

Determination Of Physical And Chemical Properties Of Fish Oil Methyl Ester, Diethyl Ether, And Butanol Blends

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Abstract

This study aims to determine the physical and chemical properties of blends consisting of fish oil methyl ester (FOME), diethyl ether (DEE), and butanol. Understanding these properties is crucial for assessing the suitability of such blends as alternative fuels for internal combustion engines. Experimental investigations are conducted to analyze parameters such as density, viscosity, flash point, cetane number, calorific value, cold flow properties and Fatty Acid Methyl Ester analysis. The results of this study provide comprehensive insights into the characteristics of FOME, DEE, and butanol blends, shedding light on their potential as viable fuel options. By examining a wide range of physical and chemical properties, the study offers valuable data to support informed decision-making in fuel formulation and selection processes. Additionally, the findings contribute to advancing research in the field of alternative fuels, offering opportunities for optimizing engine performance, reducing emissions, and promoting sustainability. The results showed that the higher concentration of the FOME, the higher the density, viscosity, calorific value, higher flash point and pour point but cetane value is lower. When addition of DEE and butanol additives except cetane value all the properties above mentioned are lower additionally Fatty Acid Methyl Ester values are reduced. This decrease is caused by differences in the heating value of the two fuels The results of this study are very important as a basis for the development of FOME blends as an environmentally friendly vehicle-fuel substitute material to conventional fuel.

Keywords: FOME, DEE, butanol, density, viscosity, flash point, cetane number, calorific value and cold flow properties

Date of Submission: 24-04-2024

Date of Acceptance: 04-05-2024

I. Over view

The combustion of fossil fuels is a significant contributor to atmospheric pollution, accounting for a substantial portion of greenhouse gas emissions. According to the International Energy Agency, combustion engines alone contribute approximately 25% of these emissions. Increased population, modernization, industrialization and urbanization have resulted in higher energy demand over the past few decades. Globally, the carbon dioxide (CO₂) emitted from energy-related activities increased from 30.4 billion metric tons (BMT) in 2010 to 31.5 BMT in 2020 (Figure 1).

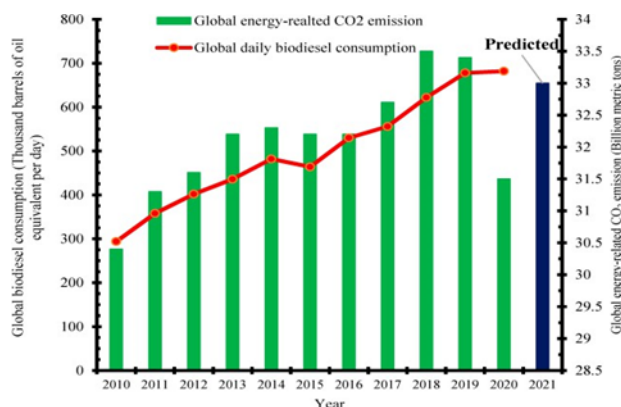


Fig. 1 Global biodiesel consumption and global energy-related CO₂ emission [1]

There is a need for more investment in the renewable energy sector to safeguard our planet from the terrible effects of fossil fuel consumption. Biodiesel has emerged as a promising alternative fuel to mitigate the environmental and health impacts associated with the combustion of petroleum-derived diesel in compression-ignition engines. Global biodiesel consumption increased from 294 thousand barrels of oil equivalent per day (mboe/d) in 2010 to 682 mboe/d in 2020 (Figure 1) [2&3].

Biodiesel offers several advantages over conventional diesel, including sustainability, carbon cycle balance, biodegradability, lubrication properties, and reduced emissions of harmful pollutants. However, a major challenge hindering the widespread adoption of biodiesel is the high cost of refined oils used as feedstock in its production. This cost can constitute a significant portion, ranging from 60% to 80%, of the overall production expenses of biodiesel. Consequently, biodiesel struggles to compete economically with petroleum-derived diesel, which is produced at a lower cost.

To address this limitation, researchers have explored alternative, low-cost feedstock options for biodiesel production. These include used vegetable oil, animal waste fats, unrefined vegetable oils, and fish waste from fishing activities. Among these alternatives, fish oil stands out as a particularly abundant and inexpensive source. It is estimated that approximately half of the fish processed globally is either discarded or sold at minimal prices for purposes such as fertilizer or animal feed. By utilizing fish oil as a feedstock for biodiesel production, researchers aim to capitalize on this abundant resource while simultaneously addressing environmental and economic concerns. By repurposing fish waste into biodiesel, this approach not only reduces waste but also provides a cost-effective solution for producing sustainable fuel.

