

Oils for energy use (biofuels or biodiesel): Composition, Applications and Analytical Considerations

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Introduction

Biofuels are renewable fuels derived from biological resources such as crops, vegetable oils, animal fats and organic waste. Their development has been strongly encouraged by international policies aimed at reducing greenhouse gas emissions, decreasing dependence on fossil fuels and promoting a more sustainable energy system. Unlike fossil fuels, which originate from ancient organic matter, biofuels are part of the short-term carbon cycle, as the carbon dioxide released during combustion is partially offset by the carbon absorbed during biomass growth.

Among the various categories, bioethanol and biomass-based diesel represent the largest shares of global biofuel production. Biomass-based diesel includes biodiesel and renewable diesel, with biodiesel being one of the most widely used alternatives to conventional petroleum diesel in transportation, power generation and industrial applications. The growing demand for biofuels has significantly increased the use of vegetable oils as primary feedstocks, particularly in the United States and Europe.

Chemical Composition

Biodiesel is produced through a chemical process known as **transesterification**, in which triglycerides present in **vegetable oils or animal fats** react with an **alcohol**, typically methanol, forming fatty acid methyl esters, commonly referred to as **FAME**, and glycerol as a by-product. The chemical composition of biodiesel therefore reflects the fatty acid profile of the original feedstock. The most commonly used vegetable oils for biodiesel production include soybean oil, rapeseed oil, canola oil, sunflower oil and palm oil. Waste-derived feedstocks such as used cooking oil, free fatty acids and animal fats are also increasingly employed, particularly within sustainability-oriented regulatory frameworks. The proportion of saturated and unsaturated fatty acid methyl esters plays a critical role in determining fuel properties. Saturated esters generally provide higher oxidation stability but poorer cold flow properties due to higher crystallization temperatures. In contrast, unsaturated esters improve low-temperature performance but are more prone to oxidative degradation. For this reason, biodiesel quality is closely linked to the fatty acid distribution and must comply with international standards such as ASTM D6751 and EN 14214.

Properties and Uses

Biodiesel is a biodegradable and clean-burning fuel that can significantly reduce greenhouse gas emissions compared to fossil diesel, depending on feedstock and production pathway. It contains no fossil carbon and can be blended with conventional diesel at various ratios, commonly up to 7 percent in many European markets, or used in higher blends and even in neat form in compatible engines. In addition to lower emissions of particulate matter, carbon monoxide and sulfur compounds, biodiesel exhibits superior lubricity compared to ultra-low sulfur diesel, contributing to reduced engine wear. It can generally be used in existing diesel engines without significant modification, making it a technically feasible and scalable alternative. However, biodiesel properties vary significantly depending on feedstock composition. Fuels rich in unsaturated esters may exhibit lower oxidation stability and require the addition of antioxidants, while those with higher saturated content may face challenges related to cold filter plugging point and cloud point, especially in colder climates. Therefore, rigorous quality control and stability monitoring are essential to ensure compliance with regulatory standards and reliable engine performance.

Essential Parameters for the Characterization of Oils Used as Biofuels

The quality of vegetable oils and waste-derived feedstocks intended for biodiesel production must be carefully controlled to ensure compliance with regulatory standards and reliable engine performance. Among the most critical parameters for feedstock characterization are **Free Fatty Acid** content, **Iodine Value** and **Peroxide Value**. These indicators provide essential information on chemical stability, suitability for transesterification and expected fuel behavior.

Free Fatty Acid (FFA)

Free Fatty Acid content is one of the most important parameters in the evaluation of oils intended for biodiesel production. FFAs are generated primarily through hydrolysis of triglycerides, a process influenced by time, temperature and moisture during storage and handling. High FFA levels indicate degradation and reduced storage stability, as free acids are more susceptible to oxidation than neutral triglycerides. From a process standpoint, elevated FFA content significantly affects alkali-catalyzed

transesterification, the most widely used method for biodiesel production. When FFA levels exceed approximately 1%, soap formation occurs in the presence of alkaline catalysts, reducing biodiesel yield and complicating downstream purification. The official determination of FFA is performed by acid–base titration, typically according to standardized procedures such as ASTM D664 for acid number determination. The oil sample is dissolved in neutralized alcohol and titrated with standardized potassium hydroxide, with results expressed as mg KOH per gram of oil or as percentage of free fatty acids. This parameter is also critical in biodiesel quality control, since residual FFAs may cause corrosion, thermal instability and oxidative degradation.

