Penn State Multi-Discipline Tribology Group and Energy Institute Studies.

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INTRODUCTION. This presentation is a summary of the current research activities on fuels and lubricants in the Multi-discipline Tribology group and the engine test group in the Combustion Laboratory of the Pennsylvania State University. The progress areas discussed in this summary include those found in Table 1.

Table 1. RESARCH AREAS

- **Diesel Engine Emission Reduction**
- **Oxygenated Fuels**
- **Improved Friction Fuels**
- **Vegetable Oil Lubricants**
- **Extended Drain Lubricants**
- **Effect of Chemical Structure on Friction and Wear**

The research is of interest either directly or indirectly to the goal of this work-shop, diesel engine emissions reduction. The current projects at Penn State in the areas listed above will be discussed.

EXPERIMENTAL.

Engine Test Facilities Facilities. The Combustion Laboratory of the Energy Institute has a number of test stands and a fully equiped emissions lab. A partial list of the engines and equipment utilized in this work are found in Table 2 and 3.

Table 2. ENGINES.

- **Cummins 24 Valve B5.9TC**
- **VW 1.9L TDI**
- **Navistar T444E TC**
- **GM 6.5L V8 IDI TCD**
- **Yanmar TS180 NA 15 HP SCTE (2 Engines)**
- **"Knock" Test Engine**

Table 3. Emissions Instrumentation.

- **Sierra BG-1 Micro Diln Unit**
- **Sartorius M3P Prec. Balance**
- **Nicolet Magna 550 FTIR**
- **Horiba On-line Analyzers (Hc, CO, & CO_2)**
- **HP 6890 GC w TCD & FID**
- **R&P Series 5100 Diesel Particle Analyzer**
- **Calif. Analytical HFID 300 THC**
- **LambdaScan Portable Scanner**
- **Rosaemount On-line O_2 Analyzer**

Fuels. The diesel fuel used throughout these studies is a low sulfur (32 ppm) commercial fuel. A series of tests have been conducted to explore the effect of oxygenates on emissions. The oxygenated fuels studied include various ether – diesel mixes and B20 diesel fuel.

Lubricants. Lubricants studied include fully formulated commercial petroleum and vegetable oils. Several base fluids found in Table 4.

Table 4. Test Fluids.

JOJOBA
CORN
CASTOR
RAPESEED
HIGH OLEIC VEG OILS
NPG, TMP and PE Type Esters

PROGRAM DISCUSSION.

Engine Studies. Current engine projects focus on various emission reduction studies. Results of some earlier studies aimed at the reduction of emissions by using oxygenated fuels. The oxygenated fuels include Dimethyl Ethers (DME), B20 fuel. In addition, work on vegetable base lubricants is in progress. Earlier studies indicate a significant reduction in the measured particulate matter are published [1 -3].

The test results show significant reduction in particulates reduction when oxygenates are added to the fuel. A follow-on study of the use of dimethyl ether (DME) as a diesel fuel additive in a vehicle involves the use of a campus shuttle bus. Tests will begin later this year upon completion of fueling facilities and vehicle and engine modifications.

A series of NOx control studies using carbon sorbents and selective NOx recirculation is also in progress. PSU is applying carbon sorbent technology developed by Sorbent Technologies to mobile source NOx .

Particulate emission reduction studies include oxygen enrichment of intake air, membrane coated diesel traps and fuel borne catalysts.

Improved Friction Fuels. Methyl esters of vegetable oils in diesel fuel result in significant particulate reduction and improve the lubricity of low sulfur diesel fuels. However, if the use of the required volume of vegetable oils exceeds the current availability of vegetable oil. Use of lower concentrations will still improve lubricity but results in lower oxygen concentration in the fuel. This makes it less effective as a particulate reduction additive. One possible solution is to add oxygen to the fuel by oxidation.

A vapor phase oxidation pilot plant, Figure 1, was developed by the tribology group to make oxygenated hydrocarbon additives for enhanced oil recovery [4] and B20 fuels for friction and wear evaluation [5]. The approach used is to conduct vapor phase oxidation of the fuels, analyze the fuels to determine the extent of oxidation and the effect of oxidation on the cetane no., and evaluate the effectiveness of the oxidized and unoxidized fuels neat and as additives.

