**Challenging use and Development of new Additives Fatty Acid Methyl Ester (FAME)**

Dharmaraj Singh1\*, Intezar Mahdi2, Nadeem Ahmad3

*1,Department of Mechanical Engineering, IFTM University, Delhi Road, Moradabad (UP), India.*

*2,Department of Mechanical Engineering, Integral University, Lucknow (UP), India.*

*3,Department of Mechanical Engineering, IFTM University, Delhi Road, Moradabad (UP), India.*

# Introduction

Absolutely, the push for economic and technological advancement has led many countries to introduce changes aimed at enhancing production efficiency and management practices, with a focus on ecological considerations within legislation. The increasing demand for fuel and the depletion of traditional resources have driven the adoption of renewable energy sources for producing transport fuel, especially for combustion engines. The adaptable nature of combustion engines allows for modernization, making plant-based fuels a feasible concept. Given the depletion of petroleum resources, plant oils have emerged as a promising alternative due to their suitability for this purpose. [1].

# Background

Indeed, several studies have highlighted the effectiveness of using fatty acid methyl ester (FAME) derived from vegetable oils to improve the lubricity of diesel fuels, which directly impacts the performance of fuel pumps and injection equipment in diesel engines. Given the significance of lubricity in engine operation, investigating the tribological performance of FAME from vegetable oils is a valuable pursuit.

Using FAME, which is already being utilized as a load-carrying additive within engine lubrication, as an additive for lubrication of external meshing machine components appears to be a viable approach. This could potentially enhance the performance and longevity of such components while also contributing to sustainable practices by repurposing FAME in a different application. [2].

# Tribology

# History of Tribology

It encompasses the study of friction, lubrication, and wear. Tribology focuses on the science and engineering of interacting surfaces in relative motion, involving the principles of friction, lubrication, and wear. The term "Tribology" was coined by Jost in 2006, originating from the Greek word "tribos," which means rubbing. While Leonardo da Vinci first described the laws of friction, his work remained unpublished, and scientific studies of wear saw limited development until the twentieth century. The industrial growth during that era drove significant advancements in tribology knowledge due to the growing demand for understanding friction, lubrication, and wear across various applications. [3].

# Friction

It's the force that opposes the motion of surfaces sliding against each other. Friction acts in the opposite direction to the initial force that sets the surfaces in motion. Surfaces have coefficients of friction (μ) that range from 0 to 1. Smooth and well-lubricated surfaces typically have a lower μ, while rough surfaces have a higher μ closer to 1.

# Wear

Wear refers to the material loss experienced by components as they slide against each other. There are two main types of wear: abrasive wear and adhesive wear. Abrasive wear occurs when a harder surface removes material from a softer surface it slides against. Adhesive wear happens when surfaces stick together during sliding, causing material loss from one surface.

In addition to these two types of wear, there's a third failure mode that can occur under low-stress conditions. If a system undergoes repetitive cycles of the same load, it can eventually fail, even if the stress applied is lower than the ultimate tensile strength of the material. This failure is triggered by minuscule imperfections in the component, leading to nearly invisible microscopic cracks. While these cracks might not be initially problematic, repeated stress cycles cause them to propagate and grow, eventually leading to failure. [4].

# Lubrication

Lubrication involves using a lubricant to reduce wear between surfaces that are in close proximity and moving relative to each other. The lubricant is interposed between the surfaces to help carry the load or pressure generated between them. The lubricant can take various forms, including solid substances like graphite or MoS2, solid/liquid dispersions, liquids, liquid-liquid dispersions, and even gases in exceptional cases. The primary goal of lubrication is to create a protective layer that minimizes friction and wear, enhancing the longevity and efficiency of the interacting components. [5].

It involves a lubrication film with the thinnest possible thickness, resulting in minimal separation between sliding components. In boundary lubrication, additives such as extreme pressure (EP) or anti-wear (AW) agents are used to prevent friction and wear, as there isn't a significant physical separation between the surfaces. This form of lubrication relies on the additives to form a protective layer that minimizes direct contact between the surfaces, thus reducing wear and enhancing the lubrication process. [6].

