

Bell Performance, Inc.tel 407-831-50211340 Bennett Drivefax 407-331-1125Longwood, FL 32750www.BellPerformance.comwww.WeFixFuel.comwww.WeFixFuel.com

Biodiesel Fuel Stability & Bio Dee-Zol Life

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Over the past eight years, biodiesel fuels have transformed from being "an expanding fuel market" to, in 2014, an integral part of the nation's diesel fuel usage landscape. Production rates in that time have skyrocketed – from 70 million gallons in 2005 and 200 million gallon in 2006 to 1.33 billion gallons in 2013. Independent of government and political mandates, fuel consumers, gravitate towards biodiesel because it is a renewable fuel (to reduce national dependence on foreign oil sources) and it is environmentally-friendly (reduces emissions). Producers of biodiesel also find that it is easy to manufacture.

Stability Issues

Despite its positive qualities, biodiesel has certain negative chemical characteristics which must be taken into consideration when using it as an alternative fuel. Of greatest concern are its problems with storage stability. It is commonly known that alternative fuels derived from biological sources (including biodiesel) are inherently more unstable than traditional petroleum fuels like diesel and gasoline.

The degradation of biodiesel follows two main chemical processes – hydrolysis and oxidation. These process are influenced by exposure to certain common environmental elements.

- Instability from Hydrolysis When biodiesel is exposed to water, a hydrolysis reaction happens across the ester linkage of the biodiesel molecule, resulting in an increase in the acidity of the fuel. An increase in the acidity of the bio-material in the fuel directly increases the rate of degradation and decomposition of the biodiesel blend. This is why it is important to know the biodiesel's total acidity, or Acid Number. A biodiesel blend that is out of spec in respect to this will not retain its fuel quality in storage.
- **Instability from Oxidation** As biodiesel is exposed to air, it reacts with the oxygen in the air to form peroxide compounds. These peroxides function as precursors in the fuel, giving rise to chain reactions that further break down normally-stable molecules in the fuel. This eventually produces gums, varnishes and other compounds which are harmful to engine components.
- **Instability from Heat** Biodiesel is generally stable in the presence of heat if it is kept away from oxygen and water. But if stored at high temperatures for long periods of time (such as in a hot climate in Florida or Texas), the fuel becomes more susceptible to the effects of other environmental factors linked to causing fuel instability (microbes, hydrolysis and oxidation).

Fuel Factors Controlling The Stability of Biodiesel

Bio-feed composition, environmental conditions, the removal of natural preservatives, and petroleum-feed composition are the most important factors controlling the stability of biodiesel fuels.



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Bio-feed Composition

By this, we mean the composition of the feedstock oil which was used to produce the bio-portion of the biodiesel blend. Different oils, such as soybean, coconut, palm or animal fats, react differently to the chemical processes used to transform the oil into usable biodiesel stock. While they indeed become transformed into combustible fuel, the biodiesel molecules forms from these kinds of feedstocks score higher on measures of oxidative instability. Their oxidative instability properties are related to the amount of olefinic or unsaturated materials produced by the conversion processes. Higher amounts of unsaturated molecules in biodiesel produced from these kinds of oils means greater storage instability.

Environmental Conditions

Water content, microbial presence, exposure to sun light, exposure to metals during transport and storage, exposure to oxygen and the presence of natural preservatives are all key influences upon instability of biodiesel.

- Water Content Exposure to water causes hydrolysis reactions to occur which increase the • acidity and instability of the fuel.
- **Microbial Presence** If water is present in the fuel, there's a greater chance that microbes are growing in the fuel as well. Microbes produce enzymes such as lipases during their life cycle which help to digest biodiesel as a food source for them, but which have deleterious effects on the fuel and its stability.
- **Exposure to Light** Exposure to light increases both the rate and the magnitude of oxidation. Light will cause peroxides to be formed, but by different mechanisms than conventional causes like exposure to air. This "light-enhanced oxidation" cannot be eliminated by conventional antioxidants, which is why it is important to keep biodiesel fuel out of contact with sunlight if being stored for longer than short periods of time.
- **Exposure to Metals** Some metals, like copper and manganese, can act as oxidation catalysts, increasing the production and decomposition of the peroxides precursors to fuel instability.

Natural Preservatives in Biodiesel

Many plant oils (like soybean oil) naturally contain vitamin E derivatives called tocopherols. These act as preservatives to extend the storage life of the plant oils, and may also act as stability improvers for the biodiesel fuels themselves. Unfortunately, biodiesel processors will often remove these compounds from the fuel in order to sell them as by-products to other industries. These contributes to lower storage stability for these biodiesel fuels.



