ORIGINAL RESEARCH ARTICLE

Evaluation of flash point and calorific value of nanostructured rapeseed **oil biodiesel as an automotive fuel**

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ABSTRACT

The growing need for energy and the emphasis on reducing emissions have brought attention to the importance of developing renewable energy sources, specifically biofuels. However, using vegetable oils directly in diesel engines is hindered by their high viscosity, low ability to evaporate, and high content of polyunsaturated fats. Nanoemulsions, which are created without traditional surfactants, have demonstrated remarkable thermodynamic stability. This offers a potential solution to the challenges encountered with biofuels. This paper aimed to study the system of rapeseed oil-ethanol and 1-heptanol to understand the effects these nanoemulsions have on the calorific value and flash point. Ternary fuel blends with varying amounts of ethanol, rapeseed oil, and 1-heptanol were studied at constant weight percentages of 20% 1-heptanol and 30% rapeseed oil. The calorific value was determined by using a bomb calorimeter, and the results show that increasing the amount of 1-heptanol and rapeseed oil was able to increase the calorific value of the blend and maintain it close to that of diesel fuel. The flash point was determined using the Pensky Martens Closed Cup Method according to the American Society for Testing and Materials D93 standard (ASTM Standard D93-02a, 2002), and results show that only blends at 20% and 30% 1-heptanol at a constant of 30% rapeseed oil complied with the flash point requirement for diesel. This finding highlights the potential of the tricomponent fuel being used in an internal combustion engine without modification to the engine. The improved calorific value and flash point of the blends could be attributed to the co-solvent behaviour of 1-heptanol on rapeseed oil and ethanol.

Key words; Biofuel, Co-solvent, kinematic viscosity, surfactant, nanoemulsion.

1.0 Introduction

Biofuels are regarded as the answer to rising energy demand and emission reduction due to their self-replenishing nature and low emission characteristics. Overreliance on fossil fuels has resulted in unpredictable price fluctuations and the release of carbon dioxide (CO_2), and

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sulphur dioxide (SO_2), which are responsible for global warming and acid rain, respectively (Khoshsima et al., 2015).

The use of biofuel in an internal combustion engine in its neat form, B100, is limited due to its high density, high viscosity, and low volatility (Vijay et al., 2018). These properties determine the quality of the fuel and have been standardised and documented by the American Society for Testing and Materials (ASTM) and the European Committee for Standardisation (CEN), as shown in Table 1.

Table 1: ASTM D6751 and EN14214 standards for biodiesel and ASTM D975 for diesel

		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	>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

Biofuels are produced through various methods such as pyrolysis, blending, transesterification, pyrolysis, and emulsification. Emulsification performs better in terms of energy efficiency and emission reduction (Murray et al., 2019). This has led to many researchers investigating emulsification more than the other techniques of biofuel production. Emulsions are formed between two immiscible liquids where one of the liquids is dispersed as small droplets in the other liquid (Woo et al., 2021). A microemulsion is a mixture of oil, water, and a surfactant that is clear and thermodynamically stable. Microemulsions in diesel can be achieved by either using water or alcohol. They are used in fuel formulation to mitigate harmful emissions associated with the use of biofuels. Water is utilised to decrease the temperatures within the combustion chamber by absorbing heat and undergoing vaporization. This process ultimately leads to a reduction in NOX emissions, as the limited energy available inhibits their formation. The high density of water works to the disadvantage of these microemulsions as it increases the kinematic viscosity of the resultant fuel. This necessitated the shift to alcohol-based microemulsions. The presence of a surfactant breaks the cohesive forces of the oil molecules, which lowers their viscosity.

Biofuel nanoemulsification produces nano-sized emulsions by mixing vegetable oil, ethanol, and a co-solvent. Khoshsima et al., (2015) developed nanoemulsions from rapeseed oil by mixing it with ethanol and different green additives. Their research proved that a

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thermodynamically stable nanoemulsion can be obtained in the absence of a surfactant. 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. Not many researchers have explored the principles behind the formation of these emulsions. Zemb et al., (2016) attributed the stability of these emulsions to the balance between entropy and hydration force. The balance between these two forces minimises the free energy available, resulting in the thermodynamic stability of the ternary mixture. Their study demonstrated that the kinematic viscosity and phase characteristics of nano-emulsified vegetable oil closely resemble those of diesel, indicating its potential direct application in diesel engines. Nanostructuring results in a change in the physicochemical properties of the materials, such as an increased surface area to volume ratio (Cheng, 2013). A high surface area-to-volume ratio speeds up thermodynamic processes by providing more surface area for the reaction with oxygen, making nanomaterials more reactive compared to bulk materials.