# Materials used in Tribology

Lubricating materials can exist as gases, liquids, solids, or even hybrid states. Their primary role is to manage friction and wear, but they also contribute to controlling temperature, preventing corrosion, transmitting power, cleaning out debris, absorbing shocks, and more.

Liquid lubricants, typically made from various sources such as petroleum, plants, animals, and synthetics, are well-known and widely used. Additionally, semi-liquid or plastic lubricants like grease are commonly employed. Solid lubricants, though less common, are highly valuable in specialized and demanding applications where their unique properties prove advantageous. Overall, lubricating materials play a crucial role in maintaining the efficiency and longevity of mechanical components.[7]. Solid lubricants are often added to other lubricants to enhance their properties. They contribute specialized advantages to the lubricant mixture. Examples of solid lubricants include graphite, mica, and lead carbonate. Various metal sulfides are also employed as solid lubricants, such as bismuth sulfide, tungsten sulfide, copper sulfide, tin sulfide, zinc sulfide, and iron sulfide. These solid lubricants offer specific benefits in certain applications, helping to reduce friction, wear, and enhance the overall performance of lubricants.

# Challenging of Tribology

One of the major difficulties is the low visibility of tribology, mainly because it's a multidisciplinary domain that requires expertise from various fields to gain a comprehensive understanding. This complexity also makes it challenging to create accurate predictive models for simulating tribological processes. Another hurdle is the intricate nature of tribology itself. Much progress has come from empirical methods involving trial and error, as well as iterative experimentation, rather than a complete understanding of the underlying mechanisms. The multifaceted nature and reliance on practical experience make tribology a fascinating yet intricate field to navigate. [8]. Absolutely, advancing in the field of tribology will indeed require increased research efforts and the integration of various component fields into a unified discipline. By bringing together expertise from multiple domains and encouraging interdisciplinary collaboration, tribology can emerge as a distinct and self-standing field. This approach will enable a more comprehensive understanding of tribological phenomena and facilitate the development of effective solutions to the challenges it presents.

# Lubricant

A lubricant, often referred to as "lube," is a substance, typically a liquid, introduced between moving surfaces to reduce friction, enhance efficiency, and minimize wear. Lubricants can also aid in dissolving or transporting foreign particles and distributing heat.

In general, lubricants consist of around 90% base oil, often derived from petroleum fractions known as mineral oils, and less than 10% additives. While mineral oils are common, vegetable oils and synthetic liquids like esters, silicone, and fluorocarbons are also used as base oils. Additives play a crucial role in enhancing lubricants by reducing friction and wear, increasing viscosity, improving viscosity index, and providing resistance to corrosion, oxidation, aging, and contamination.

Beyond industrial applications, lubricants find use in various other contexts. These include biomedical applications such as lubricating artificial joints. Lubricants play a vital role in ensuring smooth operation and extending the life of mechanical components across a wide range of fields. [9].

# Lubricants serve a range of crucial purposes, including:

* Keeping moving parts apart
* Reducing friction
* Transferring heat
* Carrying away contaminants and debris
* Transmitting power
* Protecting against wear
* Preventing corrosion
* Sealing for gases
* Mitigating the risk of smoke and fire

Each of these functions contributes to the efficient and reliable operation of mechanical systems by minimizing wear, promoting smooth movement, and maintaining the overall health and longevity of components.

Lubricants serve various purposes beyond the conventional functions:

* Assisting proper movement of parts, such as locks and switches, to ensure they function as intended.
* Providing water resistance to surfaces, helping to repel water and prevent damage.
* Preventing wear and tear from impacting surfaces, extending their lifespan.
* Facilitating the transfer of power, particularly in hydrostatic systems, where lubricants aid in power transmission.
* Transferring heat from one surface to another, helping to manage temperature and prevent overheating.
* These diverse uses of lubricants showcase their versatility in meeting specific needs across a wide range of applications and industries.

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# Base Oil

A clear distinction between refined and synthetic oils and explained the concepts of base oil and additives in lubrication.

