Exploring Low Emission Lubricants for Diesel Engines

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NREL Technical Monitor and Editor: K. Shaine Tyson

Prepared under Purchase Order No. 166234

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I. EXECUTIVE SUMMARY.

The USDOE Office of Heavy Vehicle Technologies envisions the development of flexible-fuel, energy-efficient, near-zero emissions, heavy duty U.S. diesel engine technology in all truck classes as a real and viable strategy for reducing energy requirements for commercial transportation services and the rapid growing multipurpose vehicle market. To achieve this vision, R&D goals have been set for three classes of trucks, Heavy (Class 7 & 8), Medium (Class 3 to 6) and Light (Class 1 & 2) Trucks. To achieve these goals necessitates development of future diesel vehicle technology to meet the stringent EPA 2004 emission requirements.

The chronology of the diesel NO_x and Particulate emission reductions achieved to date and the target levels for 2004 are found on Figure 1. Meeting the target levels for 2004 is even more difficult for the heavy duty diesel engine manufacturers, who, as a result of the 1998 EPA/DOJ decree, agreed to meet the EPA 2004 regulations by October 1, 2002. Meeting the targets and future regulations may result in a fuel economy penalty for large trucks. To meet the 2002 targets and future regulations will require both new emission control technologies and an improved fuel quality

A significant issue arising from the urgent need to develop post combustion catalyst and particulate trap technology is the potential impact on heavy-duty engine oils on any new technology developed. Removal of the sulfur from diesel fuel raises real issues that include the effect of the sulfur and phosphorus content of the lubricating oils on new technology and how changes in additive chemistry affect engine durability and component compatibility.

A workshop to explore the technological issues involved with the removal of sulfur from lubricants and the development of low emission diesel engine oils was held in Scottsdale, AZ on January 30, 31 and February 1, 2000. A total of 89 attendees from industry, government and academia with extensive expertise in the areas of aftertreatment technology, petroleum and alternate fuels, basestocks, lubricants, additives, tribology, and alternative lubricants participated in the workshop. The group had OEM representatives from both diesel and gasoline engine and vehicle industries.

The primary purpose of this DOE Workshop on Low Emission Diesel Engine Oils was to explore the issues and ***“To craft a shared vision for Industry - Government (DOE) R&D collaboration in diesel engine oils to minimize emissions, while maintaining or enhancing engine performance”***.

The format of the workshop was to present an overview of the current technology by means of panel discussions and technical presentations from industry, government and academia and then address the key areas (Basestocks, Additives, Alternative Fuels, Alternative Lubricants and Catalysts) in breakout sessions.

The breakout or working groups were formed on the second day of the workshop. The five groups were asked to address their area in the context of improving energy efficiency

and reducing emissions of the vehicle as a system and to establish a list of high priority R&D opportunities related to low emission diesel engine oils for industry and government collaboration. Table 1 is a summary of the priority areas.

FIGURE 1.

Decreasing Diesel Engine Emissions

Source: Cummins, modified by DOE

TABLE 1. SUMMARY OF WORKSHOP NEEDS AND STATUS

NEEDS	TECHNICAL TARGET	CURRENT BARRIER	FEASIBILITY OF SUCCESS (Reasons)
MORE TOLERANT CATALYSTS	Develop sulfur tolerant catalysts	Specific knowledge on masking & poisoning	Low (Needs revolutionary change in catalyst, Time factor, Investment High.)
ROLE OF LUBRICANT	Determine specifics on catalyst masking & poisoning	Contribution of additives to problem unknown factor. Reducing ZDP, metals and S may be adequate.	High (DECSE program partially addressing need)
ADDITIVE TYPE AND ROLE	Determine mechanism of additive involvement	Assumes all additive Sulfur, Phosphorus, Metals end up in exhaust. Volatility factors unknown.	High (Fundamental data can be determined in laboratory - Bench & Dynamometer tests).
ADDITIVE - EGR INTERACTIONS	Knowledge on type of additive & concentration factor needed.	Assumes more particulate reduces effectiveness of additives.	High (Bench and engine dynamometer tests can yield information needed)
NEW ADDITIVES	Additives non-detrimental to catalyst efficiency or durability	Extensive knowledge on current additives and how to synthesize new additives.	Medium (Time and high cost of research. Also, need to prove in new engines and field)
EGR FILTER	Effective way to remove acids and particulate from EGR stream.	Application of current filter technology. May have similar trap problems as exhaust.	High – Medium (Sizing filter is minor problem, some chemical, mechanical and durability factors)
ALTERNATIVE LUBRICANTS	Biodegradable, effective DEO with new additives	Current renewable lubricants on test, using minimal sulfur and phosphorus.	Medium (Cost, lack of engine & field testing, availability of sufficient base fluids)
FUELS	No Sulfur Fuel	Current fuels available, limited quantities	Medium (Cost of infrastructure, may need special lubricants)
ALTERNATE FUELS	Reduction of emissions and expand supplies at reasonable costs.	Availability limited, costs high, mixed emission data, efficiency loss, cold flow properties and oxidative stability.	Medium (infrastructure, studies on material compatibility, limited advanced engine and vehicle testing)

RECOMMENDATIONS:

1. The issue coming out of the workshop with the top priority is to solve the exhaust emissions aftertreatment problems resulting from fuel sulfur and possibly lubricant additives affecting the performance of the system. It is known that the level of sulfur in the fuel is a problem and a low sulfur fuel by 2002 will help solve part of the problem. It is not known to what extent the lubricant plays a role. Engine out and catalyst out information using a future engine with exhaust gas recirculation (EGR), an ultra-low or zero sulfur fuel and a test procedure are essential to resolve this issue.

The DOE Diesel Emissions Control – Sulfur Effects (DECSE) Program is addressing this issue and should be expanded if necessary to determine the effect of current lubricants and reduced sulfur and ZDP additive lubricants on the efficiency of the catalyst. (The DECSE Program was recently renamed the Advanced Petroleum-Based Fuels, Diesel Emission Control [APBF-DEC] Program; it is referred to as the DECSE Program throughout this document.) The development of PC-9 DEO involves some 10-12 engine and laboratory tests is costing the industry over \$40 million. Therefore, it is not unreasonable to consider increasing the DECSE Lubricant budget an estimated \$5 million to solve this issue.

2. The second priority that has an impact on the system is the effect of EGR on the lubricant. To develop the next generation of low emission lubricants requires resolving several issues regarding the particulate loading of the lubricant. Unless the particulate can be effectively removed from the recirculated exhaust, the loading of particulate in the lubricant is expected to more than double. As a result, excessive engine wear may occur. A tribology program to explore the effect of particulate in the lubricant is needed in order to determine the range of options available to make revolutionary changes in the lubricant.

3. The development of environmentally friendly fuels and lubricants is feasible for the 2007 timeframe. To accomplish this 1) alternative fuels, blends with diesel fuels, and selected additives need to be evaluated in the laboratory and the better fuels evaluated in advanced engines to identify the impact on emissions and if long term problems exist, and 2) biodegradable alternative lubricants need to be optimized using selected additives prior to evaluation in advanced engines and vehicles to identify problems or concerns. To accomplish this, prescreening tools to evaluate alternative fuels and lubricants, test methods and required specifications need to be agreed upon and standardized. Non-sulfur and reduced additive requirements of these oils make this approach friendly to the aftertreatment systems.

4. The nature of the particulate emitted from a future EGR engine needs to be determined. The distribution mass and number of the particles and the origin of the nanoparticles is needed. Characterization of particulate is important to the resolution of health effects issues hanging over the diesel.

5. Collaboration with existing fuel and lubricant programs is recommended to expedite completion of the research and development to enable meeting the 2004 emission requirements.

II. INTRODUCTION.

The USDOE Office of Heavy Vehicle Technologies envisions the development of flexible-fuel, energy-efficient, near-zero emissions, heavy duty U.S. diesel engine technology in all truck classes as a real and viable strategy for reducing energy requirements for commercial transportation services and the rapid growing multipurpose vehicle market. To achieve this vision, R&D goals have been set for three classes of trucks, Heavy (Class 7 & 8), Medium (Class 3 to 6) and Light (Class 1 & 2) Trucks:

Class 7 (26,001 - 33,000 lb.) & Class 8 (33,001 lb. and over) Trucks:

To develop by 2004, the enabling technologies needed to achieve a fuel efficiency of at least *10 miles per gallon* (at 65 mph) and *meet* emission standards prevailing in 2004, using petroleum based diesel fuel. __

Class 3 to 6 (10,001 to 26,000 lb.) Trucks :

By 2004, to develop and demonstrate commercially viable vehicles that achieve, on an urban cycle, at least *double the fuel economy* of comparable current (1999) vehicles, and as a research goal, reduce criteria pollutant emissions to *at least 30 percent below* EPA standards prevailing in 2004.

Class 1 (6,000 lb. and less) and Class 2 (6,001 to 10,000 lb.) Trucks:

To develop by 2004 the enabling technologies for clean diesel engines to be competitive with and *at least 35 percent more fuel efficient* than equivalent gasoline engines for light trucks, while meeting Federal and State emission standards prevailing in 2004.

OVHT plans that focus on critical R&D areas for all truck classes can be found in the OHVT Technology Roadmap (October 1997) and the OHVT Multi-year Plan for 1998 - 2002. Both can be found on the internet at <http://www.osti.gov/roadmap.pdf> and <http://www.osti.gov/multiyr.pdf>

To achieve these goals requires meeting stringernt EPA regulations by October 1, 2004. The 1988 EPA/DOJ Consent Decree with heavy-duty engine manufacturers requires that they develop the new technologies to enable them to meet the EPA 2004 emission regulations by October 1, 2002. Meeting the decree may result in a fuel economy penalty for large trucks. This fuel penalty would result in a projected ten percent loss in efficiency in heavy duty diesel engines (HDD) which equates to an increase in fuel consumption of over 10 million barrels of fuel per year.

It is anticipated that further reductions in emissions will be required for HDD in 2007. The NOx reduction goal will be approximately 90 % of 2004 standards and beginning in 2007, PM trap based reductions are expected to be 90 % lower than 1994 levels. Light duty diesel trucks and diesel passenger cars will be expected to meet Tier 2 automotive standards of 0.07g/mi. NOx and 0.01 g/mi. of particulate by 2007.

To enable the use of the new control technologies will require improved quality, ultra low sulfur fuel. A significant issue arising from the use of low sulfur fuel is the potential

impact on the heavy-duty engine oils. Real questions arise on the effect of sulfur and phosphorus content of the lubricating oils on new technology, and how changes in additive chemistry affect engine durability and component compatibility. These issues were the drivers for the “Low Emissions Diesel Engine Oils” workshop.

The primary purpose of this DOE Workshop on Low Emission Diesel Engine Oils was to explore the issues and ***“To craft a shared vision for Industry - Government (DOE) R&D collaboration in diesel engine oils to minimize emissions, while maintaining or enhancing engine performance”***.

The format of the workshop was to present an overview of the current technology by means of panel discussions and technical presentations from industry, government and academia and then address the key areas (Basestocks, Additives, Alternative Fuels, Alternative Lubricants and Catalysts) in breakout sessions. The agenda for the meeting is found in Attachment 1. The attendance list for the meeting is Attachment 2 and includes participants with outstanding expertise in the five breakout areas.

The breakout or working groups were formed on the second day of the workshop. The five groups were asked to address their area in the context of improving energy efficiency and reducing emissions of the vehicle as a system and to establish a list of high priority R&D opportunities related to low emission diesel engine oils for industry and government collaboration.

III. TECHNICAL PROGRAM.

Six sessions are listed on the agenda of the workshop. In some cases, the sessions contained a mix of presentations covering several technical areas related to achieving low emission engine oils. It was obvious from the presentations that the workshop focus on low emission diesel engine oils is only part of a larger R&D problem involving the overall system. The technical issues related to the various components of the diesel engine or vehicle system are intertwined. If the 2004 and 2007 goals are to be met, R&D efforts cannot be polarized by fixing one component of the system at a time. To better understand the needs in the individual areas, this report will first group the technical presentations by system area and then address the interrelationship of the issues in an attempt to better understand the recommendations resulting from the workshop.

A. USDOE OHVT Program Overview.

To give the participants of the workshop a detailed understanding of the DOE OHVT R&D program, its mission, goals and budget:

“Overview of the DOE Heavy Vehicle Technologies R&D Program” by Dr. James J. Eberhardt, Director of Heavy Vehicles Technologies, U.S. Department of Energy. The OHVT Mission is “To conduct, in collaboration with our heavy duty vehicle industry partners and their suppliers, a customer-focused national program to research and develop

technologies that will enable trucks and other heavy vehicles to be more energy efficient and able to use alternative fuels while simultaneously reducing emissions”.

The presentation is Attachment 3.

The outline of the presentation is as follows:

- Organizational Structure
- Rational
- Program Strategy
- Implications of Consent Decree
- Purpose of Workshop
- Summary

B. The Keynote Address.

“The Diesel Challenge” by Rodica Barenescu, Chief Engineer, Navistar International Truck and Engine Corporation and president-elect of the Society of Automotive Engineers (SAE).

Dr. Barenescu reviewed the state of the art of diesel engines, the progress that has been made in reducing emissions, a systems approach to the development of cleaner engines, clean fuels as a technology enabler and the challenges beyond the year 2000. Dr. Barenescu’s talk summarized some of the key issues that needed to be addressed at the workshop:

1. Although current heavy duty diesels have made outstanding progress in reducing engine emissions since 1974, future engines must reduce levels by 90% to near-zero levels. Also, light duty diesel trucks and diesel powered passenger cars must achieve Tier 2 type emission standards by 2007. This can only be accomplished through a systems approach.
2. Progress on after-treatment is encouraging and the engine manufacturers and suppliers are working feverishly on a number of systems. The fuel and oil must be included in the studies if we are to achieve the 2004 goals.
3. All after-treatment systems have sensitivity to sulfur and a national fuel with a sulfur level of 30 PPM is needed for the diesel to meet the 2004 standards.
4. Having a national ultra low sulfur fuel (5 PPM) fuel will enable achieving the 90% reduction in emissions from the current level.
5. Catalysts are seen as the ultimate system for reducing emissions and eliminating health effects concerns associated with the diesel engine.
6. The potential exists for a green diesel technology with near-zero emissions and a decrease in green house gases.
7. Future diesel engine advantages include reliability, fuel efficiency, durability, low emissions, and sociability.

The diesel engine supports economic development by providing the most practical and efficient transportation system on water, land and rail. It is highly utilized in agriculture,

construction, forestry, mining and industrial applications. The popularity of the diesel has stimulated interest in the field of light duty and passenger cars primarily because of its efficiency and durability. However, the newly proposed EPA emission standards for passenger cars in 2004 and beyond are particularly challenging for the diesel engine.

In passenger cars the competitive fuel economy target of 80 miles per gallon (3 liters per 100 kilometers) is pushing the envelope. The direct injection diesel engine is one of the leading alternatives. Reliability and durability of future cars will be benchmarked at 100,000 miles of operation without tune-up. The norm for commercial heavy-duty diesel trucks is currently 1 million miles. The reputation of superior durability, rugged construction and reliability is driven by competitive commercial forces between manufacturers.

Environmental requirements have made the engines virtually smokeless. Beyond 2000, regulated emissions of diesel engines will be very low in nitric oxides and particulate emissions. Sociability requires low noise, easy start, convenience of service and maintenance. The sociability benchmark comes from the domain of advanced passenger car engines. It is expected that the passenger car technology can be gradually transferred to the diesel vehicles but with some difficulty. Lastly, the cost has to be reduced to be competitive.

What are some of the benefits of the diesel engine? The first is energy savings. About 30-40 % of the energy in a barrel of crude oil can be economically processed to produce distillates that are the starting point for diesel fuels. More of the crude is naturally suited for use as a diesel fuel than gasoline. Refinery processes can be biased to produce more gasoline but it is not practical to go beyond a given point due to increasing process costs and difficulty in cracking the heavier crude components.

Fuel efficiency and carbon dioxide are the next benefits. The diesel achieves the highest thermal efficiency of current engines. A prototype with 55% efficiency has already been demonstrated in the larger engines. Current diesels can achieve 45% efficiency, significantly higher than gasoline engines.

Carbon dioxide is the green house gas associated with global warming. The diesel is the lowest emitter of carbon dioxide, it is proportional to the fuel consumption.

The reliability and durability of the diesel are positive factors for the customer who is looking for longer life.

Diesel fuel is also less flammable and therefore safer in closed spaces like garages and boathouses. The newer diesel engines are low in odor.

The biggest challenges for the diesel are emissions. It is always benchmarked against gasoline engines although from a cycle standpoint, it is a different cycle, the combustion is different, and the ignition profile is different. Gaseous hydrocarbon and carbon monoxide emissions are inherently low in the diesel. Evaporative emissions are also low

due to the low volatility of the fuel. The challenges are due to the NO_x -Particulate tradeoff. The industry has made significant progress on the reduction of emissions. The progress has been phenomenal and the industry should take some credit.

In the last 25 years of diesel engine emission developments, NO_x and Particulates, that started being regulated in 1974, have been drastically reduced. NO_x was reduced some 73% from the 1974 base, and will be reduced by 87% by 2000. Current particulate levels are reduced by 90 % from 1974 levels. Considering the fact that this is a trade-off situation, the reduction of both NO_x and Particulates achieved to date, is a credit to the advances in diesel engine technology.

In 1991 most diesel engines had mechanically controlled fuel systems. Most of the technological advances that have reduced particulates are the result of engine developments. Some of the advances include transition from the mechanical to electronically controlled fuel systems, exclusive use of direct injection, air-to-air charge cooling, improved combustion chamber designs, injection rate design and control, advanced forms of turbocharging, higher compression ratios, use of pilot injection and controlled multiple injection.

Other approaches such as exhaust gas recirculation (EGR) and aftertreatment of the exhaust with catalysts and particulate traps were investigated but not considered to be of high priority until now. EGR was effective but required good mixing with fresh air and temperature control and also increased engine wear, due to increased soot loading of the oil. . The aftertreatment systems were prone to plugging, made the engine more complex, were expensive, less durable and had poor reliability.

The effect of sulfur on particulates was demonstrated and analyzed in the early 1980's. Sulfur in the form of sulfate with bound water was a component of the total particulate in the transient diesel test method. Numerous engine tests helped to quantify the contribution of sulfur and identified the fuel as the main source of the problem. It was found that the sulfur level of the fuel, and not combustion characteristics, resulted in the higher particulate levels. In 1993, this resulted in the reduction of diesel fuel sulfur for on-road applications from 3000 to 500 PPM.

The impact of air quality goals on diesel engines and the plans of manufacturers to penetrate the light duty vehicle market makes it imperative that breakthrough progress be achieved in diesel engine emission control. We are finding that to reduce emissions in the engine, it must be treated as a system consisting of the fuel, the engine and the aftertreatment system. Methodologies of system engineering can then be applied to optimize the system for lower emissions. The proper combination of engine, exhaust aftertreatment, fuel and oil formulation can be selected, but must be kept in perspective with performance, life, reliability, cost, customer needs and sociability. Concentration of resources on one area alone, fuel, oil, aftertreatment, system, alone will not enable meeting near-zero/Tier 2 emission standards.

The presentation is Attachment 4.

C. FUELS.

The following presentations focus on petroleum and alternative fuel sources and the role of sulfur in the fuel as related to future low emission diesel engines and vehicles. The reduction of sulfur in diesel fuel is necessary for lower emissions via aftertreatment technology. The components of the system are intertwined and the introduction of very low sulfur fuels places increased performance requirements on the lubricant and the necessity to change the lubricant technology.

"Low Sulfur Diesel Fuel an Enabling Technology for Future Low Emitting Diesel Engines". Paul Machiele of the U.S. EPA, Ann Arbor, MI presented an update on fuel-related issues and EPA's concerns on fuel and lubricant sulfur.

The U.S. Environmental Protection Agency is considering setting new quality requirements for fuel used in diesel engines, in order to bring about large environmental benefits through the enabling of a new generation of diesel emission control technologies. The Advanced Notice of Proposed Rule Making (ANPRM) published last July sought comment on the merits of improving the quality of diesel fuel, as an enabler of advanced technologies for diesel emission control. These advanced sulfur-sensitive technologies have the potential to reduce diesel engine NOx and PM emissions by more than 90%. As with past changes in diesel engine technology, these changes are likely to place new demands on the composition and performance of engine lubricants. The presentation reviews these new emission control technologies and discusses the importance of the fuel and engine lubricant composition and their performance on them.

The presentation is Attachment 5.

"Fuel Formulations" Brent Bailey, Coordinating Research Council, Atlanta, GA presented a historical overview of the developments and interdependency of fuels, lubricants and engines.

Diesel engine lubricants have been developed and improved for over 100 years. This development has coincided with developments in fuel and engine technologies as each of the components in the system are interdependent. Fuel composition impacts lubricant formulation because the lubricant is exposed to the unburned fuel and to the fuel combustion products. The extent and conditions of exposure are dependent on the engine technology employed. The presentation includes a short historical review of developments in fuel composition over the last 100 years, a review of new diesel fuel formulations under investigation, and a brief glimpse into what may be expected for future fuel, engine, and lubricant development.

The fuel, engine and lubricant system has shown gradual evolutionary improvements over the years. In view of the rapidly changing requirements of today, future system improvements could experience a step change. The changes will require interdependency of the components. This interdependency is not new. It was also identified in the

development of the CLR Oil Test Engine, CRC Report No.301, June 1955, which states “....Satisfactory oil under one set of conditions may be unsatisfactory in the same engine under another set of conditions. This emphasizes the necessity for matching these four factors: oil, fuel, engine design and conditions.”

The focus of the workshop is on the lubricant but the fuel composition has to be considered. Based on previous studies, the fuel composition impacts the lubricant formulation. The lubricant is exposed to unburned fuel. Experience with the use of alcohol fuels in diesel engines shows the necessity to design the additive package to be compatible with the unburned fuel and blowby fuel combustion products. One problem at this point in time is that the future fuel composition is uncertain.

The presentation also compares the effects of various fuels on emissions, including NO_x and Particulate tradeoffs and the effect of the fuels on particulate size. CRC research studies have shown that the higher the hydrogen/carbon ratio of the fuels the lower the PM. The presence of oxygen in the fuel further reduces the PM. The presentation identifies previous CRC studies that can contribute to the research planning for the development of low emission diesel engine oils

This presentation is Attachment 6.

“Renewable Diesel Fuels” K. Shaine Tyson, Renewable Diesel Project, National Renewable Energy Laboratory, Golden, CO

The U.S. Department of Energy’s Renewable Diesel Alternatives Program focuses on expanding supplies of reasonably priced renewable diesel fuels for transportation. The program’s focus on alternative diesel fuel production and supply issues compliments the other parts of DOE’s Office of Transportation, such as the Office of Heavy Vehicle Technologies where much of the engine emission and design research originates. The program is evaluating :

1. fuels that can be used (neat or in blends with diesel) in existing compression ignition engines with little or no modification,
2. liquid fuels that may require engine modification or new engine technology,
3. gaseous fuels with their own unique engine designs, and
4. fuels for hydrogen reforming.

The goal of the evaluation is to develop a rational strategy for investing in R&D to improve production technology, reduce costs, and expand supplies of promising alternative diesel fuels.

Diesel fuel will be a dominant fuel for the next several decades, and thereafter, will play a strong if not dominant role in heavy-duty transportation. At the same time, the quality of diesel fuel will improve. Some alternative diesel fuels can play a role in that process, as blends of those fuels with diesel provide public benefits at reasonable costs. Therefore,

the program is interested in developing alternative diesel fuels that can be blended with petroleum diesel and used in existing compression ignition engines. Some of these fuels may even evolve to the point where they are used in their pure form as costs decline.

As diesel's dominance wanes, some yet unknown fuels will begin to capture large market shares. Are they hydrogen, biogas or natural gas, electric, liquid fuels, or some combination of all of these? No clear answers are available. Most fuels face some type of potential market limitation, but that may not be a good reason for suppressing an otherwise promising fuel, as we may never return to the days of one fuel dominance. The program may need to support the production of a variety of promising alternative diesel fuels, although budget limitations will restrict investment in all but a few promising "winners."

The Renewable Diesel Alternatives Program is under the Office of Fuels Development of the Office of Transportation Technologies of the DOE Office of Energy Efficiency and Renewable Energy. The mission of the Renewable Diesel Alternatives Program is "To invest in R&D to expand supplies of reasonably priced renewable diesel fuels."

This presentation is Attachment 7.

"PSU Fuel Additive Program" André L. Boehman, Assistant Professor of Fuel Science and Director of the Combustion Laboratory, The Energy Institute, The Pennsylvania State University, University Park, PA 16802

A number of studies on oxygenated fuel additives for diesel fuels are in progress. One of the more comprehensive current programs is at Penn State University. To supply technical input in this area, Dr. Boehman, Director of the Combustion Laboratory of the Energy Institute at Penn State reviewed the projects. Most of the oxygenated additives, including methyl soyate were beneficial in the diesel and reduced engine out emissions.

Dimethyl ether (DME) and a liquid fuel additive made from dimethyl ether offer the promise of reduced diesel engine emissions without any sacrifice in performance. The liquid fuel additive, CETANER™, offers the additional benefit of a seamless transition to cleaner burning, reformulated diesel fuel. Inclusion of oxygen in diesel fuel is known to reduce particulate emissions. Both, DME and CETANER™ have the additional benefit of a high cetane number. DME has a cetane number of 55 and CETANER™ can be formulated to have a cetane number as high as 125, making CETANER™ both an oxygenating and a cetane boosting fuel additive. Both fuels can lead to cleaner burning Diesel engines and potentially, to greater market acceptance of Diesel powered vehicles.

In the present work, engine combustion and emissions studies are ongoing to determine the optimal treat rates and fueling strategies for DME and CETANER™ across a range of engine platforms. These projects also involve field demonstrations and emissions measurements in on-road vehicles for verification of the laboratory results. These projects involve collaborations between the Penn State Energy Institute, the University of

California-Berkeley, Air Products and Chemicals, Inc., Cummins Engine Company, Navistar International, USA PRO (a consulting company in Southern California), the Pennsylvania Department of Environmental Protection, the Federal Energy Technology Center and the South Coast Air Quality Management District.

The status of five current PSU projects:

“Incorporating Oxygen in Diesel Fuel as a Means of Reducing Engine Emissions”,

“Effect of Oxygenated Cetane Improver on Diesel Engine Combustion and Emissions”,

“Impact of Molecular Structure”,

“Reformulated Clean Burning Diesel Demonstration Program”, and

“Development of a Dimethyl Ether (DME) - Fueled Shuttle Bus Demonstration” are briefly described.

This presentation is Attachment 8.

D. CATALYSTS/TRAPS/AFTER-TREATMENT.

“Diesel Emission Catalysts and Filters”, Dale McKinnon, MECA , Washington, DC

As emission requirements for diesel engines become stricter and manufacturers move towards cleaner diesel engines, a systems approach will be required including advanced engine technologies, advanced fuels and lubricants, and advanced emission control technologies. This presentation outlines the interactions of lubricant constituents on catalysts and filter technologies and their effects on the performance of the technologies.

This presentation is Attachment 9.

“Post Combustion Devices For Diesel Applications”, Magdi Khair, Southwest Research Institute, San Antonio, TX

This paper will review the standards, goals and research targets for diesel engine emissions. Several post combustion emission control systems and their principle of operation will be described. A comparison of the various systems will be made and their advantages and disadvantages reported. Progress in Post Combustion Technology has been made and is discussed. The studies indicate current aftertreatment technology developments do not identify a clear cut winner in the current technology systems.

This presentation is attachment 10.

"Sample Analytical Tools For Diesel Catalyst/Lube Oil Additive Studies", Magdi Khair, Southwest Research Institute, San Antonio, TX

This presentation discusses an ongoing program to address the potential poisoning effect of lubricating oil on diesel catalytic converters. The study utilizes several analytical tools to assess the problem. The effect of aging on catalysts is shown using EDX, SEM and other methods of analysis. Assessments of catalysts using fresh, aged and additized lubricants are described. The impact of sulfur is compared to other elements present in the lube oil package.

This presentation is Attachment 11.

"Diesel Emission Controls : NOx and Particulate" , John H. Johnson, Presidential Professor, Michigan Technological University, Houghton, MI

This presentation focuses on emission control research by the Vehicle Engine Cooling System Simulation (VECSS) research group in the Department of Mechanical Engineering and Engineering Mechanics at MTU.

This presentation is Attachment 12.

E. BASESTOCKS.

The development of new lubricants is a complex process involving refinery processes, bench tests and engine laboratory research. The first step in the process is in developing low emission diesel oils is the proper selection of the basestock, or base oil. Synthetic base fluids became available as the result of research efforts in World War II. Research efforts in the 1950's and 1960's led to a number of synthetic polyalphaolefins, currently designated as Type IV API Base Oils, and synthetic ester fluids, designated Type V API Base Oils. Removal of aromatic and sulfur compounds to produce high quality petroleum basestocks, started with the "super-refining" of conventional petroleum basestocks in the late 1950's. Considerable progress has been made in recent years in refining crude oils to produce high quality base oils by eliminating sulfur and aromatic components from the petroleum base oils. The presentations in this section identify some of the high quality petroleum base oils of interest to low emission diesel engine oils and describe some lessons learned from an earlier DOE lubricant study using synthetic base fluids and additives.

In addition, environmental concerns have resulted in renewed interest in biodegradable basestocks from renewable resources. Currently, these renewable base oils are used

primarily in hydraulic fluid and niche markets, relatively small markets, such as : cutting oils, two stroke engine oils, chainsaw bar oils, wire-rope oils, bicycle chain oils, railroad oils, pump oils, outboard engine oils, and drilling oils. Demands on the oils in the niche markets are less severe than in diesel engine oils. However, research in progress indicates the potential use of these renewable oils as engine base oils is feasible. Some issues related to the market development of alternative diesel engine oils may also be applicable to any novel low emissions engine oil that is not evolutionary.

"Base Oil Chemistry For Diesel Engine Lubricants" Cliff Mansfield, Equilon Enterprises, Houston, TX

Currently, Group I and II base oils along with synthetic PAO's are used in formulating diesel engine lubricants. The compositions of these base oils, along with additive chemistry, can directly impact the performance of these lubricants. Modern analytical methods are available to determine the compositions of these base oils, and the compositions can be empirically related to the performance properties such as oxidation and fuel economy. As demands on diesel engine lubricants increase through new engine design and environmental regulations, demands on base oils will also increase. Future trends may be less use of Group I base oils and more use of Group II, Group III, PAO's and PAO type base oils. Very little work has been done on the effect of base oil composition on diesel particulate emissions. The same techniques that have been used to examine oxidation and fuel economy could also be applied to this question

This presentation is Attachment 13.

"Synthetic Liquid Lube Oil Development: Lessons Learned". John W. Fairbanks, US Department of Energy, Washington , DC

Early work with the "Adiabatic" or low heat rejection (LHR) diesel engine identified a need for a high temperature synthetic liquid lubricant . Roy Kamo's LHR engine used one liquid for lubrication and cooling , Stauffer's SDL-1. Pre-contract work by Cummins and Stauffer showed possibilities of very high top ring reversal temperatures. Specifically they modified an engine and developed an advanced synthetic liquid lubricant that ran for 275 hours with top ring reversal temperatures of 875 °F and a sump temperature of 300 °F. The approach was to develop a synthetic basestock that would compensate for elimination of certain additives and develop an ashless additive pack. The overbase and detergency were achieved with a chemically active filter that allowed elimination of the conventional TBN metallic salts (Calcium Sulfonate) Materials in the ring/liner interface were important. The only ceramic material that worked was one alloyed with a transition element metal. Tribology support showed a phosphate ester anti-wear additive significantly reduced friction. Recent engine tests show a 3.2% improvement in fuel consumption with a commercially available synthetic lube oil accompanied by a 3 to 4 times increase in the oil drain interval compared to the engine builder's standard recommendation. The challenge is to maintain or enhance the fuel economy and drain

interval advantages while reducing the crankcase oil's contribution to particulate emissions.

This presentation is Attachment 14.

"The Use of Vegetable Oils as Renewable Basestocks". Sevim Z. Erhan, National Center for Agricultural Utilization Research (NCAUR), U.S. Department of Agriculture (USDA), Agricultural Research Services (ARS), Peoria, IL 61604

Annual consumption of oil-based lubricants in the U.S. is close to 10 million metric tons valued at more than \$8 billion. This is a well-established and highly competitive market growing at an average rate of less than 1% per year. More than 70% of the total lubricant volume is used as motor oils for automotive engines and 10% as hydraulic fluids. Other application areas, mostly industrial lubricants are less significant. Major components in lubricants are base stock (usually 80 % or more) and additives, which are used to enhance the most important properties, depending on application. Most of the basestocks originate from petroleum, including many synthetic esters and polyalphaolefins. Vegetable oil basestocks and other vegetable-based fluids have seen a quite promising increase in use as biodegradable lubricants over the last decade. However, still less than 2% of all basestocks are products of oleochemical and related industries. These basestocks are mostly used for hydraulic fluids and various niche markets.

Vegetable oils have a series of advantages that can be beneficial for a number of lubricant applications. They are readily biodegradable and essentially nontoxic, properties that are not exhibited by lubricants based on mineral oils. Volatility is very low due to high molecular weight triglycerides and viscosity does not change rapidly with varying temperature. Ester linkages deliver inherent lubricity and ability to adhere to metal surfaces. Solubilizing power, miscibility with contaminants and additive acceptability of vegetable oils is better than that of mineral oils, especially in the case of polar materials.

The most serious disadvantage of vegetable oils when used in lubricants is their poor oxidative stability. Bis-allylic hydrogen in methylene-interrupted polyunsaturated fatty acids is very susceptible to free radical attacks, peroxide formation and production of polar oxidation products. Oxidation results in increased acidity, corrosion, viscosity and volatility of the lubricant. Antioxidant additives improve oxidative stability of vegetable oils to only a limited extent and chemical modification is necessary to eliminate bis-allylic hydrogen. Micro-oxidation experiments identified the triglyceride ability to oxypolymerize into branched networks that may result in oxidative gelation and subsequent problems in filterability and flowability. Presence of ester linkages makes vegetable oils susceptible to hydrolysis, therefore, contamination control and demulsifiers must prevent formation of emulsions with water. Extensive low temperature testing shows that formulated vegetable oils solidify at -20 °C upon long term exposure. Therefore, chemical modifications are necessary to suppress or eliminate triglyceride crystallization. Inherently, narrow viscosity range limits the usage in various viscosity grades, especially at lower viscosities.

