ULSD/Biodiesel blend and its effect on fuel/water separation

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Abstract: The use of ULSD/biodiesel blend can cause potential on-vehicle fuel filtration problems including decreased emulsified water separation efficiency and shortened fuel filter life, thus the understanding of the fuel blend is important. In this paper, we will present our preliminary studies on the different physical and physical-chemical properties of ULSD/biodiesel blends. We will also show the effects of the blended fuel on fuel/water separator's efficiency. The biodiesel used in this study includes soybean and animal fat based fatty acid methyl esters.

Key words: Biodiesel, ULSD, fuel properties, filtration, fuel/water separation

INTRODUCTION

Vegetable oils and animal fats were investigated as diesel fuels well before the energy crisis of 1970s. However, neat vegetable oils and animal fats are about 10 times more viscous than petrodiesel fuels, and they caused some operational and maintenance problems for diesel engines, so they were eventually abandoned as alternative diesel fuels **[1]**. Biodiesel, derived from transesterification of vegetable oils or animal fat matters, on the other hand, has attracted worldwide attention in recent years as real alternative fuel of low viscosity. It is miscible with petrodiesel in all ratios.

The use of petrodiesel and biodiesel blend has been practiced in many parts of the world for diesel engines. For example, since October 2005, B2 (B2 = 2 vol % biodiesel in diesel fuel) has become a mandatory use in Minnesota in most of the state's diesel fuel supply, in spite of a temporary snag due to the use of an off-spec biodiesel. "In August 2007, Minnesota governor Tim Pawlenty announced a plan requiring the state to increase its biodiesel mandate incrementally from B2 to B20 by 2015. The governor's proposal calls for Minnesota to move to B5 by 2008, B10 by 2011, B15 by 2013 and B20 by 2015" **[2]**. However, the use of petrodiesel and biodiesel blend still causes some extent of concerns for the end users, especially when the ratio of the blend is increased from B2 to B20.

Biodiesel's storage stability, oxidative stability as well as its high affinity to dissolved water could lead to shortened fuel filter life and deteriorated fuel/water filtration efficiency. Biodiesel is known to have higher cloud point and more unsaturated hydrocarbon content, which tend to lead to earlier wax precipitation and increased intensity of fuel oxidation **[1]**. The affinity to water is attributed to the more polar nature of alkyl-esters and unsaturated acids which barely exist in No.2 petrodiesel, a mid-distillate of crude oil with boiling temperature ranging from 180°C to 340 °C. In addition, biodiesel used for field tests normally has more impurities and its quality is more variable. A qualified straight biodiesel should meet the requirement of ASTM D 6751 in the US or EN 14214 in Europe.

Per the US biodiesel standard, total glycerin must be removed to under 0.24 wt % to prevent fuel filter pre-mature plugging and fuel injector deposits. Water and sediment content should be less than 500 ppm. A possible addition of another specification to the test standard for B6 to B20 has been discussed, i.e. the cold soak filtration test. It is devised to prevent materials from falling out of solution causing filter plugging and damaging biodiesel's reputation as a transportation fuel **[3].** The good news from a recent survey conducted by National Renewable Energy Laboratory (NREL) is that, 89.6% of the 70% total B100 market sampled in 2007 was on specification, thanks to the effort made by the biodiesel industry on quality **[4].** However, as pointed out by engine manufacturers, these specifications define only the biodiesel used as the blend component with diesel fuel, they are not applicable to fuel blends purchased by the end users **[5].** The question is therefore how to manage the quality of the biodiesel in storage, blending and delivery, as well as the quality of blended fuel in application to minimize engine operational problems. According to a private communication with a biodiesel user, 40% of the problem is a result of water contamination, 20% is attributed to microbial growth, 25% due to glycerin, 10% improper blending, and 5 % others. In this paper, we will address the problem from two aspects: the qualities of fuel blend and their implication on fuel/water filtration.

FUEL PROPERTIES

I: Soy methyl ester biodiesel

Soybean oil is the major feedstock for biodiesel production in the United States. Methyl, ethyl, isopropyl and other alcohols can be used in the transesterification reaction to produce alkyl esters with 10 wt % coproduct-glycerins, a sugar that must be removed from the mixture for practical use of the biodiesel thus produced. However, virtually all the commercial production of biodiesel in the US is methyl esters due to the lower cost and the ease of recycling of methanol than other longer chain alcohols. To ensure good quality product, it is recommended to purchase biodiesel from a BQ-9000 accredited producer or marketer. However, a qualified neat biodiesel does not necessarily guarantee problem-free applications; issues to our interest are the blended fuel's effect on fuel/water separation and the fuel's filterability.

