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# Bio Dee-Zol Life® & Improving The Stability of Biodiesel Blends

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## Executive Summary

- For protecting the oxidative stability of biodiesel, **Bio Dee-Zol Life®** significantly outperformed both TBHQ and BHT traditional hindered phenol solutions for fuel stability by substantial margins - an average of **213% improvement** in Rancimat rating. *See Samples 1-8 for details.*

- **Bio Dee-Zol Life®** was especially effective in both animal-based biodiesel fuels (i.e. tallow, chicken fat, used grease) and already-unstable biodiesel fuels (with Rancimat ratings < 3.00), improving oxidative stability scores by 200-500% or more in many cases. *See Samples 1-8 for details.*

- **Bio Dee-Zol Life®** was more effective than BHT or TBHQ at protecting oxidative stability while also requiring lower treat rates to use. *See Samples 1-8 for details.*

- For protecting thermal stability of biodiesel, the hindered phenol stabilizers BHT and TBHQ were marginally effective at improving reflectance when used at 60 – 200 mg/l. **Bio Dee-Zol Life®** had more than 2x the beneficial effect on thermal stability when used at only 30 mg/l. *See Sample 9 for details.*

- BHT and TBHQ were both ineffective at protecting biodiesel oxidative stability from the effects of catalytic metals (33-77% drop in B100). **Bio Dee-Zol Life®** was highly effective, with virtually no drop in oxidative stability measurements after metal exposure. The same was true for B10 fuels measured for thermal stability. BHT and TBHQ treatment of metal-exposed B10 still saw a 48% drop in reflectance. **Bio Dee-Zol Life®** prevented virtually any reflectance reduction whatsoever. *See Sample 10 and Sample 11.*

- **Bio Dee-Zol Life®** demonstrated the ability to protect biodiesel blends against Rancimat reduction when aged biodiesel content was combined with fresh biodiesel content (mingled fuel instability). Biodiesel dosed with 1000 ppm **Bio Dee-Zol Life®** retained more than 80% of its Rancimat oxidative stability that was lost in untreated biodiesel. *See Sample 12 for details.*

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**Bio Dee-Zol Life®** was introduced by Bell Performance in 2007 as a treatment solution for stored biodiesel blends. Its primary use is for preserving the storage stability of biodiesel blends as well as for reversing the degradation of biodiesel fuel quality which has already started dropping. The recommended treat ratio is for **Bio Dee-Zol Life®** is 1:1280 (1 ounce per 10 gallons) for biodiesel blends of up to 20% concentration (B20). Biodiesel blends with higher proportions of FAME may be successfully treated with increased dosing rates.

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**Introduction**

Over the past decade, biodiesel fuels have shifted from being merely "an expanding fuel market" to 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 gallons in 2006 to 1.33 billion gallons in 2013.
In addition to being incented through government tax credits 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). More than ten years on since tax policy shifted to encourage its use, biodiesel is now universally present across the nation's diesel fuel supply, with virtually all on-road diesel fuel containing at least 2% biodiesel content.

**Stability Issues & Problems Associated With Biodiesel Blends**

Despite its positive qualities (lower emissions, increased lubricity), biodiesel fuels have certain negatives which must be taken into consideration when using them. Storage stability is, perhaps, chief among those concerns. Alternative fuels derived from biological sources (including biodiesel) are inherently less stable than traditional petroleum fuels like #2 diesel fuel and gasoline.

Several processes and factors influence the degradation of biodiesel. These processes are also 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. This acidity increase directly speeds up the rate of degradation and decomposition of the biodiesel blend. This phenomenon is reflected in the fuel's Acid Number (a measure of the biodiesel's total acidity), which users can reference in their fuel spec. A biodiesel blend that is out of spec in respect to this will not retain its fuel quality for a satisfactory period of time.

- **Instability from Oxidation (Oxidative Instability)** – As biodiesel is exposed to the oxygen in air, it reacts to form peroxide compounds. These peroxides function as precursors of instability in the fuel, kicking off chain reactions that form alcohols, aldehydes, and other molecules that attack and break down stable molecules in the fuel. The eventual result is the formation of heavy molecules like gums, varnishes and other compounds which are harmful to engine components.

- **Instability from Heat (Thermal Instability)** – Biodiesel is generally stable in the presence of heat if it is kept away from oxygen and water. If it is stored at elevated temperatures for long periods of time (such as in a hot climate in Florida or Texas), the fuel does become more susceptible to the effects of other factors linked to instability (microbes, hydrolysis & oxidation).

- **Microbial Presence** – If water is present in the fuel, there's a greater chance that microbes are growing in the fuel as well. Biodiesel, by its nature, tends to attract and hold water to a greater degree than conventional petrodiesel. 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 in the fuel. 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** – Metals can enter the fuel storage & distribution system through any number of processing and transport avenues. Some metals, like copper and manganese, can act as oxidation catalysts, increasing the formation and decomposition of the peroxide precursors to fuel instability. As this happens, the rate of fuel degradation is greatly increased.

## Fuel Characteristics Influencing Biodiesel Stability

For a fuel to be designated as biodiesel, it must meet ASTM D6751 specifications independent of the oil or fat or even the specific process used for its manufacture. And as biodiesel is a manufactured fuel, there are some fuel-specific characteristics that play a part in determining the stability (or lack thereof) of biodiesel fuels. These characteristics include *bio-feed composition, the presence (or lack thereof) of natural preservatives, and petroleum-feed composition*.