The utilization of fish oil as a feedstock for biodiesel production holds promise for reducing both environmental pollution and reliance on costly refined oils. This approach represents a significant step towards achieving economic competitiveness and environmental sustainability in the biodiesel industry.

The search for sustainable and environmentally friendly fuel alternatives has become increasingly imperative in recent years, driven by concerns over climate change and the depletion of finite fossil fuel resources. Biodiesel, derived from renewable feedstocks such as vegetable oils and animal fats, has emerged as a promising candidate for reducing greenhouse gas emissions and enhancing energy security. Among biodiesel variants, fish oil methyl ester (FOME) holds particular interest due to its abundance and potential as a sustainable fuel source.

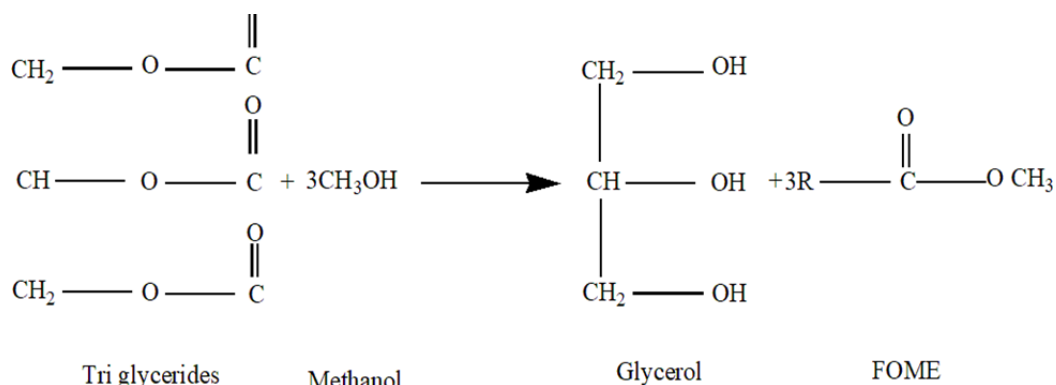


Fig. 2 Formation of FOME

However, despite its promising attributes, FOME faces challenges related to its physical and chemical properties that limit its widespread adoption. Issues such as high viscosity, poor cold flow properties, and oxidative instability pose obstacles to its efficient use in various applications, particularly in compression ignition (CI) engines. To overcome these challenges and enhance the suitability of FOME as a viable fuel option, blending strategies have been explored to modify its properties and improve performance.

Overall, while FOME holds promise as a renewable and sustainable alternative to petroleum diesel, its limitations, such as high viscosity, poor cold flow properties, and compatibility issues, need to be addressed to ensure its effective and widespread use in compression ignition engines. Continued research and development efforts are necessary to overcome these limitations and optimize the performance and viability of FOME as a biodiesel fuel [4-8].

To overcome above limitations one approach involves blending FOME with co-solvents such as diethyl ether (DEE) and alcohols like butanol. These blending agents offer unique properties that can complement and enhance those of FOME, addressing its limitations and expanding its potential applications. Diethyl ether, for instance, exhibits excellent cold flow properties and high volatility, which can help mitigate issues related to FOME's poor cold weather operability. Similarly, butanol offers advantages such as improved cetane number and combustion characteristics, contributing to enhanced engine performance and emissions control.

Diethyl ether (DEE), also referred to as 'ethyl ether,' is another ether isomer of butanol that can be produced from ethanol, which itself is derived from biomass. DEE exhibits several favorable properties for blending with diesel fuel, including a very high cetane number, reasonable energy density for on-board storage, high oxygen content, low auto-ignition temperature, and high miscibility with diesel fuel. However, it also has drawbacks such as high volatility, susceptibility to peroxidation during storage, and low lubricity.

Iso butanol is the most commonly studied isomer in diesel engine applications. It possesses a straight chain structure with the hydroxyl group located at the terminal carbon, facilitating its compatibility with diesel fuel. While research on butanol's application in diesel engines has been relatively limited compared to vegetable oils, biodiesels, or ethanol, the body of literature on the subject has been rapidly expanding, as evidenced by recent studies.

Iso butanol, derived from biomass through alcoholic fermentation, presents several advantages that make it a desirable renewable fuel option. Compared to ethanol, butanol exhibits lower hydrophilic tendency, higher heating value, cetane number, and viscosity, as well as lower vapor pressure. These properties align more closely with those of diesel fuel, making butanol a preferred candidate for blending with conventional diesel fuel.