We collected geographically biodiesel samples from four states, Texas, Florida, Maryland and Minnesota, and conducted a series of quick screening tests on each sample by measuring the following properties and the results are shown in Table 1.

- Interfacial tension (IFT) of fuel against water
- Micropsep (MSEP)
- Initial water concentration

- Initial particulate contamination
- Density
- Surface tension
- Saturated water concentration

Table 1 Properties of neat soybean methyl esters

Property	**ULSD**	**Biodiesel**			
	TX	TX	FL	MD	MN
Surface tension, mN/m	28.0	25.8	31.0	30.8	25.3
IFT, mN/m	7.4	10.1	13.5	13.3	13.0
MSEP	0	98	99	99	98
Density, g/cm^3	0.835	0.882	0.838	0.874	0.880
Initial water, ppm	107	363	474	594	361
Saturated water, ppm	153	1829	1971	1574	1738
Particulate, mg/L	0.5	5.5	23.4	6.2	7.0

Table 1 also shows the basic properties of the ULSD we used for the biodiesel blends to be discussed in the next sections. The surface tension of all the biodiesel is between 25 mN/m to 31 mN/m, similar to that of petrodiesel. The interfacial tension of these samples are much lower, ranging from 10 mN/m to 13 mN/m. This is not surprising as we expected since the biodiesel has high affinity to water even without the addition of surface active additives. Some constituents of the biodiesel are themselves surface active. According to the National Biodiesel Board, the average molecular weight of soy methyl esters is calculated to be 292.2 using the following major component esters (fatty acids) in soybean biodiesel listed in the order of their weight percentage: .

Linoleic (52%)>oleic (25%)>palmitic (12%)>linolenic (6%)>stearic (5%).

It is understood that there are other esters in the biodiesel in addition to the five shown above. The general chemical structure of all these esters (CH3-O-CR=O) has oxygen atoms in the polar head and the long chain non-polar hydrocarbon "R" in the tail, this is the reason why the biodiesel itself is surface active to some extent. However, the intensity of the surface activity of the B100 is not that much as reflected by the IFT, because the MSEP of all the biodiesel tested is very high as shown in the table. MSEP is used to characterize the level of difficulty for separating water-in-fuel emulsion with a standard coalescence material. Its rating ranges from 0 to 100. The higher the number, the easier the separation. At a microscopic and molecular level, MSEP can be translated to the surfactancy of a fuel which is related to the emulsion stability, which further correlates to the surfactant molecules, their concentration, molecular weight, HLB value (hydrophilic and lipophilic balance), mobility, viscosity, rigidity, elasticity and other variables. The very high MSEP means all these biodiesel fuels should not affect emulsified water filtration too much due to the instable nature of the water-in-fuel emulsion formed in the fuel **[6].**

The biodiesel molecules indeed have very high affinity to water though, as can be seen from the water concentration analysis. The dissolved water concentration for diesel fuel is typically in the range of 30 ppm to 180 ppm. Biodiesel does dissolve more water, over 300 ppm, and this is not a surprise considering the nature of those ester molecules, which are more polar than petrodiesel fuel molecules consisting mainly of hydrogen and carbon atoms. What's more interesting is that, when biodiesel is mixed with free water to reach phase equilibrium for water saturation in the fuel, 2.5-5 times more water is dissolved depending on the source of the original biodiesel, as shown in Table 1. This is important because we normally pay attention only to free or emulsified water filtration, but the huge increase in water solubility in neat biodiesel compared to ULSD can also be a major concern. The existence of such dissolved water can promote biodiesel hydrolysis to break down the fuel molecules, which will raise the fuel's surfactancy due to the formation of carboxylic acids; it will also promote bacteria growth and fuel oxidation, and possibly affect the fuel combustion and cause corrosion problems. The separation of significant amount of dissolved water will redirect fuel filter design in practice. However, all these problems could be mitigated by using biodiesel blend with relatively small blending ratio. The challenge to avoiding major water ingression to biodiesel therefore lies in the operational chain of fuel storage, shipping, handling and blending before the blended fuel is used to power an engine.

The particulate contamination shown in Table 1 needs to be well addressed. These particles could have been introduced during the processes of biodiesel production, storage and handling. It could be also partially a result of fuel degradation, something inherent to the unsaturated hydrocarbon bonds through auto-oxidation mechanism. The particulate contamination could become worse in winter time due to the high cloud point of biodiesel. A non-qualified biodiesel could also contain more glycerins than allowed in the standard specification. It's interesting to see that the fuel from Florida has the highest particulate contamination, making one wonder if the humidity or the salty air is part of the problem. When looking at the fuel density, we found that the fuel from Florida is the lightest, meaning the heat duty of this fuel is lower than others.