Iodine Value (IV)

The **Iodine Value measures** the degree of unsaturation of an oil, expressed as grams of iodine absorbed per 100 grams of sample. Since double bonds are reactive sites susceptible to oxidation and polymerization, iodine value is directly related to oxidative stability.

Oils with high iodine values contain larger proportions of polyunsaturated fatty acids and are therefore more prone to autoxidation, gum formation and long-term instability. While unsaturation improves low-temperature fluidity, it also reduces resistance to oxidative degradation.

Therefore, balancing unsaturation is crucial to achieving optimal biodiesel performance.

The conventional determination of iodine value is performed using halogen addition methods, typically the Wijs method, followed by titration of excess iodine with sodium thiosulfate. Although ASTM D6751 does not impose a strict limit on iodine value for biodiesel, this parameter remains essential for feedstock selection and stability assessment.

Peroxide Value (PV)

Peroxide Value is a key indicator of primary oxidation and reflects the concentration of peroxides and hydroperoxides formed during the early stages of lipid oxidation. When unsaturated fatty acids react with oxygen, peroxides are generated as initial degradation products, leading eventually to rancidity, discoloration and changes in physical properties.

For biodiesel feedstocks, a high peroxide value indicates ongoing oxidative deterioration and reduced suitability for fuel production. Although peroxide value is most informative during early oxidation stages, it remains an important indicator of storage conditions and shelf life. Oils with peroxide values below approximately 10 meq O₂/kg

are generally considered fresh, whereas significantly higher values indicate degradation.

The official determination of peroxide value is based on iodometric titration, as described in standard methods such as ISO 3960 or AOCS Cd 8b-90.

Peroxides present in the oil oxidize iodide ions to iodine, which is then titrated with standardized sodium thiosulfate. Results are expressed as milliequivalents of active oxygen per kilogram of oil.

CDR FoodLab® system for oils and fats quality control: easy, rapid and industry-friendly

CDR FoodLab® system represents a practical and efficient solution for the quality control of oils and fats used in biofuel production. Unlike traditional titration methods, which require significant sample preparation, solvent handling and skilled laboratory personnel, **CDR FoodLab®** operates with minimal sample treatment and ready-to-use reagents, reducing analytical complexity and turnaround time. The system delivers results within minutes, enabling rapid decision-making during raw material acceptance, storage monitoring and process control. Its photometric approach ensures reliable and repeatable measurements, and **results correlated with reference methods**, while limiting operator exposure to hazardous chemicals.

Compact and suitable for both laboratory and production environments, CDR FoodLab® supports industry needs for fast, accurate and regulatory-aligned analysis, contributing to improved process efficiency, cost control and consistent fuel quality.

Bibliography

- American Oil Chemists' Society (AOCS). (n.d.). *Official Method Cd 8b-90: Peroxide Value, Acetic Acid–Isooctane Method*. Champaign, IL, USA: AOCS.
- ASTM International. (n.d.). *ASTM D664 – Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration*. West Conshohocken, PA, USA: ASTM International.
- ASTM International. (n.d.). *ASTM D6751 – Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels*. West Conshohocken, PA, USA: ASTM International.
- European Committee for Standardization (CEN). (n.d.). *EN 14214 – Liquid petroleum products – Fatty acid methyl esters (FAME) for use in diesel engines – Requirements and test methods*. Brussels, Belgium.
- International Organization for Standardization (ISO). (n.d.). *ISO 3960 – Animal and vegetable fats and oils – Determination of peroxide value –*

Iodometric (visual) endpoint determination.
Geneva, Switzerland: ISO.

- Canesin, E. A., Oliveira, C. C., Matsushita, M., Dias, L. F., Pedrão, M. R., & Souza, N. E. (2014). Characterization of residual oils for biodiesel production. *Electronic Journal of Biotechnology*, 17(1).
<https://doi.org/10.1016/j.ejbt.2013.11.001>
- Kumar, M., & Sharma, M. P. (2016). Selection of potential oils for biodiesel production. *Renewable and Sustainable Energy Reviews*, 56, 1129–1138.
<https://doi.org/10.1016/j.rser.2015.12.032>
- Umeh, S. I., & Okonkwo, P. A. (2025). The essential properties of oils for biodiesel production. IntechOpen.
<https://doi.org/10.5772/intechopen.1008694>