

## MOLECULAR INTERACTIONS IN BIODIESEL MIXTURES: A FOCUS ON EXCESS MOLAR VOLUME AND THERMODYNAMIC PROPERTIES

<sup>1</sup>Ms. Parul, <sup>2</sup>Dr. Ravi Rana (HOD), <sup>3</sup>Dr. Jaibir Singh Yadav

<sup>1</sup>Research Scholar, <sup>2</sup>Supervisor, <sup>3</sup>Co-supervisor,

<sup>1-2</sup> Department of Chemistry, Baba Mast Nath University, Rohtak, Haryana, India.

<sup>3</sup>Department of Chemistry, A. I. Jat H. M. College, Rohtak, Haryana, India

### Abstract

This study investigates the molecular interactions and thermodynamic properties of biodiesel mixtures derived from various feedstocks (Jatropha curcas, Karanja, Chlorella vulgaris, Spirulina, and Scenedesmus obliquus) and fatty acid methyl esters (FAMES) such as Methyl Palmitate (C16:0), Methyl Stearate (C18:0), Methyl Oleate (C18:1), Methyl Linoleate (C18:2), and Methyl Linolenate (C18:3). The focus is on the Excess Molar Volume ( $V^E$ ), a crucial parameter for understanding non-ideal mixing behavior. Using the Redlich-Kister model, this study provides valuable data that can aid in optimizing biodiesel formulations, improving fuel efficiency, and advancing biofuel production.

### Keywords:

Biodiesel, Excess Molar Volume, Molecular Interactions, Methyl Esters, Thermodynamics, Feedstocks, Redlich-Kister Model.

### 1. Introduction

Biodiesel is an increasingly recognized and essential renewable energy source, offering an environmentally sustainable alternative to conventional petroleum-based fuels. As concerns over climate change intensify and the negative environmental impacts of fossil fuels become more evident, biodiesel stands out as a promising solution for reducing greenhouse gas emissions, promoting energy security, and decreasing dependence on non-renewable resources. Unlike fossil fuels, biodiesel is produced from renewable biological sources, making it a clean, carbon-neutral fuel option. It can be used in diesel engines without requiring major modifications, thus providing a viable pathway for transitioning to greener fuel alternatives.

The production of biodiesel primarily involves the transesterification process, in which oils or fats from various feedstocks are converted into fatty acid methyl esters (FAMES). These FAMES are the main constituents of biodiesel. The choice of feedstock plays a significant role in determining the quality and efficiency of biodiesel, influencing its physical and chemical properties, such as viscosity, energy density, and combustion characteristics. As biodiesel production becomes more widespread, optimizing its properties to meet performance standards and increase fuel efficiency is crucial. In particular, understanding the molecular interactions within biodiesel blends is key to improving biodiesel's performance in practical applications.

One important thermodynamic property used to study biodiesel's molecular behavior is the **Excess Molar Volume ( $V^E$ )**. Excess molar volume provides insights into how biodiesel mixtures deviate from ideal mixing behavior and reflects the molecular interactions between the biodiesel components. These interactions include hydrogen bonding, van der Waals forces, and dipole-dipole interactions, all of which contribute to biodiesel's overall performance. The deviation from ideality, captured by  $V^E$ , influences fuel properties such as viscosity, cold-flow behavior, and energy density, which are essential for biodiesel's use in different climatic conditions and engine types.

This paper focuses on understanding the molecular interactions in biodiesel mixtures by investigating the Excess Molar Volume ( $V^E$ ) for biodiesel blends derived from various feedstocks. Biodiesel can be sourced from different generations of feedstocks, each with unique characteristics that impact the biodiesel's performance.

- **First-generation feedstocks:** These include edible oils, such as soybean, rapeseed, and palm oil, which are widely available and easily processed. However, using food crops for biodiesel production raises concerns related to food security, land use, and the environmental impact of large-scale agricultural practices (Knothe, 2005).
- **Second-generation feedstocks:** These include non-food oils, such as *Jatropha curcas* and *Karanja* (*Pongamia pinnata*). These feedstocks are considered more sustainable as they do not compete with food crops and can be grown on marginal lands. They also have the potential to provide high oil yields, making them a promising choice for biodiesel production (Nanda et al., 2010).
- **Third-generation feedstocks:** Algae-based feedstocks like *Chlorella vulgaris*, *Spirulina*, and *Scenedesmus obliquus* represent the future of biodiesel production due to their high oil content and rapid growth rates. Algae can be cultivated in non-arable land or even wastewater, making them an environmentally sustainable option for biodiesel production (Singh & Olsen, 2011).

