American Chemistry Council

Fuel Additives: A Review of Enabling Technologies

The American Chemistry Council's (ACC) Fuel Additive Task Group (FATG), a task group of the Petroleum Additives Panel, is comprised of fuel additive manufacturers[1].

INTRODUCTION

The landscapes of diesel fuel and engine technology for transportation have been changing fast to meet challenging environmental objectives. In the United States, federal, state, and local initiatives to reduce emissions have helped spur an energy transition in the transportation sector. Original Equipment Manufacturers (OEMs), oil marketers, fleets, and additive companies all play a role in this shift. OEMs are developing lower-emission engine designs, fuel producers are increasing the availability of renewable fuels and their blends, and fleets are making technology selections to meet regulatory requirements. The additives industry has been working closely with OEMs and fuels producers to facilitate these changes by helping to solve technical challenges. The appropriate use of fuel additives provides a cost-effective way to fill performance gaps, helping alternative fuels meet operational and environmental expectations.

Interviews conducted by FATG with key stakeholders reaffirmed the role of the additives industry as a critical partner to both fuels producers and OEMs in these fast-changing landscapes. The FATG is grateful for the time and feedback provided by: Scott Fenwick of Clean Fuels Alliance America, Gary Gunter & Paul Ryder of Phillips 66, Truck and Engine Manufacturers Association (EMA) staff, Shailesh Lopes of GM, and Jeff Klopfenstein of Cummins Inc. Looking ahead, outreach to additional user groups by the additives industry to share practical additive knowledge will be helpful in expanding overall understanding of fuel additive technologies, which in turn will lead to more effective use of these chemistries.

Over the past decade, renewable fuels such as biodiesel and renewable diesel have become increasingly popular as alternatives to conventional fossil-based, mineral diesel. They can help reduce carbon footprint, and the uptake of such fuels has also improved with large scale production and financial incentives from federal and local governments.

While biodiesel and renewable diesel can be produced using the same feedstocks, their chemical and performance properties are different. Biodiesel, also known as B100 or Fatty Acid Methyl Ester (FAME), is derived from the transesterification of fats, oils, and greases with methanol. On the other hand, renewable diesel, also known as R100 or Hydrogenated Vegetable Oil HVO, is derived from hydrogenation of the same feedstock. The difference in their chemical composition has led to different performance characteristics as well as challenges in using them as fuels in their pure form (100%).

Together, these efforts to develop alternative liquid fuels support an "all-of-the-above" national energy strategy. In the transportation sector, diverse fuel and technology pathways, including

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[1] The FATG members are Afton Chemical, BASF, Chevron Oronite, Infineum, Innospec, and The Lubrizol Corporation.

advanced diesel, renewable diesel, biodiesel, and future low-carbon solutions, can coexist and complement one another. By ensuring that additive technologies help bridge performance and environmental gaps, the industry not only enhances fuel reliability and consumer confidence, but also strengthens U.S. energy security, supports domestic manufacturing and supply-chain resilience, and helps keep transportation affordable and dependable for businesses and households. This balanced approach values innovation across every available energy option, ensuring that fleets, OEMs, and consumers alike have practical, cost-effective tools to maintain competitiveness in today's rapidly evolving energy landscape.

> Shailesh Lopes, GM, described the Alliance of Automotive Innovation's low carbon liquid fuel strategy which notes that a wide range of fuel and vehicle technologies will be needed to achieve significant GHG reductions from the transportation sector going forward. Lopes noted that fuel improvements are the largest remaining ICE "system technology" lever, and that some liquid fuel improvements can benefit the entire industry by reducing GHG emissions.

This article will overview the challenges associated with biodiesel and renewable diesel and how proper additive chemistries can help address them. The article also marks the first of a series aimed at exploring these technical challenges in more detail as well as sharing excellent practices recommended by additive producers.

COMMON CHALLENGES

Filterability/Solubility

As we move away from traditional petroleum-based fuels to biomass-based distillate fuel, and blends of the two, changes in fuel properties or contaminants can give rise to new problems related to solubility and filterability.

Renewable diesel is typically highly paraffinic. There is variability in the paraffin distribution of different renewable diesels, primarily due to differences in the chemical composition of the feed stock (fats and oils), but also based on isomerization, which may be done to improve the low temperature properties of renewable diesel. With no appreciable aromatic content, it has very different solubility characteristics than traditional diesel fuels.

Contaminants that were somewhat soluble in traditional diesel fuel may have poor solubility in renewable diesel and precipitate to cause filtration issues or deposits that can lead to filter plugging. Blending renewable diesel into conventional hydrocarbon diesel fuel can improve the solubility, but higher concentrations of renewable diesel may still exhibit issues.