II. Composition Of FOME, DEE And Iso Butanol

Fish oil methyl ester (FOME) is a type of biodiesel produced through the transesterification of fish oil. The chemical composition of FOME primarily consists of fatty acid methyl esters, which are derived from the triglycerides present in fish oil. FOME consists of Fatty Acid Methyl Esters, Saturated Fatty Acid Methyl Esters, Monounsaturated Fatty Acid Methyl Esters, Polyunsaturated Fatty Acid Methyl Esters [9].

In addition to FAMES, FOME may contain minor components such as glycerol (a by-product of the transesterification reaction), residual methanol, free fatty acids, and other impurities. These components are typically present in small concentrations and can vary depending on the production process and purification methods used.

Overall, the chemical composition of FOME primarily consists of fatty acid methyl esters derived from fish oil triglycerides. The specific composition and proportions of FAMES in FOME can vary depending on factors such as the species of fish used, the processing methods, and the degree of purification.

The chemical composition of DEE and iso butanol is relatively simple, consisting of carbon, hydrogen, and oxygen atoms arranged in a specific molecular structure. This structure gives iso butanol its unique properties and makes it useful for various industrial and commercial applications, including as a solvent, fuel additive, and chemical intermediate in organic synthesis.

In summary, both butanol and diethyl ether offer promising properties for blending with FOME, providing potential solutions to enhance the physical and chemical properties of blends to make alternate fuels for CI engines. Further research and experimentation are necessary to fully explore the feasibility and benefits of incorporating these DEE and Iso butanol into FOME fuel blends.

In this context, this study aims to investigate the physical and chemical properties of blends comprising FOME, DEE, and butanol. By systematically analyzing parameters such as density, viscosity, flash point, cetane number, cold flow properties and Fatty Acid Methyl Ester analysis, this research seeks to elucidate the behavior and characteristics of these blends as alternative fuels for IC engines.

III. Materials And Methodology

The FOME samples were retrieved from fish processing units at local areas. DEE (analytical grade, 99.5%) was purchased from industrial market areas, while butanol (analytical grade, 60–100 mesh) was procured from SVM Agro processor, Nagpur. DEE is hygroscopic and, therefore, must be kept in an airtight glass jar and contact with eyes must be avoided. The butanol was collected from the stock used for frying and needs no pre-treatment, while the FOME was collected just at the point of disposal with food debris and light yellow. About one liter of butanol was collected while four liters of each FOME were collected and transported into the laboratory in a sealed glass container. This is to ensure enough FOME samples are available for testing and conversion to ester. The information obtained about the FOME, DEE and butanol samples is displayed in Table 1, while Figure 2 is the picture of the collected samples. However, the cycle of usage and the frying temperature could not be accurately ascertained. The collected FOME samples were exposed to thermal treatment by pouring them into a clean transesterification reactor and heating it to about 50 °C. The oil, now in liquid form, is subjected to physical treatments to get rid of solid food residues and other contaminants in liquid form by filtration using a laboratory filter paper that allows the oils to pass. The filtered samples were dehydrated by heating the samples to 100 °C under a vacuum of 25 mmHg for 20 min to eliminate the water molecules contained in the samples. The treated FOME samples were subjected to acid and transesterification process described in below figure 3.