II. Soybean biodiesel blend

Based on the screening test, we decided to use the biodiesel produced in Minnesota to mix with ULSD purchased from Texas, as shown in Table 1, to make the fuel blends. The Minnesota biodiesel referred here is bought from a BQ-9000 certified manufacturer. It meets the specification of ASTM D 6751. The blending was carried out in a 1000 ml beaker using a magnetic stirring bar at ambient temperature. The ULSD purchased has no biodiesel in it initially. Its IFT against water is 7.4 mN/m and its MSEP reads 0.

Fig.1 shows the interfacial tension (IFT) of the blended fuel against water. The IFT generally increases as more biodiesel is added to ULSD. The B100 has an IFT of about 12 mN/m, B5 and B20s' IFT about 8.3 mN/m. So at a blending ratio below 20 vol%, ULSD's IFT dominates the IFT of the blend. This is important because the most common application of biodiesel as a transportation fuel will be using B2 to B20. The selection of the base ULSD will determine the effective use of the biodiesel and the applicability of those filtration technologies related to fuel/water separation. This is further indicated in the MSEP measurement as shown in **Fig.2**. Only B75 and B100 show very high MSEP ratings instead of 0 for the other blends, meaning B75 and B100 should boost emulsified water filtration efficiency as compared to ULSD or other lower ratio blends. Under B50, the MSEP is all zero, indicating the additives initially residing in the ULSD still function as strong surfactants to stabilize the water-in-fuel emulsion. Their effectiveness diminishes when the ratio of biodiesel in the blend dominates possibly due to the increased interaction between ULSD additives and biodiesel molecules. Due to the different polarity of ULSD and biodiesel, the additives initially designed for ULSD may be constrained somehow by the biodiesel molecules so their concentration and mobility to and from the interface of fuel and water decreases, thus reducing the stability of the emulsion.