### *Biodiesel Feedstock Composition*

By this, we mean the composition of the feedstock oil which was used to produce the bio-portion (the FAME) of the biodiesel blend. Different oils, such as soybean, coconut, palm or animal fats, react differently to the chemical processes used to transform them into usable biodiesel stock. While they all may become transformed into combustible fuel, the biodiesel molecules formed from different feedstocks may score higher or lower on measures of oxidative instability. Their scores are related to the amounts of olefinic or unsaturated (double-bonded) material produced during these conversion processes. Higher levels of unsaturated molecules in biodiesel are linked to poor storage instability.

### *Presence of Natural Preservatives in Biodiesel*

Plant oils contains higher natural levels of 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. Processing of these plant oils into biodiesel fuel may involve removing these compounds from the fuel in order to sell them as by-products to other industries. Without these natural stabilizers, the resulting biodiesel fuels have lower storage stability scores.

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***Petrodiesel Fuel Makeup***

Beyond the biodiesel FAME itself, the substantial changes to conventional diesel itself have influenced the stability of biodiesel blends. The primary culprit for this is the EPA sulfur-removal mandates from the mid-2000s. These require diesel refiners to hydro-treat diesel fuel to remove or substantially lower sulfur content. This process 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 today's diesel fuels than in fuels from the past. And this means these processes are a contributing factor to the poor oxidative stability of biodiesel blends made with today's ultra-low sulfur diesel fuels.

**Biodiesel Fuel Stabilization Solutions**

The problem of biodiesel instability has been studied extensively over the years, as the fuel industry seeks to gain a greater understanding of the mechanisms causing this phenomenon. Over the years, the industry has looked at the pathways of fuel degradation (peroxide formation and decomposition), the by-products of decomposition formed in the fuel (aldehydes, ketones and acids), the various types of chemical reactions that take place when these by-products are interacting within the fuel, and the impact of outside factors (light, water, metal exposure) on the entire process. One thing is for certain – the storage stability problems inherent with biodiesel fuels necessitate effective fuel-borne solutions for the marketplace.

Historically, a number of chemistries have been used to address these issues. But not all of them have been proven effective at every essential function necessary to comprehensively address biodiesel instability. Hindered phenols have been the historic weapon of choice for fuel stabilization, but this chemistry doesn't effectively work in biodiesel to slow peroxide formation, or inhibit their decomposition, or blunt the effects of metal-catalyzed oxidation. Biodiesel fuels need something better.

Effectively combatting biodiesel instability requires packages or combinations of ingredients to better address all of these factors. The right package of solutions can enhance biodiesel fuel stability and delay the onset of damaging oxidation while also even correcting oxidative degradation of biodiesel fuel that has already occurred (through inhibiting the effect of some chemical by-products associated with peroxide decomposition).

To meet the needs of the market in this regard, Bell Performance offers **Bio Dee-Zol Life®**, a stabilizer treatment specific to the needs of stored biodiesel blends. Comparative testing data shows that **Bio Dee-Zol Life®** is highly effective in improving the stability characteristics of biodiesel blends exposed to different types of storage situations. It also shows that **Bio Dee-Zol Life®** offers superior performance to other conventional stability chemistries available in the marketplace.

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**Evaluating Stabilizers For Biodiesel Fuel To Counteract Oxidative and Thermal Instability**

The superiority of **Bio Dee-Zol Life®** may be seen when it is compared with alternatively available chemistries. As such, it was tested against two market-available simple hindered phenol anti-oxidants: BHT (Butylated hydroxyl toluene) and TBHQ (tert-Butylhydroquinone). BHT and TBHQ were evaluated as 100% active formulations vs. **Bio Dee-Zol Life®.** All three market options were tested for performance and enhancement of biodiesel stability under both oxidative and thermal stability testing.

**Oxidative Stability & Rancimat Testing**

ASTM D6751 states that the standard for measuring the oxidative stability of biodiesel involves utilizing the EN14112 Rancimat test method. This defines oxidative stability of biodiesel in terms of an hourly score called an induction period. The oxidative stability characteristic is valued within the industry because it is predictive of the stored fuel's stability over time, whether biodiesel or petroleum-based.

The United States standard requires biodiesel to score a minimum of three (3.00) hours of stability under the Rancimat method. The European biodiesel standard requires six (6.00) hours.

*Starting Rancimat Ratings For Fresh Biodiesel*

Surveys conducted on soy biodiesel evaluated for oxidative stability confirm that virtually all fresh biodiesel samples will initially exceed the three-hour minimum specification. This is not surprising as this is the legal requirement for them.

*Reduction of Biodiesel Fuel Rancimat Ratings Over Time*

Despite starting within specification, as this new biodiesel fuel is stored, its stability measurement diminishes over time due to factors described earlier. To illustrate this, a cross-section of aged soy biodiesel fuel samples was tested for oxidative stability. Their results showed that their measurements diminished over time. Their results are listed below.

| Fuel | Composition | Rancimat Hrs |
|---|---|---|
| A | Soy | 1.85 |
| B | Soy | 2.86 |
| C | Soy | 1.49 |
| D | Soy | 3.19 |
| E | Soy | 4.46 |
| F | Soy | 2.98 |
| G | Soy | 5.44 |
| H | Soy | 3.60 |

All of these biodiesel fuel samples initially met ASTM specifications for oxidative stability, meaning their Rancimat ratings were a minimum of 3.00 hours induction period. But after a period of time in storage, four of the samples – those with scores less than 3.00 - no longer met the specification, meaning they had already undergone oxidation and had become partially "rancid."