Currently, our research priority is given to chemical modification of vegetable oils to overcome the performance deficiencies. Criteria are being established to determine the necessary improvements in technical parameters through cooperation with industrial partners and correlating field testing data to laboratory observations. In general three possible avenues for an improved soy basestock are being investigated: 1) genetically modification to produce a more stable oil from seed, 2) chemical changes, and 3) additive technology.

This presentation is Attachment 15.

"Market Development Issues for Alternative Diesel Engine Oils", David B. Smith, Creative Energy Products, L.L.C., Moorestown, NJ 08057

Crop based fluids, produced from renewable sources such as corn, canola, soy and sunflower, have the potential to bring added market value to diesel engine oils. This presentation covers several possible ways these fluids could be interesting to current and alternative marketers. Potential value is derived from use of crop fluids as a renewable resource, from taking advantage of unique physical properties, by exploiting the active molecules of these unique lubricant base stocks or combination of all of these factors.

Crop based fluids can gain market entry by satisfying any future government regulation or mandate calling for the replacement of mineral oils with a renewable resource. Barring such government intervention, these fluids will need to solve performance issues either more economically than modern mineral oils, or provide a performance boost not possible with other known lubricant base stocks or additives. Research areas are suggested to explore and identify this potential.

The historical perspective on crop based fluids recalls poor stability at high and low temperatures. Advances in genetics and additive chemistry show promise in solving these issues. Market acceptance will come only when the stability of diesel engine oils containing these fluids is proven with full scale engine testing. This can be proof-of-performance vehicle runs, or documented sequence engine testing. Large-scale market penetration will require proof in all of the engine testing required for today's mineral diesel engine oils.

This presentation is Attachment 16.

F. ADDITIVES.

Additive concentrations in lubricants can vary from about 1 % to 20 % depending on the purpose of the lubricant. Additive packages in diesel engine oils tend to be near the higher end of the concentration range. Additives are used to slow the oxidation process, prevent wear, lower friction, disperse contaminants, keep surfaces clean and prevent

corrosion and rust. The additives must be compatible with the system and each other. Current additive technology has evolved over the years by laboratory testing of thousands of additives and additive combinations. The best technology also has undergone extensive engine testing and accumulated years of field experience. To produce low emission diesel engine oils may take an evolutionary change since the better additives currently in use contain sulfur, phosphorus, zinc and other metals that are suspect in reducing catalyst performance and durability. New low-sulfur, low-ash additives are a major departure from past experience and may pose significant market risks as they are introduced. The following presentations give an overview of current additive technology and some insight into the additive problem and some alternatives.

"Diesel Engine oil Additives for Low Emission Engines: The Challenges and Consequences", Tom Boschert, Ethyl Corporation, Southfield, MI

Diesel engine oils (DEO) garner much of their performance through additives that can comprise as much as 20% by weight of a DEO. Several of the more promising paths being pursued for low emission diesel engines require aftertreatment devices which are 'poisoned' by metallics from these oil additives. If we are to substantially decrease the use of metallics in a DEO additive system, we will be faced with many challenges in the oil formulation as well as in the engine design to be able to accomplish this task in a customer friendly fashion. There are also a number of severe consequences that may occur. These include misapplication of the new low metallic oil in older engines, misapplication of older high metallic oils in low emission engines, and a risk factor of new technology being introduced without an adequate history of field use.

This presentation is Attachment 17.

"Lubricant Additives and Strategies for Low Emission Diesel Oils", Steve Hsu, NIST, US Dept. of Commerce, Gaithersburg, MD

This presentation is a review of basic additive chemistries used in diesel engine oils. From the chemistry point of view, the issues encountered in formulating a 'clean' lubricant are discussed. Several potential strategies are offered to overcome such difficulties.

This presentation is Attachment 18.

"Challenges and Opportunities for Future Engine Oils", Ewa Bardasz, The Lubrizol Corporation, Wickliffe, OH

In light of technological progress that was made during the last century, it is difficult to predict advances, which might occur in the next decade and beyond. One thing is sure, advances are made in response to forces of change, and a look at the current most

significant market drivers, such as global emissions regulations, can provide a glimpse of what will lead additive development in the next ten plus years.

This presentation provides a historical perspective on petroleum additive industry. The traditional approaches to methodology for developing new additives and lubricating oils are contrasted to novel, alternative ways of lubricating engines of the future. We speculate that during the next decade, through the utilization of combinatorial chemistry and virtual testing, the development of intelligent, structure specific additives becomes a reality. These novel approaches can maximize the desired attributes of any chemical compound(s) while minimizing undesirable side effects and promote invention of new classes of additives with superior performance characteristics. Examples of extended oil drain interval concepts and a necessity for building an intimate interface between equipment manufactures and lubricant companies are also discussed.

This presentation is Attachment 19

G. LUBRICANTS.

Knowing the base stock and additive technology leads to a finished lubricant, a diesel engine oil in this case. However, the research and development that goes into the final step is time, resource and manpower consuming. The presentations on lubricants range from discussions on the impact of lubricants on the catalyst systems to methodology to identify the impact of lubricants on the system. The current DEO programs and costs of development of implementing a new DEO product are described.

"Lube Oil Contribution to Emissions: Emerging Issues", W. S. Key, Oak Ridge National Laboratory, Knoxville, TN 37932

Much attention has been focused on diesel fuel formulation and its impact on exhaust emissions and on emission control (EC) devices. To date a comparable effort has not been placed on evaluating the effects of lube oil formulation. Some prior work when coupled with future trends suggests that lube oil formulation may also be of concern. This concern is elevated by the increasing demands from future exhaust emission regulations as well as the sensitivity of EC devices needed to meet these regulations to some exhaust constituents such as sulfur. This talk provides the authors perspective on the current status on which issues need to be addressed in light of the concerns and the level of effort currently underway.

This presentation is Attachment 20.

"Impact of Engine Oil Consumption on Diesel Engine Emissions", Kent Froelund, Engine Research Department, Southwest Research Institute, San Antonio, TX 78228

The engine oil contributes to the engine exhaust emissions through oil consumption. Measurement methods for oil consumption mapping for steady-state conditions as well as transient conditions will be discussed. SwRI typically normalizes steady-state oil consumption data by dividing it by the engine fuel consumption. These normalized data, hereby deemed "relative oil consumption", enables a direct comparison between data obtained for different engine types, makes, displacement, etc. Examples are provided of mapping of the relative oil consumption versus engine speed and load, which leaves a characteristic "fingerprint" of an engine. Transient oil consumption is treated as well. Finally, the sensitivity of oil consumption to oil parameters such as viscosity and volatility is discussed.

This presentation is Attachment 21.

"New Emissions Regulations - Impact on Engine Design and Oil Formulation", G.P. Fetterman, Jr., Infineum USA L.P., Linden, N.J. 07036

This presentation starts with a look at the changes in the EPA emissions limits for diesel engines from 1988 through 2002, and makes the observation that the problem areas are not HC and CO, but rather the trade-off between NO_x and PM. It then looks at the historical balance between these two, and how engine design has been modified to meet limits to date. Next it looks at the need for EGR to meet the 2002 goals and discusses the new PC-9 oil category targeted to lubricate EGR equipped engines. There is a brief discussion as to why EGR is a concern and a look at the anticipated costs of PC-9 followed by the required timing of the new tests and a discussion of what could happen if the category is delayed. Finally, the paper addresses some of the expected formulation impacts of PC-9, and most of these are directly counter to the anticipated needs of future engines with exhaust gas aftertreatment.

This presentation is Attachment 22A.

Similar issues on the subject are described in an NPRA paper presented by G. P. Fetterman at the Lubricants and Waxes Meeting, November 11-12, 1999 in Houston TX.

This paper is Attachment 22B.

"Future API PC-9 Engine Oil Category", August (Augie) Birke, Equilon Enterprises LLC, Houston, TX 77082-3101

API Service Categories for HD Engine Oils are developed by those branches of the Technical Societies and Trade Associations focused on Engine Lubricants. API Service Categories for HD Oils, e.g., CH-4, CG-4, etc., designate minimum performance requirements that a lubricant must meet to insure successful performance in diesel engines. The most recent HD API Service Category is CH-4.

Currently the industry is engaged in the development of the next Service Category for HD engines equipped with EGR. These engines are designed to meet the October 2002 emissions standards for On-Road trucks.

Details on how the performance tests are selected, the procedure used to set performance limits and the costs involved will be highlighted for the next API Service Category for HD lubricants...currently designated as PC (Proposed Category) 9.

This presentation is Attachment 23.

“Catalyst Compatible Diesel Engine Oils - DECSE Phase II”, Shawn D. Whiteacre, Cummins Engine Company, Columbus, IN 47201

The continued development of high performance, low emission diesel engines will require careful integration of engines, emission control systems, fuels, and lubricants. A research program is underway to study lubricant effects on the performance and durability of advanced diesel emission control systems. The Diesel Emissions Control - Sulfur Effects (DECSE) program explored in Phase I the detriments of diesel fuel sulfur on various NO_x and PM control technologies. With drastic reductions in fuel sulfur presently under consideration, the contribution of the sulfur in the lubricant is potentially significant. Other non-sulfur containing lubricant additives may also impact exhaust catalyst durability. DOE, EMA, MECA, API, NPRA, and CMA will explore lubricant effects in a joint research endeavor within DECSE Phase II. The work group plans to identify lubricant derived emission components that are detrimental to the emission control system. This information is critical to provide formulation guidelines for future base oils and lubricant additive packages, and to identify design constraints for engine manufacturers and emission control system suppliers.

(The DECSE Program was recently renamed the Advanced Petroleum-Based Fuels, Diesel Emission Control (APBF-DEC) Program; it is referred to as the DECSE Program throughout this document.)

This presentation is Attachment 24.

H. PARTICULATE.

There has been about a 90 percent reduction in particulate emissions from diesel engines since 1974. Part of this came about because of excellent cooperative research on diesel emissions. The health effects issues of the late 70's and early 80's also stimulated in-house and cooperative research. The sulfur issue came to light at about the same time. Several SAE Technical papers in the early 1980's addressed issues such as sampling (SAE No. 852081) and composition of particulate and unregulated emissions including sulfate formation (SAE No. 840413). In March 1985, there was a Coordinating Research Council Workshop on Particulates in Dearborn, MI where some of the same issues we are debating were raised by an international group of scientists. The reductions in

emissions we have seen since then are primarily due to engine design changes. Higher compression ratios, more efficient burning of the fuel have significantly reduced the particulate emissions, but at the same time, making it a drier particulate and changing the particle morphology. Dr. Kittleson in the next presentation addresses some of these changes. He has been a leader in the particulate area since the 1970's and his knowledge of the diesel particulate composition and structure is without question a key to solving some of the needs discussed at this workshop.

"Diesel Exhaust Particle Morphology: Nanoparticle Formation", David B. Kittleson, Center for Diesel Research, University of Minnesota, Minneapolis, MN 55455

The presentation gives an experimental (physical) and theoretical description of nanoparticle formation by engines. It suggests that nanoparticles may be formed from engine exhaust during atmospheric dilution by nucleation and growth of sulfate / SOF particles, or during the expansion stroke by nucleation and growth of metallic ash particles. Evidence suggests that current on-road engines emit mainly sulfate / SOF nanoparticles while engines running with high ash fuels or metallic fuel additives emit ash nanoparticles. Sulfate / SOF nanoparticle formation is extremely sensitive to sampling and dilution conditions. As elemental carbon is removed from engine exhaust, nanoparticle formation becomes more likely because volatile nanoparticle precursors that would have otherwise been adsorbed by the carbon nucleate to form new particles. Ash and sulfur from lube oil are likely to play an increasingly important role in nanoparticle formation as the sulfur content of the fuel is reduced and combustion improvements reduce elemental carbon formation.

This presentation is Attachment 25.

I. TRIBOLOGY.

The current EPA method of measuring particulate by trapping PM on a filter at moderate temperatures has long been an issue of controversy but until a better method to measure particulate by number or mass comes along, the methodology is the best current technology available. Therefore, removal of sulfur from the fuel is necessary if the diesel engine is to meet future EPA standards, not only from the catalysts needs, but also the necessity to reduce PM. In reducing sulfur in the fuel, and possibly diesel engine oils, we must consider other system requirements. Reducing sulfur in the fuels and lubricant leads to a fluid that has poorer friction and wear characteristics and possible compatibility problems with components, such as filters and seals, in the engine. Two presentations address this issue, the one by F.A. Kelley, an eminent tribologist, will directly address the issues and needs of this workshop. The second presentation by G.R. Fenske reviews the findings of a recent DOE friction and wear workshop at ANL. Although the workshop covers many tribology issues related to other industries, some of the issues and research topics have a direct relationship to the "Low Emissions Diesel Engine Oil" issues and needs.

“Tribology Needs for Low Emission Diesel Engine Oils”, Frank A. Kelley, Program Manager, Advanced Materials Technology, Caterpillar Inc., Peoria, IL 61656

As manufacturers strive to develop engine and vehicle technologies that appropriately addresses environmental concerns while providing advances in productivity and value, a number of challenges arise which must be dealt with in key tribological systems and interfaces. Customers and users place high demands on equipment and expect to produce good results for their efforts. Changes in lubrication system technology to accommodate new system approaches to reduce emissions are particularly challenging. Implications on lubricant technology development are quite pronounced because lubricants are very tightly integrated into the relative success or failure of these systems. It is easy to show that changes in one area can have a negative impact on another. It will be important to find lubricant formulation and system design approaches that can favorably improve compatibility with the environment without sacrificing needed performance or cost. This presentation discusses the needs and expectations surrounding heavy-duty engines and vehicles and identifies a number of tribological challenges that must be addressed in achieving an appropriate balance. It will be necessary to develop a higher degree of sophistication in the development process to account for the increasing number of interacting effects that must be taken into account. This includes a need to develop faster, less costly ways to define acceptable fluid performance requirements.

This presentation is Attachment 26.

“Friction and Wear Workshop”, George R. Fenske, Argonne National Laboratory, Argonne, IL 60439

Over the past few years, the US Department of Energy Office of Transportation Technologies has sponsored a series of workshops soliciting input from industry on critical needs in the areas of aerodynamic drag, friction and wear, thermal management, and brakes and rolling resistance. Reducing friction and wear in engines and drive trains represents one of these approaches that will enable the development of fuel-flexible, energy-efficient, heavy-duty transportation systems. This presentation reviews the findings of the Workshop on Reducing Friction and Wear in Heavy Vehicles that was held at Argonne National Laboratory in March of 1999.

This presentation is Attachment 27.

J. OTHER.

Two other presentations are included in this report that review research programs related to the interests of the low emissions diesel engine oils workshop. The first one is the

Coordinating Research Council program overview and the second covers research programs in progress on soybeans, a renewable resource.

The CRC was established in 1942 with the support of API and SAE and has had continuous cooperative industry and government research efforts on fuels, lubricants and environmental areas.

The soybean program was the result of congressional action and is managed by Omni Tech International, Ltd for the United Soybean Board. Although the Soy programs are diverse in nature, new lubricants and additives research are being funded in the program.

“CRC Program Overview”, Brent K. Bailey, Coordinating Research Council (CRC), Atlanta, GA 30346

The Coordinating Research Council, Inc. (CRC) was established in 1942 with two supporting members, the American Petroleum Institute and the Society of Automotive Engineers. CRC serves as a focal point for collaborative efforts between the fuels, lubricants, and domestic equipment industries. Efforts are directed towards generating statistically valid data on interactions of fuels, lubricants, and vehicle systems on vehicle and automotive equipment performance, emissions, and resultant air quality. Information developed by CRC is made publicly available and is used 1) by industry to ensure optimum

compatibility and customer satisfaction and 2) by industry, Government, and the public to enhance joint achievement of clean air and other applicable goals.

This presentation is Attachment 28.

“New, Non-Food Uses of Soybean Products”, Blaine Rhodes, OmniTech International, Ltd, Midland, MI

The national program of the United Soybean Board for development of new commercial markets and uses of products made from soybeans are outlined, with concentration on the New Uses Section as managed by Omni Tech International, Ltd., of Midland, MI.

Examples of products developed in the subsections of the New Uses Program – Coatings and Inks, Adhesives, Lubricants, Plastics, and Specialty Products – are reviewed with special attention to automotive and diesel crankcase motor oils.

A brief report on the progress of field trials of soybean oil-containing motor oils concludes the presentation

This presentation is Attachment 29.

K. Questions & Answers

Some of the comments to questions following the technical session presentations are recorded below. The comments are not comprehensive and are included as additional input to the discussions.

API PC-9 engine builders will use EGR to meet the next level of reductions in emissions. As a result the PC-9 oil will be required to meet the engine lubrication requirements. Will be ready by 2002.

Cost of development of PC-9 will be over \$40M. Once the test matrix is developed it will cost the lubricant manufacturers over \$350,000 to certify an oil under this new category.

HDD alone is a 400 million gallon per year market. This means under the API rules the base stocks have to be available to all manufacturers to keep a level playing field.

PC-9 is an evolution from the previous CH-4. After API finalizes the tests and procedures it requires one year before an oil can be licensed and put on the market. This is to allow all manufacturers and formulators the opportunity to get an oil on the market.

PC-10 will be the 2007 oil category. Discussions have already started on this category. This is where involvement should be. PC-9 is too far along.

ZDDP was first used in 1941 by Lubrizol. Serious questions remain whether complete removal is practical. Reducing concentration may be a fix.

ZDDP is the most widely used and effective additive and is the highest total contributor of sulfur in the oil (0.25 to 0.6 % sulfur)

Base oils in GP II contain only 0.001 to 0.003 % Sulfur. Group I can be from 0.1 to 0.4 % sulfur. The question is whether a sufficient quantity of GP II will be available at refineries. Currently the base stock mix is 2/3 GP 1 and 1/3 GP 2. Regarding availability of GP 2 and 2 1/2+, seven years is not a long time to get ready.

Oil consumption is now 2000 mi. / qt, shooting for 4000 mi. / qt. Therefore, additives must do a better job.

Considering reducing ZDDP in half. May have to change dispersant/detergent package.

Easiest fix is to come up with a sulfur tolerant catalyst.

Lubricants must be new and old engine compatible.

DOE-MECA-EMA started DECSE in 1998. Oil used in phase I. had 0.35 % sulfur. See information on internet.

Evolutionary approach means there is no radical change in the field. Revolutionary

changes in additives can result in significant field failures even though lab and dynamometer tests are satisfactory. The metallurgy may also have to be changed if new additives are used.

DECSE agreed on set of study questions:

- What are the effects of emissions out - oil composition effects.
- How to study aged oil.
- Oil consumption effects.
- Additive contribution effects.
- Sulfated ash, zinc, phos, volatility, olefins, etc. need to be looked at.

Task 1. Select an engine with EGR and measure engine out emissions.

Task 2. Conduct bench tests using knowledge from Task 1.

EGR will mean an increase in soot and additional additives will be needed. Indications are soot adsorbs additives and renders them ineffective. Need to understand the fundamentals.

Closed crankcase needed? Maybe.

Oil consumption rate - need good way to measure rate? Look at specific lubricant component as a tracer. Also need new and better sensors.

PM filters do have size exclusion limits.

The smaller the particulates the higher the surface area.

Method to trap sulfur? Absorber.

Sulfur products the same from fuel and lubricant? Some are, some are not.

Ceramic engine? May be a way. Need to design whole system.

L. BREAKOUT GROUP INPUT

Five work or breakout groups were charged to take into account all of the workshop presentations, the knowledge and experience of the group members and to come up with their views on program(s) that DOE should consider participating in. Each group was to come up with priorities, program recommendations, key participants and estimates of time and cost of the proposed programs.

The five areas covered by the groups were: 1) Additives, 2) Basestocks, 3) Alternative Lubricants, 4) Alternative Fuels and 5) Catalysts.

A. Additives.

Additive issues: Main issue is the extent of catalyst deactivation that can result from current lubricant additive packages.

If revolutionary additive package changes result in low or no sulfur and phosphorus, low or no ash & metals, the results on the catalysts are unknown. Need to determine what a revolutionary additive change would do to solve the aftertreatment problems. Also, what would the compatibility be with other components in the system. May require development of components such as seals, gaskets, etc.

Projects:

- Need a good catalyst deactivation test,
- Need engine durability tests (3 engines),
- Fundamental test and model development needed to study additive mechanisms for catalysts deactivation and wear,
- Revised engine parts development may be necessary,
- Particulate effects on additives unknown.

Prioritized Work Scope:

1. Develop a test to study catalyst effectiveness and to evaluate oils. Cost may be \$3M. Need data by 2002. (Some aspects of this project parallels the DECSE lubricant program and could be integrated with the DECSE lubricant study). Program already has a group of industry and government people cooperatively involved.
2. EGR will result in increased particulate loading . The effect of up to 8% particulate in the lubricant on properties, morphology/ultrafines (increased surface area) and especially the additive effectiveness needs to be established. Determine effect of particulate loading on additives. Two-year program, cooperative university - industry program, estimated cost \$500K.
3. Development of new additives: Estimate an evolutionary approach would require about \$1M DOE research/ \$9M in research by additive mfrs. Target - 2004.
4. Determination of what hardware changes will be requires for new oils. Overlaps with additive development; an additional \$500K is required.

B. Basestock Breakout Group:

Basestocks: The basestock comprises 80 % or more of the DEO. Need to determine basestock options and what properties influence the suitability of the basestock:

- Volatility, low sulfur, low nitrogen, low aromatics;
- Balance of aromatics and saturates;
- Dependence on additives selected.

Need to develop newer and faster methods of characterizing properties of basestocks and the additive effectiveness in new and used basestocks.

Projects: Piggyback on lubricants work being pursued on other programs.

1. Need evaluations of basestocks using low/zero sulfur fuels, common DI/VI package, GP 1 oil (Group 1, GF-3) oil, GP 2 oil, GP 2+ oil , GP 4 oils and engine emissions with new and used oils. Target 2004, Cost \$1M.
2. Engine oil/market capacity evaluation (NPRA should do).
3. Engine population and growth survey to evaluate demand for new oils (EMA should do).
4. Methods development for product characterization.

C. Alternative Fuels Breakout Group:

Two leading alternative fuels for diesel engines are the Fischer-Tropsch and Biodiesel. Initial use will most likely involve use of alternate fuels as blends (20%) in low sulfur diesel fuel. Both NOX and Particulates are reduced when using FT. Some needs include:

- Alternate fuels effect on lubricants,
Fischer - Tropsch
Biodiesel
- Need monitoring of fate of fuels and some monitoring of effect on lubricants.
- Screening studies - MeOH type (MeOH blowby products in crankcase were detrimental to the lubricant. Extraction of additives occurred).
- Need to start studies using 2007 fuels.
- Quality control of vegetable oils and products such as methyl soyate need better product control if they are be used as a fuel or as an additive in diesel fuel.
- Maintenance studies limited. Need data.
- Compatibility of alternative fuels and lubricants with system components
- Ability to meet performance, durability and emissions requirements.

Projects:

1. Screening studies of alternate fuels and lubricant incompatibilities.
2. Industry standards organizations assessment of role of alternate fuel in low sulfur fuel.
3. Market development of alternate fuel, performance, PC-9 type testing.
4. Follow-up development & testing of engine, lubricant, basestock, & additive package.

Cost: \$2M, 5 years

D. Alternative Lubricants Breakout Group:

Alternate lubricants include vegetable oils, synthetic esters and polyolesters, polyolefins. Two other options discussed in the meeting were using a segregated system and vapor

phase lubrication. The vegetable oils and synthetics fluids have the added interest in that they are biodegradable.

Alternative Lubricant Issues:

- What happens to lubricants in conversion from sump to exhaust?
- What additives are needed to overcome drawbacks and what is their compatibility with system and their effects on emissions?
- Lubricant blends screening and evaluation (Government / Academia)
- Engine design - split engine system. (Industry / Academia)
- Recycling/disposal issues (Industry / Government / University)
- Contaminant removal (University)
- Vapor phase lube studies (University / Industry)
- Effect of lubricant on morphology - ultrafines.

Projects:

1. Current programs exist that have developed basic data on vegetable oils and have overcome low temperature and oxidation problems through blending and use of selective additives. Indications are significant PM reductions in emissions are obtained with these lubricants. Need is to extend laboratory testing to engine testing to evaluate long-term performance using low sulfur, FT and BD20 fuels. Conduct program to develop these lubricants as an alternative. 5 years, \$1M.
2. Evaluate alternative lubricant effect on particulate morphology and particle distribution. 2 years, \$1M.
3. Vapor phase lubricant of a single cylinder engine was demonstrated in the late 1980's. Develop a segregated system using vapor phase lubrication. 5 years, \$1M.

E. Catalysts/Traps/Aftertreatment:

Issue: Impact of lubricant changes on emission control devices.

Projects:

1. Evaluation of fundamental deactivation & effects fields
2. Feasibility & demonstration of integrated systems (evaluation)
3. Evaluation of fundamental mechanisms in conjunction with different materials.

Conduct all three. Time: 5 years, Cost: \$3 - 5 M. Integrate with DECSE Project.

4. Basic research to develop; 1) a post-combustion system compatible with current lubricating oils when using ultra low sulfur fuel and 2) an effective EGR particulate removal trap. Time: 4 years, \$40million.

This is an accelerated comprehensive 4-year program was discussed that would include an extensive literature search of developments the past two years, followed by an extensive fundamental research project dealing with understanding the interaction of selected known catalyst deactivators and various catalyst formulations. This would include extensive research on trap materials and their structural characteristics, their resistance to heat and temperature, developing the regeneration process and evaluating the economics of these processes. A third phase would cover the system development from the mechanical and electronic stand-point with emphasis on advanced development engines for heavy duty and light duty diesel applications. The final phase would involve durability evaluation of the entire package both in controlled environments and field tests. The cost of the overall program would be \$8 - 10 million per year.

IV. DISCUSSION.

1. CATALYSTS/TRAPS/AFTERTREATMENT.

It was essentially a consensus of the group that the efficiency and durability of the current Post-Combustion Systems (Catalysts/Traps) are reduced due to the presence of sulfur, phosphorus and metals in the exhaust stream being treated. The problem is the lack of specific information on the mechanism and to what extent each species causes problems. Several analytical tools are available to study systems but care must be taken to interpret results since reactions are not homogeneous in the systems. Analysis location (front, middle, and back) can lead to different conclusions. There is a need to obtain data on the mechanism and extent of poisoning and coating of active sites of aftertreatment traps and catalysts by the fuel and lubricant.

The ultimate fix would be to develop a sulfur tolerable catalyst. This would require revolutionary change. Time and investment costs make this an unlikely solution by the 2007 timeframe. The next best solution is to have a nation-wide ultra low sulfur fuel to enable optimizing current post combustion aftertreatment technologies. To do this will require development of an engine test to quantify the rate of deactivation due to each of the species of concern, sulfur, phosphorus and metals. This would allow establishing long term catalyst efficiency and durability.

Testing to establish engine out and catalyst out information will vary with engine design. Multiple (3 or more) engine designs will most likely be required to establish baseline data.

Several systems should be evaluated since there is no obvious winner of any of the systems described at the conference.

2. FUEL ALTERNATIVES.

Fuel alternatives include Ultra-low sulfur fuel, Fischer-Tropsch, B20 biodiesel, alcohols, Natural Gas, Hydrogen, Oxygenates. These fuels and fuel additives cover a wide range of properties and considerable data exists on these fuels, neat and in blends.

A critical review of the available data is needed to select the better candidates for the near future.

To compete in a non-crisis environment, a fuel must be available in sizable supply with a distribution infrastructure in place. The fuel should run in both available and next generation engines, have acceptable performance and public acceptance.

Both biodiesel and Fischer-Tropsch reduce emissions but the quantity available in the near future may be an issue. Best approach may be to use blends. Blending can occur upstream or downstream and use current distribution infrastructure. Using blends needs in future generation vehicles needs to be considered in R&D programs. This means that fuel property tests, emissions and other screening tools need to be standardized for evaluating these fuels. Astm standards will be required for new fuels and blends.

New fuels will also require screening tests to determine compatibility with the lubricants. Field data over time will be essential to establishing system durability.

3. LUBRICANTS.

The same problem exists here as was discussed for fuel sulfur. There is not any good quantitative data on the extent to which lubricant additives interfere with after-treatment systems. Zinc, phosphorus and some metal additives are suspect but it is not clear whether elimination, modification or simple reduction of the common additives in the oil is required to solve the problem. There is a question as to the role of the additives and whether the problem gets worse with aging (use) of the oil.

EGR will be required by most diesel engines to meet 2004 regulations. Cooled EGR results in condensation and recirculation of nitric acid and sulfuric acid into the engine combustion chamber and increases the particulate level in the lubricant. This leaves a number of issues to be resolved. There is the issue of how to resolve the TBN requirements. To deal with the additional acid may require modification of the TBN. Lower levels of a more active TBN or higher levels of a less active TBN are two options to be considered. In addition, increased soot levels may require a more potent or higher levels of a soot dispersant. The soot problem is complicated by the fact that the extremely large surface area of the soot may absorb additives and lead to increased wear problems. The soot may also affect the required concentration levels to insure adequate lubricant performance.

The lubricant problem is further complicated by the increased stress occurring as a result of customer demands for better oil control and increased drain periods. Current 2000 mile per quart oil consumption rates will approach 4000 mile per quart levels, or higher in the next decade. Higher risks in engine reliability and durability will occur if the low emissions diesel engine oil requires a revolutionary change in additives.

It is difficult to isolate problems in engines due to the complexity of chemical and mechanical processes occurring simultaneously. This leads to a need for innovative bench tests to explore the problems prior to engine testing.

The industry is struggling to meet difficult deadlines with PC-9 and PC-10 requirements for diesel engine oils for 2002 and 2007, respectively. Cooperative efforts between the engine, additive and basestock manufacturers to develop the PC-9 specifications and test requirements is high. Cost of development of the test matrix for PC-9 is estimated to be over \$40 million. Once the test matrix is developed, cost to the lubricant manufacturers to certify an oil and obtain an API license under the new category will be over \$340,000, assuming the oil passes the test matrix on its first try.

Alternative lubricants containing a mix of synthetic fluids and vegetable oils may be a possible route to low emissions diesel engine oils. Current programs have shown the potential for such lubricants but there is a need to accelerate current programs (USDA/PSU/SwRI) and include an increase in engine and field testing.

4. BASESTOCKS.

The role of the basestocks is usually underestimated. They make up 80 to 86 % of current finished DEO and can range from essentially pure synthetics to very complex hydrocarbon mixtures. As a result, there are many questions on what properties are key to the suitability of basestocks - volatility, low sulfur, low nitrogen, low aromatics. The properties of the basestock can be a factor in engine out emissions and they can also be a factor in fuel economy.

Impact of basestock composition on particulate emissions is not known at this point. Factors that appear to impact particulates are viscosity, volatility, oxidation and thermal stability of compounds, and the deposit forming tendencies (can result in loss of oil control). API Group 2, 3 and 4 type base oils have reduced or no sulfur. Additional data on additive compatibility and effectiveness as sulfur and aromatics is reduced needs to be obtained. A big question with these base oils is whether they will be available in sufficient quantity to satisfy the volume requirements. Heavy duty diesel engine oil volume alone is over 400 million gallons per year.

Vegetable oils are possible alternative basestocks. Currently, they are used in niche markets and may only become a viable engine oil basestock if the government, for environmental reasons, imposes requirements for increased biodegradability on the use of petroleum basestocks. Even then, blending vegetable oils with biodegradable synthetics would be required to meet the lubricant volumes required.

5. ADDITIVES.

Current additive technology is the result of decades of evolution and the technology is built on a solid base of laboratory, engine and field tests. This gives current DOE's a

large safety factor. Developing the next generation of low sulfur, metals, and phosphorus DEO, without relying on current additive technology, is no longer an evolutionary process. Even to cut the sulfur content in half may require a revolutionary approach. To accomplish this will require an understanding of both the additive and additive-materials reactions.

Conceptual strategies for consideration for development of low emissions DEO ranged from super-stable to decomposable base fluids that had fuel value. Others include:

- An environmentally friendly lubricant with low volatility and new additives that have limited or no effect on aftertreatment system.
- A low or non-ash consumable lubricant containing reduced sulfur and phosphorous;
- A segregated system using vapor-phase lubrication.
- A reduced or non-additive lubricant with component modifications such as coatings, modified materials, or self lubricated components.

Again, as in the case of alternative fuels, the first step is to quantify the extent to which additives result in reduced catalyst efficiency. This includes evaluation of aging (use) of on additive effectiveness and engine out emissions.

6. PARTICULATES

In addition to after-treatment studies, research on particulate morphology and the related health effects issues need to be resolved. Kittleson's work at the U of Minn. is the most advanced in the U.S. on particle characterization. The presence of nanoparticles and whether they are soot or non-soot organic and inorganic materials needs to be resolved. Once characterized, the health effects issues of the particulate can be addressed. Particulate matter reduction through reduction of the soluble organic fraction by tailoring the basestock is possible. Alternative and synthetic basestocks have shown the feasibility of this. Tailoring of Group 2 and 3 petroleum base stocks may also reduce PM.

The second major particulate issue is the fact that EGR will increase the soot loading in the lubricant. Some work is already in progress to develop baseline information using samples containing up to 3-4 % soot loading. With EGR the soot loading may go as high as 8% and there is a need to determine how this affects the reformulating of the next generation of lubricants. Characterization of the soot in the oil also needs to be done. Surface area and activity of the soot with additives will help define the additive mix required for the next generation of lubricants.

PC-9 and PC-10 are the next two DEO classifications. The test matrix for these oils is still unresolved and the particulate is a significant issue in the final test matrix to be established for these oils.

7. TRIBOLOGY.

The removal of sulfur from the fuel and reduction of current sulfur and phosphorus containing additives in the lubricants will impact the friction and wear of the engine

system. Current customer demands are for longer drain intervals on lubricants, extended warranty, and increasing time periods before overhaul are in opposition to the needs to solve the after treatment problems.

