Proceedings of the Sustainable Research and Innovation Conference
JKUAT Main Campus, Kenya
6 - 7 October, 2021

Characterization of nanostructured rapeseed oil as an automotive biodiesel

Christopher M. Ong'era[1], Benson B. Gathitu[1], Sylvia I. Murunga[1], Patrick W. Kuloba[2], Jeremiah W. Gathirwa[3]

Abstract**—** Nanoemulsions produced by the use of co-solvents show unexpected thermodynamic stability without the use of conventional surfactants. We study the system rapeseed oil – ethanol – 1-heptanol to be able to understand the effects of these nanoemulsions on biofuel properties. Ternary fuel blends prepared at a constant weight percentage of 20% 1-heptanol while varying the mass of ethanol and rapeseed oil and also at a constant weight percentage of 30% rapeseed oil while varying the mass of ethanol and 1-Heptanol were investigated for particle size, zeta potential and kinematic viscosity. The Particle sizes of the blends were determined by dynamic light scattering at $25^{O}C$. Complete nanoemulsions with droplet sizes of 92.29 nm and 47.76 nm were observed in the 2:3:3 and 2:4:4 (1-heptanol: ethanol: rapeseed oil) blends respectively. The kinematic viscosity of all blends prepared at 30% wt of rapeseed oil was between 2.67 – 5.6 mm^2/s which met the ASTM D6751 biofuel standards. The improved kinematic viscosity of the blends could be attributed to the co-solvent behaviour of 1-heptanol on rapeseed oil and ethanol.

Keywords**—** Biofuel, Co-solvent, Kinematic viscosity, Surfactant, Nanoemulsion.

I. INTRODUCTION

THE rising energy demand coupled with the need to reduce emissions has necessitated the need to develop renewable energy sources such as biofuels. Renewable energy sources are self-replenishing and therefore do not face the risk of depletion like fossil fuels. But the development of these renewable energy sources such as biofuels has run into various challenges which have hindered their full exploitation. The main constraints in the use of biofuel in unmodified compression ignition engines lie in its properties. Some of the critical physicochemical properties of biofuel include density, viscosity, calorific value, pour point, cloud point and flash point [1]. These properties determine the quality of the fuel and have been standardized and documented by the American Society for Testing and Material (ASTM) and European Committee for Standardization (CEN) as shown in Table 1.

The fatty acid composition of vegetable oils influences their chemical and physicochemical properties. The knowledge of the fatty acid composition is, therefore, important in looking for ways to improve the properties of these oils. The degree of saturation and the length of the fatty acid chain are very critical in determining the fuel properties. A high degree of saturation results in high density and oxidation instability while a longer carbon chain results in high viscosity [2]. The nature, number and position of the double bond in the oil molecule affect the kinematic viscosity of the oil. Depending on their position, an increase in the double bonds results in lower kinematic viscosity of the vegetable oil [3]. The cetane number of the fuel also increases as the length of the carbon chain increases [4].

Viscosity plays an important role during the injection of the fuel into the cylinder. The higher the viscosity, the poorer the atomisation leading to incomplete combustion of the fuel. Poorly atomised fuel will have bigger droplets which reduce their ability to combine with oxygen for complete combustion [5]. Smaller droplets have a large surface area to volume ratio thus providing more surface for the reaction with oxygen during the combustion process.

Blending, transesterification, pyrolysis and emulsification are the main methods by which biofuels are produced. Emulsification performs better in terms of energy efficiency and emission reduction compared to transesterification [6]. This has led to more research being carried out on emulsification to lower the kinematic viscosity and increase the volatility of vegetable oils. Nanoemulsification produces nano-sized emulsions by mixing vegetable oil, ethanol and a co-solvent. Surfactant free nanoemulsions have been proven to exist in ternary mixture provided the two solvents are immiscible and the third solvent which acts as a co-solvent is soluble in one of the solvents [7]. These emulsions lack the hydrophilic head provided by the surfactant which necessitates the need to have organic material in the mixture to provide the OH- group required to dissolve the hydrophobic dyes. The organic material in this case is the co-solvent which provide polar bonding thus causing solubility. Not many researchers have explored the principle behind the formation of these emulsions. Zemb *et. al* [8] attributed the stability of these emulsions to the balance in hydration forces and entropy. The balance in entropy and hydration forces minimises the free energy available resulting

