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BIOdiesel Tech NOTES

Comparison of Oxidative Stability Additives for Biodiesel

One of the environmental advantages of biodiesel is that it degrades more quickly than petro-diesel, and so does not pose a long-term harm to the environment. However, this can also be a disadvantage if the fuel degrades before it can be used. In 2006, a specification was added to ASTM 6751 (the U.S. biodiesel quality specification) in order to ensure that biodiesel has adequate protection from oxidation.

Biodiesel degrades due to oxidation, contact with water, and/or microbial activity. The oxidation of biodiesel can produce various acids or polymers, which, if in high enough concentration, can cause fuel system corrosion and deposits which in turn can lead to filter clogging and fuel system malfunctions.

Most raw vegetable oils contain vitamin E (tocopherols), a naturally occurring antioxidant. However, vitamin E can be destroyed during the oil refining process. To avoid oxidation and extend the shelf life of biodiesel, commercial antioxidants can be added.

Most commercial antioxidants contain a combination of synthetic materials. These include butylated hydroxytoluene (BHT), butylated hydroxyanisol (BHA), tertiary-butylhydroquinone (TBHQ) and propyl gallate (PG).

Additionally these products may contain a chelating agent such as citric acid, phosphoric acid, or amino acids. These acids can have a synergistic antioxidant effect by removing metal ions which tend to catalyze the oxidation reaction (Knothe, 2007, pp. 671-672).

Fuels and Additives Tested

To investigate the effectiveness of commercial products, we tested four different brands of oxidative stability additives to see how they compared (company name is in parentheses):

- Baynox Plus (Lanxess)
- Ethanox 4760E (Albemarle)
- Bioextend (Eastman)
- BF 320 (Kemin)

The instructions for all these types of antioxidant treatments emphasize that the additive should be mixed with freshly made fuel. We tested the additives with fresh fuel at 200 parts per million, which is the standard recommendation. We also tested them at 500 parts per million, because with some fuels 200 ppm might not be enough to meet the specifications, especially the European specification.

The fresh fuels tested were:

- Canola methyl ester (CME)
- Canola ethyl ester (CEE)
- Mustard methyl ester (MME)
- Soy methyl ester (SME)

Although oxidative stability additives are meant to be added to fresh fuel, we were curious about whether older fuel could be treated with these additives to bring the fuel in line with U.S. and European Union specifications. Therefore, we also tested four fuels that had been sitting in storage for about two years. We are including the acid value and viscosity because they provide an indication of the extent to which the oil had degraded.

- Rapeseed Ethyl Ester (Aged REE) – Acid value 0.37; viscosity 6.18
- Palm Methyl Ester (Aged PME) – Acid value 1.22; viscosity 4.66
- Tallow Methyl Ester (Aged TME) – Acid value 0.98; viscosity 4.48
- Mustard Methyl Ester (Aged MME) – Acid value 1.25; viscosity 5.15

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In three of the four aged oils, the acid value had increased to well above the ASTM limit of 0.5 mg KOH/gram. The viscosity values of these samples were all within the normal range. The REE sample had an acid value that was within the ASTM limit, but a higher viscosity. This lower acid value and higher viscosity is mostly due to the presence of over 50% erucic acid (22:1), which is only mono-unsaturated. Thus, it is relatively stable against oxidation, but has a naturally high viscosity because of its longer chain length.

The fatty acid profile of the feedstock is of interest because it indicates how stable the fuel may be (see Table 1). Fuel made from feedstocks with more saturated fats (myristic, palmitic, and stearic) tend to be more stable than fuels made from unsaturated fats.

Testing and Results

To test the fuels, we used an instrument called a Biodiesel Rancimat (manufactured by Metrohm, a Swiss company with U.S. headquarters in Riverview, FL), which accelerates the degradation process by heating the fuel to 110 degrees C and then bubbling dry room air through it. The time required for the oil to reach its induction time, as indicated by the onset of rapid oxidation, is measured. To meet the U.S. ASTM specification for biodiesel, the fuel must remain stable for at least three hours during the Rancimat test. The European EN specification is more stringent: fuel must remain stable for at least six hours.

Figure 1 shows how the fresh fuels performed when the antioxidants were added at 200 parts per million and 500 parts per million.