**Enhancement of Oxidative Stability in Biodiesel**

To illustrate its effectiveness, **Bio Dee-Zol Life®** was evaluated with the two other dominant stability chemistries – BHT and TBHQ – for the enhancement of biodiesel oxidative stability under the Rancimat method. Three different samples of soy biodiesel were tested, each with differing initial stabilities (unstable, moderately stable, and stable). Soy biodiesel was chosen because it is the most common bio feedstock used for biodiesel in the United States.

Rancimat ratings were taken in soy biodiesel with treatment rates of 0 (untreated baseline), 100 mg/l, 300 mg/l, 600 mg/l and 1000 mg/l. The exceptions were that **Bio Dee-Zol Life®** was not tested at 1000 mg/l (due to having satisfactory test results at levels below this) and that the BHT chemistry was only tested at 1000 mg/l.

*Sample 1 – Unstable Soy Biodiesel*

Following are the test results from an unstable soy biodiesel with starting Rancimat rating of 2.02 hours, which is well below the minimum acceptable rating of 3.00.

| Soy Biodiesel (#1) | 2.02 | | | | |
|---|---|---|---|---|---|
| | | Treat Rate mg/l (ppm) / (% Improvement from Untreated) | | | |
| | 0 | 100 | 300 | 600 | 1000 |
| BIO DEE-ZOL LIFE® | | 2.37 (+17%) | 2.90 (+43%) | 3.49 (+72%) | |
| BHT | | | | | 4.75 (+135%) |
| TBHQ | | 2.23 (+10%) | 2.49 (+23%) | 3.04 (+50%) | 4.03 (+99%) |

**Results:** All three chemistries showed improvement of the out-of-spec soy biodiesel. **Bio Dee-Zol Life®** improved the fuel's Rancimat rating by a greater % than TBHQ at the same treat rates. BHT produced the highest improvement, but only at the highest treat rate of 1000 mg/l, and was not evaluated at the lower treat rates. It took a minimum of **600 mg/l** of both **Bio Dee-Zol Life®** and TBHQ to bring the unstable biodiesel back up to spec for oxidative stability.

*Sample 2 – Moderately Stable Soy Biodiesel*

Next, a moderately stable soy biodiesel was tested, with starting Rancimat rating of 3.23 hours which meets the minimum stability specification of 3.00.

| Soy Biodiesel (#2) | 3.23 | | | | |
|---|---|---|---|---|---|
| | | Treat Rate mg/l (ppm) / (% Improvement from Untreated) | | | |
| | 0 | 100 | 300 | 600 | 1000 |
| BIO DEE-ZOL LIFE® | | 4.01 (+24%) | 4.65 (+44%) | 5.44 (+68%) | |
| BHT | | | | | 4.96 (+53%) |
| TBHQ | | 3.29 (+1%) | 3.95 (+22%) | 4.79 (+48%) | 6.63 (+105%) |

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**Results: Bio Dee-Zol Life®** showed superior results vs. both BHT and TBHQ in this moderately stable biodiesel. Just 100 mg/l of **Bio Dee-Zol Life®** produced a greater improvement than 300 mg/l of TBHQ. 600 mg/l of **Bio Dee-Zol Life®** improved the fuel's stability more than 1000 mg/l of BHT.
*Sample 3 – Stable Soy Biodiesel*

Next, a stable soy biodiesel was tested with a starting Rancimat rating of 5.26 hours. This fuel would be considered "very stable".

| Soy Biodiesel (#3) | 5.26 | | | | |
|---|---|---|---|---|---|
| | | Treat Rate mg/l (ppm) / (% Improvement from Untreated) | | | |
| | 0 | 100 | 300 | 600 | 1000 |
| BIO DEE-ZOL LIFE® | | 6.97 (+32%) | 9.54 (+81%) | 12.70 (+141%) | |
| BHT | | | | | 7.36 (+40%) |
| TBHQ | | 7.06 (+34%) | 11.52 (+119%) | 14.64 (+178%) | |

**Results:** Both **Bio Dee-Zol Life®** and TBHQ performed better, in terms of % improvement, in this stable fuel than they did in the less stable samples. The improvement was similar at 100 mg/l (32% vs. 34%), but TBHQ improved the biodiesel's stability by a greater extent at the higher treat rates (300 and 600 mg/l). Both of these chemistries were superior to BHT in this stable fuel.

**Bio Dee-Zol and Correction of Poor Oxidative Instability**

Stabilizers are added to biodiesel (and conventional petrodiesel) to guard against and prevent the fuel from degrading. In certain instances, these stabilizers may also correct oxidative degradation which has already occurred. This is more clearly defined as the stabilizer increasing the Rancimat rating of a fuel sample who's Rancimat rating has started to decrease due to oxidative instability development. This means that such a stabilizer can be used to, in effect, reverse and correct existing fuel instability.