C. M. Ong'era, Department of Agricultural and Biosystems Engineering, Jomo Kenyatta University of Agriculture and Technology (JKUAT) (phone: +254725476806; e-mail: chrismandela@gmail.com).
B. B. Gathitu, Department of Agricultural and Biosystems Engineering, JKUAT, (email: bbgathitu@jkuat.ac.ke).
S. I. Murunga, Department of Agricultural and Biosystems Engineering, JKUAT, (email: smurunga@jkuat.ac.ke).
P. W. Kuloba, Engineering Division, Kenya Industrial Research and Development Institute (KIRDI), (email: kulobap@ymail.com).
J. W. Gathirwa, Centre for Traditional Medicine and Drug Research, Kenya Medical Research Institute (KEMRI) (email: jgathirwa@gmail.com).

TABLE I

ASTM D6751 and EN14214 standards for biodiesel and ASTM D975 for diesel [9], [10], [11]

		Biodiesel B100		Diesel
		ASTM D6751	EN14214	ASTM D975
Property	Units	Limits	Limits	Limits
Density at 15^{O}C	kg/m^3	880	860-900	820-860
Kinematic viscosity	mm^2/s	1.9-6.0	3.5-5.0	2.0-4.5
Flash point	^{O}C	130 Min	>101	60-80
Cloud point	^{O}C	-3 to -12	-	-15 to -5
Cetane number		>47	>51	46
Lower calorific value	MJ/kg	-	35	42

in the thermodynamic stability of the ternary mixture. Biofuel nano-emulsification produces nano-sized emulsions by mixing vegetable oil, ethanol and a co-solvent. Khoshsima *et. al* [12] developed nanoemulsions from rapeseed oil by mixing it with ethanol and different green additives [13]. Their research proved that a thermodynamically stable nanoemulsion can be obtained in the absence of a surfactant. The kinematic viscosity of the resultant fuel was found to fulfil the requirement of the American Society for Testing and Materials (ASTM) D6751 at 25^{O}C and 40^{O}C [14]. Their work suggests that nano emulsified vegetable oil can be used directly in a diesel engine based on phase behaviour and kinematic viscosity.

II. MATERIALS AND METHODS

A. *Materials*

Ethanol (Purity ≥99.9%) and 1-Heptanol (≥99%) were purchased from Kobian Kenya Limited. Rapeseed was a generous gift from Agventure Limited Timau. All chemicals were used without further purification.

TABLE II

Equipment and devices

Item No.	Equipment	Measurement range	Accuracy
1	Zetasizer Nano ZSP (Malvern Instruments, UK)	Particle size = 0.3nm to 10µm Zeta potential = 3.8nm to 100µm	±2%
2	Redwood's Viscometer	20 to 2000 seconds	Temperature ±0.2°C
3	Fourier Transform Infrared spectrometer	wavenumber range of 4,000 to 400 cm^{-1}	± 0.01 cm^{-1}
4	Shimadzu GC-14A gas chromatograph	Linear Dynamic Range: 10^6	± 10%

B. *Methods*

1. *Oil extraction*

Rapeseeds were dried to a moisture content of 3% [15] before cold pressing using a screw press to obtain the oil. The oil was afterwards filtered using a 150-micron screen to ensure that it is free of particles.

2. *Nanoemulsion preparation*

Ternary fuel blends are prepared by mixing different proportions of rapeseed oil, ethanol and 1-heptanol by mass. The blends are prepared at a constant weight percentage of 20% 1-heptanol and also at a constant weight percentage of 30% rapeseed oil [14] as illustrated in the ternary phase diagram in Fig. 1 and 2. The weight fractions were calculated from the mass obtained by precise weighing of the individual components.

