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Status and Issues for Biodiesel in the United States

A Discussion Paper for Clean Cities Coalitions and Stakeholders to Develop Strategies for the Future

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State of the Technology

Biodiesel consists of mono-alkyl esters of fatty acids, which are typically methyl esters and are sometimes referred to as FAME, or fatty acid methyl esters. These mono-alkyl esters are produced today from fat, grease, or vegetable oil feedstocks using a chemical reaction called transesterification. The process technology for transesterification is well established and not currently a limiting factor in the biodiesel marketplace. This renewable fuel is primarily used as a 2%- to 20%-by-volume blend with petroleum diesel. Biodiesel blends are referred to as 'Bxx'; for example, B5 indicates a 5% by volume biodiesel blend.

Current Market Status

In 2008, the U.S. biodiesel industry produced 682 million gallons of B100.[1] A significant fraction of this production was exported. A 2004 study indicates that U.S. resources are available to produce about 1.7 billion gallons of biodiesel annually.[2] The National Biodiesel Board indicates that current installed production capacity is well over 2 billion annual gallons – significantly more than the current market.[3]

For quality specification purposes in the United States, to ensure trouble free operation, and to qualify for a blender's tax credit, biodiesel must meet the requirements of ASTM D6751. This ASTM specification is for B100 that can be used for blending at up to 20% by volume. The standard has been improved several times over the past few years, and the process continues today. The specification ensures that blends up to 20% are compatible with diesel engines and associated fuel system hardware.

A survey of B100 quality was conducted recently to determine the degree to which U.S. biodiesel producers were meeting the D6751 specification.[4] Samples were tested for the most critical properties in D6751. Production volume information from the National Biodiesel Board was used to estimate the volume percentage of biodiesel production passing or failing each requirement. The 56 producers that provided samples represented 52% of the producers in the marketplace, but 70% of the volume of biodiesel produced. The study found that 90% of the biodiesel was on specification, a positive result given that earlier, less comprehensive studies had found a lower compliance rate. On the negative side, as much as 10% of the product being produced when these samples were collected was failing to meet legal requirements due to negligence on the part of a small number of biodiesel producers.

Many vehicle owners refer to the engine owner's manual to determine which fuels are suitable for their engines. Thus, the written policy of the engine manufacturer regarding biodiesel has a significant impact on biodiesel markets. In most manufacturers' literature, B5 and lower blends are approved, as long as the biodiesel meets D6751 and/or EN14214, the European biodiesel specification, and some manufacturers recognize higher blend levels. The ASTM specification for conventional diesel fuel, D975, allows up to 5% biodiesel in conventional diesel fuel. A separate specification, D7467, describes the required property limits for B6 to B20 blends.

Vehicles/Engines

There has been concern regarding the potential for using biodiesel during winter months because of a higher than expected incidence of cold weather fuel filter plugging experienced in the past for biodiesel blends. This problem was caused by the presence of minor components in biodiesel

that, for long cooling times, could precipitate out of the blend and plug the fuel filter. In October 2008 ASTM published a new version of the D6751 specification that included a new requirement intended to limit the presence of these minor components. This requirement, known as the cold soak filtration test, appears to have been successful as fuel filter plugging events were much less frequent in the 2008-2009 winter. For biodiesel meeting the cold soak filterability requirement, cloud point and other common metrics of low-temperature operability are good predictors of actual performance.[5]

Long-term engine durability tests[6] and fleet studies[7] with B20 have not shown significant negative effects of B20 or lower blends. However, how biodiesel will perform with advanced emission control equipment such as diesel particle filters and NOx emission control catalysts is largely unknown. These are being introduced into the U.S. market in 2007 to 2010. Questions remain about both the short-term performance of these devices and their long-term durability when used with biodiesel. In particular, catalyst manufacturers are concerned that low-levels of metals (sodium, potassium, calcium, and magnesium) and phosphorus that are allowable in biodiesel today could be high enough to damage DPFs or NO_x control catalysts, or lead to more frequent maintenance requirements. The interaction of biodiesel with engine lubricant is also of concern. It is normal for lube oil to contain a certain fraction of fuel; however, the effect of biodiesel on lube oil performance has not been well quantified. Advanced emission control technologies also put more strain on the lube oil because for these systems it can be diluted with fuel at higher levels. This happens because, in some engines, late in-cylinder fuel injection is used to regenerate particle filters and NO_x traps. Under these conditions, biodiesel's impacts on lubricant performance have not been well studied. A robust engine and emission control component testing program is thus required to address these issues.

Infrastructure

Local regulatory authorities typically require storage tanks (both above ground and underground), associated piping and leak detectors, as well as fuel dispensers and hoses to have third party certification as being safe and compatible with the fuels being handled. For these items the third party certifying their performance is Underwriters Laboratories (UL). UL has indicated that D975-compliant diesel fuels containing up to 5% biodiesel will be treated the same as diesel fuel, and thus items listed by UL for use with diesel fuel are also acceptable for use with blends up to B5. No equipment is currently listed by UL for use with higher biodiesel blends. Thus, an important barrier to larger markets for biodiesel is UL listing of fuel tanks, dispensers, and associated equipment for use with B20.

Today relatively few petroleum products terminals are able to store and in-line blend biodiesel. Thus, preparation of biodiesel blends is done by splash blending into the transport truck, which may require visiting separate sites to load the biodiesel and diesel fuel. Incentives for installation of biodiesel storage and blending capability at terminals are recommended.

Currently, biodiesel is moved to blending terminals by truck, rail, and occasionally barge. Biodiesel blends are produced at petroleum pipeline terminals and refinery truck racks, as well as by independent fuel jobbers. They are then moved to fleets and retail outlets by truck. A number of efficiencies could be gained if biodiesel blends could be prepared at refineries and moved to market in petroleum product pipelines. Biodiesel in blends will not separate or partition into water, as can occur for ethanol blended into gasoline under some conditions, which

makes pipeline transport feasible. In July 2006, Countrymark Co-op, a refiner and marketer of petroleum products in the U.S. Midwest, successfully transported 210,000 gallons of B5 through a 238-mile private pipeline.[8] In August 2006, 75,000 barrels of B5 were transported from Houston, Texas, to Linden, New Jersey, in a common carrier pipeline operated by Colonial Pipeline.[9] The test was successful in that the B5 blend did not degrade during transport. However, the next batch of diesel fuel was contaminated with low levels of biodiesel. Recently Kinder Morgan announced commercial shipment of B5 blends in the Plantation Pipeline in the Southeast U.S. Though it is not a concern for diesel fuel, there is some concern that jet fuel could become contaminated with FAME in a multiproduct pipeline. Studies show that 1% FAME in jet fuel can reduce oxidative stability, leading to increased deposits.[10] However, at levels below a few hundred ppm, no decrease in stability was observed.[11] A test method for analysis of FAME in jet fuel at ppm levels has recently been developed and is currently being balloted at ASTM. Jet engine testing to show that these engines can operate with up to a few hundred ppm biodiesel in the fuel will be required before biodiesel blends can be routinely transported on multiproduct pipelines that also ship jet fuel.

Supply

As noted, a 2004 study indicates that U.S. resources are available to produce about 1.7 billion gallons of biodiesel annually.[2] There are several sources of additional feedstock that could be developed in the near-term. Currently, about 60% of soybeans are crushed for oil extraction. This percentage could increase if markets for soy meal used as high-protein animal feed increase more rapidly than projected. Future increases in soybean yields and oil content could also increase feedstock oil production. A large potential source of vegetable oil feedstock is corn oil recovered from dry-mill ethanol production. Theoretically, this source could supply more than 500 million gallons at current ethanol production rates. A number of other terrestrial crops also might lead to increases in the availability of feedstocks, such as camelina, pennycress, canola rotation with wheat, and jatropha. One transformational technology that could lead to a dramatic increase in lipid feedstock production is aquaculture of algae. This technology is in its infancy but has the potential to yield several thousand gallons per acre, compared to roughly 60 gallons per acre of soy oil (note that soy oil is a byproduct of soy protein production).[12]

Available Federal and State Incentives

Policies supporting the use of biodiesel include the federal biodiesel blender's tax credit of $1 per gallon. More recently, the U.S. Energy Independence and Security Act of 2007 (Pub. L. No. 110-140) mandates the use of 1 billion gallons per year of biomass-based diesel by 2012 and 21 billion gallons of advanced biofuel by 2022. Biodiesel qualifies as both biomass-based diesel and likely qualifies advanced biofuel.

Emission Benefits

The U.S. Environmental Protection Agency's (EPA's) national air pollutant emission trends report shows that in 2000 diesel vehicles produced approximately 7% of U.S. mobile-source hydrocarbon emissions and 5% of mobile-source carbon monoxide (CO).[13] However, diesel vehicles produced 45% of U.S. mobile-source oxides of nitrogen (NO_x) and 60% of mobile source particulate matter ($PM_{2.5}$ or PM). In addition, diesel PM can contain 20% to 40% organic compounds that have known mutagenic and carcinogenic properties.[14] Thus, the impact of biodiesel on NO_x and PM emissions is of greatest interest.

In the United States, engine dynamometer tests are used for heavy-duty (HD) engine emissions compliance testing.[15] Results for hydrocarbon, CO, NO_x, and PM are reported in g/bhp-h (0.7457 g/bhp-h = 1 g/kW-h). Allowable levels of HD emissions have been reduced dramatically over the past 25 years, resulting in a continuous evolution of diesel engine and emission control technology. A reduction in the allowable NO_x level from 4 g/bhp-h in 1998 to 1.2 g/bhp-h in 2007 was made possible by exhaust gas recirculation, higher pressure fuel injection, and more advanced fuel injection control strategies. Beginning in 2006, sulfur in on-highway diesel fuel was lowered from 500 to 15 ppm (ultra-low-sulfur diesel) to allow the introduction of diesel particle filters (DPF) and NO_x reduction catalysts. All 2007 model-year HD engines in the United States were equipped with diesel particle filters to meet a PM emission standard of 0.01 g/bhp-h, a factor of 10 below the previous standard. A lower NO_x standard of 0.2 g/bhp-h by 2010 will be achieved by using adsorbent and catalyst systems.