**Bio Dee-Zol Life®** can be shown to do exactly this – correct and reverse existing fuel instability. To show this, **Bio Dee-Zol Life®** was evaluated by the Rancimat method in comparison with the two other dominant stability chemistries – BHT and TBHQ – in three different feedstocks known for having poor oxidative stability – tallow, used grease and chicken fat. As with the previous three sample tests, Rancimat ratings were taken at 0 (untreated), 100 mg/l, 300 mg/l, 600 mg/l and 1000 mg/l.

*Sample 4 – Unstable Tallow*

Following are the test results from an unstable tallow biodiesel with starting Rancimat rating of just 1.86 hours, which is well below the minimum acceptable rating of 3.00.

| Tallow Biodiesel (#4) | 1.86 | | | | |
|---|---|---|---|---|---|
| | | Treat Rate mg/l (ppm) / (% Improvement from Untreated) | | | |
| | 0 | 100 | 300 | 600 | 1000 |
| BIO DEE-ZOL LIFE® | | 7.96 (+328%) | 12.39 (+566%) | 15.73 (+746%) | 20.05 (+977%) |
| BHT | | | | | 5.92 (+218%) |
| TBHQ | | 2.88 (+55%) | 5.15 (+177%) | 7.70 (+314%) | |

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**Results:** The difference in effectiveness between **Bio Dee-Zol Life®** and BHT/TBHQ is substantial. At the lowest treat rate of 100 mg/l, TBHQ cannot bring the tallow up to minimum specification, while **Bio Dee-Zol Life®** has improved oxidative stability by 328%. The differences at the higher treat rates are just as substantial. **Bio Dee-Zol Life®** shows itself to be much more effective at correcting unsatisfactory stability properties in tallow biodiesel.

*Sample 5 – Unstable Tallow*

Following are the test results from an unstable tallow biodiesel with starting Rancimat rating of just 1.06 hours, which is well below the minimum acceptable rating of 3.00. This is the worst biodiesel sample tested, which means there is the greatest room for improvement.

| Tallow Biodiesel (#5) | 1.06 | | | | |
|---|---|---|---|---|---|
| | | Treat Rate mg/l (ppm) / (% Improvement from Untreated) | | | |
| | 0 | 100 | 300 | 600 | 1000 |
| BIO DEE-ZOL LIFE® | | 2.06 (+94%) | 3.75 (+253%) | 8.94 (+743%) | |
| BHT | | | | | 5.57 (+425%) |
| TBHQ | | 1.61 (+52%) | 2.12 (+100%) | 2.85 (+169%) | |

**Results:** From the onset, one noticeable fact is that the starting Rancimat rating is so low, the % improvements will be larger by definition. With that in mind, we can still see a substantial difference in effectiveness between **Bio Dee-Zol Life®** and the other chemistries. It does take 300 mg/l of **Bio Dee-Zol Life®** to raise the tallow stability rating above the minimum 3.00 standard. But TBHQ was not able to reach this standard even at twice that treat rate (600 mg/l). BHT successfully improved the stability rating at 1000 mg/l, yet **Bio Dee-Zol Life®** outperformed BHT at a much lower treat rate (600 for **Bio Dee-Zol Life®** vs. 1000 for BHT).

*Sample 6 – Unstable Used Grease*

Following are the test results from an unstable used grease biodiesel with starting Rancimat rating of 2.56 hours, which is below the minimum acceptable rating of 3.00 (but not as bad as Samples 4 or 5).

| Used Grease Biodiesel (#6) | 2.56 | | | | | | |
|---|---|---|---|---|---|---|---|
| | | Treat Rate mg/l (ppm) / (% Improvement from Untreated) | | | | | |
| | 0 | 100 | 200 | 300 | 400 | 600 | 1000 |
| BIO DEE-ZOL LIFE® | | 3.38 (+32%) | | 6.18 (+141%) | | 8.35 (+226%) | |
| BHT | | | | | | | 4.85 (+89%) |
| TBHQ | | | 4.62 (+80%) | | 6.68 (+161%) | 9.05 (+254%) | |

**Results:** All three chemistries were able to bring the Used Grease biodiesel into spec, albeit at differing treat rates. **Bio Dee-Zol Life®** did it at just 100 mg/l. Indeed, **Bio Dee-Zol Life®** and TBHQ appeared to be similarly effective up to 600 mg/l, at which point TBHQ was somewhat more effective (226% vs 254%). BHT was substantially less effective than both (only 89% improvement at the highest treat rate).

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*Sample 7 – Unstable Chicken Fat*

Following are the test results from an unstable chicken fat biodiesel with starting Rancimat rating of just 1.94 hours, which is well below the minimum acceptable rating of 3.00.

| Chicken Fat Biodiesel (#7) | 1.94 | | | | |
|---|---|---|---|---|---|
| | | Treat Rate mg/l (ppm) / (% Improvement from Untreated) | | | |
| | 0 | 200 | 400 | 600 | 1000 |
| BIO DEE-ZOL LIFE® | | 14.02 (+622%) | 24.00 (+1137%) | | |
| BHT | | | | | 11.07 (+470%) |
| TBHQ | | 5.00 (+157%) | 7.60 (+292%) | 11.79 (+507%) | |

**Results:** The difference in effectiveness is substantial. **Bio Dee-Zol Life®** improved the fuel's stability by over 6x at just 200 mg/l treat rate. It improved stability to a greater extent at this low treat rate than TBHQ did at three times the amount (200 vs. 600 mg/l), and greater than BHT did at five times the amount (200 vs. 1000 mg/l).