Refined oils, such as Paraffinic and naphthenic oils, are obtained through the refining of crude oil. The references to long chain molecules and ring structures are associated with paraffinic and naphthenic oils, respectively, and help explain their properties.

On the other hand, synthetic oils are manufactured rather than being derived from crude oil. These synthetic oils offer specific characteristics tailored to particular applications.

In all lubricants, the base oil is a fundamental component, forming the foundation before blending with additives or thickeners in the case of grease. This mixture of base oil and additives enhances the lubricant's performance and effectiveness in various applications. [10]. Selecting the appropriate base oil for a given application can indeed be a complex decision. Factors such as performance requirements, operating conditions, and budget constraints play a role in this choice. Understanding the differences between mineral oils and synthetic oils can help you make an informed decision.

Mineral oils are derived from crude oil through refining processes. They offer good general lubrication properties and are cost-effective, suitable for many applications.

Synthetic oils, on the other hand, are manufactured to precise specifications, offering tailored properties like higher viscosity index, better stability at extreme temperatures, and improved resistance to oxidation. While synthetics can provide enhanced performance, they are typically more expensive.

To make the right choice, assess your application's demands. If you need improved performance under extreme conditions or specific requirements, synthetic oils might be preferable. However, for standard applications, mineral oils can be a practical and economical option. Consider consulting with lubrication experts or referring to industry guidelines to ensure you make the most suitable base oil selection for your needs.

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# Base Oil Categories

This classification helps in understanding the different types of lubricants available:

**Mineral Oil:** Derived from crude oil, mineral oils vary in quality based on the refining process. They are versatile and cover a wide range of applications.

**Synthetic Oil:** Synthetics are artificially created through a synthesis process. They come in various formulations tailored for specific purposes, offering distinct properties like high temperature stability or better performance in extreme conditions.

**Vegetable Base Oil:** Derived from plant oils, these represent a small fraction of lubricants. They are primarily used for environmentally-friendly and renewable reasons.

Understanding these distinctions helps in selecting the most suitable lubricant for a given application based on its performance requirements, environmental considerations, and other specific needs. [11].

# Fatty Acid Methyl Ester (FAME)

FAME, derived from various vegetable oils and fats, shares physical properties with conventional diesel fuel. Its versatility allows it to serve as a blending component in fossil diesel or as a pure fuel, often referred to as B100. FAME's non-toxic and biodegradable nature has contributed to its adoption as a renewable alternative fuel, and it's interesting to note that FAME, along with Bioethanol, ranks as one of the leading renewable liquid fuels globally. In Sweden, FAME holds the position of the second-largest renewable liquid fuel in the market. [12]. the exclusive use of rapeseed methyl ester (RME) for FAME in the Swedish market reflects a commitment to meeting climate-related regulations. Rapeseed-based FAME aligns with the sustainability goals and requirements, showcasing how specific feedstock are chosen to support environmental objectives in different regions.

# Primary area of use

FAME is often referred to as biodiesel and is used as a fuel for diesel engine vehicles. It's commonly blended with fossil diesel to increase the renewable component in the fuel, with the current European diesel standard allowing up to 7% v/v of FAME in diesel without vehicle or distribution system modifications. FAME enhances lubricating properties and is fully miscible with fossil diesel. While it's biodegradable and nontoxic if spilled, its biodegradable nature can affect storage time, necessitating consumption within six months to prevent oxidation and polymerization issues. Vehicles using pure FAME (B100) need manufacturer approval to ensure compatibility with materials and engine settings. Additionally, FAME's sensitivity to cold climate is an important consideration. [13]. It's great to hear that an increasing number of trucks, buses, and light transportation vehicles have gained approval for using pure FAME (B100). The growth of the B100 market in Sweden and its rapid expansion suggests a positive trend towards adopting renewable fuels. However, you're right that there might still be a need to spread knowledge about this fuel to the rest of Europe. Raising awareness about the benefits, considerations, and approvals required for using pure FAME could contribute to its broader acceptance across the continent.