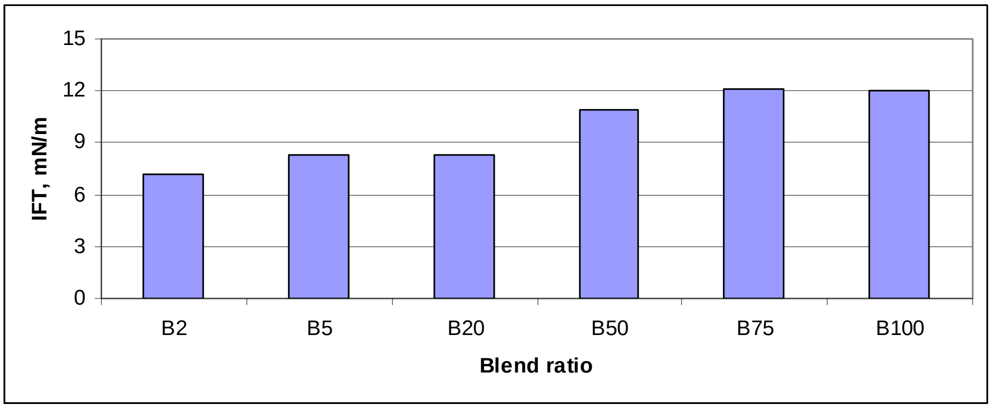

Fig.1 Interfacial tension vs. blending ratio

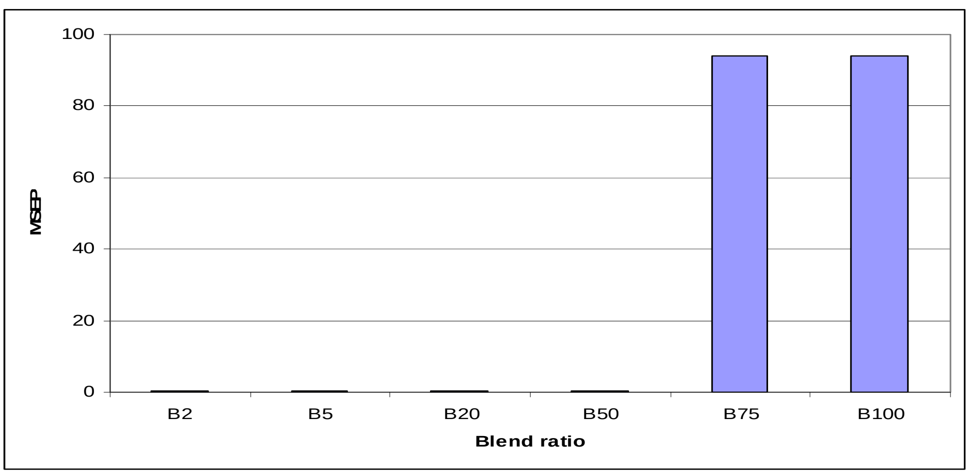

Fig.2 MSEP vs. blending ratio

The similar trend happens to the surface tension of the blends as shown in **Fig.3**. Diesel fuel generally has good wettability to solid surfaces. If the fuel has more solvent power, which is the case for biodiesel, it will tend to attack more aggressively the materials used in the fuel delivery line, and the low surface tension will allow the fuel to find its way to wet, spread and penetrate the solid surfaces for the chemical damage to occur more easily. Therefore, material's compatibility with biodiesel must be addressed in fuel delivery system, which is the case for the end users.

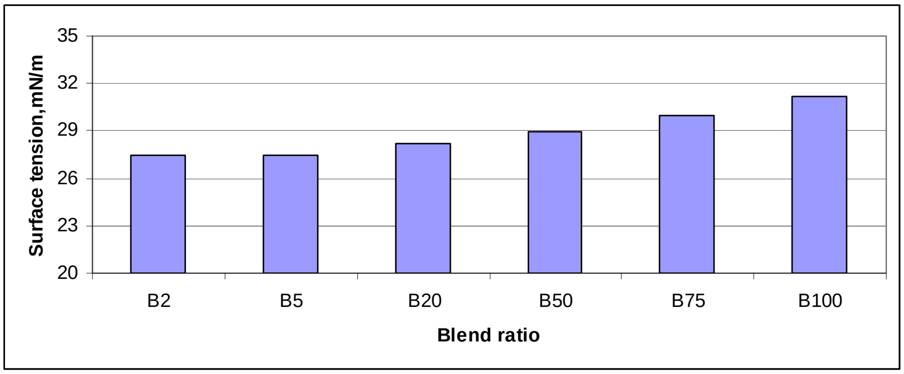

Fig.3 Surface tension vs. blending ratio

Fig. 4 shows the original water and particulate contamination, respectively. The amount of dissolved water and particulate contamination increases with increasing blending ratio. However, the relationship is non-linear. The contamination concentration rises more quickly when the blending ratio is under 20vol%. Putting particulate contamination into perspective, a concentration of 3 mg/L means that about 23 grams of particles will go through a fuel filter assuming a heavy duty truck's average diesel consumption rate is 6 miles per gallon and 12,000 miles are accumulated. Keep in mind that these particulate contamination was collected by a 0.8 um membrane and was analyzed gravimetrically. In reality, most commercial fuel filters would not be able to remove particles smaller than 5 um effectively but are designed to remove sufficient amount of ISO dusts for filters to last longer.

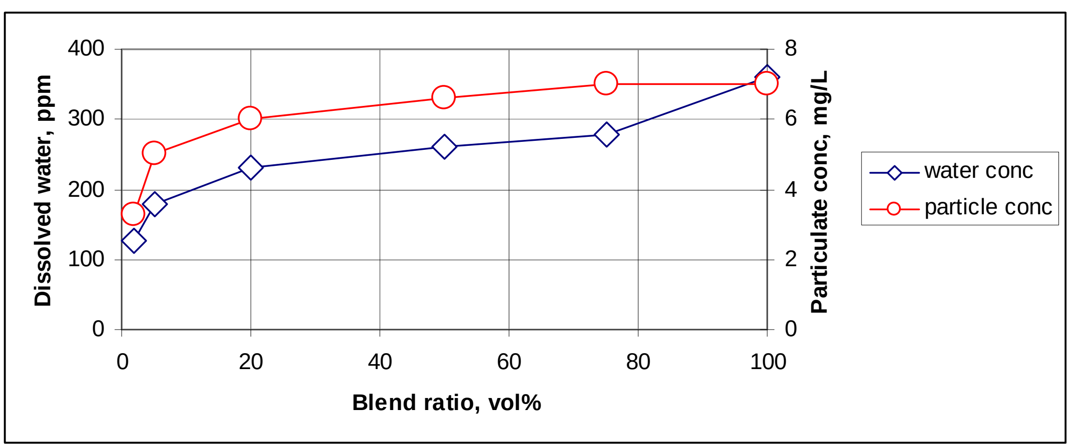

Fig.4 Dissolved water concentration and particulate contamination

Viscosity of the biodiesel blend decreases when temperature increases as shown in **Fig. 5**, a general phenomenon typically seen for a liquid. Within the temperature range that viscosity was measured, B2, B5 and B20 overlap, and a linear correlation can be found for these blends between viscosity and temperature, which can to some extent justify the use of the blended fuel up to B20. The cloud point of the neat biodiesel is around 0 °C, a quick viscosity increase at temperatures below 0°C takes place for B50 and B100, particularly for B100. The exponential increase in viscosity at low temperature for B100 could lead to engine operational problems.