Changes in the friction and wear characteristics of the lubricant with age is another area that additional research is needed. The effect on current materials is a factor in this study. Design of the system requires development of information on both the lubricant and material pairs involved. There is considerable data in this area that needs to be revisited prior to undergoing a revolutionary change in the lubricant alone. Engine component design and oil changes need to proceed together.

The removal of sulfur from the fuel raises friction and wear issues for the fuel injection system. Additives will be required to maintain adequate life of this component of the system.

The effect of sulfur removal on other relevant properties such as viscosity, water solubility (important for low-temperature operations) need to be considered in addition to friction and wear.

A related area is that of oil filtration in the engine. This may be one method of controlling the necessary additive levels required for proper lubrication of the system.

V. CONCLUSIONS AND RECOMMENDATIONS.

1. The issue coming out of the workshop with the top priority is to solve the exhaust emissions aftertreatment problems resulting from fuel sulfur and possibly lubricant additives affecting the performance of the system.

It is known that the level of sulfur in the fuel is a problem and a nationally available low sulfur fuel by 2002 will be needed to help solve part of the 2004 problem. An ultra-low sulfur fuel will be required to meet future regulations.

It is not known to what extent the lubricant plays a role. Engine out and catalyst out information using a future engine with EGR, a ultra-low or zero sulfur fuel and a test procedure are essential to resolve this issue.

The DOE DECSE Program is addressing this issue and should be expanded, if necessary, to determine the effect of current lubricants and reduced sulfur and ZDP additive lubricants on the efficiency of the catalyst.

The DECSE Program has an impressive group of industry and government participants and additional funding should be considered to ensure the basic information needed to solve the aftertreatment problems is obtained. To achieve this, the funding of the DECSE lubricant program needs to be increased. The development of PC-9 involving some 10-12 engine and laboratory tests is costing the industry over \$40M. It is not unreasonable to consider increasing the DECSE lubricant budget by \$5M to solve this issue.

2. The second priority that has an impact on the system is the effect of EGR on the lubricant. To develop the next generation of low emission lubricants requires resolving several issues regarding the particulate loading of the lubricant. Unless the particulate can be effectively removed from the recirculated exhaust, the loading of particulate in the lubricant is expected to better than double.

A tribology program to explore the effect of particulate in the lubricant is needed to determine the range of options available to revolutionary changes in the lubricant. This program would take 3 years at \$1 million per year.

3. Alternative fuels and lubricants issues need to be considered in the DECSE program. The DECSE testing program should be expanded to include testing of alternative fuels and alternative fuel blends with low - and ultra low - sulfur diesel fuels. This will resolve some of the emission reduction and lubricant compatibility issues, as well as identifying potential problem areas. This would involve adding an additional \$2 million to the DECSE lubricants program.

4. Development of alternative biodegradable lubricants should be pursued and if commercially ready in time, included in the DECSE lubricants program. This program would take 3 years and \$1.5 million per year.

5. The nature of the particulate emitted from a future EGR engine needs to be determined. The distribution mass and number of the particles and the origin of the nanoparticles is needed. If the nanoparticles are organic or inorganic, catalytic and trap removal are feasible. Characterization of particulate is important to the resolution of health effects issues hanging

over the diesel. The characterization studies would take 3 years and \$1 million, The health effects issues studies will depend on the extent of the studies required and could range from \$1 to over \$10 million per year.

6. Prescreening tools for alternative fuels and blends with low-sulfur diesel fuels and alternative lubricants need to be standardized. This could be done, in part, cooperatively with technical societies. Time would be 5 years at a cost of \$500K per year.

7. Collaboration with existing fuel and lubricant programs is recommended.

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FEBRUARY 21, 2000

ATTACHMENTS 1 and 2

AGENDA & ATTENDANCE

AGENDA

USDOE/NREL Workshop
"EXPLORING LOW EMISSION DIESEL ENGINE OILS"

HOLIDAY INN SUNSPREE RESORT
SCOTTSDALE, ARIZONA
JANUARY 30, JANUARY 31 AND FEBRUARY 1

MEETING AGENDA

JANUARY 30, 2000:

Registration 6-9PM
Reception (cash bar) 7PM -9PM

LOCATION

Apache Foyer
Navajo 1 & 2

JANUARY 31, 2000:

7:30 AM Continental Breakfast Apache A & B
8:20 Introductory and Administrative Comments - J.Perez Apache A & B

Session I, "The Diesel Challenge"

Apache A & B

Chairperson: K. Shaine Tyson, NREL

8:30 Welcome - NREL -Shaine Tyson/Wendy Clark
8:45 Diesel Keynote Speech "*The Diesel Engine Challenge*" Rodica Baranescu,
NAVISTAR International Transportation Corp.
9:30 Environmental Keynote Speech "*Low Sulfur Diesel Fuel an Enabling
Technology for Future Low Emitting Diesel Engines,*" Byron Bunker, EPA
10:00 Coffee Break

Session II, "Snapshots of Needs" Panel Discussion

Apache A & B

Chairperson: S. Goguen

10:15 -12:00 Panel

- "*New Emissions Regulations-Impact on Engine Design and Oil Formulation,*" - Pat Fetterman, Infinium USA LP
- "*Diesel Emission Catalysts and Filters,*"- Dale McKinnon, MECA
"*Future API PC-9 Diesel Engine Oil Category,*" - Augie Birke, Equilon Enterprises LLC
- "*Diesel Engine Oil Additives for Low Emission Engines - The Challenges and Consequences,*" Tom Boschert, Ethyl Petroleum Additives
- "*Catalyst Compatible Diesel Engine Oils*"- S.D. Whitacre, Cummins Engine Co. (DECSE Program).
- "*Engine Oil Developments for Advanced Diesel Engines,*" John Fairbanks, DOE

Panel -Audience Discussion

12:00 Lunch

Apache C & D

1:00 - 3:30 Session III, "Engine Oil Technology"

Apache A & B

Chairperson: W. Clark, NREL

- ***"Base Oil Composition and Performance in Diesel Engine Lubricants,"***
Cliff Mansfield, Equilon Enterprises, LLC
- ***"The Use of Vegetable Oils as Renewable Basestocks,"***
Sevim Erhan, USDA, NCAUR, ARS
- ***"Lubricant Additives and Strategies for Low Emission Diesel Oils",***
Steve Hsu, NIST
- ***"Challenges and Opportunities for Future Engine Oils,"***
Ewa Bardasz, Lubrizol Corp.
- ***"Tribology Needs for Low Emission Diesel Engine Oils"***
Frank Kelley, Caterpillar, Inc.

(3:30 - 3:45 Break)

Apache A& B

3:45-5:15 Session IV, "Particulate Studies"

Apache A & B

Chairperson: Kevin Stork, ANL

- ***"Engine Oil Contribution to Emissions"***
Kent Froelund, SwRI
- ***"Diesel Emissions Controls - NOx / Particulates,"***
John Johnson, MTU
- ***"Diesel Engine Particulate Morphology: Nanoparticle Formation,"***
Dave Kittleson, U of Minn

5:15 -7:00 PM Reception and Dinner

Apache C & D

7:00-9:00 Session V, Open Forum .

Apache C & D

Chairperson: J. Perez, PSU

After Dinner Speaker: James Eberhardt, Director, OHVT, USDOE "Overview of the DOE Heavy Vehicles Technologies Program,"

- **Blaine Rhodes - Omni Tech International Projects;**
- **B. Bailey - CRC Program Overview;**
- **A. Boehman, Penn State Univ. - Penn State Fuel Additive Projects;**
- **G. Fenske, Argonne -Review of critical Friction & Wear issues identified at DOE/Argonne Workshop (March 1999);**
- **M. Khair, SwRI - Sample Analytical Tools for Diesel Catalyst/Lube Oil Additive Studies**
- **Others - TBD**

FEBRUARY 1, 2000

7:30 Registration

Apache Foyer

8:00 AM Continental Breakfast

Apache Foyer

8:30 - 10:30 Session VI, "Emerging Issues"

Apache A & B

- *Session Chairperson: G. Fenske, ANL*

- *"Fuel Formulations,"- Brent Bailey, CRC*
- *"Alternative Fuels," K. Shaine Tyson, NREL*
- *"Post Combustion Devices for Diesel Applications , " Magdi Khair, SwRI*
- *"Engine Oil Contribution to Emissions: Emerging Issues" Bill Keys, ORNL*
- *"Market Development Issues for Low Emission Alternative Diesel Engine Oils," - David Smith (Retired Mobil), Creative Energy Products, LLC*

(10:30 -1045 Coffee Break)

Apache Foyer

Break-out Workgroups

Group 1 Apache A	Additives
Group 2 Pima	Basestocks
Group 3 Papago	Alternative Lubricants
Group 4 Zuni	Alternative Fuels
Group 5 Apache B	Catalysts

10:45 - 12 Noon -Worksessions **See Workgroup Assignments in Handout**

12:00-1:00 Lunch **TBD - North Terrace, Pool Patio or Apache C & D**

1:00 - 2:30 Break-out Workgroups **Same as above.**

2:30 - 2:45 Break **Outside: Papago, Zuni, & Pima and one by Apache A & B**

3:00- 4:30 Break-out Group Reports

Apache A & B

Wrap-up and Thanks

5:00 Adjournment of Workshop.

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January 30-February 1, 2000

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Low Emission Diesel Engine Oils
January 30-February 1, 2000

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January 30-February 1, 2000

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January 30-February 1, 2000

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Low Emission Diesel Engine Oils
January 30-February 1, 2000

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Rodica Baranescu	622875	NAVISTAR
Ewa Bardasz	622735	The Lubrizol Corporation
Mike Berg	622785	Octel Starreon LLC
Mark Bezek	622752	Sunoco Lubricants
Barry Bhatt	622754	NOXTECH Inc.
Augie Birke	622747	Equilon Enterprises LLC
Andre Boehman	622744	Penn State University
Stacy Bond	622768	PerkinElmer Auto Reserach
Thomas Boschert	622729	Ethyl Corporation
Briana Bowen	622786	Octel Starreon LLC
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Total Number of Attendees for LOW: 81

ATTACHMENT 3

"Overview of the DOE Heavy Vehicle Technologies R&D Program" by Dr. James J. Eberhardt, Director of Heavy Vehicles Technologies, U.S. Department of Energy.

ATTACHMENT 4

Keynote Address

"The Diesel Challenge" by Rodica Barenescu, Chief Engineer, Navistar International Truck and Engine Corporation and president-elect of the Society of Automotive Engineers (SAE).

Overview of the DOE Heavy Vehicle Technologies R&D Program

Dr. James J. Eberhardt, Director
Office of Heavy Vehicle Technologies
U.S. Department of Energy

Presented at the
Workshop on Low Emission Diesel Engine Oils
Scottsdale, AZ
January 30 to February 1, 2000

OHVT Mission

To conduct, in collaboration with our heavy vehicle industry partners and their suppliers, a customer-focused national program to research and develop technologies that will enable trucks and other heavy vehicles to be more energy efficient and able to use alternative fuels while simultaneously reducing emissions.

DOE Office of Energy Efficiency and Renewable Energy

Office of Heavy Vehicle Technologies

- ◆ The U.S. Department of Energy - Secretary
 - ◆ Efficiency and Renewables - Deputy Assistant Secretary, Transportation Technologies
 - ◆ **Office of Heavy Vehicle Technologies**
 - ◆ Created in the DOE/Office of Transportation Technologies restructuring (March 1996)
 - ◆ Focuses research and development on critical areas identified with heavy vehicle customers

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Office of Heavy Vehicle Technologies Program Coordination Structure

The Magnitude of Our Energy Problem

	1973	1997
U.S.	74 Quads	91 Quads
World	225 Quads	365 Quads

1 Quad of energy is equivalent to 340,000 tank cars of crude oil stretched from Miami to Seattle (3,300 miles).

Rationale for a Heavy Vehicle Technologies R&D Program

Since the 1973 Oil Embargo Essentially All of the Increase in U.S. Highway Fuel Consumption has been due to Trucks

Source: EIA Annual Energy Outlook, 1999
Federal Highway Administration, Highway Statistics

A Healthy National Economy Depends Upon Efficient Heavy Vehicle Transportation

Increasing Use of Class 7 and 8 Trucks

Source: 1982, 1987, 1992 Truck Inventory and Use Survey, 1997 Vehicle Inventory and Use Survey, U.S. Census Bureau

OHVT Customers/Stakeholders

OHVT program targets joint Industry/Government needs identified with customers and stakeholders

- ◆ U.S. Diesel engine manufacturers
- ◆ Heavy vehicle manufacturers
- ◆ U.S. automakers (truck divisions)
- ◆ Component manufacturers
- ◆ Fleet operators/owners
- ◆ Industry trade organizations
- ◆ Fuel suppliers
- ◆ Materials suppliers
- ◆ Universities/research organizations

DOE/Industry Collaborative R&D Efforts Target Common Interests

OHVT Plans Focus on Critical R&D Areas for All Truck Classes

OHVT Technology Roadmap

Office of Heavy Vehicle Technologies (OHVT)
Office of Transportation Technologies

October 1997

<http://www.osti.gov/roadmap.pdf>

<http://www.osti.gov/multiyr.pdf>

OHVT Technology Roadmap Development

Industry stakeholders provide input to Technology Roadmap

- ◆ Initial draft developed by DOE and the National Laboratories as recommended by industry stakeholders attending the initial OHVT customer-focus workshop.
- ◆ **OHVT Executive Steering Committee Meeting** held in conjunction with SAE Truck and Bus Show (October 1996).
 - ◆ **Draft OHVT Technology Roadmap** presented to industry stakeholders for review.
- ◆ Additional **targeted workshops** and **one-on-one meetings** with industry stakeholders provided feedback and comments.
- ◆ Final version released (October 1997).
- ◆ Technology Roadmap updated/revised by OHVT Team (May 1999).
- ◆ Revised OHVT Technology Roadmap presented to industry stakeholders at the 1999 SAE International Truck and Bus Meeting and Exposition (November 1999).

OHVT Technology Roadmap

Office of Heavy Vehicle Technologies (OHVT)
Office of Transportation Technologies

November 1999

OHVT Technology Roadmap

R&D needs of three groups of trucks are addressed

- ◆ Class 7 and 8, heavy-duty on-highway trucks
- ◆ Class 3-6, medium duty trucks such as urban delivery vans and transit buses.
- ◆ Class 1 and 2 light trucks (pickups, vans, and sport utility vehicles)

Truck Classification (by Gross Vehicle Weight)

	CLASS 1 6,000 lbs. & Less		CLASS 5 16,001-19,500 lbs.
	CLASS 2 6,001-10,000 lbs.		CLASS 6 19,501-26,000 lbs.
	CLASS 3 10,001-14,000 lbs.		CLASS 7 26,001-33,000 lbs.
	CLASS 4 14,001-16,000 lbs.		CLASS 8 33,001 lbs. & Over

DOE/OHVT Advanced Truck Technologies R&D Goals

Heavy (Class 7-8) Trucks

To develop by 2004, the enabling technologies needed to achieve a fuel efficiency of at least **10 miles per gallon (at 65 miles per hour)** and **meet** emissions standards prevailing in 2004, using petroleum-based diesel fuel.

Medium (Class 3-6) Trucks

By 2004, to develop and demonstrate commercially viable vehicles that achieve, on an urban driving cycle, at least **double the fuel economy** of comparable current (1999) vehicles, and as a *research goal*, reduce criteria pollutant emissions to at **least 30 percent below** EPA standards prevailing in 2004.

Light (Class 1-2) Trucks

To develop by 2004 the enabling technologies for clean diesel engines to be competitive with and **at least 35-percent more fuel efficient** than equivalent gasoline engines for light trucks, while meeting Federal and state emissions standards prevailing in 2004.

OHVT Technology Roadmap

Technical Plan -- Class 7 & 8

Technology Thrust Areas

- ◆ Engine Efficiency
- ◆ Power Requirements (@65 mph)
- ◆ Emissions
- ◆ Fuels and Lubricants

Heavy (Class 7-8) Truck Technologies R&D

October 1998 EPA/DOJ Consent Decree with Heavy-Duty Engine Manufacturers

- ◆ EPA alleges use of “defeat devices” by manufacturers to control NO_x during certification.
- ◆ Manufacturers deny allegations and claim full compliance with emissions limits.
- ◆ Manufacturers cannot use current “injection timing strategies.”
- ◆ EPA 2004 heavy-duty emissions regulation must be met by October 1, 2002.
- ◆ Manufacturers must develop new technologies to meet emissions levels.

Impact of EPA/DOJ Consent Decree on Heavy-Duty Engines

- ◆ Efficiency will be sacrificed (about 10 percent penalty) to meet emissions regulations. This could well mean a 0.5 to 1.0 mpg fuel economy penalty for a Class 8 truck.
- ◆ New emission control technologies are required to achieve emissions and maintain current efficiency.
- ◆ Improved fuel quality (very low sulfur) may well be necessary for some control technologies to be effective.

Decreasing Diesel Engine Emissions

Source: Cummins, modified by DOE

Increasing Diesel Cycle Engine Efficiency

Potential Impact of EPA/DOJ Consent Decree on Heavy-Duty Engine Lube Oil

- ◆ Sulfur/phosphate content of lube oil are real issues
 - Near-zero sulfur/phosphate lube oil may well be necessary for effective emissions control if exhaust aftertreatment is required (e.g., lean-NO_x catalysts).
- ◆ Durability issues
 - Change in lubricity?
 - Impact on seals?
 - Impact on fuel injectors?

Workshop on Low Emission Diesel Engine Oils

Purpose

To craft a shared vision for
Industry-Government (DOE)
R&D collaboration in diesel engine oils
to minimize emissions, while maintaining
or enhancing engine performance.

R&D Needs for Low Emission Diesel Engine Oils

*Within the context of improving energy
efficiency and reducing emissions
of the vehicle as a system*

what are the high priority R&D opportunities
in diesel engine lubricating oils
for Industry/Government collaboration?

OHVT Budget by Activities

	FY 1996	FY 1997	FY1998	FY1999	FY2000
		Appropriation			
		(In Millions)			
Vehicle Technologies R&D					
Advanced Combustion Engine R&D					
♦ Combustion and Aftertreatment R&D	1.95	1.5	1.8	3.4	3.147
♦ Light Truck Engine	--	5.6	9.4	14.8	18.0
♦ Heavy Truck Engine	3.45	--	--	--	5.0
Heavy Vehicle Systems R&D					
♦ Hybrid Systems R&D	--	--	1.7	1.5	3.0
♦ Heavy Vehicle Propulsion Systems	--	--	--	--	4.0
Fuels Utilization R&D					
Advanced Petroleum Based Fuels					
♦ Heavy Trucks	0.0	0.0	2.4	2.7	4.0
Alternative Fuels					
♦ Heavy Trucks	9.3	12.4	3.765	3.27	4.3
♦ Medium Trucks	0.0	0.0	6.31	4.7	4.3
♦ Fueling Infrastructure	0.0	0.0	0.0	0.2	2.0
Transportation Materials Technologies					
Propulsion Materials Technology					
♦ Heavy Vehicle Propulsion System Materials	8.0	5.0	4.95	5.3	6.05
Lightweight Materials Technology					
♦ High Strength Weight Reduction Materials	2.5	2.8	3.1	4.2	5.95
High Temperature Materials Laboratory	5.2	4.7	5.2	5.5	8.5
TOTAL Heavy Vehicle Technologies	30.4	32.0	38.625	45.57	68.247

Summary

- ♦ Commercial truck highway transportation energy use continues to grow both in the U.S. and the world.
- ♦ EPA/DOJ Consent Decree may exact unacceptably high fuel consumption penalties for heavy-duty truck owners and operators.
- ♦ There are some serious engine lubricating oil concerns as emissions control strategies tend toward catalytic exhaust aftertreatment.
- ♦ An early consensus on high priority opportunities for Government/industry collaboration in diesel engine lubricating oil R&D could lead to more timely solutions to heavy vehicle emissions and fuel efficiency challenges.

Flat Emissions Map

Compliance Over Wider Range of Engine Operating Conditions

THE DIESEL ENGINE CHALLENGE

Dr. Rodica A. Baranescu

Chief Engineer, Engine Group

International Truck and Engine Corporation

USDOE/NREL Workshop

EXPLORING LOW EMISSIONS DIESEL ENGINE OILS

Scottsdale, Arizona, January 30 - February 1, 2000

Outline

- § Introduction
- § Requirements for State-of-the-Art Engine
- § Benefits and Challenges of Diesels
- § Progress in Reducing Diesel Emissions
- § Emission Challenges beyond 2000
- § Further Development (System Approach)
- § Clean Fuel - Technology Enabler
- § Conclusions

REQUIREMENTS FOR THE STATE-OF-THE ART ENGINE

Diesel Engine Benefits

- § **Energy Use**
- § **Fuel Efficiency and CO₂ Emissions**
- § **Durability and Reliability**
- § **Safe Fuel Handling**

Diesel Engine Challenges

- § Benchmark against Gasoline Engine
- § NOx Emissions Profile
- § Particulate Emissions
- § Nox/Particulate Trade-off

Progress In Reducing HD Truck PM Emissions

Technology Trail

Progress in Reducing HD Truck NOx Emissions

EPA Proposal Adds Stringency to 2004 Regulation

- § Requires compliance over a wider range of ambient conditions
- § Requires Compliance over a wider range of engine operating conditions
- § Requires Not To Exceed Limits
(Flatter Emissions Maps)

Compliance Over Wider Range of Ambient Conditions

- § No timing compensations for temperatures over 55°F
- § No timing compensations for altitudes below 5 500 ft contrary to current practices.

Flat Emissions Map

Compliance Over Wider Range of Engine Operating Conditions

High Pressure Fuel Common Rail Comparison System Schematic

NO_x Reduction as a Function Of EGR

Evolution Of Electronic Controls

Message:

Engine Industry is working diligently to develop cost-effective 2004 complying engines that will provide the performance and durability that meets our customer needs.

Critical Questions Concerning 2004 Engines

- § Fuel Economy?
- § Oil Drain Intervals?
- § Engine Durability?
- § Engine Costs?

Tier 2 Standards for LD Applications

- § Proposal affects Passenger Cars and LD trucks (under and over 6000 lb.)
- § 0.07 gr/mi Nox; 0.01g/mi Particulates (fleet average emissions)
- § gradual phase-in 2004-2007
- § Standards are fuel neutral
- § Proposal represents about 90% reduction in emissions from today's level

Engine System Development

- § Engine
- § Aftertreatment of exhaust
- § Fuel
- § Lubricant

Aftertreatment Options

- § Diesel Oxidation Catalysts
- § Diesel Particulate Filters
- § Non-Catalysed Particulate Filters w/
Fuel Borne Catalyst
- § Lean NO_x Catalyst
- § Selective Catalytic Reduction

The Barrier

§ 2004 Truck compliance

- HD problematic
- LD unlikely

§ Needs 30 ppm sulfur national fuel

The Breakthrough To The Next Level!

§ The development of adv. aftertreatment devices, (Lean NOx catalyst & NOx Adsorber)

§ We need ultra-low national sulfur fuel

§ Potential to achieve added 90% reduction of NOx & PM emissions

Why Breakthrough the Barrier?

- § Eliminate Health Concerns
- § Maximize Potential of “Green” Diesel Technology
- § Provide best overall value to Heavy-Duty & Light-Duty Customers

Impact of Fuel Sulfur on Aftertreatment

Impact of Fuel Sulfur

- § Sulfate Generation
- § Catalyst Inhibition
- § Catalyst Poisoning

Diesel Fuel Quality Sulfur Content

§ 30PPM Sulfur

- Required for Utilizing DeNOx Catalysts
- Required for Aggressive Oxidation Catalysts

§ 5PPM Sulfur

- Nox Adsorber
- Particulate Trap

Why A National Low Sulfur Diesel Fuel?

- § Reduces PM inventory by reducing SO₄ emissions from all diesels
- § Enables the introduction of advanced aftertreatment devices

Navistar Supports

- § Fuel Neutral Standards
 - Subject to Clean Fuel Availability
- § Phased Approach to Reducing Emission of NO_x and Particulates
 - Technology Advancements of Base Engine
 - Leverage of Catalytic Aftertreatment
 - Sulfur Reduction in Fuel
 - Development of Adequate Lubricants

Conclusions

Conclusions

- § Diesel Emissions Regulations which are Challenging but Technologically Feasible will Drive Investment in Diesel Technology
- § Low Sulfur Fuel is a “Technology Enabler” which will Allow Diesels to meet Stringent Fuel Neutral Standards

Conclusions (cont'd)

- § Diesel is the only Technology that can Provide Short Term and Long Term Greenhouse Gas Benefits
- § Light Duty Diesel Technology will be Applicable to Heavy Duty Engines

Conclusions (cont'd)

- § Lubricant plays an Increasing Role in Catalytic Emission Control System. The Development of Advanced Lubricants Should be Pursued.

Conclusions (cont'd)

- § Diesel is the only Technology that can Provide Short Term and Long Term Greenhouse Gas Benefits
- § Light Duty Diesel Technology will be Applicable to Heavy Duty Engines

FUELS

ATTACHMENTS 5, 6,7 & 8

“Low Sulfur Diesel Fuel an Enabling Technology for Future Low Emitting Diesel Engines”. Paul Machiele of the U.S. EPA, Ann Arbor, MI

“Fuel Formulations” Brent Bailey, Coordinating Research Council, Atlanta, GA

“Renewable Diesel Fuels” K. Shaine Tyson, Renewable Diesel Project, National Renewable Energy Laboratory, Golden, CO

“PSU Fuel Additive Program” André L. Boehman, Assistant Professor of Fuel Science and Director of the Combustion Laboratory, The Energy Institute, The Pennsylvania State University, University Park, PA 16802

Low Sulfur Diesel Fuel an Enabling Technology for Future Low Emitting Diesel Engines

Paul Machiele
U.S. EPA

DOE/NREL Workshop
Exploring Low Emission Diesel Engine Oils

January 31, 2000
Scottsdale, AZ

Diesel Popularity

- Diesel sales now top a million a year
- 4% annual growth in diesel truck-miles since mid-80's
- Nonroad applications proliferating
- Dieselization trend to smaller engines continues:
 - Industry preparing to introduce new models for light-duty truck market

Diesels and Air Quality

Rapid progress in emissions control BUT...

- NOx and PM inventories still large
- Diesel PM increasingly of concern:
 - Fine PM (~all diesel PM is <2.5 microns)
 - Air toxics (cancer, other respiratory effects)
 - Localized high concentrations

Increasing number and use of diesel vehicles and equipment

Increasing concern over emissions from diesel engines

Pressure to do everything to minimize emissions from diesel

“Reconcile the diesel engine with the environment”

Highway Diesels: Phase 1

Proposal Last Fall:

- Affirms 2 g/hp-hr NO_x for 2004 diesels
- Codifies consent decree (in-use control) requirements for all diesel manufacturers

Highway Diesels: Phase 2

- Control focus is shifting to aftertreatment (PM traps, NO_x adsorbers)
- Potential for 90%+ emission reductions in NO_x, PM, and HCs -- gasoline-like levels
- Magnitude of control similar to auto's in 70's

Heavy-Duty PM Standards

Heavy-Duty NOx Standards

Pressure to Reduce Engine Oil Ash

- Inorganic ash from engine oils
 - is captured by the diesel particulate filter
 - builds up over time
 - Requires periodic maintenance
- High oil ash will cause more frequent PM filter maintenance intervals

More Flexibility on TBN

- Sulfur in diesel fuel contributes to acidification of engine lubricating oils
- Lower sulfur diesel fuel should simplify TBN control

What does this mean for Diesel Engine Lubricating Oils?

Pressure to Reduce Engine Oil Sulfur Concentration

Sulfur in engine oil raises similar issues as sulfur in diesel fuel

Assuming:

- 1oz Oil consumption per 100 lbm fuel consumption
- an average oil sulfur level of 5,000 ppm
- Is equivalent to ~3 ppm S in the fuel
- Could be much higher

Regulating the Fuel and Vehicle as a Single System

- Past rulemakings: separate fuel and vehicle programs
- Sulfur impact on diesel aftertreatment requires a systems approach:
 - Ultra-low sulfur diesel fuel by mid-2006...
 - ... in time for new standards in 2007

Why Sulfur Alone?

Some Preliminary Data On Fuel Effects

Barrier is Sulfur

Impact of Sulfur: NOx Adsorbers

- Sulfur
 - “blocks” NOx storage sites
 - reduces NOx conversion efficiency
 - leads to a sulfur removal fuel penalty

Impact of Sulfur: Catalyzed Diesel Particulate Filters

- Sulfur
 - is converted to PM (hydrated sulfuric acid)
 - inhibits filter regeneration
(DECSE: sulfur increase from 3 to 30 ppm
increases balance point 25°C)

NO_x Adsorber Catalyst

Rich (HC injection) Phase:

A Catalytic PM Trap Cell

A Continuously Regenerating PM Trap Cell

Barrier is Sulfur

What Does This Mean?

- EPA anticipates that these 2007 standards will lead to a new generation of engine oils
 - Lower sulfur content of oil
 - Low ash oils
 - TBN?
- We anticipate as in the past that industry will rise to this challenge

Fuel Formulations

Brent K. Bailey
Coordinating Research Council

Session VI - Emerging Issues
U.S. DOE/NREL Workshop on:
"Exploring Low Emission Diesel Engine Oils"

Holiday Inn Sunspree Resort
Scottsdale, Arizona
January 31-February 1, 2000

Introduction

- Over 100 years of diesel engine lubricant development
- Engine, fuel, and lubricant development are interdependent
- ◊ Fuel/Engine/Lubricant system gradual continuous improvement
- ◊ Future systems could experience a step change

Interdependency

" . . . Satisfactory oil under one set of conditions may be unsatisfactory in the same engine under another set of conditions. This emphasizes the necessity for matching these four factors: oil, fuel, engine design, and conditions."