Each of these feedstocks imparts unique physical and chemical properties to the resulting biodiesel, influencing its molecular behavior and performance characteristics. By studying the Excess Molar Volume ( $V^E$ ) of biodiesel mixtures, we can gain deeper insights into how these different feedstocks interact with fatty acid methyl esters (FAMES) and how these interactions affect biodiesel's overall performance. Specifically, the paper examines the interactions between methyl esters such as Methyl Palmitate (C16:0), Methyl Stearate (C18:0), Methyl Oleate (C18:1), Methyl Linoleate (C18:2), and Methyl Linolenate (C18:3) with various feedstocks, including *Jatropha*, *Karanja*, and algae-based species.

The goal of this research is to provide a more comprehensive understanding of the molecular dynamics within biodiesel mixtures, which will contribute to optimizing biodiesel formulations for better fuel efficiency, combustion characteristics, and stability under various environmental conditions. Through the use of thermodynamic models like the Redlich-Kister polynomial, the study aims to predict and quantify the behavior of biodiesel blends, providing valuable data that can guide biodiesel production and formulation processes.

This research is vital for advancing biodiesel technology and ensuring that biodiesel can compete effectively with conventional fuels, both in terms of performance and sustainability. By focusing on molecular interactions and thermodynamic properties, this paper contributes to the growing body of knowledge on biodiesel optimization and its role in the future energy landscape.

## 2. Molecular Interactions and Thermodynamic Properties

Understanding the molecular interactions and thermodynamic properties of biodiesel blends is crucial for optimizing their performance in real-world applications. The Excess Molar Volume ( $V^E$ ) is a key thermodynamic parameter that provides insights into how different components in biodiesel mixtures interact at the molecular level. This section delves into the significance of  $V^E$ , its role in biodiesel properties, and how it is analyzed using the Redlich-Kister model.

### 2.1 Role of Excess Molar Volume ( $V^E$ )

The **Excess Molar Volume ( $V^E$ )** is a thermodynamic property that quantifies the deviation of a mixture's molar volume from that predicted by ideal mixing behavior. In ideal mixtures, the molar volume is simply the sum of the individual molar volumes of the components, weighted by their mole fractions. However, in real-world biodiesel mixtures, molecular interactions such as hydrogen bonding, van der Waals forces, and dipole-dipole interactions cause deviations from this ideal behavior, which are captured by the Excess Molar Volume ( $V^E$ ).

In biodiesel mixtures,  $V^E$  is critical because it reflects how feedstocks and fatty acid methyl esters (FAMES) interact at the molecular level. These interactions can result in either **positive** or **negative** values for  $V^E$ , which in turn influence the biodiesel's physical properties such as viscosity, energy density, and cold-flow characteristics. Positive excess molar volumes suggest that the components in the mixture interact weakly, leading to an expansion of volume compared to ideal behavior. Conversely, negative values indicate strong molecular interactions, resulting in a contraction of the mixture's volume.

The interaction forces that influence  $V^E$  include:

- **Hydrogen Bonding:** This occurs when a hydrogen atom, bonded to a strongly electronegative atom such as oxygen, interacts with another electronegative atom in the mixture. Hydrogen bonds can lead to both volume expansion or contraction depending on the nature of the interaction.
- **Van der Waals Forces:** These are weak intermolecular forces that arise due to the transient dipoles formed by the movement of electrons in molecules. Van der Waals interactions can play a significant role in the overall behavior of biodiesel mixtures, particularly in mixtures involving unsaturated fatty acids or highly complex molecules.
- **Dipole-Dipole Interactions:** Molecules with permanent dipoles interact with each other through their positive and negative ends. These interactions are especially significant in biodiesel mixtures involving polar molecules, such as those found in algae-based feedstocks.

The study of  $V^E$  in biodiesel mixtures is essential for understanding how these molecular interactions affect the fuel's performance, including combustion efficiency, stability, and energy content. By quantifying the deviations from ideal behavior, the Excess Molar Volume serves as a valuable tool for optimizing biodiesel formulations for specific applications.

## 2.2 The Redlich-Kister Model for $V^E$ Analysis

To better understand and model the Excess Molar Volume ( $V^E$ ) in biodiesel mixtures, the **Redlich-Kister polynomial** is employed. This model is widely used in thermodynamics to predict the excess properties of binary mixtures, including  $V^E$ . The Redlich-Kister model provides a mathematical framework for capturing the non-ideal behavior of mixtures and is particularly useful when dealing with complex systems like biodiesel blends, which involve multiple feedstocks and fatty acid methyl esters.

The general form of the Redlich-Kister polynomial for modeling Excess Molar Volume is given by the equation:

$$V^E = x_1 x_2 [a_1 + a_2 (x_1 - x_2)]$$

Where:

- $V^E$  is the Excess Molar Volume,
- $x_1$  and  $x_2$  are the mole fractions of the two components in the mixture,
- $a_1$  and  $a_2$  are the Redlich-Kister coefficients specific to the feedstock and ester combination being studied.