*Sample 8 – Stable Canola*

This final test used a canola biodiesel with a satisfactory stability rating of 5.60.

| Canola Biodiesel (#8) | 5.60 | | | | |
|---|---|---|---|---|---|
| | | Treat Rate mg/l (ppm) / (% Improvement from Untreated) | | | |
| | 0 | 100 | 300 | 600 | 1000 |
| BIO DEE-ZOL LIFE® | | 6.31 (+12%) | 7.01 (+25%) | 8.43 (+50%) | |
| BHT | | | | | 10.12 (+80%) |
| TBHQ | | 6.15 (+10%) | 7.52 (+34%) | 9.18 (+64%) | |

**Results:** Because the canola biodiesel was already stable, the value here is in observing the improvement in the rating. TBHQ showed itself to be the most effective here, though the difference was much smaller than in previous samples. As the treat rate increased, the difference in percent improvement widened, but only by small amounts. For example, at 300 mg/l, the percent improvement for TBHQ was 9 index points better than **Bio Dee-Zol Life®** (34% vs 25%), while at 600 mg/l, the gap widens to 14% (64% vs 50%). Still, these are the smallest performance gaps among the 8 samples tested.

*Summary of Oxidative Stability Tests*

Putting the data from all eight sample tests together can better help us see how the performance of the three stabilization chemistries stack up against one another. In this summary, we've grouped the data according to treat rate as the primary indicator, followed by baseline stability. This enables us to see how the performance of the stabilizer chemistries compares as the baseline stability ratings and treat rates change.

For ease of interpretation, any Rancimat rating of treated fuel that does not meet the 3.00 minimum standard is highlighted **in red**. Furthermore, the top performance for each test is highlighted **in green**.

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| Stabilizer Performance by Treat Rate – 100 mg/l | | | | | |
|---|---|---|---|---|---|
| | | | Rancimat Rating / (% Improvement From Baseline) | | |
| **Feedstock** | **Treat Rate** | **Baseline** | **Bio Dee-Zol Life®** | **TBHQ** | **BHT** |
| Tallow | 100 | 1.06 | **2.06 (+94%)** | **1.61 (+52%)** | |
| Tallow | 100 | 1.86 | **7.96 (+328%)** | **2.88 (+55%)** | |
| Soy | 100 | 2.02 | **2.37 (+17%)** | **2.23 (+10%)** | |
| Used Grease | 100 | 2.56 | 3.38 (+32%) | | |
| Soy | 100 | 3.23 | **4.01 (+24%)** | 3.29 (+1%) | |
| Soy | 100 | 5.26 | 6.97 (+32%) | **7.06 (+34%)** | |
| Canola | 100 | 5.60 | **6.31 (+12%)** | 6.15 (+10%) | |

100 mg/l was the lowest treat rate used for evaluation, with seven test comparisons. BHT was not evaluated at this treat rate. In 5 of the 6 test comparisons, **Bio Dee-Zol Life®** outperformed TBHQ, often by substantial margins. The 7th test comparison, in Used Grease biodiesel, did not have a comparison to **Bio Dee-Zol Life®** at that treat rate. The performance difference was greatest in the biodiesels with the poorest stability (lowest baseline Rancimat), and the difference was also greatest in animal fat-based biodiesel vs. plant-based.

In the tests where **Bio Dee-Zol Life®** performed the best, the average difference was **+69%.** In the only test where TBHQ performed the best, the difference was only **+2%.**

| Stabilizer Performance by Treat Rate – 200 mg/l | | | | | |
|---|---|---|---|---|---|
| | | | Rancimat Rating / (% Improvement From Baseline) | | |
| **Feedstock** | **Treat Rate** | **Baseline** | **Bio Dee-Zol Life®** | **TBHQ** | **BHT** |
| Chicken Fat | 200 | 1.94 | **14.02 (+622%)** | 5.00 (+157%) | |
| Used Grease | 200 | 2.56 | | 4.62 (+80%) | |

Only two test comparisons were conducted at 200 mg/l, and one of them only saw TBHQ tested in order to establish a comparison. In the Chicken Fat test, **Bio Dee-Zol Life®** far outperformed TBHQ; **+465%** better.

| Stabilizer Performance by Treat Rate – 300 mg/l | | | | | |
|---|---|---|---|---|---|
| | | | Rancimat Rating / (% Improvement From Baseline) | | |
| **Feedstock** | **Treat Rate** | **Baseline** | **Bio Dee-Zol Life®** | **TBHQ** | **BHT** |
| Tallow | 300 | 1.06 | **3.75 (+253%)** | **2.12 (+100%)** | |
| Tallow | 300 | 1.86 | **12.39 (+566%)** | 5.15 (+177%) | |
| Soy | 300 | 2.02 | **2.90 (+43%)** | **2.49 (+23%)** | |
| Used Grease | 300 | 2.56 | 6.18 (+141%) | | |
| Soy | 300 | 3.23 | **4.65 (+44%)** | 3.95 (+22%) | |
| Soy | 300 | 5.26 | 9.54 (+81%) | **11.52 (+119%)** | |
| Canola | 300 | 5.60 | 7.01 (+25%) | **7.52 (+34%)** | |

