Biodiesel Quality—The Science and Production

Quality Control of Biodiesel

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Biodiesel is an oxygenated (10%) alternative fuel for diesel engines that burns cleanly and is receiving great attention worldwide. It is attractive because it can be produced from a great variety of feedstock (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut) and animal fats (usually tallow).

It is also attractive because it is nontoxic, biodegradable, and reduces emission of harmful pollutants (mainly particulates) from diesel engines (80% less CO_2 emissions, 50% less sulfur dioxide) but emissions of nitrogen oxides (precursor of ozone) are increased. However, the relative simplicity of biodiesel production can disguise the importance of maintaining high quality standards of the fuel supplied to the modern diesel engine. There is currently an excess production of vegetable oils in an oilseed protein driven market, so the use of bulk fat of the excess fats and oils worldwide will most likely be in the industrial sector.

There are already several large cities in the United States, Europe, and Asia that uses biodiesel to power truck and transportation bus fleets. Keeping with the trend, the Food Protein R & D Center of Texas A&M University organ-

Participants of Texas A&M's Practical Short Course on Biodiesel and Industrial Applications of Vegetable Oils August 20-23 2006.

ized a "Practical Short Course on Biodiesel and Industrial Application of Vegetable Oils." Key issues related to biodiesel production, the feedstock qualities, reaction conditions, and quality control aspects were discussed at large.

One of the most important factors of brewing biodiesel is making sure one has the quality fuel before running in their diesel engines. Bad quality fuel containing water and sediments, excess methanol, and/or leftover catalyst can damage key engine components and may cause breakdowns of the engine.

There are several ways to reduce the high viscosity of the vegetable oils to enable their use in diesel engines, including blending with petrodiesel, pyrolysis, microemulsification, and transesterification. However, transesterification is by far the most common method employed for biodiesel production since it reduces the viscosity of the original oil by one-tenth. The most commonly prepared esters are methyl esters because methanol is the least expensive alcohol in the United States. Generally, transesterification can proceed by base or acid catalyst, however, homogenous catalysis, alkali catalysis (sodium or potassium hydroxide, alkoxide) is a more rapid process than acid catalysis. In addition to the type of catalyst, reaction parameters, the molar ratio of alcohol to the vegetable oil, temperature, reaction time, and degree of refinement of the vegetable oil plays an important role for a good quality biodiesel.

To produce biodiesel, it requires on average about 20% methanol, 79% oil, and 0.5% sodium methylate. For example, for every 100 grams of oil, one would add 20 grams of methanol and 1.7 grams of 30% sodium methylate. The most important part of quality control is to ensure that the reaction went properly in the first place. Refined, bleached and deodorized (RBD) oil should be used routinely for production of quality biodiesel. At the end, make sure two distinct layers—one of glycerin and one of biodiesel—is clear and visible. Drain the maximum glycerin off the bottom of the fuel and wash the fuel thoroughly until the water coming out has no soap in it. Once all of these steps are followed, it is time to test the fuel for quality.

Making biodiesel is an easy process but one should always keep in mind, especially those who are interested in investing large capital for biodiesel production, to be familiarized and to follow some standard protocols, either national or international. In the United States, diesel fuel is characterized by the ASTM standard D 6751 to ensure quality of biodiesel in the marketplace and to provide confidence to consumers. Other test methods developed by professional oleochemical organizations, such as the American Oil Chemists' Society (AOCS), may also be suitable or even more appropriate because they were developed for fats and oils and not for petroleum-derived material.

Feedstock quality is very important for biodiesel quality. Higher concentration of free fatty acids (FFA), moisture, and phosphatides are the minor components of most vegetable oils (2-3%); however, if not removed prior to transesterfication, they will react with the catalyst and form soap, causing fuel-system deposits and reduced pump and filter life. FFA and phosphatides are not converted into biodiesel but react with the catalyst and produce gum. Animal fats may contain around 8-14% FFA whereas, soybean, rapeseed, and sunflower seed oil contains around 3.2, 2.5 and 1.5% of total phosphatides respectively. Depending on the raw material, biodiesel can contain more or less unsaturated fatty acids in its composition and unsaturated fatty acids are susceptible to oxidation reactions accelerated by exposure to oxygen and high temperatures, will lead into polymerized compounds.