Effects on Hydrocarbon, CO, and Particulate Matter

In 2002, the EPA reviewed published biodiesel emissions data, which consisted almost entirely of data for HD engines in the 1988 to 1998 model-year range.[16] On average, using biodiesel as a blend or in neat form resulted in substantial reductions in emissions of PM, CO, and hydrocarbons for engines from that decade. The conclusions of EPA's review of the impacts of biodiesel on total hydrocarbon, CO, and PM emissions have been confirmed in many recent studies of newer engines.[17] The overall database, however, remains unrepresentative of the current on-highway U.S. fleet. For example, more than 20% of the available test data are for 2-stroke engines that today make up less than 0.2% of the in-use fleet.

Data are quite limited on the emission performance of engines equipped with DPFs. Boehman and coworkers demonstrated that the blending of biodiesel could increase the oxidation reactivity of PM in a DPF, which may improve DPF performance in some situations.[18] Biodiesel blends were shown to lower the balance-point temperature (BPT), the temperature at which the rate of PM accumulation on the DPF is equal to the rate of PM combustion. Williams and coworkers subsequently showed that B20 could reduce the BPT by as much as 40ºC, and they demonstrated that as little as 5% biodiesel in the fuel could increase the rate of DPF regeneration measurably.[19] Additional data are required to understand if these observations translate into a benefit for biodiesel in terms of DPF operation, with potentially fewer regeneration events and reduced fuel economy penalty for regeneration.

While current emission regulations limit the total PM mass, health impacts are thought to correlate more closely with the number of very small particles that are emitted. Limited studies have been conducted of the impact of biodiesel on particle size distribution, all for engines not equipped with a DPF with sometimes conflicting results. Clearly, additional research is warranted on the impact of biodiesel on particle size distribution.

Impact on NO_x Emissions

NO_x emissions are of concern because of the potential for NO_x to participate in atmospheric reactions that lead to ozone formation; although the importance of NO_x in ozone formation has recently been questioned.[20] The EPA review cited above concluded that biodiesel caused a small increase in emissions of NO_x relative to petroleum diesel, which averaged 2% for B20. However, some data suggest that this may not always be the case. For example, a significant fraction of the 785 NO_x observations for B20 included in the EPA's review show a decrease in

NO_x. Factors that affect NO_x emissions from biodiesel include biodiesel source material,[21] driving cycle and average load,[22] as well as engine and fuel system design and operating strategy.[23] Tests conducted by EPA showed that the increasing NO_x effect was greater for higher average load driving cycles.[22] In addition, NO_x increased in proportion to the biodiesel blend level for one engine tested. The Cummins engine company examined the effect of biodiesel both on combustion and on engine control system parameters.[23] The study showed how NO_x could increase or decrease at different engine speed/load setpoints and how the engine computer control system could respond to biodiesel in different situations, to either increase or decrease NO_x. The Cummins study also presented data suggesting that the effect of biodiesel on NO_x is less than the NO_x variation caused by the normal range of variation in petroleum diesel fuel properties (aromatic content and cetane number, for example).

Ongoing analyses of all the available data continue to show, on average, a small increase in NO_x for B20. Yet, as noted, the engines included in the available dataset are not representative of the current on-highway fleet. Nevertheless, the potential for biodiesel to increase NO_x could become a significant barrier to market expansion if the volume of biodiesel used were to become so large that the effects were detrimental to air quality.

This issue will have to be reevaluated for engines equipped with the NO_x emission control catalysts that will be phased in beginning 2010, because there are as yet only limited data showing the performance of those catalysts with biodiesel blends. These early studies suggest that the small NO_x increase coming out of the engine will have little effect on NO_x downstream of the NO_x reduction catalyst, for short term operability effects.[24,25] Extensive testing is required to determine the long-term durability impacts of biodiesel on NO_x emission control technologies.

Toxic Compound Emissions and Health Effects

Sharp and coworkers performed detailed chemical characterizations of exhaust from one 1995 and two 1997 model-year engines.[26] Species quantified included C_1 to C_{12} hydrocarbons, C_1 to C_8 aldehydes, and several specific polyaromatic and nitro-polyaromatic hydrocarbons from both the semi-volatile and particle phase. Results for B100 showed large reductions in mass emissions of all groups of compounds; B20 resulted in smaller reductions overall and no significant change for some species. These results indicate that B20 has a very positive impact on toxic compound emissions; however, diesel engine technology has changed significantly since the study was conducted. Thus, measurement of toxic compound emissions for B20 in newer engines remains a pressing research need.

Studies have used bioassays to compare biodiesel and conventional diesel particulate matter extracts. For mutagenicity, some groups found no significant difference for PM extracts of the two fuels.[27, 28, 29, 30] However, Kado and Kuzmicky report higher mutagenic activity per particle mass for biodiesel fuels but lower total mutagenic emission rates because of the significantly lower particle mass emission rate.[31] Krahl and coworkers recently showed higher mutagenicity for biodiesel PM from several different engines.[32] Swanson and coworkers used airway epithelial cell bioassays to evaluate the inflammatory potential of extracts from diesel and biodiesel PM. Exposure to biodiesel PM extracts appeared to be a more potent inflammatory stimulant than exposure to diesel PM extracts.[33] These results suggest that biodiesel PM extracts contain some bioactive compounds that have not been identified in toxic compound emission speciation studies. Nevertheless, Finch and coworkers studied the exposure of rats to inhalation

of engine exhaust generated by burning 100% soy-derived biodiesel.[34] The animals were exposed to diluted exhaust over a range of PM concentrations. This study demonstrated health effects similar to those from exposure to conventional diesel exhaust.

A key feature of these studies is that few are very recent. Considerable additional work is required to understand how biodiesel impacts emissions of toxic compounds, health impacts, and to assess risk.

Petroleum and Carbon Reduction Benefits

Life-cycle analysis shows that biodiesel contains from 2.5 to 3.5 units of energy for every unit of fossil energy input in its production; and because very little petroleum is used in production of biodiesel, its use displaces petroleum at nearly a 1-to-1 ratio on a life cycle basis.[35, 36, 37, 38] Life-cycle analysis also shows reductions total greenhouse gas emissions (CO_2+CH_4+N_2O) ranging from 60% to over 90%, for direct effects. While many studies find marginal indirect land use change effects for vegetable oil-derived biodiesel, it remains to be seen how EPA will rule on this aspect of biodiesel's sustainability.

Barriers that are preventing significant deployment in the marketplace

As noted above, there are significant barriers associated with a lack of knowledge regarding compatibility of biodiesel blends with advanced emission control systems such as diesel particle filters and NO_x emission control catalysts. Additional issues may exist for compatibility with engine lubricants, especially for systems using late in-cylinder injection for regeneration of catalysts and filters. On the other hand, some tests show potential benefits for biodiesel in terms of DPF regeneration frequency. Additional data are required to understand if these observations translate into a benefit for biodiesel in terms of DPF operation, with potentially fewer regeneration events and reduced fuel economy penalty for regeneration. Extensive testing is also required to determine the long-term durability impacts of biodiesel on NO_x emission control technologies. A robust engine and emission control component testing program is thus required to address these issues.

Studies show that NO_x emissions increase for biodiesel blends in some engines. Because only a limited number of the many engine models on the road have been tested, the average effect of B20 on NO_x emissions is unclear. However, the potential for biodiesel to increase NO_x could become a significant barrier to market expansion if the volume of biodiesel used were to become so large that the effects were detrimental to air quality. Additional research is warranted on the impact of biodiesel on particle size distribution, and measurement of toxic compound emissions.

No equipment is currently listed by UL for use with biodiesel blends containing more than 5% biodiesel. Thus, an important barrier to larger markets for biodiesel is UL listing of fuel tanks, dispensers, and associated equipment for use with B20.

Major economic advantages could be gained for biodiesel if biodiesel blends could be transported by pipeline. The key issue here is potential contamination of jet fuel by biodiesel. Jet engine testing to show that these engines can operate with up to a few hundred ppm biodiesel

in the fuel will be required before biodiesel blends can be routinely transported on multiproduct pipelines that also ship jet fuel.

Another major barrier to more widespread deployment of biodiesel is the need for increased feedstock supply at reduced cost. Currently biodiesel market price is well over $3.50 per gallon, while petroleum diesel fuel is less than $3.00 per gallon. The primary driver of biodiesel price or cost is the cost of feedstock. Major initiatives to promote production of additional feedstock for making biodiesel should drive down cost.

According to the National Biodiesel Board (NBB), increasing the number of terminals that blend biodiesel will increase the quality of the final product, as well as lower the cost and increase potential availability. Currently, only 70 of the 1,500 petroleum terminals blend biodiesel.

Current Available Resources; Activities or Strategies Being Implemented

To a greater or lesser extent, all of the barriers listed above are being worked on through various government and industry R&D programs. The DOE's National Renewable Energy Laboratory (NREL) and NBB have an ongoing collaboration to examine biodiesel effects on advanced emission control equipment. Additional work in this area is being conducted at other DOE laboratories. NREL and other labs are also beginning to examine biodiesel impacts on particle number and toxic compound emissions.

NBB is working with UL to initiate testing of B20 blends in storage tanks and dispensers. NBB is also working with a large industry consortium to test jet engines with jet fuel containing 400 ppm of biodiesel. If these tests are successful, the allowable level of biodiesel in jet fuel would be raised to 100 ppm (a 4x safety factor) and petroleum product pipelines will be able to transport B5 blends. This would be a major development for biodiesel markets, potentially leading to a large increase in utilization.