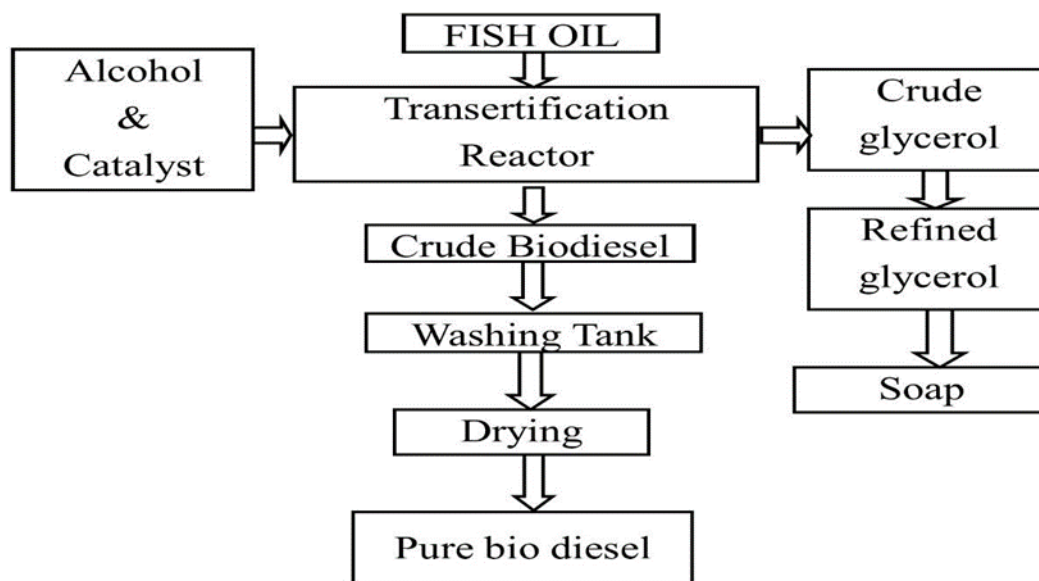


Fig. 3 Transesterification process of Raw fish oil to FOME

Initially Fish oil methyl ester (FOME) (considered as base fuels) itself examined later FOME is mixed with 15% by vol of DEE fixed quantity [10] and butanol (supplement fuels) is varying, showing no separation after mixing for a long period. It is stated that Iso butanol and DEE are isomers, thus containing the same amount of fuel-bound oxygen on a mass (and roughly volumetric) basis, while in the FOME contains depends on quantity of FAME (fatty acid methyl esters) ~10% fuel-bound oxygen. Thus, the comparison of all the blends is affected on the basis of an almost equal parameter, which is known to affect strongly the combustion behavior via the ‘local’ air-fuel ratio in the various ‘zones’ and, consequently, the temperatures and emissions formation, by also noting that the air aspirated by the engine is constant for the same load and speed conditions. Parameters of the blends such as (mainly) viscosity, density, and calorific value are equal in general [11].

The properties of the FOME, Iso-butanol, and DEE are summarized in Table 1. Only the density and lower calorific values were used in the computations, with all the other cited properties referred to here for comparative purposes, in order to explain qualitatively the relative behavior of the different fuel blends. All density values were measured at the laboratory and the others are mean values taken from various sources in the literature, such as mainly for the Iso-butanol [12], for the diethyl ether [13] and for the FOME.

Table 1 Physical properties for base fuels

Name	Units	FOME	DEE	BTN
Density	kg/m ³	0.88	0.76	0.81
Cetane Number		51	125	25
Calorific Value	kJ/kg	39000	29500	34370
Viscosity	mm ² /sec	4.44	0.22	3.25
Flash Point		165	45	37.5
Pour point		10	42.5	75

The properties of density, cetane number, calorific value, viscosity, flash point and fire point for FOME each blend of FOME or its biodiesel with any of the bio-fuel supplements are easily calculated from the ‘lever’ law, by knowing the bio-fuels volume fraction and their densities (taken from Table 1). By knowing the Cetane Number (% by weight) for each bio-fuel (taken from Table 1), the fuel-bound oxygen in the blend (% by weight) can be easily calculated, which as stated above constitutes an important basis for comparison. The above parameters are given in Table 2 for all blends used in this study.

IV. Results And Discussions

The pretreated FOME and its blends samples were analyzed and the results were compared with ASTM standards. At the end of the transesterification reaction, the FOME and its blends samples were converted into crude biodiesel. The biodiesel samples were separated in a separating funnel where the impurities were drained off. The crude biodiesel samples were purified to remove the excess moisture, catalyst and methanol trapped in the crude biodiesel. The clean FOME and its blends samples are kept in an airtight glass vial for

analysis. The results of the physical analysis of the samples are shown in Table 2.

Table 2 Physical properties for blends

Name	Units	FOME85DEE15	FOME50DEE15BTN35	FOME25DEE15BTN60
Density	kg/m ³	0.85	0.83	0.81
Cetane Number		62.1	53.0	46.5
Calorific Value	kJ/kg	37575	35955	34797
Viscosity	mm ² /sec	3.8	3.4	3.1
Flash Point		147.0	102.4	70.5
Pour point		14.9	37.6	53.9

Density

The variation of density of a FOME and its blends is influenced by its composition shown in figure 4. If FOME blends contain additional components or diluents with lower densities than FOME itself variation of density is shown in figure 4, it could contribute to an overall decrease in density with values for FOME 0.88kg/m³, FOME85DEE15 0.85kg/m³, FOME50DEE15BTN35 0.83kg/m³, FOME25DEE15BTN60 0.81kg/m³. While adding the DEE density is slightly decreased but butanol decreases density hugely compare to pure form of FOME.

