recorded. Further, 10 ml of ethyl alcohol and 10 ml of propanol 2 was measured with the aid of 25 ml beakers in a 100-ml Erlenmeyer, with 2 drops of phenolphthalein added in the Erlenmeyer and the solution of ethyl alcohol and propanol 2 was titrated with the KOH 0.1 N solution until a pink color appears that persists for thirty seconds. Thereafter, the Erlenmeyer was placed on the scale, the value of the mass of solution titrated was recorded by designating the mass per m_o, and the scale was zeroed.

With the aid of a dropper pipette, we measure approximately 1.00 g of sample (oil) and record the value (m_1); titrate the sample with the KOH 0.1 N solution until it appears with a persistent pink color and registers the volume spent on the titration (V_1). The procedure is repeated at least four more times. If any of the values are not in agreement and are rejected, the experimental procedure was repeated until three concordant values are obtained. The acid value is determined according to Equation 3.

$$\mathrm{Ia} = \frac{\mathrm{V_m \times C_{Real} \times 56.11}}{\mathrm{m_m}} \tag{3}$$

Where I_a- acid value, m_m- oil mass, V_m- médium volume of the solution.

Kinematic viscosity was determined using the Redwood viscometer. Initially, the viscometer hole is closed through the ball valve. The 100 ml volumetric flask was placed under the hole opening; the cylindrical cup was filled with oil to the desired level; the viscometer bath was filled with water; the thermometers were inserted in their respective places to measure the temperatures of the oil and water bath; the bath was heated, the water stirred and a uniform temperature was maintained. As soon as the water and oil temperature stabilizes at 40ºC, the spherical valve was lifted, the oil was collected in the 50-ml volumetric flack, and the time required in seconds was recorded to collect 50 ml of oil. A stopwatch was used to measure the spent and the procedure was repeated by recording the values. After this, the kinematic viscosity was calculated using Equation 4.

$$\mathrm{v} = \mathrm{A} \cdot \mathrm{t} - \frac{\mathrm{B}}{\mathrm{t}} \tag{4}$$

Table 1. Results of the physic-chemical characteristics of kanyu oil.

Parameter	Unit	Experimental data	Other authors	
Density	a 25°C [kg/m³]	$899.85 \pm 2.1\times10^{-3}$	877 ± 15.74	Enweremadu and Rutto (2016)
			973	Gandure and Ketlogetswe (2013)
			900	Vermaak et al. (2011)
kinematic Viscosity	a 40°C [mm²/s]	53.85 ± 0.26	38.2	Hundessa (2014)
			41	Robinson et al. (2012)
				Ejilah et al. (2017)
Acid value	[mgKOH/g]	9.18 ± 0.18	8.41	Ahmed et al. (2015)
			3.60	Hundessa (2014)
			4.20	Francis and Tahir (2016)
Induction time	a 110°C, 10 l/h, [h]	11.93 ±0.13	8.41	Enweremadu and Rutto (2016)
			27.10	Kivevele and Huan (2015)
			37	Kleiman et al. (2008)

Where *A* and *B* are constants of the viscometer respectively; A=0.247 and B=65, t (s).

The induction time or oxidative stability has used the method of Rancimat 743 Metrohm: placing the vessel inside the analytical balance and zeroing the scale; measuring 7 g of oil and recording its value; repeating the procedure for at least three vessels; connecting the vessels and measurement using the right tubes; placing the vessels in such a way that they are all connected in the heating block by adjusting the temperature to 110ºC; commencing the gas flow to check in advance that everything is correctly connected to the final check and initiating realization on the graph under the construction that appears on the computer monitor. The procedure was then repeated at least twice.

RESULTS AND DISCUSSION

52 kg of kanyu seeds resulted in 7.62 kg of almonds, producing 300 ml of oil. The results of the characterization of the physico-chemical properties of the oil are presented in Table 1.

The oil density obtained is 899.85 ± 2.1 x 10^{-3}kg/m^3, which is within the range recommended by the institutions (ANVISA, 2008; Silva et al., 2019), ASTM and EN of oil legislation for the production of cosmetics of 950 -1050 kg/m^3, for human consumption and biodiesel production of 860 - 900 kg/m^3. The density value obtained was closer to that observed by Vermaak et al. (2011) at 900 kg/m^3.

The density of vegetable oil increases with the length of the alkyl-ester carbon chain, being considered a property related to the quality of the fuel since it occurs with storage time (Machado, 2014).