Development of new feedstocks is being pursued by many different parties, including NBB, USDA, and industrial interests both large and small. This work involves modification of existing crops to have higher oil content, development of new oilseed crops that have benefit for farmers as a rotation or winter cover crop, as well as aquaculture of algae and other biotechnology based approaches.

Opportunities in the Marketplace and Technology Deployment Needs

The major strategy pursued by both DOE and the biodiesel industry for expansion of biodiesel markets has been to make biodiesel blends suitable for all diesel applications. This effort has been largely successful for pre-2007 engines without advanced emission controls and work is ongoing to ensure compatibility with post-2007 engines. A key factor for deploying biodiesel in the full range of diesel applications appears to be overcoming barriers to transport of B5 blends by pipeline. B5 blends are considered the same as conventional diesel fuel by ASTM and UL. If transportable by pipeline, a large fraction of the U.S. diesel market could become B5 (potentially as much as 3 billion gallons of biodiesel if B5 were used in all distillate fuel applications).

Biodiesel Availability

As of August 2009, there are 697 U.S. biodiesel fueling sites dispensing B20 and higher blends. Of these stations, approximately 50% are open to the public. To help fleets and consumers easily locate fueling sites, NREL developed the Alternative Fueling Station Locator and TransAtlas tools, which live on DOE's Alternative Fuels and Advanced Vehicles Data Center Web site (www.afdc.energy.gov). Launched in 1995, the Alternative Fueling Station Locator (www.afdc.energy.gov/afdc/locator/stations/) allows fleets to identify and map routes to fueling sites locally and nationwide. The TransAtlas tool (http://rpm.nrel.gov/transatlas/launch/) displays maps of fueling stations, vehicle densities, and production facilities throughout the country.

NBB also tracks biodiesel stations, including those that dispense blends of lower than B20. In fiscal year (FY) 2010, NREL will work more closely with NBB to share fueling site data.

Retail Price of Biodiesel

According to Clean Cities' Alternative Fuel Price Report, from September 2005 to April 2009 the nationwide average retail prices for B2 to B5 blends average about 1% less than petroleum diesel. B20 blends are approximately 2% more expensive, while B99-B100 blends are approximately 21% more expensive than petroleum diesel.

Average Cost to Install a Biodiesel Dispenser

The incremental cost of installing a dispenser for biodiesel blends of B6 and higher is not significant when compared to the price of a conventional diesel dispenser. As per ASTM D975, conventional diesel fuel can contain up to 5% biodiesel, so there are no physical differences between a conventional diesel fuel and a B5 dispenser.

Educating Fleets and Consumers

NREL and Clean Cities actively produce fact sheets, research reports, and online tools to educate fleets and consumers about biodiesel. In doing so, NREL and Clean Cities work hand-in-hand with NBB. Two examples of this partnership are NREL's "Biodiesel Handling and Use Guide" and Clean Cities' "Biodiesel Clears the Air in Underground Mines" fact sheet.

NREL consults with NBB about updating and distributing the handling and use guide. NBB not only reviews the documents, it distributes it to its members to ensure industry's consistent use of biodiesel. More recently, NBB expressed to Clean Cities a need for a biodiesel and mining fact sheet. Seeing an opportunity for coordinators to expand their reach within their communities, Clean Cities wrote and produced this previously mentioned fact sheet, which is posted on the AFDC and distributed by NBB.

In FY 2010, NBB and NREL and Clean Cities plan to partner on project to analyze data from trucking operator JB Hunt's biodiesel experience and produce a report that will help other trucking companies incorporate biodiesel into their operations. This report will help both coordinators and NBB promote biodiesel use to trucking stakeholders.

In addition to publications, NREL and Clean Cities are launching a new online training program in October 2009. Titled Clean Cities University (CCU), this new project educates coordinators and stakeholders about all of Clean Cities' technology areas. NREL and Clean Cities will work

with NBB to produce biodiesel-specific training courses for CCU and to host existing NBB-produced training modules in CCU.

Biodiesel Market Potential for Light-Duty Diesel Vehicles

According to J.D. Power Automotive Forecasting, demand for light-duty diesel vehicles could almost double, increasing from $15 million sales in 2005 to $29 million in 2015. As stated earlier, most manufacturers' literature approves B5 and lower blends for use in their vehicles as long as the biodiesel meets ASTM D6751 and/or EN14213 standards. Because most consumers defer to their owner/operator manual for what fuels are allowed in their vehicle, having manufacturer approval can significantly impact the market acceptance of biodiesel.

Clean Cities and Dealers and Manufacturers

On the local level, Clean Cities continues to create educational opportunities and participate in outreach activities—some of which target general consumers. Based on responses to the 2008 annual Clean Cities questionnaire, 1,310 activities were reported by coordinators and estimated to reach more than 113 million people—almost three times the number reached in 2007. Media events and advertisements dominated the field, combining to represent 97% of the total number of people reached.

Coordinators were asked to judge how much they thought they were responsible for the number of people reached at each event in contrast to the contribution of other event sponsors and participants. An analysis of the responses shows that, on average, coordinators felt they were responsible for 57% of the 113 million people reached.

The general public was most often cited as a target audience, followed by government then fleets in general. Specialized applications—airports, waste management, delivery trucks, utility trucks, and mass transit—were identified as audiences in one-third of the outreach activities. Other audiences were cited as audience types in 13% of the activities reported.

Many Clean Cities coordinators agree that partnerships local dealerships are an opportunity for growth. In general, Clean Cities coalitions have good relationships with national-level vehicle manufacturers but lack ongoing working relationships with many local dealerships.

Fleet Experiences

Throughout the country, there are a wide variety of fleets utilizing biodiesel for a variety of reasons and with varying success. Clean Cities captures the biodiesel implementation stories of many fleets in the Fleet Experiences (www.afdc.energy.gov/afdc/progs/fleet_exp_fuel.php/BD) section of the AFDC. NREL developed this section to inspire fleets to use alternative fuels and advanced vehicles.

Minnesota's Blend Requirement

Many states are implementing programs to expand the use of biodiesel. However, the state of Minnesota has made it a priority to be a leader in the development of the biodiesel industry. The Minnesota Legislature has enacted number of bills toward this goal, as well as creating taskforces and committees that focus on biodiesel and their expanding industry.

Currently all diesel sold in Minnesota must be B5. Future mandates are for B10 by May 2012, and B20 by May 2015. Content levels apply only during warm-weather months (April-October), with B5 required during the remainder of the year unless a fuel standard is in place to address cold-weather diesel issues. The increases are not automatic, however. There is built-in flexibility, including an approval process before moving to higher blends. This will allow all interested parties from the legislature, state agencies, end users, consumers and biodiesel producers to gauge the economic, supply, and environmental impacts before moving to a higher blend.

Within Minnesota Statute 239.77 – Biodiesel Content Mandate, there is a provision that the commissioners of agriculture, commerce and pollution control must submit progress reports to the legislature so that informed decisions are made prior to each increase in the biodiesel requirement. This provision highlights the importance of quality assurance in the successful implementation of the mandate, which is supported by the Department of Commerce's testing method for determination of FAME content in blends of biodiesel. In an additional effort to ensure proper implementation of the mandate, the Minnesota Biodiesel Technical Cold Weather Issues Team Handling Subcommittee has produced a Biodiesel Blend Handling Guide.

Challenges and Opportunities

According to NBB, 690 million gallons of biodiesel were sold in 2008. Sales are expected to decline in 2009 due to economics. If biodiesel plants were built or plants planned expansion based on the Renewable Fuels Standard 2 (RFS2) being in place, the delay of RFS2 may cause some plants to produce at less than capacity or delay expansion.

It is unlikely that any biodiesel producers are significantly profitable, due to the high cost of the feedstock and the downward price pressure from lower costs of conventional diesel fuel.

References

[1] Energy Information Administration, http://www.eia.doe.gov/emeu/mer/renew.html, accessed July 13, 2009.

[2] Tyson, K.S., Bozell, J., Wallace, R., Petersen, E. and Moens, L. *Biomass Oil Analysis: Research Needs and Recommendations*; NREL Technical Report No. TP-510-34796, National Renewable Energy Laboratory, 2004.

[3] National Biodiesel Board, http://www.biodiesel.org/pdf_files/fuelfactsheets/Production_Capacity.pdf, accessed August 26, 2009.

[4] Alleman, T.L. and McCormick, R.L. *Results of the 2007 B100 Quality Survey*, NREL Report No. TP-540-42787, National Renewable Energy Laboratory, 2008.

[5] McCormick, R.L., Chandler, J.,Gault, R., Howell, S., Nikanjam, M., Buczynsky, A., Jetter, J., Barenescu, R., Arters, D., Forester, D., Mitchell, K., "Biodiesel Blend Low-Temperature Performance Validation", CRC Project: DP-2a-07 , June 2008.

[6] Bartoli, Y. 1000 Hour Durability Evaluation of a Prototype 2007 Diesel Engine with Aftertreatment Using B20 Biodiesel Fuel. Presented at the National Biodiesel Conference, Orlando, FL, Feb. 5, 2008.

[7] Proc, K., Barnitt, R., Hayes, R.R., McCormick, R.L., Ha, L. and Fang, H.L. 100,000 Mile Evaluation of Transit Buses Operated on Biodiesel Blends (B20). SAE Tech. Pap. No. 2006-01-3253, 2006.

[8] Biofuels International. Latest News Page. Biodiesel Pipeline First. http://www.biofuels-news.com/news/pipeline_first.html (accessed June 23, 2008).

[9] Northville Products and Services and Colonial Pipeline. B5 Soy Test Data and Report: Bio Diesel Trial NPS-73-441, Soy Blended Low Sulfur Diesel, 2007. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/20070201_gen384.pdf (accessed June 23, 2008).