Oxidations were conducted at 350 and 375^{o}C. A series of analyses were conducted on the original feed to the column and the oxidized products. Solid – liquid chromatographic column analyses indicated oxygen was added to up to 40 percent of the fuel molecules in the vapor phase oxidation process. Gas chromatography comparisons of the feed and the oxidized fuels showed minimal cracking of the feed stock. Heat of combustion tests indicarted oxidaion resulted in a reduction of energy content of the fuel of about 10%. Since the oxidized fuels are to be used as an additive, this energy loss is minimal.

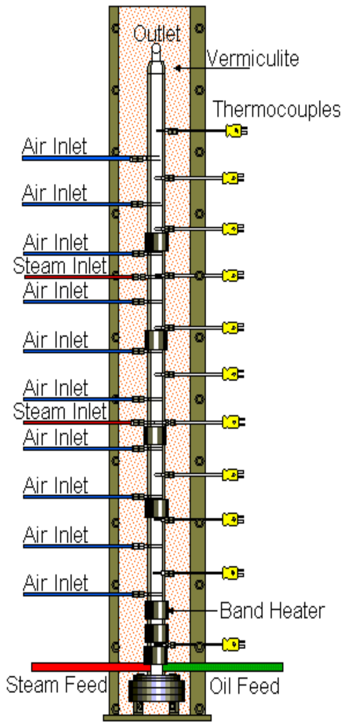

Fig.1. Vapor Phase Oxidation Reactor

To evaluate friction and wear, a modification of the Penn State four-ball method was developed. Due to the higher volatility of the fuels, a temperature was selected to allow completion of the tests with adequate fuel remaining in the ball pot to cover the test specimens. The load was selected to optimize the observed changes in the wear scars. The conditions selected are found in Table 5.

Both friction and wear of the fluids were evaluated. All of the oxidized fuels exhibited a wear reduction when compared to the original low sulfur diesel fuel. The friction was also lower for all the fuels.

Typical friction results are found on Figure 2 (Diesel Fuel) and Figure 3 (B20 Fuel).

Table 5. Four-Ball Test Conditions for Fuel Evaluations

- **load 10 kg**
- **speed = 600 rpm**
- **test temperature = 60 °C**
- **AINSI 52-100, 1.27 cm diam. balls**
- **test times,**
  - **30 min break-in**

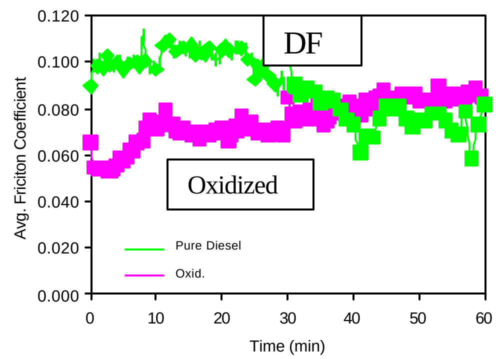

Fig.3. Friction – Low Sulfur Diesel Fuel

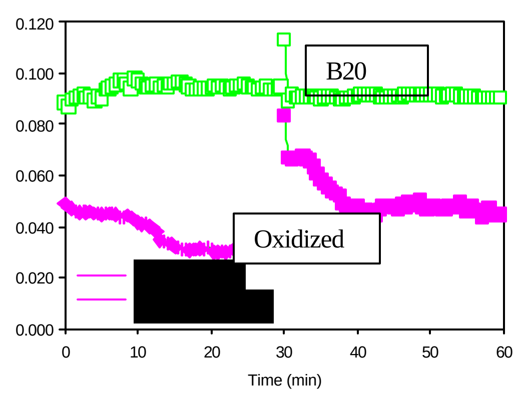

Fig.4. Friction – B20 Fuel

The wear characteristics of all of the oxidized fuels were better than the unoxidized low sulfur fuel. Typical data are found on Figure 5.

Testing was conducted using various concentrations of the oxidized fuels in the diesel fuel. The concentrations ranged from 0 to 20% . Both friction and wear were measured. The optimum effect on wear was obtained with approximately 10 % by weight of the oxidized fuels in the low sulfur diesel fuel. Friction was lower in all cases.