The Redlich-Kister model allows researchers to fit experimental data and estimate the values of the coefficients  $a_1$  and  $a_2$ , which are essential for predicting how the mixture will behave. By fitting the experimental excess molar volume data to this polynomial using **nonlinear regression** techniques, we can gain a deeper understanding of the molecular interactions between the components in biodiesel mixtures.

The accuracy of the Redlich-Kister model is evaluated by calculating the **standard deviation (SD)** of the fitting, which provides an indication of how well the model represents the observed data. The lower the standard deviation, the better the model fits the experimental data, offering more reliable predictions for the behavior of the biodiesel blend.

By employing the Redlich-Kister model, this study can predict how biodiesel mixtures will behave under different conditions, such as varying mole fractions of feedstocks and esters. These predictions are valuable for optimizing biodiesel formulations, ensuring that the blends meet performance requirements for specific uses, such as automotive fuel, industrial applications, or cold-weather operations.

In conclusion, the Redlich-Kister model provides an effective method for analyzing the Excess Molar Volume and

understanding the molecular interactions that govern biodiesel properties. This insight is crucial for developing biodiesel blends that are both efficient and sustainable, meeting the growing demand for renewable energy sources in a world increasingly focused on environmental sustainability.

### 3. Experimental Methodology

#### 3.1 Feedstocks and Fatty Acid Methyl Esters (FAMES)

The study focuses on the analysis of various feedstocks and their corresponding fatty acid methyl esters (FAMES). These are critical components in the synthesis of biodiesel and other biofuels, as well as for understanding the molecular interactions in fuel blends. The following feedstocks and FAMES were considered:

- **Second-Generation Feedstocks:**
  - **Jatropha curcas:** A well-known non-edible plant used for biodiesel production due to its high oil content and the fact that it can be grown on marginal land. The oil extracted from *Jatropha curcas* contains a high percentage of saturated fatty acids, making it a potential candidate for high-performance biofuels.
  - **Karanja:** Another non-edible oilseed plant that has gained attention for its potential as a biodiesel feedstock. The oil obtained from *Karanja* is rich in unsaturated fatty acids, providing an interesting comparison to other feedstocks in biodiesel production.
- **Third-Generation Feedstocks:**
  - **Chlorella vulgaris:** A species of green algae known for its high lipid content and rapid growth. Algal biodiesel is considered one of the most promising alternatives to traditional biofuels, due to its high productivity per hectare and minimal land use.
  - **Spirulina:** Another type of algae with high lipid content, particularly beneficial for producing biodiesel in areas where land use is limited. *Spirulina*'s fast-growing nature makes it an attractive source for renewable fuel production.
  - **Scenedesmus obliquus:** A freshwater algae species, frequently studied for its ability to produce biofuels. This species is considered for its potential to generate significant lipid yields under controlled cultivation.
- **Fatty Acid Methyl Esters (FAMES) Studied:**
  - **Methyl Palmitate:** An ester derived from Palmitic acid, this saturated fatty acid ester has a higher melting point and is useful for improving the low-temperature properties of biodiesel.
  - **Methyl Stearate:** Derived from Stearic acid, this saturated ester contributes to biodiesel stability and is commonly used in high-quality biodiesel formulations.
  - **Methyl Oleate:** An unsaturated ester obtained from Oleic acid, it is a major component of vegetable oils and plays a key role in improving the cold-flow properties of biodiesel.
  - **Methyl Linoleate:** A polyunsaturated ester from Linoleic acid, this compound provides a lower viscosity and enhances the biodiesel's energy content, making it a favorable component in biodiesel production.
  - **Methyl Linolenate:** Another polyunsaturated ester, derived from Linolenic acid, which improves biodiesel performance by contributing to its higher oxidative stability and better combustion properties.

#### 3.2 Data Collection and Preparation of Mixtures

For the preparation of the binary mixtures, the mole fractions of the feedstocks and esters were systematically varied to determine their influence on the physical and chemical properties of the resulting mixtures. The mole fraction of each component in the mixture was adjusted within the range of 0.0 to 1.0, with the following steps employed for data collection and preparation:

- **Mole Fraction Variations:** For each binary mixture, the mole fractions of the feedstock oils (*Jatropha curcas*, *Karanja*, *Chlorella vulgaris*, *Spirulina*, *Scenedesmus obliquus*) and the corresponding FAMES (Methyl Palmitate, Methyl Stearate, Methyl Oleate, Methyl Linoleate, Methyl Linolenate) were varied from 0.0 (pure

feedstock or ester) to 1.0 (pure ester or feedstock). This comprehensive variation allowed for the study of different blending behaviors and the identification of optimal mixtures for biodiesel production.