[10] Wilson, G., Thom, M. and Serino, P. Effect of FAME on Thermal Oxidative Stability. In Proceedings of the 10th International Conference on Stability, Handling and Use of Liquid Fuels Tucson, AZ, USA, October 7-11, 2007; see www.iash.net (accessed June 23, 2008).

[11] Anderson, S. FAME in Jet Fuel. Presented at the IATA Aviation Fuel Forum, Istanbul, Turkey, November 5-8, 2007.

[12] Hu, Q., Sommerfeld, M., Jarvis, E., Ghirardi, M., Posewitz, M., Seibert, M. and Darzins, A. Microalgal Triacylglycerols as Feedstocks for Biofuel Production: Perspectives and Advances. *The Plant Journal* **2008**, *54*, 621–639.

[13] U.S. Environmental Protection Agency. *National Air Quality and Emissions Trends Report*; 2003 Special Studies Edition, EPA Report No. 454/R-03-005, U.S. EPA, Washington, DC, 2003.

[14] U.S. Environmental Protection Agency. *Health Assessment Document for Diesel Engine Exhaust*, Report No. EPA/600/8-90/057F, U.S. EPA, Washington, DC, 2002.

[15] United States Code of Federal Regulations, Title 40, Part 86, Subpart N, Emission Regulations for New Otto-Cycle and Diesel Heavy-Duty Engines; Gaseous and Particulate Exhaust Test Procedures.

[16] U.S. Environmental Protection Agency. *A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions,* Draft Technical Report No. EPA420-P-02-001, U.S. EPA, Washington, DC, 2002.

[17] McCormick, R.L., Williams, A., Ireland, J., Brimhall, M. and Hayes, R.R. *Effect of Biodiesel Blends on Vehicle Emissions.* NREL Report No. MP-540-40554, National Renewable Energy Laboratory, Golden, CO, 2006.

[18] Boehman, A.L., Song, J. and Alam, M. Impact of Biodiesel Blending on Diesel Soot and the Regeneration of Particle Filters. *Energy & Fuels* **2005**, *19*, 1857-1864.

[19] Williams, A., McCormick, R.L., Hayes, R.R., Ireland, J. and Fang, H.L. Effect of Biodiesel Blends on Diesel Particulate Filter Performance. SAE Tech. Pap. No. 2006-01-3280, 2006.

[20] Lawson, D.R. The weekend ozone effect—The weekly ambient emissions control experiment. *Environmental Management* **2003**, *July,* 17-25.

[21] McCormick, R.L., Alleman, T.L., Graboski, M.S, Herring, A.M. and Tyson, K.S. Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine. *Environ. Sci. Technol*. **2001**, *35*, 1742-1747.

[22] Sze, C., Whinihan, J., Olson, B.A., Schenk, C.R. and Sobotowski, R. Impact of Test Cycle and Biodiesel Concentration on Emissions. SAE Tech. Pap. No. 2007-01-4040, 2007.

[23] Eckerle, W., Lyford-Pike, E., Stanton, D., LaPointe, L., Whitacre, S.D. and Wall, J.C. Effects of Methyl Ester Biodiesel Blends on NO_x Emissions. SAE Tech. Pap. No. 2008-01-0078, 2008.

[24] Tatur, M., Nanjundaswamy, H., Tomazic, D. and Thornton, M. Effects of Biodiesel Operation on Light-Duty Tier 2 Engine and Emission Control Systems. SAE Tech. Pap. No. 2008-01-0080, 2008.
[25] Williams, A., Pedersen, D., Ireland, J., McCormick, R.L., Fang, H.L. "Effect of Biodiesel Blends on Urea Selective Catalytic Reduction Catalyst Performance with a Medium-Duty Engine" SAE Tech. Pap. No. 2008-01-2484, 2008.
[26] Sharp, C.A., Howell, S.A. and Jobe, J. The Effect of Biodiesel Fuels on Transient Emissions from Modern Diesel Engines, Part II, Unregulated Emissions and Chemical Characterization. SAE Tech. Pap. No. 2000-01-1968, 2000.
[27] Bagley, S.T., Gratz, L.D., Johnson, J.H. and McDonald, J.F. Effects of an Oxidation Catalytic Converter and a Biodiesel Fuel on the Chemical, Mutagenical and Particle Size Characteristics of Emissions from a Diesel Engine. *Environ. Sci. Technol*. **1998**, *32*, 1183 –1191.
[28] Bünger, J., Krahl, J., Franke, H.U., Munack, A. and Hallier, E. Mutagenic and Cytotoxic Effects of Particulate Matter of Biodiesel Compared to Fossil Diesel Fuel. *Mutat. Res*. **1998**, *415*, 13–23.
[29] Rantanen, L., Mikkonen, S., Nylund, L., Kociba, P., Lappi, M. and Nylund, N.O. Effect of Fuel on the Regulated, Unregulated and Mutagenic Emissions of DI Diesel Engine. SAE Tech. Pap. No. 932686, 1993.
[30] Turrio-Baldassarri, L., Battistelli, C.L., Conti, L., Crebelli, R., De Berardis, B., Iamiceli, A.L., Gambino, M. and Iannaccone, S. Emission Comparison of Urban Bus Engine Fueled with Diesel Oil and 'Biodiesel' Blend. *Sci. Total Environ.*, **2004**, *327,* 147-162.
[31] Kado, N.Y. and Kuzmicky, P.A. *Bioassay Analyses of Particulate Matter from a Diesel Bus Engine Using Various Biodiesel Feedstock Fuels.* NREL Report No. SR-510-31463, National Renewable Energy Laboratory, Golden, CO, 2003.
[32] Krahl, J. "Exhaust Gas Emissions and Mutagenic Effects of Diesel Fuel, Biodiesel and Biodiesel Blends" SAE Tech. Pap. No. 2008-01-2508, 2008.
[33] Swanson, K., Kado, N., Madden, M.C. and Ghio, A.J. Release of IL-8 and IL-6 by BEAS-2B Cells Following In Vitro Exposure to Biodiesel PM Extracts. *Toxicol.* **2007,** *96*, 813(A).
[34] Finch, G.L., Hobbs, C.H., Blair, L.F., Barr, E.B., Hahn, F.F., Jaramillo, R.J., Kubatko, J.E., March, T.H., White, R.K., Krone, J.R., Ménache, M.G., Nikula, K.J., Mauderly, J.L., Van Gerpen, J., Merceica, M.D., Zielinska, B., Stanowski, L., Burling, K. and Howell, S. Effects of Subchronic Inhalation Exposure of Rats to Emissions from a Diesel Engine Burning Soybean Oil-Derived Biodiesel Fuel. *Inhal. Toxicol*. **2002**, *14*, 1017–1048.
[35] Sheehan, J., Camobreco, V., Duffield, J., Graboski, M. and Shapouri, H. *An Overview of Biodiesel and Petroleum Diesel Life Cycles;* NREL Technical Report No. TP-580-24772, National Renewable Energy Laboratory, Golden, CO, 1998.
[36] Hill, J., Nelson, E., Tilman, D., Polansky, S. and Tiffany, D. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. *Proceedings of the National Academy of Sciences.* **2006,** *103*,11206–11210.
[37] Huo, H., Wang, M., Bloyd, C. and Putsche, V. *Life-Cycle Assessment of Energy and Greenhouse Gas Effects of Soybean-Derived Biodiesel and Renewable Fuels,* Argonne National Laboratory ANL/ESD/08-2, March 2008.
[38] Van Gerpen, J. Presentation at the National Biodiesel Conference, Orlando, FL, February 3-6, 2008. http://nbb.grassroots.com/08Releases/EnergyBalance/.

STATUS AND ISSUES FOR BIODIESEL IN THE UNITED STATES

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State of the Technology

Biodiesel consists of mono-alkyl esters of fatty acids, which are typically methyl esters and are sometimes referred to as FAME, or fatty acid methyl esters. These mono-alkyl esters are produced today from fat, grease, or vegetable oil feedstocks using a chemical reaction called transesterification. The process technology for transesterification is well established and not currently a limiting factor in the biodiesel marketplace. This renewable fuel is primarily used as a 2%- to 20%-by-volume blend with petroleum diesel. Biodiesel blends are referred to as 'Bxx'; for example, B5 indicates a 5% by volume biodiesel blend. One of the major advantages of biodiesel is the fact that it can be used in most existing engines and fuel injection equipment in blends up to 20 percent with no impact to operating performance. A dedicated vehicle is not required for biodiesel use. Biodiesel is one of the best-tested alternative fuels and the only alternative fuel to meet all of the testing requirements of the 1990 amendments to the Clean Air Act. A number of independent studies – performed by the U.S. Department of Energy, the U.S. Department of Agriculture, Stanadyne Corp. (the largest diesel fuel injection equipment manufacturer in the U.S.), Lovelace Respiratory Research Institute, and Southwest Research Institute – have shown that biodiesel performs similar to petroleum diesel with substantial benefits to the environment and human health.

Effective November 1998, Congress approved the use of biodiesel as an Energy Policy Act (EPAct) compliance strategy. The legislation allows EPAct-covered fleets (federal, state and public utility fleets) to meet their alternative fuel vehicle purchase requirements simply by buying biodiesel and burning it in new or existing diesel vehicles in at least a 20% blend with diesel fuel. The Congressional Budget Office and the U.S. Department of Agriculture confirmed that the biodiesel option is the least-cost alternative fuel option for meeting the Federal government's EPAct compliance requirements.

Current Market Status

In 2008, the U.S. biodiesel industry produced 682 million gallons of B100.[1] A significant fraction of this production was exported. A 2004 study indicates that U.S. resources are available to produce about 1.7 billion gallons of biodiesel annually.[2] The National Biodiesel Board indicates that current installed production capacity is well over 2 billion annual gallons – significantly more than the current market.[3]

For quality specification purposes in the United States, to ensure trouble free operation, and to qualify for a blender's tax credit, biodiesel must meet the requirements of ASTM D6751. This ASTM specification is for B100 that can be used for blending at up to 20% by volume. The standard has been improved several times over the past few years, and the process continues

today. The specification ensures that blends up to 20% are compatible with diesel engines and associated fuel system hardware.