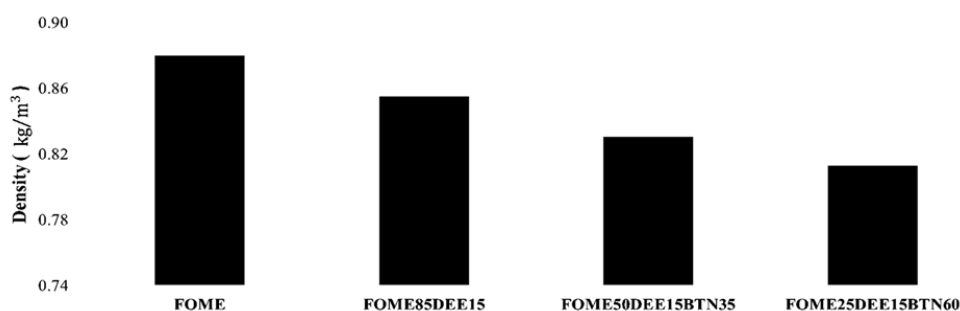


Fig. 4 Densities of FOME and its blends

The density of a material can be affected by intermolecular interactions between its components. Blending FOME with DEE and butanol may result in phase separation, where components with different densities segregate into distinct phases. Blended samples exhibit little bit phase separation, the overall density of blend sample lower due to the presence of less dense phases. The arrangement of molecules within a material influences its density. If the molecular packing in FOME blends is less efficient compared to pure FOME, perhaps due to molecular differences or structural disruptions caused by blending, it could result in a lower overall density. The blending process may introduce voids or empty spaces within the material, reducing its overall density. This could occur if air or other gases become trapped during blending, or if the blending process causes structural defects or disruptions in the material.

These experimental values can help explain the density of FOME blends may be lower than that of pure FOME. However, experimental validation and further analysis would be necessary to confirm the specific mechanisms at play in a given system.

Calorific value

Heat capacity between FOME blends and pure FOME could affect the combustion process. If the blends have lower heat capacities, they may not release energy as efficiently during combustion, leading to lower calorific values. Blending FOME with other substances could lead to structural changes in the molecules or overall composition of the blend. These structural changes may affect the easy of combustion or the energy released during combustion, ultimately impacting the calorific values.

The calorific value of the FOME and blends of DEE, butanol shows the heat produced from the combustion process. If the combustion is perfect, then the optimal thermal energy can be obtained. Test results obtained shows in figure 5 that the caloric value of FOME is 3900kJ/kg . After mixing the DEE and butanol calorific value is lower i.e, for FOME85DEE15 37575kJ/kg, FOME50DEE15BTN35 35955kJ/kg and FOME25DEE15BTN60 34797kJ/kg. Table 2 shows that the higher the concentration of butanol added to the FOME, the lower the calorific value. This decrease is caused by the difference in the heating value between the additives. The National Standards Agency (BSN) has set FOME quality standards with a minimum heating value of 4500 kJ/kg. Based on the quality standards set by BSN, the blend FOME and DEE, butanol produced in this

study were following the standards.



Fig. 5 Calorific values of FOME and its blends

Cetane number

Blending FOME with other substances, especially those with higher cetane numbers i.e., DEE, can increase the overall cetane rating of the blend. If the blends contain additives with higher cetane numbers than FOME, the overall cetane number of the blend would increase. The cetane number of a fuel is influenced by its chemical composition, particularly the presence of long-chain hydrocarbons. Blending FOME with DEE cetane value increased and compare to pure FOME with an increasing 22.5%, but when butanol added cetane value is decreased due to alter the chemical composition of the fuel, leading to a decrease in cetane number.