Kinematic viscosity obtained from 53.85±0.26 mm^2/s at a temperature of 40ºC, is much above the recommended value for consumption 20 to 40 mm^2/s according to the standard ANVISA, 3.5 to 5,0 mm^2/s for EN 14214 and 1.9 to 6.0 mm^2/s for ASTM D6751.

Viscosity indicates the evidence of oil degradation (Farah, 2002). In addition, viscosity is related to the molecular weight of fatty acids and the composition of carbon chains present in the oil (Hundessa, 2014).

The viscosity of 53.85 ±0.26 mm^2/s is above the result observed by Hundessa (2014), Robinson et al. (2012) and Ejilah et al. (2017) at 38.2 and 41 mm^2/s, respectively.

The acid value obtained is 9.18 ± 0.18 mgKOH/g of oil, which proved to be very high for human consumption, as well as for direct use as biodiesel. The high acid value confirms the presence of a high number of free fatty acids (20.7%) in the oil, and its susceptibility to oxidation (Robinson et al., 2012).

The acid value of 9.18 ± 0.18 mgKOH/g is above that observed (8.41 mgKOH/g) (Ahmed et al., 2015). This value is very high due to contact with hydraulic press metals.

According to ANVISA, the maximum acid value for unrefined cold-pressed oil is 4.0 mgKOH/g, but it should be noted that the extraction of this oil was not cold and hence did not meet the parameters for this type of extraction, let alone for kanyu oil specifically.

The oil induction time is 11.93 ± 0.13 h, which proved to be within the range allowed for human consumption, as well as for use as biodiesel. This value is above the limits established by the standard EN 14214 of 6 h and for ASTM D6751 of 3 h, along with the production of biodiesel oil (Moser, 2011).

This time of 11.93 ± 0.13 is higher than that observed (8.41 h) (Enweremadu and Rutto, 2016) by solvent extraction, and much lower than that observed by Kivevele and Huan (2015) at 27.10 h and 37 h for kanyu oil (Kleiman et al., 2008).

Kanyu (marula) oil have greater oxidative stability due to its rich composition of mono-unsaturated fatty acids (Vermaak et al., 2011).

The stability behavior of kanyu oil is attributed to the presence of a smaller number of unsaturated bonds that are prone to oxidation by air oxygen (Enweremadu and Rutto, 2016).

Therefore, the impressive stability value of kanyu oil is attributed to the presence of the high level of saturated and mono-unsaturated fatty acids, along with the low level of polyunsaturated linolenic and linoleic acid.

Conclusion

The parameters studied were in agreement with the existing literature on the physico-chemical characteristics for kanyu oil. The acid value and kinematic viscosity found were high, which is justified by the material used in oil extraction.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

REFERENCES

Ahmed AI, Babeker A M, Elamin AMA, Ibrahim EA (2015). Physicochemical Evaluation of Seeds and Oil of Nontraditional Oil Seeds. Turkish Journal of Agriculture - Food Science and Technology 3(8):687-691

ANVISA (2008). National Health Surveillance Agency of Brazil. Quality Control Guide for Cosmetic Products. Ministry of Health. Second, ed. Brasília. ANVISA, resolution nº36, 3 June.

Bila J M, Vaz I C (2017). Potencialidades de *Sclerocarya birrea* em *Chigubo província* de Gaza, Moçambique. Pesquisa Florestal Brasileira 37(90);213-217.

Bressan RT (2018). Physical-Chemical Analysis and Optimization of Crambe Pressing in Mechanical Extruder under Variations of Temperature and Relative Humidity of Grains. Master's Thesis, State University of Western Paraná, Energy Engineering at Agriculture.

Carvalho AC. (2017). Physico-chemical characteristics of Edible Vegetable Oils. Monograph, State University of Norte Fluminense, Department of Chemistry, Rio de Janeiro, Brazil.

Ejilah R, Kamal D, Gambo BA (2017). Influence of Marula Oil Methyl Ester – Diesel Fuel Mixtures on the Performance of a Variable Load Compression Ignition Engine. European Journal of Advances in Engineering and Technology 4(6):457-465.

Enweremadu CC, Rutto HL (2016). Performance Characteristics of Green Diesel from Marula (*Sclerocarya birrea*) Oil in Diesel Engine. Journal of Biobased Materials and Bioenergy 10(3):159-167.