A survey of B100 quality was conducted recently to determine the degree to which U.S. biodiesel producers were meeting the D6751 specification.[4] Samples were tested for the most critical properties in D6751. Production volume information from the National Biodiesel Board was used to estimate the volume percentage of biodiesel production passing or failing each requirement. The 56 producers that provided samples represented 52% of the producers in the marketplace, but 70% of the volume of biodiesel produced. The study found that 90% of the biodiesel was on specification, a positive result given that earlier, less comprehensive studies had found a lower compliance rate. On the negative side, as much as 10% of the product being produced when these samples were collected was failing to meet legal requirements due to negligence on the part of a small number of biodiesel producers.

Vehicles/Engines

As noted, biodiesel blends up to B20 can be used in most engines and vehicles with no modification. Many vehicle owners refer to the engine owner's manual to determine which fuels are suitable for their engines. Thus, the written policy of the engine manufacturer regarding biodiesel has a significant impact on biodiesel markets. In most manufacturers' literature, B5 and lower blends are approved, as long as the biodiesel meets D6751 and/or EN14214, the European biodiesel specification, and some manufacturers recognize higher blend levels. The ASTM specification for conventional diesel fuel, D975, allows up to 5% biodiesel in conventional diesel fuel. A separate specification, D7467, describes the required property limits for B6 to B20 blends. Blends of B20 or higher are now accepted by more than 17 OEMs, compared to only 2 manufacturers supporting up to B5 at the start of the OEM Outreach Program in 2005. Companies supporting B20 now include some Chrysler and GM models, Case IH, Case Construction, Caterpillar, Cummins, International/Navistar, John Deere, New Holland, Arctic Cat, Buhler, Fairbanks Morse, Hayes Diversified Technologies, Perkins, TomCar, Toro and Valtra. Conversations and biodiesel training sessions continue with Ford, GM, Volkswagen and Chrysler, as well as numerous manufacturers new to the U.S. diesel market, to ensure OEMs recognize the importance of biodiesel compatibility, and embrace the concept of biodiesel approval as a marketing tool as demand for green vehicles grows. Ford's 2011 Ford F-Series Super Duty® diesel pickups will be fully compatible with a 20 percent biodiesel blend (B20). Researchers at J.D. Power & Associates predict that diesel sales will approximately triple in the next 10 years, accounting for more than 10 percent of U.S. vehicle sales by 2015 – up from 3.6 percent in 2005.[5]

Diesel fuel itself is required to lubricate certain components of the engine fuel system, and thus must have adequate lubricity. The addition of biodiesel, even in very small quantities, has been shown to provide increases of 60% in fuel lubricity using a variety of bench scale test methods. Biodiesel has been tested, at varying concentrations, with poor lubricity Number 2 and Number 1 diesel fuels representative of that on the market after 1993 (i.e. fuel refined to meet a 500 ppm maximum sulfur content). For the Number 2 diesel fuel, 1% biodiesel was sufficient to achieve the desired increase in lubricity, while the Number 1 diesel fuel took almost 2%. In addition, the data show that most of the lubricity benefits of the biodiesel were achieved by adding only 2% biodiesel to either Number 1 or Number 2 diesel. More recent work shows that biodiesel also

imparts adequate lubricity to ultra-low sulfur diesel (<15 ppm maximum sulfur content) at 2% addition rate.

There has been concern regarding the potential for using biodiesel during winter months because of a higher than expected incidence of cold weather fuel filter plugging experienced in the past for biodiesel blends. This problem was caused by the presence of minor components in biodiesel that, for long cooling times, could precipitate out of the blend and plug the fuel filter. In October 2008 ASTM published a new version of the D6751 specification that included a new requirement intended to limit the presence of these minor components. This requirement, known as the cold soak filtration test, appears to have been successful as fuel filter plugging events were much less frequent in the 2008-2009 winter. For biodiesel meeting the cold soak filterability requirement, cloud point and other common metrics of low-temperature operability are good predictors of actual performance.[6] However, the biodiesel market could benefit from outreach and education regarding proper precautions and procedures for utilizing biodiesel blends in cold temperatures.

Long-term engine durability tests[7] and fleet studies[8] with B20 have not shown negative effects of B20 or lower blends and performance is generally very similar to petrodiesel. However, how biodiesel will perform with advanced emission control equipment such as diesel particle filters and NOx emission control catalysts is not fully understood. These are being introduced into the U.S. market in 2007 to 2010. Questions remain about the long-term durability of these devices when used with biodiesel. In particular, catalyst manufacturers are concerned that low-levels of metals (sodium, potassium, calcium, and magnesium) and phosphorus that are allowable in biodiesel today could be high enough to damage DPFs or NO_x control catalysts, or lead to more frequent maintenance requirements. Despite rumors to the contrary, new light-duty vehicles that utilize an emissions control system with in-cylinder post-injection are also compatible with biodiesel blends, even those B10 and higher. However, increased engine oil dilution associated with the systems call for more frequent oil changes to mitigate any concerns running on biodiesel blends. This is predominantly limited to the light duty diesel product offerings from Volkswagen, Audi, Mercedes and BMW, which are a small portion of the U.S. market. The other light, medium and heavy duty diesel engine manufacturers do not generally use late in-cylinder injection of raw fuel and have not reported problems with B20 compatibility or excessive engine oil dilution in their new diesel models. They have opted for systems that utilize an exhaust-stream injection of fuel to regenerate the particulate traps, therefore mitigating the risk of engine oil dilution. Nevertheless, some questions remain and a robust engine and emission control component testing program is thus required to address these issues.

Infrastructure

Biodiesel is distributed utilizing the existing fuel distribution infrastructure with blending occurring both at fuel terminals and "below the rack" by fuel jobbers. But today relatively few petroleum products terminals are able to store and in-line blend biodiesel. Thus, preparation of biodiesel blends is done by splash blending into the transport truck, which may require visiting separate sites to load the biodiesel and diesel fuel. Incentives for installation of biodiesel storage and blending capability at terminals are recommended.

A number of efficiencies could be gained if biodiesel blends could be prepared at refineries and moved to market in petroleum product pipelines. Biodiesel in blends will not separate or partition into water, as can occur for ethanol blended into gasoline under some conditions, which

makes pipeline transport feasible. In July 2006, Countrymark Co-op, a refiner and marketer of petroleum products in the U.S. Midwest, successfully transported 210,000 gallons of B5 through a 238-mile private pipeline.[9] In August 2006, 75,000 barrels of B5 were transported from Houston, Texas, to Linden, New Jersey, in a common carrier pipeline operated by Colonial Pipeline.[10] The test was successful in that the B5 blend did not degrade during transport. However, the next batch of diesel fuel was contaminated with low levels of biodiesel. Recently Kinder Morgan announced commercial shipment of B5 blends in the Plantation Pipeline in the Southeast U.S. Though it is not a concern for diesel fuel, there is some concern that jet fuel could become contaminated with FAME in a multiproduct pipeline. Studies show that 1% FAME in jet fuel can reduce oxidative stability, leading to increased deposits.[11] However, at levels below a few hundred ppm, no decrease in stability was observed.[12] A test method for analysis of FAME in jet fuel at ppm levels has recently been developed and is currently being balloted at ASTM. Jet engine testing to show that these engines can operate with up to a few hundred ppm biodiesel in the fuel will be required before biodiesel blends can be routinely transported on multiproduct pipelines that also ship jet fuel.

Local regulatory authorities typically require storage tanks (both above ground and underground), associated piping and leak detectors, as well as fuel dispensers and hoses to have third party certification as being safe and compatible with the fuels being handled. For these items the third party certifying their performance is Underwriters Laboratories (UL). UL has indicated that D975-compliant diesel fuels containing up to 5% biodiesel will be treated the same as diesel fuel, and thus items listed by UL for use with diesel fuel are also acceptable for use with blends up to B5. No equipment is currently listed by UL for use with higher biodiesel blends. Thus, an important barrier to larger markets for biodiesel is UL listing of fuel tanks, dispensers, and associated equipment for use with B20.

Supply

As noted, a 2004 study indicates that U.S. resources are available to produce about 1.7 billion gallons of biodiesel annually.[2] There are several sources of additional feedstock that could be developed in the near-term. Currently, about 60% of soybeans are crushed for oil extraction. This percentage could increase if markets for soy meal used as high-protein animal feed increase more rapidly than projected. Future increases in soybean yields and oil content could also increase feedstock oil production. A large potential source of vegetable oil feedstock is corn oil recovered from dry-mill ethanol production. Theoretically, this source could supply more than 500 million gallons at current ethanol production rates. However, corn oil from distiller's dried grains may require some upgrading to remove impurities before it could be used to make biodiesel. A number of other terrestrial crops also might lead to increases in the availability of feedstocks, such as camelina, pennycress, canola rotation with wheat, and jatropha. One transformational technology that could lead to a dramatic increase in lipid feedstock production is aquaculture of algae. This technology is in its infancy but has the potential to yield several thousand gallons per acre, compared to roughly 60 gallons per acre of soy oil (note that soy oil is a byproduct of soy protein production).[13]

Available Federal and State Incentives

Policies supporting the use of biodiesel include the federal biodiesel blender's tax credit of $1 per gallon. More recently, the U.S. Energy Independence and Security Act of 2007 (Pub. L. No. 110-140) mandates the use of 1 billion gallons per year of biomass-based diesel by 2012 and 21

billion gallons of advanced biofuel by 2022. Biodiesel qualifies as both biomass-based diesel and likely qualifies advanced biofuel. However, the Biomass-based Diesel volumes required by law have not been implemented due to delays in RFS-2 rulemaking process. A workable RFS-2, expected in early 2010, will create the potential for a 1.15 billion gallon market demand before the end of next year.