Development of CER Oil Test Engine
CRC Report No. 301 June 1955

Background

- ◆ Fuel composition impacts lubricant formulation
 - Lubricant exposed to unburned fuel
 - Lubricant exposed to fuel combustion products
- ◆ Future fuel composition uncertain

Presentation Overview

Brief history of fuel development in last century

Current research fuel formulations

Future fuel composition

The first advanced fuel from last century -- 1903

- Fuel distilled from Pennsylvania crude oil
- Octane number estimated to be 38
- Half gallon, gravity feed fuel tank
- Wright brother's engine 4.4:1 CR; fixed 1200 rpm

Early Fuel Research

- Detonation discovered by Gibson 1915
- TEL discovered 1921 by Midgley & Boyd
- Ricardo explains detonation 1923
- Waukesha CFR engine 1929
- ◆ U.S. Army Air Corps Flight Testing 1935
 - 30% power increase
 - 40% increase in rate of climb
- ◆ British decide to modify all engines 1937

Results of Technical Cooperation -- The Battle of Britain*

"The RAF fighters, outnumbered almost three to one by the Luftwaffe, won the Battle of Britain by a narrow margin . . . Had the Luftwaffe gained control of the air . . . the then vastly superior German military forces could probably have invaded England successfully. With Britain occupied, it is difficult to conceive how a subsequent invasion of Europe could have been accomplished. . . ." *Ogston, SAE 810848

A Century of Cooperative Research in Review

- Cooperative Fuel Research Comm., 1922
- War Dept. Comm. 100 Octane Fuel, 1935
- Coordinating Research Council, 1942
- CLR Oil Test Engine Group, 1950
- Octane race, ca. 1950s - 60s
- Cat. converters and unleaded, ca. 1970
- PFI deposit control, ca. 1985
- The Auto/Oil Program, 1989-1997

Selected Diesel Fuel Formulation Research

- CRC Report #120 "Investigation of High and Low Sulfur Diesel Fuels" 1945
- CRC Report #507 "Diesel Exhaust Odor Analysis System (DOAS)" 1979
- CRC Project #CAPE-32-80, "Effects of Fuels and Engine Variables on Light-Duty Diesel Engine Emissions" 1985
- CRC Project #VE-1, "Evaluation of Fuel and Engine Variables on Heavy-Duty Diesel Engine Emissions" 1990
- CRC Project #VE-10, "Effects of Fuel Oxygenates, Cetane Number, and Aromatic Content on Emissions from Low-Emission Heavy-Duty Diesel Engines" 1995
- SAE Paper #972966, "Influence of Future Fuel Formulations on Diesel Engine Emissions - A Joint European Study" 1997
- SAE Paper #981357, "Emissions Comparison of Alternative Fuels in an Advanced Automotive Diesel Engine" 1998

Recent PNGV Test Fuels Evaluated on a Daimler-Benz OM11 Engine

2D - EPA 2-D Certification Diesel Fuel

CARB - "Pseudo"-CARB

LS - Ultra Low Sulfur

◇ FT100 - Fischer Tropsch Synthetic Diesel

◇ FT20 - 20% FT Synthetic Diesel in LS

◇ B20 - 20% Biodiesel in LS

◇ DMM15 - 15% DMM in LS

Test Fuels

Fuel Code

Fuel

2D

EPA 2-D Certification Diesel

CARB

"Pseudo"-CARB

LS

Ultra Low Sulfur

FT100

Synthetic Diesel (Fischer-Tropsch Process)

FT20

20% Synthetic Diesel in LS

B20

20% Biodiesel in LS

DMM15

15% DMM in LS

Fuel Properties

Property	Units	ASTM Method	Baseline Fuel (2D)	California Diesel (CARB)	Low-Sulfur Diesel (LS)	Synthetic Diesel (FT100)	Blodiesel Blend (B20)	Synthetic Diesel Blend (FT20)	DMM Blend (DMM15)
Density @ 15°C	g/mL	D 4052	0.849	0.831	0.811	0.781	0.826	0.806	0.817
Distillation		D 86							
IBP	°C		194	194	241	215	241	238	42
10%	°C		224	217	246	258	249	247	61
50%	°C		265	249	251	289	259	255	249
90%	°C		312	285	261	325	329	281	259
95%	°C		328	318	266	332	339	301	262
End Point	°C		344	344	285	337	347	322	281
Cetane Number		D 613	46	45	67	84	65	79	63
Aromatics	vol. %	D 5186	33.3	8.9	1.2	0.2	0.6	0.6	0.7
Flash Point	°C	D 93	74	69	101	98	104	100	< 9
Kin. Viscosity, 40°C	cSt	D 445	2.71	2.42	2.41	3.21	2.64	2.55	1.49
Carbon	mass %	D 5291	86.6	86	85.6	84.8	83.7	85.3	80.8
Hydrogen	mass %	D 5291	13.4	13.9	14.4	15.1	14.0	14.6	14.0
Oxygen	mass % difference		0.0	0.1	0.0	0.1	2.3	0.1	5.2
Sulfur	ppm	D 2622	340	300	< 10	< 10	< 10	< 10	< 10
Nitrogen		D 4629	97.0	7.3	7.6	7.8	7.4	7.7	7.3
Net Heat of Comb.	MJ/kg	D 240	42.9	43.1	43.4	43.9	42.1	43.5	40.4

Range of Fuel Properties Tested

- ◆ Density, g/mL: 0.849 to 0.781
- ◆ IBP, deg C: 194 to 42 (241)
- ◆ EP, deg C: 344 to 281 (347)
- ◆ Cetane No.: 46 to 84 (45)
- ◆ Aromatics, vol%: 33 to 0.2
- ◆ Hydrogen, wt%: 13.4 to 15.1
- ◆ Oxygen, wt%: 0.0 to 5.2
- ◆ Sulfur, ppm: 340 to < 10
- ◆ Net Heat of Combustion, MJ/kg: 42.9 to 43.9

Comparison of Average HC Emissions

Comparison of Average CO Emissions

Equally weighted average of 13 modes

Average Particulate Size Distribution

Particulate Emissions Correlated with Hydrogen/Carbon Ratio

Fuel/Lubricant/Engine Interactions

- Significant differences in fuel composition
 - Fuel/lubricant compatibility
 - Lubricant performance requirements
- Emission benefits in unmodified engine
 - Lubricant benefits possible in formulation
 - Direct lubricant emissions become significant

New Drivers for Fuel Change

- ◆ EPA emissions standards
- ◆ Energy efficiency
- ◆ Resource availability
- ◆ New technology developments

The Process for Change Historically Established

- ◆ Continuous improvement path?
 - Engine and emission control systems modified
 - Fuels modified for improved systems
 - Lubricants modified for improved systems
- ◆ Step change in technology?
 - Coordinated industry/government development
 - Joint systems development for optimal performance

Alternative Diesel Fuels

K. Shaine Tyson

National Renewable Energy Laboratory

DOE Office and Program Structure

Alt. Diesel Fuels Feedstocks

- Coal
 - Natural gas
 - Electricity
 - Biomass
 - All of the above could allow a transition to renewable fuels
-
- Natural gas/biogas
 - Electricity
 - Hydrogen
 - Ethanol/methanol
 - Fischer-Tropsch
 - Biodiesel
 - DMM, DEE, DME,

Transition Approach

- Track the development of ADF engine and vehicles
- Identify fuels, current feedstocks, supply issues
 - Identify where renewable fuels can augment traditional fuel supplies
 - Identify where renewable fuels can play significant long-term roles
- Target R&D priorities for ADF

ADF Success Factors

- Able to compete in a non-crisis environment
 - Sizable supply base
 - Public benefits
 - Appropriate engine/vehicle technology
 - Public acceptance
 - Good fit with application
-
- Unable to predict which fuel(s) may dominate future markets at this time

ADF Categories

• Liquid fuels that do not require engine or vehicle modifications

- Liquid fuels requiring modified or unique engines and vehicles
- Gaseous fuels
- Electricity
- Hydrogen fuels

ADF for Existing CI Engines

- Intuitively attractive
 - no new engine or vehicle purchases
 - no new infrastructure requirements
 - large immediate market potential - near term benefits
 - consumer flexibility
 - transitions from blends to pure in the future
 - useful in crises situations - put in existing vehicles
 - driven by perceived benefits
 - “stretches out petroleum supplies”
 - consumer may be unaware of changes

Drivers for ADFs in Diesel Mkt

- Improve on diesel fuel characteristics
 - Improve lubricity or cold flow properties
 - Increase Cetane number
 - Reduce aromatics and sulfur
 - Reduce regulated emissions (NO_x & PM) ←
 - Reduce smell or air toxics
 - Improve fuel efficiency or performance
 - Reduce cost
- Global warming, Fuel diversity & Energy security not monetarized

ADF Fuel Requirements

- Improved Emissions
- No phase separation in presence of
 - water, metal catalysts, etc.
- Good stability
- No undesirable fuel-fuel interactions
 - or material compatibility problems
- Long-term field performance record
- Reasonable cost for performance
- Properties within ranges set by ASTM D 975
 - either blended or pure

Pure ADF for Existing Engines

- Neat Fuels
 - Fischer - Tropsch Diesel
 - Biodiesel
- Others may exist but not evaluated yet

Fischer-Tropsch

Conventional 3-Step Approach

Biodiesel

Pure Fuel Properties

	<u>Diesel</u>	<u>Biodiesel</u>	<u>Fischer</u> <u>Tropsch</u>
Fuel Standard	ASTM D975	ASTM PS 121	n/a
Fuel composition	C10-C21 HC	C12-C22 FAME	C_nH_{2n+2}
Lower Heating Value, Btu/lb	130,250	120,910	121,300
Kin. Viscosity, @ 40 °C	1.3-4.1	1.9-6.0	3.21-3.57
Specific Gravity kg/l @ 60 °F	0.85	0.88	0.783
Density, lb/gal @ 15°C	7.079	7.328	6.52
Water, ppm by wt	161	.05% max	
Carbon, wt %	87	77	85
Hydrogen, wt %	13	12	15
Oxygen, by dif. wt %	0	11	neg.
Sulfur, wt %	.05 max	0	<.001
Boiling Point			
°F	370-650	360-640	350-670
°C	188-343	182-338	177-354

Pure Fuel Properties

	<u>Diesel</u>	<u>Biodiesel</u>	<u>Fischer</u> <u>Tropsch</u>
Flash Point, °C	60-80	100-170	60-81
Cloud Point, °C	-15 to 5	-3 to 12	-23 to 8
Pour Point, °C	-35 to -15	-15 to 16	-20 to 11
Cetane Number	40-55	>48	>74
Autoignition Temperature			
°F	600		600
°C	316		316
Stoichiometric Air/Fuel Ratio, wt./wt.	15	13.8	15.2
Flammability Limits, Vol. % Rich	7.6		
Flammability Limits, Vol. % Lean	1.4		
RVP			
psi @ 100 °F	<0.2	n/a	n/a
kPa @ 37.8 °C	<1	n/a	n/a
BOCLE Scuff, grams	3,600	>7,000	1,700-2,300
HFRR, microns	685	314	

HD FTP Hot Start Emissions

	% Change from Diesel No. 2			
	PM	NOx	CO	HC
FT 1	-26.94	-9.12	-44.91	-46.06
FT 2	-31.90	-6.68	-47.48	-25.46
FT 3	-28.10	-9.13	-44.58	-41.26
FT 4	-13.33	-14.26	-38.89	-42.77
FT 5	-15.57	-6.50	-12.89	-8.74
FT 6	-37.00	-6.00	-27.00	-50.00
FT 7	-21.30	-27.94	-32.90	-59.09
FT 8	-22.74	-27.38	-34.20	-50.00
Average	-24.61	-13.38	-35.36	-40.42

Market Issues for FT

- Fischer-Tropsch
 - No domestic supplies, limited international supply
 - Price uncertainty, but premium value assured
 - No available field test info
 - Need ASTM standard or other
 - Material compatibility as a pure fuel
 - Cold weather issues
 - Higher value as a blend stock initially
 - Dedicated engines for FT with NOx/PM aftertreatment may provide higher emission benefits

Biodiesel HD FTP Emissions

B100	% Change from Diesel No. 2				Test
	PM	NOx	CO	HC	
Soy	-66.00	11.46	-46.99	-43.90	FTP Avg
Rape	-14.15	-2.52	-35.37	-63.33	FTP Avg
Rape	-24.53	3.43	-38.78	-70.00	FTP Avg
Grease	-78.09	2.81	-52.31	-100.00	FTP Hot
Grease	-74.31	4.46	-41.56	-45.27	FTP Hot
Tallow	-73.56	0.94	-44.14	-39.19	FTP Hot
Tallow	-74.69	1.92	-46.74	-31.08	FTP Hot
Lard	-73.94	1.29	-52.07	-25.00	FTP Hot
Canola	-70.92	10.41	-41.89	-32.09	FTP Hot
Soy	-69.40	13.69	-34.32	-23.98	FTP Hot
Soy	-28.30	13.13	-45.33	-95.65	FTP Avg
Soy	-49.02	11.33	-38.26	-83.33	FTP Avg
Soy	-36.72	4.26	-38.05	-74.19	FTP Avg
Grease	-42.50	4.36	-48.87	-61.20	FTP Hot
Avg	-55.44	5.78	-43.19	-56.30	

Market Issues for Biodiesel

- Biodiesel
 - Cost high but declining (\$1.30/gal 1/2000)
 - Material compatibility as pure fuels
 - NOx emissions need reducing
 - as fuel cost declines and market expands, "optimized" biodiesel engines may be developed
 - additive testing underway
 - Long term field experience
 - Cold weather issues
 - Dedicated engines for BD with a NOx/PM aftertreatment may provide higher emission benefits

ADF for Blends with Diesel

- **Fuel Blends**

- Fischer-Tropsch Diesel
- Biodiesel
- Methylal
- Diethyl ethers
- Ethanol

- **Blend Benefits**

- reduce material compatibility concerns
- Reduce impact of “poor” fuel properties
- Reduce impact of cost
- Meet diesel emission goals
- Meet diesel fuel quality goals
 - Cetane
 - Lubricity
 - Lower S and aromatics

ADF Blend Issues

- “Optimal” blend levels not well established
 - depend on objectives & tradeoffs
- Data on blended fuel properties scarce
 - Emissions data
 - Properties of blended fuels
- Fuel supply issues vague
- EPA 211(b) Health Effects and “Sub Sim” regs may add substantial costs

FT Blends - Emission Data

% FT	% Change from Diesel No. 2				Test
	PM	NOx	CO	HC	
20	-27	-6	-20	-42	13 M avg
50	-9.84	-5.48	-5.89	-10.76	FTP Hot
30	0.36	-12.48	-17.23	-40.91	FTP Hot
50	-4.33	-18.87	-24.28	-50.00	FTP Hot
80	-13.00	-24.82	-31.59	-59.09	FTP Hot

Biodiesel Blends - Emissions

% BD	% Change from Diesel No. 2				Test
	PM	NOx	CO	HC	
5 Soy	-4.40	0.65	-8.03	0.00	FTP Hot
10 Soy	-10.30	2.06	0.00	-10.34	FTP Avg
20 Soy	-14.91	3.16	-3.64	-18.97	FTP Avg
20 Soy	-24.60	3.04	-17.79	-11.69	FTP Hot
20 Soy	-3.77	4.16	-14.67	-17.39	FTP Avg
20 Soy	-13.73	3.56	-7.38	0.00	FTP Avg
20 Soy	-14.84	1.91	-21.46	-32.26	FTP Avg
20 Soy	-9.09	-0.85	-9.29	25.00	FTP Hot
20 Soy	-9.39	2.48	-15.88	-7.87	FTP Avg
20 Soy	-13.67	1.14	-7.11	-12.80	FTP Avg
20 Soy	-17.12	-3.99	-18.77	-20.83	FTP Avg
20 Soy	-16.52	0.51	-5.12	14.53	FTP Hot
20 Soy	-32.00	0.00	-20.00	-31.00	13 mode avg
20 Grease	-59.17	1.68	-34.16	-4.35	FTP Hot
20 Grease	-13.50	2.29	0.72	-5.74	FTP Hot
20 Tallow	-10.86	-2.03	-2.54	-30.06	FTP Hot
35 Soy	-26.00	0.97	-17.72	-9.76	FTP Avg
50 Grease	-31.67	-0.09	-38.95	-29.77	FTP Hot
50 Rape	-13.21	-2.75	-29.93	-43.33	FTP Avg
50 Rape	-17.92	-1.60	-34.01	-46.67	FTP Avg
65 Soy	-45.00	4.60	-28.71	-26.83	FTP Avg
B20 Average	-18.08	1.22	-12.65	-10.96	

Fuel Property Data

	Diesel	Methylal	DEE	Ethanol
Fuel Standard	ASTM D975	n/a	n/a	n/a
Fuel composition	C10-C21 HC	CH ₃ OCH ₂ OCH ₃	C ₂ H ₅ OC ₂ H ₅	C ₂ H ₅ O
Lower Heating Value, Btu/lb	130,250	73,067	86,521	76,00
Kin. Viscosity, @ 40 °C	1.3-4.1	0.33	0.23 (68°C)	
Specific Gravity kg/l @ 60 °F	0.85	0.86	0.714	0.794
Density, lb/gal @ 15°C	7.079	8.33	5.946	6.612
Water, ppm by wt	161	773		
Carbon, wt %	87	47.37	52	
Hydrogen, wt %	13	10.13	13	
Oxygen, by dif. wt %	0	42.5	35	
Sulfur, wt %	.05 max	0	0	
Boiling Point				
°F	370-650	107	94	172
°C	188-343	42	34	

Fuel Property Data

	Diesel	Methylal	DEE	Ethanol
Flash Point, °C	60-80	-28	-49	
Cloud Point, °C	-15 to 5	<-52	very low	
Pour Point, °C	-35 to -15	very low	very low	
Cetane Number	40-55	24	55-60 to 125	<5
Autoignition Temperature				
°F	600	459	320	793
°C	316	228-237	160	
Stoichiometric Air/Fuel Ratio, wt/wt.	15	7.1	11.1	9
Flammability Limits, Vol. % Rich	7.6	14.9	36	19
Flammability Limits, Vol. % Lean	1.4	3.3	1.9	4.3
RVP				
psi @ 100 °F	<0.2	12.2	9-16	2.3
kPa @ 37.8 °C	<1	84-86	110	
BOCLE Scuff, grams	3,600			
HFRR, microns	685	700	810	

DMM Blends - Emission Data

% DMM	PM	% Change from Diesel No. 2			Test Procedure
		NOx	CO	HC	
5	-5.08	-7.29	-9.22	40.82	9 mode avg SS
10	-13.56	-6.56	2.31	38.10	9 mode avg SS
15	-52	-4	-36	-24	13 mode avg. SS
20	-27.12	-4.94	19.40	32.65	9 mode avg SS
30	-25.42	-11.88	59.65	68.71	9 mode avg SS

DEE Blends - Emission Data

% DEE	PM	% Change from Diesel No. 2			
		NOx	CO	HC	
5	10.17	-5.59	-2.21	11.56	9 mode avg SS
10	-11.86	-1.32	1.63	29.93	9 mode avg SS
20	-16.95	-3.54	11.91	89.12	9 mode avg SS
30	-23.73	-8.56	26.03	118.37	9 mode avg SS
50	17.39	-40.12	47.61	128.86	Pt. SS, 1500 rpm
50	-30.91	-26.23	90.70	166.67	FTP Hot

"Oxydiesel"* Emission Data

Percentage change in Emissions

	10% Ethanol	15% Ethanol
CO	-20	-27
NOx	-4	-5
PM	-27	-41
HC	+71	+110

***Ethanol + emulsifier + Cetane improvers + diesel fuel**

Summary

- Current List a beginning
- ADF may be viewed as "new" or "expanded" diesel capacity
- ADF provides flexibility when reformulating diesel fuel
 - lower aromatics & sulfur, higher Cetane & lubricity
- Blending can occur down stream or upstream

Summary

- Cities and States very interested in blends
 - air quality concerns
- Emission benefits equate to price premium
- FT and BD leading the way
- Customers appear to like blended fuels
 - no new vehicle or infrastructure expense
 - no new ES&H or training issues with FT or BD
 - “Seamless” transition for consumer
 - distributor has burden of learning curve

Conclusions

- Unresolved issues remain:
 - Monitor material compatibility
 - Monitor fuel oil interactions
 - Need more field experience
 - Need fuel standards
 - for pure fuels and/or for the blended products
 - Need standardizing testing for new products
 - streamlining and cost reduction issues
 - Need more sophisticated engine-fuel sensors and computer mapping

INCORPORATING OXYGEN IN DIESEL FUEL AS A MEANS OF REDUCING ENGINE EMISSIONS

Howard Hess, Shirish Bhide, Elana Chapman,
William Greenland, James Szybist, Brice O and André Boehman

Department of Energy and Geo-Environmental Engineering
The Combustion Laboratory of the Penn State Energy Institute
College of Earth and Mineral Sciences
The Pennsylvania State University

Incorporating Oxygen in Diesel Fuel

Sponsors

- Air Products and Chemicals, Inc.
- Pennsylvania Department of Environmental Protection
- Federal Energy Technology Center
- General Motors Powertrain Division
- Navistar International
- Cummins Engine Company
- Texaco Additives, Inc.
- Mobil Oil Company
- Volkswagen AG
- Champion Motor Coach
- PACCAR (Peterbilt-Kenworth)
- Lubrizol
- Ethyl Additives
- DuPont

Engine and Emissions Equipment

- 400 Hp Eddy Current Dyno
- 250 Hp Eddy Current Dyno Being Installed
- 50 Hp Water-Brake Dyno
- Waukesha CFR Octane Rating Engine
- Refurbished Horiba On-Line Gas Analyzers and Sample Conditioners
- Nicolet Magna 550 FTIR Spectrometer
- HP 6890 GC with TCD and FID
- HP 5890 GC with FID
- Sierra Instruments BG-1 Micro Dilution Test Stand
- R&P Co. Inc. Series 5100 Diesel Particulate Analyzer
- California Analytical Hot-FID Analyzer
- Kistler Pressure Sensors and Crank Angle Encoders
- Navistar T444E, V-8, DI Turbodiesel with HEUI Fuel Injection
- Cummins B5.9, 6 Cyl., 24-valve, DI Turbodiesel with Electronic Controls
- Volkswagen 1.9L TDI, DI Turbodiesel
- Yanmar TS-180 Single-Cylinder IDI

Combustion Laboratory Single-Cylinder Engine Test Cell

Combustion Laboratory Multi-Cylinder Engine Test Cell

Effect of Oxygenated Cetane Improver on Diesel Engine Combustion and Emissions

A Proposal to the Strategic Alliance Committee

by

André L. Boehman and Peter J.A. Tijm

Objectives

- **Examine Emissions and Combustion Behavior of Diesel Fuels Doped with Oxygenates**
- **Clarify the Effects of an Oxygenate with High Cetane Number**
- **Study Both Emissions Reductions and Combustion Behavior by Sampling the Exhaust and Monitoring In-Cylinder Pressure**

Benefits of CetanerTM

- Development of Transportation Fuel Additives from Synthesis Gas
 - Complies with US DoE Federal Energy Technology Center "Vision 21" Mission - Cleaner and More Efficient Use of Coal
 - Producing Cetane Enhancers from Inexpensive Feedstocks
 - Projected to Have a Cost Equal to Diesel Fuel

Comparison of Some Oxygenated Fuel Additives

Property	Chemical formula	Cetane Number	Characteristics
Diesel	$C_{15}H_{32}$	40-55	base fuel, tendency to soot and form NO_x during the diesel combustion process due to chemical and physical properties
Diethyl Ether (DEE)	$C_4H_{10}O$	55-60	gas, unstable fuel, offers minimal improvement to cetane number
Dimethyl Ether (DME)	CH_3OCH_3	55-60	gas, not readily mixed with diesel fuel, offers minimal improvement to cetane number
Dimethoxy Methane (Methylal, DSM)	$CH_3(OCH_3)_2$	55-60	liquid, boils at 50° C
Methyl tert-butyl ether (MTBE)	$CH_3OC(CH_3)_3$	< 5	liquid, negative impact on cetane number, potential carcinogen that is showing up in California water reservoirs because of its use in reformulated gasoline
Methanol	CH_3OH	5	liquid, high octane number, difficult to autoignite, low solubility in diesel fuel
Cetaser	mixture	60-125	liquid, high cetane number, soluble in diesel fuel, mixture of dimethoxymethane (DMM), 1,2-dimethoxyethane (DMET) and methanol

Yanmar TS180 Single-Cylinder IDI Diesel Engine in the 50 hp Test Cell

Oxygenate Blends Evaluated

Oxygenate Blended	Structure	Notation	Wt% oxygen	Blend Ratio
diethylene glycol methyl ether	$\text{CH}_3\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$	DGME	40.0	10/90
Triethylene glycol dimethyl ether	$\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_3\text{CH}_3$	Triglyme	36.0	11/89
Diethylene glycol dimethyl ether	$\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_2\text{CH}_3$	Diglyme	35.8	11/89
1,2-dimethoxyethane	$\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_1\text{CH}_3$	Glyme	35.6	11/89
CETANER™ *		CETANER™	36.5	11/89
96% Glyme	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$		(35.6)	
4% dimethoxymethane	$\text{CH}_3\text{OCH}_2\text{OCH}_3$		(59.3)	
Methyl Soyate	Mixed esters	Me Soyate	11.0	35/65

*Simplified mixture chosen to represent a potential CETANER™ formulation.

Oxygenated Fuel Properties

Oxygenate Blend Tested	Saybolt Viscosity (SUS), 100°F	Gravity (°API)	Cloud Point (°F)	Flash Point (°F)	Heat of Combustion (BTU/lb)
ASTM Specification	32.6-40.1	Min 30	Max 0	Min 125	-----
Premium Diesel Fuel	34.8	45	<0	160	19,707
DGME	35.7	41	<0	157	19,118
Triglyme	32.3	44	<0	173	18,909
Diglyme	34.0	51	<0	147	18,856
Glyme	32.0	48	<0	<67	18,613
CETANER™	34.3	45	<0	<67	18,867
Methyl Soyate	41.4	43	8	180	18,793

Total Brake-Specific Particulate Emissions, g/kWhr

Oxygenate Fuel Blend Evaluated	% wt Oxygen In Blend	BS PM, g/kWhr	% Reduction from Baseline (*)
Premium Diesel Fuel	—	0.728	—
DGME	4.12	0.661	9.3 ± 8.2%
Triglyme	3.96	0.607	16.6 ± 5.3%
Diglyme	3.94	0.511	29.8 ± 6.8%
Glyme	3.97	0.512	29.7 ± 7.0%
CETANER™	4.00	0.524	28.0 ± 5.8%
Methyl Soyate	3.88	0.539	26.0 ± 8.1%

* Error range based upon 95% Confidence Interval.

Specific Fuel Consumption

Specific Energy Consumption

Specific CO Emissions

Specific NOx Emissions

Total Particulate Emissions

VW 1.9L TDI Turbo Diesel Engine Multi-Cylinder Engine Test Cell

TDI Testing Protocol

	Mode 1	Mode 2	Mode 3	Mode 4	Mode 5	Mode 6
Speed (RPM)	3500	3000	2700	2400	2100	1800
% rated speed	100%	85.7%	75%	68.6%	60%	51.4%
Power (hp)	36	30	25	20	15	10
% rated Power	85.6%	71.4%	59.5%	47.6%	35.7%	23.8%
Torque (ft-lb)	55.70	52.52	48.63	43.71	37.51	30.89
Torque (mV)	138.2	130.3	120.7	108.6	93.1	76.7

Engine Test Matrix
VW L5 L TDI

Total Brake-Specific Particulate Emissions, g/kWhr

Brake-Specific NO_x Emissions, g/kWhr

Conclusions

- Oxygenated blends can achieve up to ~30% particulate matter reduction in diesel fuels when blended at a level of 4% oxygen content
- There are significant differences between the effectiveness of different oxygenates - presumably due to molecular structure and accessibility to oxygen
- Specific Fuel Consumption increased for all the oxygenated fuel blends, but Specific Energy Consumption remained unchanged
- CETANER™ has demonstrable performance benefits over other oxygenated fuels

Impact of Molecular Structure

all oxygenates are not the same

Oxygenate Blended	Structure	Notation
Triethylene glycol dimethyl ether	$\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_3\text{CH}_3$	Triglyme
Diethylene glycol dimethyl ether	$\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})_2\text{CH}_3$	Diglyme
1,2-dimethoxyethane	$\text{CH}_3\text{O}(\text{C}_2\text{H}_4\text{O})\text{CH}_3$	Glyme
CETANER™	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$	CETANER™
20% Glyme		
80% Diglyme		
CETANER™ formulation for latest tests

Glyme

Diglyme

Triglyme

Future Work

- Complete VW IDI testing sequence
- Monitor combustion and heat release rates using Kistler pressure probe and AVL heat flux probe in a Yanmar single-cylinder engine
- Move to laboratory and field tests in commercial 3-cylinder engine

Reformulated Clean Burning Diesel Demonstration Program

Funded by
the South Coast Air Quality Management District

- Determine Engine Combustion and Emissions for Blends of Diesel Fuel and Cetaner in Medium-Heavy Duty Engine Application
 - Develop an Operational Database and Optimized Engine Parameters for Use of Cetaner in Medium-Heavy Duty Engine Applications
 - Verification of Laboratory Engine Performance Data Through On-Road Field Testing
- The Energy Institute
 - Air Products and Chemicals, Inc.
 - USA PRO
 - University of California - Berkeley
 - Cummins Engine Co.
 - PACCAR (Kenworth-Peterbilt)

Cummins 5.9L V-8 Turbodiesel in the 250 hp Test Cell

PM COMPARISON BY MODE

NOx COMPARISON BY MODE

Current Status

- Cummins B5.9 Engine Installed in the Test Cell and has been Operated on the AVL 8-Mode Test
- Cummins is Machining the Head for Pressure Probe Installation
- UC-Berkeley Testing is Ongoing
- Dodge Ram Truck Has Been Received by USA PRO from Chrysler Test Fleet for 18 Month Period
- Field Emissions Measurement Strategy Under Development with Assistance from Clean Air Technology and R&P Co.
- US EPA Supporting Collaborative Work with Our Field Emissions System

Development of a Dimethyl Ether (DME)-Fueled Shuttle Bus Demonstration Project

A Project Sponsored by the Pennsylvania
Department of Environmental Protection
with
Additional Support from the Federal Energy Technology Center

Air Products and Chemicals, Inc.
The Pennsylvania Transportation Institute
and
The Energy Institute at Penn State

Objectives

- **Determine the Emissions and Combustion Performance for DME-Diesel Fuel Blends**
- **Determine Injection System Durability Criteria for Use of DME-Diesel Blends**
- **Determine the Viscosity and Bulk Modulus of DME-Diesel Blends**
- **Develop Protocol for DME Fueling Based on Fuel Blends**
- **Detailed Speciation of Particulate Matter**
 - Said to be smokeless, but perhaps not under all conditions
- **How Much DME is Optimal?**
- **Demonstrate DME-Diesel Fueling in a Campus Shuttle and Operate the Shuttle on DME-Diesel**

Research Plan Blending and Additives

- **Combine Lubricity Studies with Engine Combustion Studies**
- **Prior to Running DME/Diesel Blends; Examine Their Phase Behavior, Viscosity, Compressibility and Wear Rate Characteristics**
- **Protect Fuel Injectors and Pump by Anticipating Fuel Mixtures that will Lead to Excessive Wear**
- **Examine Several Lubricity Additives: Lubrizol, Ethyl and Methyl Soyate**

High Pressure Viscometer

High Pressure Viscometer Initial Determination of Viscometer Constant

Navistar T444E V-8 Turbodiesel in the 400 hp Test Cell

CAM Encoder Mounted on Navistar T444E V-8 Turbodiesel

Current Status

- Navistar Engine Acquired and Installed in the Test Cell
- Engine Dressed with Help from Allegheny Truck and Navistar
- Pressure Sensor and Crank Angle Marker Operational
- High Pressure Viscometer Operational for Measurements of Viscosity and Bulk Modulus of DME-Diesel Blends
- Penn State Fleet Services Has Acquired the Champion "Defender" Shuttle Bus
- PTI has Performed Emissions, Performance and Efficiency Tests on the Shuttle Bus on Diesel Fuel
- DME/Diesel Fuel Delivery System Under Construction

Acknowledgement

- Peter Tijm, Fran Waller, Bob Quinn of Air Products and the Strategic Alliance Committee
- Mike Nowak and John Winslow of DoE/FETC
- Susan Summers of PA/DEP
- Fred Minassian and Cindy Sullivan of SCAQMD
- Pranab Das, X. Gui, David Schuh and Len Stanley of Navistar
- Vinod Duggal and Peter Woon of Cummins
- Rafal Sobotowski of BP Oil Company (now with Cummins Engine Company)
- Gib Jersey of Mobil Oil Company
- Tony Zarger of GM Powertrain
- Bill Buscher formerly of Texaco Inc.
- Allen Aradi of Ethyl Additives, Inc.
- John Lueszler, DuPont

CATALYSTS/TRAPS/AFTERTREATMENT

ATTACHMENTS 9, 10, 11 & 12

“Diesel Emission Catalysts and Filters”, Dale McKinnon, MECA , Washington, DC

“Post-Combustion Emission Control Devices For Diesel Applications”, Magdi Khair,
Southwest Research Institute, San Antonio, TX

“Sample Analytical Tools For Diesel Catalyst/Lube Oil Additive Studies”, Magdi Khair,
Southwest Research Institute, San Antonio, TX

“Diesel Emission Controls : NO_x and Particulate” , John H. Johnson, Presidential
Professor, Michigan Technological University, Houghton, MI

Lubricants and Advanced Integrated Exhaust Emission Control Technologies

Manufacturers of Emission Controls Association

Exploring Low Emission Diesel Engine Oils

USDOE/NREL Workshop

January 30 – February 1 2000

Presentation Outline

- Introduction
- Background
- Diesel Emission Control Technologies
- Deactivation Mechanisms
- Lubricant Considerations
- Conclusions

Existing Technologies Provide Many Options and Emerging Technologies Show Much Promise

Existing Exhaust Emission Controls:

- Oxidation Catalysts
- Diesel Particulate Filters

Advanced Emission Control Technologies

- NOx Catalysts
- SCR
- NOx Adsorbers
- Plasma Technology
- Combined Systems

MECA

Diesel Oxidation Catalysts

Oxidation Catalysts Oxidize CO, HC, and SOF to Reduce PM, CO, HC, and Toxic Emissions.

MECA

Diesel Oxidation Catalysts Are Efficient and Have Excellent Operating Experience

Oxidation Catalyst Control Capabilities

PM -- 20-50% Reduction

CO and HC -- >90%

Toxic HCs -- >70%

Oxidation Catalyst Operating Experience

>5,000,000 Light-Duty Vehicles in Europe

>1.5 Million HDEs in the U.S.

>250,000 Nonroad Engines

MECA

Diesel Particulate Filters Address Most Controlled Emissions

Diesel Particulate Filters Trap Carbon and Adsorbed SOF and Can Be Used to Oxidize CO, and HC to Reduce PM, CO, HC, and Toxic Emissions.