Water and sediments are two housekeeping issues for biodiesel. Petroleum based diesel fuel can absorb ~ 50 ppm of water, whereas, biodiesel can absorb as much as 500 ppm (hydrophilic) and therefore the level of water should be minimized to 0.05% by volume. Sulfated ash and the carbon content should be minimized to $\leq 0.02\%$ and $< 0.05\%$ (100% distillation) respectively.

It is highly recommended that for quantitative determination of free and total glycerol one should consider using a gas chromatographic method since it is a well established and widely used technique. An open tubular column with a 5% phenylpolydimethylsiloxane bonded and cross lined phase internal coating, which can withstand an upper temperature limit of at least 400°C is recommended. Columns, either 10 m or 15 m in length with a 0.32 mm internal diameter, and 0.1 μm film thickness have been found satisfactory. However, any column with better chromatographic efficiency and selectivity can be used. Internal standard 1,2,4-butane triol and tricaprin are reliable standards for quantitative analysis of triacylglycerol (TAG), monoglycerol (MG) and diglycerol (DG) respectively. Glycerols may cause problems during storage or in the fuel system due to separation of glycerol leads to injector fouling or formation of higher aldehydes. The limit for free glycerol content of biodiesel is $\leq 0.02\%$ (m/m) and for total glycerol of $\leq 0.24\%$.

The National Biodiesel Accreditation Program is a cooperative and voluntary program for the accreditation of producers and marketers of biodiesel fuel called BQ-9000. The program is a unique combination of the ASTM standard for biodiesel, ASTM D 6751, and a quality systems program that includes storage, sampling, testing, blending, shipping, distribution, and fuel management practices. BQ-9000 is open to any biodiesel manufacturer, marketer, or distributor of biodiesel and biodiesel blends in the United States and Canada.

Making biodiesel is an easy process, however, expensive instruments are needed for quality control purposes. All biodiesel facilities should be equipped with a laboratory so that the quality of the final biodiesel product can be monitored.

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**Biodiesel Quality—
The End-User's Perspective**

Fuel School: Biodiesel and Your Truck's Engine

Engine manufacturers say there are still some issues to be worked out with biodiesel

Terry Scruton

The word "biodiesel" is on the tips of many tongues these days. In some states, such as Minnesota, Washington, and Colorado, the use of biodiesel is becoming a matter of public policy.

But what about engine manufacturers? With new ultra-low-sulfur-diesel regulations on the way and 2007 just around the corner, engine makers would seem to have plenty on their plates already.

But they'd better make room for more, because biodiesel doesn't appear to be going away any time soon.

Most of the major truck engine manufacturers—Caterpillar, Cummins, and Detroit Diesel—have policies in place regarding the use of biodiesel in their engines and are continuing research into the subject. But several areas of concern have already been identified.

To B20 or not to B20

While B20—a 20-percent blend of biodiesel—is a popular blend among retailers, that popularity doesn't necessarily extend to engine manufacturers. The Engine Manufacturers Association (EMA) recommends a blend of no higher than B5, and most manufacturers seem to agree.

The EMA's recommendations state that higher biodiesel blends could cause problems such as filter plugging, piston ring sticking and breaking, and elastomer seal swelling.

In its statement on biodiesel, Cummins states that it does not, at this time, recommend blends higher than 5 percent and will not until it completes evaluations on the other blends. A spokeswoman for Cummins told *Land Line* magazine that the company is still working on those evaluations and will modify its position once they are complete.

While Detroit Diesel agreed with Cummins on the B5 limit, Caterpillar, in its biodiesel standards, said it "neither approves nor prohibits the use of biodiesel fuels." Unlike Cummins, Caterpillar said it "is not in a position to evaluate the many variations of biodiesel fuels and the long-term effects on performance, durability, and emissions compliance of Caterpillar products."

Joe Suchecki, a spokesman for the EMA, said that even the B5 recommendation could change in light of what happened in Minnesota. Trucking operations in that state experienced fuel filter problems in late 2005 after a mandate went into effect requiring all diesel sold in the state to be a 2-percent biodiesel blend.