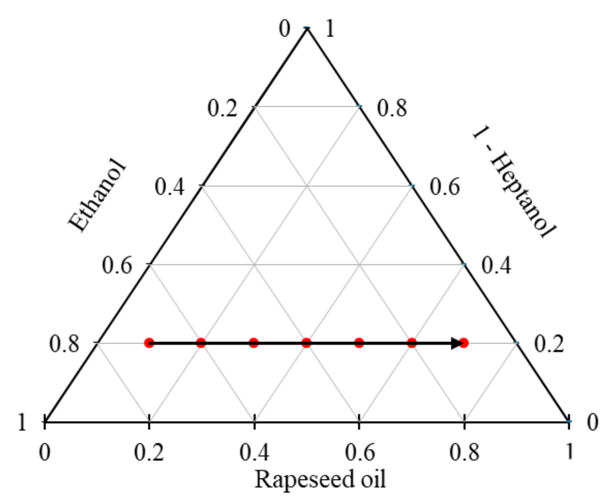

Fig. 1 Ethanol, Rapeseed oil and 1-Heptanol Blends at 20% 1-Heptanol Path

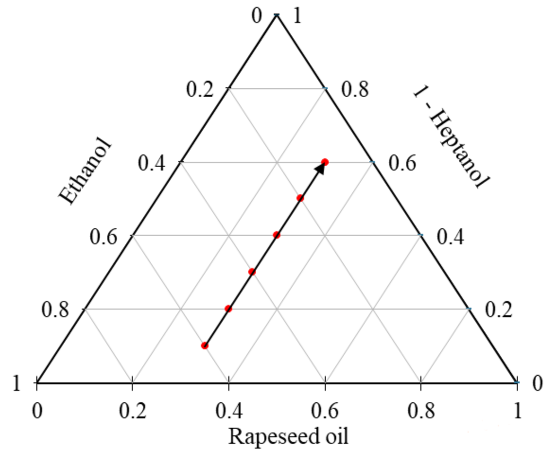

Fig. 2 Ethanol, Rapeseed oil and 1-Heptanol Blends at 30% Rapeseed oil Path

3. *Fatty acid profiling*

The fatty acid composition of total lipids and their different classes were determined on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector and capillary column (25 m × 0.2 mm id) coated with polyethene glycol. A temperature program for the column oven was 180 ^{O}C-5^{O}C/min-220^{O}C, while injector and detector temperatures were maintained at 230 and 250^{O}C, respectively. The chromatogram was recorded by a chromatopac integrator (C-R8A, Shimadzu, Japan). The peaks are identified by comparing their relative retention times with those of authentic standards run under the same parameters.

4. *Fourier-transform infrared spectroscopy*

The absorption and transmission spectra of the rapeseed oil were analysed using FTIR spectrometer with Diamond crystal cell ATR (path length: 1.66 µm; Bruker Optics, Model-Alpha, Germany) at 4 cm^{-1} resolutions, 0.2 cms^{-1} scan speed, and 24 scans at 30^{O}C in the wavenumber range of 4000 cm^{-1}-400 cm^{-1}.

5. *Particle size determination*

Size characterization was done by dynamic light scattering using a Zetasizer Nano ZSP (Malvern Instruments, UK) using a 4 mW He–Ne laser operating at a wavelength of 633 nm and a detection angle of 173^{O}. A plastic disposable cuvette, PCS1115 (Malvern Panalytical, UK) manufactured specifically for DLS measurements was filled with 1.5 ml of the biofuel blend and fitted with a thermal cap before being inserted into the cell area. All the measurements were done at 25^{O}C. The intensity size distribution was obtained by analysing the correlation functions using the general-purpose algorithm in the instrument's software.

6. *Zeta potential*

Zeta potential measurements were done on the Zetasizer Nano ZSP using a folded capillary with gold-coated electrodes. 40 volts was applied to the gold plated electrode after which the effective charge as a result of the applied field was determined.

7. *Kinematic viscosity measurements*

The kinematic viscosity was determined using a Redwood viscometer according to ASTM D445 standards. Biodiesel was poured into the viscometer cup and heated by a water bath to 40^{O}C. The time taken to collect 50ml of the heated biodiesel sample from the redwood viscometer was then recorded. Equation (1) was used to calculate the viscosity of the fuel.

$$kV = at - \tfrac{b}{t} \tag{1}$$

Where kV = Kinematic viscosity, a = 0.26, b = 172, t = time in seconds

III. RESULTS AND DISCUSSION

A. *Fourier transform infrared spectroscopy*

The objective of the Fourier Transform Infrared (FTIR) analysis was to assess the chemical bond and structure of the rapeseed oil. The Mid –IR spectrum (400 cm^{-1}– 4000 cm^{-1}) was used in the analysis. The rapeseed oil has 22 peaks which imply it is a complex molecule as shown in Fig. 3 and Fig. 4. The single bond area has several peaks with the peak at 3565 cm^{-1} indicating the existence of oxygen-related bonding. The lack of peak between 3000 cm^{-1}– 3200 cm^{-1} informs that there is no aromatic structure in the oil. There is a presence of aldehydes because of the peaks at 2731 cm^{-1} and 2855 cm^{-1}. Aldehydes are known to promote the combustion of the fuel and therefore their presence in the rapeseed oil will help in improving the combustion properties [16]. The oil has no triple bond with the sharp peak at 1745 cm^{-1} informing the presence of carbonyl double bond which is from the esters. The presence of double bond and oxygen-related bonding explains the reason why pure rapeseed oil has a high density and kinematic viscosity [17]. High viscosity is not desirable for fuel as it causes poor atomization which results in incomplete combustion. To improve the kinematic viscosity, the long carbon chain needs to be broken down into smaller carbon chains.