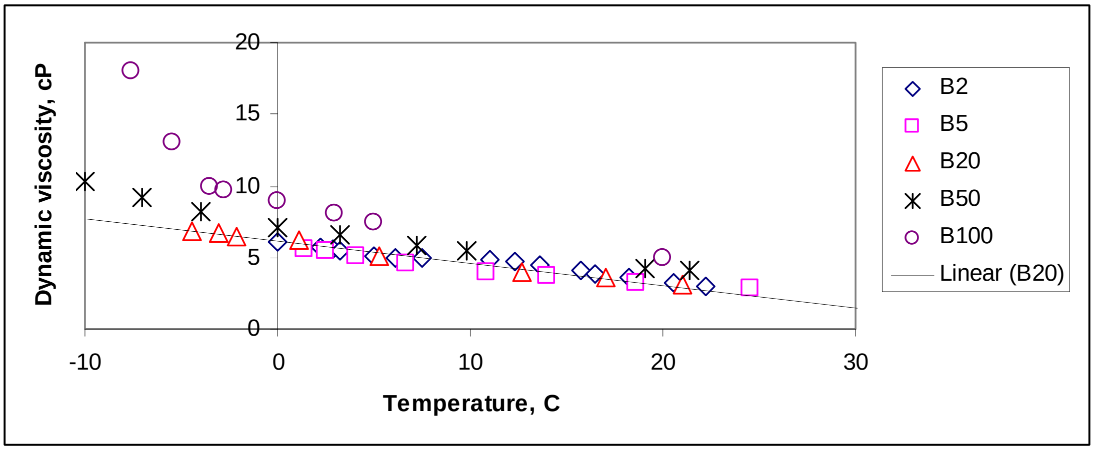

Fig. 5 Blended fuel viscosity as a function of temperature

Biodiesel stability is a major specification for its quality control in which the oxidation stability can be measured using the Rancimat test (EN14112). The oxidation stability of biodiesel blend can also be measured using the same method. In this test the highly volatile organic acids produced by autoxidation are absorbed in water and used to indicate the induction time. The longer the induction time, the more stable the fuel to oxidation. **Fig. 6** shows the measurement result of the different blends at 110 °C.

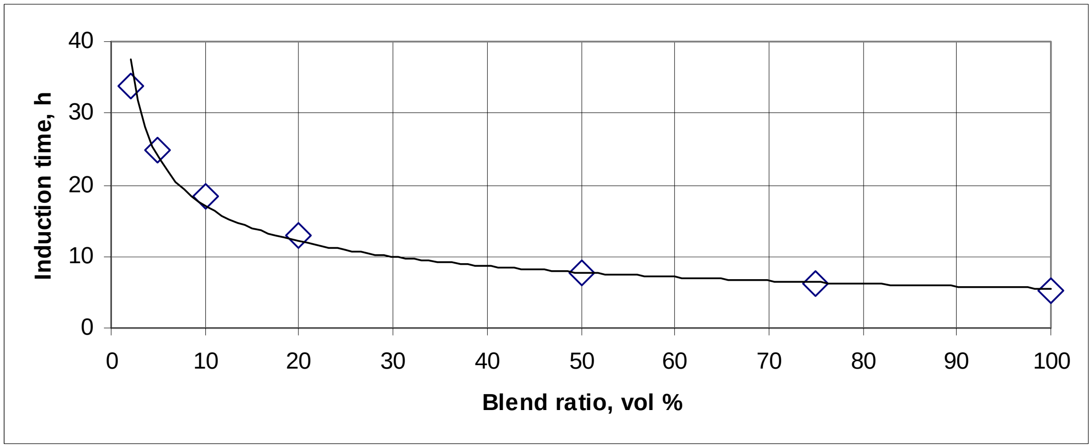

Fig.6 Soybean biodiesel/ULSD oxidation stability vs. blend ratio

As expected, the fuel blend oxidation stability (induction time) drops dramatically as more biodiesel is added to the ULSD for blends under B20, and then it levels off. The first four data points in **Fig. 6** correspond to B2, B5, B10 and B20. In the US, the induction time of an in-spec biodiesel should be at least 3 hours; in Europe it is 6 hours. High oxidation stability prevents deposits in the engine and filters and increases both reliability and working life. However, it was discovered that a fuel's oxidation stability does not necessarily correlate to the formation of the solid contamination that causes filter plugging **[7].**