**Properties**

It's evident that the production and sustainability aspects of biodiesel (FAME) have been a subject of comprehensive study within various IEA-AMF tasks, including Task 45, Task 37, Task 34-1, and Task 30. The global trend towards using biodiesel as a substitute for diesel fuel is on the rise, with volumes of production and consumption growing significantly. This transition, from minimal usage in the mid-1990s to over 10 M-toe in 2009, is indicative of the increasing interest and adoption of biodiesel as an alternative and sustainable fuel source. [14]. By 2015, global biodiesel production had reached a substantial level of 23.5 M-toe (30.1 billion liters), making up 22% of the total biofuels production. However, along with this promising growth, certain technical challenges need to be addressed. These challenges include issues like oxidative stability, elastomer incompatibility, low-temperature flow properties, elevated NOx emissions, and competition for resources used in the food industry.

To maximize the impact of bio-derived fuels, it's important to adopt a diversified approach that utilizes various biomass feedstock and produces a wider range of fuel options. This would allow for a more comprehensive array of fuel choices, covering both gasoline and diesel replacements, while addressing the technical barriers associated with specific feedstock and climates. [15].

Absolutely, the concept of a flexible bio refinery is gaining importance as the world looks to diversify manufacturing processes. Paraffinic fuel options like HVO (Hydrogenated Vegetable Oil) are also emerging in this context.

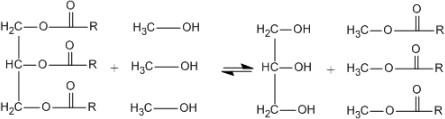
FAME biodiesel has acceptable ignition properties, often boasting a cetane number over 50. Its advantages include low sulfur and aromatic content, as well as good lubricity. However, there are drawbacks to consider, such as its high viscosity, poor performance in cold conditions, elevated boiling point, and the presence of impurities like triglycerides, glycerol, alcohols, sodium, potassium, and phosphorus. These factors underscore the need for continued research and development to enhance the overall performance of biodiesel fuels.

**Chemical structure**

Indeed, the process of transforming various raw materials like vegetable oils, animal fats, and recycled cooking greases into biodiesel involves a chemical reaction known as transesterification. This process, as illustrated in Figure 2, converts triglycerides and/or free fatty acids in these materials into esters by reacting them with alcohol. Sodium or potassium hydroxide is commonly used as a catalyst. The byproduct of this reaction is glycerol.

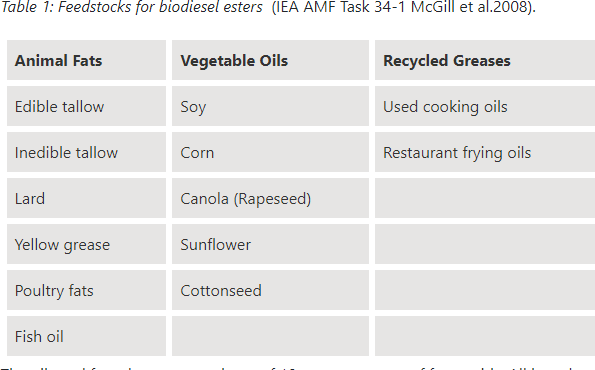
Currently, methanol is the predominant alcohol used in biodiesel plants. The processes and catalysts employed are optimized for methanol. While higher alcohols have the potential to be used, their yields tend to be lower compared to methanol. Interestingly, using higher alcohols may lead to an increase in cetane number (ignition quality) but could also raise viscosity. It's important to note that this discussion specifically focuses on fatty acid methyl esters (FAME), one of the key types of biodiesel. [16].

