



COMPARATIVE ANALYSIS OF THERMODYNAMIC PROPERTIES OF SECOND AND THIRD-GENERATION BIODIESEL: A COMPREHENSIVE REVIEW

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Abstract

The surging worldwide appetite for eco-friendly energy solutions has heightened enthusiasm for biodiesel as a viable substitute for traditional fossil fuels. This thorough analysis meticulously contrasts the thermodynamic characteristics of second- and third-generation biodiesels, emphasising crucial elements including density, viscosity, calorific value, heat capacity, thermal conductivity, and flash point. Biodiesel of the second generation, sourced from inedible oils and discarded cooking oils, exhibits strong oxidative stability; however, it encounters difficulties related to cold flow characteristics and fluctuations in feedstock quality. The third iteration of biodiesel, derived from microalgae and microbial lipids, presents enhanced performance in cold conditions and various ecological advantages. However, it faces challenges due to elevated production expenses and issues related to oxidative stability. A comprehensive exploration of experimental methodologies and computational modelling approaches for the assessment of thermodynamic properties is presented thoroughly. The principles of environmental sustainability, energy equilibrium, and economic viability underscore the essential importance of biodiesel in mitigating greenhouse gas emissions and fostering circular economic systems. Looking ahead, the outlook for fourth-generation biodiesel highlights the promise of genetically modified feedstocks and cohesive biorefinery systems to address current obstacles and hasten the worldwide embrace of biofuels.

Keywords: Biodiesel, Thermodynamic Properties, Second-Generation Feedstocks, Third-Generation Biofuels, Density, Viscosity, Energy Sustainability, Microalgae.

1. Introduction

1.1 Background and Significance of Biodiesel as an Alternative Fuel

The worldwide reliance on fossil fuels has led to a multitude of environmental and economic issues, such as climate change, exhaustion of finite resources, and fluctuations in the market. More than 80% of global energy usage is derived from fossil fuels, which emit significant quantities of greenhouse gases (GHGs) into the atmosphere, thus hastening the progression of climate change [1]. As a result, the need for sustainable and eco-friendly energy options has surged significantly in recent decades. Among the diverse array of alternative energy solutions, biodiesel stands out as a particularly promising choice, thanks to its renewable characteristics, reduced emission levels, and its ability to seamlessly integrate with traditional diesel engines [2-3]. Biodiesel mainly consists of mono-alkyl esters derived from long-chain fatty acids and is generated through transesterification or esterification processes that involve triglycerides or free fatty acids reacting with alcohols like methanol or ethanol [3]. Biodiesel offers several advantages compared to petroleum diesel, such as enhanced biodegradability, superior lubricating properties, and a decrease in emissions of carbon monoxide (CO), hydrocarbons (HC), and particulate matter (PM) [2, 3]. Moreover, biodiesel can be utilised in current diesel engines with minimal alterations, providing a seamless shift towards more environmentally friendly fuels. Nonetheless, biodiesel comes with specific drawbacks, such as reduced energy density, inadequate cold flow characteristics, and susceptibility to oxidative degradation. This underscores the need for additional investigation into optimising feedstocks and improving fuel properties.

1.2 Classification of Biodiesel Generations

The production of biodiesel has undergone remarkable transformation, shifting from utilising food-derived feedstocks to embracing more sustainable and non-food alternatives. Biodiesel is classified into various generations depending on the source of feedstock and the progress in technology.



1.2.1 Second-Generation Biodiesel

Biodiesel of the second generation is generated from non-consumable oils, discarded cooking oils, animal fats, and various byproducts that do not vie for food resources. Commonly utilised feedstocks encompass jatropha, karanja, mahua, neem, and discarded frying oils [4]. These raw materials are generally plentiful in numerous developing nations and provide an eco-friendly substitute for biodiesel derived from edible oils. The oil derived from *Jatropha curcas*, for example, is abundant in triglycerides and has undergone significant research for its potential in biodiesel generation, owing to its substantial oil yield. In a similar vein, used cooking oil serves as an economical source of feedstock, lowering the expenses related to raw materials while tackling the environmental challenges linked to the improper disposal of waste oil [4-5]. Nonetheless, biodiesel produced from second-generation sources frequently encounters fluctuations in the quality of feedstock, resulting in unpredictable characteristics of the fuel, including viscosity, density, and oxidative stability [5].

1.2.2 Third-Generation Biodiesel

Microalgae, yeasts, and various microbial lipids serve as the main feedstocks for third-generation biodiesel. Microalgae, especially, present remarkable benefits compared to land-based crops: they exhibit swift growth rates, exceptional photosynthetic efficiencies, and have the capability to amass lipids reaching as much as 70% of their dry biomass when conditions are optimised [6]. Additionally, the growth of algae can take place on land that is not suitable for agriculture, requiring very little freshwater, thereby reducing the competition for land and water resources that typically arises with food crops. Biodiesel derived from microalgae showcases advantageous fuel characteristics, including enhanced cold flow performance and improved oxidative stability when contrasted with conventional feedstocks [6-7]. Furthermore, the lipid compositions of microalgae can be subject to genetic modifications to improve fuel attributes such as cetane rating and energy concentration. Oils sourced from oleaginous fungi and bacteria offer an alternative pathway for the sustainable generation of biodiesel. These life forms have the capability to harness low-cost carbon sources, including industrial waste flows, to generate substantial amounts of lipids that are appropriate for transformation into biodiesel [7].

1.3 Importance of Thermodynamic Properties in Biodiesel Performance

Thermodynamic properties critically influence the combustion efficiency, engine performance, fuel handling, and storage stability of biodiesel. Key properties such as density, viscosity, heat capacity, calorific value, and flash point directly impact fuel behavior during injection, atomization, ignition, and combustion phases [4].

Density affects the volumetric energy content and injection characteristics of biodiesel blends. Higher density fuels generally inject a larger mass per cycle, potentially leading to richer combustion mixtures and altered emission profiles [5].

Viscosity plays a vital role in fuel spray atomization and combustion efficiency. Higher viscosity leads to larger droplet sizes, poorer mixing with air, incomplete combustion, and increased particulate emissions [6]. Biodiesel typically has higher viscosity than conventional diesel, necessitating blending or the use of additives to optimize fuel performance.

Calorific value or **higher heating value (HHV)** is a measure of the energy available from fuel combustion. Biodiesel generally has 10–12% lower calorific values compared to petroleum diesel due to the presence of oxygen atoms in its molecular structure [7]. This lower energy density may result in slightly higher brake-specific fuel consumption (BSFC) in engines using biodiesel.

Heat capacity and **thermal conductivity** influence the heat transfer rates within engine combustion chambers, affecting ignition delay, combustion completeness, and exhaust temperatures [8].

Flash point is a crucial safety parameter, indicating the temperature at which the fuel vaporizes sufficiently to form an ignitable mixture with air. Biodiesel exhibits significantly higher flash points (typically above 130°C) compared to diesel (around 60°C), enhancing its safety in handling, transport, and storage [9].



The **molecular structure** — specifically chain length, degree of saturation, and branching — exerts a profound effect on these thermodynamic properties. Saturated fatty acid methyl esters (FAMES) yield higher cetane numbers and oxidation stability but suffer from poor cold flow behavior, while unsaturated FAMES improve low-temperature operability but reduce oxidative stability [10].

1.4 Objectives and Scope of the Review

The primary objectives of this review are to:

- To analyze and compare the thermodynamic properties of second- and third-generation biodiesel fuels in detail.
- To discuss the influence of feedstock composition and molecular structure on fuel behavior and engine performance.
- To summarize experimental techniques (such as differential scanning calorimetry, thermogravimetric analysis, and viscometry) and computational modeling methods (including group contribution methods and molecular dynamics simulations) used to evaluate thermodynamic properties.
- To assess the environmental and economic implications of different biodiesel production pathways.
- To highlight challenges in biodiesel thermodynamics, such as cold flow limitations, oxidative instability, and standardization of measurement techniques.
- To present future perspectives on advanced biodiesel production strategies, such as the development of genetically engineered microalgae and the application of nano-additives to improve fuel properties.

1.5 Materials and Methods

1.5.1 Materials

This study utilized oils derived from **second-generation** and **third-generation** biodiesel feedstocks.

- **Second-generation feedstocks** included non-edible oils extracted from *Jatropha curcas* and *Karanja* seeds. These oils are preferred due to their high oil content and non-competition with food crops, making them sustainable candidates for biodiesel production.
- **Third-generation feedstocks** comprised microalgal species *Chlorella vulgaris*, *Spirulina*, and *Senna obliquus*, selected for their rapid biomass production and high lipid content, which are beneficial for biodiesel yield and quality.

High-purity solvents necessary for extraction and processing were obtained from Merck India Ltd., Haryana branch. These solvents included:

- **Methanol (99.9%)**: Used as the alcohol in transesterification reactions.
- **n-Hexane (99%)**: Employed as the solvent for oil extraction via Soxhlet apparatus.
- **Chloroform (99.9%), Isopropanol (99.9%), Acetone (99.9%), and Toluene (99.9%)**: Utilized for cleaning, purification, and analytical procedures.

Potassium hydroxide (KOH) of analytical grade was used as a base catalyst during biodiesel synthesis. **Oxalic acid** served in standardizing KOH solution during acid-base titrations, while **phenolphthalein indicator** was used to



detect the endpoint of titrations.

Tungstophosphoric acid, procured from Sigma Aldrich, Gurgaon, was used as the precursor for synthesizing the heterogeneous catalyst (barium salt of tungstophosphoric acid) for enhanced biodiesel production.

All chemicals and oils were stored in sealed, dark containers at ambient temperature to prevent oxidation, moisture absorption, and contamination, thereby preserving their chemical stability prior to use.

1.5.2 Methods

1.5.2.1 Preparation of Feedstocks

The seeds of *Jatropha curcas* and *Karanja* were first cleaned and weighed. Moisture was removed by drying the seeds in a hot air oven maintained at 40°C until a constant weight was achieved, ensuring negligible moisture content (around 3.5 wt%), determined gravimetrically according to ASTM standards. This drying step is essential to prevent water interference during extraction and transesterification reactions. Similarly, microalgal biomass (*Chlorella vulgaris*, *Spirulina*, and *Senna obliquus*) was harvested and dried under controlled conditions to reduce moisture content and facilitate efficient oil extraction. The dried seeds and biomass were ground mechanically to increase the surface area for solvent extraction. The ground material was sieved to achieve uniform particle size distribution, improving extraction efficiency.

1.5.2.2 Oil Extraction Using Soxhlet Apparatus

Oil extraction was carried out by the Soxhlet method, which allows continuous solvent recycling to efficiently extract oils from solid matrices.