III. Animal fat biodiesel blend

The animal fat biodiesel (Pork fat, C14-C24 methyl esters) we used for tests was purchased from another BQ- 9000 accredited US company. Its kinematic viscosity at 40 °C is 4.62mm^2/s. Animal fat biodiesel typically has fewer double bonds **[8]** and is free of multiple double bonds, so it is less susceptible to fuel oxidation and polymerization. This has been reflected in fuel oxidation stability test using Rancimat method as shown in **Fig. 7**

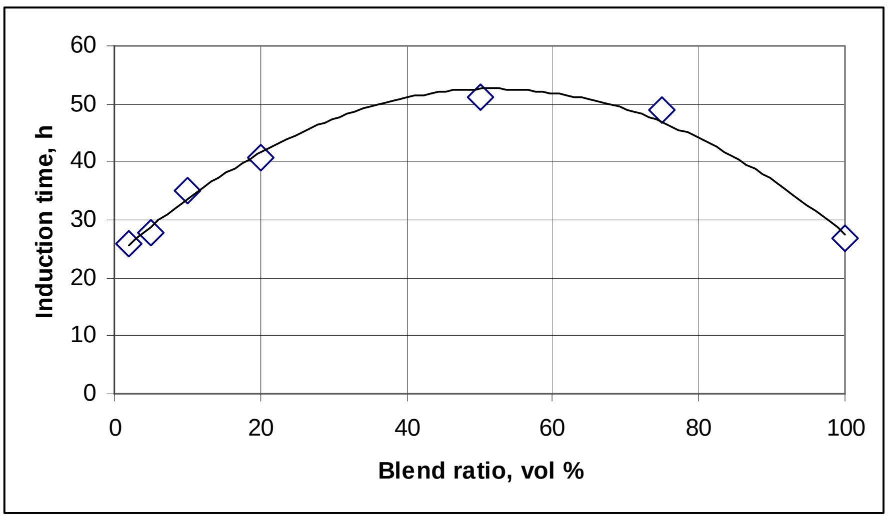

Fig.7 Animal fat biodiesel/ULSD oxidation stability vs. blend ratio

The B100 induction time for the animal fat biodiesel is over 25 hours as contrast to 5 hours for the soy biodiesel as shown in **Fig.7**. The induction time for the B20 animal fat blend is about 40 hours as compared to 13 hours for the B20 soy biodiesel blend. However, the stability trend is drastically different from that for soybean biodiesel/ULSD blend. We repeated the experiments three times for each ratio of blend and used the averaged data to make the plot. We can see that the stability initially increases with the blending ratio, then decreases after reaching a maximal point. The maximum induction time appears to be around B50. We thought the induction time of the animal fat biodiesel/ULSD blend should behave similarly to that of the soybean biodiesel/ULSD blends as shown in **Fig. 6**, but it did not, and we cannot offer any in-depth explanation at the moment. Interestingly, the particle contamination we measured for the animal fat biodiesel/ULSD blends is around 1 mg/L, much lower than that of soybean biodiesel, independent of the biodiesel blend ratio. This could be another supportive indication that animal fat biodiesel is more stable, and that is why it is cleaner.

However, the better oxidation stability of animal fat biodiesel does not necessarily justify it as a better quality fuel in application, since it has much higher cloud point of about 9 °C compared with 0 °C for the soybean biodiesel. Therefore the use of high percentage animal fat biodiesel blend could cause more engine operational problems in cold climate. The possible solutions to this are to use cold-flow enhancing additives, adding heaters to the fuel delivery line or store the vehicles in or near a building.

Fig.8 shows the viscosity change against temperature for the animal fat biodiesel/ULSD blends. It can be seen that when the blending ratio is above 50%, the blended fuel starts to thicken quickly at temperature below 0 °C. For B100, the starting temperature for fuel thickening is around 10-15 °C, much higher than B50 and B75, and higher than soybean B100. When the blending ratio is between 2% to 20%, the viscosity increases almost linearly with decreasing temperature, and the application of these blends generally should not cause fuel gelling problems.