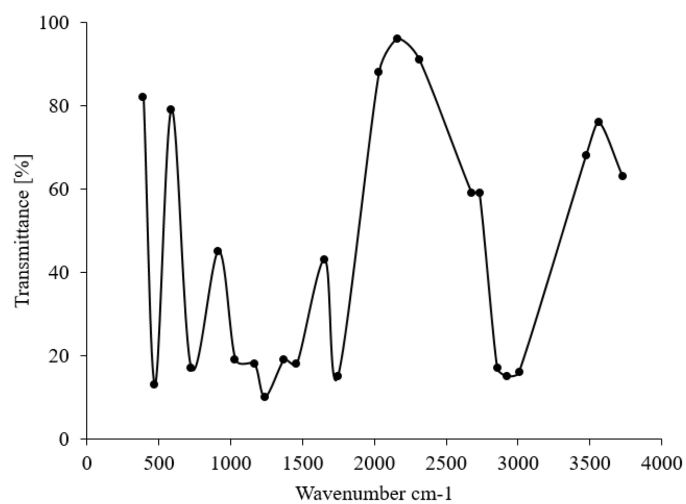

Fig. 3 Fourier Transform Infrared Transmittance Spectrum

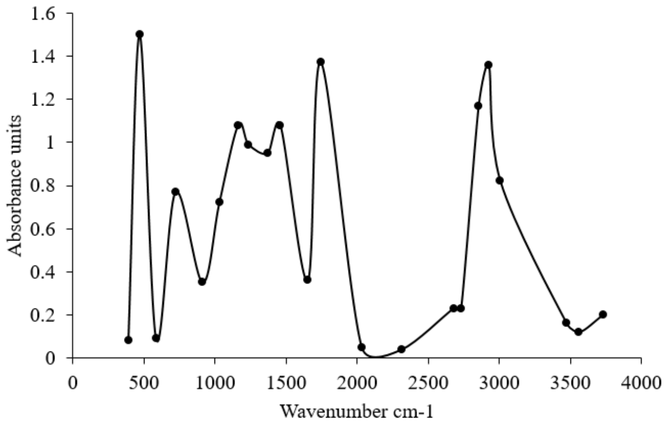

Fig. 4 Fourier Transform Infrared Absorbance Spectrum

B. *Fatty acid composition*

The composition of Fatty acid was analysed using the gas chromatography method. The fatty acid composition is as shown in Table III.

It can be inferred that rapeseed oil consists of a higher percentage of unsaturated fatty acids than saturated fatty acid with linolenic acid constituting the bulk of unsaturation. The major source of unsaturation in the rapeseed oil is linolenic and oleic acids. The source of saturation is majorly from palmitic and stearic acid. The saturated fatty acids provide desirable properties to the rapeseed oil such as high cetane number and better ignition properties [18].

TABLE III
Fatty acid composition of pure rapeseed oil

Item No.	Sample ID	% composition
1	Solvent front	
2	Butyric	0.00
3	Caprylic	0.00
4	Capric	0.38
5	Lauric	0.00
6	Myristic	0.36
7	Penta	0.10
8	Palmitic	6.73
9	Palmitoleic	0.00
10	Heptadecanoic	0.14
11	Stearic	13.77
12	Oleic	21.34
13	Linoleic	7.54
14	Linolenic	35.26
15	Arachidic	9.17
16	Arachidonic	1.46
17	Behenic	0.33
18	Lignoceric	1.38
19	Nervonic	0.22
20	Unknown	1.82
	Total	100

C. *Particle size and zeta potential*

The hydrodynamic sizes of the studied nanodroplets were obtained with multi-angle dynamic light scattering (DLS) measurements using a Zetasizer Nano ZSP. A laser light hits the droplet which then scatters the light at an angle. The angle of the scattered light is inversely proportional to the size of the droplet. The DLS result shows that nanoemulsions occur at a lower amount of rapeseed oil. Optimum nanoemulsions were obtained at 30% and 40% wt rapeseed oil when 1-heptanol was kept constant at 20% wt. At a higher amount of rapeseed oil, 1-heptanol is not able to fully dissolve rapeseed oil in ethanol.