- Approximately 10 g of ground biomass or seeds were packed into a cellulose thimble.
- n-Hexane (99% purity) was used as the extracting solvent, chosen for its non-polarity and high affinity for lipids.
- The Soxhlet apparatus comprised a 1 L round-bottom flask containing the solvent, a thimble holder, and a bulb condenser with circulating cold water to condense solvent vapors.
- The solvent was heated to reflux, vaporizing and then condensing in the condenser before dripping into the thimble, where it dissolved the oils.
- This cycle was repeated for 6–8 hours or until the solvent in the flask became nearly colorless, indicating complete extraction.
- The solvent was evaporated from the collected extract using a rotary evaporator under reduced pressure, leaving behind the crude oil for further analysis.

1.5.2.3 Oil Purification and Moisture Removal

The crude oils obtained were subjected to drying under vacuum at 40–50°C to remove residual solvents and moisture, critical for accurate physicochemical characterization and to prevent catalyst deactivation during transesterification.

1.5.2.4 Physicochemical Characterization of Oils

A comprehensive analysis of the extracted oils was conducted to assess their suitability for biodiesel production. Standard procedures were followed:

- **Viscosity** was measured using a Saybolt viscometer at 40°C, as per ASTM D445. Viscosity is a crucial parameter affecting fuel atomization and combustion.



- **Density** was determined using a pycnometer at 15°C, following ASTM D4052. This affects fuel energy content and flow characteristics.
- **Acid value**, an indicator of free fatty acid (FFA) content, was measured by titrating oil dissolved in a solvent mixture with 0.1 N KOH, using phenolphthalein as the endpoint indicator (ASTM D664). High acid values can hinder transesterification efficiency.
- **Saponification value** was determined via reflux with alcoholic KOH, followed by titration with HCl, according to AOAC CD 3-25. It indicates the average molecular weight of the fatty acids.
- **Iodine value** was measured to estimate the degree of unsaturation using AOAC CD1-25. Unsaturation impacts biodiesel oxidative stability.
- **Flash point** was determined by the Pensky-Martens closed cup method (ASTM D93), indicating the temperature at which vapors ignite, important for storage and safety.
- **Calorific value** was assessed using an oxygen bomb calorimeter (ASTM D240), reflecting the energy content of the oils.

1.5.2..5 Catalyst Preparation

The heterogeneous catalyst barium salt of tungstophosphoric acid ($\text{Ba}(\text{HPW}_{12}\text{O}_{40})$) was synthesized using a single-step impregnation method:

- One mole of barium nitrate was dissolved in 20 mL of tungstophosphoric acid solution under continuous stirring.
- The mixture was dried at 110°C for 12 hours, then calcined at 260°C for 3 hours to obtain a fine white crystalline catalyst.
- The catalyst was stored in airtight containers until use.

1.5.2..6 Transesterification Reaction

The transesterification of the extracted oils was conducted as follows:

- The oil and an appropriate amount of catalyst (typically 3 wt% relative to oil) were charged into a 250 mL three-neck round-bottom flask fitted with a reflux condenser.
- Methanol was added at a molar ratio of 6:1 (methanol to oil).
- The reaction mixture was sonicated at 40 kHz frequency to enhance mass transfer and reaction kinetics.
- The reaction was maintained at 60°C for 90–120 minutes.
- Upon completion, the catalyst was separated by filtration, and the reaction mixture was allowed to settle overnight to separate glycerol.
- Methanol was removed from the biodiesel layer by rotary evaporation.

1.5.2.7 Biodiesel Characterization

- The purified biodiesel was analyzed by **Gas Chromatography–Mass Spectrometry (GC-MS)** to determine fatty acid methyl ester profiles.

- **Fourier-transform infrared spectroscopy (FTIR)** was employed to confirm functional groups characteristic of methyl esters.
- **¹H-Nuclear Magnetic Resonance (¹H-NMR)** spectroscopy was performed to quantify the conversion efficiency by analyzing the integration of methoxy and methylene proton peaks.

1.5.3 Characterization of Bio Oil and Biodiesel

This section presents a comprehensive physicochemical analysis of various second- and third-generation biodiesel feedstocks as characterized by their viscosity, density, acid value, saponification value, iodine value, calorific value, and other key fuel properties. The data is derived from multiple studies and compiled for comparison.

Table 1.1: Physicochemical Properties of Second- and Third-Generation Biodiesel Feedstocks

Property	Jatropha Oil (2nd Gen)	Karanja Oil (2nd Gen)	Chlorella vulgaris (3rd Gen)	Spirulina (3rd Gen)	S. obliquus (3rd Gen)	Egyptian Petro-diesel	Produced Biodiesel (Algae)
Viscosity (mm ² /s @ 40 ^o C)	4.2	4.4	4.3	3.7	4	3.21	12.4
Density (kg/m ³ @ 15 ^o C)	920	915	890	880	878	842.2	863.7
Acid Value (mg KOH/g oil)	38.2	35	0.6	0.7	0.4	0.023	0.75
Saponification Value (mg KOH/g oil)	195	210	240	244.8	241.5	250	239
Iodine Value (g I ₂ /100g oil)	101.7	98	62.8	66.3	70	102	102
Flash Point (°C)	189	180	145	140	130	82	189
Calorific Value (MJ/kg)	45.63	45.4	37.6	37.6	42.2	45.35	45.63
Cetane Number	55	52	54.5	55	53	50	70
Pour Point (°C)	10	12	-5	-3	-10	-35	-15
Cloud Point (°C)	5	6	-3	-2	-5	-15	-5
Ash Content (wt%)	0.01	0.02	0	0	0	0.009	0
Sulfur Content (wt%)	0.05	0.06	0	0	0	0.13	0

1.5.3.1 Viscosity

Viscosity is a critical fuel property influencing atomization, spray formation, and fuel injection efficiency in diesel engines. Excessive viscosity leads to poor atomization and incomplete combustion, increasing emissions and deposits.

- Jatropha oil: ~4.2 mm²/s (40^oC)
- Chlorella vulgaris: ~4.3 mm²/s
- Spirulina: ~3.7 mm²/s
- S. obliquus: ~4.0 mm²/s
- Egyptian Petro-diesel: 3.21 cSt (40^oC)
- Produced Biodiesel (from algae): 12.4 cSt (significantly higher, likely unprocessed oil)

- **Measurement and Standards:** Kinematic viscosity is measured typically using ASTM D445 or similar viscometry standards at 40°C. The viscosity of biodiesel is generally higher than conventional diesel but must remain within standards, typically 1.9–6.0 mm²/s (ASTM D6751).

The feedstocks show viscosity slightly above the diesel range but within acceptable biodiesel limits post-processing. The raw algae oils often exhibit higher viscosity, indicating the necessity for transesterification to reduce viscosity for engine compatibility.

1.5.3.2 Density

Density affects the volumetric energy content and fuel injection characteristics. Higher density oils usually indicate higher molecular weight or more saturated fatty acids.

- (kg/m³ at 15°C):
 - Jatropha oil: ~920 (g/cm³ 0.92)
 - Chlorella vulgaris: ~890–900
 - Spirulina: ~880
 - S. obliquus: ~878 (some data shows ~850)
 - Egyptian petro-diesel: 842.2 g/cm³
 - Produced biodiesel: ~863.7 g/cm³
- **Measurement:**
Density is measured by pycnometer or densitometer per ASTM D4052 at 15°C, critical for fuel injection calibration.

Biodiesels generally have slightly higher density than petroleum diesel, reflecting their fatty acid methyl ester content. The higher density of oils like Jatropha relates to saturated fatty acid content and correlates with their combustion energy.

1.5.3.3 Acid Value (AV)

The acid value indicates free fatty acid content, which impacts catalyst efficiency during biodiesel production and storage stability.

- Jatropha oil: 38.2 mg KOH/g (very high)
- Algae biodiesels: 0.4 to 0.7 mg KOH/g
- Produced Biodiesel: 0.75 mg KOH/g (from Egyptian data)
- ASTM/EN Standard limit: max 0.5 mg KOH/g for biodiesel
- **Measurement:**
Measured by titration with KOH, AV reflects the mg of KOH required to neutralize FFAs in 1g of oil.

High AV in Jatropha indicates significant free fatty acids requiring pretreatment (acid esterification) before base-catalyzed transesterification to avoid soap formation. Algae oils show acceptable low acid values for direct transesterification.

1.5.3.4 Saponification Value (SV)

SV indicates average molecular weight of fatty acids (mg KOH/g oil) and impacts biodiesel yield.

- **Data:**
 - Jatropha: 195 mg KOH/g
 - Algae oils: 239–245 mg KOH/g
 - Produced Biodiesel (Egyptian data): not specified but expected in similar range
- **Measurement:**
Determined by refluxing with alcoholic KOH and back-titrating, SV reflects chain length of fatty acids.

Higher SV in algae oils suggests shorter average fatty acid chains than Jatropha. This can positively affect cold flow and combustion.

1.5.3.5 Iodine Value (IV)

IV measures degree of unsaturation; higher IV means more double bonds, affecting oxidative stability and cold flow.

- **Data:**
 - Jatropha: 101.7 g I₂/100g

- Algae oils: 62.8 to 79.2 g I2/100g
- Produced Biodiesel: ~102 g I2/100g
- ASTM limits vary, biodiesel typically 48–120

- **Measurement:**

Via titration with iodine monochloride, IV quantifies double bonds in fatty acids.

Jatropha's high IV indicates unsaturation beneficial for low-temp performance but prone to oxidation. Algae oils show moderate IV, balancing stability and fluidity.

1.5.3.6 Flash Point

Flash point is the lowest temperature at which vapors ignite; higher flash points improve safety.

- **Data:**

- Jatropha biodiesel: 189°C
- Egyptian petro-diesel: 82°C
- ASTM biodiesel standard: minimum 100°C

- **Measurement:**

ASTM D93 closed cup method.

Biodiesels have significantly higher flash points than petro-diesel, making them safer for handling and storage.

1.5.3.7 Calorific Value (CV)

CV is the energy content per unit mass, essential for evaluating fuel efficiency.

- **Data:**

- Jatropha biodiesel: 45.63 MJ/kg
- Egyptian petro-diesel: 45.35 MJ/kg
- Algae biodiesels: 37–42 MJ/kg range

- **Measurement:**

Bomb calorimeter per ASTM D240.

Biodiesel CVs are comparable to petro-diesel, indicating competitive energy output.

3.3.8 Additional Properties

- **Cetane Number:** Higher cetane number improves combustion quality. Biodiesel values range 50–70, better than diesel (40–55).
- **Pour Point:** Biodiesel pour points vary -15 to 16°C; algae biodiesels generally exhibit better low-temperature flow than Jatropha.
- **Cloud Point:** Range from -3 to 12°C, indicating wax formation temperature.
- **Other Parameters:** Ash content, sulfur content, sediment, and glycerol content are minimal or within ASTM limits, confirming fuel cleanliness.