As you can see, all of the additives at 200 ppm boosted the stability of the fresh fuels enough to meet the U.S. specification. All of the fuels also met the European specification with at least one of the additives. At 500 ppm, all the fresh fuels with additives passed the U.S. specification, and three of the fresh fuels plus additives passed the European specification. The only exception was mustard methyl ester, which passed the European specification only

Table 1: Fatty acid profiles of common biodiesel feedstocks

Fatty Acid %	Canola	Soy	Rapeseed	Palm	Tallow	Mustard
Myristic (14:0)					3	
Palmitic (16:0)	4	8	3	41	25	3
Stearic (18:0)	2	4	1	5	14	2
Oleic (18:1)	59	25	14	40	38	24
Linoleic (18:2)	18	55	10	11	1	21
Linolenic (18:3)	8	8	5			9
Eicosanoic (20:1)	2		8			12
Erucic (22:1)	1		54			23

Figure 1: Oxidative stability of fresh fuels with additives

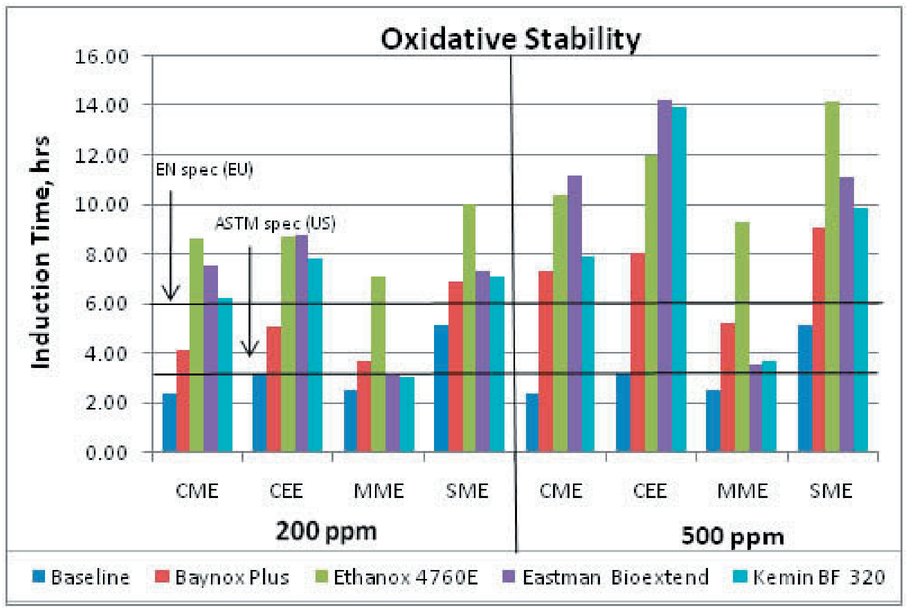
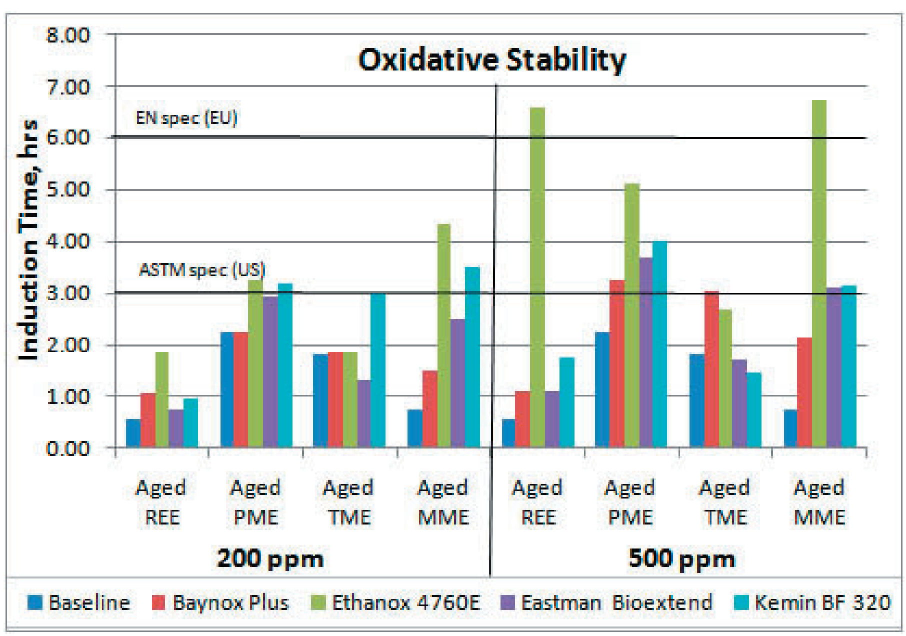


Figure 2: Oxidative stability of aged fuels with additives



with the addition of Ethanox 4760E.