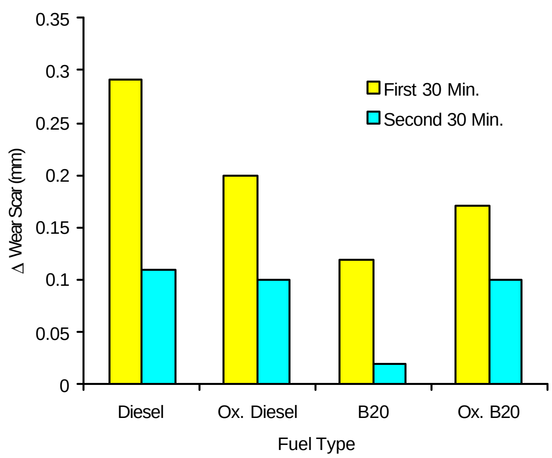

Fig.5. Effect of Oxid'n of Fuels on Wear

The research on oxidized fuels demonstrates one approach to reducing friction and wear in low sulfur diesel fuels. Studies on the effectiveness of the increase oxygen content of these fuels on particulates needs to be determined.

VEGETABLE OILS.

Research on vegetable oils as hydraulic fluids, industrial oils and engine oils at Penn State is continuing. It is aimed at improving the oxidation stability and the low temperature properties of these oils [6-9]. Research involves the use of genetically modified vegetable oils, chemically modified oils and additive effectiveness in a wide range of applications.

All three of these approaches can be shown to improve the oxidation stability of the vegetable oils studied, allowing formulation of single and multi-grade lubricants that perform in laboratory tests as well as petroleum base oils. Coupled with the low volatility and excellent viscosity-temperature properties, the vegetable oils become more attractive as engine oil lubricants.

In the current studies, the effect of the material surface on the thermo-oxidative properties of lubricants and the use of coatings to passivate the surfaces in an engine is demonstrated.

Oxidation and volatility studies are conducted using the Penn State Microoxidation (PSMO) test, Figure 6.

Fig.6. Thin-film PSMO Test Unit [10]

In this thin-film test, 40 ul of test fluid is put under an inert (nitrogen) or an oxidizing (air) atmosphere at selected conditions and the volatiles, oxidized products and deposits measured.

The effect of oxidation and active metal surfaces on the volatiles and the deposit forming tendency were studied. The data in Figure 7 were obtained from tests of a high oleic soybean oil in the PSMO. The thin-film tests were conducted using nitrogen to obtain evaporation data and air to obtain the oxidation related volatiles. As can be seen the evaporative losses are only about one-fourth of the total oxidative volatiles. This comparison was also run on normal soybean oil, a trimethylol propane ester and a chemically modified soybean oil. In all cases, the evaporation was one-third or less of the total oxidative volatiles. This has to be taken into account when comparing system fluid losses or modeling a system.

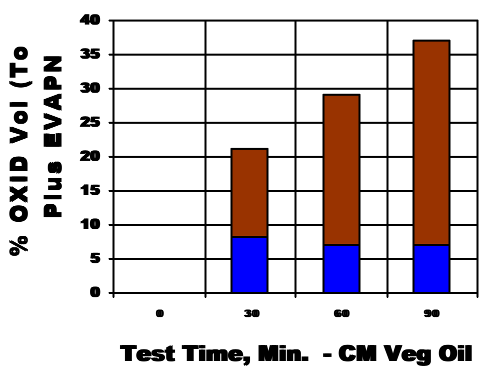

Fig.7. Comparison of Evaporation and Oxidative Volatiles.

Another effect to consider is the catalytic effect of the metal surface on the rate of oxidation. Several fluids were evaluated using low carbon steel and more inert aluminum test specimens. The more active steel results in a higher rate of oxidation and more volatiles, Figure 8.

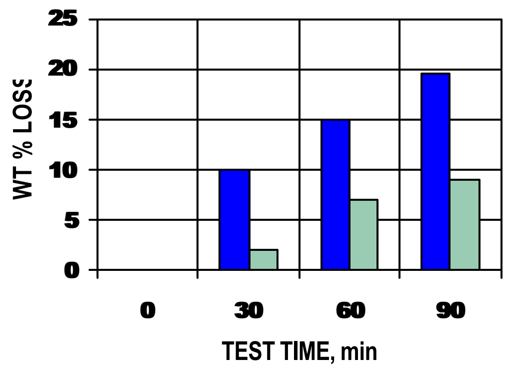

Fig.8. Effect of Surface on Oxidative Volatiles – LCS vs Al.

In this case the volatiles produced on the more active steel surface are about twice that of aluminum. This is attributed to the presence of active sites on the LCS entering into the oxidation mechanism. One approach to reducing the rate of oxidation is to neutralize the active sites by the use of surface coatings

A proprietary coating [11] that is used as an inert coating inside high temperature gas chromatographic columns and in environmental gas collection canisters was explored as a possible coating to slow the oxidation rate and products that lead to the formation of deposits. The coating was first used in the PSMO test. Test coupons were coated to evaluate the coating thickness. The thickness was varied from 900 to 1200 angstroms.