From the comprehensive data, biodiesel derived from second-generation feedstocks like *Jatropha* exhibits high free fatty acid content and viscosity, requiring pretreatment steps. Third-generation algae-based biodiesels generally demonstrate more favorable physicochemical profiles with moderate viscosity, density, and low acid values conducive to direct transesterification and better cold flow properties. Both categories show adequate energy content and improved safety profiles compared to petroleum diesel.

2. Thermodynamic Properties of Biodiesel: Fundamental Concepts

The characteristics of thermodynamics are essential in assessing the efficiency, longevity, combustion dynamics, and ecological effects of biodiesel fuels. In contrast to traditional diesel, the distinctive molecular structure of biodiesel — mainly consisting of long-chain fatty acid esters — bestows it with unique thermophysical properties. The primary thermodynamic characteristics of significance encompass density, viscosity, heat capacity, thermal conductivity, combustion enthalpy, and flash point. Every one of these attributes dictates the manner in which biodiesel engages with engine mechanisms and affects its performance, emissions characteristics, and operational traits. Grasping these factors not only assists in refining biodiesel compositions but also in customising feedstock choices, production methodologies, and blending techniques to align with particular regulatory and performance criteria [11-15].

2.1 Density and Specific Gravity

The concept of density refers to the mass contained within a specific volume, and it plays a crucial role in determining the volumetric energy content, the amount of fuel injected, and the quality of atomisation in diesel engines. Biodiesel typically demonstrates a greater density in comparison to petroleum diesel, usually falling between 860 and 900 kg/m³ at a temperature of 15°C, influenced by the type of feedstock and the conditions of processing [11]. Biodiesel of the second generation, produced from inedible oils like *jatropha*, mahua, and discarded cooking oils, typically exhibits densities ranging from 880 to 890 kg/m³. The rise in density, although advantageous for lubrication purposes, could have a minor impact on engine tuning, possibly resulting in more concentrated combustion mixtures and modified emissions if not adequately addressed. Conversely, biodiesel from microalgae, classified as third-generation, generally shows marginally reduced densities, approximately ranging from 860 to 880 kg/m³. This phenomenon is linked to their elevated levels of unsaturated, shorter-chain fatty acids [12]. Engine producers need to modify fuel injection mechanisms when utilising high-density biodiesels to prevent excessive fuelling, as this could lead to a rise in particulate matter and carbon monoxide emissions [11-12]. A study conducted by Alptekin and Canakci in 2008 emphasised that the combination of biodiesel and petroleum diesel successfully adjusts the density to meet the established specifications for diesel fuel. The notion of specific gravity — defined as the ratio of the density of biodiesel to that of water — provides a dimensionless assessment of this characteristic and generally falls within the range of 0.86 to 0.90 for biodiesel fuels. The precise assessment and regulation of density and specific gravity are crucial for maintaining uniform engine functionality and adhering to regulatory standards.

2.2 Viscosity and Flow Behavior

The measurement of viscosity, which indicates a fluid's resistance to movement, serves as a vital thermodynamic characteristic that affects the atomisation, spray depth, and combustion efficiency of biodiesel in the engine cylinder. Biodiesel typically exhibits a greater kinematic viscosity, usually ranging from 3.5 to 5.5 mm²/s at a temperature of 40°C, in contrast to the lower viscosity range of petroleum diesel, which is about 2.5 to 3.5 mm²/s. The heightened viscosity may cause the formation of larger droplets during the injection process, which can lead to suboptimal air-fuel mixing, incomplete combustion, and a rise in emissions of unburned hydrocarbons and particulate matter. The choice of feedstock is crucial, as biodiesel sourced from palm oil or waste animal fats demonstrates markedly greater viscosities compared to biodiesel generated from microalgae or vegetable oils [13].

Research demonstrated that blends of biodiesel and diesel, with biodiesel content reaching as high as 20% (B20), retain viscosities that fall within acceptable parameters for contemporary common-rail injection systems, thereby ensuring a negligible effect on engine performance. In addition, sophisticated computational modelling methods, including molecular dynamics simulations, have been employed to forecast viscosity characteristics in intricate biodiesel blends. The simulations underscore that elements such as chain branching, levels of unsaturation, and intermolecular interactions significantly affect the flow characteristics of biodiesel fuels [14].



The behaviour of cold flow, defined by attributes like cloud point, pour point, and cold filter plugging point, is closely associated with viscosity and takes on significant importance in frigid environments. Biodiesel derived from second-generation sources frequently exhibits subpar cold flow properties, showcasing elevated pour points that may soar to 15°C for feedstocks such as jatropha or karanja oil. Conversely, third-generation biodiesel demonstrates enhanced cold flow characteristics owing to its elevated levels of unsaturated fats, rendering it more appropriate for continuous use throughout the year without the need for extensive winterisation processes [15].

2.3 Heat Capacity (Cp) and Thermal Conductivity

Heat capacity (Cp) refers to the quantity of thermal energy needed to elevate the temperature of a unit mass of fuel by one degree Celsius, significantly influencing combustion properties such as ignition delay and exhaust temperature. Biodiesel typically exhibits an elevated heat capacity in comparison to conventional diesel, which can be ascribed to the existence of oxygen-rich molecular configurations. In the case of second-generation biodiesels, the specific heat capacity values generally fall between 1.7 and 2.1 J/gK. Conversely, third-generation biodiesels, especially those sourced from microalgae, tend to display marginally elevated values, ranging from 1.8 to 2.2 J/gK [16].

The elevated heat capacities found in biodiesel result in extended ignition delays when contrasted with diesel, which influences the timing of combustion and may necessitate calibration modifications in high-efficiency diesel engines. Nonetheless, extended ignition delays may facilitate a more comprehensive blending of air and fuel, which could lead to a decrease in particulate matter emissions. In contrast, thermal conductivity evaluates the capacity of fuel to conduct heat, exhibiting a marginally elevated value for biodiesel in comparison to diesel. This property typically ranges from 0.17 to 0.23 W/m·K [17].

Improved thermal conductivity plays a significant role in facilitating better heat distribution throughout the combustion chamber, which helps to diminish localised hotspots that encourage the formation of nitrogen oxides (NO_x). Techniques like differential scanning calorimetry (DSC) and transient hot-wire methods have been widely employed to analyse the thermal characteristics of biodiesel fuels [18].

2.4 Enthalpy of Combustion (ΔH)

The enthalpy of combustion (ΔH), also known as the higher heating value (HHV), signifies the overall energy emitted when a unit mass of fuel undergoes complete combustion. Biodiesel, because of its oxygen composition, naturally has a reduced heating value in comparison to petroleum diesel. The usual higher heating values (HHV) for biodiesel fall within the range of 37 to 41 MJ/kg, in contrast to conventional diesel, which shows elevated values between 42 and 46 MJ/kg [19].

Within the realm of second-generation biodiesels, those extracted from feedstocks that are rich in saturation, like palm oil and animal fats, generally exhibit marginally elevated heating values, nearing the range of 40 to 41 MJ/kg. Conversely, biodiesel of the third generation, derived from microalgae, typically exhibits higher heating values ranging from 36 to 39 MJ/kg, a result of the lipid composition that is primarily characterised by polyunsaturated fatty acids [20].

The integration of bioadditives like ethyl levulinate and the application of blending techniques with alcohols have been investigated to improve the overall energy content and combustion performance of biodiesel. Nonetheless, the delicate equilibrium between enhancing calorific value and preserving advantageous cold flow and oxidation stability requires meticulous consideration, particularly for extensive applications in frigid areas [21].

2.5 Flash Point and Ignition Characteristics

The flash point, defined as the minimum temperature at which a liquid can create a flammable mixture with air, is an essential safety characteristic. Biodiesel demonstrates notably elevated flash points, generally exceeding 130°C, in contrast to petroleum diesel, which hovers around 60°C. This characteristic markedly improves safety in the processes of handling, transportation, and storage. Biodiesel from the second generation typically exhibits flash points ranging from 150 to 170°C. In contrast, biodiesel from the third generation tends to have marginally lower

flash points, attributed to its elevated levels of volatile unsaturated esters, which usually fall between 130 and 150°C [22].

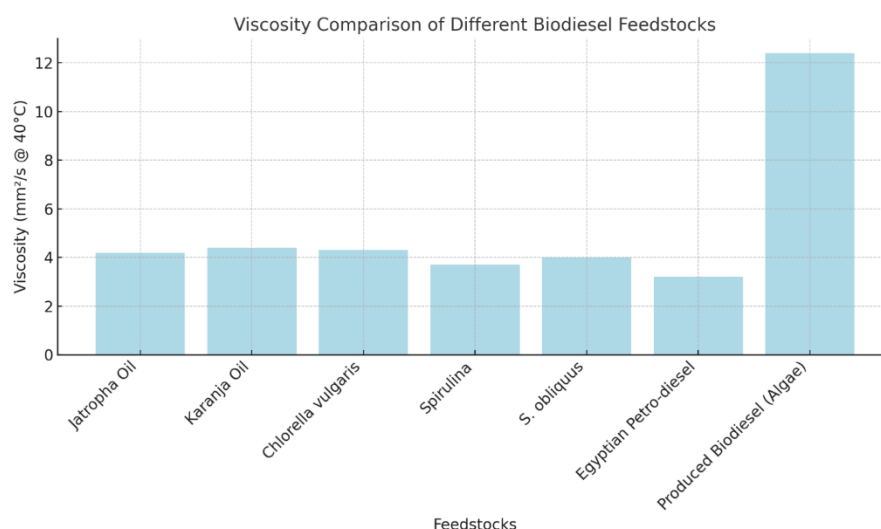
The quality of ignition, frequently measured by cetane number, plays a vital role in assessing the combustion properties of biodiesel. FAMES that are saturated, like methyl stearate, generally demonstrate elevated cetane numbers, resulting in reduced ignition delays and more seamless combustion. Conversely, unsaturated esters tend to reduce the cetane number, which may lead to a longer ignition delay while simultaneously enhancing performance in cold weather conditions [23].

Cutting-edge research employing ultrasonic and spectroscopic methodologies has validated the relationship among molecular architecture, ignition characteristics, and thermodynamic efficiency. In summary, the elevated flash point and satisfactory cetane ratings of biodiesel render it a more secure and environmentally friendly option compared to diesel. However, obstacles like difficulties with cold starts and the potential for oxidative degradation continue to be significant concerns [24].