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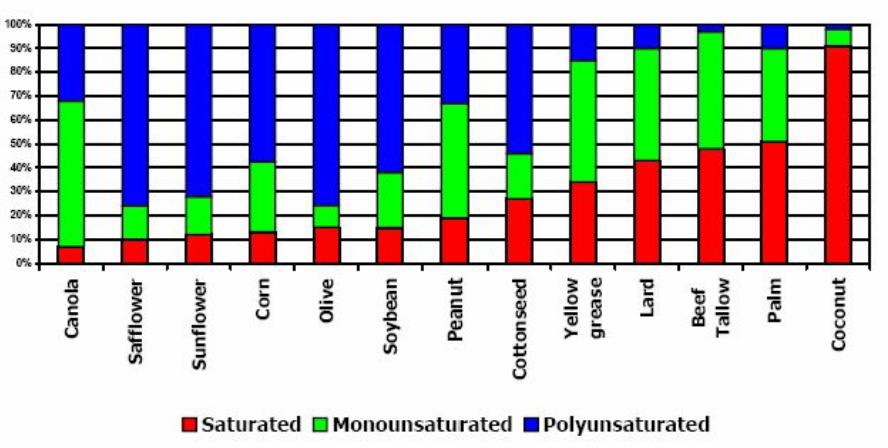


R= Carbon chain of fatty acid.

Certainly, the production of biodiesel esters can utilize a range of vegetable oils and fats, as indicated in Table 1. This diversity in feedstock sources provides flexibility and options for creating biodiesel that align with both availability and specific goals related to feedstock sustainability and performance.



The composition of the oils and fats listed earlier consists of 10 common types of fatty acids. These fatty acids typically have carbon atom counts ranging from 12 to 22, with the majority falling between 16 and 22 carbon atoms. Their saturation levels vary, with some being fully saturated, others monounsaturated (containing one double bond), and some polyunsaturated (containing multiple double bonds) in their fatty acid chains. This diversity in fatty acid composition contributes to the variability in properties and characteristics of the resulting biodiesel esters. [17].Certainly, the varying proportions of saturated, monounsaturated, and polyunsaturated fatty acids in the different feedstock’s you mentioned are depicted in Figure 3.

This distribution of fatty acid types among the feedstock’s influences the resulting properties and characteristics of the biodiesel produced from each source. It's this unique composition that contributes to the wide range of biodiesel options available, each with its own set of attributes and potential applications.

An essential aspect of biodiesel production – the varying degrees of saturation in different feedstocks significantly impact the properties of the final biodiesel fuel. This consideration becomes crucial when choosing the most suitable feedstock for the intended application of the biodiesel fuel. This relationship is effectively demonstrated in Table 1, which highlights the correlation between the degree of saturation in the feedstock and three key fuel properties: cetane number, cloud point, and stability.

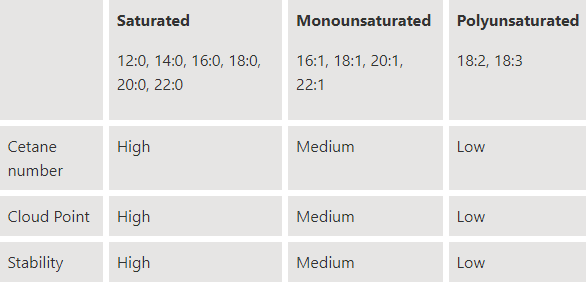
In this context, it's evident that fuels derived from saturated fatty acids generally exhibit better performance in terms of cetane number and stability. As the number of double bonds increases, the performance in these properties tends to degrade. This information underscores the importance of feedstock selection in achieving desired fuel characteristics for specific applications.[18].

The interconnected relationship between feedstock selection, biodiesel production, and engine performance. The choice of feedstock impacts the resulting biodiesel's characteristics, which in turn influence engine performance. In the context of diesel engines, various fuel parameters including cetane number, density, boiling range, aromatic compound content, and sulfur content significantly affect both engine performance and emissions. Additionally, properties like viscosity, lubricity, and impurity content play a critical role in determining engine durability.

It's also important to recognize that these properties can vary by region due to climate and other factors. Therefore, a holistic understanding of the entire cycle, from feedstock to engine performance, is essential in making informed decisions about biodiesel production and use, ensuring optimal engine operation, emissions control, and overall sustainability.

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The National Renewable Energy Laboratory (NREL) likely compiled this information in 2006 to illustrate how different feedstock compositions lead to different biofuel characteristics. Such tables are valuable tools for understanding the relationships between feedstock and final product properties, aiding in the selection of the best feedstock for specific applications.