Adding detergent/dispersants to renewable fuel blends can improve the solubility of contaminants and prevent them from precipitating out of solution.

> Scott Fenwick of CFAA, agrees that detergency challenges overlap with filterability. Investigating fuel blends of fossil and biomass-based diesel fuels, and the relationship of aromatics and solubility, may demonstrate that additive solutions are effective.

During production, there can be trace metals left in the biodiesel, such as sodium or potassium, which are either left over from the catalysts used in the esterification process or are already present in the fats and oils. These contaminants can react with the biodiesel itself, or with additives like corrosion inhibitors, to form salts that can precipitate out of solution and contribute to filter plugging. In addition, there are other naturally occurring molecules in feedstock fat or oil, or incomplete or unwanted reaction products that might contribute to filter plugging. There have been instances of filter plugging caused by insoluble and unwanted side products in biodiesel. Distilling biodiesel or treating biodiesel blends with diesel detergent/dispersants can prevent the precipitation of these contaminants and avoid filter plugging.

Specifications for the use of biodiesel as a blending component include limits on metals content and performance in cold soak filterability testing as ways to control undesirable chemical components. As the blend percentage increases, there may be a need to revisit these limits.

Lubricity

The lubricating properties of fuel play a critical role in the use of fuel in equipment in order to provide sufficient boundary lubrication between metal components in the fuel system. Equipment utilizing fuels with poor lubricating properties may incur damage to fuel system components such as the fuel pump, bearings, or other fuel-wetted surfaces where metals move in contact with one another.

> According to Paul Ryder, ensuring that lubricity additives are appropriate and effectively protect equipment is crucial to maintaining the long-term reliability of fuel systems.

Renewable diesel is comprised of n-paraffins and iso-paraffins, which are non-polar materials. These non-polar materials are not surface active and have limited lubricating performance when measured by the high frequency reciprocating rig (HFRR). The lubricity of n-paraffins increases as their carbon chain length increases.

In the production process of renewable diesel, the predominant carbon chain lengths present are C15-C18. Given both the purity and distribution of carbon chain lengths in renewable diesel, it’s not expected that renewable diesel will have sufficient lubricating properties to meet the ASTM D975 specification of less than 520 µm for High Frequency Reciprocating Rig Wear Scar Diameter without the use of additives.

Biodiesel Stability

Biodiesel stability[2], which includes oxidative, storage, and thermal stability, can vary greatly between different sources of biodiesel. Biodiesel made from feedstocks with a higher degree of unsaturation tends to be less stable than those made from more saturated feedstocks. As biodiesel and biodiesel blends age, organic peroxides, carboxylic acids, aldehydes, higher molecular weight and polymerization products, insolubles and other degradation products may form, potentially impacting the physical and performance properties of the fuel. For example, certain organic acid degradation products may interfere with the performance of cold flow improver components, resulting in poorer cold sedimentation test results and greater separation of fuel components in cold climates. These degradation products may also impact fuel conductivity. Insoluble components

[2] Jain, S. and Sharma, M.P. (2009). Stability of biodiesel and its blends: A review. Renewable and Sustainable Energy Reviews, 14(2), 667-678. https://doi.org/10.1016/j.rser.2009.10.011

and polymerization products may impact filtration performance and the visual appearance of the fuel as well. Overall, the formation of degradation products from poor stability may impact various fuel properties and performance parameters including, but not limited to, density, viscosity, color, clarity, filtration, sedimentation, cold flow performance and conductivity. Environmental factors including the presence of oxygen and water, temperature, light, and interaction with contaminants, may impact fuel degradation, and should be considered when storing and handling biodiesel blends.

According to EMA staff, EMA members are aware of the use of additives to improve the stability of biodiesel blends. They generally defer additive selection to fuel providers and simply focus on the desired finished-fuel requirements.

Additives such as antioxidants can help slow the aging process where high levels are biodiesel are involved. An effective way of reducing the impact of degradation products on fuel stability is to add an antioxidant into the fuel as early as possible. This helps prevent and delay the formation of degradation products from the start, before the fuel may become too far oxidized to recover. In cases where oxidation has already begun, certain additives may be able to neutralize the resulting organic acids, thereby reducing the potential negative effect on cold sedimentation and filtration. Lab evaluations conducted prior to field use can help identify the most effective type and dose of additive for the given biodiesel blend.