The structural composition of biodiesel fuels — encompassing factors such as carbon chain length, level of unsaturation, and branching — significantly influences their thermodynamic characteristics. Esters derived from long-chain fatty acids typically demonstrate increased viscosity and density, which enhances oxidative stability while resulting in diminished cold flow characteristics. On the other hand, an increased level of unsaturation, marked by the presence of several double bonds, leads to a reduction in oxidative stability while simultaneously improving performance in cold conditions by decreasing crystallisation temperatures. The formation of branches in the molecular framework, typically accomplished via isomerisation or the incorporation of particular microbial lipids, interferes with crystal arrangement and lowers pour points, thereby enhancing performance in low-temperature flow dynamics. Simulations of computational molecular dynamics have shown to be extremely beneficial in forecasting these impacts, illustrating how minor alterations at the molecular scale can result in considerable enhancements in the behaviour of fuels on a macroscopic level. In addition, the incorporation of biodiesel with alcohols or the introduction of oxygenated bioadditives like dimethyl carbonate has demonstrated the ability to refine molecular interactions, thereby enhancing viscosity, density, and combustion properties. Recent breakthroughs in the genetic modification of microalgae have created opportunities for customising lipid compositions aimed at generating biodiesel with improved thermodynamic characteristics, signalling a shift towards the next generation of biofuels.

3. Comparative Analysis of Second vs. Third-Generation Biodiesel

Viscosity Analysis

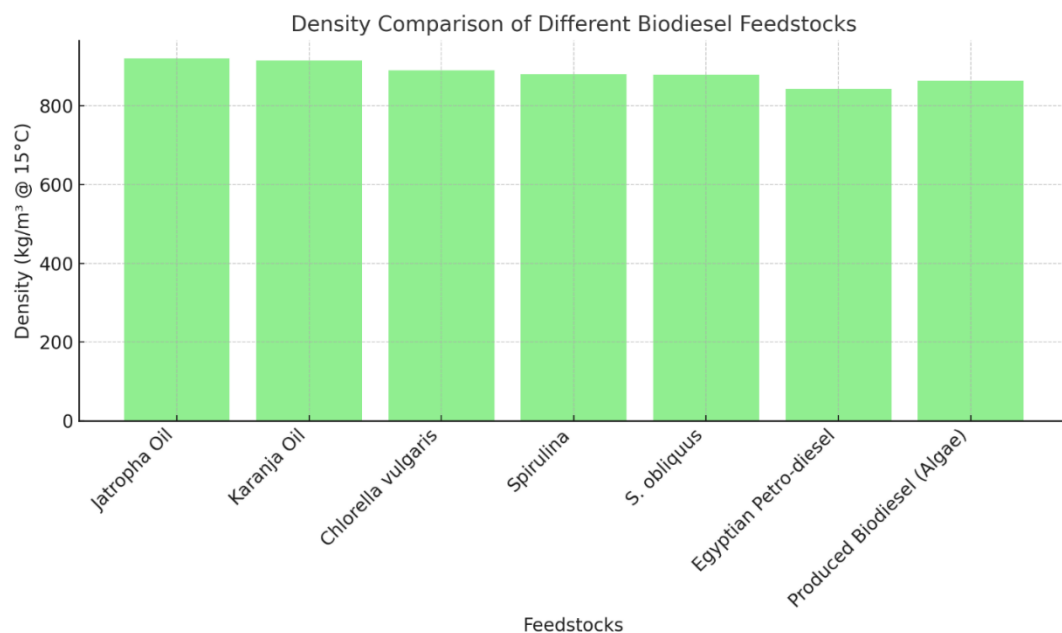


- **Jatropha Oil** has a viscosity of 4.2 mm²/s, which is typical for oils with higher saturated fatty acids. This higher viscosity could result in poor fuel atomization and incomplete combustion, necessitating additives or blending with conventional diesel.

- **Karanja Oil** exhibits a similar viscosity of 4.4 mm²/s, also indicating the presence of saturated fatty acids.
- **Chlorella vulgaris** and **Spirulina** show viscosities slightly higher than conventional diesel but within acceptable ranges. Algae-based biodiesel tends to have lower viscosity, facilitating better fuel atomization and engine performance, compared to second-generation oils.
- **S. obliquus** has a viscosity of 4.0 mm²/s, comparable to Jatropha and Karanja oils.
- **Egyptian Petro-diesel** is the baseline, with a lower viscosity of 3.21 mm²/s, making it easier to atomize.
- **Produced Biodiesel (Algae)** has a significantly higher viscosity of 12.4 mm²/s, indicating that it might be an unprocessed oil that requires further refining to reduce viscosity for engine compatibility.

Second-generation biodiesels like Jatropha and Karanja oils show higher viscosities, which could lead to poor atomization and combustion efficiency. On the other hand, third-generation biodiesel (like from algae) demonstrates better cold flow properties and is more adaptable, though it might require additional processing.

Density Analysis

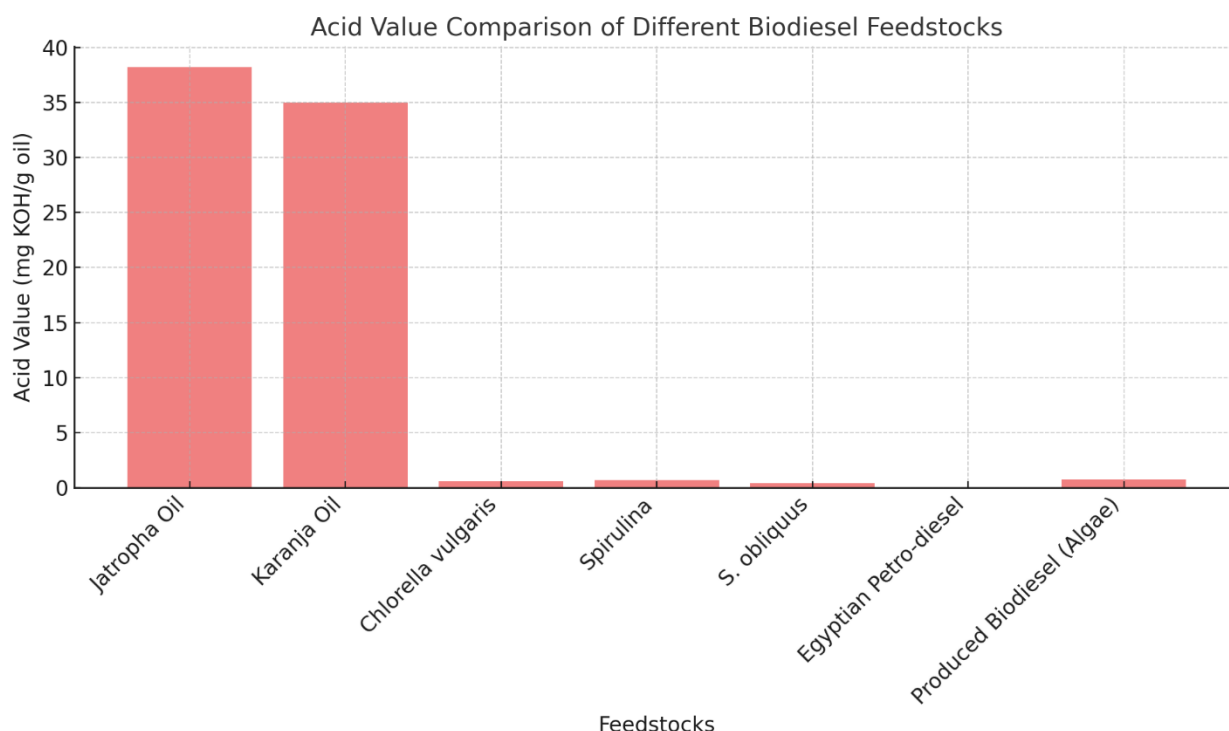


- **Jatropha Oil** has a density of 920 kg/m³, which is slightly higher than typical diesel (around 842.2 kg/m³). This increased density could suggest that Jatropha oil has a higher molecular weight and more saturated fatty acids, contributing to higher combustion energy.
- **Karanja Oil** also has a similar density (915 kg/m³), pointing to similar properties as Jatropha oil.
- **Chlorella vulgaris** has a lower density (890–900 kg/m³), which suggests that algae-based biodiesels have a more fluid consistency and a lower molecular weight compared to second-generation oils.
- **Spirulina** and **S. obliquus** have densities of 880 and 878 kg/m³, respectively, indicating their oil's lighter characteristics.
- **Egyptian Petro-diesel** has a density of 842.2 kg/m³, setting the baseline.

- **Produced Biodiesel (Algae)** has a density of 863.7 kg/m^3 , which is somewhat higher than standard petrodiesel, but it remains within a reasonable range for biodiesel.

Second-generation oils, such as Jatropha and Karanja, exhibit higher density, likely due to higher saturation in their fatty acid profiles. Third-generation biodiesel, especially algae-based oils, tend to have lower density, which contributes to better fuel injection and atomization characteristics.