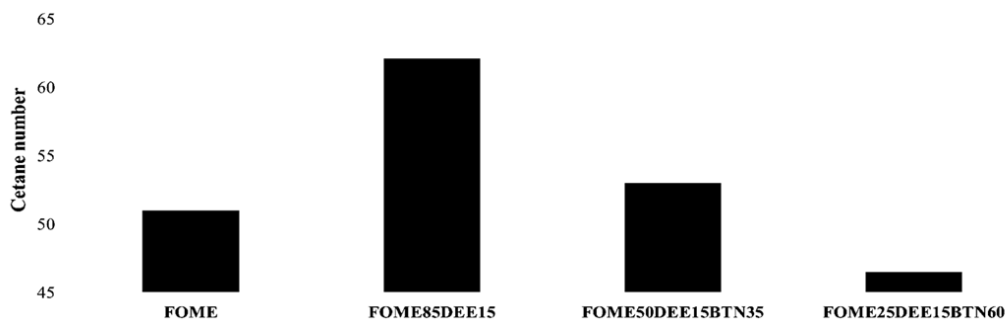


Fig. 6 Cetane number of FOME and its blends

Viscosity

FOME typically has larger molecular sizes compared to DEE and butanol. Larger molecules tend to experience stronger intermolecular forces, leading to higher viscosity. Blending FOME with DEE and butanol, which have smaller and potentially less complex molecular structures, may reduce the overall viscosity of the blend due to the dilution effect caused by the smaller molecules.

The blend viscosity in various concentrations of FOME and butanol fuel is shown in figure 7. In the figure 7, it appears that the higher the concentration of the FOME, the higher the blend's viscosity. Fuel viscosity can affect the fogging process. Fuels that have high viscosity are difficult to atomize. Conversely, fuels with low viscosity are easier to atomize. Fuels that are more easily atomized are also easier to ignite and also more perfect for combustion.

The result of the FOME was a value of 4.4 mm²/sec, while that when DEE added to FOME its decreased to of 3.81 mm²/sec. After mixing butanol to above blend tremendously, the data obtained showed that the higher the concentration of FOME higher viscosity but addition of DEE which enhances the oxidation property which increases the combustion quality. This is thought to be influenced by the viscosity of butanol, which is lower than the FOME and FOME+DEE viscosity.

The blending process might result in phase separation or the formation of microstructures within the blend. Additives i.e., DEE and butanol structures influence viscosity differently than in pure FOME, it could lead to variations in viscosity between the blends and pure FOME. These practical considerations provide potential explanations for the viscosity of FOME samples might be higher than its blends with DEE and butanol.

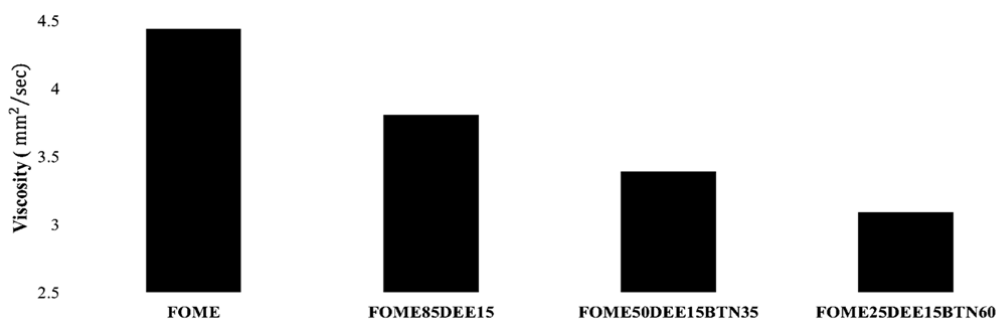


Fig. 7 Viscosity of FOME and its blends

Flash point

FOME typically consists of fatty acid methyl esters, which may have higher flash points compared to other components present in the blends, such as DEE (Diethyl Ether) and butanol. The chemical composition of FOME, with its longer carbon chains, may contribute to higher flash points due to increased molecular weight and stronger intermolecular forces. DEE and butanol are typically more volatile substances compared to FOME. Their lower molecular weights and simpler molecular structures may lead to easier vaporization and lower flash points. Blending FOME with these substances could lower the overall flash point of the blend due to the presence of more volatile components.