The stability of the biodiesel blends was estimated from the zeta potential measurements. Zeta potential is recorded in millivolts because it is an electromagnetic potential at the slipping plane of the electrically charged particle in the emulsion. Zeta potential indicates the stability of the nanoemulsion. Nanoemulsions having zeta potential values >+25mV or <-25mV [19] usually exhibit a high degree of stability compared to those having lower values of zeta potential.

The results indicate that above 40% 1-heptanol based on weight fraction, the zeta potential was above 25mV pointing to very stable nanoemulsion being formed as shown in Fig. 5. High values of zeta potential imply that the particles or droplets are highly charged and will repel each other[20]. The repulsion of the particles prevents agglomeration resulting in stability. All the blends that were prepared at a constant weight fraction of 20% 1-heptanol exhibited very low zeta potential as shown in Fig. 6 implying that the nanoemulsions are not stable and will agglomerate with time. The blends with low zeta potential also had large droplet sizes which may have led to an increase in interfacial tension resulting in flocculation [21]. For automotive fuel, this is not a desirable property as it will impact negatively on the spray pattern of the fuel during atomization. Agglomeration of the droplets also means that during long time storage there will be sediments formed in the storage tanks.

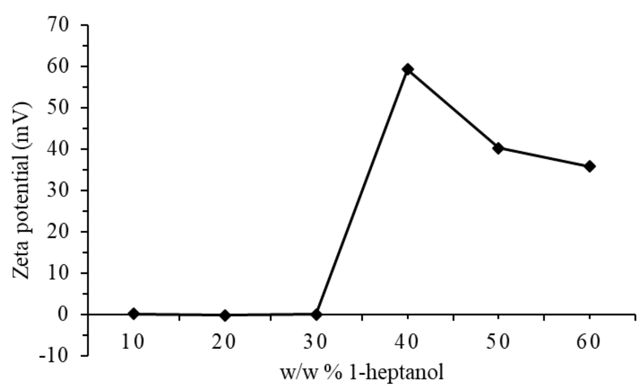

Fig. 5 Effect of 1-Heptanol on Zeta Potential

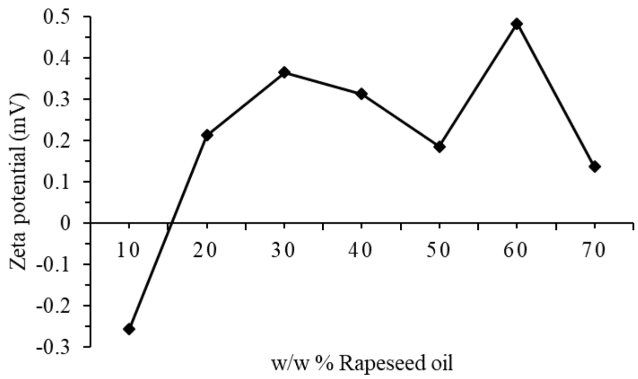

Fig. 6 Effect of Rapeseed oil on Zeta Potential

D. Kinematic viscosity

Fig. 7 depicts the kinematic viscosity as a function of the weight percentage of rapeseed in the presence of a constant weight percentage of 30% 1-heptanol. The kinematic viscosity measurements are performed at 40^{O}C using a redwood viscometer. A continuous increase in the kinematic viscosity of the blend appears with an increasing amount of rapeseed oil. This fact can be attributed to the higher kinematic viscosity of rapeseed oil. At a low amount of rapeseed oil, the kinematic viscosity is within the required value of the ASTM D6751 standards. High viscosity causes poor atomization during injection and deposits in the engine affecting the performance of the fuel [22]. Therefore, the kinematic viscosity of the formulated fuel is a very important parameter that cannot be overlooked in the production of biodiesel.