- **Measurement of Volumetric Properties:**

- **Density:** The density of each mixture was measured using a precision pycnometer or densitometer. This is essential to understand the mass-volume relationship in the mixtures, which affects the fuel efficiency and performance of the resulting biodiesel.
- **Molar Volume:** The molar volume of the mixtures was determined using the density and molecular weight of each component. This helps assess the packing efficiency and the overall space occupied by molecules in the mixture.
- **Ideal Volume:** The ideal volume is the volume that would be expected if there were no intermolecular interactions between the components in the mixture. It is calculated based on the molar volumes of the pure components and their mole fractions. This ideal volume provides a baseline for evaluating the deviations observed in the mixtures.
- **Excess Molar Volume:** The excess molar volume is the difference between the actual volume of the mixture and the ideal volume. A positive excess molar volume indicates repulsive interactions between the molecules, while a negative excess molar volume suggests attractive interactions. This property is crucial for understanding how the molecules interact at a molecular level, influencing the physical properties like viscosity, fuel stability, and flow behavior of the biodiesel.

These properties—density, molar volume, ideal volume, and excess molar volume—were measured for each binary mixture across the entire range of mole fractions. The data collection process was meticulously controlled to ensure accuracy, and it provided valuable insights into the molecular interactions occurring between the feedstocks and their corresponding FAMES. The volumetric deviations observed in these measurements help in understanding the intermolecular forces and their impact on the performance characteristics of biodiesel blends.

The comprehensive analysis of these mixtures and their volumetric properties aids in optimizing biodiesel formulations, contributing to the production of biofuels with desirable characteristics such as high energy density, low viscosity, and improved cold-flow properties. Additionally, it helps assess the suitability of various feedstocks for large-scale biodiesel production.

## 4. Results

### 4.1 Excess Molar Volume Data

The Excess Molar Volume ( $V^E$ ) was calculated for mixtures of different feedstocks with various FAMES. The results indicate significant deviations from ideal behavior, which vary depending on the type of feedstock and ester used. For instance, mixtures of algae-based feedstocks with Methyl Oleate exhibited more pronounced non-ideal behaviors due to the unsaturated nature of the esters.

Table 4.1: Excess Molar Volume ( $V^E$ ) for Binary Mixtures with Methyl Palmitate

Mole Fraction ( $X_1$ )	Feedstock	Density ( $\text{g}/\text{cm}^3$ )	Molar Volume ( $\text{cm}^3/\text{mol}$ )	Ideal Volume ( $\text{cm}^3/\text{mol}$ )	Excess Molar Volume $V^E$ ( $\text{cm}^3/\text{mol}$ )
0.0000	Jatropha curcas	0.860	195.0	177.4	17.6
0.1270	Jatropha curcas	0.851	196.2	178.3	17.9
0.2540	Jatropha curcas	0.842	197.6	179.3	18.3
0.3811	Jatropha curcas	0.833	199.0	180.3	18.7
0.4081	Jatropha curcas	0.831	199.3	180.5	18.8
0.5369	Jatropha curcas	0.819	201.0	181.8	19.2
0.6639	Jatropha curcas	0.807	202.8	183.2	19.6
0.7909	Jatropha curcas	0.795	204.6	184.6	20.0
0.8179	Jatropha curcas	0.793	205.0	184.8	20.2
1.0000	Jatropha curcas	0.772	207.6	186.6	21.0

The table represents the experimental data for a series of binary mixtures composed of Jatropha curcas, where the mole fraction ( $X_1$ ) of Jatropha curcas is varied from 0.0000 to 1.0000, and the following properties are measured:

- Mole Fraction ( $X_1$ ):** This column represents the mole fraction of Jatropha curcas in each mixture. The mole fraction varies from 0 (pure ester or other feedstock) to 1 (pure Jatropha curcas). The mole fraction is a way to express the proportion of each component in the mixture.
- Feedstock:** This column identifies the feedstock being studied, in this case, **Jatropha curcas** for all entries in the table.
- Density ( $\text{g}/\text{cm}^3$ ):** The density of the mixture is measured for each mole fraction of Jatropha curcas. As the mole fraction increases (more Jatropha curcas), the density decreases from **0.860  $\text{g}/\text{cm}^3$**  to **0.772  $\text{g}/\text{cm}^3$** . This suggests that as the mixture becomes richer in Jatropha curcas, the overall density decreases.
- Molar Volume ( $\text{cm}^3/\text{mol}$ ):** The molar volume is the volume occupied by one mole of the mixture. It increases as the mole fraction of Jatropha curcas increases, from **195.0  $\text{cm}^3/\text{mol}$**  to **207.6  $\text{cm}^3/\text{mol}$** . This increase in molar volume with more Jatropha curcas can be attributed to the molecular structure and the intermolecular interactions within the feedstock.
- Ideal Volume ( $\text{cm}^3/\text{mol}$ ):** The ideal volume is calculated assuming there are no intermolecular interactions between the components of the mixture. It increases with increasing mole fraction of Jatropha curcas, from **177.4  $\text{cm}^3/\text{mol}$**  to **186.6  $\text{cm}^3/\text{mol}$** , as expected when a larger proportion of Jatropha curcas (a higher molar volume component) is included in the mixture.
- Excess Molar Volume ( $V^E$ ) ( $\text{cm}^3/\text{mol}$ ):** This column represents the difference between the actual molar volume and the ideal volume. It indicates the degree of molecular interaction between Jatropha curcas and the other components in the mixture. A positive excess molar volume suggests that the molecules are experiencing repulsive interactions, while negative excess volume would suggest attractive interactions. In this case, the excess molar volume increases with mole fraction, from **17.6  $\text{cm}^3/\text{mol}$**  to **21.0  $\text{cm}^3/\text{mol}$** , which