Six test comparisons were run at 300 mg/l, while a 7th test (Used Grease biodiesel) saw only one product tested. BHT was not evaluated at this treat rate. In 4 of the 6 comparisons, **Bio Dee-Zol Life®** outperformed TBHQ. As with the testing at 100 mg/l, the difference was greatest in animal-based biodiesel with the lowest baseline Rancimat ratings – in other words, the least stable fuels. TBHQ outperformed **Bio Dee-Zol Life®** in plant-based biodiesel that already had satisfactory stability ratings. But the differences in performance (TBHQ was 38% and 11% better) were not close to the differences in performance for the poorest stability fuels (**Bio Dee-Zol Life®** was 153-389% better).

In the tests where **Bio Dee-Zol Life®** performed the best, the average difference was **+146%.** In the tests where TBHQ performed the best, the average difference was only **+25%.**

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| Stabilizer Performance by Treat Rate – 600 mg/l | | | | | |
|---|---|---|---|---|---|
| | | | **Rancimat Rating / (% Improvement From Baseline)** | | |
| **Feedstock** | **Treat Rate** | **Baseline** | **Bio Dee-Zol Life®** | **TBHQ** | **BHT** |
| Tallow | 600 | 1.06 | **8.94 (+743%)** | **2.85 (+169%)** | |
| Tallow | 600 | 1.86 | **15.73 (+746%)** | 7.70 (+314%) | |
| Chicken Fat | 600 | 1.94 | | 11.79 (+507%) | |
| Soy | 600 | 2.02 | **3.49 (+72%)** | 3.04 (+50%) | |
| Used Grease | 600 | 2.56 | 8.35 (+226%) | **9.05 (+254%)** | |
| Soy | 600 | 3.23 | **5.44 (+68%)** | 4.79 (+48%) | |
| Soy | 600 | 5.26 | 12.70 (+141%) | **14.64 (+178%)** | |
| Canola | 600 | 5.60 | 8.43 (+50%) | **9.18 (+64%)** | |

Seven test comparisons were run at this higher treat ratio of 600 mg/l. An 8th test (Chicken Fat) saw only TBHQ tested at that treat ratio. **Bio Dee-Zol Life®** outperformed TBHQ in 4 of the 7 tests. This means TBHQ was the better performer in the remaining 3 tests. **Bio Dee-Zol Life®** tended to perform better in the poorest stability fuels.

In the tests where **Bio Dee-Zol Life®** performed the best, the average difference was **+262%.** In the tests where TBHQ performed the best, the average difference was only **+26%.**

| Stabilizer Performance by Treat Rate – 1000 mg/l | | | | | |
|---|---|---|---|---|---|
| | | | **Rancimat Rating / (% Improvement From Baseline)** | | |
| **Feedstock** | **Treat Rate** | **Baseline** | **Bio Dee-Zol Life®** | **TBHQ** | **BHT** |
| Tallow | 1000 | 1.06 | | | 5.57 (+425%) |
| Tallow | 1000 | 1.86 | **20.05 (+977%)** | | 5.92 (+218%) |
| Chicken Fat | 1000 | 1.94 | | | 11.07 (+470%) |
| Soy | 1000 | 2.02 | | | 4.75 (+135%) |
| Used Grease | 1000 | 2.56 | | | 4.85 (+89%) |
| Soy | 1000 | 3.23 | | **6.63 (+105%)** | 4.96 (+53%) |
| Soy | 1000 | 5.26 | | | 7.36 (+40%) |
| Canola | 1000 | 5.60 | | | 10.12 (+80%) |

In most of the tests at this highest treat rate of 1000 mg/l, only BHT was tested. This leaves only one test each where **Bio Dee-Zol Life®** and TBHQ were directly compared to BHT. In both of those tests, **Bio Dee-Zol Life® (+759%)** and TBHQ (**+52%)** outperformed BHT.

The biggest takeaway from looking at the results of these oxidative stability Rancimat tests is:

> ***Bio Dee-Zol Life®*** *outperformed TBHQ and BHT in most of the tests across multiple treats (low and high) and multiple feedstocks (animals and plant). In the minority of tests where TBHQ outperformed* ***Bio Dee-Zol Life®*** *, the difference was considerably smaller than the converse.*
>
> ***Bio Dee-Zol Life®*** *outperformed TBHQ and/or BHT in 15 of 22 tests, by an average difference of* ***+213%.***
>
> *TBHQ/BHT outperformed* ***Bio Dee-Zol Life®*** *in 7 of 22 tests, by an average difference of* ***+26%.***

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**Enhancement of Biodiesel Thermal Stability**

Beyond the Rancimat test, ASTM D6468 (Standard Test Method for High Temperature Stability of Distillate Fuels) is the second industry-standard test used to predict storage stability of fuels. D6468 is considered a predictive test, whereas EN14112 Rancimat is considered more likely to indicate a fuel's current stability condition. The D6468 test measures fuel stability by a percentage of reflectance of a filter pad used to filter the fuel after a period of thermal stressing (hence, the predictive aspect). A higher percentage of reflectance indicates *greater* fuel stability.