The calorific value is an indicator of the energy content of the fuel. The higher the calorific value, the more energy the fuel has. Generally, biofuels have a slightly lower calorific value (≈ 39 MJ kg-1) compared to diesel (≈ 43 MJ kg-1) (Oliveira and da Silva, 2013). This has been attributed to the oxygen content of biofuels (Sani et al., 2018). The higher oxygen content of the biofuels helps in the combustion process and helps reduce oxidation. The lower calorific value also leads to more fuel consumption to obtain the same amount of energy when compared to diesel.

The flashpoint is the lowest temperature at which the vapour of the fuel will burn in the presence of an ignition source. A low flash point presents the risk of self-ignition, making the fuel a fire hazard. Although biodiesel is classified as non-hazardous when it comes to fire risk categories, the flashpoint is an indicator of the presence of volatile contaminants in the biodiesel, which tend to lower the flashpoint (Saxena et al., 2013). The flashpoint of biodiesel serves as a quality indicator rather than a safety precaution.

Rapeseed, *Brassica napus* subsp. Napus, is cultivated for its oil-rich seeds. Rapeseed oil has a high calorific value (36 MJ/kg), which is comparable to that of diesel (42 MJ/kg), and a high kinematic viscosity (36mm^2/s) (Laza and Bereczky, 2011). Its use in an internal combustion engine is limited by both its physicochemical and combustion properties. This research aims to study the effect of nanoemulsions without surfactants on the calorific value and flash point of rapeseed oil emulsified by mixing with ethanol and 1-heptanol.

2.0 Materials and methods

2.1 Materials

1-Heptanol (purity≥99%) and Ethanol (purity≥99.9%) were purchased from Sigma-Aldrich (Steinheim, Germany) through their authorised Kenyan supplier, Kobian Kenya Limited. Rapeseed was a generous contribution from Agventure Limited, located in Timau, Kenya. All chemicals were used without further purification.

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2.2 Methods

2.1.1 Extraction

Rapeseed oil was obtained through mechanical extraction using a screw press after drying the rapeseeds to a moisture content of 3% (Gaber et al., 2018). The low moisture content enabled maximum extraction of oil from the seeds (Singh et al., 2019). The oil was extracted through cold pressing to avoid significant alteration of the oil properties using a belt drive screw expeller press (XEMPLAR-5-KE/T/2005/058411, Kenya) fabricated by Prof. Shitanda Douglas at the School of Agricultural and Biosystems Engineering workshop. The oil was then filtered using a 150-micron screen.

The density at 40°C, kinematic viscosity at 40°C, calorific value, and flash point of the extracted oil were then measured according to the ASTM standards and recorded as shown in Table 2.

Table 2: Comparison of the properties of the extracted rapeseed oil to diesel (Murray et al., 2019)(Woo et al., 2021)(Cheng, 2013)(Oliveira and da Silva, 2013)(Sani et al., 2018)(Saxena et al., 2013)(Laza and Bereczky, 2011)(Gaber et al., 2018)(Singh et al., 2019)

Properties	Rapeseed oil	Diesel
Density @ 40°C	883.80 kg/cm^3	910 – 925 kg/cm^3
Kinematic viscosity	37.35 mm^2/s	2.00 – 4.50 mm^2/s
Calorific value	33.12 MJ/kg	42.00 MJ/kg
Flash point	224°C	60 – 80°C

Source: Diesel standards adopted from ASTM standards

Fig. 1: Moisture determination using oven drying method

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2.1.2 Nanoemulsion preparation

Tri-component blends of rapeseed oil, 1-heptanol, and ethanol were prepared using weight fractions at a constant weight percentage of 20% 1-heptanol and at a constant weight percentage of 30% rapeseed oil, as illustrated in the ternary phase diagram in figures 2 and 3.