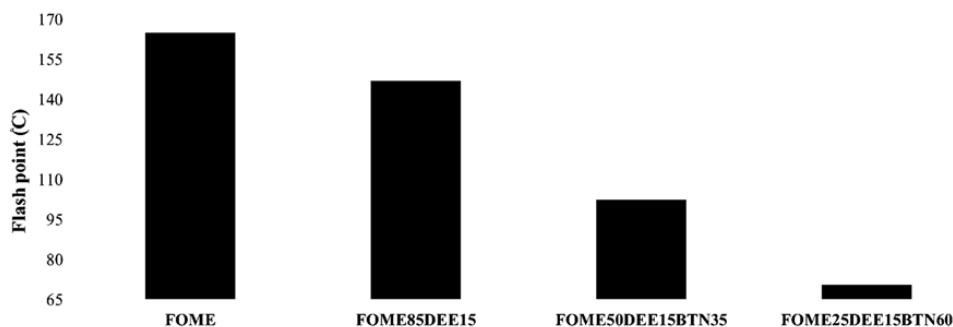


Fig. 8 Flash point of FOME and its blends

Flash point of FOME+DEE is 11% lower compare to pure form of FOME, when Butanol added flash point lowers highly compare to above blend which is averagely 50% lower compare to pure form of FOME, in particular, is capable of forming hydrogen bonds due to the presence of hydroxyl (-OH) groups. Hydrogen bonding can increase the stability of the liquid phase and raise the flash point. However, if butanol is blended with FOME, it might disrupt the hydrogen bonding network, resulting in a lower flash point for the blend. Blending FOME with DEE and butanol may dilute the overall composition, leading to a decrease in flash point. If the concentration of FOME in the blend is reduced compared to pure FOME, it could contribute to a lower flash point due to the presence of more volatile components.

Pour point

Figure 9 shows that the influence pour point FOME by the addition of DEE and butanol significant. Due to the very low pour point of DEE relative to that of FOME, it can be expected that FOME+DEE blends will depict a lower value compared to that of FOME. This improvement is possible as long as DEE remains soluble in FOME. Figure 9 shows that pour point increases when DEE added to FOME which means fuel flow improving in the fuel injection system. However, FOME50DEE15BTN35 and FOME25DEE15BTN60 pour point shows an unusual result that is caused by phase separation when temperature decreases, which leads the automatic testing device to display DEE pour point instead of blend pour point. FOME solidifies at a higher temperature than ethanol, so the temperature at which the fuel can no longer be poured due to gel formation is not detected in the blend fuel but in the ethanol component. This behavior becomes stronger due to the fact that the tested FOME flow improver additives and it is known that, at low temperatures, FOME is usually blended with DEE and butanol or low temperature-flow improving additives to avoid fuel gelling. The low concentration of DEE in FOME and rapid decrease in temperature reproduced by the device may have prevented the phase separation in samples FOME50DEE15BTN35 and FOME25DEE15BTN60 [14&15].

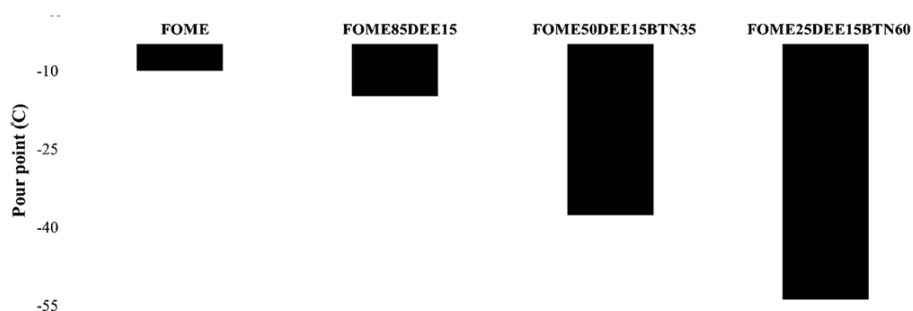


Fig. 9 Pour point values of FOME and its blends

Gas Chromatography analysis

The Fatty Acid Methyl Ester (FAME) composition analysis, as depicted in Figure 10, reveals significant disparities between the original FOME samples and their blends. This variance is primarily attributed to the influence of food and thermal contamination during the transesterification process. Transesterification is a chemical reaction utilized in biodiesel production, where fatty acids in oils or fats are converted into methyl esters, commonly known as biodiesel, through the reaction with an alcohol like methanol or ethanol.

Fish oil, known for its high content of palmitic acid and eicosenpentanoic acid, undergoes this process to produce FOME. However, the composition of fatty acids in FOME blends differs notably from that of pure FOME due to various factors, including the addition of compounds like diethyl ether (DEE) and butanol.

Gas chromatography analysis, as illustrated in Figure 10, provides a detailed breakdown of the fatty acid composition in both FOME and its blends. While palmitic acid remains prominent in fish oil, the addition of DEE and butanol during the transesterification process introduces alterations in the composition of fatty acids. It's observed that after transesterification, there isn't a substantial change in the overall composition of different fatty acids. However, the addition of DEE and butanol seems to affect the concentration of palmitic acid.

Compared to the pure form of FOME, the presence of DEE and butanol leads to a reduction in palmitic acid levels, followed by a shift in the distribution of other fatty acids.