# Legislation and standards

International standards for biodiesel fuels are crucial to ensure a certain level of quality and consistency across the industry. These standards are designed to guarantee that specific requirements are met during the fuel production process. For instance, they address key factors such as low sulfur content, as well as the absence of substances like glycerin, alcohol, catalyst, and free fatty acids. These standards play a vital role in maintaining fuel quality, compatibility, and performance, and they provide a common framework for both producers and consumers to follow. [19]. Basic industrial tests to determine whether the products conform to standards are specified in the standards rules.

The international standards for biodiesel in Europe and North America. In Europe, the EN 14214 standard outlines the requirements and test methods for FAME (biodiesel) before blending with diesel fuel. In the U.S. and Canada, the ASTM D6751 standard is referenced for neat biodiesel (B100) prior to blending. ASTM D6751 includes two grades, No. 1-B and No. 2-B, with the former having more stringent controls for minor components in raw materials.

Blended fuel standards are also established: ASTM D975 for on/off-road diesel up to 5% biodiesel (B5), ASTM D7467 for B6-B20 on/off-road applications, and ASTM D396 for heating oil up to 5% biodiesel. For these standards, B100 used must meet ASTM D6751 (either No. 1-B or No. 2-B grade) before blending.

This system of standards ensures that biodiesel fuels meet specific quality and performance criteria for safe and effective use. More detailed information can be accessed from ASTM's website (ASTM.ORG) or the National Biodiesel Board's website (NBB.ORG). [20]:

It's clear that these standards play a crucial role in ensuring the quality and compatibility of biodiesel fuels with different vehicles and engines. Standards such as EN590, EN16734, and EN16709 in Europe, as well as JISK 2204:2007 in Japan, outline the acceptable levels of FAME content in diesel fuels for different applications.

It's also worth noting that the World Wide Fuel Charter (WWFC) provides guidelines for fuels, including 100% FAME biodiesel, and helps manufacturers and consumers understand compatibility and performance.

Table 2 provides a comparison of biodiesel properties (Rapeseed Methyl Ester, RME) with the requirements outlined in EN 14214 and ASTM D6751 for 100% FAME biodiesel. This comparison is essential for understanding how biodiesel properties align with the established standards. It's great to see such detailed information that contributes to a better understanding of biodiesel standards and their impact.

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# FAME/Biodiesel projects

The FAME industry has faced concerns due to unclear political steering, debates on land usage, and changes in tax incentives, particularly in Sweden.

Despite these challenges, the global biodiesel development continues, with new production plants being established. While the political situation in the EU remains uncertain, several European countries are eager to increase biodiesel usage further. The approval of the new European Standard EN 16709 in August 2015, allowing B20 and B30 blends in fossil diesel, reflects this commitment to biodiesel expansion.

However, it's important to note that the application of this standard is not yet valid in Sweden due to the country's transportation fuel law, which restricts the marketing of diesel fuels containing more than 7% v/v of FAME. This highlights the complexity of navigating regulations and policies in different regions, and how they can impact the growth and direction of the biodiesel industry.

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# Physical & Chemical Properties of FAME

The characteristics of FAME (biodiesel) that distinguish it from hydrocarbon-only diesel fuel:

* FAME has higher viscosity, density, and different distillation properties.
* The lower energy content of FAME can lead to higher volumetric fuel consumption in diesel fuels containing FAME.
* FAME is a more effective solvent that can dissolve sediments in fuel tanks and systems, contributing to potential filter plugging.
* FAME exhibits distinct cold flow properties, often having a higher pour point, cloud point, and cold filter plugging point (CFPP) compared to conventional diesel fuels. [21].
* Impurities within FAME can have poor solubility both in FAME itself and in blended diesel fuel, which can negatively impact cold temperature performance and filterability.
* FAME is not compatible with certain metals, plastics, and coatings commonly used in fuel supply and distribution systems.
* Generally, FAME exhibits lower oxidation and thermal stability in comparison to hydrocarbon-only diesel. [22].