Figure 2 shows the aged fuels with additives at 200ppm and 500ppm. The increase in stability was much smaller for the aged fuels. At 200 ppm, three of the aged fuels, palm methyl ester, mustard methyl ester, and tallow methyl ester, were able to meet the U.S. specification with at least one of the additives, but none of the aged fuels met the European specification. At 500 ppm, all of the aged fuels met the U.S. specification with the addition of one or more additives, and two of the aged fuels met the European specification with the addition of Ethanox.

Another interesting finding was that most of the products performed better on the canola ethyl esters vs. canola methyl esters among the fresh fuels, but displayed consistently worse effectiveness on the rapeseed ethyl esters vs. the other aged methyl esters. Some of the apparent increase in stability for the ethyl ester may be due to their greater molecular weight and thus their lesser number of oxidatively sensitive double bonds per unit of mass.

Of the products tested, Ethanox 4760E gave the best overall performance on both sets of fuels. However, the Eastman Bioextend and the Kemin BF 320 outperformed it on canola ethyl ester at the 500 ppm level.

Cost of Antioxidant Additives

Figure 3 shows the cost per gallon of biodiesel for each of the antioxidants in this study. Evaluating the cost of using these products showed that Eastman Bioextend was the most expensive overall while Baynox Plus was the least.

Small producers will generally pay more as most of the companies offer a price break for quantity. Baynox Plus, however, is available in only one size, so there is no price break for larger quantities. Table 2 shows the cost per standard quantities of the products we used.

The cost of using antioxidants at an average of about one cent per gallon is low-cost insurance for a greatly improved shelf life for biodiesel.

Figure 3: Cost of antioxidants at two load rates

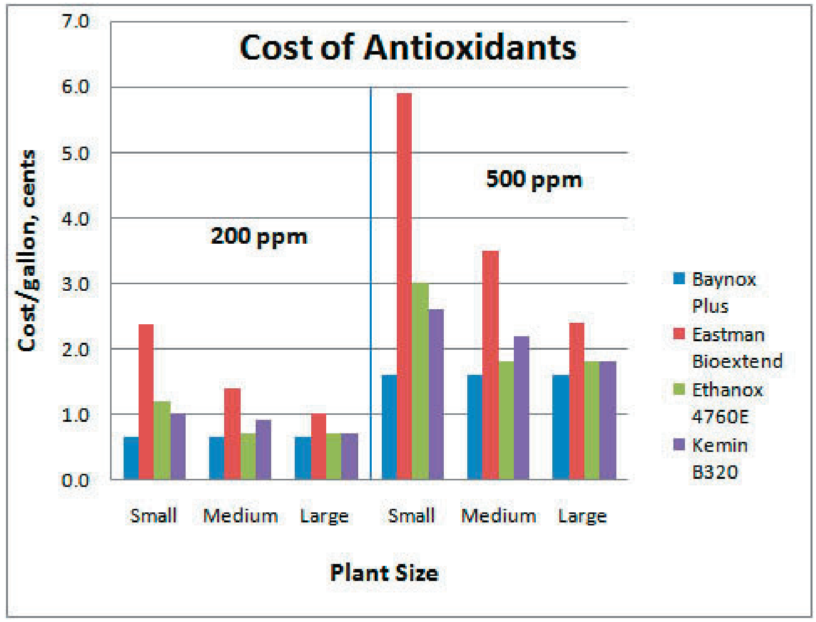


Table 2: Cost of Antioxidants per container and per pound

Additive	Quantity	Cost per container (as of 2010)	Cost per pound
Baynox Plus	Powder (33 lb bag)	$142	$4.30
Bioextend	5 gallons	$79	$15.82
Bioextend	55 gallons	$512	$9.30
Bioextend	275 gallons	$1,757	$6.39
Ethanox	5 gallons	$41	$8.12
Ethanox	55 gallons	$263	$4.79
Ethanox	275 gallons	$1317	$4.79
Kemin BF 320	5 gallons	$34	$6.83
Kemin BF 320	55 gallons	$321	$5.83
Kemin BF 320	275 gallons	$1328	$4.83

Works Cited

Knothe, Gerhard. "Some Aspects of Biodiesel Oxidative Stability." Fuel Processing Technology 88 (2007) 669–677.

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