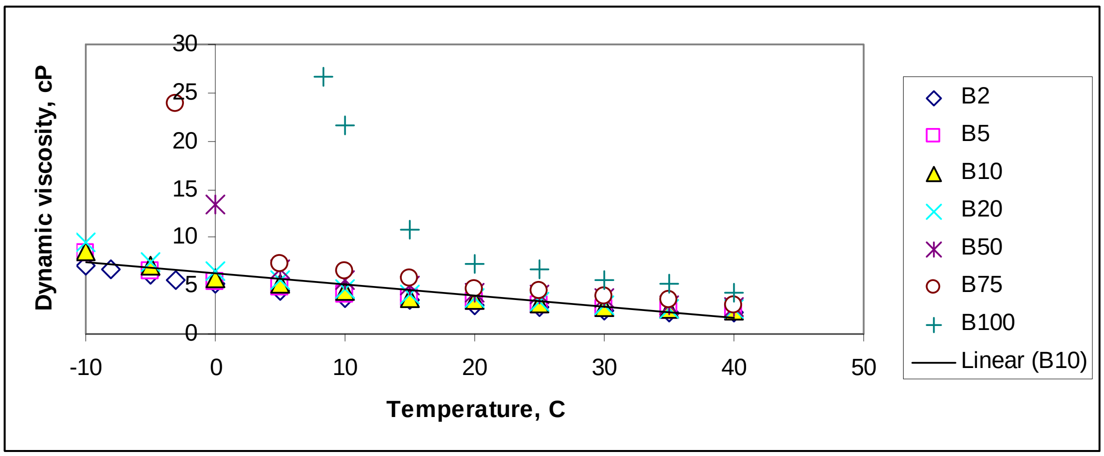

Fig.8 Viscosity of animal fat biodiesel/ULSD blends

Table 2 shows some other properties of the blended fuel using animal fat biodiesel and ULSD. The surface tension of the blends at different blending ratios behaves similarly to soybean biodiesel blends. The interfacial tension and MSEP are higher at every blend ratio than the soybean biodiesel, except at B2. This is an indication that the interaction of the tested animal fat biodiesel with ULSD is chemically different than that of soybean biodiesel. This also implies that the fuel/water separation efficiency for animal fat biodiesel/ULSD blend can be easier than that for soybean biodiesel/ULSD blend. Increasing blend ratio for animal fat biodiesel may also enhance fuel/water separation efficiency due to the increase in MSEP rating. The reason for this has been explained in Ref **[6].** For the soybean biodiesel, it's hard to predict the trend of the fuel/water separation efficiency as the blending ratio gets higher, since the MSEP under B50 is all zero as shown in **Fig. 2**.

Table 2 Properties of animal fat biodiesel/ULSD blends

Fluid Type	Density (g/ml)	IFT (mN/m)	Surface tension (mN/m)	MSEP	Water saturation ppm
B2	0.840	13.0	28.3	0	140
B5	0.841	13.3	27.9	43	173
B10	0.845	13.4	28.3	52	170
B20	0.845	15.4	28.5	66	265
B50	0.853	17.9	28.8	62	698
B75	0.862	18.5	29.9	98	701
B100	0.871	19.5	30.7	99	1604

The water saturation level of the blends merits more discussion**.** The experiments were conducted by contacting the blended fuel with water in a bottle with mild magnetic stirring for 16 hours without mixing the two phases; the fuel sample was then taken for water titration. The dissolved water concentration of the original B100 without such phase contact for equilibrium is 214 ppm, less than that for the neat soybean biodiesel which is 361 ppm. The dramatic increase in water content from B50 to B100 after water equilibration also impacts the visual quality of the fuel as we observed. The fuel starts to become hazy and turbid with small water droplets dispersed in the fuel without quick fuel/water phase separation as illustrated in **Fig. 9** even a few more days were allowed for the bottled sample to settle. For neat petrodiesel fuel, we barely observed such a phenomenon. The water does not fall out of high percentage biodiesel blend quickly is a further indication of the higher solvent power and polarity that biodiesel has over petrodiesel. It may also cause over-dissolved water separation problems using a filter media due to the high affinity of water to fuel. In terms of fuel quality control, if high biodiesel blend is to be used, other fuel additives such as demulsifiers or dehazers might be needed to prevent fuel from becoming over-saturated with water to cause other problems.