These differences highlight the need for careful consideration when handling, storing, and blending FAME, as well as the importance of selecting appropriate materials and monitoring fuel quality to ensure safe and efficient use.

# Challenges from FAME Use

The chemistry and composition differences between fatty acid methyl ester (FAME) and hydrocarbon-only fuels can indeed lead to challenges when blending FAME into diesel fuels. These challenges encompass various stages of the fuel production, blending, distribution, and supply processes. It's important to ensure that these challenges are effectively managed to maintain fuel quality, engine performance, and compliance with regulations. [23]. These include the effect of FAME as a neat product and as a blend component in diesel fuel on:

**Oxidation Stability:** Ensuring stable fuel quality over time and preventing oxidation-related issues, especially in terms of both thermal stability and longer-term storage conditions.

**Cold Flow Properties and Filterability:** Addressing potential challenges related to cold weather performance, including pour point, cloud point, cold filter plugging point, and the potential impact on filterability.

**Microbiological Growth:** Managing the potential for microbial contamination and growth within the fuel, which can lead to fuel degradation and clogged filters.

**Water Content:** Understanding how FAME might affect water content in diesel fuel, potentially leading to issues like degraded water shedding ability and increased dissolved water content.

**Material Compatibility:** Ensuring that FAME-blended fuels are compatible with the materials used in refineries, distribution systems, and fuel supply chains.

**Contaminant Removal:** Addressing the removal of dirt, rust, and other solid contaminants within the supply and distribution systems.

**Transport in Pipelines:** Considering the transportation of FAME/diesel blends through multi-product pipelines and other distribution systems, ensuring compatibility and safe handling.

**Safety and Waste Handling:** Implementing appropriate safety measures, firefighting procedures, and waste handling protocols related to FAME-blended fuels.

**Additive Performance and Compatibility:** Assessing the performance and compatibility of additives commonly used in distillate fuels when blended with FAME.

These challenges underscore the intricate nature of blending FAME with hydrocarbon fuels and the importance of addressing these considerations to ensure the quality, performance, and safety of the final blended fuels. [24].

# Fuel Additive Performance

It's crucial to ensure that the FAME used for blending doesn't contain additives beyond oxidation-stability improving additives to prevent compatibility issues with diesel fuel additives. Adding performance additive packages during or after blending can help optimize the fuel's properties.

Moreover, it's good to know that FAME is generally considered safe to use. However, caution should still be exercised to prevent rapid oxidation when exposed to air, especially for FAME with high iodine values. Proper handling and disposal of materials used with neat FAME are important to avoid potential hazards like spontaneous combustion. [25].

These additives are crucial for enhancing the performance, efficiency, and safety of various fuel types, whether they're used for transportation or electricity generation. They are designed to address operational challenges and improve specific performance features, and they can be used at different stages, from refining to distribution and end use.

Additives can be applied individually to address specific issues, or they can be combined to create multi-functional packages that cater to the needs of the automotive industry, for example. The treat levels of these additives are generally low, with varying dosages depending on the desired benefits. It's interesting to note that additive treat levels are considerably lower than the amounts of fuel blending components like ethanol or fatty acid methyl esters (FAME), which are typically added at levels of 3-20% of the hydrocarbon base fuel volume.

# Development of new additives

Absolutely, innovation is a constant requirement in the fuel additives industry, often driven by changing regulations and the need for higher quality fuels. Legislation altering fuel specifications, not just for automotive fuels, often triggers the development of new additives. For instance, the reduction of sulfur content in middle distillate fuels has necessitated the creation of lubricity additives to safeguard diesel injector pumps.

In other cases, there might be a demand for advanced multi-functional additive packages, which could involve novel additive components. These packages can contribute to improving vehicle fuel efficiency while minimizing the emission of regulated exhaust pollutants. The increasing use of diesel exhaust particulate filters has also driven the creation of fuel borne catalyst additives to aid in the cleaning or regeneration of these filters onboard vehicles. All these examples showcase the industry's need for ongoing innovation to meet evolving requirements and challenges. [27].

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