Emission Benefits

The U.S. Environmental Protection Agency's (EPA's) national air pollutant emission trends report shows that in 2000 diesel vehicles produced approximately 7% of U.S. mobile-source hydrocarbon emissions and 5% of mobile-source carbon monoxide (CO).[14] However, diesel vehicles produced 45% of U.S. mobile-source oxides of nitrogen (NO_x) and 60% of mobile source particulate matter ($PM_{2.5}$ or PM). In addition, diesel PM can contain 20% to 40% organic compounds that have known mutagenic and carcinogenic properties.[15] Thus, the impact of biodiesel on NO_x and PM emissions is of greatest interest.

In the United States, engine dynamometer tests are used for heavy-duty (HD) engine emissions compliance testing.[16] Results for hydrocarbon, CO, NO_x, and PM are reported in g/bhp-h. Allowable levels of HD emissions have been reduced dramatically over the past 25 years, resulting in a continuous evolution of diesel engine and emission control technology. A reduction in the allowable NO_x level from 4 g/bhp-h in 1998 to 1.2 g/bhp-h in 2007 was made possible by exhaust gas recirculation, higher pressure fuel injection, and more advanced fuel injection control strategies. Beginning in 2006, sulfur in on-highway diesel fuel was lowered from 500 to 15 ppm (ultra-low-sulfur diesel) to allow the introduction of diesel particle filters (DPF) and NO_x reduction catalysts. All 2007 model-year HD engines in the United States were equipped with DPF to meet a PM emission standard of 0.01 g/bhp-h, a factor of 10 below the previous standard. A lower NO_x standard of 0.2 g/bhp-h by 2010 will be achieved by using adsorbent and catalyst systems.

Effects on Hydrocarbon, CO, and Particulate Matter

In 2002, the EPA reviewed published biodiesel emissions data, which consisted almost entirely of data for HD engines in the 1988 to 1998 model-year range.[17] On average, using biodiesel as a blend or in neat form resulted in substantial reductions in emissions of PM, CO, and hydrocarbons for engines from that decade. The conclusions of EPA's review of the impacts of biodiesel on total hydrocarbon, CO, and PM emissions have been confirmed in many recent studies of newer engines.[18] The overall database, however, remains unrepresentative of the current on-highway U.S. fleet. For example, more than 20% of the available test data are for 2-stroke engines that today make up less than 0.2% of the in-use fleet.

Data are quite limited on the emission performance of engines equipped with DPFs. Boehman and coworkers demonstrated that the blending of biodiesel could increase the oxidation reactivity of PM in a DPF, which may improve DPF performance in some situations.[19] Williams and coworkers demonstrated that as little as 5% biodiesel in the fuel could increase the rate of DPF regeneration measurably.[20] Additional data are required to understand if these observations translate into a benefit for biodiesel in terms of DPF operation, with potentially fewer regeneration events and reduced fuel economy penalty for regeneration.

While current emission regulations limit the total PM mass, health impacts are thought to correlate more closely with the number of very small particles that are emitted. Limited studies have been conducted of the impact of diesel or biodiesel on particle size distribution, all for engines not equipped with a DPF with sometimes conflicting results. Clearly, additional research is warranted on the impact of biodiesel on particle size distribution.

Impact on NO_x Emissions

NO_x emissions are of concern because of the potential for NO_x to participate in atmospheric reactions that lead to ozone formation; although the importance of NO_x in ozone formation has recently been questioned.[21] The EPA review cited above concluded that biodiesel caused a small increase in emissions of NO_x relative to petroleum diesel, which averaged 2% for B20. However, some data suggest that this may not always be the case. For example, a significant fraction of the 785 NO_x observations for B20 included in the EPA's review show a decrease in NO_x. Factors that affect NO_x emissions from biodiesel include biodiesel source material,[22] driving cycle and average load,[23] as well as engine and fuel system design and operating strategy.[24] Tests conducted by EPA showed that the increasing NO_x effect was greater for higher average load driving cycles.[23] In addition, NO_x increased in proportion to the biodiesel blend level for one engine tested. The Cummins engine company examined the effect of biodiesel both on combustion and on engine control system parameters.[24] The study showed how NO_x could increase or decrease at different engine speed/load setpoints and how the engine computer control system could respond to biodiesel in different situations, to either increase or decrease NO_x. The Cummins study also presented data suggesting that the effect of biodiesel on NO_x is less than the NO_x variation caused by the normal range of variation in petroleum diesel fuel properties (aromatic content and cetane number, for example).

Ongoing analyses of all the available data continue to show, on average, a small increase in NO_x for B20. Yet, as noted, the engines included in the available dataset are not representative of the current on-highway fleet. Nevertheless, the potential for biodiesel to increase NO_x could become a significant barrier to market expansion if the volume of biodiesel used were to become so large that the effects were detrimental to air quality.

This issue will have to be reevaluated for engines equipped with the NO_x emission control catalysts that will be phased in beginning 2010, because there are as yet only limited data showing the performance of those catalysts with biodiesel blends. These early studies suggest that the small NO_x increase coming out of the engine will have little effect on NO_x downstream of the NO_x reduction catalyst, for short term operability effects.[25,26] Extensive testing is required to determine the long-term durability impacts of biodiesel on NO_x emission control technologies.

Toxic Compound Emissions and Health Effects

Sharp and coworkers performed detailed chemical characterizations of exhaust from one 1995 and two 1997 model-year engines.[27] Species quantified included C_1 to C_{12} hydrocarbons, C_1 to C_8 aldehydes, and several specific polyaromatic and nitro-polyaromatic hydrocarbons from both the semi-volatile and particle phase. Results for B100 showed large reductions in mass emissions of all groups of compounds; B20 resulted in smaller reductions overall and no significant change for some species. These results indicate that B20 has a very positive impact on toxic compound emissions; however, diesel engine technology has changed significantly

since the study was conducted. Thus, measurement of toxic compound emissions for B20 in newer engines remains a pressing research need.

Studies have used bioassays to compare biodiesel and conventional diesel particulate matter extracts. For mutagenicity, some groups found no significant difference for PM extracts of the two fuels.[28, 29, 30, 31] However, Kado and Kuzmicky report higher mutagenic activity per particle mass for biodiesel fuels but lower total mutagenic emission rates because of the significantly lower particle mass emission rate.[32] Krahl and coworkers recently showed higher mutagenicity for biodiesel PM from several different engines.[33] Swanson and coworkers used airway epithelial cell bioassays to evaluate the inflammatory potential of extracts from diesel and biodiesel PM. Exposure to biodiesel PM extracts appeared to be a more potent inflammatory stimulant than exposure to diesel PM extracts.[34] These results suggest that biodiesel PM extracts contain some bioactive compounds that have not been identified in toxic compound emission speciation studies. Nevertheless, Finch and coworkers studied the exposure of rats to inhalation of engine exhaust generated by burning 100% soy-derived biodiesel.[35] The animals were exposed to diluted exhaust over a range of PM concentrations. This study demonstrated health effects similar to those from exposure to conventional diesel exhaust.

A key feature of these studies is that few are very recent. Considerable additional work is required to understand how biodiesel impacts emissions of toxic compounds, health impacts, and to assess risk. Notably, the same statement could be made regarding petroleum diesel.

Petroleum and Carbon Reduction Benefits

Life-cycle analysis shows that biodiesel contains from 2.5 to 4.5 units of energy for every unit of fossil energy input in its production; and because very little petroleum is used in production of biodiesel, its use displaces petroleum at nearly a 1-to-1 ratio on a life cycle basis.[36, 37, 38, 39] Life-cycle analysis also shows reductions total greenhouse gas emissions (CO_2+CH_4+N_2O) ranging from 60% to over 90%, for direct effects. While many studies find marginal indirect land use change effects for vegetable oil-derived biodiesel, it remains to be seen how EPA will rule on this aspect of biodiesel's sustainability.

Barriers that are preventing significant deployment in the marketplace

While there are a number of barriers to expanded deployment of biodiesel, the three most significant near term challenges are 1) increased biodiesel distribution, 2) verifying in-use data and information, and 3) educating or bringing together key sectors impeding greater acceptance and use this alternative fuel.

1. Increase Biodiesel Distribution

A significant limiting factor remains the fact that few petroleum distribution terminals currently have storage and blending capability for biodiesel. One terminal can make B20 available at a lower cost and a higher quality to dozens of fuel distributors and hundreds of fleets in one location. Development of partnerships, coalitions, and funding for terminal blending infrastructure is thus a pressing need, and should proceed before encouraging B20 public pumps. For expanded availability of B20 at public pumps, the fact that o equipment is currently listed by UL for use with biodiesel blends containing more than 5% biodiesel must be addressed. Thus,

an important barrier to larger markets for biodiesel is UL listing of fuel tanks, dispensers, and associated equipment for use with B20.

2. Verifying Data or In-Use Information
Fleet demonstrations, data collection and information dissemination of new biodiesel markets such as off-road diesel engines, mining, and boating are critical activities for expanding biodiesel markets. Clean Cities Coalitions can work with biodiesel users , other stakeholders, and other DOE programs to develop projects to collect and disseminate this information.

3. Educating Key Stakeholders
As biodiesel becomes more main stream, education and training for those distributing and handling the fuel and vehicles continues to be limited. Clean Cities Coalitions should continue to offer outreach and training to the OEMs, up/downstream petroleum distributors, retailers, mechanics, first responders and fleet managers, especially in the form of fuel quality. A second issue where education of stakeholders is critical is the wintertime use of biodiesel in cold climates.

A number of no-less significant longer term challenges also exist. Major economic advantages could be gained for biodiesel if biodiesel blends could be transported by pipeline. The key issue here is potential contamination of jet fuel by biodiesel. Jet engine testing to show that these engines can operate with up to a few hundred ppm biodiesel in the fuel will be required before biodiesel blends can be routinely transported on multiproduct pipelines that also ship jet fuel.