MECA

Diesel Particulate Filters Are Efficient and Are Developing an Impressive Track Record

Filter Control Capabilities

PM -- >80% Reduction

CO and HC -- >90%

Toxic HCs -- >90% Reduction

Based Filter Operating Experience

- Several Thousand Trucks and Buses in Commercial, Retrofit Operation in Europe
- Peugeot Will Offer Filter-Equipped LDVs in 2000
- Over 10,000 Non-Road Engines Equipped (Both OE Installed and Retrofit)

MECA

NOx Technology Overview

<u>Technology</u>	<u>Performance Range</u>				<u>Potential Commercial Availability</u>
	NOx	CO	HC	PM	
Active Lean NOx	25-50	>70	>70	~ 30	2000
NOx Adsorber	50-70	>70	>70	> 30	2004
SCR Urea	>80	>50	>70	≥ 30	2000
Compact SCR	>90	>70	>70	≥ 30	2004
Plasma / NOx Cat.	>65	>50	>50	~ 30	Post - 2004

MECA

State-of-The Art SCR System has NO₂ Generation and Oxidation Catalyst to Eliminate Ammonia Slip

Source: Schaefer-Sindlinger, Degussa, 9-99

MECA

SCR Systems Can Achieve 80+% Efficiency under Reasonable Conditions

DeNO_x Map (with pre-catalyst)

Source: Schaefer-Sindlinger, Degussa 9-99

MECA

NO_x Adsorber Conversion Ratios Are Getting into the High-80% Efficiencies at Reasonable Temperatures

Source: Geckler, FEV 9-99

MECA

NO_x Technologies Are in Various Stages of Development

- Passive Lean-NO_x Catalysts Used on PC in Europe
- SCR Used on Stationary Sources, Marine Vessels, Locomotives and Have Been Used in Truck and PC Demonstration Programs
- NO_x Adsorbers Are in Vehicle Trials
- Plasma Technology Is in the Laboratory Stage and Emerging on Vehicles

MECA

Integrated Systems

MECA

Integrated System Using a DOC, DPF, and SCR

MECA

Integrated System -- Lean NO_x Catalysis + Filter

Integrate heat transfer and chemistry
for simultaneous reduction of
NO_x, CO, HC, & PM

Catalyst Deactivation Mechanisms

Thermal Sintering
Masking
Chemical Poisoning

MECA

Thermal Sintering

MECA

Masking

MECA

Lube Oil Components Can:

Increase Light-Off Temperature

Reduce Emission Control Performance

Compete for Desired Reactions

Upstream NOx Catalyst Assisted Filter

· Increase Backpressure

· Decrease Regeneration Potential

Oxidation Catalysts and Filters

· Create Particulate

Affect Durability

MECA

*Low Emission Diesel
Engine Oils
Conference*

**Post-Combustion Emission Control
Devices For Diesel Applications**

By Magdi Khair

January 30 - February 1, 2000

Presentation Outline

- **Standards, Goals, and Research Targets**
- **Post Combustion Emission Control Devices**
- **Description & Principle of Operation**
- **Advantages and Disadvantages**
- **Summary**
- **Conclusion**

Standards, Goals, and Research Targets

Post Combustion Emission Control Technology Options

Post Combustion Emission Control Systems

- Diesel Oxidation Catalyst (DOC)
- Diesel Particulate Filters (DPFs or Traps)
- Lean NO_x Catalyst (LNC)
- Lean NO_x Trap (LNT)
- Selective Catalytic Reduction (SCR)
- Combinations

Diesel Oxidation Catalyst (1)

Diesel Oxidation Catalyst (3)

Diesel Oxidation Catalyst (2)

Diesel Particulate Filters (1)

Most Common Filter Element Wallflow Construction

Diesel Particulate Filters (2)

Methods For Active Regeneration

Diesel Particulate Filters (3)

Methods For Passive Regeneration

- With Catalytic Coating Assist

- Self Regenerating

Diesel Particulate Filters (4)

Combination Catalyst and Particulate Filter

Catalyzed Soot Filter

Continuously Regenerated Trap

Lean NOx Catalyst (2)

(COMPOSITE GENERATED FROM INDUSTRY EXPERIENCE)

Lean NOx Trap (1)

Selective Catalytic Reduction

Advantages and Disadvantages

Diesel Oxidation Catalyst

Advantages

- Passive Device for PM Control
- SOF Conversion Eff. of 50-70%
- Some Formulations Show Gas-Phase Activity
- Good Durability
- Proven Reliability

Disadvantages

- Effective on High SOF Engines Only
- Sulfur Deactivation Concerns
- Lube Oil Additive Package Deactivation Concerns
- Ineffective With EGR Systems
- Highly Active DOCs Can Also Form Sulfate

Diesel Particulate Filters

Advantages

- Greater Than 90% PM Removal
- Highest Potential For Reducing Fine Particles
- Has Synergistic Value When Used With EGR
- Passive Regeneration Techniques Are Attractive

Disadvantages

- Cost
- Complex Controls
- Durability and Reliability Concerns
- High Back Pressure
- Potential of Plugging

Lean NOx Catalyst

Advantages

- Can Use Same On-Board HC
- Good Resistance to Sulfur
- No Appreciable Hydrothermal Deactivation For Low Temp.
- Some Limited Success For Passive Systems

Disadvantages

- Low NOx Conversion
- Narrow Temperature Range
- Void of NOx Conversion Between Low and High Temp. Catalysts
- N₂O Formation With Low T. Cat.
- Lack of Durability of High T. Cat.
- PM & Fuel Consumption Concerns

Lean NOx Trap

Advantages

- Experience With DI Gasoline
- Active in 250 - 450°C Range
- Potential For High NOx Conversion (>50%)
- Compatible With Total Engine/Aftertreatment Control Schemes

Disadvantages

- Serious Sulfur Deactivation
- May Require DOC in Rich Regime
- Relatively New For Diesel Applications
- Requires Sophisticated Controls
- Adverse Impact on Fuel Economy

Selective Catalytic Reduction

Advantages

- NOx Conversion of 70%
- Established Technology (Stationary)
- Good Durability at Low- & Mid-Range Temperatures
- Maintain Engine Durability and Performance By Avoiding EGR and Timing Retard

Disadvantages

- Additional On-Board Fluid
- Requires Sophisticated Controls
- Infrastructure For Urea Distribution
- Ammonia Slip Concerns
- US Regulators Non-Committal--May Have to Carry Life-Time Supply

Combination Systems

Advantages

- Overcome Limitations of Other Systems
- CRT Technology Holds Good Promise--Requires 50ppm or less Sulfur
- Field Experience With Peugeot system
- Designed to Achieve Extremely Low Emissions

Disadvantages

- They Each Have Limitations
- Requires Sophisticated Controls
- Are Application Specific
- CRT's Efficiency and Viability Depends on Availability of Low Sulfur Fuel
- Trap Regeneration Remains a Challenge

Summary

Progress in Post Combustion Emissions Reduction Technologies (Summary-1)

Progress in Post Combustion Emissions Reduction Technologies (Summary-2)

<i>Technology</i>	<i>Pros</i>	<i>Cons</i>
<i>DOC</i>	<i>Passive/Cost/Durability</i>	<i>Low Conv. Efficiency</i>
<i>DPF</i>	<i>Efficiency</i>	<i>Cost/Reliability & Durability</i>
<i>LNC</i>	<i>Reductant Common With Onboard Fuel</i>	<i>Fuel Consumption & Low Conv. Efficiency</i>
<i>LNT</i>	<i>Reductant Common With Onboard Fuel</i>	<i>Unproven-Durability Fuel Consumption-Sulfur</i>
<i>SCR</i>	<i>High NO_x Conversion</i>	<i>Add. Fluid Onboard/ Cost/Infrastructure...</i>

Concluding Comments

- There is no clear winner among the various aftertreatment systems
- Trap systems have the potential for PM control but still suffer from high cost, low durability, and low reliability
- CRT appears to have good passive regeneration qualities but requires ultra low sulfur fuel
- LNT for diesel engines is still new and requires more research--We know that it requires very low sulfur content

EXPORTING

Low Emission Diesel Engine Oils Conference

Sample Analytical Tools For Diesel Catalyst/Lube Oil Additive Studies

By Magdi Khair

January 30 - February 1, 2000

Potential Poisoning Effect Of Lubricating Oil On Diesel Catalytic Converters

Catalyst Description

Catalyst Detail

Catalyst Designation

Lube Oil Description

Content	Baseline	Additized
Mn	<1	<1
Mg	8	8
Fe	1	1
Cr	<1	<1
Cu	<1	<1
B	<1	<1
Ba	<1	<1
Ag	<1	<1
Al	1	1
Zn	1248	5166
Sn	1	<1
Si	<1	2
Sb	<1	<1
P	1147	4592
Pb	<1	3
Ni	1	<1
Mo	<1	<1
S	0.39	1.063
Ca	2061	1956
K. Vis. 100 cST.	14.28	13.79
K. Vis., 40 cST.	99.57	96.95
ASH, ASTM D-482, wt%	0.78	2.03
ASH, ASTM D-482, wt%	0.88	2.06

Units in ppm unless otherwise noted

Catalytic Converters Aging

Catalytic Converters Assessment

Sample Result For HC Conversion

Catalytic Converters Preparation

Analytical Methods

BET		Brunauer-Emmett-Teller	(Surface Area/Unit Mass)
SEM		Scanning Electron Microscope	(Determine Topographical Features of Catalyst Surface)
PIXE		Proton-Induced X-ray Emission	(Determine Presence of Noble Metal & Poisons)
XRD		X-ray Diffraction	(Determine Changes in Washcoat Crystalline Structure)
EDX		Energy Dispersive X-ray	(Determine Spectrum of Surface Elements)

Catalytic Converters Assessment (BET Surface Area Drop For Two Catalyst Formulations)

Catalytic Converters Assessment

(Amplified SEM Photographs)

Fresh

Aged
(1K Hrs.-Add. Lube)

222-Front

Catalytic Converters Assessment

(Amplified SEM Photographs - Sulfur Distribution By EDX)

Front

Regular Lube

Additized Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photograph - Sulfur Distribution By EDX)

Front

Regular Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photograph - Sulfur Distribution By EDX)

Front

Additized Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Sulfur Distribution By EDX)

Front

Regular Lube

Additized Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photographs - Phosphorous Distribution By EDX)

Front

Regular Lube

Additized Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photograph - Phosphorous Distribution By EDX)

Front

Regular Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photograph - Phosphorous Distribution By EDX)

Front

Additized Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photographs - Phosphorous Distribution By EDX)

Front

Regular Lube

Additized Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photographs - Zinc Distribution By EDX)

Front

Regular Lube

Additized Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photograph - Zinc Distribution By EDX)

Front

Regular Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photograph - Zinc Distribution By EDX)

Front

Additized Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photographs - Zinc Distribution By EDX)

Front

Regular Lube

Additized Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Sulfur/Phosphorous/Zink Distribution By EDX)

Front

Regular Lube

Additized Lube

222 Aged For 1000 Hours

Catalytic Converters Assessment

(Sulfur/Phosphorous/Zink Distribution By EDX)

Front

Regular Lube

Additized Lube

211 Aged For 1000 Hours

Catalytic Converters Assessment

(Amplified SEM Photographs)

Fresh

Aged

(1K Hrs.-Add. Lube)

211-Front

Concluding Comments

- Several analytical tools are available to study the interactions between catalyst and lube oil formulation
- Careful attention is advised when interpreting results of any of these analytical methods.
- Analysis of the catalyst front face may lead to different conclusions than the middle or the rear of the catalyst.
- Impact of sulfur should be viewed in light of effect of other elements in lube oil package such as phosphorus and especially, zinc.

EXPLORING LOW EMISSION DIESEL ENGINE OILS WORKSHOP, Jan 30 - Feb 1, 2000 Scottsdale, AZ

DIESEL EMISSION CONTROLS : NO_x AND PARTICULATE

Presented By

Dr. JOHN H. JOHNSON, Presidential Professor

MICHIGAN TECHNOLOGICAL UNIVERSITY

Jan 30, 2000

**Department of Mechanical Engineering & Engineering Mechanics
Michigan Technological University**

OVERVIEW

- **Overall Approach**
- **EGR System**
- **Catalyst Systems**
- **Recuperator**
- **Catalyzed Filters**
- **Modeling**

**Department of Mechanical Engineering & Engineering Mechanics
Michigan Technological University**

VECSS OVERVIEW

Vehicle Engine Cooling System Simulation (VECSS) Research Group
Michigan Technological University, Houghton

CONFIGURATION OF THE VECSS (ver. 8.1)

Component	Model No./ type	Manufacturer
Engine	Series 60, 12.7 L	Detroit Diesel Corporation
Radiator	405-16366-001	Behr McCord
Condenser	BM 19757	Behr McCord
Charge air cooler	01-23132-00	Allied Signal
Coolant thermostat	-	Detroit Diesel Corporation
Fan	DST variable speed clutch	Kysor Cooling Systems
Oil Cooler	-	Harrison Division-GMC
Oil thermostat	-	Detroit Diesel Corporation
Turbocharger	-	Garrett Automotive

Vehicle Engine Cooling System Simulation (VECSS) Research Group
Michigan Technological University, Houghton

VECSS Conventional Schematic

MichiganTech

Vehicle Engine Cooling System Simulation-VECSS Group
Department of Mechanical Engineering-Engineering Mechanics

Comparison of Varying EGR at 1500 rpm, 50% load, 55 mph, 70F, 12/19/99

Radiator Heat Rejection at 1500 rpm, 100% load, 20 mph, 100F, 1/9/00

Radiator Heat Rejection at 1500 rpm, 50% load, 55 mph, 70F

Wisconsin_06_99 age 12

FEV

QuadCAT Flow Schematic

- © Integrate heat transfer and chemistry for simultaneous reduction of NOx, CO, HC, & PM

Heat Recuperator Platform

- ◎ Recycle heat from exothermic reactions
- ◎ Increase catalyst and filters temperatures with minimum fuel penalty

ceryx

Heat Recuperation Elevates Catalyst Temperatures

ceryx

Integration Makes Full Use of Resources

Injecting supplementary HC provides:

Energy source for DPF regeneration
 $\text{HC} + \text{O}_2 \rightarrow \text{Heat}$

Reducing agent for NOx catalyst
 $\text{HC} + \text{NOx} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2$

Light-Duty QuadCAT Converter

© A QuadCAT Converter field unit installed on a Ceryx test vehicle

CPF DIMENSION NOMENCLATURE

CPF Specifications

EX 80 - 100 Cell Density
 Engelhard Catalyst
 Diameter - 10.5 inches
 Length - 12 inches
 Volume - 17 liters

W- Porous wall thickness = 0.017 inches
 H- Cell width = 0.083 inches
 L- Cell length = 12 inches

Department of Mechanical Engineering & Engineering Mechanics
 Michigan Technological University

CATALYZED FILTERS

Normalized Number Distribution

Department of Mechanical Engineering & Engineering Mechanics
 Michigan Technological University

CATALYZED FILTERS

NORMALIZED VOLUME DISTRIBUTION

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CATALYZED FILTERS

Normalized Number Distribution

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CATALYZED FILTERS

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MODELING

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MODELING

COMPARISON OF EXPERIMENTAL & MODEL DATA - EX 80 (100 CD)

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MODELING

EX 66 - COMPARISON OF EXPERIMENTAL AND MODEL DATA

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BASESTOCKS

ATTACHMENTS 13, 14, 15, & 16

"Base Oil Chemistry For Diesel Engine Lubricants" Cliff Mansfield, Equilon Enterprises, Houston, TX

"Synthetic Liquid Lube Oil Development: Lessons Learned". John W. Fairbanks, US Department of Energy, Washington , DC

"The Use of Vegetable Oils as Renewable Basestocks". Sevim Z. Erhan, National Center for Agricultural Utilization Research (NCAUR), U.S.Department of Agriculture (USDA), Agricultural Research Services (ARS), Peoria, IL

"Market Development Issues for Alternative Diesel Engine Oils", David B. Smith, Creative Energy Products, L.L.C., Moorestown, NJ

BASE OIL CHEMISTRY FOR DIESEL ENGINE LUBRICANTS

**CLIFF MANSFIELD
EQUILON ENTERPRISES
31 JANUARY 2000**

API BASE OIL GRADES

- **GROUP I BASE STOCK**
 - CONTAINS <90% SATURATES
 - CONTAINS >0.03% SULFUR
 - HAS A VISCOSITY INDEX >80 AND <120
- **GROUP II BASE STOCK**
 - CONTAINS > 90% SATURATES
 - CONTAINS <0.03% SULFUR
 - HAS A VISCOSITY INDEX >80 AND <120
- **GROUP III BASE STOCK**
 - CONTAINS >90% SATURATES AND <0.03% SULFUR
 - HAS A VISCOSITY INDEX >120

LUBRICANT BASE OILS

- BASE OILS MAKE UP APPROX. 80 TO 86% OF FINISHED DIESEL LUBRICANT
- MINERAL BASE OILS - PROCESSED PETROLEUM FRACTIONS, GENERALLY IN THE C20 TO C40 CARBON NUMBER RANGE
- TYPICAL 10W-40 BASE OIL WILL HAVE AN AVERAGE CARBON NUMBER OF ~31-32
- SYNTHETIC BASE OILS - POLYALPHAOLEFINS - MADE BY POLYMERIZATION OF DECENE UNITS

POSSIBLE ALKANE ISOMERS

CARBON NUMBER	NO. OF ISOMERS
C10	75
C20	366,319
C30	4,111,846,763
C40	62,491,178,805,831

BASE OIL COMPOSITION

- **TASK MADE DIFFICULT BY LARGE NUMBER OF POSSIBLE ISOMERS**
- **AT THE LEAST, ONE IS REDUCED TO THE ANALYSIS OF COMPOUNDS BY CLASS, E.G.**
 - **% SATURATES, % AROMATICS, % POLARS**
- **AT THE BEST, ONE CAN ANALYZE BY COMPOUND TYPE**
 - **% PARAFFINS, % MONOCYCLOPARAFFINS, % DICYCLOPARAFFINS, % TRI.....**
 - **% MONOAROMATICS, % DIAROMATICS, % TRI.....**
- **CAN DO ELEMENTAL ANALYSIS, E.G., S AND N**

BASE OIL COMPOSITION

- **API BASE OIL CATEGORIES ARE DEFINED USING ASTM D2007 - NOT RELIABLE METHOD**
- **TYPICAL BASE OIL ANALYSIS WOULD INVOLVE SEPARATION OF COMPOUND CLASSES BY D2549 OR RELATED METHOD TO GIVE SATURATES, AROMATICS, AND POLAR FRACTIONS**
- **FRACTIONS ANALYZED BY SOME TYPE OF MASS SPECTROMETRY METHOD TO GIVE % OF VARIOUS COMPOUND TYPES, e.g., % paraffins, % mononaphthenes, % dinaphthenes, ...**

COMPOSITIONAL PROPERTIES FOR FUEL ECONOMY

PROPERTIES NEEDED FOR BETTER FUEL ECONOMY (LOWER PVC)

- REDUCED POLYAROMATICS**
- REDUCED POLYNAPHTHENES**
- LONG ALKYL CHAINS**

BASE OIL IMPACTS ON DIESEL PARTICULATES

- COMPOSITIONAL FACTORS NOT KNOWN AT THIS POINT**
- KNOWN LUBRICANT FACTORS THAT IMPACT PARTICULATES**
 - VISCOSITY**
 - DEPOSIT FORMING TENDENCIES**
- MORE STUDIES NEEDED**

COMPOSITION IMPACTS IN OTHER TESTS

- MACK T-8 / T-8E - BEST PERFORMANCE WITH HIGH SATURATES BASE OILS AND BOOSTED ASHLESS DISPERSANTS PACKAGES WITH MODERATE DETERGENT LEVELS
- CAT 1K, 1N, AND 1P - BEST PERFORMANCE WITH HIGH DETERGENCY, HIGH AROMATICS, AND MODERTE SULFATED ASH

R. A. Cherillo and A. Huang, "The Increasing Significance of Base Oils in the Evolution of Heavy-Duty Diesel Engine Oils", NPRA Paper, 1999

AROMATICS DO CONTRIBUTE TO SOLVENCY

	GROUP I	GROUP II
% POLARS AT 10K MILES	26.1	18.7
% POLARS IN CLEAR TOP	12.6	6.4
DIFFERENCE	13.5	12.3

COMPOSITIONAL FACTORS AFFECTING OXIDATION

- HETEROAROMATIC COMPOUNDS - N AND S
- POLYAROMATICS
- POLYNAPTHENES
- MONOAROMATICS
- MONONAPTHENES
- PARAFFINS

DECREASING
POTENTIAL FOR
OXIDATION

OXIDATION IN SEQUENCE IIIE (FIXED ADDITIVE PACKAGE)

GROUP I > GROUP II > GROUP III $\geq$ GROUP IV

NOTE: THIS IS A GENERALIZATION. DEPENDING ON COMPOSITION, SOME GROUP II'S MIGHT OUT PERFORM SOME GROUP III'S. SOME GROUP III'S CAN PERFORM AS WELL AS GROUP IV'S.

FI-MS OF SATURATE FRACTION OF 10W-40 BASE OIL BLEND

FI-MS OF PAO

COMPOSITION OF SOME TYPICAL BASE OILS

	GROUP I	GROUP II	GROUP III
% PARAFFINS	15.52	21.39	41.63
% MONONAP	26.28	35.59	38.11
% POLYNAP	36.2	39.4	20.12
% MONOARO	14.79	1.39	na
% POLYAROM	3.86	1.4	na
% THIO	1.4	0.21	na

IMPACT OF COMPOSITION ON PROPERTIES

- PERFORMANCE PROPERTIES OF DIESEL LUBRICANT DEPEND ON BOTH BASE OIL AND ADDITIVE CHEMISTRY
- HOLDING THE ADDITIVE PACKAGE CONSTANT, ONE CAN MAKE CERTAIN GENERALIZATIONS ABOUT BASE OIL CHEMISTRY FOR
 - OXIDATION
 - FUEL ECONOMY
 - SOLVENCY

Synthetic Liquid Lube Oil Development: Lessons Learned

John W. Fairbanks
U.S. Department of Energy
Washington, D.C.

Presented at
Exploring Low Emissions: Diesel Engine Oils
Scottsdale, Arizona
January 30 - February 1, 2000

OHVT Mission

To conduct, in collaboration with our heavy vehicle industry partners and their suppliers, a customer-focused national program to research and develop technologies that will enable trucks and other heavy vehicles to be more energy efficient and able to use alternative fuels while simultaneously reducing emissions.

Synthetic Liquid Lubricant Anticipated Problem with "Adiabatic" or Low Heat Rejection (LHR) Diesel Engine

- ◆ European engine companies working on LHR engines indicated a need for a high temperature liquid lubricant
- ◆ Roy Kamo used Stauffer's SDL-1
- ◆ Program evolved to develop advanced synthetic liquid lubricant
 - Improve understanding of high temperature liquid lubricant technology
 - Develop comprehensive technology base
 - Increase rate of further development
 - Commercialization of advanced lubricants
- ◆ Conventional anti-wear and overbase additives cause deposit formation
 - Top ring reversal temperatures 370- 425 °C
- ◆ Conventional anti-wear agents (zinc dithiophosphates) ineffective temperatures >345 °C
- ◆ Looking for combination ashless anti-wear additives
 - Function temperature range ambient 600 °C
- ◆ Ashless to prevent
 - Ring clogging
 - Other deposit formation

Stauffer/Cummins Synthetic Liquid Lubricant Program

- ◆ Stauffer developed SDL-1 used in Kamo's adiabatic diesel engine
 - Ideas for improving
- ◆ Stauffer developed synthetic lube oils used in most aircraft gas turbine engines
- ◆ Stauffer working with Cummins in Columbus (precontract)
 - Demonstrated synthetic liquid lube that allows operation at TRR temperature of ~875 °F for 275 hours
 - No other testing reported at these temperatures
- ◆ LE-55 (LHR Engine Program)
 - Did not require high temperature synthetic lube oil
 - Current engines do not require synthetic liquid lube oil
 - Porsche and Mercedes recommend synthetic lube oil

Basestock Function As:

1. Dispersants
2. Viscosity index improvers
3. Pour point depressants
4. Seal swelling agents
5. Anti-wear agents

Synthetic Lubricant Basestock Candidates

1. Diesters
2. Polyol esters
3. Phosphate esters
4. Poly- α -olefins
5. Silicones
6. Ethers
7. Alkyl benzenes
9. Petroleum base oils

Criteria for Basestock for Crankcase Lubrication

1. Good film former
2. Carrier for additives
3. High oxidation resistance
4. Carrier for blow-by products and fluid decomposition
5. Localized cooling medium
6. Proper viscosity characteristics
7. Compatible with additives and engine materials
8. No deposits if decomposition
9. Available in quantity at reasonable cost

Basestock Experience

1. Basestocks either decomposed via predictable, concerted mechanism
 - > yielding volatile decomposition productsor
2. Basestocks decomposed via a random, high energy pathway
 - > resulting in polymers and carbon deposits

Basestock Incorporating Additive Demonstrated Enhanced Performance

- ◆ Elimination of polymeric viscosity index improvers
 - > Lessens deposit
 - > Stabilizes viscosity to shear down
- ◆ Elimination of polymeric pour point suppressants
 - > Lessens deposits
 - > Eliminates cold start fluctuations
- ◆ Elimination of antioxidants
 - > Reduces costs
 - > Precludes catastrophic lubricant failure due to additive depletion
- ◆ Extends drain intervals

Lubricants Based on Ester Basestock

1. Thermally stable and resists oxidation
 - Less likely to form deposits
2. Ester based lubricant would assist the additive package with
 - Dispersancy
 - Deposit control
 - Seal swell
 - Improved viscometrics
3. Some additives eliminated could improve performance

Ashless Additive Concerns

- ◆ Conventional oil additives cannot be used
 - Not compatible with synthetic basestocks
 - Poor performance at high temperatures
- ◆ Viscosity index improvers and pour point depressants at elevated temperatures
 - Tendency to degrade rapidly
 - Deposit formation

Viscosity Index Improvers

- ◇ Polymeric additives which alter basestock temperature/viscosity curve
- ◇ Allow low temperature flow properties while preventing thinning of basestock at high temperatures
- ◇ Polymers not stable under high shear stress or at high temperatures
- ◇ Synthetic basestock must provide proper viscosity index for temperature

Anti-wear Additive

- ◇ Zinc dithiophosphates (ZDP)
 - Classical anti-wear additive petroleum oils
 - Also an anti-oxidant
 - Effective in conventional engines to 315 °C
 - Does not work well with ceramic surfaces
- ◇ Problem above 315 °C
 - Deposit formation of non-volatile zinc salts or oxides
 - Typically found in ring groove area
 - Contributes to ring stressing
- ◇ Approach
 - Replace ZDP with ashless anti-wear agents
 - Phosphate and dithiophosphate esters
 - Also need ashless anti-oxidants to function in synthetic basestock

Pour Point Suppressants and Advanced Synthetic Basestocks

- ◆ Pour point suppressants
 - Inhibit wax formation
 - Enhance low temperature fluidity
 - Thermally unstable
 - Lead to deposit formation
- ◆ Advanced synthetic basestocks
 - No wax
 - Can provide wide temperature viscosity
 - No pour point suppressants

Primary Ashless Additives Incorporated to Improve

1. Anti-wear properties
2. Oxidation resistance
3. Anti-foaming properties
4. Detergency and dispersancy
5. Corrosion inhibition

Overbase and Detergent Additives

- ◆ Metallic salts of phenates and sulfonates
 - > Neutralize acidity
 - > Minimize deposit formation
- ◆ Result
 - > Extending oil drain interval
 - > Reduce deposits
- ◆ Problem
 - > Decompose at high temperature
 - > Cannot be used above 315 °C
 - > LHR engine tests with conventional additives
 - > 50% of ring deposits were from overbase and detergency additives
- ◆ Solution
 - > Chemically active filter with alternative substances activates on filter surface

High Temperature Liquid Lubricant Formulation

Selection of the finished formulation will be based on:

1. Oxidation resistance
2. Deposit control
3. Wear particles
4. Wide temperature operation
5. Good elastohydrodynamic film forming capabilities and high temperature, high shear viscosity
6. Other properties related to high temperature operation, i.e., detergency, dispersancy
7. Materials compatibility

Diesel Engine Friction Losses

- ◆ Friction losses are an order of magnitude less than thermal losses
- ◆ Improves engine power and fuel economy from reduced friction losses
 - > Piston/ring interface
 - > Valve gear
 - > Crankshaft and other bearings (maximum heat contributor)
 - > Accessories
- ◆ 250kW heavy duty truck engine
 - > 35kW heat dissipated from oil (20% from piston liners)
- ◆ Lubricant
 - > Reduce friction
 - > Reduce emissions
 - > Priority

Performance of Mineral and Synthetic Liquid Lube Oils (Reported at SAE by Caterpillar and Mobil)

- ◆ Fleet tests with 2 mineral oils and 2 synthetic oils in diesel engines
 - > Synthetic oils improved fuel consumption by an average of 3.2%
 - > Drain interval for fully synthetic diesel oils
 - > 45,000 to 60,000 miles depending on engine type
 - > 3 to 4 times the engine builder's standard recommendation

Series 60 engines operated on SYN-DEO versus the CF-4 reference (Petroleum base lube oil)

Ref: SAE 982718

Lessons Learned

- ◆ Basestock chosen to eliminate additives with temperature problems
- ◆ Ashless additive pack
 - Anti-wear, anti-oxidant, anti-foam, corrosion inhibitor
- ◆ TRR temperature can exceed lube oil boiling point
 - Volatile products can provide lubrication
- ◆ Achieve TBN (overbase) and detergency
 - Chemically active filter
- ◆ Ring/liner surface chemistry important
 - Only ceramic with transition metal alloyed work
- ◆ Phosphate ester- replaced ZDP
 - Reduced friction
- ◆ Current synthetics replacing petroleum oils
 - Average fuel economy benefit of 4.7%
- ◆ Need fuel economy benefit with minimal particulate emissions

The Use of Vegetable Oils as Renewable Basestocks

S. Z. Erhan

National Center for
Agricultural Utilization Research
USDA/ARS, Peoria, IL 61604

Lubricants and Hydraulic Oils

- Lubricant market in the U.S. is about \$8 billion
- More than 90% of all lubricants are based on petroleum
- Hydraulic oils comprise about 10% of all lubricants
- The demand for biodegradable lubricants is expected to grow at about 10% annual rate

Concerns

💧 Environmental

- 💧 Pollution- Air, Water and Soil
- 💧 Ecological Balance

💧 Handling and Toxicity

- 💧 Health
- 💧 Contamination

💧 Disposal

- 💧 Biodegradability
- 💧 Cost

Primary Functions of Lubricants

- 💧 Reduce friction and minimize wear
- 💧 Dissipate heat
- 💧 Disperse deposits
- 💧 Inhibit rust/corrosion
- 💧 Seal critical contact joints

Consumption of lubricants

~ 20 M tons / year in US

Commercial Uses of Biodegradeable Lubricants

- 💧 Chain saw lubricants
- 💧 Drilling oils
- 💧 Food industry fluids
- 💧 Gear oils
- 💧 Greases
- 💧 Hydraulic fluids
- 💧 Marine lubricants
- 💧 Pump oils
- 💧 Railroad lubricants
- 💧 Shock absorber fluids
- 💧 Mould release oils
- 💧 Two stroke engine oils

Biodegradability is delivered by **basestock**, not additives.

Basestock: 80-100% of Lubricant

Flowchart of Lubricant Development

Screening protocols depend on application

Basestock Screening

***Lubricity
more
dependent
on additives
than on
basestock***

- 💧 Biodegradability
- 💧 Viscosity
- 💧 Low Temperature Solidification
- 💧 Volatility
- 💧 Oxidative Stability
- 💧 Deposit Forming
- 💧 Hydrolytic Stability
- 💧 Solvency / Miscibility
- 💧 Seal Compatibility
- 💧 Special Requirements
(e.g. heat conductivity,
transparency, density,
electric resistance, etc.)

Types of Additives Used in Lubricants

- 💧 Viscosity Index Improvers: (Few %)
- 💧 Oxidation Inhibitors: (0.5-1%)
- 💧 Detergent Dispersants (2-20%)
- 💧 Rust Inhibitors (~1%)
- 💧 Antiwear Agents (Few %)
- 💧 Pour Point Depressants (~1%)

Options in biodegradable basestocks

**Poly alpha
olefins (PAOs)**

**Synthetic
Esters**

Comparison of Major Basestocks

Base	\$ / lb	Bio- degradability	Stability		Low-T Performance
		CEC-L-33	Oxidative	Hydrolytic	
Vegetable Oils	0.5	95%+	Poor	Poor	Poor
Synthetic Esters	1.5	80%+	Good	Moderate	Excellent
Poly alpha olefins	1.0	70%+	Good	Excellent	Excellent
Mineral Oil	0.2	30%+	Good	Excellent	Good

Rate of Oxidation

Bond Dissociation Energies (D.E.)

Bond	Bond Type	Fatty Acid	D.E. Kcal/mole
$\text{CH}_2 - \text{H}$	Aliphatic	na	104
$\text{CH} - \text{H}$	Aliphatic	Stearic	96
$\text{CH} = \text{CHCH} - \text{H}$	Allylic	Oleic	85
$\text{CH} = \text{CHCH} - \text{H}$ $\text{CH} = \text{CH}$	Doubly Allylic	Linoleic Linolenic	76

Sample analysis in micro oxidation

Preparation Injection Microoxidation Washing in THF

- %evaporation (negligible for vegetable oils)
- % solidified products
- % oxypolymers

Investigating oxidative stability: micro oxidation

Oxypolymerization of Vegetable Oils

- * Fast oxypolymerization with increasing polyunsaturation.
- * Test sufficiently accurate for kinetic studies.

Oxidative Stabilities of Biofluids

Low temperature performance

ASTM D 97 Pour point
and cold storage testing

Pour Point

Soybean oil - 9°C
90% oleic
sunflower -12°C
Canola oil -21°C
Castor oil -24°C

Needed:
pour points below -36°C

no solidification at -25°C
for 7 days

Mod. SBO Improves Low T Behavior

	Pour Point	Days at -25°C
VO* / diluent** (50:50)	-24°C	0
VO / diluent (50:50) + 1% PPD	-30°C	1
mod. SBO / diluent (50:50)	-18°C	0
mod. SBO / diluent (50:50) + 1% PPD	-36°C	7+
mod. SBO / diluent (65:35) + 1% PPD	-41°C	7+

* VO - high oleic (>80% oleic) Vegetable Oil

** diluent - low pour pt. polyalphaolefin or synthetic ester

Approaches to Improve the Drawbacks of Vegetable Oils

- 💧 Genetic modification to alter F.A.
- 💧 Chemical modification
 - 💧 Polymerization
 - 💧 Reduction
 - 💧 Branched chains (methylation)
 - 💧 Interesterification
- 💧 Separation techniques
 - 💧 Fractionation
- 💧 Formulation
 - 💧 Additive technology

Conclusions

- 💧 Government regulations restricting the use of petroleum lubricants provide an opportunity for vegetable oil based lubricants.
- 💧 Veg. oils are non-toxic, biodegradeable, renewable, and possess good boundary lubrication, a high viscosity index, a high flash point, low wear and a high load carrying capacity.
- 💧 High oleic vegetable oils with improved oxidative stability and low temperature properties show great promise as lubricant base stocks.
- 💧 Further improvements in genetic engineering and chemical modifications coupled with optimized additive technology will lead to a range of veg. oil products for environmentally sensitive markets.

MARKET DEVELOPMENT ISSUES FOR ALTERNATIVE DIESEL ENGINE OILS

David B. Smith

February 2, 2000

CREATIVE ENERGY PRODUCTS, L.L.C.

PRESENTATION FOCUS

CROP SOURCED FLUIDS

Canola

Corn Oil

Soy Oil

Sunflower Oil

CREATIVE ENERGY PRODUCTS, L.L.C.

MARKET POTENTIAL OF CROP SOURCED FLUIDS

- Total Loss Applications**
 - ♦ Relatively Low Volume
 - ♦ Do Not Require High Temperature Stability
- Biodegradable Hydraulic Fluids**
 - ♦ Initial Large Volume Potential Use
 - ♦ Can Be Short on Performance vs. MO
- Motor Oils**
 - ♦ Attractive Volume Potential (Even @ Low %)
 - ♦ Usefulness Needs To Be Proven

CREATIVE ENERGY PRODUCTS, L.L.C.

QUESTION ?

**Why Would Anyone Want To
Market a Diesel Engine Oil
Containing a Crop Based Fluid?**

CREATIVE ENERGY PRODUCTS, L.L.C.

WHY CONSIDER CROP SOURCED FLUIDS FOR ENGINE OILS?

ATTRACTIVE PROPERTIES

- Renewable**
- Biodegradable**
- Non-Toxic**

CREATIVE ENERGY PRODUCTS, L.L.C.

WHY CONSIDER CROP SOURCED FLUIDS FOR ENGINE OILS?

POTENTIAL PERFORMANCE BOOSTS

- Very Low Volatility**
- Very High Viscosity Index**
- Active Molecule Potential**
 - » Improved Anti-wear**
 - » Better Fuel Economy**

CREATIVE ENERGY PRODUCTS, L.L.C.