indicates that as the mole fraction of *Jatropha curcas* increases, the molecules of the mixture are less compatible, leading to more repulsive interactions.

In summary, the table shows the effects of increasing the mole fraction of *Jatropha curcas* on the physical properties of the mixture, highlighting the changes in density, molar volume, and excess molar volume as a result of molecular interactions. These properties are crucial for understanding how different feedstocks blend together and their potential implications for biodiesel production.

#### 4.2 Trends in Excess Molar Volume for Various Feedstocks

The excess molar volume was found to be highest for combinations of Methyl Stearate with Karanja and lowest for mixtures of Methyl Linoleate with *Jatropha*. These findings suggest that certain combinations of feedstocks and esters result in more stable and efficient biodiesel mixtures.

**Table 4.2: Excess Molar Volume ( $V^E$ ) for Binary Mixtures with Methyl Stearate**

Mole Fraction ( $X_1$ )	Feedstock	Density ( $\text{g}/\text{cm}^3$ )	Molar Volume ( $\text{cm}^3/\text{mol}$ )	Ideal Volume ( $\text{cm}^3/\text{mol}$ )	Excess Molar Volume $V^E$ ( $\text{cm}^3/\text{mol}$ )
0.0000	Karanja	0.861	195.4	178.9	16.5
0.1270	Karanja	0.854	196.7	179.0	17.7
0.2540	Karanja	0.847	198.1	179.2	18.9
0.3811	Karanja	0.840	199.5	179.4	20.1
0.4081	Karanja	0.839	199.8	179.4	20.4
0.5369	Karanja	0.827	201.7	179.7	22.0
0.6639	Karanja	0.815	203.7	180.0	23.7
0.7909	Karanja	0.802	205.2	180.3	24.9
0.8179	Karanja	0.800	205.6	180.5	25.1
1.0000	Karanja	0.772	207.6	186.6	21.0

The table shows data for the molecular interactions of Karanja (*Pongamia pinnata*) as a feedstock for biodiesel mixtures with varying mole fractions ( $X_1$ ) of a fatty acid methyl ester (FAME). For each mole fraction, the table presents the corresponding **density**, **molar volume**, **ideal volume**, and **excess molar volume ( $V^E$ )**, which measures the deviation from ideal mixing behavior.

Starting with a mole fraction of 0.0000 (pure Karanja), the density of the mixture is  $0.861 \text{ g}/\text{cm}^3$ , the molar volume is  $195.4 \text{ cm}^3/\text{mol}$ , and the ideal volume is  $178.9 \text{ cm}^3/\text{mol}$ , with an excess molar volume ( $V^E$ ) of  $16.5 \text{ cm}^3/\text{mol}$ . As the mole fraction increases, corresponding changes in the density, molar volume, and excess molar volume are observed. For instance, at a mole fraction of 0.1270, the density decreases to  $0.854 \text{ g}/\text{cm}^3$ , and the molar volume increases to  $196.7 \text{ cm}^3/\text{mol}$ , while the excess molar volume increases to  $17.7 \text{ cm}^3/\text{mol}$ , indicating more significant molecular interaction between the ester and the feedstock.

As the mole fraction continues to increase (up to 1.0000), the density gradually decreases to  $0.772 \text{ g}/\text{cm}^3$ , and the molar volume increases to  $207.6 \text{ cm}^3/\text{mol}$ . The excess molar volume also shows a general increasing trend, peaking at  $25.1 \text{ cm}^3/\text{mol}$  at a mole fraction of 0.8179, and reaching  $21.0 \text{ cm}^3/\text{mol}$  at the pure feedstock ( $X_1 = 1.0000$ ). These observations suggest that as the proportion of ester increases, the molecular interactions between Karanja and the ester components grow stronger, resulting in larger deviations from ideal mixing behavior. This is reflected in the increasing values of excess molar volume, which influence the overall fuel properties of the biodiesel mixture, such as viscosity, energy density, and performance under different conditions.

In summary, the data reveals how varying the mole fraction of the ester affects the thermodynamic properties of Karanja-based biodiesel mixtures. The increasing excess molar volume with the mole fraction highlights the non-ideal behavior of the mixture, which plays a crucial role in understanding and optimizing biodiesel performance for specific applications.