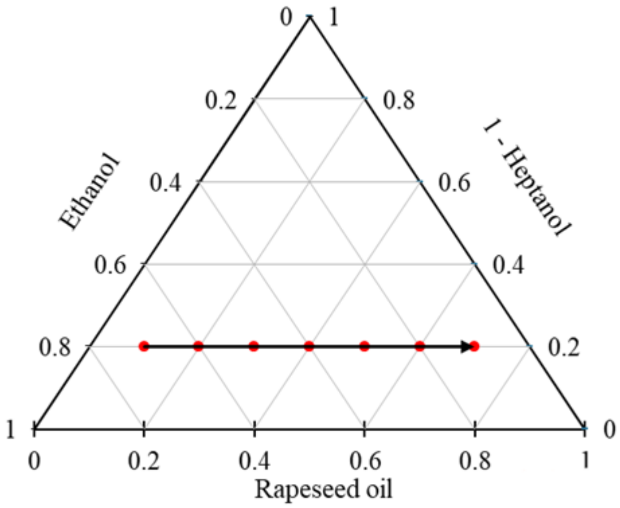

Fig. 2: Ethanol, Rapeseed Oil, and 1-Heptanol Blends at 20% 1-Heptanol Path

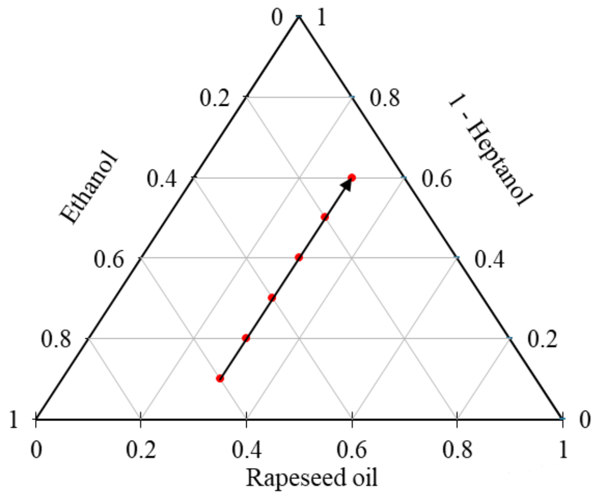

Fig. 3: Ethanol, Rapeseed Oil, and 1-Heptanol Blends at 20% 1-Heptanol Path

2.1.3 Calorific value determination

The calorific value was determined in a bomb calorimeter according to ASTM D240 standards, where a sample of the rapeseed oil biofuel was burned in the oxygen bomb calorimeter under controlled conditions. The heat content of the fuel was then computed from the temperature observations made before, during, and after the combustion. An allowance for thermochemical and heat transfer corrections was then made, and the calorific value was calculated by applying equation 1.

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$$C = \frac{(W_w + W_e) * c * [(T_2 - T_1) + T_c]}{W_f}$$

C = calorific value (higher) of fuel (KJ/kg), w_f = weight of fuel sample (kg), (1)
w = weight of water (kg), c = specific heat of water $(J/kg{\cdot}K)$,
w_e = water equivalent of calorimeter (kg),
t_1 = initial temperature of water and calorimeter (K),
t_2 = final temperature of water and calorimeter (K), t_c = radiation cautions

2.1.4 Flash point determination

The flashpoint was determined using the Pensky Martens Closed Cup Method according to the ASTM D93 standard (ASTM Standard D93-02a, 2002). A brass cup of diameter 53.90mm and height 55.75 mm is filled with rapeseed oil up to a height of 34.03 mm, covered, and heated while being stirred at specified rates. An ignition source was then introduced to the test cup at intervals until a flash was detected. The flashpoint was recorded when the vapour of the rapeseed oil biofuel ignited.

3.0 Results and discussion

3.1 Calorific value

The calorific value measures the energy content of the fuel. When compared to diesel, biofuels have a lower calorific value, which translates to less energy being released for the same amount of diesel fuel (Oliveira and da Silva, 2013). Fig. 4 and Fig. 5 show the variation of the calorific value with the increasing percentage of rapeseed oil and 1-Heptanol, respectively, in the ternary biofuel blends.