Traditional stability treatments like simple hindered phenols (i.e. BHT and TBHQ) have not shown to be as effective at enhancing thermal stability of biodiesel as much as enhancing the fuel's oxidative stability. On the contrary, these phenolic stabilizers have been shown to promote formation of gums and deposits, especially if they are used at higher treat rates. This is not an ideal situation if you are trying to protect the quality of stored biodiesel fuels.

To evaluate enhancement of biodiesel thermal stability, the ASTM D6468 test method was used to assess the performance of **Bio Dee-Zol Life®** and the BHT and TBHQ hindered phenol treatments. All three were tested in B10 blend fuel prepared by mixing an unstable biodiesel (Rancimat = 1.00 hours) with a stable ULSD base fuel. In this test, the B100 was first treated with the appropriate stability additive, then was used to create the B10 test fuel.

Results were measured as % reflectance of the filter pad. Remember that higher scores indicate better performance (better stability).

*Sample 9 – Thermal Stability of B10 Blends*

| Additive | | Treat Rate (mg/l) In The B100 | | | |
|---|---|---|---|---|---|
| | 0 | 30 | 60 | 100 | 200 |
| Base Fuel | 18 | | | | |
| BIO DEE-ZOL LIFE® | | 64 | 74.2 | | |
| BHT | | | | 24 | 29.5 |
| TBHQ | | 17 | 34.2 | | |

**Results:** The untreated base fuel started with a reflectance of only 18%. An initial examination of results seems to indicate superior thermal stability performance by **Bio Dee-Zol Life®** compared to BHT and TBHQ. 30 mg/l treatment with TBHQ yielded no significant difference in reflectance, while a doubling of treat rate to 60 mg/l only improved the fuel's thermal stability to around 34%. BHT performed even less satisfactorily, as the fuel's thermal stability did not break 30% even at a high treat rate of 200 mg/l. **Bio Dee-Zol Life®** needed only 30 mg/l treat rate to improve the fuel's thermal stability to 64.

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**Bio Dee-Zol Life® and Instability Caused by Metallic Exposure in B100 (Oxidative Stability)**

As referenced earlier, exposure to transition metals like copper can have an extreme negative effect on the stability of biodiesel blends. Some research shows the presence of a transition metal in the fuel can cause up to a 50% loss in oxidative stability. Therefore, in order to be truly effective, any stabilizer for biodiesel must be able to counteract transition metal-induced instability. As such, **Bio Dee-Zol Life®**, along with BHT and TBHQ, was evaluated for its ability to help in this area. The evaluation was conducted using a moderately stable soy biodiesel with a Rancimat rating of 4.77. The B100 was dosed with 0.16 ppm of soluble copper complex. The Rancimat rating of the metal-exposed B100 fuel was then evaluated with and without stability additive.

*Sample 10 – Metal-Induced Biodiesel Instability*

| Fuel | Treat Rate (mg/l) | Cu Conc. (mg/l) | Rancimat (Hours) | Loss (%) |
|---|---|---|---|---|
| Base fuel | | | 4.77 | |
| Base fuel + Cu | | 0.16 ppm | 2.65 | -44.44% |
| **Additive** | | | | |
| Fuel + BHT | 1000 | | 7.38 | |
| Fuel + BHT + Cu | 1000 | 0.16 ppm | 4.90 | -33.60% |
| Fuel + TBHQ | 300 | | 15.86 | |
| Fuel + TBHQ + Cu | 300 | 0.16 ppm | 3.51 | -77.87% |
| Fuel + Bio Dee-Zol Life® | 300 | | 5.96 | |
| Fuel + Bio Dee-Zol Life® + Cu | 300 | 0.16 ppm | 6.16 | **+3.36%** |

Reviewing the data for Sample Set 10, we can draw out a few facts:

- The base fuel lost almost **45%** of its Rancimat induction upon exposure to copper.
- Fuels treated with BHT and TBHQ lost **33.6%** and **77.87%** of their Rancimat induction periods upon copper exposure.
- **Bio Dee-Zol Life®** clearly did a superior job at retarding metal-mediated oxidation, with no loss in Rancimat rating.

This data seems to confirm the inability of hindered phenol treatments like BHT and TBHQ at solving fuel oxidation problems when exposure to catalytic metals comes into play.

**Evaluation of Bio Dee-Zol Life® To Counteract Metal-Catalyzed Instability in B10 Fuels (Thermal Stability)**

The other part of the picture is the effect of stabilizers on metal-catalyzed instability in blended B10 fuels (in contrast to B100 fuels). To evaluate this, a B10 fuel was prepared by blending a stable biodiesel (Rancimat = 6.00 hours) with a stable ULSD base fuel. The B100 itself was first treated with stability additives, then the treated B100 was used to prepare the B10 biodiesel blend.
0.16 ppm of soluble copper was then added to the prepared B10 blend fuel. Both treated and untreated B10s were evaluated under the ASTM D6468 method for determining thermal stability

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*Sample 11 – Metal-Induced Biodiesel Instability in B10 Fuel (ASTM D6468 - % Reflectance)*

| Base | Base | Bio Dee-Zol Life® | BHT | TBHQ |
|---|---|---|---|---|
| Treat Rates (mg/l) | 0 | 30 | 100 | 30 |
| As Rec'd | 81.2 | 89.1 | 86 | 84.1 |
| As Rec'd + Cu, + Additives | 44.8 | 88.8 | 51.6 | 45.6 |

Reviewing the data for Sample 11, we can see the following:

- Exposure of the B10 base fuel to the copper metal caused a reflectance reduction from **81.2** to **44.8 (48%)**
- Both hindered phenol treatments, BHT and TBHQ, saw similar substantive reductions in reflectance, both dropping **over 40%**.
- B10 treated with 30 mg/l of **Bio Dee-Zol Life®** saw virtually no reduction to its thermal stability.