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Petrodiesel Fuel Makeup

The EPA mandates from the mid-2000s to lower the sulfur content of diesel fuel down to 15 ppm (thus producing ultra-low sulfur diesel, or ULSD) requires diesel refiners to hydrotreat the fuel to remove the sulfur. The chemical process of hydrotreating both removes and changes the structure of certain molecules in the fuel that previously would have protected the fuel against oxidation and instability. For this reason, polymers, varnishes and gums tend to form more quickly in ultra-low sulfur diesel than in higher-sulfur diesel fuel. Thus, the removal of sulfur to satisfy ULSD production requirements has a negative impact upon the oxidative stability of biodiesel blends made with ultra-low sulfur diesel.

Improving Biodiesel Fuel Stability: Bio Dee-Zol Life

To combat this problem of instability, Bell Performance has introduced a multi-purpose biodiesel additive called **Bio Dee-Zol Life**, designed to help stabilize biodiesel blends. Test data on the active ingredients in **Bio Dee-Zol Life** show that it is highly effective in improving the stability measurements for biodiesel blends exposed to different types of storage situations.

The Rancimat Rating for Fuel Stability

Measuring biodiesel stability involves utilizing the ASTM D6751 specification for biodiesel, which assigns a Rancimat rating to define a measurement of stability for biodiesel. The United States standard requires biodiesel to maintain three hours of stability under the Rancimat method. The European biodiesel standard requires six hours.

In surveys conducted on soy biodiesel evaluated for oxidative stability, it has been determined that most fresh biodiesel samples will initially exceed the three hour minimum specification. However, as this new biodiesel is stored, the stability measurement diminishes over time due to factors described earlier in this paper.

Bio Dee-Zol Life and Oxidized Fuel Stabilization

Traditional stabilizers are added to biodiesel to guard against and prevent the fuel from degrading. In certain instances, these stabilizers can correct oxidative degradation which has already occurred, defined as increasing the Rancimat rating of a fuel sample who's Rancimat rating has started to decrease due to oxidative instability development. This benefit is in contrast to cold flow improvers, which can be used to prevent fuel gelling but cannot reverse gelling once it has occurred.

Testing with the active ingredients in **Bio Dee-Zol Life** showed that biodiesel fuels treated with the ingredients had Rancimat ratings increased by 100-150% as compared to measurements before additizing with the ingredients. This shows that the active ingredient in **Bio Dee-Zol Life** was effective in correcting instability issues associated with aged and oxidized biodiesel fuel.



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Bio Dee-Zol Life and Mingled Fuel Instability

It is inevitable sometimes that fresh biodiesel and aged biodiesel end up mixed together within storage tanks. Adding old and new biodiesel together adversely impacts the stability of the entire blend – research has shown that the Rancimat rating for such a blend decreases as the percentage of aged biodiesel increases.

- Adding just 10% aged biodiesel to fresh biodiesel reduces the Rancimat rating of the blend by almost 50%.
- Increasing the percentage to 25% cuts the Rancimat rating by over 70%.

So it becomes evident that adding as little as 15% of an unstable biodiesel to fresh fuel can drag the stability of a high quality biodiesel fuel out of specification.

The active ingredients in **Bio Dee-Zol Life** have been shown to minimize the Rancimat depression that occurs when blending old and new biodiesel together. For example, a blend of old and new fuel with an out-of-spec Rancimat rating of just 2.03 hrs was treated with stabilizer and saw an improvement in its stability rating of 160%, up to 5.32 hrs - well above the standard specification requirement. So the **Bio Dee-Zol Life** product proves very useful for minimizing potential problems if the need arises to store old and new biodiesel fuels together.

Bio Dee-Zol Life and Instability Caused by Metallic Exposure

Research shows that the presence of a transition metal like copper will cause up to a 50% loss in oxidative stability. When treated with the active stabilizer in **Bio Dee-Zol Life**, the reduction in Rancimat rating was reduced by 90%, such that the biodiesel samples remained above specification for stability when exposed to these catalytic metals.

Conclusion

Biodiesel users can better take advantage of the fuel's great qualities if the downsides of the fuel can be minimized. Factors such as oil feedstock composition, exposure to oxygen, water, and sunlight, and metallic storage containers can all cause the fuel to degrade more quickly than it is supposed to. The use of a high quality stabilization product such as **Bio Dee-Zol Life** can minimize fuel-related problems and associated potential equipment problems encountered by unstable biodiesel fuel.

For more information on **Bio Dee-Zol Life** and other high quality Bell Performance products for biodiesel, ethanol, gasoline and diesel, visit their web site at <u>www.BellPerformance.com</u> or call 407-831-5021.

Erik Bjornstad is Technical Sales Director for Bell Performance. He can be reached at 407-831-5021 x233 or by email at <u>ebjornstad@bellperformance.net</u>.