MOTOR OIL - Base Oil Properties

NOACK Volatility

PAO 4	12
GROUP III	15
GROUP II+	15
GROUP II	23
GROUP I	29
CROP FLUID	1

Viscosity Index

PAO 4	120
GROUP III	120-145
GROUP II+	115-120
GROUP II	95-115
GROUP I	95-100
CROP FLUID	220

CREATIVE ENERGY PRODUCTS, L.L.C.

CROP BASED FLUIDS

**ATTRACTIVE COMBINATION OF
VERY HIGH VI AND VERY LOW
VOLATILITY**

**– Potential Blending Component to Reduce
Oil Consumption**

CREATIVE ENERGY PRODUCTS, L.L.C.

MARKETING CROP SOURCED FLUIDS FOR ENGINE OILS

**SUCCESS WILL DEPEND ON
FINDING ECONOMIC ADVANTAGE
FOR SOME OR ALL OF THESE
UNIQUE PROPERTIES**

CREATIVE ENERGY PRODUCTS, L.L.C.

HISTORICAL PERSPECTIVE ON CROP SOURCED FLUIDS

**Early Lubricants
Wide Variety of Crop Sources
Varying Compositions
Performance Issues
 High Temperature Stability
 Cold Flow**

CREATIVE ENERGY PRODUCTS, L.L.C.

MARKETING CROP SOURCED FLUIDS FOR ENGINE OILS

**SUCCESS WILL ALSO DEPEND ON
PROVING THE PERFORMANCE OF
THESE FLUIDS IN FULL-SCALE
ENGINE TESTING**

CREATIVE ENERGY PRODUCTS, L.L.C.

HOW CROP SOURCED FLUIDS CAN BE USED IN ENGINE OILS

What Is Known

- ◆ VI & Volatility Can Be Controlled With a Crop Fluid
 - Cost Vs Current Alternates?
- ◆ Engines Can Be Lubricated With Motor Oils Containing 20+ % of a Crop Fluid
- ◆ High Temperature Stability Can Be Controlled
 - High Oleics Better
- ◆ Notational Fuel Economy
- ◆ Indications of Improved Anti-wear

CREATIVE ENERGY PRODUCTS, L.L.C.

HOBS

High Output Engine Demos

Source: RLI

- ◆ High Output 358 V-8
- ◆ 800 Lap Break-In
- ◆ Short Track
- ◆ 8000 - 8300 RPM
- ◆ Gasoline Fueled
- ◆ SAE 20W-50 with 20% Crop Fluid

- ✓ Engine - No Change After Day's Run
- ✓ Idle Oil Pressure Stabilized
- ✓ 200-300 More RPMs

CREATIVE ENERGY PRODUCTS, L.L.C.

Dow AgroSciences

STABILIZATION OF HIGH OLEIC CROP FLUID (HOCF)

Micro-Oxidation Test
(30 Min @ 225°C)

HOCF - No Additives

HOCF Plus Chemistry

A = HO Soy

B = Holly Canola

C = HO Corn

D = HO Sun

Source: RLI

CREATIVE ENERGY PRODUCTS, L.L.C.

ANTI-WEAR INDICATION OF HIGH OLEIC CROP FLUIDS (HOCF)

	4-Ball Steady State 30 Min mm Scar	4-Ball Scuffing Load kg
Mineral Oil	0.64	40
Sunflower Oil	0.51	50

Lower = Better

Higher = Better

Source: RLI

CREATIVE ENERGY PRODUCTS, L.L.C.

HOW CROP SOURCED FLUIDS CAN BE USED IN ENGINE OILS

What Is Not Known

- ◆ Performance in Sequence Engine Tests
 - Cost Factor
- ◆ Solid Reason for OEMs / Oil Marketers To Be Interested

CREATIVE ENERGY PRODUCTS, L.L.C.

PRAGMATICS OF BRINGING CROP SOURCED FLUIDS TO DIESEL ENGINE OIL MARKET

CREATIVE ENERGY PRODUCTS, L.L.C.

Usage Considerations

Better Potential For Impact

- Blending Component**
- Additive**

Lower Potential

- Major Base Fluid Component**

CREATIVE ENERGY PRODUCTS, L.L.C.

USING ATTRACTIVE PROPERTIES

Renewable Aspect

Need Help From Governments

Regulations / Mandates

Biodegradability

May Not Matter

Non-Toxicity

May Not Matter

CREATIVE ENERGY PRODUCTS, L.L.C.

PRAGMATICS OF USING POTENTIAL PERFORMANCE BOOST

High VI & Low Volatility

Potential Component

Active Molecule Impact

**Need Targeted Research To Quantify
Potential Benefits & Cost Effectiveness**

CREATIVE ENERGY PRODUCTS, L.L.C.

PRAGMATICS OF USING POTENTIAL PERFORMANCE BOOST

Ideas for Targeted Research

- ◆ Fully Document Improved Fuel Economy Vs. Industry Specifications
- ◆ Unique Engine Component Durability
- ◆ Enhanced Exhaust Control System Durability
- ◆ Ability to Economize with Additive Packages
- ◆ Other?

CREATIVE ENERGY PRODUCTS, L.L.C.

PRAGMATICS OF BRINGING CROP SOURCED FLUIDS TO DIESEL ENGINE OIL MARKET

THE BOTTOM LINE

**Once There Is A Reason To Use - Performance
Must Be Documented**

Two Ways To Approach Performance

- 1 Proof-of-Performance Truck Testing
- 2 Full-Scale Engine Testing

Which Ever Way You Start -

**Both Must Be Done To Achieve
Large Volume Use!**

CREATIVE ENERGY PRODUCTS, L.L.C.

ADDITIVES

ATTACHMENTS 17, 18, & 19

“Diesel Engine oil Additives for Low Emission Engines: The Challenges and Consequences”, Tom Boschert, Ethyl Corporation, Southfield, MI

“Lubricant Additives and Strategies for Low Emission Diesel Oils”, Steve Hsu, NIST, US Dept. of Commerce, Gaithersburg, MD

“Challenges and Opportunities for Future Engine Oils”, Ewa Bardasz, The Lubrizol Corporation, Wickliffe, OH

DEO Additives for Low Emission Engines The Challenges and Consequences

DOE Conference: Low Emission Diesel Engine Oils

Tom Boschert

Ethyl Corporation

January 31, 2000

Diesel Engine Oils (DEO) Perform Many Functions

- Wear Reduction
 - In boundary and hydrodynamic lubrication
- Friction Reduction
- Cooling
- Anti-corrosion
- Cleaning Action
- Sealing
- Hydraulic media

Diesel Engine Oils (DEO)

Perform Many Functions

- Base oils alone cannot provide these functions
- Requires use of additives
- Additives can comprise as much as 20% or more of a Multi-grade DEO formulation

Types of Additives Typically Found in DEOs

- Detergents & Detergent/Inhibitors
 - Sulfonates
 - Phenates, Salicylates
- Dispersants
 - Nitrogen and Hydrocarbon based
- Anti-wear
 - Zincdithiophosphate (ZDDP) predominate
- Rust and Corrosion Inhibitors
 - Detergents, ZDDP, Triazoles, Thiodiazoles

Types of Additives Typically Found in DEOs

- Anti-oxidants
 - ZDDP, Phenates, Phosphonates, Salicylates
 - Phenolics, amines, carbamates, copper compounds, molybdenum compounds
 - Many A/O's are sulfur containing
- Anti-foam
 - Silicone oils
- Friction Modifiers
 - Various
- Viscosity Index improvers & PPD's
 - Hydrocarbon and oxygen based

Additive Package Development Evolutionary Rather than Revolutionary

- ZDDP first used in 1941
- Succinimide type dispersants widely adopted in 1970's
- Most additives are variations of known compounds and have evolved over the last 30 years - little 'revolutionary' development

Additive Package Development Evolutionary Rather than Revolutionary

- Advantages of Evolutionary Approach
 - No radical change from year to year
 - Extensive history of field performance
 - Engines and metallurgy designed with knowledge of engine oil limitations
 - In the past decade, oil changes yield better performance - backward compatibility
 - Plants, processes, application remain common

Ethyl

DEO Additives Harmful to Aftertreatment?

- There are a number of paths to developing low emission engines.
- Some of the more promising aftertreatment systems are currently harmed by products of combustion coming from sulfur, phosphorous and metallics from the additives
- In general if sulfur can be decreased, other metallics will decrease also

Ethyl

Typical DEO Formulation

<u>Component</u>	<u>% wt. Sulfur</u>
ZDDP	0.20 - 0.25
Detergent	0.05 - 0.25
Other (A/O, VII, FM)	0.0 - 0.10
Total	0.25 - 0.60
Typical Group II Base Oil	0.001 - 0.003

Lube Oil Sulfur Contribution

Shawn D Whitacre 11-99

How Could we decrease Metallics into Aftertreatment Systems?

- Use Group II or higher base oils
- Decrease ZDDP, detergents, and other additives, or substitute with new additives
- Improve engine oil consumption
- Negate metallics by traps or other treatment before they move into aftertreatment devices

How will we decrease Metallics into Aftertreatment Systems?

- Lets ASSUME we need to cut the sulfur contribution of lube oil by a factor of 4
 - Improve engine oil consumption by 2X
 - Cut the sulfur in engine oil additives by 1/2
 - Use of group II base oils

Lube Oil Sulfur Contribution

Shawn D Whitacre 11-99

Challenges of reducing DEO sulfur by 1/2

- Reduction of most effective anti-wear - ZDDP - replacement?
- Reduction of most detergents and some types of A/O's, FM's and VII's - replacement?
- Engine metallurgy and design must take into account these reductions
- Durability, combustion processes, pressures and temperatures all must be studied
- Proof of performance

The Consequences of 1/2 Sulfur DEO

Oil Suitable for Low Emission Engine Only

- Limited Backward Compatibility**
- Different Drain Interval?**
- Different engine metallurgy?**

Older Classification oil in new engine could harm the aftertreatment

New 'revolutionary' additives rather than evolutionary - will not have comfort factor from long history of use

Decreased oil consumption will strain oil in sump

Summary

- Additives are necessary for DEO performance
- Additives and formulations have evolved over many years giving large factor of safety
- Several aftertreatment technologies; those with higher success factors require low sulfur, phosphorous & metallics in engine exhaust
- If DEO must decrease sulfur in oil by 1/2
 - Many challenges, potentially revolutionary additives
 - A number of substantial risks
- We must strive to minimize the challenges and Risks

Summary

- The oil and additive industry can & will respond to the challenge for low sulfur, phosphorous and metallics in engine oils - we have seen this in the passenger car side
- Because of the risks involved we must carefully weigh all the options before we commit to this path

Lubricant Additives

Strategies for Low Emission Diesel Oils

Dr. Stephen Hsu
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Heavy Duty Truck Technology

- Fuel economy
- Durability
 - MM miles
 - Engine built for life
- Emissions
 - Hydrocarbons
 - Nanoparticles

Lubricants

- Base oils
 - Paraffins & cycloparaffins
 - Polynuclear aromatics
 - Polar speices (0.5 - 3%) (sulfur & oxygen)
- Additives
 - dispersants
 - detergents
 - inhibitors (antiwear, antioxidants, corrosion, rust)
 - Viscosity Index Improver
- Base oil - Additives interactions ► Lubricant performance

Lubricant Performance

- Largely controlled by design, operating parameters, fuel/combustion, duty cycles
- Lubricant defines the limits of operability for a given set of conditions
- So far, base oil is a given, different formulations are developed for a base oil and a performance level
- Lubricant performance is defined by additive combination, individual additive concentration, & materials

Material-Lubricant Relationship

- Most additives are metal-specific (steel assumed)
- Antiwear additives demand can be substantially reduced if steel surfaces are not used
- Engineered surfaces can also substantially reduce the antiwear demand
- Changing the materials can substantially change the additive chemistry requirement

Surface Texture Engineering

- Surface texture to control friction
- Surface texture to provide fine particle trapping
- Perpetual surface texturing by surface layering composite material
- Control flow path of vapor and soot

Additive Chemistry

- Dispersant: succinimides, Mannich reaction prods
- Detergents: sulfonates, phenates, salicylates
- Antiwear: Zinc dithiophosphates
- Friction modifiers
- Anticorrosion
- Antirust
- Pour depressant
- antifoam
- Viscosity Index Improvers

Antiwear Additives

- Zinc dithiophosphates
 - alkyl vs aryl
 - primary vs secondary
 - decomposition temps
- Tricresyl phosphate
 - acid phosphate
 - phosphites
- Phosphate esters

VI IMPROVER GENERAL
STRUCTURAL REPRESENTATION

OIL SOLUBLE, HIGH MOLECULAR WEIGHT
 (20,000-1,000,000) LINEAR POLYMER

Lubricant oxidation is a free radical chain reaction involves chain initiation, propagation, branching, and termination.

Antioxidants

- Hindered phenol
 - simple titration
 - radical termination
- Amines
 - complex reactions
 - different radicals
 - longer inhibition

Irganox L 08
Where R = C₈H₁₇

Irganox L 57

Where R, R' = H, C₂H₅ or C₈H₁₇ and other alkyl chains

Irganox L 109

Irganox L 118

Irganox 1035

Irganox L 135

Polymerization Mechanism

- Condensation
- Example (Aldol Condensation)

Modelling Oil Degradation:

- To characterize the lubricant in terms of reaction, the following factors must be determined:
 - Evaporation
 - Thermal degradation
 - Oxidation
 - Oxidative volatility
 - Polymerization
 - Deposit formation

Polymer Formation

- Molecular weight increase with oxidation time

GPC Differential Refractometer Chromatograms of PRL4247
Oxidized in the Micro-Oxidation Reactor at 225°C and 275°C.

Final simulation results:

Lubricant	CT5113	CT5126	CT5213	CT5214	CT5215
Test Time, hr	252	125	252	252	252
Engine Test					
WDK	526	577	214	242	328
TGF	50%	100%	10%	50%	24%
Oil Consumption (g/kW h)	0.48	3.84			
Simulation					
TGF	42%	85%	8%	60%	25%
Oil Consumption (g/kW h)	0.42	3.69	0.31	0.5	0.5

Reaction Model

where:

- RH : the original lubricant
- Q : primary oxidation products
- P : polymer (high MW products)
- D : deposit
- E : evaporation
- k_n : rate constants
- k_{Ar} : evaporation rate const.
- k_{O_2} : oxidative evap. rate const.

Corrosion Inhibitors

Reocor 12

Succinic acid half ester

Reocor D88G

Reocor 190

Amino O

Sarkosyl O

COMMERCIAL OILS vs HPL-3

DSC AT 220°C

Current Lubricant Technology

- Polarity stacking (preferential attachment to rubbing surfaces)
- Chemical kinetic rate selectivity (antiwear always react the fastest to the rubbing surfaces)
- Optimum reactivity of additives towards the surfaces in terms of concentrations, aggregation tendencies, aggregation sizes, free molecules available in base oils

Dispersancy vs Solvency

- Base oils containing aromatics or esters can disperse insoluble particles or aggregations
- Dispersants are used to help to keep these particles in solution to prevent deposition onto surfaces
- to keep the amount of insolubles low by altering the reaction pathways (stop polymerization)
- to allow the base oil structures to carry more dispersancy or solvency

Figure 6.13 The size and composition of a PIB-TEPA micelle

Figure 6.11 The size and shape of a ZDDP micelle

NORMAL CALCIUM SULFONATE
(NCS)

OVERBASED CALCIUM SULFONATE MICELLE
(WHERE = NCS)

Figure 3—Normal and Overbased Sulfonates

Nanoparticles Emission

- Measurement issues: accuracy, precision
- Dust particle contamination
- Lack of calibration standards

Definitive measurement techniques

- Transmission microscope
- AFM tapping mode in clean room

Lubricant to reduce Nanoparticles

- Sulfur free lubricant
 - * ZDDP major issue--wear
 - * Sulfonate free -- detergent
 - * Synthetic base oil
- Metal free lubricant
 - * Ca major issue -- detergent
 - * Carbon soot accumulation

CLEAR TOPPER

Strategies for low emission lubricants

- Super-stable lubricant
 - Base oils
 - Additives
 - LHRE engine experience
- Decomposable lube.
 - Polylactone structure
 - tailored MW
 - largely inhibitors
 - almost once through
- Multifunctional baseoil structures
- Additive that blocks the polymerization reactions
- additive that promotes decompositions
- Do we really need VII in diesel oils?

Strategy for LEO

- Revolutionary rethinking lubricant composition
- Simpler additive package
- Cleaner additive chemistry
- Combination of base oil structure and additive structure as a designed package rather than take one and tailor to it.

Challenges and Opportunities for Future Engine Oils

Dr. Ewa A. Bardasz
The Lubrizol Corporation
Wickliffe, Ohio USA

January 31st, 2000

OUTLINE

- Chronological additive technology advances
- Traditional lubricants development approaches
- Composition of typical crankcase lubricants
- Future lubricants development approaches
- Future lubricant concepts
 - Examples
 - How a lubricant can function differently

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Additive Advances in the 20th Century

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Additive Component Chronology

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Traditional Additive Development Approaches

- Chemical
- Formulating
- Testing

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Lubricant Development

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Common Additive Components for Engine Lubricants :

Additive	Gasoline Engine Oils	Diesel Engine Oils	Natural Gas Engine Oils	Two Cycle Engine Oils
Dispersant	•	•	•	•
Detergent	•	•	•	•
Antiwear/EP Agent	•	•	•	•
Oxidation Inhibitor	•	•	•	•
Corrosion Inhibitor/ Metal Deactivator	•	•	•	•
Friction Modifier	•			
Pour Point Depressant	•	•	•	
Foam Inhibitor	•	•	•	
Viscosity Modifier	•	•		

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Functions of a Passenger Car Lubricant

Lubricant Marketer	Formulation Component	Possible Elements
Fluidity	Mineral or synthetic oil	H, C, O
Additive Supplier		
Multigrade	Viscosity modifier	
Low temperature flow	Pour point depressant	
Suspend contaminants	Ashless dispersant	N, B
Rust protection	Detergent	Ca, Mg, Na
Cleanliness		
Acid neutralization		
Wear control	Zinc dithiophosphate	Zn, P, S
Oxidation protection	Ashless antioxidants	N
Friction reduction	Friction modifier	Mo, S
Foam control	Antifoam	Si

• Functions of the performance package

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Current Market Drivers

- Extended life, improved durability
- Environmental/societal issues (such as emissions) and concerns
- Economics - more for less
- Product Stewardship - cradle to cradle

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Diesel Engine Emission Regulations

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Future Additive Development Approaches

- Chemistry → Combinatorial Chemistry
- Formulating → Artificial Intelligence
- Testing → Diagnostic Systems, Virtual Testing

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Combinatorial Chemistry

A technology by which large numbers of structurally distinct molecules may be synthesized in a time and resource-effective manner and rapidly tested for desirable properties.

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Combinatorial Chemistry Quantitative Structure Activity Relationship (QSAR)

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Artificial Intelligence New Two-Cycle Additive

Program Input:

Performance Parameters: Piston Varnish ≥ 8.8 , Ring Stick ≥ 8.6
Intermediate Constraints: 0 % Component A (too expensive)
Cost Targets: Minimum Cost

Program Output:

New TC Formulation:

23.5% Component H
10 % Component D
1 % Component F
0.2% Component B
0.3% Component C

Predicted Performance:

Piston Varnish = 8.8
Ring Stick = 8.60
Tot. Treat Wt. % = 35.00
Cost = 20% reduction

Westbend Test Results:

Piston Varnish
Ring Stick

Predicted Results:

8.88
8.60

Actual Results:

9.3
8.6

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Extended Drain Intervals

Benefits

Consumer friendly - reduced maintenance
Reduced disposal

Concerns

Lubricant cost: is synthetic needed?
Qualification methods
Adequate for engine durability
Fuel economy retention
Octane requirement increase (ORI)
Escalating oil consumption with usage
Diverse use patterns
Hazardous waste classification

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Future Lubricant Concepts

- Consumable lubricant
 - Fuel value
 - Environmentally friendly
 - Fuel quality improvement possible
- Alternative fuels
- Lubricants and fuel additives
- Lubricant/coolant

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Extended Oil Drain Interval Concepts Smart Drain Intervals

- 'based on engine operating and oil condition parameters
- engine operating parameters include
 - revolutions, load, speed, distance/time traveled
- oil condition parameters include
 - temperature, level/consumption, pressure before/after filter
- oil sensors for assessing performance reserve ?

• e.g., Jelden and Paehr (Volkswagen) DE 44 01 835 A1, 1994

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Extended Oil Drain Interval Concepts Increased Oil Volume

- auxiliary reservoir supplements sump oil
- sump level detector triggers automatic leveling
- service interval is increased by increasing the volume of oil in the system
 - oil contaminants are diluted
 - additive level is increased

• Renault (Renault), FR 2 581 700 A, 1986

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Extended Oil Drain Interval Concepts Lubricant Temperature Control

- lubricant temperature is kept constant irrespective of engine load
- heat can be fed or drawn off from the lubricant circuit
- oil temperature sensor / heat exchanger / regulating unit
- higher load temperature can be maintained during lower load operation

- Gasthuber, *et. al.* (Daimler-Benz) GB 2 312 246 A, 1997

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Extended Oil Drain Interval Concepts Lubricant/Coolant

- engine oil also serves as engine coolant
- engine oil volume is increased
 - oil contaminants are diluted
 - additive level is increased
- simplified engine block

- e.g., Valev (Steyr-Daimler-Puch), US 4,926,800, 1990

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Extended Oil Drain Interval Concepts Dual Lubrication Systems

- lubrication system 1 valve train, camshaft (subjected to excessive wear)
 - lubricate with conventional oil (Yasuhara)
 - blowby eliminated, wear reduced
 - lubricant life prolonged
 - lubrication system 2 crankshaft, pistons (not subjected to excessive wear)
 - lubricate with diesel fuel (Yasuhara)
 - wear reduced by constant application of fresh lubricant
- Yasuhara (Nissan), US 4,392,463, 1983; Skupien (Renault), FR 2 605 677 A, 1988

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Extended Oil Drain Interval Concepts On-Board Oil Reconditioner

Pinmore Ltd. (UK)

- heated/magnetized stainless steel discs (electronic control)
 - water, fuel, coolant, and corrosive gases flashed from the oil
 - additives remain intact
 - metal particles removed
- functions in partial bypass

- Assali and Ramirez, WO 96/25996

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Extended Oil Drain Interval Concepts Reconditioning Packages

TF Purifiner (US)

- aftermarket retrofit product for Heavy Duty Diesel
 - bypass reconditioner
 - bypass oil filter (> 1 micron)
 - time-release additives in filter
- users change filters, perform oil analysis, and add makeup oil
- 1 million miles without drains in fleet study
- certified as "Pollution Prevention Technology" by California EPA

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Extended Oil Drain Interval Concepts Automatic Oil Change

- spent oil is pumped into holding tank
- new oil is pumped into sump from supply tank
- oil quality stabilized
 - contaminant buildup minimized
 - additives constantly replenished
- pumping operation may be dictated by oil condition sensors

- e.g., Merrill, US 4,674,456, 1987; Nelson, US 5,390,762, 1995

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Extended Oil Drain Interval Concepts Consumable Engine Oil

- spent oil is pumped into fuel system
- new oil is pumped into sump from supply tank
- oil quality stabilized
 - contaminant buildup minimized
 - additives constantly replenished
- pumping operation may be dictated by oil condition sensors

• e.g., Nelson, US 4,869,346, 1989; Yasuhara (Nissan), US 4,417,561, 1983
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Extended Oil Drain Interval Concepts Consumable Engine Oil

Cummins Centinel

- aftermarket retrofit product for Heavy Duty Diesel
 - crankcase oil pumped into fuel
 - makeup oil pumped to crankcase from supply tank
 - high efficiency oil filters
 - electronic controls constantly monitor the engine and synchronize system with engine's actual duty
- oil drains: 300,000 miles; oil filter changes: 75,000 miles
(c.f. 22,000 miles)

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Extended Oil Drain Interval Concepts Advanced Engine Materials

- diamond-like carbon coatings
- vacuum deposition with an arc created by a laser
- coated piston rings, tappets, conrods
- lubricating qualities of graphite, hard as diamond, durable
- reduce wear
- self-lubricating
 - reduce frictional loss and fuel consumption
 - decreased oil volume, extended oil drain interval

BMW Functional Coatings Group / Fraunhofer Institute for Materials and Ray Technology (Dresden) / Federal Institute for Materials Research and Testing (Berlin)

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Extended Oil Drain Interval Concepts Advanced Engine Materials

- solid film lubricant coatings
 - MoS₂, graphite, BN, thermoset polymer base
 - composites of M/MO_x (M = Fe, Ni, Cu, Mo)
- coated cylinder bores, piston rings, valve train components, bearings
- reduce friction, improve wear and corrosion resistance
- promote rapid formation of tenacious oil films
- pores in films serve as lubricant replenishing reservoirs

e.g., Rao, et al. (Ford), US 5,313,919, 1994; WO 97/13884

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Extended Oil Drain Interval Concepts Oil-Free Tribosystems

- piston rolling bearings require no, minimum quantity, or lifetime lubrication
- electromagnetic or electrohydraulic valve control requires no lubricant
- main crankshaft and crank pin/connecting rod bearings require:
 - lifetime lubrication in encapsulated form
 - separate lubricant circuit (diesel fuel or synthetic lubricant)
 - ferrofluid lubricant
- no oil changes
- oil consumption, HC, and PM reduced

Gasthuber, *et. al.* (Daimler-Benz) GB 2 315 812 A, 1998; DE 196 30 215 A1, 1998

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Consumable Engine Oil

Benefits

- Consumer friendly - reduced maintenance
- Consistent lubricant quality
- Deposit control: Combustion chamber, injectors
- Fuel value
- Environmental disposal
- Control over fuel additive quality

Concerns

- Vehicle design changes
- Emissions
- Octane effects
- Product distribution
- Governmental regulation

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Continuous Consumption Simulated Data

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Test Lubricants

	Typical	"Fail" Reference	"Pass" Reference
Base Stock	75% 150N 25% 600N	86% 150N 14% 150B	Low S 150N
Viscosity Modifier	7.5%w OCP	14% Hi SSI VM	10% Thickener
Pour Point Dep.	0.2%w Pour Pt.	0.3%w Pour Pt.	0.3%w Pour Pt.
Additive	13.5%w CG-4 Add.	14.7%w Med. Ash	18%w Exptl Add
Viscosities			
@ 150°C, cP	3.91	4.19	2.56
@ 100°C, cSt	13.74	14.59	7.71
@ 40°C, cSt	101.4	113.2	50.5
CCS @ -15°C	2910	3220	2190
CCS @ -20°C	9600	--	3910
Chemical Properties			
% Ash	0.9	1.3	0.2
% Ca	0.15	0.33	0.01
% Mg	0.04	--	0.02
% Zn	0.12	0.12	--
% P	0.11	0.11	0.03
% S	0.66	0.67	0.07

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Particulate Matter

Fuel + 3% Lubricant, gm/mile

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Diesel Injector Deposit Test

3% "Fail" Reference

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Diesel Injector

After Transient Emissions Matrix

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Combustion Chamber after Matrix

Piston Crown

Cylinder Head

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Transient Emissions Cycle

1994 11-Litre HD Diesel, 365hp, 500hr Audit

Fuel Treatment (in LSRD fuel)	Crankcase Lubricant	Particulate Matter	Run Order
1994 Max. Limit		0.100 gm/hp-hr	
None	Factory Fill	0.123	1
None	Synthetic OEM	0.111	6
None	"Fail" Exptl.	0.111	3
1% "Fail" Exptl.	"Fail" Exptl.	0.112	2
3% "Fail" Exptl.	"Fail" Exptl.	0.138	4
3% "Pass" Exptl.	"Fail" Exptl.	0.126	5

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A Way Forward

- Many new approaches for newer lubrication systems
- Need for a paradigm shift
 - Future lubricants can not be developed in dated hardware
 - Future hardware can not be developed with dated lubricants
- Mechanical, chemical and electronic technology integration is need to create a newer and richer lubricant technology, capable of meeting the market demands of the next decade.

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LUBRICANTS

ATTACHMENTS 20, 21, 22A, 22B, 23 & 24

"Lube Oil Contribution to Emissions: Emerging Issues", W. S. Key, Oak Ridge National Laboratory, Knoxville, TN 37932

"Impact of Engine Oil Consumption on Diesel Engine Emissions", Kent Froelund, Engine Research Department, Southwest Research Institute, San Antonio, TX 78228

"New Emissions Regulations - Impact on Engine Design and Oil Formulation", G.P. Fetterman, Jr., Infineum USA L.P., Linden, N.J. 07036

NPRA paper presented by G.P. Fetterman, Jr. at the Lubricants and Waxes Meeting, November 11-12, 1999 in Houston TX.

"Future API PC-9 Engine Oil Category", August (Augie) Birke, Equilon Enterprises LLC, Houston, TX 77082-3101

"Catalyst Compatible Diesel Engine Oils - DECSE Phase II", Shawn D. Whiteacre, Cummins Engine Company, Columbus, IN 47201

Lube Oil Contribution to Emissions

W. S. Key
Oak Ridge National Laboratory

Emerging Issues

Oak Ridge National Laboratory
W.S. Key
Thang Dam
John M. Storey
Feb. 1, 2000

Motivation – Future Changes Will Elevate the Importance of Lube Oil

- Further Tightening of Heavy Duty Regulations
 - Might Expect Convergence to Light Duty Regulations
- Regulation of Currently Unregulated Toxic Emissions (PAH's, etc.) and regulation of Ultrafine Particulates
- Modifications to the Engine:
 - EGR
 - High Pressure Injection
 - Addition of PCV to Heavy Duty Engines
- More Complex (and perhaps more sensitive) Emission Controls
- Evolution of Fuel & Lube Formulations Changing the Lube/Fuel Combustion Chemistry

Motivation

- Studies to Date Are Sparse, Contradictory, or Lack Consistency
 - Northern Front Range Air Quality Study
 - Suggested That High Emitter Vehicles Had High Contributions to PM From Lube
 - "Preliminary Indications Are That the Nuclei Mode Particles Are Solid and Formed From...metallic Ash From Lubrication Oil Additives."
 - (Abdul-Khalek, et.al., SAE 980525)
 - Ultrafines Have No Solid Core Downstream of EC Devices
 - (Luders, et.al., [FEV], SAE 981374)
 - Lube Oil Contribution to Exhaust is 3 – 7 ppm Fuel Equivalent
 - (DECSE)
 - Lube Oil Contribution of Exhaust is ~20 ppm Fuel Equivalent
 - (Nigel Clark per Schaberg, SAE 972898)

Issues

- What is Lube Oil's Contribution to: PM/SOF/NOx/Sulfur?
- How Does Lube Oil Formulation Change the Contribution to Emissions
 - Viscosity
 - Additives
 - Sulfur
- What is the Range of Change of Contributions to Emissions?
- What Effect Do Lube Oil Emissions Have on EC Devices
- **Will Lube Oil Need to be Reformulated?**

Additional Issues

- What is Lube Oil's Contribution to Solid Core Ultrafines?
- How Does Lube Oil Formulation Affect the Contribution to Unregulated Toxic Emissions?
- How is the Contribution Affected by Fuel Formulation?
- How do Transient Operations Affect Lube Oil Contributions?
- **Will Lube Oil Need to be Reformulated?**

Contributing Constituents

- Hydrocarbons
- Sulfur
 - Base Stock
 - Zinc Dithiophosphate
- Detergents
- Lubricity Agents
 - Zinc (ZDDP)
 - Calcium
 - Magnesium
- Anti Wear, pH Neutralizers, etc.

Volatiles

- Much of Past Work Has Been With SI Engines – Probably Not Relevant to Diesel Because:
 - SI Has Lower Compression
 - Fuel More Volatile
- Studies Indicate That Consumed Lube Oil Is Emitted as Volatiles
- Lube Oil is a Greater Source of PAHs (SAE 940342)

Particulates - Sulfur

- Lube Oil Sulfur Can Become the Dominant Source of the Sulfur in the Exhaust as Fuel Sulfur Declines, Thus:
 - May Become the Principal Source of Catalyst Poisoning or Deactivation
 - May Become the Principal Source of Particulate Sulfates

Particulates – Ash and Metals

- Ash and Metals Can Coat EC Devices Reducing the Number of Active Sites and Reducing Performance
- Are There Metal Constituents Which Could be Subject to Regulation?

Metals for Potential Regulation

EPA's and ARB's Air Toxics Lists

EPA Mobile Source HAPs

Acetaldehyde	Mn compounds
Acrolein	Hg compounds
As compounds	MTBE
Benzene	Naphthalene
1,3 Butadiene	Ni compounds
Cr compounds	POM as 7 PAHs
Dioxin/Furans	Propanal
Diesel PM Styrene	
Ethylbenzene	Toluene
Formaldehyde	Xylene
n-Hexane	
Lead Compounds	

ARB Diesel Exhaust TACs

(same as EPA plus:)

aniline	phenol
Antimony (Sb)	P compounds
Be compounds	Se compounds
phthalates	o-xylene
Cadmium	p-xylene
Chlorine (?)	m-xylene
Chlorobenzene	minus MTBE
Co compounds	
methanol	
MEK	
4-nitrobiphenyl	

Sulfur Contribution

Exhaust SO₄ Levels As A Function of Sulphur Mass Percent
For Various Diesel Test Fuels (SAE 972898)

Plot by Nigel Clark, WVU

Sulfur Contribution

- Preliminary Finding:
 - Deduce an ~ 0 ppm Fuel Sulfur Equivalent

Sulfur Contribution Mercedes A170

Sulfur Contribution

Preliminary data suggest engine out SO_2 due to lube is insignificant for modern LD Diesel

Measuring Sulfur Contribution

■ Method Using SO_2 Measurement

- Initial assumption is that dilute exhaust is similar to ambient air; use ambient SO_2 analyzer (pulsed fluorescence type)
- Pro: sensitive to 50 ppb
- Con: slow (2 min) so only suitable for bag or steady-state measurement
- Ambient NO is small so no significant interference
- Dilute NO is not small, so correction curve developed – makes a big difference

Measuring Sulfur Contribution

Without correction for NO in analyzer,
different conclusion!