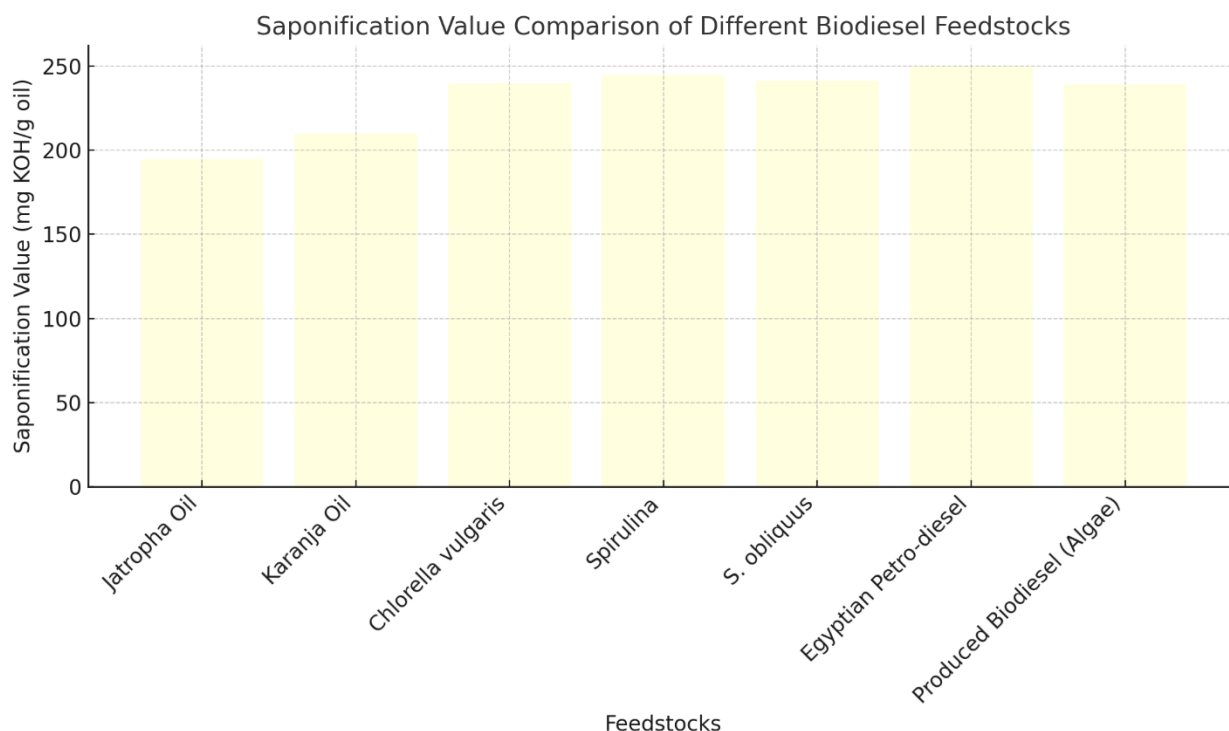
Acid Value Analysis



- **Jatropha Oil** has a notably high acid value of 38.2 mg KOH/g , indicating a high concentration of free fatty acids (FFAs). This high AV suggests that Jatropha oil requires pretreatment, like acid esterification, before transesterification to avoid soap formation and ensure efficient biodiesel production.
- **Karanja Oil** has a slightly lower acid value of 35 mg KOH/g , also requiring pretreatment before conversion to biodiesel.
- **Chlorella vulgaris**, **Spirulina**, and **S. obliquus** have very low acid values ($0.6\text{--}0.4 \text{ mg KOH/g}$), which indicates they have a minimal FFA content. This allows for direct transesterification without the need for additional pretreatment, making algae-based biodiesel more efficient to produce.
- **Egyptian Petro-diesel** has an extremely low acid value (0.023 mg KOH/g), as expected for refined petroleum-based fuel.
- **Produced Biodiesel (Algae)** has an acid value of 0.75 mg KOH/g , indicating a low FFA content and making it easier to process compared to second-generation feedstocks.

Second-generation biodiesels like Jatropha and Karanja oils have much higher acid values, indicating they require pretreatment for efficient biodiesel production. Third-generation biodiesels, especially algae-based oils, have much lower acid values, which simplifies their conversion process and enhances fuel quality.

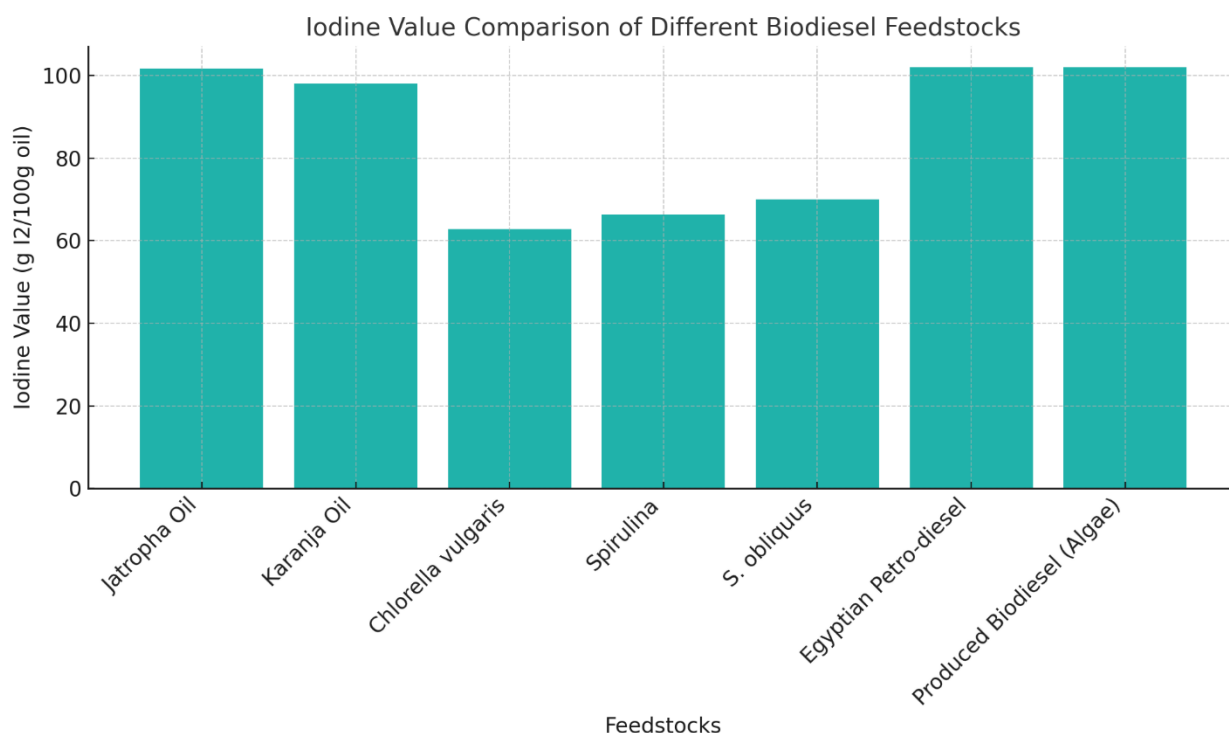
Saponification Value Analysis



- **Jatropha Oil** has a saponification value of 195 mg KOH/g, which suggests that it contains longer fatty acid chains. This longer chain length can contribute to higher viscosity and lower cold flow properties, but it can also lead to better combustion characteristics in diesel engines.
- **Karanja Oil** has a higher saponification value (210 mg KOH/g), indicating a slightly shorter average fatty acid chain compared to Jatropha. This may contribute to improved cold flow properties.
- **Chlorella vulgaris**, **Spirulina**, and **S. obliquus** exhibit higher saponification values (240–245 mg KOH/g). This suggests that algae oils have shorter fatty acid chains, which can improve the cold flow and combustion properties of biodiesel.
- **Produced Biodiesel (Algae)** has a similar saponification value of 239 mg KOH/g, again indicating shorter fatty acid chains compared to second-generation biodiesels.
- **Petro-diesel** is not applicable here as it is a refined product.

The higher saponification values in algae-based biodiesels reflect the presence of shorter fatty acid chains, which generally enhance the cold flow and combustion characteristics, making them more suitable for use in cold climates. In comparison, second-generation oils like Jatropha and Karanja have longer fatty acid chains, affecting the flow and cold weather performance.

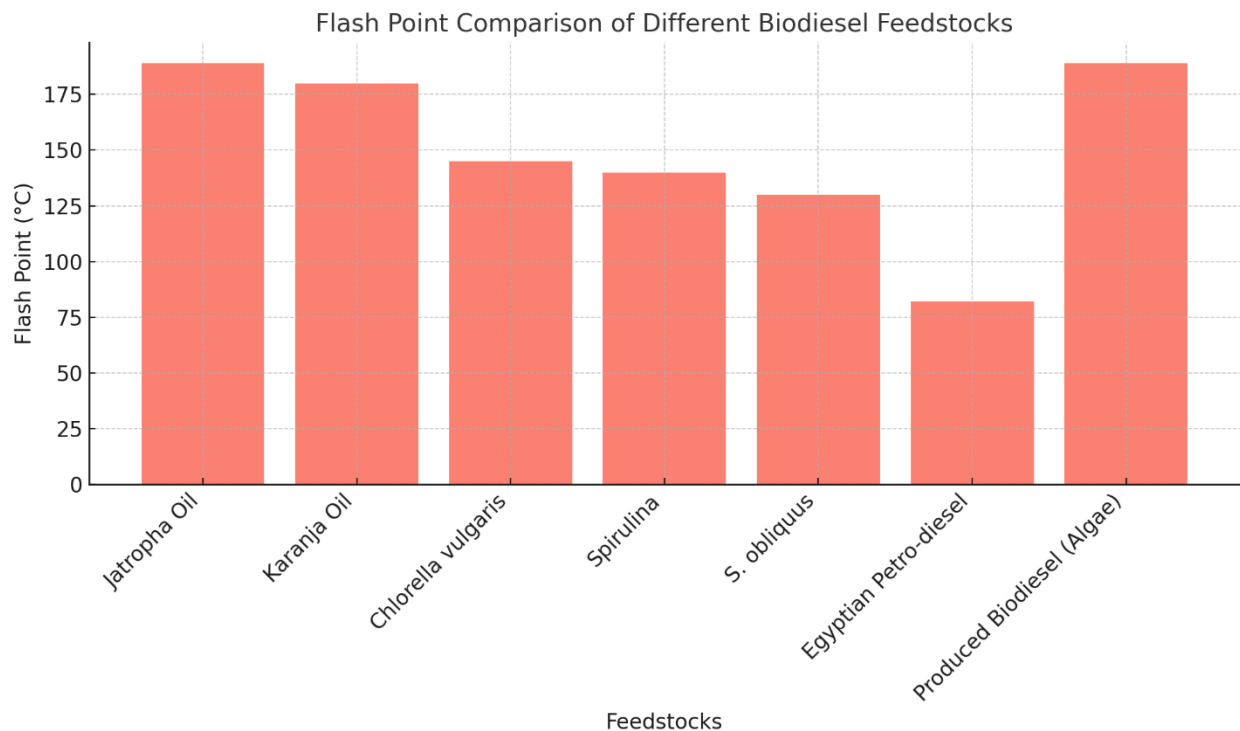
Iodine Value Analysis



- **Jatropha Oil** has an iodine value of 101.7 g I₂/100g, indicating a high level of unsaturation. This contributes to lower oxidative stability but better low-temperature performance. High iodine values are beneficial for cold flow but make the oil more susceptible to oxidation over time.
- **Karanja Oil** has a slightly lower iodine value (98), indicating a similar level of unsaturation as Jatropha, with a balance between performance in colder temperatures and oxidative stability.
- **Chlorella vulgaris**, **Spirulina**, and **S. obliquus** exhibit iodine values ranging from 62.8 to 70, which reflect a moderate level of unsaturation. These values indicate that algae-based oils have improved oxidative stability compared to Jatropha but still maintain good low-temperature performance.
- **Produced Biodiesel (Algae)** has a high iodine value of 102, indicating a high degree of unsaturation, similar to Jatropha oil.
- **Petro-diesel** is not applicable here, as its iodine value is irrelevant.

Algae oils have lower iodine values compared to Jatropha and Karanja oils, indicating that they are more resistant to oxidation, though still effective for cold flow. High iodine values in oils like Jatropha indicate better performance in colder conditions but pose a risk for oxidation without proper stabilizing additives.