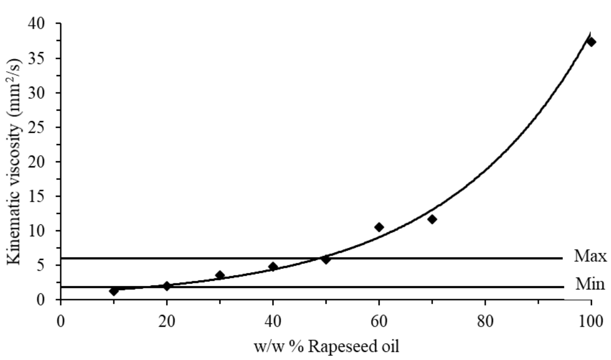

Fig. 7 Effect of Rapeseed oil on Kinematic Viscosity

All the blends prepared at an increasing amount of 1-heptanol in the presence of a constant weight percentage of 30% rapeseed oil had kinematic viscosity that met the ASTM D6751 biodiesel standard. From the results, it can also be observed that as the amount of 1-heptanol increases, the kinematic viscosity reduces further but is still within the limits of the ASTM standards. This reduction can be attributed to the low kinematic viscosity of 1-heptanol.

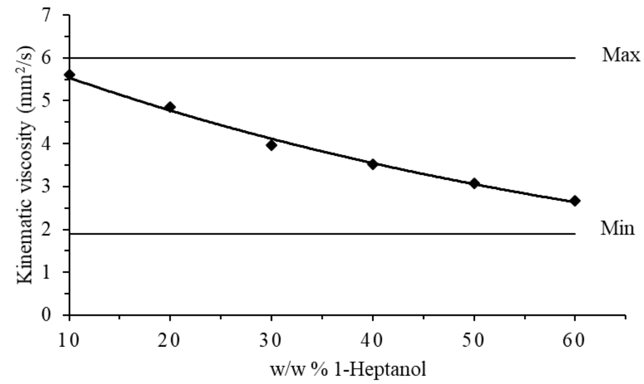

Fig. 8 Effect of 1-Heptanol on Kinematic Viscosity

IV. CONCLUSION

The main objective of this study was to find out how nanostructuring affects the properties of biodiesel without the use of a surfactant. The research on surfactant-free nanoemulsions is still at its infancy stage with few researchers reporting on it. The physicochemical properties of biodiesel are very important as they determine how the fuel performs in terms of atomisation. Biodiesel in its raw form has a high density and viscosity which limits its use in unmodified diesel engines. But after nanostructuring its well within the allowable limit.

Few researchers have reported on the formation of surfactant-free nanoemulsions and their effects on the physicochemical properties of biodiesel. Though they are similar work in terms of the physicochemical properties, in the present study we investigate further the effects on zeta potential. Zeta potential is a parameter that measures the magnitude of the charge between particles and is important in determining the storage stability of the sample. From this study, we conclude that the formulated biodiesel meets the ASTM standards in terms of kinematic viscosity. The biodiesel is also stable in storage as exhibited by the high zeta potential.

Therefore, the formulations obtained by mixing rapeseed oil and ethanol with 1-heptanol should be considered as potential biofuel for use directly in an unmodified diesel engine. How this nanostructured biodiesel performs in the engine is another interesting area for further research.

ACKNOWLEDGEMENT

We are grateful to the Centre for Traditional Medicine and Drug Research (CTMDR), KEMRI for providing the experimental facilities for particle size and zeta potential measurements.

Our gratitude also goes out to Agventure farm Limited Timau for their generous gift of rapeseed.

The authors acknowledge the assistance of the staff at the thermo-fluid laboratory at Jomo Kenyatta University of Agriculture and Technology.

REFERENCES

[1] M. T. Vertonha, L. A. Delgado, and G. V. B. Lukasievicz, “Characterization of the Physicochemical Properties of Different

Biodiesel Samples," *Brazilian Arch. Biol. Technol.*, vol. 61, no. spe, 2018.

[2] Wahyudi, I. N. G. Wardana, A. Widodo, and W. Wijayanti, "Improving vegetable oil properties by transforming fatty acid chain length in jatropha oil and coconut oil blends," *Energies*, vol. 11, no. 2, 2018.

[3] G. Knothe and K. R. Steidley, "Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components," *Fuel*, vol. 84, no. 9, pp. 1059–1065, 2005.

[4] P. Tamilselvan *et al.*, "Influence of saturated fatty acid material composition in biodiesel on its performance in internal combustion engines," *Mater. Today Proc.*, vol. 33, pp. 1181–1186, 2020.