## 5. Discussion

### 5.1 Implications for Biodiesel Optimization

The study offers crucial insights into the molecular interactions that underpin biodiesel's performance. These molecular interactions, captured by the **Excess Molar Volume ( $V^E$ )**, provide an understanding of how feedstocks and fatty acid methyl esters (FAMEs) blend at the molecular level and how these interactions influence key biodiesel properties, including **viscosity, stability, energy output, and combustion efficiency**.

**Viscosity** is a critical property for biodiesel, as it affects fuel atomization and combustion efficiency in diesel engines. The study's findings indicate that as the mole fraction of ester increases, the excess molar volume also increases, reflecting stronger molecular interactions that may lead to increased viscosity. In such cases, optimizing the proportion of feedstock and ester components in biodiesel formulations can help adjust the viscosity to desired levels for efficient engine operation.

**Cold-flow properties** are another important consideration, particularly in regions with colder climates. Unsaturated fatty acids, which are typically present in higher concentrations in algae-based and other non-edible feedstocks, play a significant role in determining the cold-flow characteristics of biodiesel. The presence of these unsaturated compounds causes more substantial deviations from ideal mixing behavior, which in turn influences the crystallization temperature and flowability of biodiesel in cold temperatures. The study suggests that the molecular interactions in biodiesel blends with higher levels of unsaturated fatty acids will require careful optimization to ensure biodiesel remains fluid in low-temperature environments.

Furthermore, **fuel stability** is an essential aspect of biodiesel performance. The study's insights into excess molar volumes suggest that blending biodiesel with certain feedstocks or esters may influence its oxidative stability, affecting how quickly the fuel degrades when exposed to air and heat. By fine-tuning the feedstock-ester ratios, it may be possible to enhance biodiesel's long-term stability, reduce the formation of sediments, and improve storage and shelf life.

By utilizing the excess molar volume data, biodiesel formulations can be tailored to meet specific application requirements. These formulations can be optimized to provide better **combustion efficiency** (the ability to produce energy from fuel in an internal combustion engine), improve **energy density** (the amount of energy stored per unit volume), and increase overall fuel performance. These findings are valuable for improving biodiesel blends and ensuring they perform optimally under diverse operational conditions.

### 5.2 Future Research Directions

The study opens several avenues for further research aimed at optimizing biodiesel formulations for specific needs. One important direction is exploring the **temperature dependence of excess molar volumes**. As biodiesel blends experience different temperatures during transportation, storage, and engine use, understanding how their thermodynamic properties change with temperature could provide essential insights for improving fuel performance in varying environmental conditions. The temperature dependence could help researchers design biodiesel formulations with improved cold-flow properties, ensuring that they remain fluid and effective even in sub-zero temperatures.

Another promising area of research lies in **ternary biodiesel mixtures**, which involve blending multiple feedstocks and esters. Currently, the study primarily focuses on binary mixtures of one feedstock with one ester, but real-world biodiesel formulations often include a variety of feedstocks (such as combinations of vegetable oils, animal fats, and algae oils) and esters. Ternary mixtures are more complex and may exhibit unique molecular interactions that can

further influence biodiesel properties like viscosity, energy output, and combustion behavior. By studying these ternary blends, researchers can develop biodiesel formulations that better meet the requirements of diverse applications and operating conditions.

Moreover, future studies could delve deeper into the long-term **stability and performance** of biodiesel blends. The impact of environmental factors such as humidity, sunlight, and temperature on biodiesel's molecular interactions, oxidative stability, and overall performance over extended periods is still not fully understood. Research focused on the aging characteristics of biodiesel can help optimize formulations to maintain their quality over time, reducing the risk of fuel degradation and improving shelf life.

Finally, **biorefinery integration** offers an exciting frontier for research. By incorporating advanced molecular understanding of biodiesel's properties into the broader context of biofuel production, biodiesel formulations could be optimized in combination with other renewable biofuels, such as bioethanol or biogas. This could lead to the development of more efficient, sustainable, and integrated biofuel systems that optimize feedstock use, reduce waste, and maximize the overall efficiency of biofuel production.

## 6. Conclusion

In conclusion, this study offers valuable insights into the **molecular interactions** that govern biodiesel mixtures, with a specific focus on the **Excess Molar Volume ( $V^E$ )**. By exploring how different feedstocks and fatty acid methyl esters interact at the molecular level, this research contributes to the optimization of biodiesel formulations for better **fuel performance, energy output, and combustion efficiency**. The data derived from excess molar volume studies can help biodiesel producers tailor blends to meet the demands of specific applications, particularly in terms of **viscosity, stability, and cold-flow properties**.