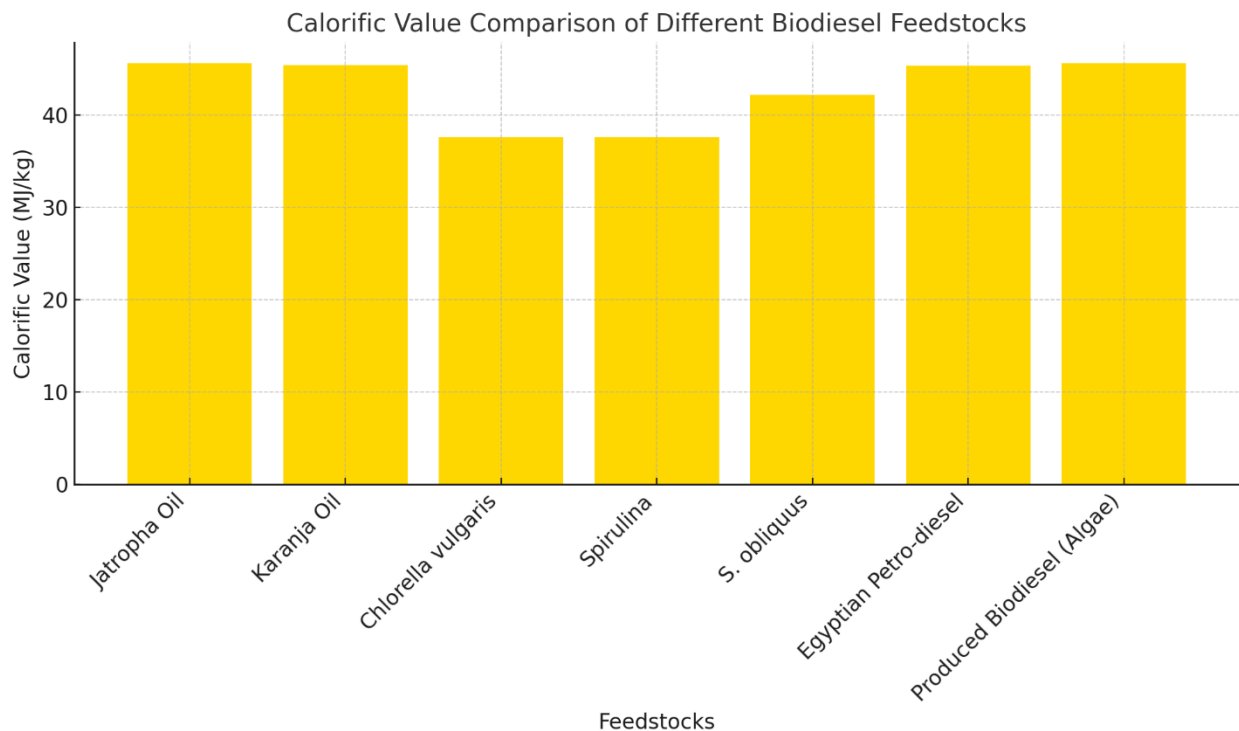
Flash Point Analysis



- **Jatropha Oil** has a flash point of 189°C, which is significantly higher than conventional diesel (82°C). The high flash point improves the safety of biodiesel during storage and handling by reducing the risk of ignition.
- **Karanja Oil** has a flash point of 180°C, indicating similar safety characteristics to Jatropha oil.
- **Chlorella vulgaris**, **Spirulina**, and **S. obliquus** have lower flash points (145–130°C), which suggests a greater tendency to ignite at lower temperatures. However, these flash points are still higher than conventional diesel.
- **Egyptian Petro-diesel** has a low flash point of 82°C, making it more dangerous to handle, particularly in high-temperature environments.
- **Produced Biodiesel (Algae)** has a flash point of 189°C, similar to Jatropha oil, indicating good storage safety.

Second-generation oils (like Jatropha and Karanja) have much higher flash points compared to third-generation algae oils, which is beneficial for safety during storage and transportation. Third-generation biodiesel may require additional safety measures in high-temperature conditions.

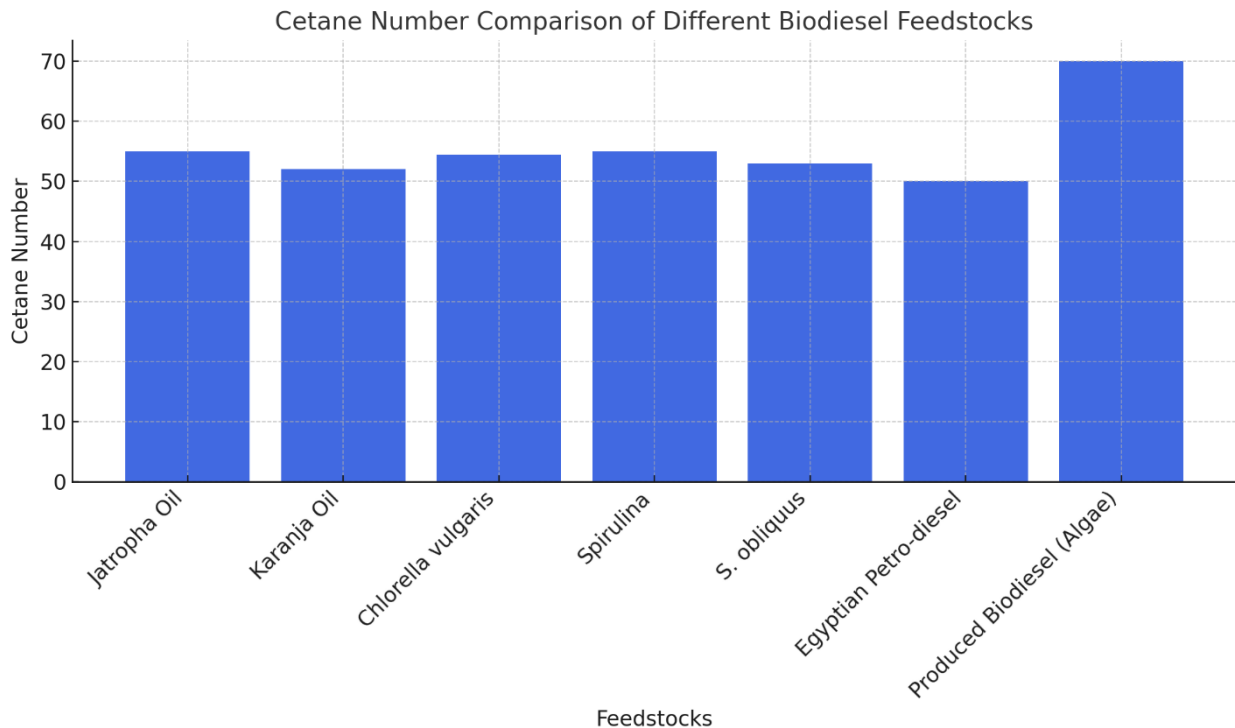
Calorific Value Analysis



- **Jatropha Oil** and **Produced Biodiesel (Algae)** have the highest calorific values (45.63 MJ/kg), which is close to that of conventional diesel (45.35 MJ/kg). This indicates that both oils provide high energy output.
- **Karanja Oil** has a calorific value of 45.4 MJ/kg, which is also quite close to conventional diesel, making it a viable alternative fuel with a comparable energy density.
- **Chlorella vulgaris**, **Spirulina**, and **S. obliquus** have calorific values ranging from 37.6 to 42.2 MJ/kg. While slightly lower than Jatropha and Karanja oils, these values are still competitive and suggest that algae-based biodiesel has reasonable energy content.
- **Egyptian Petro-diesel** serves as the baseline with a calorific value of 45.35 MJ/kg.

Second-generation biodiesels like Jatropha and Karanja offer comparable energy output to petro-diesel, while third-generation algae-based biodiesels provide slightly lower energy content but remain competitive in terms of efficiency. The difference in calorific value doesn't significantly affect performance, as algae biodiesel's improved cold flow properties and engine efficiency can offset the slight decrease in energy density.

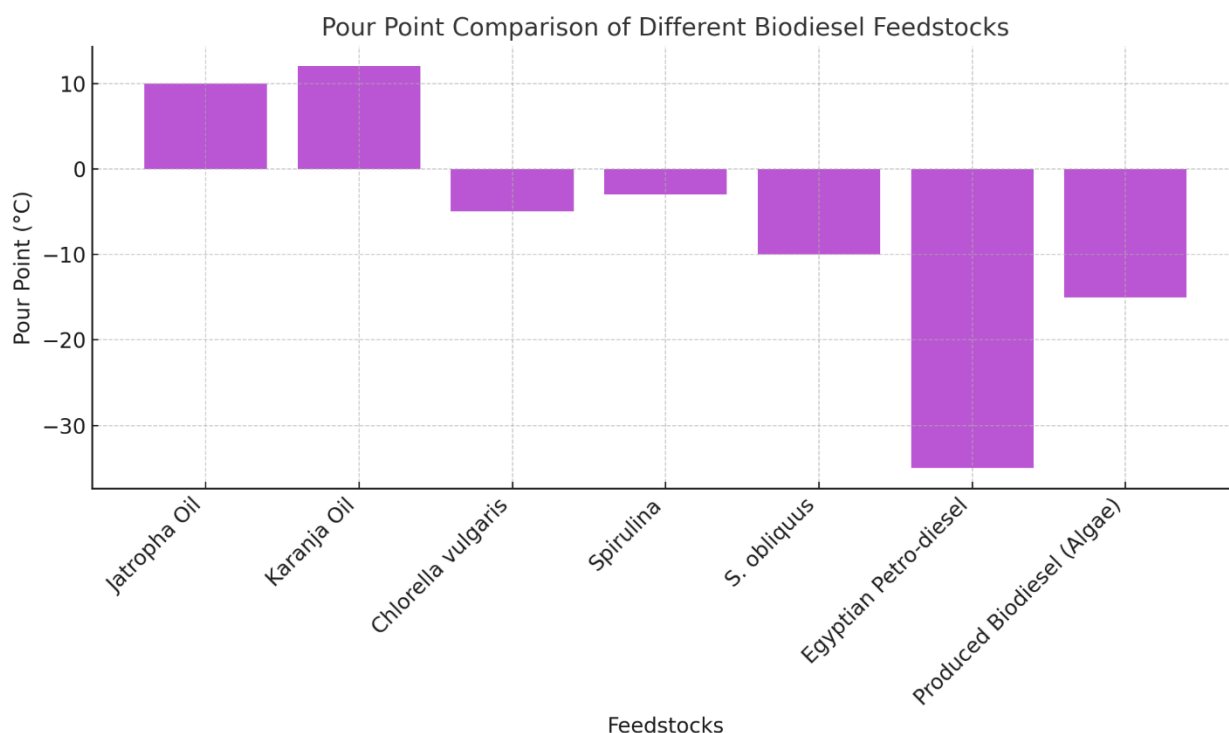
Cetane Number Analysis



- **Jatropha Oil, Spirulina, and Produced Biodiesel (Algae)** have cetane numbers around 55, which is quite high and indicative of good combustion efficiency. A higher cetane number results in shorter ignition delays, leading to more complete combustion and reduced emissions.
- **Karanja Oil** has a slightly lower cetane number of 52, which still falls within an acceptable range for biodiesel but may lead to slightly longer ignition delays compared to Jatropha or algae-based biodiesel.
- **Chlorella vulgaris** and **S. obliquus** have cetane numbers around 54.5 and 53, respectively, which are good for efficient combustion in diesel engines.
- **Egyptian Petro-diesel** has a cetane number of 50, which is lower compared to most biodiesel but still within the range considered acceptable for diesel engines.