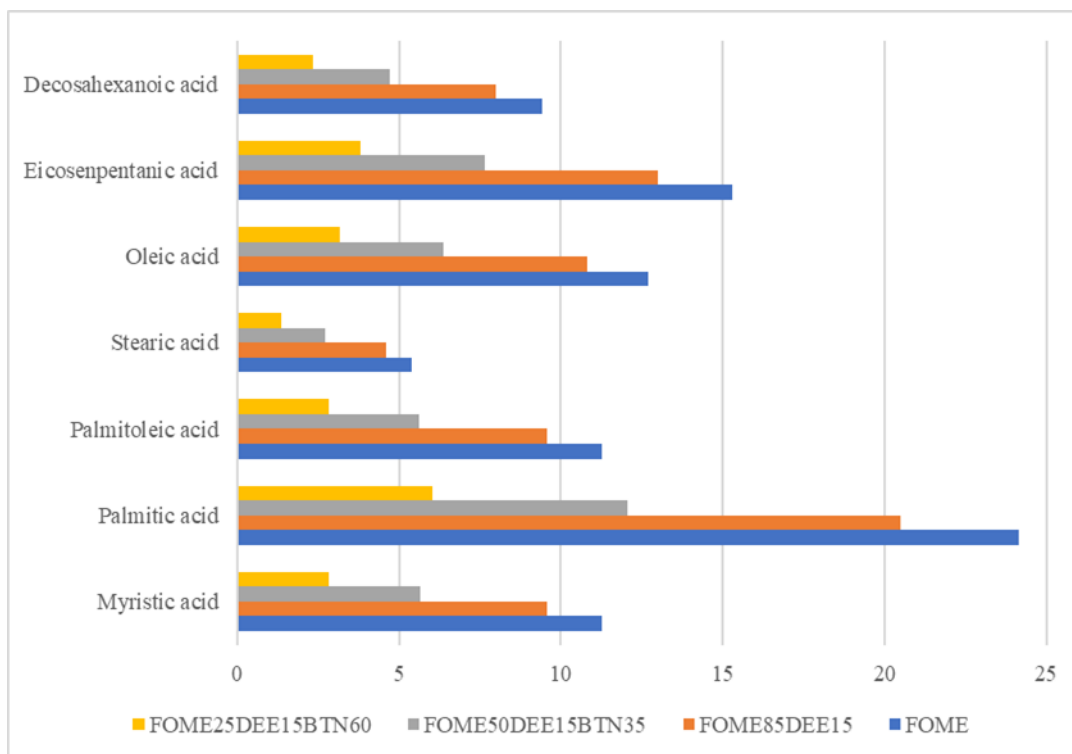


Fig. 10 Gas Chromatography analysis of FOME and its blends

V. Conclusions

In the current effort, we have investigated the impacts of DEE and butanol blend in to FOME physicochemical properties. The physicochemical properties and spectroscopic behavior of palm oil are distorted by high temperature frying and the transesterification process. The outcome of this research can be summarized as follows

- The density of the FOME, DEE, and Butanol blends might differ from that of pure FOME. Depending on the specific composition and concentration of components, the density of the blends may decrease due to the inclusion of less dense substances or changes in molecular packing efficiency.
- The viscosity of the FOME, DEE, and Butanol blends tends to decrease compared to pure FOME. This reduction in viscosity can be attributed to the dilution effect caused by blending FOME with DEE and Butanol, as well as the differences in molecular size, structure, and hydrogen bonding capabilities between the components.
- The flash point values of the FOME, DEE, and Butanol blends are lower than that of pure FOME. This decrease in flash point can be explained by the presence of more volatile components in the blends, such as DEE and Butanol, as well as potential disruptions to hydrogen bonding networks and changes in intermolecular interactions.
- The cetane number of the FOME, DEE, and Butanol blends may vary depending on the composition and concentration of the components. Blending FOME with DEE and Butanol could lead to changes in combustion properties and ignition characteristics, influencing the cetane number of the blends compared to pure FOME. FOME and DEE blend shown higher cetane value compare to pure FOME and butanol blends due to higher presence of oxygen values
- There is reduced in a Fatty Acid Methyl Ester of blends by the addition of additives, but by the addition of DEE the cetane value increased, this significant variation does not show any effects on combustion and ignition characteristics.

These conclusions highlight the complex interplay of physical and chemical properties when blending FOME with DEE and Butanol and underscore the importance of comprehensive characterization to inform practical applications and potential uses of these blends among all the blends FOM85DEE15 and FOME50DEE15BTN35 shows good characteristics compare to pure form of FOME and remaining blends.

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