Fig.9 Color change of blended fuels saturated with water

FUEL/WATER FILTRATION

Much work has been conducted by the Southwest Research Institute (SwRI) on biodiesel fuel/water separation **[9]**. The general conclusion is that regardless of the type of filter media, as low as 5% biodiesel blend will dramatically reduce the emulsified water filtration efficiency from the blended fuel, independent of the biodiesel production feedstock, whether it being soybean oil, yellow grease or rapeseed. In their experiments, biodiesel reduces the interfacial tension of the ULSD they used for the test from above 25 mN/m to below15 mN/m. To evaluate a fuel/water filter's performance with a low IFT ULSD blended with biodiesel, we conducted a series of tests and observed that the fuel/water separation efficiency may either go down or remain unchanged. The base ULSD also plays a critical role in the blended fuel. In our test per SAE J1488, we controlled the IFT at 15 dynes/cm and MSEP close to 0. The filter we used for the tests is a standard fuel/water separator that typically works well for low sulfur diesel fuel, and the result is shown in **Fig.10**. It can be seen that the efficiency does not decrease as we increase the blending ratio up to 20 vol% for the animal fat biodiesel. For the soybean biodiesel, on the other hand, the efficiency drops by about 20% when the blending ratio reaches 10 vol% and then it becomes flat. The efficiency of the filter in neat ULSD is about 70%, at a reduced fuel flow rate of 0.75gal/min due to the high surfactancy of the fuel.

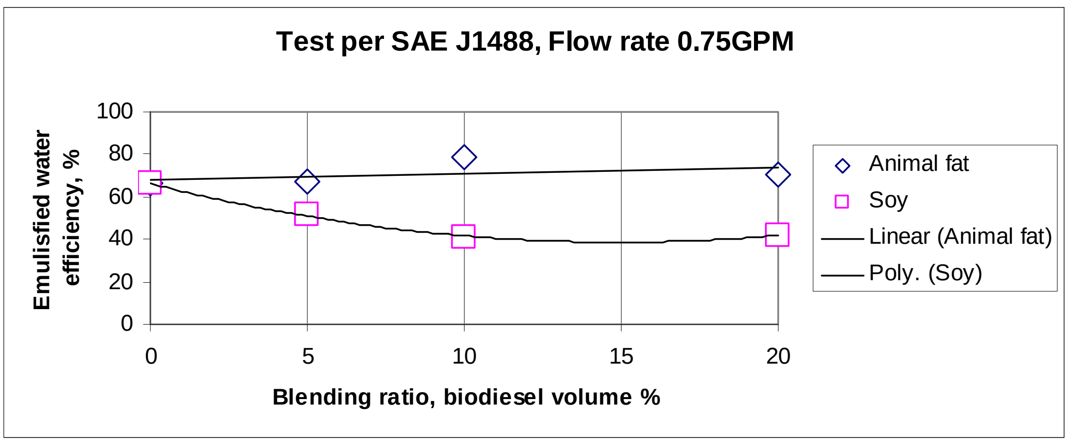

Fig. 10 Emulsified water separation efficiency as a function of biodiesel blend ratio

This result is complementary to SwRI's research. As we observed, for biodiesel/ULSD blends, a fuel/water separator's efficiency is strongly dependent on the fuel properties just as in ULSD **[6].** The scientific questions to ask for the blended fuel are therefore (1) how much surfactancy is additionally introduced or reduced by the biodiesel molecules derived from different feedstocks and (2), how do biodiesel molecules interact with the additives, especially those lubricity additives in ULSD, if the interaction does occur. From the engineering standpoint, the task is to develop a filtration technology that will handle not only ULSD, but also ULSD/biodiesel blend with high water/fuel separation efficiency. At the same time, test standards need to be better established to include the standardization of the base ULSD and the biodiesel for the tests.

CONCLUDING REMARKS

1. Biodiesel derived from different feedstocks makes the petrodiesel/biodiesel blend properties different. Those properties closely related to transportation fuel filtration such as IFT, MSEP, particle and water contamination as well as viscosity should be looked at carefully to understand how the blended fuel affects engine operation.
2. The base petrodiesel fuel used for the fuel blend is equally as important as the biodiesel. Some interaction among the different fuel molecules and the fuel additives may take place during blending, which will significantly affect fuel filtration and fuel/water separation.
3. The animal fat biodiesel we studied is more stable than soybean biodiesel, and its use under B20 does not seem to affect emulsified water filtration in our research. Soybean biodiesel reduces the effectiveness of a fuel/water separator.
4. Provided the biodiesel's quality meets ASTM D6751 or EN14214, a systematic understanding of the impact of biodiesel/ULSD blend on engine fuel filtration and fuel/water separation is still essential.

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