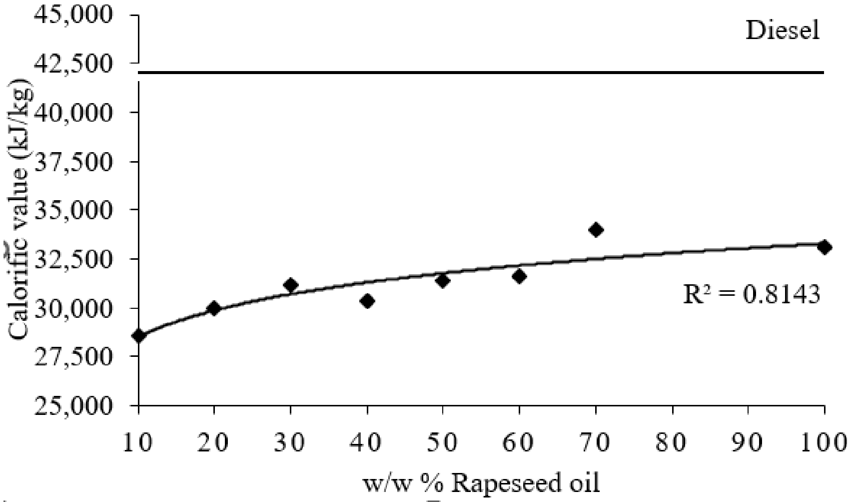

Fig. 4: Calorific Value as a Function of the w/w% of Rapeseed Oil

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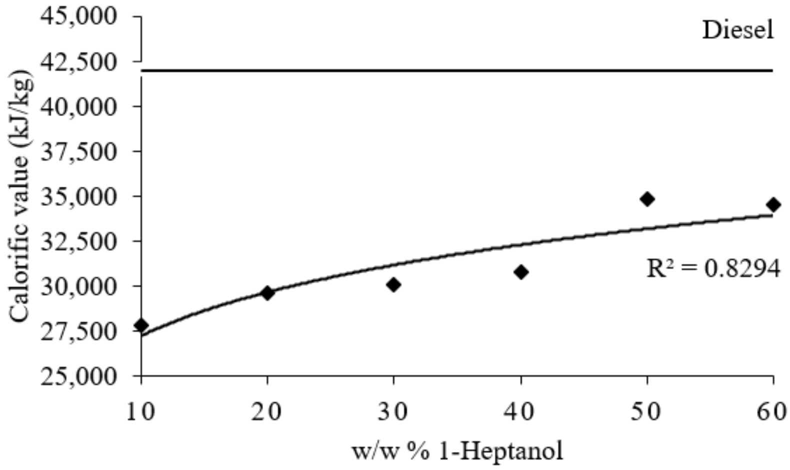

Fig. 5: Calorific Value as a Function of the w/w% of 1-Heptanol

As the amount of rapeseed oil and 1-heptanol in the ternary blend increased, the calorific value increased, pointing to a very strong correlation between the calorific value and the amount of rapeseed oil and 1-heptanol in the mixture. The reduction in the calorific value of the mixture can be attributed to the low calorific value of ethanol, 29.78 MJ/kg (Nwufo et al., 2016), when compared to that of rapeseed oil, 36 MJ/kg (Laza and Bereczky, 2011), and 1-heptanol, 39.91–40.59 MJ/kg (Lide et al., 2010). The limit for the calorific value is not specified in the ASTM standard.

3.2 Flash point

The flash point is the lowest temperature at which a volatile substance gives sufficient vapour to ignite in the presence of an ignition point (Fu, 2019). Biodiesels are classified as non-hazardous in fire risk categories because of their high flash point, therefore presenting no risk of self-ignition. The flash point serves as an important quality determination parameter for biofuels as it indicates the presence of contaminants in the fuel (Saxena et al., 2013). Figs. 6 and 7 show the results of the flash point variation with respect to the increasing percentage of rapeseed oil and 1-heptanol, respectively, in the ternary biofuel. The flash point result obtained can be compared to the ASTM D975 standard for diesel outlined in Table 1. The ASTM D975 standard for flash points for diesel specifies that the fuel must have flash point limits between 60^{O}C– 80^{O}C. Comparing the flash points of the blends, it’s clear that only blends at 20% and 30% 1-heptanol at 30% rapeseed oil complied with the flash point requirement for diesel. The reduction in the flash point of the ternary fuel blend can be attributed to the presence of ethanol in the blends, which tends to lower the flash point due to its high volatility (Gouveia et al., 2017).