As biodiesel continues to gain prominence as a renewable energy source, the ability to optimize its properties for diverse operational conditions is crucial for advancing its role in the global energy landscape. The findings of this study are therefore of significant importance not only for biodiesel producers but also for researchers focused on the development of more efficient, sustainable, and high-performance biofuels.

## References

- Adhikesavan, C., Ganesh, D., & Augustin, V. C. (2022). Effect of quality of waste cooking oil on the properties of biodiesel, engine performance, and emissions. *Clean Chemical Engineering*, 4, 100070. <https://doi.org/10.1016/j.cce.2022.100070>
- Ateeq, E. A. (2015). *Biodiesel viscosity on flash point determination* (Master's thesis). An-Najah National University, Nablus, Palestine.
- Cisek, J., & Mruk, A. (2012). Characteristic of a diesel engine fuelled by natural rape oil. *Proceedings of the Institute of Vehicle Engineers, Warsaw University of Technology*, 1, 5–16.
- Cisek, J., Mruk, A., & Hlavna, V. (2011). The properties of a HDV diesel engine fuelled by crude rapeseed oil. *Teka Kom. Motoryz. I Energetyki Rol.*, 11, 29–39.
- El-Hagar, M. M. E.-G. (2020). Effect of fuel cetane numbers on reducing the ignition delay period and exhaust emissions from DI diesel engine. *WSEAS Transactions on Heat and Mass Transfer*, 99, 99–105.
- Gad, M. S., Abdel Aziz, M. M., & Kayed, H. (2022). Impact of different nano additives on performance, combustion, emissions and exergetic analysis of a diesel engine using waste cooking oil biodiesel. *Propulsion and Power Research*, 11, 209–223. <https://doi.org/10.1016/j.jprr.2022.01.009>
- Gao, J., Wang, Y., Li, X., Wang, S., Ma, C., & Wang, X. (2022). Catalytic effect of diesel PM derived ash on PM oxidation activity. *Chemosphere*, 299, 134445. <https://doi.org/10.1016/j.chemosphere.2022.134445>
- Government of Poland. (2024). *Production of biocomponents in 2023*. <https://www.gov.pl/web/kowr/produkcja-biokomponentow-w-2023r> (accessed August 9, 2024)
- Greena. (2024). And do you recycle your used cooking oil at home? *Greena*. <https://www.greena.com/publication/and-do-you-recycle-your-used-cooking-oil-at-home/> (accessed August 9, 2024)
- Guo, S., Yang, Z., & Gao, Y. (2016). Effect of adding biodiesel to diesel on the physical and chemical properties and engine performance of fuel blends. *Journal of Biobased Materials and Bioenergy*, 10, 34–43. <https://doi.org/10.1166/jbmb.2016.1450>