Sulfur Contribution

Current Projects

- Ad Hoc Auto/Energy Test:
 - Determine the Contribution of Lube Oil to PM and NO_x in an Advanced Diesel Engine
 - Will Synthetic Engine Oils Reduce the VOF of PM as well as NO_x and Other Regulated Gas Emissions?
- Advanced Petroleum Based Fuels Lube Oil Testing (Preliminary):
 - Effect of Lube Oil Properties & Composition on Emissions
 - Effect of the Emissions on EC Device Performance (w/EGR)
 - Influence of Oil Age on Emissions and Subsequently on ECs
- Comparative Toxicity Study (SwRI, DRI)
- Dayton Research Institute – Study Under Development

What Needs to be Done

- Standardize Test Procedures and Test Methods
- Add Longevity Testing to Current Plans to Develop Aging Effects (Wear) During a Vehicles Regulated Life
- Characterize the Effect of Lube Oil Age (Oil Change Interval) on Lube Oil Contributions to Emissions
- Configure HD Engines with/without EGR and PCV to Quantify Effects
- Perform Fundamental Combustion Experiments to Determine Effects of Interactions of Fuel and Lube Oil Formulations on Exhaust Products
- Conduct Transient Testing to Determine Lube Oil Contributions During this Driving Mode

IMPACT OF ENGINE OIL CONSUMPTION ON DIESEL ENGINE EMISSIONS

USDOE/NREL WORKSHOP

**Dr. Kent Froelund
Diesel Engines
Engine Research Department
Southwest Research Institute**

Outline

- ☞ Motivation - Impact of Oil Consumption on Emissions**
- ☞ Measurement Methods**
- ☞ Sensitivity to Engine Make, Engine Type, and to Operating Conditions**
- ☞ Sensitivity to Oil Properties**
- ☞ Real-Time Steady-State Measurements**
- ☞ Real-Time Transient Measurements**

Motivation for R&D in Oil Impact on Emissions

- ☞ Customer Satisfaction
- ☞ Regulated Engine-Out Emissions
- ☞ Regulated Tailpipe-Out Emissions - Catalyst Deterioration
- ☞ Unregulated Emissions

Measurement Methods

- ☞ Gravimetric (Direct)
- ☞ Volumetric
- ☞ Tracer
 - SO₂
 - Tritium
 - Pyren
 - Oil Additives
- ☞ This Presentation Will Focus on Results Obtained With SwRI's SO₂-Analyzer

Experimental Setup: SO₂-Tracer Technique

Advantages SO₂-Tracer Technique

- ☞ Real-Time Steady-State Engine OC
- ☞ Real-Time Transient Engine OC
- ☞ Component Break-Down OC:
 - ☞ Power-Cylinder
 - ☞ Valve
 - ☞ PCV-Valve
 - ☞ Turbocharger
- ☞ Burned and Unburned Engine OC

Sensitivity to Operating Conditions

HD DI-MEDIUM

MY 1994, ~7 l

*Absolute Oil Consumption Not Appropriate
for Comparison Between Operating Conditions*

Sensitivity to Operating Conditions

DI-MEDIUM

MY 1997, 2 l, I-4

*Good Diesel Engine As of Today Less Than 0.10%
Relative Oil Consumption Regardless of Operating
Condition*

Sensitivity to Operating Conditions

HD DI-MEDIUM
MY 1993, ~7 l, I-6

Characteristic: Low Speed Problems

Sensitivity to Operating Conditions

HD DI-LARGE
MY 1994, >10 l, I-6

Characteristic: Low Load Problems

Sensitivity to Operating Conditions

Relative Oil Consumption Enables A Comparison Between Operating Conditions and Engines!

Summary of Findings

- ➡ **Relative Oil Consumption is a Good Data Analyzing Tool for Comparing Engine Conditions and Engine Makes**
- ➡ **Gasoline Engines With Less Than 0.2% Relative Oil Condition Is Considered Good (1998)**
- ➡ **Diesel Engines With Less Than 0.1% Relative Oil Consumption is Considered Good (1998)**

Summary of Findings (Cont'd)

- ➡ Every Engine is Exhibiting its Own Oil Consumption Characteristics - It Leaves a "Fingerprint"

Viscosity

Decreasing Viscosity Increases Oil Consumption!

Ref.: Furuhami et al., Lub. Eng. 1977

Ref.: Froelund et al., SAE Paper 971699

Volatility

Oil Consumption Index Versus Noack
6 Cylinder, SI-engine, 5W30 Oil

Increasing Volatility Increases Oil Consumption!

Ref.: Hanada et al., Nissan Motors, JSAE Review 1990

Coupling Viscosity and Volatility

Evaporation Versus Base Oil Viscosity
NOAC (DIN 51851)

Desirable Oil: Lowest Volatility at Any Given Viscosity!

Ref.: Kiovsky et al., BP Oil Company, Lub. Eng. 1993

800 rpm Under 0% Load (Idle)

☞ TOC Constant in Time

☞ IOC Constant Among Cylinders

6000 rpm Under 100% Load (Rated Power)

☞ TOC Constant in Time

☞ IOC Constant Among Cylinders

4000 rpm Under 25% Load 1'st Run

- ☞ TOC Fluctuates in Time
- ☞ IOC Varies Among Cylinders

4000 rpm Under 25% Load 1'st Run

- ☞ TOC Fluctuates in Time
- ☞ IOC Varies Among Cylinders

4000 rpm Under 25% Load 2'nd Run - Repeat Next Day

- ☞ TOC Constant in Time
- ☞ IOC Varies Among Cylinders

New Emissions Regulations - Impact on Engine Design and Oil Formulation

**NPRA Fall 1999 Meeting LW-99-132
G.P. Fetterman, Jr. Infineum USA L.P.
Greg Shank, Mack Trucks, Inc.**

Overview of Topics

- **Historical look at emissions regulations and the co-evolution of high performance diesel engines and their equally high performance lubricants**
- **Emission limit changes in 2002 will require new control technology - Exhaust Gas Recirculation (EGR)**
- **EGR - equipped engines will require new lubricants**

Overview of Topics

- ASTM is working on new PC-9 category for EGR engines
- PC-9 development timing, costs, and alternatives
- Probable oil formulation impact of PC-9 tests
- Summary

Table One
U.S. EPA Diesel Engine Emission Standards

Year	1988	1991	1994	1998	2002
Unburned HC	1.3	1.3	1.3	1.3	1.3
NOx	10.7	5.0	5.0	4.0	2.0*
Carbon Monoxide	15.5	15.5	15.5	15.5	15.5
Particulate Matter	0.6	0.25	0.1	0.1	0.1

All values are measured in grams per brake horsepower-hour

* Alternate target is a total of 2.5 for combined NOx and non-methane hydrocarbons

Limits apply to engines at "end of useful life"

NOx Versus Particulate Matter Balancing Act

Reduce PM-Agravate NOx

- **Improved combustion**
 - Inlet air swirl
 - High pressure injection
 - Advanced timing
 - Reduced crevice volume
- **High peak temperature**

Reduce NOx-Agravate PM

- **Less effective combustion**
 - Retarded injection timing
- **Lower peak temperature**

New NOx Limit in October 2002

- **NOx limit in EPA test cycle drops by 50%**
 - Current 4.0 g/hp-h drops to 2.0 g/hp-h (or 2.5 incl HC)
- **Cannot be met with existing NOx control technology**
 - Beyond operational limit of retarded timing
- **All engine manufacturers plan to use Exhaust Gas Recirculation (EGR) to meet 2002 NOx limits**
 - EGR is expected to dramatically impact engine oil performance requirements

New Oil Category PC-9

- Anticipated performance needs of EGR-equipped engines is PC-9 driver
- Three new engine tests with EGR
 - Mack T-10 (Ring and Liner wear)
 - Cummins M11-EGR (Valve Train wear/Sludge/Filter Pressure)
 - Caterpillar 1Q (Piston Deposits)
- Performance parameters similar to CH-4 tests-
 - T-9, M11, and 1P but using EGR
 - None of the new tests currently available

EGR...What's The Worry?

The combustion process:

- In the textbook
 - $C_xH_y + O_2 \Rightarrow CO_2 + H_2O + \text{Heat}$
- In the real world
 - $\text{Fuel} + \text{Air} \Rightarrow CO_2 + H_2O + \text{Heat} + CO + HC + NO_x + SO_x + \text{Particulate Matter} + ??$
 - At high temperatures not a problem
- Cooled EGR condenses nitric and sulfuric acids
 - Recirculated into engine power assembly

PC-9 Is Not Just Three New Tests

Current engine test proposal to define PC-9:

– Mack T-10	New test - \$65,000
– Cummins M11-EGR	New test - \$85,000
– Caterpillar 1Q	New test - \$60,000
– Caterpillar 1N	CG-4 test - \$22,000
– Mack T-8E	CH-4 test - \$43,000
– John Deere JDQ-78A	New test - \$60,000
– RFWT	CH-4 test - \$12,000
– EOAT	CH-4 test - \$ 7,000

Total, one time pass = \$354,000

PC-9 Costs

- One time pass in just HD tests > \$350,000
- Add in PCMO test costs > \$500,000
 - To approve one core data set in one viscosity grade
 - Engine tests only - slight increase to include bench tests
- If testing volume is similar to CH-4 experience, PC-9 reformulation cost could approach \$40 million
 - Reduced by about \$3,000,000 if Sequence IIIF could be substituted for JDQ-78A

Summary of Events Required for PC-9 Licensing Brent Shoffner 9/21/99

ID	Task Name	Start	Finish	1999	2000	2001	2002
1							
2	Define PC-9 Performance Parameters	3/16/99	3/16/99				
3	Design Prec. Mtx. Finalized	3/17/99	10/7/99				
4	PC-9 Funding MOU Signed	10/8/99	12/20/99				
5	Designate Base Stocks for Prec. Mtx.	11/1/99	11/1/99				
6	Select additive suppliers for Prec. Mtx.	11/2/99	12/15/99				
7	Identify Test Oils (with validation)	10/1/99	1/17/00				
8	Blend Prec. Mtx. Oil Formulations	1/18/00	3/29/00				
9	Final Acceptance of New Engine Tests *	2/9/00	2/9/00				
10	Final Acceptance of Test Parameters	2/9/00	2/9/00				
11	PC-9 Demonstration Oil Is Validated	6/15/00	6/15/00				
12	PC-9 Precision Matrix Testing	3/30/00	8/9/00				
13	Precision Matrix Data Analysis	8/10/00	9/15/00				
14	HDEOCP Post Matrix Test Acceptance	9/18/00	10/17/00				
15	Finalize Pass/Fail Criteria (Sub B Mtg)	10/18/00	12/29/00				
16	New Product Development	1/1/01	12/31/01				
17	API Licensing Allowed	1/1/02	1/1/02				

* Acceptance of each engine test (by HDEOCP) for discrimination and preliminary precision prior to starting the precision matrix. What is the criteria? Minimum of one test on 100S-1 and one on a prototype PC-9 oil?

PC-9 Alternatives

- **Past history suggests PC-9 will not be developed in time for a January 1, 2002 API first licensing**
- **EPA emission deadline is firm**
 - **EGR required to meet NOx limits**
 - **New oils required to protect engines**
- **OEM specifications already exist**
 - **Mack has EO- X oil approval lists**
 - **Cummins has CES 200XX oil specifications**
 - **Will be upgraded as required to protect engines**

PC-9 Oil Formulation Implications

- **EGR and its attendant acid formation will stress the acid neutralization capability of oils**
 - **More TBN?**
 - **More or less reactive TBN?**
 - **A balance of both?**
- **Increased soot loading with PC-9 tests will require increased dispersant potency**
- **High soot also leads to wear concerns**
 - **Possible need for high anti-wear treats at odds with low phosphorus / catalyst compatibility for light duty oils**

Continued Formulation Implications

- **“Backward compatibility” has always been a key part of the API oil category system**
 - **Newer / higher quality oils can be recommended for use in engines which originally called for lower categories**
- **Potential need for higher TBN/SASH oils to meet PC-9 performance could cause difficulties**
 - **The 1P test in CH-4 is very difficult for high SASH oils**
- **Industry guidance is that protection of EGR engines outweighs backward compatibility**

Summary

- **EPA emission regulations reduce NOx in 2002**
- **New limits will require EGR**
- **EGR will recirculate acids into the engine**
- **PC-9 under development for EGR engines**
 - **Many tests / high cost to reformulate**

Summary

- **Very tight time schedule, delay likely**
 - **OEM's will do whatever is required to protect engines**
- **PC-9 oils expected to differ significantly from current CH-4/SJ formulations**

Summary (continued)

- **Although the development process will be difficult, it is likely that the combination of EGR-equipped engines and PC-9 quality lubricants will successfully continue the historic co-evolution of high performance diesel engines and their equally high performance oils.**

LW-99-132

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NEW EMISSIONS REGULATIONS – IMPACT ON ENGINE DESIGN AND OIL FORMULATION

by

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Presented at the

1999 Lubricants & Waxes Meeting
November 11-12, 1999
Omni Hotel, Houston, TX

NEW EMISSIONS REGULATIONS – IMPACT ON ENGINE DESIGN AND OIL FORMULATION

Abstract: For the past eleven years changes in heavy-duty diesel engine emission limits have driven changes in engine design. In turn, these changes in engine design have made the service environment of the engine lubricant more severe and necessitated the development of increasingly higher quality heavy-duty oils. This paper will review the historical co-evolution of emissions limits, engines, and lubricants as a background to what may be the most dramatic change in emissions control technology yet considered.

This new technology is exhaust gas re-circulation (EGR), and although it offers the possibility of allowing diesel engines to reach significantly lower levels of exhaust emissions; it also brings with it an array of new concerns and potential problems. A new API performance category, which is currently known as PC-9, is being developed to meet the lubrication needs of these EGR-equipped engines. This paper will provide an overview of the early development status of this new category along with a description of the new engine tests being considered. Although none of these new tests are yet available for new product development, some very preliminary data points are available using CH-4 quality oils in the new tests. A quick review of these results will be contrasted against the known performance of these products in the current CH-4 tests.

By extrapolating these results from specific tests to general performance needs, this paper will finally predict the probable implications of these tests on the formulation requirements of PC-9 quality lubricants.

Background: For many years, in fact until 1988, diesel engine exhaust emissions were largely uncontrolled by the U.S. Environmental Protection Agency. Although there were some limitations on black smoke, the more conventional pollutants such as unburned hydrocarbons (HC), nitrogen oxides (NO_x), and carbon monoxide (CO) were left uncontrolled for diesel engines long after they had been brought under strict control for passenger cars. To some extent this was a reasonable position, as diesel engines offer inherently low levels of HC and CO in their exhaust streams due to their operation with a dramatic excess of air compared to a spark-ignited engine as used in a passenger car.

In fact, a review of the EPA limits on HC and CO as shown in Table One reveals that the limits first imposed on these two pollutants in 1988 do not tighten as the years progress. It should also be noted that these limits are not really constraining for diesel engines as they can easily be met with no changes to the engine hardware. The battleground for the diesel engine designer lies in the trade-off between the other two controlled pollutants, NO_x and particulate matter (PM). Although the details of the combustion chemistry are more complicated, it is useful to consider the control of both NO_x and particulate matter as the two horns of a dilemma. Generally, things done to improve the combustion process i.e. to burn the fuel more completely will reduce the engine out particulate matter. Unfortunately, this good combustion leads to very high peak flame temperatures which also generates high levels of NO_x. Conversely, anything which “messes up” the combustion event can bring down both the peak flame temperature and the generation of NO_x, but at the same time it will directionally increase the particulate matter. Of course all of the trade-offs to control NO_x and PM must be balanced to maintain the best possible fuel economy.

Some of the engine design changes to control diesel engine emissions were described in the 1995 NPRA paper by Fetterman and Shank. Generically, the control of PM is done with changes which

improve the combustion of the fuel in the engine. These include such things as much higher injection pressures in order to form smaller fuel particles, increasing the rate of "swirl" of the air in the combustion chamber, reducing the amount of dead space in the combustion chamber, and even slowing down the rated engine speed to allow more time for the fuel to burn completely. During this time the control of NOx has been handled by retarding the timing of the injection of the fuel into the combustion chamber. By delaying the injection event until closer to top dead center, the combustion event is changed so that the peak flame temperature drops and NOx generation drops.

Unfortunately, this delay in injection timing means that the fuel injector is still firing after the piston passes through top dead center and begins to move back down the cylinder. This, combined with the extremely high fuel injection pressures involved can cause some of the fuel to spill over the top of the combustion chamber bowl. Some portion of this fuel is coked by the high temperature of the combustion zone, and it is converted to soot. In turn, some portion of this soot reaches the cylinder liner and becomes entrained in the lubricant film and transported into the bulk lubricant in the engine sump. Thus, one impact of the control of engine out NOx has been a significant increase in the soot loading of the engine oil.

Both of the last two API performance categories, CG-4 and CH-4, have had the control of oil entrained soot as key portions of their engine test requirements. Some tests, such as the Mack T-8 and T-8E look at an oil's ability to prevent excessive increases in viscosity when it is loaded with 4 to 6% soot. Other tests such as the Cummins M11 and the Roller-Follower Wear Test address the oil's ability to prevent excessive wear in the valve train with similar levels of soot loading, while the Mack T-9 looks at ring and liner wear with about 2% soot in the oil. Again, in all of these tests at least one of the key pass/fail parameters is a measure of how well the oil can cope with the increased soot loading which comes from retarded timing to control NOx.

If we look at the impact these engine changes have had on oil formulations, several trends evolve. First, the dramatic increase in soot loading from 1-2% in pre-emission controlled engines to 6+% in 1999 emissions compatible engines has required a significant increase in dispersant potency. At the same time, piston design changes combined with increased specific engine output (not an emission requirement, but a part of the real world none-the-less) have lead to the need for enhanced oxidation stability and piston cleanliness / detergency. Finally, the need to control engine wear in a high soot environment has lead to a careful balance of the dispersant and antiwear components in the oil. The good news for additive suppliers is that, generally, these new engines like to have more additives! The bad news for them is that the U.S. lubricant market is extremely competitive and cost sensitive, so these additives must be delivered in a well-optimized, cost effective package.

Up to this point, this background discussion has been historic...a review of what has happened to date. From here on, it will be looking forward to what is coming and that is a 50% reduction in the NOx limits in October of 2002. Although the engine manufacturers, the EPA, and the California Air Resources Board had mutually set this target level of performance several years ago, the original target timing was to be 2004. It was accelerated to 2002 as a part of several consent decrees signed in late 1998 between the various engine manufacturers in the U.S. and the EPA.

As discussed earlier, NOx reductions from the 1988 limits through 1999 have been met by retarding the injection timing. According to the engine design experts at all of the engine manufacturers, reducing NOx from today's limit of 4.0 g/bhp-h to the 2002 limit of 2.0 g/bhp-h is beyond the capability of additional retardation of timing. A new emission control technology is required to meet these NOx reductions. This new technology is known as exhaust gas recirculation (EGR). EGR reduces NOx by putting non-combustible components into the incoming air-fuel

charge, once again reducing peak flame temperature and NOx generation. In addition to this simple dilution effect of EGR, even greater benefits can be seen if the exhaust gas is cooled before it is returned to the engine. One part of this advantage is the cooler intake charge allows better filling of the cylinder and thus better power generation. The other part of the advantage is that the EGR components have higher specific heat values than the incoming air and fuel, so they even further cool the combustion mixture and allow more power / better fuel economy at a fixed NOx generation level.

Developing API quality level PC-9: The anticipated lubricant needs of these new EGR-equipped diesel engines is the sole driving factor for the developing PC-9 quality level. Figure one shows a schematic diagram of a generic cooled EGR system. Exhaust gas is taken from the high pressure area upstream of the turbo-charger turbine and passed through a cooler. This cooled gas is mixed with fresh intake air as it exits from the intake charge-air cooler, and then the mixture of fresh air plus EGR is drawn into the engine. (N.B. the engineering effort required to make this happen is not insignificant, but it is well beyond the scope of this paper.)

One of the major concerns about the use of EGR with high-output diesel engines stems from the need to cool the exhaust gases before returning them to the engine intake. The problem with this is that diesel fuel contains sulfur. Even "low-sulfur" diesel fuel still contains 300 to 400 ppm as a typical level of sulfur. When the fuel is burned in the engine, this sulfur is converted to SOx. In addition, one of the main by-products of the combustion of a hydrocarbon fuel is water vapor, so the exhaust stream contains some level of NOx, SOx, and water vapor. In the past these have not been a problem, because the exhaust gases have been extremely hot which keeps these components in a dis-associated gaseous state. However, when the EGR stream is cooled before it is returned to the engine, the mixture drops below the dew point, and liquid water condenses out. This water reacts with the NOx and SOx components to form a mist of nitric and sulfuric acids in the EGR stream. This mixture is then fed back into the power assembly of the engine where it has been seen to cause catastrophic increases in ring and liner wear. In addition, the use of EGR with no change in injection timing will also cause an increase in soot generation. The little bit of good news coming with EGR is that it is so efficient in controlling NOx that engine designers expect to be able to advance injection timing which will both reduce soot and improve fuel economy.

The engine manufacturers concern over the impact of EGR is so great that they have proposed and started development of three new EGR-equipped engine tests for PC-9. These tests are the Mack T-10, the Cummins M11-EGR, and the Caterpillar 1Q. It is anticipated that each of these tests will measure similar performance attributes to their CH-4 counter-parts, the T-9, M11, and 1P, except they will evaluate these parameters in an engine equipped with EGR.

To re-cap their expected duties, both the T-9 and T-10 will look at ring and liner wear as well as bearing corrosion protection. The M11 and M11-EGR will address sliding valve train wear, filter plugging, and sludge control; and both the 1P and 1Q will evaluate the oils ability to control piston deposits. As this paper is being written, none of these tests is yet available to industry, so much of what is said is based on plans and predictions. With that disclaimer, what follows is a discussion of each new test.

Mack T-10: The Mack T-10 is a new test using an in-line six cylinder, turbo-charged and after-cooled diesel engine which has been modified to use EGR. An ASTM Task Force reporting to the HDEOCP has been formed to develop this test for PC-9. Several shake-down tests have been run in the Mack test laboratory in Hagerstown, MD. By the end of October, 1999, Mack plans to have seven engines distributed to industry labs as well as a preliminary draft of a test procedure. It is

anticipated that this test will run for 300 hr. with two phases...similar to the T-9 test. The first phase will run for 100 hr. with retarded timing to pre-condition the oil with soot, and the second phase will run 200 hr. at low speed and extremely high firing pressure to generate ring and liner wear. Again, both of these operating conditions are similar to the T-9, but the use of EGR in the T-10 is expected to dramatically increase the wear rates compared to the CH-4 test. The current development plan calls for a discrimination mini-matrix to start in late 1999 and for the test to be ready for the ASTM precision and BOI matrix testing in the Spring of 2000.

Cummins M11-EGR: The Cummins M11-EGR is also a new test using an in-line six cylinder, turbo-charged and after-cooled diesel engine which has been modified to use EGR. The test is at roughly the same level of development as the T-10 with some testing done in Cummins engine laboratory in Columbus, IN. and ten engines expected to be distributed to industry by October, 1999. An ASTM Task Force has also been formed to develop the M11-EGR test. The test procedure is expected to vary somewhat from the M11 test, in that it will use a 100 hr. pre-sooting phase (similar to the T-10), followed by a 250 hr. cycling phase with variations in engine speed, load, EGR rate and cooling. The original expectation was that the M11-EGR test might generate 10-12% soot in the oil, but more recent data suggests the level will be more like 8-10%. Still, this represents a dramatic increase in soot loading compared to the 5-7% soot required for CH-4 / Mack EO-M PLUS / Cummins CES20076 test requirements. Based simply on the test length, EGR cycling, and soot loading, it would appear that the M11-EGR test could be the defining test for PC-9.

Caterpillar 1Q: The Caterpillar 1Q test is also a new test for PC-9, but in this case it is a single-cylinder laboratory test engine which has been modified to use EGR. The test engine assembly which Cat identifies as the 1Y3700 Single Cylinder Oil Test Engine (SCOTE) uses the same block and head as the 1P test. However, for the 1Q test it uses a new piston design as well as EGR. Since all engine labs have 1Y3700 SCOTE installations and the new piston is readily available, the power-producing portion of the 1Q can be run today. In fact, Caterpillar have released a test procedure for a test which they call the pre-Q. It uses the proposed 1Q operating conditions but without EGR, and both Caterpillar and the other industry labs have experience running this test. However, the availability of EGR-conversion kits for the 1Y3700 engines is somewhat behind the other two new tests. Cat's original design used a variable venturi to help draw EGR into the intake air stream, and this design proved to be plagued with deposit problems. A new EGR system has been designed using increased back-pressure to drive the EGR stream, similar to both the T-10 and M11-EGR tests.

Industry status: As indicated earlier, the industry need is to have API licensed oils meeting the needs of EGR-equipped engines available no later than October of 2002 when the new EPA emissions limits become effective. However, many engine manufacturers would like to have oils available even earlier, as they can accrue credits for early introduction of lower NOx engines. To support this desire, ASTM is targeting January 2002 as the desired first allowable use date. Working back from January 2002, the API typically requires a minimum of one year development time for a new category to insure that all parties have sufficient time for reformulation testing. This means that all ASTM test development work and limit setting must be complete by January 2001. Figure two shows the official HDEOCP timeline as of September 1999, and based on this plan it is possible that PC-9 could be developed in time. However, a review of the early timeline plans for both API CG-4 and CH-4 would show that both categories slipped by one year. Considering the dramatic increase in engine severity expected with EGR-equipped tests combined with the fact that

none of the new tests are available as of the September 1999 timeframe, it requires a very optimistic outlook to predict an on-time delivery for PC-9. Still, all parties are working diligently to develop PC-9 as quickly as possible since the EPA emissions timing is non-negotiable, and these new oils will be required to protect EGR-equipped engines.

While the new test hardware is slightly behind the OEM's desired schedule, progress has been made on many of the development supporting activities. Potential test matrix designs have been developed, and agreement in principle has been reached on the matrix funding. Final selection of the basestocks to be used in the matrix is expected at the November API lubes committee meeting, and a task force has been working on defining the matrix test oils. At this time, it would seem that on-time delivery of PC-9 is still a possibility, but it will require a full share of good luck combined with continued hard work by all shareholders to maintain the aggressive schedule for on-time delivery of the new tests.

In addition to the three new EGR-equipped engine tests being developed for PC-9 there are a significant number of other tests which will define PC-9. Eight of the CH-4 engine and bench tests are planned to be carried forward either at the CH-4 performance level or, perhaps, with tightened limits for pass/fail. These carry-forward tests are:

The 6.5 liter Roller Follower Wear Test

The Engine Oil Aeration Test

The Caterpillar 1N Aluminum Piston Deposit Test

The Mack T-8E

The Cummins High Temperature Corrosion Bench Test

ASTM D892 Foaming Test

ASTM D6278-98 Shear Stability Test

ASTM D5800 Volatility Test

The original PC-9 request from EMA also contained a number of tests which have been formally dropped from the category definition. Still, there remain several requested performance parameters which have not been dropped, but final agreement has not been reached on the test which will be used to measure that parameter. First among these is an oxidation test. The EMA requested the John Deere JDQ-78A oxidation test as part of their original category definition. This test has not been well received by the oil and additive company members of the HDEOCP. Although the EMA members have indicated early support for the test, they have also indicated a willingness to consider other options to measure an oil's oxidation protection. At the September 99 HDEOCP meeting a Task Force was formed to look at meeting the oxidation test requirements of PC-9.

In addition to all of the above tests there are two new bench tests which are also being considered for PC-9. The first is a seal compatibility test similar in intent to the CARS test developed for passenger car lubricants. In concept, this test will identify reference oils which show aggression towards seals in glassware tests, but which have shown acceptable field performance. These reference oils will be used by seal suppliers to develop new seal compounds, and oil suppliers will screen their new products against the performance of these reference oils to insure that more aggressive products are not brought to the market. The final bench test will look at the low temperature performance of heavily-sooted used engine oils. Data is being collected on drain oils from the Mack T-8E to assess these low temperature performance concerns.

Cost considerations: The development of both the new PC-9 category tests and new oils to meet the required performance level will be expensive propositions. The planned budget for the "funded" portion of the test precision and BOI matrix is approximately \$2,000,000. However, the "funded" portion of the testing represents only a fraction of the actual matrix cost as the test labs must fund that portion of the cost which would be required for test stand calibration. Of course, even though the labs provide the up front funding, these costs are eventually passed back to the oil and additive companies which conduct tests for oil approvals. The entire cost of the development matrix, including the "funded" tests as well as the calibration tests is projected to approach \$7,000,000 depending on which matrix design is finally selected.

Once the development testing is complete, oil formulators still face an impressive bill to qualify a finished lubricant. Using published costs for the carry over tests and industry estimates of \$85,000 for an M11-EGR, \$65,000 for a T-10, \$60,000 for a 1Q, and \$60,000 for a JDQ-78A (should it remain in the category), the cost to deliver a one-time pass in all of the proposed PC-9 tests is close to \$360,000 for one core program in one basestock and one viscosity grade. If some consideration is given for a less than one out of one pass ratio plus the need for testing to qualify for the latest API "S" category, it is not too difficult to imagine one core program costing well over \$1/2 million!

In June of 1998, an industry estimate of the reformulation cost for CH-4 was made based on RSI test registrations. At that time industry had spent just under \$30,000,000 on engine tests to qualify oils for CH-4. If a similar estimate is made using the tests proposed for PC-9 along with their attendant prices, the probable reformulation cost for PC-9 is \$39,500,000, or roughly 30% greater than the cost of CH-4. That cost could be reduced by close to \$3,000,000 if the Sequence IIIF test could be substituted for the JDQ-78A test for oxidation.

Alternatives to PC-9: Given the EPA deadline for reduced NOx emissions in October 2002 and the absolute need to use EGR to reach those target levels of NOx, there is a definitive need to have PC-9 quality lubricants available. Although industry still has time to deliver this new category on time, history would suggest that the probability of success is not high. Like the test developments for both CG-4 and CH-4, it is likely that ASTM will deliver fit-for-purpose tests, but they will probably not be done by the required date of January, 2001. If this happens, the response of the OEM's is again likely to be exactly as it was for the previous delayed categories. Assuming the new test development programs actually complete sometime during the year 2001, on or about January 1, 2002 Cummins will probably issue a new lubricant specification, CES200XX; and on or about April 1, 2002 Mack will issue their EO-N specification. If industry has reached consensus limits to define PC-9, both of these specs will probably align with those limits. On the other hand, if consensus limits cannot be reached, both OEM's will establish whatever limits they feel are needed to protect their engines in the field. The bottom line is that API PC-9 quality oils will exist in the 2002 time frame either as an API category or a series of OEM specifications.

Formulation implications: Since none of the new PC-9 tests are available to begin development of new oil formulations, any implications listed here are pure prognostication. That said, there are a number of known changes which allow the prediction of at least directional differences from CH-4 tests. First, since it is known that EGR will result in acidic mist being fed into the engine power assemblies, it is likely that additional TBN will be required for the PC-9 tests. What is not known is whether bulk oil TBN is sufficient, or if some special method is required to deliver this TBN to the ring and liner interface. Is it better to have more reactive TBN or more stable TBN, or most likely a proper balance of both?

One of the directional impacts which is easy to predict is the need for increased dispersant potency. The target for soot loading in the M11-EGR is in the range of 8-10%, this represents roughly a 50% increase from the 6.5% rating point for CES20076 approvals. There is absolutely no doubt that this increase in soot will require a step increase in dispersant potency from CH-4 or any of the current OEM specifications.

Another concern at these very high soot loadings is how they will impact the oil's anti-wear performance. It is possible that wear control may require either very high ZDDP treats or some kind of supplemental anti-wear component. If this happens, it could drive a wedge between the anti-wear needs of heavy duty engines and the low phosphorus / catalyst compatibility needs of light duty engines. Although it is just speculation at this time, it is possible that the divergent performance needs of PC-9 and GF-3 could spell the end of the "universal" oil market in the U.S.

During the early planning for PC-9, the industry shareholders indicated a desire to maintain the long standing API protocol of "backward compatibility". That is, oils formulated to meet the newest, highest performance category can also be used to lubricate older engines which originally specified earlier API performance levels. There is some concern that the potential need for increased TBN and SASH to meet the performance tests in PC-9 may make the Caterpillar 1P test from CH-4 very difficult if not impossible. Acknowledging this concern, the NCET in its category needs statement indicated that backward compatibility is desirable, but it should not be used as an excuse to degrade PC-9 engine protection. The need to protect EGR-equipped engines outweighs the need for backward compatibility.

Initial engine data: Mack have been running T-10 test development studies in their Engine Test Laboratory in Hagerstown, MD. Some of this work has been done using the CH-4 category reference oil, TMC1005. Early testing with 12% EGR rate showed that all of the TBN reserve of TMC1005 was consumed in less than 100 hrs. Mack revised the EGR rate to just under 10%, a level which they feel may be reasonable for high-load NOx control, and TMC1005 was able to complete the 100 hr. oil conditioning phase with 3.5 TBN reserve. The used oil wear metals analysis showed 23 ppm of copper, 165 ppm of iron, and 16 ppm of lead. Contrasting these results to the T-9 test at 100 hours reveals that TMC 1005 still retains 6.3 TBN, and the used oil wear metals are 5 ppm of copper, 58 ppm of iron, and 4 ppm of lead. Clearly the EGR addition to the T-10 test attacks the TBN reserve of the oil and causes an increase in wear metals compared to the T-9. Obviously this comparison pits a single test development result against a well established data base, but the result does suggest that PC-9 performance will require a significant formulation change from CH-4.