[5] P. Krause and R. Labuda, "The Influence of Liquid Viscosity on Atomized Fuel Mean Droplet Size Determined by the Laser Diffraction Method," *New Trends Prod. Eng.*, vol. 1, no. 1, pp. 435–441, 2018.

[6] R. Murray, G. King, and R. Wyse-Mason, "Micro-emulsification vs. transesterification: an investigation of the efficacy of methanol use in improving vegetable oil engine performance," *Biofuels*, vol. 0, no. 0, pp. 1–10, 2019.

[7] M. L. Klossek, D. Touraud, T. Zemb, and W. Kunz, "Structure and solubility in surfactant-free microemulsions," *ChemPhysChem*, vol. 13, no. 18, pp. 4116–4119, 2012.

[8] T. N. Zemb *et al.*, "How to explain microemulsions formed by solvent mixtures without conventional surfactants," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 113, no. 16, pp. 4260–4265, 2016.

[9] ASTM, "ASTM D6751, Specification for Biodiesel (B100) – ASTM D6751-08, Filtration, no. June, pp. 9000–9000, 2008.," *Filtration*, no. June, pp. 9000–9000, 2008.

[10] British Standard Institution. Bs En 14214:2008 + a1:2009 Automotive fuels—Fatty acid methyl esters (FAME) for diesel engines—Requirements and test methods. Br. Stand. Inst. 2010, 1, 1–11, no. June, 2014.

[11] T. ASTM D975, Information, "Technical Information ASTM D975 Diesel Fuel Specification Test," *Wear*, pp. 1–3, 2017.

[12] A. Khoshsima, M. R. Dehghani, D. Touraud, J. Marcus, O. Diat, and W. Kunz, "Nanostructures in clear and homogeneous mixtures of rapeseed oil and ethanol in the presence of green additives," *Colloid Polym. Sci.*, vol. 293, no. 11, pp. 3225–3235, 2015.

[13] D. Brock *et al.*, "Nanostructuring in ethanol/'ethanolotrope'/rapeseed oil automotive biofuels," *Colloids Interface Sci. Commun.*, vol. 14, pp. 1–3, 2016.

[14] A. Khoshsima, D. Brock, D. Touraud, and W. Kunz, "Pre-formulation of biofuels: Kinematic viscosities, low-temperature phase behaviour and nanostructuring of ethanol/'ethanolotrope'/rapeseed oil mixtures," *Fuel*, vol. 191, no. March, pp. 212–220, 2017.

[15] G. Singh, A. K. Singh, and P. Singh, "Effect of Moisture Content on the Mechanical Oil Extraction of Canola Seeds," vol. 8, no. 03, pp. 965–977, 2019.

[16] P. Hellier, M. Talibi, A. Eveleigh, and N. Ladommatos, "An overview of the effects of fuel molecular structure on the combustion and emissions characteristics of compression ignition engines," *Proc. Inst. Mech. Eng. Part D J. Automob. Eng.*, vol. 232, no. 1, pp. 90–105, 2018.

[17] F. Jafarihaghighi, M. Ardjmand, M. Salar Hassani, M. Mirzajanzadeh, and H. Bahrami, "Effect of Fatty Acid Profiles and Molecular Structures of Nine New Source of Biodiesel on Combustion and Emission," *ACS Omega*, vol. 5, no. 26, pp. 16053–16063, 2020.

[18] F. AYDIN and S. ÇALIŞKAN, "Evaluation of biodiesel produced from tea seed oil in terms of fatty acid components," *Int. J. Energy Appl. Technol.*, vol. 7, no. 1, pp. 13–19, 2020.

[19] A. J. Shnoudeh *et al.*, *Synthesis, Characterization, and Applications of Metal Nanoparticles*. Elsevier Inc., 2019.

[20] S. Samimi, N. Maghsoudnia, R. B. Eftekhari, and F. Dorkoosh, *Lipid-Based Nanoparticles for Drug Delivery Systems*. Elsevier Inc., 2018.

[21] J. M. Montes de Oca-Ávalos, R. J. Candal, and M. L. Herrera, "Nanoemulsions: stability and physical properties," *Curr. Opin. Food Sci.*, vol. 16, pp. 1–6, 2017.

[22] N. Isioma, Y. Muhammad, O. Sylvester, D. Innocent, and O. Linus, "Cold Flow Properties and Kinematic Viscosity of Biodiesel," *Univers. J. Chem.*, vol. 1, no. 4, pp. 135–141, 2013.