Second-generation biodiesels generally have excellent cetane numbers, contributing to efficient combustion. Third-generation biodiesels (especially from algae) also perform well in terms of cetane number, making them suitable for use in modern diesel engines with minimal ignition delay.

Pour Point Analysis



- **Jatropha Oil** and **Karanja Oil** both have pour points of 10°C and 12°C, respectively, which indicate relatively high temperatures at which these oils may start to thicken or gel. This can lead to issues in colder environments.
- **Chlorella vulgaris**, **Spirulina**, and **S. obliquus** have much lower pour points (-5°C to -10°C), which reflects better performance in cold climates. The ability of algae-based biodiesels to flow at lower temperatures makes them more suitable for colder regions.
- **Egyptian Petro-diesel** has a pour point of -35°C, making it ideal for cold-weather performance.
- **Produced Biodiesel (Algae)** has a pour point of -15°C, indicating improved cold flow properties, especially in comparison to Jatropha and Karanja oils.

Third-generation algae-based biodiesels outperform second-generation biodiesels in terms of pour point, indicating better performance in low-temperature environments. This makes algae biodiesel a suitable option for colder climates without the need for additional additives or blending.

4. Experimental and Computational Methods for Thermodynamic Characterization

Innovative methodologies are crucial for precise thermodynamic analysis of biodiesel fuels, delivering vital information regarding attributes like phase changes, thermal resilience, viscosity, and heat capacity. Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and viscometry stand out as the most significant laboratory techniques used.

Differential Scanning Calorimetry (DSC) is extensively employed to investigate phase transition phenomena such as melting temperatures, pour points, crystallization temperatures, and specific heat capacity. In the realm of biodiesel investigation, DSC facilitates the accurate assessment of cold flow characteristics, which are essential for analyzing the low-temperature functionality of second- and third-generation biodiesels. For example, saturated methyl esters obtained from palm oil display distinct endothermic peaks, signifying crystallization at elevated



temperatures, in contrast to microalgal esters, which present wider and lower-temperature transitions. DSC assessments exhibit a notable sensitivity to contaminants and variations in blends, highlighting the necessity for stringent sample preparation procedures. [14]

Thermogravimetric Analysis (TGA) is used to evaluate the thermal resilience and oxidative deterioration characteristics of biodiesel fuels. By employing regulated heating in either inert or oxidative environments, TGA yields significant insights regarding the initial degradation temperatures, the activation energy associated with decomposition, and the formation of residues. Biodiesel fuels from the second generation exhibit elevated decomposition temperatures, indicating enhanced thermal stability in contrast to third-generation biodiesels, which are abundant in unsaturated lipids. Integrated TGA-DSC analysis helps distinguish between the phenomena of physical evaporation and chemical decomposition, which is essential for comprehending fuel dynamics in engine environments [15-16].

Viscometry continues to be an essential technique for analyzing the flow characteristics of biodiesel and its mixtures. Standardized kinematic viscometers, also known as rotational viscometers, are employed to gauge the flow resistance of fuel samples under regulated temperature conditions, usually set at 40°C for the evaluation of biodiesel. Studies have demonstrated the effectiveness of blending second-generation biodiesel with fossil diesel. This combination significantly lowers viscosity to levels deemed acceptable, which is essential for contemporary diesel engine injectors designed to operate with low-viscosity fuels. Additionally, advanced micro-viscometry methods, such as oscillating capillary viscometers, have been established to examine small-volume biodiesel samples derived from innovative third-generation feedstocks like oleaginous yeasts and microalgae [23].

Additional complementary techniques include assessing flash points using the Pensky-Martens apparatus, calorimetric bomb approaches for evaluating higher heating values (HHV), and gas chromatography for comprehensive profiling of fatty acid methyl esters (FAME), which plays a vital role in correlating molecular architecture with observable characteristics.

4.2 Predictive Models (Group Contribution Methods, Molecular Dynamics)

Although experimental techniques yield exceptionally dependable information, they frequently demand significant resources and can be quite time-consuming. As a result, predictive computational models are being utilized more and more to accurately and efficiently estimate the thermophysical characteristics of biodiesel fuels. There are two notable methodologies: the group contribution techniques (GCTs) and molecular dynamics (MD) simulations.

Group Contribution Methods (GCMs) assess large-scale characteristics by analyzing the molecular architecture of constituents, aggregating the inputs from the functional groups found within a molecule. In the realm of biodiesel fuels, GCMs have proven to be highly effective in forecasting various properties, including density, viscosity, boiling point, flash point, and HHV, all derived from the established structures of FAMEs. Research has illustrated the effectiveness of GCMs in forecasting the thermodynamic characteristics of biodiesel-diesel binary blends, offering a valuable resource for the preliminary evaluation of possible feedstocks. In a similar vein, GCM-based methodologies have been used to forecast the effects of alterations in fatty acid chain length and saturation levels on the cold flow and combustion characteristics of biodiesel [27-29].

Molecular Dynamics (MD) Simulations provide detailed, atomistic perspectives on how biodiesel molecules behave when subjected to different temperature and pressure environments. By employing interatomic potential fields, molecular dynamics simulations are capable of forecasting various properties, including density, heat capacity, viscosity, thermal conductivity, and self-diffusion coefficients. MD simulations can represent ternary mixtures comprising biodiesel, ethanol, and diesel, effectively forecasting the viscosity and thermal characteristics that were experimentally observed. Furthermore, MD investigations have the capability to replicate oxidation processes, offering valuable understanding of the oxidative breakdown routes of biodiesel, which is an essential element influencing its stability during prolonged storage [34-35].

Various computational methods, such as quantum chemical assessments and molecular docking, have been investigated to forecast reaction pathways in transesterification processes. These frameworks enable investigators to refine the choice of catalysts and the parameters of reactions to improve both the yield and quality of biodiesel. Although predictive models serve a valuable purpose, they frequently necessitate verification via experimental data to guarantee precision, especially when extending beyond the limits of training datasets. The integration of

computational techniques alongside experimental methodologies creates a robust and synergistic strategy for investigating the thermodynamics of biodiesel.

Table 3: Summary of Experimental and Computational Methods for Biodiesel Thermodynamic Characterization

Method Type	Technique	Purpose
Laboratory	Differential Scanning Calorimetry (DSC)	Measure cold flow properties (pour point, cloud point), heat capacity (Cp), phase transitions.
Laboratory	Thermogravimetric Analysis (TGA)	Analyze thermal stability, oxidation degradation, decomposition kinetics.
Laboratory	Viscometry	Measure kinematic viscosity for flow behavior assessment at different temperatures.
Laboratory	Flash Point Testing (Pensky-Martens Method)	Assess ignition characteristics and fuel handling safety.
Laboratory	Bomb Calorimetry	Determine Higher Heating Value (HHV) of biodiesel samples.
Laboratory	Gas Chromatography (GC)	Analyze fatty acid methyl ester (FAME) profiles; link molecular structure to macroscopic properties.
Computational	Group Contribution Methods (GCMs)	Predict density, viscosity, HHV based on molecular structure without full experiments.
Computational	Molecular Dynamics (MD) Simulations	Model microscopic molecular interactions; predict viscosity, density, thermal properties.
Computational	Quantum Chemical Calculations	Study reaction mechanisms, optimize catalysts and process conditions.
Computational	Predictive Thermodynamic Modeling	Simulate binary/ternary blends; optimize cold flow, energy properties.

4.3 Challenges in Measurement and Standardization

In spite of notable progress, numerous obstacles continue to exist in the evaluation and uniformity of thermodynamic characteristics of biodiesel. A significant concern lies in the intrinsic variability of biodiesel formulations, which arises from the diversity of feedstocks, variations in processing techniques, and seasonal fluctuations. Variations in cultivation conditions, timing of harvest, and techniques for oil extraction can result in significant alterations in density, viscosity, and energy content, even when considering a single feedstock like jatropha or microalgae [34].

The inconsistency in measurements is further intensified by the absence of standardised protocols for testing



biodiesel. While global benchmarks outline criteria for biodiesel quality, variations in the calibration of testing equipment, methods of sample preparation, and environmental conditions can lead to discrepancies in the measurement of properties. Furthermore, contemporary biodiesel feedstocks like microbial oils and genetically engineered algae present difficulties for uniform testing, as their chemical compositions might deviate from the anticipated standards set for first- and second-generation biodiesels [23].

Methods of analysis like DSC and TGA necessitate meticulous calibration and baseline adjustments to produce dependable outcomes, especially when assessing blended or multicomponent biodiesel fuels. The assessment of viscosity is highly responsive to variations in temperature, necessitating rigorous isothermal regulation. Moreover, the efficacy of predictive models is significantly influenced by the calibre of input parameters and force fields, frequently constraining their use to systems that are thoroughly characterized [23-24].

Innovative fourth-generation biodiesel technologies — such as genetically modified microalgae designed for specific lipid synthesis — are expected to necessitate the development of novel measurement protocols and predictive algorithms for properties. Consequently, initiatives aimed at standardisation need to adapt in order to embrace the increasing variety of biodiesel origins and formulations. Global partnerships between research entities, standards bodies, and industrial sectors are crucial for the advancement of reliable and reproducible techniques for the thermodynamic analysis of biodiesel. This collaboration guarantees the safe, effective, and sustainable integration of biodiesel into worldwide energy markets.

5. Environmental and Economic Implications

5.1 Sustainability of Feedstock Sources

The ecological viability of biodiesel manufacturing is significantly influenced by the selection of raw materials. Biodiesel of the second generation, derived mainly from non-consumable oils like jatropha, karanja, and discarded cooking oils, presents significant advantages by harnessing agricultural byproducts and repurposing waste materials. This method diminishes the rivalry for agricultural produce, tackles waste management challenges, and fosters the principles of a circular economy [35]. Nonetheless, the farming of specialized non-consumable oil plants on less productive terrains can occasionally result in alterations to land use, a decline in biodiversity, and heightened water requirements, potentially negating certain ecological advantages.