As noted above, there are significant barriers associated with a lack of knowledge regarding compatibility of biodiesel blends with advanced emission control systems such as diesel particle filters and NO_x emission control catalysts. Additional issues may exist for compatibility with engine lubricants, especially for systems using late in-cylinder injection for regeneration of catalysts and filters. On the other hand, some tests show potential benefits for biodiesel in terms of DPF regeneration frequency. Additional data are required to understand if these observations translate into a benefit for biodiesel in terms of DPF operation, with potentially fewer regeneration events and reduced fuel economy penalty for regeneration. Extensive testing is also required to determine the long-term durability impacts of biodiesel on NO_x emission control technologies. A robust engine and emission control component testing program is thus required to address these issues.

Studies show that NO_x emissions increase for biodiesel blends in some engines. Because only a limited number of the many engine models on the road have been tested, the average effect of B20 on NO_x emissions is unclear. However, the potential for biodiesel to increase NO_x could become a significant barrier to market expansion if the volume of biodiesel used were to become so large that the effects were detrimental to air quality. Additional research is warranted on the impact of biodiesel on particle size distribution, and measurement of toxic compound emissions.

Current Available Resources; Activities or Strategies Being Implemented

To a greater or lesser extent, all of the barriers listed above are being worked on through various government and industry R&D programs. The DOE's National Renewable Energy Laboratory (NREL) and NBB have an ongoing collaboration to examine biodiesel effects on advanced

emission control equipment. Additional work in this area is being conducted at other DOE laboratories. NREL and other labs are also beginning to examine biodiesel impacts on particle number and toxic compound emissions.

NBB is working with UL to initiate testing of B20 blends in storage tanks and dispensers. NBB is also working with a large industry consortium to test jet engines with jet fuel containing 400 ppm of biodiesel. If these tests are successful, the allowable level of biodiesel in jet fuel would be raised to 100 ppm (a 4x safety factor) and petroleum product pipelines will be able to transport B5 blends. This would be a major development for biodiesel markets, potentially leading to a large increase in utilization.

Development of new feedstocks is being pursued by many different parties, including NBB, USDA, and industrial interests both large and small. This work involves modification of existing crops to have higher oil content, development of new oilseed crops that have benefit for farmers as a rotation or winter cover crop, as well as aquaculture of algae and other biotechnology based approaches.

Opportunities in the Marketplace and Technology Deployment Needs

The major strategy pursued by both DOE and the biodiesel industry for expansion of biodiesel markets has been to make biodiesel blends suitable for all diesel applications. This effort has been largely successful for pre-2007 engines without advanced emission controls and work is ongoing to ensure compatibility with post-2007 engines. A key factor for deploying biodiesel in the full range of diesel applications appears to be overcoming barriers to transport of B5 blends by pipeline. B5 blends are considered the same as conventional diesel fuel by ASTM and UL. If transportable by pipeline, a large fraction of the U.S. diesel market could become B5 (potentially as much as 3 billion gallons of biodiesel if B5 were used in all distillate fuel applications).

Biodiesel Availability

As of August 2009, there are 697 U.S. biodiesel fueling sites dispensing B20 and higher blends. Of these stations, approximately 50% are open to the public. To help fleets and consumers easily locate fueling sites, NREL developed the Alternative Fueling Station Locator and TransAtlas tools, which live on DOE's Alternative Fuels and Advanced Vehicles Data Center Web site (www.afdc.energy.gov). Launched in 1995, the Alternative Fueling Station Locator (www.afdc.energy.gov/afdc/locator/stations/) allows fleets to identify and map routes to fueling sites locally and nationwide. The TransAtlas tool (http://rpm.nrel.gov/transatlas/launch/) displays maps of fueling stations, vehicle densities, and production facilities throughout the country.

NBB also tracks biodiesel stations, including those that dispense blends of lower than B20. In fiscal year (FY) 2010, NREL will work more closely with NBB to share fueling site data.

Retail Price of Biodiesel

According to Clean Cities' Alternative Fuel Price Report, from September 2005 to April 2009 the nationwide average retail prices for B2 to B5 blends average about 1% less than petroleum diesel. B20 blends are approximately 2% more expensive, while B99-B100 blends are approximately 21% more expensive than petroleum diesel.

Average Cost to Install a Biodiesel Dispenser

The incremental cost of installing a dispenser for biodiesel blends of B6 and higher is not significant when compared to the price of a conventional diesel dispenser. As per ASTM D975, conventional diesel fuel can contain up to 5% biodiesel, so there are no physical differences between a conventional diesel fuel and a B5 dispenser.

Educating Fleets and Consumers

NREL and Clean Cities actively produce fact sheets, research reports, and online tools to educate fleets and consumers about biodiesel. In doing so, NREL and Clean Cities work hand-in-hand with NBB. Two examples of this partnership are NREL's "Biodiesel Handling and Use Guide" and Clean Cities' "Biodiesel Clears the Air in Underground Mines" fact sheet.

NREL consults with NBB about updating and distributing the handling and use guide. NBB not only reviews the documents, it distributes it to its members to ensure industry's consistent use of biodiesel. More recently, NBB expressed to Clean Cities a need for a biodiesel and mining fact sheet. Seeing an opportunity for coordinators to expand their reach within their communities, Clean Cities wrote and produced this previously mentioned fact sheet, which is posted on the AFDC and distributed by NBB.

In FY 2010, NBB and NREL and Clean Cities intend to consider a partnership to analyze data from a long-haul trucking operator who has biodiesel experience. The partnership would potentially produce a report that will help other trucking companies incorporate biodiesel into their operations. This report will help both coordinators and NBB promote biodiesel use to trucking stakeholders.

In addition to publications, NREL and Clean Cities are launching a new online training program in October 2009. Titled Clean Cities University (CCU), this new project educates coordinators and stakeholders about all of Clean Cities' technology areas. NREL and Clean Cities will work with NBB to produce biodiesel-specific training courses for CCU and to host existing NBB-produced training modules in CCU.

Biodiesel Market Potential for Light-Duty Diesel Vehicles

According to J.D. Power Automotive Forecasting, demand for light-duty diesel vehicles could almost double, increasing from $15 million sales in 2005 to $29 million in 2015. As stated earlier, most manufacturers' literature approves B5 and lower blends for use in their vehicles as long as the biodiesel meets ASTM D6751 and/or EN14213 standards. Because most consumers defer to their owner/operator manual for what fuels are allowed in their vehicle, having manufacturer approval can significantly impact the market acceptance of biodiesel.

Clean Cities and Dealers and Manufacturers

On the local level, Clean Cities continues to create educational opportunities and participate in outreach activities—some of which target general consumers. Based on responses to the 2008 annual Clean Cities questionnaire, 1,310 activities were reported by coordinators and estimated to reach more than 113 million people—almost three times the number reached in 2007. Media events and advertisements dominated the field, combining to represent 97% of the total number of people reached.

Coordinators were asked to judge how much they thought they were responsible for the number of people reached at each event in contrast to the contribution of other event sponsors and participants. An analysis of the responses shows that, on average, coordinators felt they were responsible for 57% of the 113 million people reached.

The general public was most often cited as a target audience, followed by government then fleets in general. Specialized applications—airports, waste management, delivery trucks, utility trucks, and mass transit—were identified as audiences in one-third of the outreach activities. Other audiences were cited as audience types in 13% of the activities reported.

Many Clean Cities coordinators agree that partnerships local dealerships are an opportunity for growth. In general, Clean Cities coalitions have good relationships with national-level vehicle manufacturers but lack ongoing working relationships with many local dealerships.

Fleet Experiences

Throughout the country, there are a wide variety of fleets utilizing biodiesel for a variety of reasons and with varying success. Clean Cities captures the biodiesel implementation stories of many fleets in the Fleet Experiences (www.afdc.energy.gov/afdc/progs/fleet_exp_fuel.php/BD) section of the AFDC. NREL developed this section to inspire fleets to use alternative fuels and advanced vehicles.

Minnesota's Blend Requirement

Many states are implementing programs to expand the use of biodiesel. However, the state of Minnesota has made it a priority to be a leader in the development of the biodiesel industry. The Minnesota Legislature has enacted number of bills toward this goal, as well as creating taskforces and committees that focus on biodiesel and their expanding industry.

Currently all diesel sold in Minnesota must be B5. Future mandates are for B10 by May 2012, and B20 by May 2015. Content levels apply only during warm-weather months (April-October), with B5 required during the remainder of the year unless a fuel standard is in place to address cold-weather diesel issues. The increases are not automatic, however. There is built-in flexibility, including an approval process before moving to higher blends. This will allow all interested parties from the legislature, state agencies, end users, consumers and biodiesel producers to gauge the economic, supply, and environmental impacts before moving to a higher blend.

Within Minnesota Statute 239.77 – Biodiesel Content Mandate, there is a provision that the commissioners of agriculture, commerce and pollution control must submit progress reports to the legislature so that informed decisions are made prior to each increase in the biodiesel requirement. This provision highlights the importance of quality assurance in the successful implementation of the mandate, which is supported by the Department of Commerce's testing method for determination of FAME content in blends of biodiesel. In an additional effort to ensure proper implementation of the mandate, the Minnesota Biodiesel Technical Cold Weather Issues Team Handling Subcommittee has produced a Biodiesel Blend Handling Guide.

Challenges and Opportunities

According to EIA, 682 million gallons of biodiesel were sold in 2008. Sales are expected to decline in 2009 due to economics. If biodiesel plants were built or plants planned expansion based on the Renewable Fuels Standard 2 (RFS2) being in place, the delay of RFS2 may cause some plants to produce at less than capacity or delay expansion.

References

[1] Energy Information Administration, http://www.eia.doe.gov/emeu/mer/renew.html, accessed July 13, 2009.