- Knothe, G. (2014). A comprehensive evaluation of the cetane numbers of fatty acid methyl esters. *Fuel*, 119, 6–13. <https://doi.org/10.1016/j.fuel.2013.11.065>
- Kukana, R., & Jakhar, O. P. (2022). Performance, combustion and emission characteristics of a diesel engine using composite biodiesel from waste cooking oil—Hibiscus Cannabinus oil. *Journal of Cleaner Production*, 372, 133503. <https://doi.org/10.1016/j.jclepro.2022.133503>
- Kurczyński, D., & Łagowski, P. (2019). Performance indices of a common rail-system CI engine powered by diesel oil and biofuel blends. *Journal of Energy Institute*, 92, 1897–1913. <https://doi.org/10.1016/j.joei.2019.05.008>
- Kurczyński, D., Łagowski, P., & Wcisło, G. (2021). Experimental study of fuel consumption and exhaust gas composition of a diesel engine powered by biodiesel from waste of animal origin. *Energies*, 14(10), 3472. <https://doi.org/10.3390/en14103472>
- Kurczyński, D., Łagowski, P., & Wcisło, G. (2021). Experimental study into the effect of the second-generation BBuE biofuel use on the diesel engine parameters and exhaust composition. *Fuel*, 284, 118982. <https://doi.org/10.1016/j.fuel.2020.118982>
- Mattos, R. A., Bastos, F. A., & Tubino, M. (2015). Correlation between the composition and flash point of diesel-biodiesel blends. *Journal of the Brazilian Chemical Society*, 26, 393–395. <https://doi.org/10.5935/0103-5053.20150031>
- Mehregan, M., & Moghiman, M. (2018). Effects of nano-additives on pollutants emission and engine performance in a urea-SCR equipped diesel engine fueled with blended-biodiesel. *Fuel*, 222, 402–406. <https://doi.org/10.1016/j.fuel.2018.02.102>
- OECD & FAO. (2023). *OECD-FAO agricultural outlook 2023–2032*. OECD Publishing. <https://doi.org/10.1787/3b9f918b-en>
- Pattanaik, B. P., & Misra, R. D. (2017). Effect of reaction pathway and operating parameters on the deoxygenation of vegetable oils to produce diesel-range hydrocarbon fuels: A review. *Renewable and Sustainable Energy Reviews*, 73, 545–557. <https://doi.org/10.1016/j.rser.2017.01.115>
- Raj, F. R. M. S., & Sahayaraj, J. W. (2010). A comparative study over alternative fuel (biodiesel) for environmentally friendly emission. In *Proceedings of the Recent Advances in Space Technology Services and Climate Change 2010 (RSTS & CC-2010)* (pp. 80–86). Chennai, India.
- Rosiak, E., Łopaciuk, W., & Krzemiński, M. (2011). *Produkcja biopaliw i jej wpływ na światowy rynek zbóż oraz roślin oleistych i tłuszczów roślinnych*. Instytut Ekonomiki Rolnictwa i Gospodarki Żywnościowej—Państwowy Instytut Badawczy IERiGŻ-PIB.
- Saxena, P., Jawale, S., & Joshipura, M. H. (2013). A review on prediction of properties of biodiesel and blends of biodiesel. *Procedia Engineering*, 51, 395–402. <https://doi.org/10.1016/j.proeng.2013.01.056>
- Sayyed, S., Das, R. K., & Kulkarni, K. (2022). Experimental investigation for evaluating the performance and emission characteristics of DIC engine fueled with dual biodiesel-diesel blends of Jatropha, Karanja, Mahua, and Neem. *Energy*, 238, 121787. <https://doi.org/10.1016/j.energy.2021.121787>
- Semorile, N. F., Alviso, D., & Romano, S. D. (2023). Flash point and refractive index measurements of diesel and biodiesel, and their binary blends with n-butanol and n-pentanol. *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, 45, 28. <https://doi.org/10.1007/s40940-023-00970-7>
- Sharma, V., Hossain, A. K., Ahmed, A., & Rezk, A. (2022). Study on using graphene and graphite nanoparticles as fuel additives in waste cooking oil biodiesel. *Fuel*, 328, 125270. <https://doi.org/10.1016/j.fuel.2022.125270>
- Szabados, G., & Bereczky, A. (2018). Evaluation analysis of particulate relevant emission of a diesel engine running on fossil diesel 1 and different biofuels. *Energy*, 161, 1139–1153. <https://doi.org/10.1016/j.energy.2018.07.096>
- Thapa, S., Indrawan, N., & Bhoi, P. R. (2018). An overview on fuel properties and prospects of Jatropha biodiesel as fuel for engines. *Environmental Technology and Innovation*, 9, 210–219. <https://doi.org/10.1016/j.eti.2018.03.008>
- Thompson, W., & Meyer, S. (2013). Second generation biofuels and food crops: Co-products or competitors? *Global Food Security*, 2, 89–96. <https://doi.org/10.1016/j.gfs.2013.03.002>
- Varuwel, E. G., Mrad, M., Tazerout, M., & Aloui, F. (2012). Experimental analysis of biofuel as an alternative fuel for diesel engines. *Applied Energy*, 94, 224–231. <https://doi.org/10.1016/j.apenergy.2012.01.019>
- Wcisło, G. (2013). *Analysis of the impact of rapeseed varieties on the properties of RME biofuels and diesel engine operation parameters*. FALL Publishing House.
- Wcisło, G. (2013). Determination of the impact of FAME biocomponent on the fraction composition of diesel engine fuels. *Combustion Engine*, 154, 1098–1103.
- Wcisło, G. (2014). Determination of the rheological properties of biofuels containing SBME biocomponent. *Teka. Kom. Motoryz. I Energetyki Rol.*, 14, 185–190.

- Weisło, G., & Pracuch, B. (2016). Determination of the distillation parameters of the milesPLUS® diesel fuel comprising a bio-component in the form of methyl esters of corn oil. *Teka. Kom. Motoryz. I Energetyki Rol.*, 16, 83–86.
- Yadav, A. K., Khan, M. E., Dubey, A. M., & Pal, A. (2016). Performance and emission characteristics of a transportation diesel engine operated with non-edible vegetable oils biodiesel. *Case Studies in Thermal Engineering*, 8, 236–244. <https://doi.org/10.1016/j.csite.2016.06.001>
- Zhang, Y., Lou, D., Tan, P., Hu, Z., Fang, L. (2022). Effects of waste-cooking-oil biodiesel blends on diesel vehicle emissions and their reducing characteristics with exhaust after-treatment system. *Journal of Cleaner Production*, 381, 135190. <https://doi.org/10.1016/j.jclepro.2022.135190>

The logo for IJEEETE is a large, light green shield-shaped emblem. At the top, the acronym 'IJEEETE' is written in a bold, grey, sans-serif font. Below the text is a stylized flower with six petals in various colors: red, cyan, purple, yellow, and two shades of green. The flower is surrounded by a laurel wreath of green leaves. The entire emblem is set against a white background.

IJEEETE