Summary: Over the last eleven years on-highway diesel engines have been under increasingly tighter exhaust emissions controls by the U.S. Environmental Protection Agency. In order to meet these controls, the design of diesel engines has gone through a series of evolutionary developments. A number of these changes have been aimed at reducing particulate emissions, and in general they are designed to improve the combustion process and to more completely burn the fuel injected into the combustion chamber. Unfortunately, most of these changes to improve combustion also raise the peak flame temperature and cause an increase in the generation of NOx, another controlled pollutant. Conversely, other design changes have been designed to "mess up" the combustion process, drop the peak flame temperature, and reduce NOx emissions. Unfortunately these changes tend to aggravate the generation of particulate matter. Up to and including the 1999 emissions targets engine designers have been able to balance the trade-off between NOx and particulate

Table One

U.S. EPA Diesel Engine Emission Standards

Year	<u>1998</u>	<u>1991</u>	<u>1994</u>	<u>1998</u>	<u>2002</u>
Unburned HC	1.3	1.3	1.3	1.3	1.3
NOx	10.7	5.0	5.0	4.0	2.0*
Carbon Monoxide	15.5	15.5	15.5	15.5	15.5
Particulate Matter	0.6	0.25	0.1	0.1	0.1

All values are measured in grams per brake horsepower-hour

* Alternate target is a total of 2.5 for combined NOx and non-methane hydrocarbons

Limits apply to engines at “end of useful life”

FIGURE ONE:

FIGURE TWO:

"EXPLORING LOW EMISSION DIESEL ENGINE OILS"

Scottsdale, AZ January 30 - February 1, 2000

FUTURE API PC-9 ENGINE OIL CATEGORY

August (Augie) Birke

EQUILON
ENTERPRISES LLC

"EXPLORING LOW EMISSION DIESEL ENGINE OILS"

EQUILON
ENTERPRISES LLC

“EXPLORING LOW EMISSION DIESEL ENGINE OILS”

Participants in the New Categories Development Process

“EXPLORING LOW EMISSION DIESEL ENGINE OILS”

API PC-9 Development Time Table (Projected)

3/2002 First Marketing of Licensed Fluids Allowed
10/2002 EPA Mandated Date for Meeting New Emission Limits

EQUILON
ENTERPRISES LL

“EXPLORING LOW EMISSION DIESEL ENGINE OILS”

Proposed API PC-9 Performance Parameters

Performance Parameter	EMA Proposed Test	Approximate Cost
Fe Piston Deposits, Oil Con.	Cat 1Q-EGR (1)	\$60,000.00
Al Piston Deposits	Cat 1N (2)	\$22,000.00
Ring/Liner Wear Brg. Corrosion	Mack T-10-EGR (3)	\$65,000.00
Soot Related VTWT	GM 6.5L (4)	\$12,000.00
Soot and EGR related VTWT	Cummins m11-EGR (5)	\$85,000.00
Thermal Oxidation	Deere JDQ (6)	\$60,000.00
Oil Aeration	Navistar 7.3L (7)	\$7,000.00
Soot Related Viscometrics	Mack T-8E (8)	\$44,000.00
Used Oil (Low Temp) Vis.	Based on T-8E?	5,000 +
High Temp. Corrosion Bench	CH-4 Bench Test (HTCBT)	
Shear Stability	CH-4 Bench Test (Bosch)	
Volatility	Bench Test (NOACK)	
Foaming	CH-4 Bench Test (D892)	
HTHS Viscosity Min	CH-4 Bench Test	
Seal Compatibility	Bench -D471 Based	
	Approximate Total	360,000 +
(X) New Engine Test	(X) Current Engine Test

"Catalyst Compatible" Diesel Engine Oils

DECSE Phase II

Shawn D. Whitacre

"Exploring Low Emission Diesel Engine Oils"

Scottsdale, AZ

Cummins Engine Company

January 31, 2000

1

Outline

- **Background**
- **Recent trends in engines and oils**
- **DECSE program**
- **Technical hurdles**

2

Meeting the Needs of the Customer

Background

- Final rule on Tier II
 - potential for diesel engine penetration
- EPA presently considering:
 - Future HD emissions standards for NO_x, PM
 - Aftertreatment *forcing*
 - Diesel fuel sulfur reductions
 - Aftertreatment *enabling*

Critical Sub-system Linkages

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Trends Influencing Oil Formulation

- Demands for longer maintenance intervals
- Retarded injection timing
 - Need improved soot handling
- Exhaust Gas Recirculation (EGR)
 - Corrosion protection
 - Oxidation resistance at elevated temperatures
- Closed Crankcase Ventilation (CCV)
 - More oil in exhaust
 - Maintain turbocharger efficiency

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Lubricant Development Trends

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DECSE Program

- Diesel Emission Control - Sulfur Effects
 - Phase 1 investigated **fuel sulfur** effects on:
 - NOx adsorber catalysts
 - Diesel oxidation catalysts
 - Lean NOx catalysts
 - PM filters/traps
 - Lubricant used in testing contained 0.35% S
 - Summary: <http://www.ott.doe.gov/decse/>

➤ Phase 2 research to focus on lubricant effects

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DECSE Phase 2 Research

- Government/industry participation:
 - DOE and National labs
 - EMA
 - API/NPRA
 - CMA
 - MECA
- Program initiation: January 2000
- Planned duration: 3 years

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DECSE Research Focus

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Study Questions

- What are the effects of lubricant properties and composition on engine-out/catalyst-in emissions?
- How do these effects influence the performance and durability of diesel engine emission control systems (ECS)?
- What is the impact of oil age?

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What Is Known....

- Emission control systems vary in sulfur sensitivity, but in general "the lower, the better"
- Lubricant contributes small, but potentially significant level of sulfur
- Automotive three-way catalysts have known incompatibilities

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Lube Oil Sulfur Contribution

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Sources of Lube Oil Sulfur

- Base oil

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Sources of Lube Oil Sulfur

- Sulfur containing additives
 - Anti-wear agents (ZDDP, others)
 - Detergents (sulfonates, phenates)
 - Corrosion inhibitors
 - Friction modifiers
 - Anti-oxidants

Sulfur Coupled Phenate

Sulfonate

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Other Characteristics of Interest....

- Sulfated ash
 - May plug PM traps
- Zinc and phosphorous
 - Known incompatibility with automotive three-way catalyst
- Volatility/distillation characteristics
- Aromatic level and type
- Viscosity
- Nitrogen
- Olefins

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Approach

- Task 1
 - Multi-cylinder engine tests to determine lubricant effects on engine-out emissions
 - Medium displacement engine equipped with EGR and CCV
- Task 2
 - Bench-scale analysis to determine if lube derived emissions impact performance of ECS
- Task 3
 - Confirm task 2 results on catalyst equipped engine
 - ECS durability

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Desired Outcome

- To determine which (if any) lube derived emission components are detrimental to ECS performance/durability
- Guidelines for lubricant formulation:
 - Basestock
 - Additive
- Design guidelines:
 - Engine manufacturers
 - ECS suppliers

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Technical Hurdles

- Maintaining backward compatibility
 - Older engines still on the road
 - Implications of misapplication
- Conflicting demands
 - Compliance may necessitate EGR + aftertreatment which differ in appetite

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Outlook....

- As we strive to produce high performance, low emissions products we must...
 - First establish an understanding of fundamentals
 - Be creative in development
 - Form partnerships in anticipation of challenges

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PARTICULATE

ATTACHMENT 25

"Diesel Exhaust Particle Morphology: Nanoparticle Formation", David B. Kittelson,
Center for Diesel Research, University of Minnesota, Minneapolis, MN 55455

TRIBOLOGY

ATTACHMENTS 26 & 27

"Tribology Needs for Low Emission Diesel Engine Oils ", Frank A. Kelley, Program
Manger, Advanced Materials Technology, Caterpillar Inc., Peoria, IL 61656

"Friction and Wear Workshop", George R. Fenske, Argonne National Laboratory,
Argonne, IL 60439

OTHER

ATTACHMENTS 28 & 29

"CRC Program Overview", Brent K. Bailey, Coordinating Research Council (CRC),
Atlanta, GA 30346

" New, Non-Food Uses of Soybean Products", Blaine Rhodes, OmniTech International,
Ltd, Midland, MI

Diesel Exhaust Particle Morphology

David B. Kittelson
Center for Diesel Research
University of Minnesota

presented at
USDOE /NREL Workshop
Exploring Low Emission Diesel Engine Oils
31 January 2000

Background

- Current emission standards are mass based. Recently interest in other measures, i.e, size, number, surface, has increased.
- Concerns about particle size
 - New ambient standards on fine particles
 - Correlations between fine particles and excess deaths
 - Increased asthma in children living near roadways
 - Special concerns about ultrafine and nanoparticles
 - Indications that reductions in mass emissions may increase number emissions
 - HEI study on old and new technology engines
 - High number concentrations downstream of some exhaust filters
 - Removing carbon from exhaust may make formation of tiny particles from fuel and lube oil derivatives more likely
 - Difficulties associated with measurement of ultrafine and nanoparticles
 - Often more than 90% of particle number are formed during exhaust dilution
 - Particle dynamics during sampling and dilution are highly nonlinear - large changes in of particle number may result from small changes dilution and sampling conditions

Typical Diesel Particle Size Distribution - Log Scale

Particle Composition and Structure

Particles consist mainly of highly agglomerated solid carbonaceous material and ash and volatile organic and sulfur compounds.

Typical Composition of Diesel Particulate Matter: Lube oil contributes to SOF, ash, sulfate

Typical P - T (average) plot for modern Diesel (adapted from Cummins, SAE 1999-01-0516)

Atmospheric Dilution Leads to Nucleation, Absorption, and Adsorption

A dilution ratio of 1000 may be reached in 1 - 2 s

Particle Formation History: From the Start of Combustion to the Nose

Significant Gas to Particle Conversion Takes Place as the Exhaust Dilutes and Cools

- More than 90% of the particle number may form through homogeneous nucleation of nanoparticles
- From 5 to more than 50% of the particle mass may form through adsorption, absorption, and nucleation
- These processes are *extremely* sensitive to dilution conditions
- Thermodynamics and fluid mechanics of mixing during dilution are very complicated and vary widely

Studies of Diesel Nanoparticle Formation Using a Variable Residence Time Dilution System

Sensitivity of Diesel Particle Number Emissions to Dilution Conditions - Residence Time and Temperature Effects

Sensitivity of Diesel Particle Size Distribution to Dilution Conditions - Residence Time Effects

Nanoparticle formation downstream of an exhaust filter may be even more sensitive to dilution conditions

Our results suggest nanoparticles are mainly volatile, we have demonstrated this with a catalytic stripper

Typically more than 99% of the nanoparticles disappear by 300 C, the residue is likely to be metallic ash

For typical diesel exhaust conditions, saturation ratio may not be high enough for nucleation, $S > \sim 3$

Influence of Dilution Upon Extractables

What does nucleate? Consider the threshold for Binary H_2SO_4 - H_2O nucleation

- An extreme dependence of the nucleation rate upon temperature, H_2SO_4 , and H_2O concentrations makes theoretical predictions of nucleation difficult.
- Seinfeld and Pandis give an empirical expression to predict the onset of nucleation in this system:

$$C_{\text{crit}} = 0.16 \exp(0.1T - 3.5RH - 27.7)$$

where C_{crit} is the threshold H_2SO_4 concentration in $\mu\text{g}/\text{m}^3$, T is temperature, RH is relative humidity (0 to 1).

- I have used this expression and mass and energy balances applied to the dilution process to predict the ratio of the actual H_2SO_4 concentration to the critical one, C/C_{crit} . When this critical concentration ratio exceeds one, nucleation is likely.

Influence of Fuel and Exhaust Conditions on Sulfuric Acid Nucleation

H₂SO₄ Nucleation Is Suppressed by Adsorption on Carbon Particles

Nanoparticle Nucleation and Growth

- It appears that with current engines binary sulfuric acid - water nucleation triggers the process.
- The initial size of these nuclei is about 1 nm.
- In most cases there is not enough sulfuric acid present in the exhaust to explain the observed rates of particle growth.
- Hydrocarbons normally associated with the soluble organic fraction apparently are absorbed by the concentrated sulfuric acid nuclei leading to the observed growth rates.
- Solid carbon in the exhaust adsorbs particle precursors and suppresses both nucleation and growth of nanoparticles
- Fast dilution decreases the influence of solid carbon and the time available for nucleation and growth

Lubricating oil and emissions

- Direct influences on particulate emissions
 - Sulfur in oil contributing to sulfuric acid in the exhaust
 - Lube oil contribution to SOF
 - Adsorbed SOF mass on solid carbon particles
 - High SOF leads to faster nanoparticle growth, especially with low solid carbon emitters
 - Ash particles
 - Most ash incorporated into accumulation mode on current engines
 - Direct ash nucleation to form nanoparticles may be an issue with low solid carbon emission engines
- Other Influences on Emissions
 - Sulfur and phosphorus damage to aftertreatment devices
 - Crankcase fumes and positive crankcase ventilation

The lube oil may contribute more sulfur to the exhaust than the fuel with future ultra-low sulfur fuels

Calcium from the oil will form exhaust solids as the products of combustion cool during expansion stroke

Modern Engines Have Particle Mass Concentrations in the Range of 8 mg/m^3

If there is little carbon formed by combustion, ash particles may nucleate to form solid nanoparticles

Number Concentrations of Calcium Particles -
Assumes all of the calcium compounds nucleate to form 7 nm diameter nanoparticles.

Summary - 1

- A significant amount of particulate matter (e.g. 90 % of the number and 30% of the mass) is formed during exhaust dilution from material present in the vapor phase in the tailpipe, principally sulfuric acid from sulfur in the fuel and lube oil and SOF constituents from the fuel and lube oil.
 - New particles are formed by nucleation. This is likely to be the source of most of the ultrafine and nanoparticles (and particle number) associated with engine exhaust.
 - Preexisting particles grow by adsorption or condensation.
 - Nucleation and adsorption are competing processes. Soot agglomerates provide a large surface area for adsorption that suppresses nucleation. Thus, engines with low soot mass emissions may have high number emissions.

Summary - 2

- Nanoparticle measurements are very strongly influenced by the sampling and dilution techniques employed.
 - Nucleation, adsorption, absorption, and coagulation during sampling and dilution depend upon many variables, including dilution rate, (or residence time at intermediate dilution ratio), humidity, temperature, and relative concentrations of carbon and volatile matter.
 - Changes of more than two orders of magnitude in nanoparticle concentration may occur as dilution conditions are varied over the range that might be expected for normal ambient dilution, e.g., 0.1 to 2 s dilution time scales.
- Sampling systems should mimic atmospheric dilution to obtain samples representative of the tailpipe to nose process.

The most difficult problem associated with exhaust particle measurement is understanding the dilution process from tailpipe to nose -- this is being examined in the CRC E-43 program

Summary - 3

- Currently most nanoparticles are volatile. However, with cleaner engines, metallic ash particles from the lube oil (or fuel if metallic additives are present) may become more important.
 - Solid particles raise new issues...
 - But they are easy to control with exhaust filters
- Spark ignition engines have much lower fine PM mass emission rates than diesels but their greater numbers may make them an important fine PM source.
 - SI particles are considerably smaller than those from diesel engines so that they will be a much larger relative contributor to nanoparticle emissions than to mass emissions
 - Lube oil also plays an important role in SI PM emissions
 - Much of the mass is lube oil related SOF in older high emitters
 - With clean low emitters, lube oil ash may be the principal PM constituent (Leeds University)

Tribology Needs for Low Emission Diesel Engine Oils

Frank A. Kelley
Program Manager
Advanced Materials Technology

"Exploring... Low Emission Diesel Engine Oils"
Scottsdale, AZ
January 31 - February 1, 2000

Topics Covered

CATERPILLAR

- Needs & Expectations
 - Environmental Acceptability
 - Reduced Operating Costs
- Development Challenges
 - Engine/Lube System Development
 - Specifications and Standards

CATERPILLAR

Emissions/Environmental Concerns

- Meet Regulations
 - All Applications
 - Environmentally Friendly
 - Biodegradability/Toxicity
 - Vegetable-based Fluids
 - Need better high temperature stability
 - Need better low temperature viscometrics
 - Synthetics
 - Need lower cost
 - Need synergistic additives
 - Extended Oil Change Periods/Fill-For-Life
 - Recycling
-

CATERPILLAR

Reduced Operating Costs

- Fuel Economy Improvement
 - Higher Temperatures, Loads and Stresses
 - Impact on Fluid Performance Characteristics
- Durability and Reliability
 - Less Downtime
 - Enhanced Productivity
- Fill-For-Life (FFL) Strategy
 - Long Life Fluids
 - New Filtration Concepts
 - On-Board Monitoring
 - Optimized System Design

CATERPILLAR

Customer Expectations

- Truck Engines & Vehicles
 - Lower Operating Cost
 - Improved Fuel Economy
 - Reduced Maintenance
 - Durability/Reliability
 - 1,000,000 Miles/20,000 Hours to Overhaul
 - Reduced Infant Mortality Failures

CATERPILLAR

The stakes are high

- Customers demand *Optimum* lubricant performance

Development Challenges in Tribology for Low Emission Diesel Oils

- Reduced SOF & Lower Oil Consumption
 - New oils/additives
 - New ring/cylinder designs & materials
- EGR Systems, Contamination Handling
 - Catalyst Compatibility
- Higher Fuel Injection Pressures
 - Fuel Lubricity & Contamination
 - Oil Interactions
- Lubricant Performance Prediction
 - Ring belt zone
 - Valve train/Bearings
 - Remaining Useful Life Of Oil
- Application of Boundary Lubrication Concepts

CATERPILLAR

Fluid Performance Characteristics

CATERPILLAR

- Deposit Formation Tendency
- Viscosity
- Low Volatility
- Thermal Stability
- Materials Compatibility
- Contamination Handling Characteristics

CATERPILLAR

HDD Engine Oil Specifications

<u>API Category</u>	<u>CF-4</u>	<u>CG-4</u>	<u>CH-4</u>	<u>PC-9</u>
Introduced	1990	1995	1998	6/2002
Emissions Std.	1991	1994	1998	2002
Primary Fuel	High S	Low S	Low S	Low S
<u>Critical Engine Tests</u>				
Piston Deposits & Oil Consumption	Cat 1K	Cat 1N	Cat 1P & 1K	Cat 1Q* & 1N
Soot Handling	T-7	T-8	T-8E	T-8E
Ring/Liner Wear	T-6	n/a	T-9	T-10 *
Rolling VTW	n/a	GM 6.2L	GM 6.5L	GM 6.5L
Sliding VTW	n/a	n/a	M11	M11 *
Oxidation Control	n/a	IIIE	IIIE	JDQ-78

* with EGR

CATERPILLAR

HD Oil Development - Testing Costs

Summary

- Address Environmental Concerns Proactively and From All Angles.
 - Maintain and Further Enhance Performance Advantages.
 - Work Towards a Higher Level of Sophistication in the Development Process.
 - Identify More Timely, Less Costly Ways to Define Fluid Performance Requirements.
-

Friction & Wear Workshop

George R. Fenske
Argonne National Laboratory
presented @
'Exploring Low Emission Diesel Engine Oils'
Scottsdale, AZ
Jan 30 - Feb 1, 2000

Why Have a Workshop on Friction and Wear?

Argonne National Laboratory

Energy Technology Division

■ Optimization of tribological systems critical to achieve:

- Fuel Economy
- Emissions Reduction
 - | Better use of fuel
 - | Implementation of emission reduction strategies
- Reliability and Durability
 - | Million-mile warranties
- Safety

■ Friction & wear often addressed after-the-fact

■ Lack of coordinated R&D efforts that address topics germane to a wide range of applications

■ DOE/OTT/OHVT - Parasitic energy loss workshops

- Friction & Wear, Aerodynamic Drag, Thermal Management, Brakes & Rolling Resistance

Workshop on Research Needs for Reducing Friction and Wear in Transportation

Argonne National Laboratory

Energy Technology Division

Objective(s):

- Obtain input from industry (OEMs end-users, and suppliers) on their critical needs to reduce friction and wear
- Develop a multi-year R&D plan to address critical barriers that industry identified
- Establish R&D teams to address critical needs
- Increase governmental awareness of issues and needs

Workshop Agenda

Argonne National Laboratory

Energy Technology Division

Keynote Presentations

- | Effect of Friction & Wear on Fuel Efficiency
- | Role of Lube Oil on Nanoparticulate Emissions

Industry Needs

- | OEMs, engine manufacturers, suppliers, end-users

Technical State-of-the-Art Updates

- | Materials, Coatings, Lubricants, Design Methods, & Characterization

Breakout Sessions to Develop Research Agendas

- | Materials, Coatings, Lubricants, Design Methods

Site Visits

Multi-Year Program Plan - Final (December 1999)

Issue - Solution - Barrier Approach

Argonne National Laboratory

Energy Technology Division

Example: General Public

- secure fuel supplies	-reduce demand by use of alternative fuels -increase thermal efficiency of engine -reduce mechanical & parasitic losses	- low lubricity of alternative fuels - wear of high(er) pressure fuel system parts - wear with low(er) viscosity lubes -

Customer Needs/Issues

Argonne National Laboratory

Energy Technology Division

Customer	Issue
General Public	<ul style="list-style-type: none"> - secure fuel supply - environment
Fleet Operators	<ul style="list-style-type: none"> - owning & operating costs - maintenance costs (oil change interval)
Truck Manufacturers	<ul style="list-style-type: none"> - cost effectiveness of vehicle - meeting emission standards
Off-Road Vehicles	<ul style="list-style-type: none"> - uptime - owning & operating costs - emissions
Engine Manufacturers	<ul style="list-style-type: none"> - emissions - fuel efficiency - durability/reliability - power density

Customer Needs/Issues cont'd

Argonne National Laboratory

Energy Technology Division

Customer	Issue
Automobile Manufacturers	<ul style="list-style-type: none"> - fuel economy (CAFE) standards - performance - durability - alternative fuels - manufacturing costs
Suppliers	<ul style="list-style-type: none"> - ring, rod, camshaft frictional losses - low-sulfur fuel systems - high power-density bearings - low-friction, durable seals - high power-density transmissions
Lubricant Suppliers	<ul style="list-style-type: none"> - emissions - catalyst poisoning - extended life lubes - universal lubes - speciality/segmented lubes

Customer Needs/Issues cont'd

Argonne National Laboratory

Energy Technology Division

Customer	Issue
Railroads	<ul style="list-style-type: none"> - operating costs - emissions - safety
Locomotive Manufacturers	<ul style="list-style-type: none"> - emissions - efficiency - durability

Common Research Topics

Argonne National Laboratory

Energy Technology Division

Quantitative understanding of failure mechanisms

- A quantitative understanding of failure mechanisms such as wear, scuffing, and fatigue is essential both for the development of computational design codes to mitigate and possibly avoid those problems and for the development of bench-top tests to predict full-scale behavior. This will require combining the results of basic research into those mechanisms, applied research into how those mechanisms are manifest in an engine or drive train, testing to develop correlations between fundamental properties and component behavior, and analytical and computational approaches to codify the understanding

Common Research Topics (cont'd)

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Bench-top tests that are predictive of full-scale behavior

- While a quantitative understanding of the various failure mechanisms would be extremely helpful in designing bench-top tests, in the meantime it should be possible to develop better correlations between lab behavior and full-scale behavior by taking greater care to duplicate in the laboratory the essential conditions that prevail in an operating engine or drive train

Common Research Topics (cont'd)

Argonne National Laboratory

Energy Technology Division

■ Affordable surface-modification technologies suitable for various components in various fuels or lubricants, and under various operating conditions

- ∴ For many situations where stresses, temperatures, or environments are becoming more severe, current bulk materials have reached, or soon will reach, their performance limits, and surface modification remains the only viable alternative for additional improvements. Surface-modification techniques for consideration include various coatings, thermal treatments (perhaps by lasers), ion implantation methods, and texturing or smoothing.
- It is unlikely that any single surface-modification technique will be suitable for all applications. Therefore, a variety of techniques or coatings need to be characterized and, perhaps, further developed.

Common Research Topics (cont'd)

Argonne National Laboratory

Energy Technology Division

■ Better understanding of the chemistry of lubricants and how additives affect their interactions with rubbing surfaces

- Formulation of additive packages is largely empirical. A more scientific understanding of the role of additives would form the foundation for developing new lubricants that will be longer lasting, environmentally friendly, capable of handling increased soot loadings for EGR, compatible with catalysts (probably with very low sulfur and phosphorous levels), and/or compatible with nonferrous materials.
- ∴ Some question the validity of current protocols to evaluate catalysts. A fundamental understanding of how lubricant additives such as S, P, and Cl poison catalysts is needed.

Common Research Topics (cont'd)

Argonne National Laboratory

Energy Technology Division

- **Advanced computer codes that model friction, wear, distribution of lubricants, and lubricant interactions with surfaces**

A general friction/wear/lubrication model is needed along with more specific models of lubrication and vapor-phase lubrication.

- **Affordable high-performance steels to withstand the higher stresses resulting from increasing power density and fuel pressure**
- **Improved rotary-seal systems for longer life**
- **Improved brake systems to compensate for heavier loads and reduced aerodynamic drag**

Benefits of Improving Friction and Wear Performance

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- **Fuel Savings**
- **Emission Reduction - Quality-of-Life**
 - use less fuel
 - enabling emission reduction strategies
- **Reduced Downtime - higher productivity**
- **Reduced Maintenance Costs**
- **Improved Safety**

What do we do next?

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Establish teams & projects

- ⋮ National labs and universities to do initial research and materials evaluations
- ⋮ Lubricant (and fuel), and additive supplier
- ⋮ Suppliers to make prototype parts
- ⋮ Vehicle and engine manufacturer for overall guidance and field tests

DOE Solicitation for R & D Projects

- ⋮ Friction and Wear
- ⋮ Aerodynamic Drag
- ⋮ Thermal Management
- ⋮ Brakes and Rolling Resistance

Acknowledgment

Argonne National Laboratory

Energy Technology Division

Ray Fessler

DOE

Industry

COORDINATING RESEARCH COUNCIL

CRC Program Overview

Timothy C. Belian
Brent K. Bailey
Coordinating Research Council, Inc.

Session V - Open Forum
U.S. DOE/NREL Workshop on
“Exploring Low Emission Diesel Engine Oils”

Holiday Inn Sunspree Resort
Scottsdale, Arizona

January 31-February 1, 2000

COORDINATING RESEARCH COUNCIL

Overview

- Established in 1942 with two members - American Petroleum Institute & Society of Automotive Engineers
- Serves as the focal point for collaborative efforts between the fuels, lubricants and domestic equipment industries. Direct efforts towards generating statistically valid data on interactions of fuels, lubricants and vehicle systems on vehicle and automotive equipment performance, emissions and resultant air quality. Information will be publicly available and will be used:
 - by industry to ensure optimum compatibility and customer satisfaction
 - by industry, Government and the public to enhance joint achievement of clean air and other applicable goals.

Overview - (Continued)

- Provides a means of cooperation with the Government
- Research carried out by committees
 - cooperative studies among participating laboratories
 - contract studies directed by small group of experts

CRC Organization

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Performance Committee Role

- Relate physical and chemical properties of automotive fuels and lubricants to vehicles and vehicle component performance as it affects customer satisfaction. Performance shall refer to, but not be limited to, driveability, acceleration, knock, fuel economy, and durability.
- Develop laboratory engine and vehicle test procedures, including methods of quantifying results, to measure effects of fuel and lubricant properties on vehicle and vehicle component performance. Tests will be used in commerce to provide customer satisfaction and/or to assure compliance with regulatory requirements.

Examples of Current Performance Committee Research

CCD Test Development

- 1999 Hot Fuel Handling Program to determine critical volatility parameters for predicting hot fuel handling performance in fuel injection vehicles
- 1999 Octane Workshop to measure octane number requirement of knock sensor equipped vehicles

Emissions Committee Role

- Define effects that changes in automotive hardware, fuel composition, and their interactions have on automotive emissions related to air quality and air-borne toxic issues.
- Determine vehicle/fuel source emissions contribution to the environment and how current computer models reflect these contributions.
- Address current and anticipated regulatory concerns.

Examples of Current Emissions Committee Research

- E-43 - Diesel Particulate Sampling Methodology
- E-37 - Effect of A/C on Tailpipe Emissions
- E-23 - Remote Sensing of High Emitters
- E-47 - Sulfur/LEV Reversibility Program

Advanced Vehicle, Fuel, and Lubricants Committee Role

- Define effects that changes in advanced automotive hardware, new fuel formulations, and their interactions have on automotive emissions.
- Evaluate the durability and operability of new fuel formulations in advanced hardware.

Examples of Current Advanced Vehicle, Fuel, and Lubricants Committee Research

- AVFL-2 - Operability and Compatibility Characteristics of Advanced Technology Diesel Fuels
- AVFL-5 - Evaluation of NO_x Aftertreatment Technologies for GDI Engines

Atmospheric Impacts Role

- Improve the ability to predict the impact of emissions on air quality and airborne toxics by promoting and participating in leveraged programs to improve emissions inventories, reducing uncertainties in the atmospheric chemistry of emissions, and comparing performance of air quality models.
- Predict the atmospheric impact of emerging data.
- Address current and anticipated regulatory concerns.

Examples of Current Atmospheric Impacts Committee Research

- A-23 - Biogenic Emissions Contribution to Urban Ozone and PM2.5
- A-28 - Meteorological Models for Inter-Regional Transport
- A-36 - Weekday vs. Weekend Emissions

CRC Web Site

www.crcao.com

New, Non-Food Uses of Soybean Products

Blaine Rhodes
Omni Tech International, Ltd.
Midland, Michigan, USA

Presented at
Exploring Low Emission Diesel Engine Oils
Scottsdale, Arizona
January 30 – February 1, 2000

*Soy.
A natural
renewable
feedstock
for industry.*

Inedible Soybean Oil Domestic Consumption

Source: US Commerce Department. Nov-Oct 12 Month Trailing Total

THE SOYBEAN CHECKOFF PROGRAM

- Established by Congress in 1991
- 0.5% of soybean market price collected from 60¢ soybean farmers
- MISSION: Create an environment within which U. S. soybean producers can maximize profits

UNITED SOYBEAN BOARD MAJOR PROGRAM AREAS

- PRODUCTION
- INTERNATIONAL
- DOMESTIC MARKETING
- NEW USES

New Uses Committee Mission

Create new soy demand through the
discovery, development and introduction of
new soy-based products and applications

Program Goals And Objectives

New usage demand – (millions of bushels)

Cumulative New Product and Application Introduction Goals

Future Product Candidates Coatings

- **Interior primer paint – ICI / Glidden**
 - Introduction planned for March 2000
- **Paint ingredients**
 - University of Missouri/Rolla
 - University of Southern Mississippi
 - Michigan Molecular Institute

Future Product Candidates Printing Inks

- **Faster drying printing inks** - Iowa State
- **UV-cured Inks** - Lehigh University - Radco
- **Textile printing inks** - Kansas State

Market Segment- Adhesives

Finger Jointed 2x4

Lubricants Market Segment

AREAS OF MAJOR EMPHASIS

- Total loss lubricants
- Hydraulic fluids
- Crankcase lubricants
- Working fluids

Soy Lube For Steel Cables

Lubricants

- High lubricity
- High viscosity index
- Low evaporation loss
- High flash point

- Chemical modification
- Genetic modification
- Additive use

MARKET SEGMENT- Plastics

MARKET SEGMENT- Specialty

*Soy.
A natural,
renewable
feedstock for
industry.*

ATTACHMENT 30

List of Acronyms

LIST of ACRONYMS

ANL	Argonne National Laboratory
ANPRM	Advanced Notice of Proposed Rule Making
APBF	Advanced Petroleum Based Fuels
API	American Petroleum Institute
ARS	Agricultural Research Services
BD20	Biodiesel (20% MeSoyate in Diesel Fuel)
CLR	Cylinder, Liner, Ring
CMA	Chemical Manufacturers Association
CO	Carbon Monoxide
CRC	Coordinating Research Council, Inc.
DECSE	Diesel Emissions Control - Sulfur Effects
DENOX	Diesel Engine Nitric Oxide Catalyst
DEO	Diesel Engine Oil
DI	Dispersant Inhibitor
DME	Dimethyl Ether
EC	Emission Control
EDX	Electron Dispersive X-ray
EGR	Exhaust Gas Recirculation
EMA	Engine Manufacturers Association
EPA	Environmental Protection Agency

DOJ	Department of Justice
FT	Fischer-Tropsch
FTV	Federal Test Vehicle
HC	Hydrocarbons
HDD	Heavy Duty Diesel
LEDEO	Low Emission Diesel Engine Oil
LHR	Low Heat Rejection
MECA	Manufacturers Emissions Control Association
MeOH	Methanol
MTU	Michigan Technological University
NCAUR	National Center for Agricultural Utilization Research
NO _x	Nitric Oxides
NIST	National Institute of Standards and Technology
NPRA	Notice of Proposed Regulatory Action
NREL	National Renewable Energy Laboratory
OHVT	Overview of Heavy Vehicle Technologies
OEM	Original Equipment Manufacturer
PAO	Polyalphaolefin
PC-9	Proposed Category 9
PC-10	Proposed Category 10
PM	Particulate Material
PPM	Parts per minute
PSU	The Pennsylvania State University

R&D	Research and Development
SAE	Society of Automotive Engineers
SCR	Selective Catalytic Reduction
SDL-1	Synthetic Diesel Lubricant
SEM	Scanning Electron Microscope
SOF	Soluble Organic Fraction
SwRI	Southwest Research Institute
TBN	Total Base Number
USDA	U.S. Department of Agriculture
USDOE	United States Department of Energy
VECSS	Vehicle Engine Cooling System Simulation
VI	Viscosity Index
ZDDP	Zinc Dialkyl Dithiophosphate
ZDP	Zinc Dithiophosphate
ZDTP	Zinc Diaryl Dithiophosphate

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE June 2000	3. REPORT TYPE AND DATES COVERED Subcontract Report	
4. TITLE AND SUBTITLE Exploring Low Emission Lubricants for Diesel Engines		5. FUNDING NUMBERS BF006001	
6. AUTHOR(S) J.M. Perez			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Perez Consulting and Technical Services 1762 Princeton Drive State College, PA 16803		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Boulevard Golden, CO 80401-3393		10. SPONSORING/MONITORING AGENCY REPORT NUMBER NREL/SR-570-28521	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A workshop to explore the technological issues involved with the removal of sulfur from lubricants and the development of low emission diesel engine oils was held in Scottsdale, Arizona January 30 through February 1, 2000. It presented an overview of the current technology by means of panel discussions and technical presentations from industry, government, and academia.			
14. SUBJECT TERMS diesel, sulfur, lubricants, low emission diesel		15. NUMBER OF PAGES 475	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102