This B10 data is consistent with the previous data reviewed on B100. **Bio Dee-Zol Life®** far outperforms hindered phenols like BHT and TBHQ for protecting biodiesel fuel against metal-induced instability.

**Bio Dee-Zol Life® and Mingled Fuel Instability**

In the field, it is often unavoidable that fresh biodiesel and aged biodiesel end up being mixed together within storage tanks. The mixing of 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. And the impact is not linear.

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

To further illustrate this phenomenon, biodiesel blend samples comprised of different proportional mixes of stable and unstable biodiesel were each tested for Rancimat rating.

- As expected, the 100% unstable sample scored lowest – less than 1 hour on the Rancimat scale. The 100% stable biodiesel sample score at over 6.00.
- Increasing the percentage of stable biodiesel in the blend also tended to improve the blend's Rancimat rating.

| Fuel Mix | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| % Stable Biodiesel | | 100 | 95 | 90 | 85 | 75 | 50 | 25 |
| % Unstable Biodiesel | 100 | | 5 | 10 | 15 | 25 | 50 | 75 |
| Rancimat Hrs | <1 | 6.00+ | 4.01 | 3.31 | 2.47 | 1.72 | 0.64 | 0.42 |

This data shows that it took as little as 15% unstable biodiesel content to take a biodiesel fuel with a healthy Rancimat rating of over 6.00 and bring it out-of-spec for overall stability. Specifically, just 15% aged biodiesel content reduced the blend's Rancimat rating down to 2.47.

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*Sample 12 – Protecting Biodiesel Blend Oxidative Stability From Aged Biodiesel Content*

**Bio Dee-Zol Life®** was evaluated for its ability to protect blends of old and new biodiesel from Rancimat rating depression. A fresh B100 with Rancimat rating over 6.00 was dosed with 1000 ppm **Bio Dee-Zol Life®**. A new biodiesel blend was then created using 85% treated fresh biodiesel and 15% aged biodiesel (Rancimat = <1.00). Unadditized biodiesel blend samples with no stabilizer treatment were also evaluated.

| Additive | 85% Fresh, 15% Aged | |
|---|---|---|
| Bio Dee-Zol Life® | 0 | 1000 |
| Rancimat Hrs | 2.03 | 5.32 |

Without any stabilizer treatment, the Rancimat rating of the blend dropped to just 2.03 hours, well below the required specification. In contrast, treatment with **Bio Dee-Zol Life®** protected the blend's oxidative stability, dropping only down to 5.32 – still well within satisfactory specifications.

**Results Summary**

After the conclusion of testing across multiple scenarios, it is clear that **Bio Dee-Zol Life®** is superior to other biodiesel stability solutions when it comes to the essential task of preserving biodiesel stability quality in storage.

- ***For protecting oxidative stability of biodiesel***, **Bio Dee-Zol Life®** significantly outperformed both TBHQ and BHT (traditional hindered phenol solutions for fuel stability) by substantial margins - an average of **213% improvement**. *See Samples 1-8 for details.*

- **Bio Dee-Zol Life®** was especially effective in both animal-based biodiesel fuels (i.e. tallow, chicken fat, used grease) and already-unstable biodiesel fuels, improving oxidative stability scores by 200-500% or more in many cases. *See Samples 1-8 for details.*

- In most cases, **Bio Dee-Zol Life®** was more effective at protecting oxidative stability while also requiring lower treat rates to use. *See Samples 1-8 for details.*

- ***For protecting thermal stability of biodiesel***, the hindered phenol stabilizers BHT and TBHQ were marginally effective at improving reflectance when used at 60 – 200 mg/l.
**Bio Dee-Zol Life®** had more than 2x the beneficial effect on thermal stability when used at only 30 mg/l. *See Sample 9 for details.*

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- ***Catalytic metal instability*** - BHT and TBHQ were both ineffective at protecting biodiesel oxidative stability from the effects of catalytic metals (33-77% drop in B100). **Bio Dee-Zol Life®** was highly effective, with virtually no drop in oxidative stability measurements after metal exposure. The same was true for B10 fuels measured for thermal stability. BHT and TBHQ treatment of metal-exposed B10 still saw a 48% drop in reflectance. **Bio Dee-Zol Life®** prevented virtually any reflectance reduction whatsoever. *See Sample 10 and Sample 11 for details.*

- ***Mingled fuel instability*** **- Bio Dee-Zol Life®** demonstrated the ability to protect biodiesel blends against Rancimat reduction when aged biodiesel content was combined with fresh biodiesel content. Biodiesel dosed with 1000 ppm **Bio Dee-Zol Life®** retained more than 80% of its Rancimat oxidative stability that was lost in untreated biodiesel. *See Sample 12 for details.*

**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.

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