[2] Tyson, K.S., Bozell, J., Wallace, R., Petersen, E. and Moens, L. *Biomass Oil Analysis: Research Needs and Recommendations*; NREL Technical Report No. TP-510-34796, National Renewable Energy Laboratory, 2004.

[3] National Biodiesel Board, http://www.biodiesel.org/pdf_files/fuelfactsheets/Production_Capacity.pdf, accessed August 26, 2009.

[4] Alleman, T.L. and McCormick, R.L. *Results of the 2007 B100 Quality Survey*, NREL Report No. TP-540-42787, National Renewable Energy Laboratory, 2008.

[5] J.D. Power and Associates. J.D. Power and Associates Reports: Global Demand for Diesel-Fueled Light Vehicles to Nearly April 16, 2006.

[6] McCormick, R.L., Chandler, J.,Gault, R., Howell, S., Nikanjam, M., Buczynsky, A., Jetter, J., Barenescu, R., Arters, D., Forester, D., Mitchell, K., "Biodiesel Blend Low-Temperature Performance Validation", CRC Project: DP-2a-07 , June 2008.

[7] Bartoli, Y. 1000 Hour Durability Evaluation of a Prototype 2007 Diesel Engine with Aftertreatment Using B20 Biodiesel Fuel. Presented at the National Biodiesel Conference, Orlando, FL, Feb. 5, 2008.

[8] Proc, K., Barnitt, R., Hayes, R.R., McCormick, R.L., Ha, L. and Fang, H.L. 100,000 Mile Evaluation of Transit Buses Operated on Biodiesel Blends (B20). SAE Tech. Pap. No. 2006-01-3253, 2006.

[9] Biofuels International. Latest News Page. Biodiesel Pipeline First. http://www.biofuels-news.com/news/pipeline_first.html (accessed June 23, 2008).

[10] Northville Products and Services and Colonial Pipeline. B5 Soy Test Data and Report: Bio Diesel Trial NPS-73-441, Soy Blended Low Sulfur Diesel, 2007. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/20070201_gen384.pdf (accessed June 23, 2008).

[11] Wilson, G., Thom, M. and Serino, P. Effect of FAME on Thermal Oxidative Stability. In Proceedings of the 10th International Conference on Stability, Handling and Use of Liquid Fuels Tucson, AZ, USA, October 7-11, 2007; see www.iash.net (accessed June 23, 2008).

[12] Anderson, S. FAME in Jet Fuel. Presented at the IATA Aviation Fuel Forum, Istanbul, Turkey, November 5-8, 2007.

[13] Hu, Q., Sommerfeld, M., Jarvis, E., Ghirardi, M., Posewitz, M., Seibert, M. and Darzins, A. Microalgal Triacylglycerols as Feedstocks for Biofuel Production: Perspectives and Advances. *The Plant Journal* **2008**, *54*, 621–639.

[14] U.S. Environmental Protection Agency. *National Air Quality and Emissions Trends Report*; 2003 Special Studies Edition, EPA Report No. 454/R-03-005, U.S. EPA, Washington, DC, 2003.

[15] U.S. Environmental Protection Agency. *Health Assessment Document for Diesel Engine Exhaust*, Report No. EPA/600/8-90/057F, U.S. EPA, Washington, DC, 2002.

[16] United States Code of Federal Regulations, Title 40, Part 86, Subpart N, Emission Regulations for New Otto-Cycle and Diesel Heavy-Duty Engines; Gaseous and Particulate Exhaust Test Procedures.

[17] U.S. Environmental Protection Agency. *A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions,* Draft Technical Report No. EPA420-P-02-001, U.S. EPA, Washington, DC, 2002.

[18] McCormick, R.L., Williams, A., Ireland, J., Brimhall, M. and Hayes, R.R. *Effect of Biodiesel Blends on Vehicle Emissions.* NREL Report No. MP-540-40554, National Renewable Energy Laboratory, Golden, CO, 2006.

[19] Boehman, A.L., Song, J. and Alam, M. Impact of Biodiesel Blending on Diesel Soot and the Regeneration of Particle Filters. *Energy & Fuels* **2005**, *19*, 1857-1864.

[20] Williams, A., McCormick, R.L., Hayes, R.R., Ireland, J. and Fang, H.L. Effect of Biodiesel Blends on Diesel Particulate Filter Performance. SAE Tech. Pap. No. 2006-01-3280, 2006.
[21] Lawson, D.R. The weekend ozone effect—The weekly ambient emissions control experiment. *Environmental Management* **2003**, *July,* 17-25.
[22] McCormick, R.L., Alleman, T.L., Graboski, M.S, Herring, A.M. and Tyson, K.S. Impact of Biodiesel Source Material and Chemical Structure on Emissions of Criteria Pollutants from a Heavy-Duty Engine. *Environ. Sci. Technol*. **2001**, *35*, 1742-1747.
[23] Sze, C., Whinihan, J., Olson, B.A., Schenk, C.R. and Sobotowski, R. Impact of Test Cycle and Biodiesel Concentration on Emissions. SAE Tech. Pap. No. 2007-01-4040, 2007.
[24] Eckerle, W., Lyford-Pike, E., Stanton, D., LaPointe, L., Whitacre, S.D. and Wall, J.C. Effects of Methyl Ester Biodiesel Blends on NO_x Emissions. SAE Tech. Pap. No. 2008-01-0078, 2008.
[25] Tatur, M., Nanjundaswamy, H., Tomazic, D. and Thornton, M. Effects of Biodiesel Operation on Light-Duty Tier 2 Engine and Emission Control Systems. SAE Tech. Pap. No. 2008-01-0080, 2008.
[26] Williams, A., Pedersen, D., Ireland, J., McCormick, R.L., Fang, H.L. "Effect of Biodiesel Blends on Urea Selective Catalytic Reduction Catalyst Performance with a Medium-Duty Engine" SAE Tech. Pap. No. 2008-01-2484, 2008.
[27] Sharp, C.A., Howell, S.A. and Jobe, J. The Effect of Biodiesel Fuels on Transient Emissions from Modern Diesel Engines, Part II, Unregulated Emissions and Chemical Characterization. SAE Tech. Pap. No. 2000-01-1968, 2000.
[28] Bagley, S.T., Gratz, L.D., Johnson, J.H. and McDonald, J.F. Effects of an Oxidation Catalytic Converter and a Biodiesel Fuel on the Chemical, Mutagenical and Particle Size Characteristics of Emissions from a Diesel Engine. *Environ. Sci. Technol*. **1998**, *32*, 1183 –1191.
[29] Bünger, J., Krahl, J., Franke, H.U., Munack, A. and Hallier, E. Mutagenic and Cytotoxic Effects of Particulate Matter of Biodiesel Compared to Fossil Diesel Fuel. *Mutat. Res*. **1998**, *415*, 13–23.
[30] Rantanen, L., Mikkonen, S., Nylund, L., Kociba, P., Lappi, M. and Nylund, N.O. Effect of Fuel on the Regulated, Unregulated and Mutagenic Emissions of DI Diesel Engine. SAE Tech. Pap. No. 932686, 1993.
[31] Turrio-Baldassarri, L., Battistelli, C.L., Conti, L., Crebelli, R., De Berardis, B., Iamiceli, A.L., Gambino, M. and Iannaccone, S. Emission Comparison of Urban Bus Engine Fueled with Diesel Oil and 'Biodiesel' Blend. *Sci. Total Environ.*, **2004**, *327,* 147-162.
[32] Kado, N.Y. and Kuzmicky, P.A. *Bioassay Analyses of Particulate Matter from a Diesel Bus Engine Using Various Biodiesel Feedstock Fuels.* NREL Report No. SR-510-31463, National Renewable Energy Laboratory, Golden, CO, 2003.
[33] Krahl, J. "Exhaust Gas Emissions and Mutagenic Effects of Diesel Fuel, Biodiesel and Biodiesel Blends" SAE Tech. Pap. No. 2008-01-2508, 2008.
[34] Swanson, K., Kado, N., Madden, M.C. and Ghio, A.J. Release of IL-8 and IL-6 by BEAS-2B Cells Following In Vitro Exposure to Biodiesel PM Extracts. *Toxicol.* **2007,** *96*, 813(A).
[35] Finch, G.L., Hobbs, C.H., Blair, L.F., Barr, E.B., Hahn, F.F., Jaramillo, R.J., Kubatko, J.E., March, T.H., White, R.K., Krone, J.R., Ménache, M.G., Nikula, K.J., Mauderly, J.L., Van Gerpen, J., Merceica, M.D., Zielinska, B., Stanowski, L., Burling, K. and Howell, S. Effects of Subchronic Inhalation Exposure of Rats to Emissions from a Diesel Engine Burning Soybean Oil-Derived Biodiesel Fuel. *Inhal. Toxicol*. **2002**, *14*, 1017–1048.
[36] Sheehan, J., Camobreco, V., Duffield, J., Graboski, M. and Shapouri, H. *An Overview of Biodiesel and Petroleum Diesel Life Cycles;* NREL Technical Report No. TP-580-24772, National Renewable Energy Laboratory, Golden, CO, 1998.
[37] Hill, J., Nelson, E., Tilman, D., Polansky, S. and Tiffany, D. Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels. *Proceedings of the National Academy of Sciences.* **2006,** *103*,11206–11210.
[38] Huo, H., Wang, M., Bloyd, C. and Putsche, V. *Life-Cycle Assessment of Energy and Greenhouse Gas Effects of Soybean-Derived Biodiesel and Renewable Fuels,* Argonne National Laboratory ANL/ESD/08-2, March 2008.
[39] Pradhan, A., Shrestha, D.S., McAloon, A., Yee, W., Haas, M., Duffield, J.A., Shapouri., H. *Energy Life-Cycle Assessment of Soybean Biodiesel,* USDA Agricultural Economic Report Number 845, September 2009.