The innovative potential of third-generation biodiesel, sourced from microalgae and microbial lipids, offers a groundbreaking avenue for the creation of sustainable fuel solutions. Microalgae have the potential to be grown on lands that are unsuitable for traditional agriculture, utilizing saline water or wastewater, and necessitating significantly less freshwater and fertilizers in comparison to conventional crops. Moreover, algae exhibit remarkable photosynthetic capabilities, capturing significant quantities of CO₂ and reducing greenhouse gas emissions throughout their growth process [35-36]. Systems utilizing algae facilitate the incorporation of wastewater treatment, thereby improving resource recovery and promoting sustainability.

Nonetheless, the ecological impact of microalgal biodiesel is significantly influenced by the techniques used for cultivation, harvesting, and lipid extraction. The processes of energy-demanding harvesting, such as centrifugation, along with solvent-based extraction methods, have the potential to greatly elevate the energy requirements throughout their life cycle and contribute to greenhouse gas emissions if not properly optimized [36]. Consequently, to fully realize the environmental benefits of third-generation biodiesel, it is essential to achieve technological progress in energy-efficient and sustainable processing methods.

5.2 Energy Balance and Lifecycle Assessment

The energy equilibrium of biodiesel pertains to the comparison between the energy produced (fuel energy) and the energy consumed (cultivation, processing, transportation). Biodiesel derived from waste oils in its second generation typically demonstrates highly advantageous energy balances, as the feedstock is essentially a byproduct of waste, necessitating only a minimal amount of energy for cultivation [37]. Evaluations of the lifecycle of biodiesel derived from waste cooking oil consistently demonstrate favorable net energy ratios exceeding 3:1, signifying a remarkable level of overall energy efficiency.



Conversely, biodiesel produced from non-food crops like jatropha or karanja may exhibit greater fluctuations in energy balances, influenced by factors such as farming methods, water requirements, and alterations in land utilization. For example, the establishment of Jatropha plantations necessitates preliminary land preparation and ongoing maintenance, contributing to the overall embodied energy of the fuel [38].

The third-generation biodiesel derived from microalgae presents a remarkable opportunity for achieving an exceptionally favorable energy balance, attributed to its elevated lipid yield per hectare. However, this potential can only be realized through the optimization of cultivation, harvesting, and extraction techniques. Conventional raceway ponds present reduced energy demands in comparison to enclosed photobioreactors; however, they are more vulnerable to contamination and losses due to evaporation. The combination of algal cultivation with CO₂ emissions from industrial facilities or wastewater discharges can greatly enhance lifecycle emissions and the overall energy equilibrium [37-38].

In summary, optimal lifecycle performance is realized when the production of biodiesel is seamlessly incorporated into current waste management practices, carbon capture technologies, and renewable energy frameworks, highlighting the significance of adopting a holistic systems-thinking perspective.

5.3 Cost-Effectiveness of Production Processes

The financial feasibility continues to be a significant obstacle for the extensive implementation of biodiesel. In the case of second-generation biodiesel, the expenses associated with feedstock represent a significant portion, comprising 70–90% of the overall production costs. The utilization of waste cooking oil for biodiesel production presents a financially appealing option, as the raw materials are both cost-effective and easily accessible. Nonetheless, the inconsistency in quality and levels of contamination necessitates pre-treatment, which in turn increases operational expenses [39].

The production of biodiesel from non-food crops like jatropha has encountered various obstacles, including yields that fall short of expectations, pest-related problems, and challenges in managing large-scale plantations. These factors contribute to its diminished economic viability unless supported by government subsidies or carbon credit programs.

The production of third-generation biodiesel is presently more costly compared to both second-generation biodiesel and fossil diesel. This is mainly attributed to elevated expenses associated with cultivation (nutrient input), harvesting, and lipid extraction. Research suggests that in the absence of significant technological advancements, the expenses associated with algal biodiesel production may fall between \$3 and \$7 for each liter [40]. The expenses related to the energy required for dewatering algal biomass present significant challenges, frequently representing 20–30% of the overall energy expenditure.

Innovations like bioflocculation, direct transesterification, and integrated biorefineries that simultaneously generate biodiesel and valuable byproducts such as pigments, proteins, and nutraceuticals have the potential to significantly enhance the financial viability of microalgal biodiesel. Support for public policy via tax incentives, carbon pricing, and mandates for renewable energy can further expedite reductions in costs [40].

In the end, the financial viability of biodiesel, particularly from advanced third-generation sources, will hinge on ongoing advancements in biotechnology, process engineering, and cohesive waste-energy systems.

6. Current Challenges and Future Perspectives

6.1 Limitations in Thermodynamic Performance

In spite of the various ecological and energy benefits, biodiesel — particularly from second- and third-generation origins — continues to encounter significant thermodynamic constraints that hinder its wider acceptance. A significant concern is its relatively diminished calorific value when compared to traditional petroleum diesel. The Higher Heating Value (HHV) of biodiesel experiences a decrease of around 10–12% as a result of its natural oxygen composition. The decrease in energy density leads to an increase in brake-specific fuel consumption (BSFC) while



the engine is running, a finding that has been repeatedly documented in various experimental investigations [41].

A further notable constraint in thermodynamics pertains to the characteristics of cold flow. Biodiesel of the second generation, especially derived from saturated feedstocks such as palm and tallow oils, demonstrates elevated pour and cloud points, which significantly affects its functionality in colder environments. While third-generation biodiesel derived from microalgae exhibits enhanced performance in low-temperature conditions owing to its increased unsaturation, this benefit is counterbalanced by a reduction in oxidative stability, rendering the fuel more susceptible to rapid degradation over time [42].

Challenges related to viscosity continue to endure. Biodiesel typically exhibits greater viscosity in comparison to petroleum diesel, which results in suboptimal atomisation and, as a result, can lead to incomplete combustion and increased particulate emissions under specific circumstances. Additionally, prolonged storage results in polymerisation and the development of sediment, which impacts thermodynamic characteristics and the longevity of the engine. The constraints highlighted emphasise the necessity for continuous investigation into the enhancement of feedstock, the alteration of chemical properties, and the refinement of fuel treatments to ensure that biodiesel can stand on equal footing with fossil fuels.

6.2 Advances in Biodiesel Modification (Additives, Blending)

In order to surpass the fundamental thermodynamic constraints, extensive investigations have concentrated on the chemical and physical alterations of biodiesel via blending, the integration of additives, and advancements in the transesterification process. The integration of biodiesel with petroleum diesel (such as B5 and B20 mixtures) has emerged as a highly effective approach to enhance cold flow characteristics, viscosity, and energy density. The research revealed that the use of ternary blends comprising biodiesel, ethanol, and diesel can enhance spray properties and diminish particulate emissions, all while maintaining energy density at a satisfactory level [43].

Chemical additives, especially those such as cold flow improvers, antioxidants, and cetane boosters, have demonstrated their essential role in enhancing the thermophysical and combustion characteristics of biodiesel. Cold flow enhancers, including polymethacrylates and pour point depressants, have proven to be effective in reducing pour points by as much as 10°C. In a similar vein, substances such as BHT (butylated hydroxytoluene) and TBHQ (tert-butylhydroquinone) are frequently incorporated to improve oxidative stability, particularly in third-generation biodiesels that are abundant in polyunsaturated esters [44].

Additionally, the straightforward alteration of fatty acid compositions via partial hydrogenation or the application of genetically modified microalgae represents a developing approach. The process of hydrogenation serves to diminish unsaturation levels, thereby enhancing oxidative stability. However, it is crucial to exercise caution to prevent over-saturation, which can negatively impact cold flow characteristics. Recent advancements in transesterification techniques involving nano-catalysts and enzymatic pathways present promising opportunities to generate biodiesel exhibiting enhanced thermodynamic characteristics while operating at reduced processing temperatures and minimising reaction durations [45].

In addition, the application of predictive modelling through Group Contribution Methods and Molecular Dynamics simulations is becoming more prevalent for the purpose of crafting ideal fuel mixtures and additives before undergoing experimental confirmation, thereby conserving both time and resources.

6.3 Potential for Fourth-Generation Biodiesel

The fourth generation of biodiesel signifies a groundbreaking advancement in biofuel exploration, offering potential solutions to the existing thermodynamic, economic, and sustainability hurdles faced by previous generations. The current generation harnesses cutting-edge biotechnology, innovative genetic manipulation, and cohesive carbon capture techniques to create tailored, high-performance biodiesel fuels [46].

Microalgae strains that have been genetically modified to generate lipids featuring particular fatty acid compositions — including elevated levels of monounsaturated fats — can greatly enhance the cold flow characteristics, oxidative stability, and energy density of biodiesel all at once. As an illustration, the enhancement of *Chlorella* or



Nannochloropsis varieties to elevate oleic acid levels beyond 70% can yield biodiesel characterised by exceptional ignition properties and improved storage longevity [47].

Furthermore, fourth-generation systems strive for environmentally beneficial production methods by integrating biodiesel production with carbon dioxide capture and wastewater management. Algal biorefineries that can simultaneously generate biodiesel, biogas, biohydrogen, and valuable compounds like carotenoids and polyunsaturated fatty acids present a significant opportunity to enhance the financial viability of biofuel production [48].

Innovative harvesting techniques, including magnetic separation, bio-flocculation, and membrane filtration, paired with energy-efficient lipid extraction processes, are essential for rendering fourth-generation biodiesel financially feasible. Additionally, the incorporation of renewable energy systems like solar-powered photobioreactors can significantly diminish lifecycle emissions and operational expenses.

7. Conclusion

Second- and third-generation biodiesels offer unique advantages and challenges in the transition towards sustainable energy. Second-generation biodiesel, derived from non-edible oils such as Jatropha, Karanja, and waste cooking oils, provides a stable and reliable alternative to fossil fuels with a high calorific value. However, it suffers from poor cold flow properties, which limits its performance in colder environments. Moreover, feedstock quality inconsistencies require pre-treatment and can result in fluctuating fuel properties. Third-generation biodiesel, primarily derived from microalgae, overcomes many of these issues by offering superior cold flow properties and the potential for customization of lipid profiles. This makes it more adaptable to varying environmental conditions, but its production remains costly, largely due to expensive cultivation and extraction processes. Despite these economic challenges, algae-based biodiesel has environmental benefits, including the use of non-arable land and low water consumption. The future of biodiesel will likely lie in the optimization and integration of both generations, alongside technological innovations such as bio-additives and genetically modified feedstocks. These advances, coupled with improved production techniques, will enhance fuel properties and make biodiesel a more competitive, sustainable alternative to fossil fuels. Integrating second- and third-generation biodiesel could offer a comprehensive, environmentally friendly energy solution.

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