Farah AF (2002). Characterization of vegetable oils as an alternative to the cooling medium used in the thermal tempering treatment. Ph.D. thesis, University of São Paulo, Materials Science and Engineering, São Carlos - São Paulo.

Francis K A, Tahir A R (2016). Evaluation of the Physicochemical Properties of Northern Ghana *Sclerocarya Birrea* Seed Oil and Proximate Analysis of the Process Waste. African Journal of Food Science 10(4):48-53.

Gandure J, Ketlogetswe C (2011). Marula Oil and Petrodiesel: A Comparative Performance Analysis on a Variable Compression Ignition Engine. Energy and Power Engineering 3(3):339-342.

Gandure J, Ketlogetswe C (2013). *Sclerocarya birrea* Biodiesel as an Alternative Fuel for Compression Ignition Engines. Advances in Internal Combustion Engines and Fuel Technologies 185

Hundessa G (2014). Extraction, Optimization and Characterization of Ethiopian Marula (*Sclerocarya birrea*) and Zigba (Podocarpus Falcatus) Oils; master´s degree, Addis Ababa University, Chemical Engineering (Food Engineering), Addis Ababa.

Kivevele T, Huan Z (2015). Review of the Stability of Biodiesel Produced from Less Common Vegetable Oils of African Origin. South African Journal of Science 111(9/10):25-31.

Kleiman R, Ashley DA, Brown JH (2008). Comparison of two seed oils used in cosmetics, moringa and marula. Industrial Crops and Products 28(3):361-364.

Leewen J V, Gomes F, Alves T, Sousa, CD (2015). Marula plant of Mozambique: The importance of local knowledge in the development of native species. I National workshop of native fruit trees. Maputo: Institute for Agricultural Research of Mozambique.

Liu XJ, Zhang HY, Ai N, Lu MZ, Li YM, Yu FW, Ji JB (2013). Deacidification of Jatropha Curcas Oil by Extraction for Biodiesel Production. In Applied Mechanics and Materials. Trans Tech Publications Ltd.. 291:207-211

Machado YDL (2014). Evaluation of oxidative stability and determination of oxidation kinetics of vegetable oils, oleic acid, and biodiesel using the PetroOXY method (ASTM D7545). Ph.D. Thesis, Federal University of Rio Grande do Norte, Chemical Engineering, and Journal American Oil Chemistry Society 91:1139-1145.

Mariod AA, Abdelwahab SI (2012). *Sclerocarya birrea* (Marula), An African Tree of Nutritional and Medicinal Uses A Review. Food Reviews International 28(4):375-388.

Moser BR. (2011). Biodiesel production, properties, and feedstocks. Biofuels pp. 285-347.

Muok BO, Khumalo SG, Tadesse W, Alem S (2011). *Sclerocarya Birrea*; Marula. Conservation and Sustainable Use of Genetic Resources of Priority Food Tree Species in Sub-Saharan Africa.

Nadaletti WC, Bariccatti RA, Alves HJ, Melegari SN. (2014). Factorial planning and surface response methodology in oxidative stability evaluation of biodiesel blends from soybean, crambe, babassu and swine fat. Journal of Food, Agriculture and Environment 12(2):1030-1032.

Rei PA (2007). Laboratory procedures for the quality control of Biodiesel. Master's Dissertation, Technical University of Lisbon, Department of Chemical Engineering, Lisbon.

Robinson E, Lukman A, Beiio A (2012). Review of *Sclerocarya birrea* Seed Oil Extracted as a Bioenergy Resource for Compression Ignition Engines. International Journal of Agricultural and Biological Engineering 5(3):59-67.

Silva FVF, Santos M C, Neiva LDB, Oliveira MAC, Leal BS, Moreira FAS, Santos PN, Cavalcante GL, Sousa J P S, Neto MPL (2019). Development and quality control of an anti-acne gel-cream based on the oil of cup *officinalis* L. (Copaíba). Electronic Magazine Health Collection (30):1-10.

Souza AP (2016). Study of the Reduction of the Acidity Index of Residual Vegetable Oils Aiming at Biodiesel Production. Master's Thesis, Universidade Federal Alagoas, Agrarian Sciences, Rio Largo - Al.

Vermaaka I, Kamatoua GPP, Komane-Mofokenga B, Viljoen AM, Beckett K (2011). African Seed Oils of Commercial Importance — Cosmetic Applications. South African Journal of Botany 77(4):920-933.