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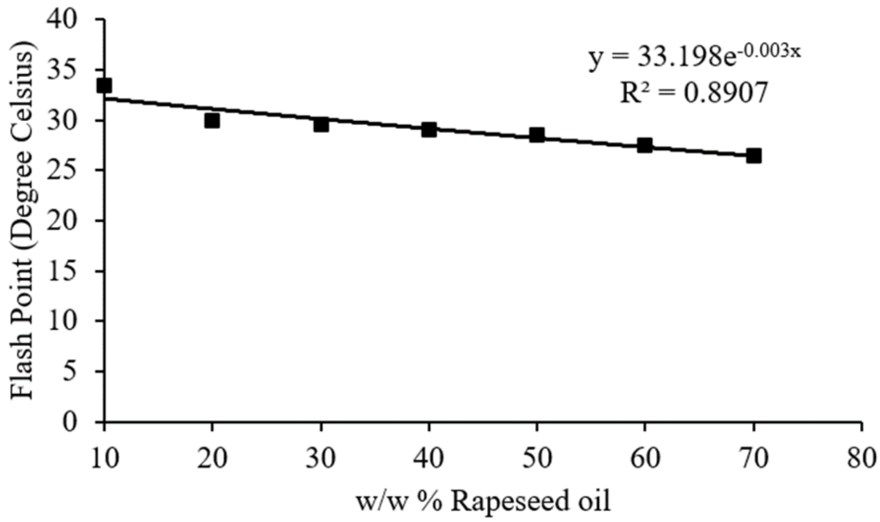

Fig. 6: Flash point as a function of w/w% of rapeseed oil (Nwufo et al., 2016)(Laza and Bereczky, 2011)(Lide et al., 2010)(Fu, 2019)(Saxena et al., 2013) (Gouveia et al., 2017)

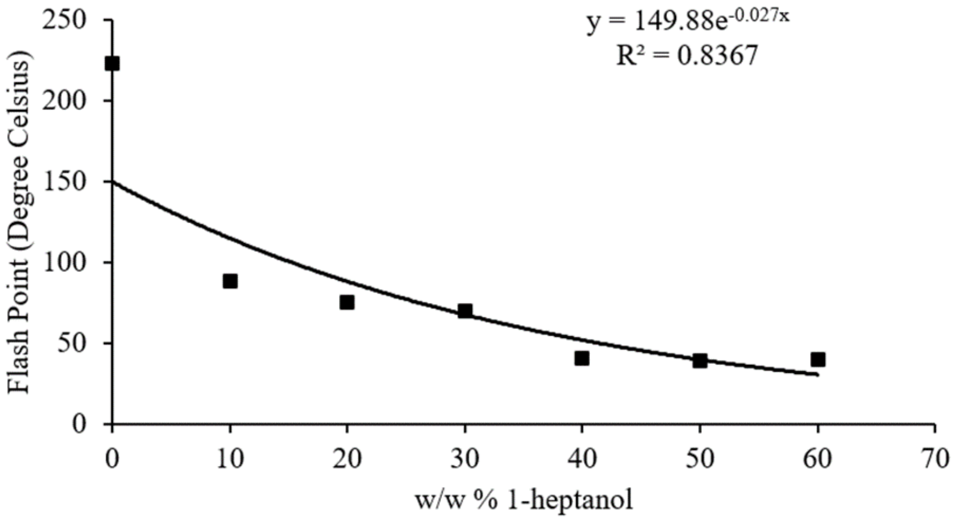

Fig. 7: Flash point as a function of w/w% of 1-Heptanol

4.0 Conclusions

The experimental results have led to several key findings. The blending led to significant alterations in the properties of rapeseed oil biodiesel, highlighting its potential as a sustainable and energy-efficient alternative. Notably, an increase in both rapeseed oil and 1-heptanol content within the blend was demonstrated to increase the calorific value, suggesting enhanced energy efficiency. Moreover, the observed reduction in flash point can be attributed to the higher presence of 1-heptanol, which possesses a marginally lower flash point.

Secondly, the evaluation of the compliance of the fuel blends to ASTM D975 specifications has shown differing results. The calorific value of biofuel is not specific to ASTM standards, but the

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result obtained was close to that of diesel. However, only blends at 20% and 30% 1-heptanol at a constant of 30% rapeseed oil complied with ASTM D975 specifications for flash point. These outcomes not only underscore the potential of this blend as a renewable energy source but also open avenues for further research and development in the field of sustainable fuels.

5.0 Acknowledgements

5.1 Funding

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5.2 General acknowledgement

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5.3 Conflict of interest

None.

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