Cold Flow

Both renewable and conventional diesels contain n-alkanes. In conventional diesel, at low temperatures, these n-alkanes precipitate as thin rhombohedral plates. In contrast, depending on production process, renewable diesel may contain larger numbers of n-alkanes that precipitate in a rapid and uncontrolled manner resulting in larger amounts of random shaped wax crystals. This not only leads to a challenge in transporting the fuel during winter due to high pour points, but these wax crystals can also cause significant issues in terms of blocking vehicle fuel filters when temperature drops below the fuel's Cloud Point.

For biodiesel, a similar mechanism can be seen. If not treated, saturated biodiesel will precipitate out of solution and lead to similar filter blocking problems. In addition to saturates, precipitation of impurities such as Saturated Mono-Glycerides (sMG) and Sterol Glucosides (SG) can also lead to filter blocking above cloud point.

According to Gary Gunter of P66, cold flow additives may also help the capacity of renewable diesel facilities that use isomerization by achieving a lower isomerization rate while still reaching a cold flow target. Alternatively, if materials don't get isomerized the first time around, a facility may have to ramp up its recycle rate, which can reduce capacity.

The amount of n-alkane in renewable diesel and saturates in biodiesel limits their use in the pure forms in the United States, particularly during the cold months. Furthermore, even when used as a blend component with conventional diesel, their level of use is also limited. Engineering solutions such as deeper isomerization, and cold filtration can be employed to help improve cold flow characteristics, therefore expanding their usage. However, these processes can be expensive and therefore increase the cost of final product. In many circumstances, Cold Flow Additives are used as an economical, and effective solution to address these cold flow problems and promote usage of renewable diesel and biodiesel geographically broadly and deep into the cold season.

> Scott Fenwick, of CFAA, reminded us that challenges like cold flow aren't new issues. Increasing the usage of renewable diesel can contribute to those issues and new chemistry and new data is going to be needed.

These additives co-crystalize with wax molecules at early stage, then work to modify their structures in such a way that they don't cause issues such as filter blocking. While treating renewable diesel and biodiesel in their pure form is still a challenge and requires very specialized chemistries, many commercially available chemistries today are often capable of addressing cold flow problems of renewable diesel and biodiesel blends, thereby promoting usage of these alternative fuels.

Deposit Control

Fuel injection equipment (FIE) has a critical role in vehicle operation. Fuel injectors have a high degree of precision to ensure the proper metering of fuel which allows for smooth vehicle operation. Improper timing can lead to power loss, reduction of efficiency, increase in emissions, or engine damage.[3] Injector deposits are one of the most common causes of injector performance deterioration. These deposits can come from a variety of sources including metal deposits and degradation of fuel. Deposit control additives, DCAs, have long been used to reduce and maintain a clean injector in mineral diesel and biodiesel blends.[4]

> Jeff Klopfenstein of Cummins pointed out instances where additive could be used to address deposits during investigations of the root cause of field issues.

Renewable diesel and its blends can also benefit from the use of DCAs. Due to its paraffinic nature, renewable diesel can have many benefits including its oxidation stability and high cetane number. The increased stability of 100% renewable diesel may help mitigate the formation of carbonaceous deposits that interfere with injector performance, but it does not remove any existing deposits that may be formed from the usage of other fuel blends. With the current availability of renewable diesel in the U.S. still limited, the use of a DCA in renewable diesel could help facilitate its use in petroleum and biodiesel blends to help ensure optimal operation of FIE.

As renewable diesel continues to grow in the U.S., it will likely start to utilize the same infrastructure as petroleum diesel. This may increase the risk of metal contamination with renewable diesel. Even miniscule levels of metal contaminants in the fuel can cause injector deposits. The use of DCAs has been proven to remove and mitigate the formation of these deposits. Additionally, with the increase of renewable diesel, there could be an increase in the blending of renewable diesel with biodiesel and/or mineral diesel which would lead to similar issues we see now with mineral/biodiesel blends.

Use of a DCA can help achieve optimal performance of FIE systems.

[3] SAE 911710 https://doi.org/10.4271/911710
[4] SAE 932737 https://doi.org/10.4271/932737

LOOKING FORWARD

Engine technology and the fuel landscape will continue to evolve together in the coming years. If liquid fuel is being used, similar opportunities and challenges described here will continue to exist. Therefore, the additive industry will continue to play an important role in not only solving these problems but also raising awareness of additive technologies to different user groups which ultimately will lead to improved deployment effectiveness in the field. By leveraging appropriate additive technologies, renewable fuels can be used more effectively, ensuring reliable engine operation and supporting a sustainable energy future.

According to Gary Gunter of P66, the FATG additive companies work well in industry; additive company participation at CRC is appreciated. Involvement at industry venues like CRC, ASTM, TOP TIER, etc. provides value to all participants, which is important to maintaining a knowledge base for future employees.