"That was really a surprise to us," he said. "But we understand that the fuel didn't meet quality specifications." Minnesota officials concluded that the problems were isolated to a few specific batches of biodiesel and said they expected to put the 2-percent blend mandate back in effect Feb. 10.

Quality Assurance

Suchecki said quality specifications are something the engine manufacturers have been pushing for and insisting on from biodiesel producers. Currently there are no federal regulations when it comes to biodiesel quality assurance.

In addition to working with the National Biodiesel Board, Suchecki said the EMA is urging state and federal governments to insist that any subsidies or incentives provided to biodiesel producers come with a requirement to meet certain quality specifications.

The National Biodiesel Board has its own voluntary quality specifications, known as BQ-9000. The standards are part of the National Biodiesel Accreditation Program, which is run by the Biodiesel Board. Thus far, the standard is a voluntary one, though Minnesota is considering making BQ-9000 certification mandatory for biodiesel producers in the state.

Suchecki said it is also important that any fuel, biodiesel or otherwise, used in a truck engine meet the standards for diesel and biodiesel set up by the American Society for Testing and Materials (ASTM).

The ASTM standards are used in the BQ-9000 accreditation, along with a quality systems program that includes standard practices for storage, sampling, testing, blending, shipping, distribution and fuel management.

Suchecki said that engine manufacturers are holding to the position that, until a national standard for quality assurance is developed, they won't officially recommend any biodiesel product higher than a B5 blend.

"Any alternative fuel needs to meet the specifications and be of high quality or else you're going to have those problems," he said.

The Ultra-Lowdown

One big issue that Suchecki said has yet to be resolved, as far as the engine makers are concerned, is that of ultra-low-sulfur diesel (ULSD). "That's a long-term issue that hasn't been resolved yet," he said. "How biodiesel will (affect) engines and emissions once the ultra-low-sulfur diesel is used."

The Biodiesel Board said in its official statement on ULSD that biodiesel contains virtually no sulfur, so it shouldn't be an issue. What's more, the board maintains that biodiesel can help with one of the key problems facing the switch to ULSD: lubricity.

Removing the sulfur from diesel seriously lowers its lubricity, which can gum up the inner workings and cause serious problems for engines. The Biodiesel Board's statement says biodiesel has a higher lubricity than ULSD, even in low blends.

The board said that a study done by Stanadyne Automotive Corp.—a manufacturer of diesel engine components—found that a 2-percent blend of biodiesel could increase lubricity by as much as 65 percent.

Suchecki said that's all well and good, but the engine manufacturers are still taking a cautious approach, waiting to see what happens once ULSD is actually on the road, before making any further recommendations with regard to biodiesel.

"There (have) been a lot of comments on using biodiesel to increase the lubricity of ULSD," he said. "That's up to the fuel producers, if they want to use that. But whatever the fuel is, it's going to have to have the proper lubricity requirements whether it's biodiesel or another additive, so we're not really concerned about that."

2007 & Beyond

Perhaps an even bigger issue facing biodiesel, in terms of engine performance, is the impact of the 2007 engine requirements from the Environmental Protection Agency (EPA).

According to the EPA rules, engine manufacturers are required to reduce on-highway emissions of particulate matter and nitrogen oxides by 90 percent. While Suchecki said the engine manufacturers are ready, this rule presents something of a problem for biodiesel.

Particulate matter may not be much of an issue, but one of the drawbacks to biodiesel is that it actually increases emissions of nitrogen oxides.

"In terms of 2007, using biodiesel by itself will not be sufficient to meet those emission requirements," Suchecki said. "We still need the particulate filters and we're getting close to when those are going to be produced."

Those new particulate filters in the 2007 engines pose another potential problem. Suchecki said the engine manufacturers are still testing and researching, but if the problems in Minnesota are any indication, biodiesel could still have a long road ahead. Suchecki said in the long run, where engine manufacturers are concerned, biodiesel has both its advantages and disadvantages.

"We see a lot of value to the environmental benefits," he said. "But beyond that, there's really no added value or harm from it, so it's kind of a non-issue."

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