It was found that the deposit formation induction time went from 0 minutes for the uncoated specimen to 60 and 120 minutes for coatings of 900 and 1200 angstroms, respectively.

Pistons for the Yanmar single cylinder diesel engine were coated and evaluated in a 50-hour steady-state engine test at full load and rated speed. The test results were dramatic, Figure 9.

In the case of the uncoated piston, the top ring was stuck at the end of the test and was broken in trying to remove it. The piston rings for the coated piston were clean. The coated piston was significantly cleaner than the uncoated piston.

EXTENDED DRAIN LUBRICANT STUDY.

By extending the oil drain period of vehicles, oil use is reduced, the quantity of used oil for disposal is reduced and the maintenance requirements are reduced resulting in less vehicle down time. A study in progress involves the evaluation of the properties of several engine oils in an extended drain fleet test.

Four oils are under study. The base stocks for each of the oils differs. Oil A is an API Type 1, Oil B is a Type III Oil and Oil C and D are Type IV base. Each oil is in use in 4-6 trucks and the oil change periods for the oils range from 75,000 to 100,000 miles. Samples for analysis are taken at approximately 10,000 to 14,000 miles. The oils are continuously being replenished by addition of a small quantity of makeup oil. Physical and chemical properties are monitored.

Friction and wear studies were conducted using the Penn State Sequential Four-Ball Test [13]. The wear characteristics of the test fluids deteriorated with use, Figure 10. However, the friction data indicated slight trend towards lower friction with mileage.

The wear increase is attributed an increase in soot in the oil from none to about 4 % at 100K miles. Soot was measured by FTIR, Figure 11.

Viscosity did not change significantly over the oil change period and the TBN drop was within desired levels.

Deposit forming tendencies of the oils were measured using the PSMO. The new and used oils had acceptable deposit levels in the PSMO test up to about 80,000 miles at which time the deposits started to increase.

EFFECT OF CHEMICAL STRUCTURE ON WEAR.

The effect of unsaturation on the friction and wear properties of a fluid and additive effectiveness are being studied. The current study involves three base fluids and five additives [12]. The fluids include a highly unsaturated vegetable oil, a TMP ester with oleic acid (one double bond) as side chains and a TMP ester with saturated side chains. The study to date indicates the sulfur containing additives and the phosphorus containing additives perform differently depending on the degree of unsaturation of the base fluid.

The neat base fluids exhibit different wear characteristics and the more highly unsaturated vegetable oil produces more debris and higher wear than the saturated TMP. The oleic-TMP is intermediate in the wear debris The debris is similar to that obtained in thin-film oxidation tests and suggests that the contact temperatures in the contact area exceed 225 ^{o}C.

SUMMARY. The current research in the Multidixcipline Tribology Group and the Combustion Laboratory of the Energy Institute at Penn State University is a broad program with several areas related to both the reduction of exhaust emissions of diesel engines and the conservation of petroleum resources.

Research on oxygenated fuels including vegetable B20 fuel show

significant reductions in particulate emissions when the oxygenates are added to low sulfur diesel fuels. The vegetable oil also improves friction and wear characteristics of the fuel.

Vapor phase oxidation of fuels is an approach to increase the oxygen content of fuels for the purpose of producing fuel additives that reduce friction and wear.

Extended drain periods in trucks can effectively increase maintenance intervals and reduce disposal costs associated with used oils. In a properly designed system, drain intervals of over 80,000 miles are feasible. Wear increases as soot increases in the used oil. Friction tends to decrease slightly with mileage possibly due to the nature of the oxidation products.

Vegetable oil studies indicate that surface materials need to be considered in evaluating oxidation stability and deposit forming tendencies.
Use of a proprietary coating significantly improved the cleanliness of pistons in a single cylinder diesel test.

Studies on fluids containing various amounts of unsaturation show that the chemical structure not only affects the oxidation stability of the fluid, it is a factor in the wear properties and the effectiveness of additives in the fluid.

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Fig.9. Comparison of Uncoated and Coated Pistons from Yanmar Single Cylinder Diesel Engine Tests. Test Conditions Include: Steady Speed @ 2200 RPM, Full-Load, Test Time – 50 Hrs Fuel – No. 2 (39 ppm S), Lube Oil – 10W30

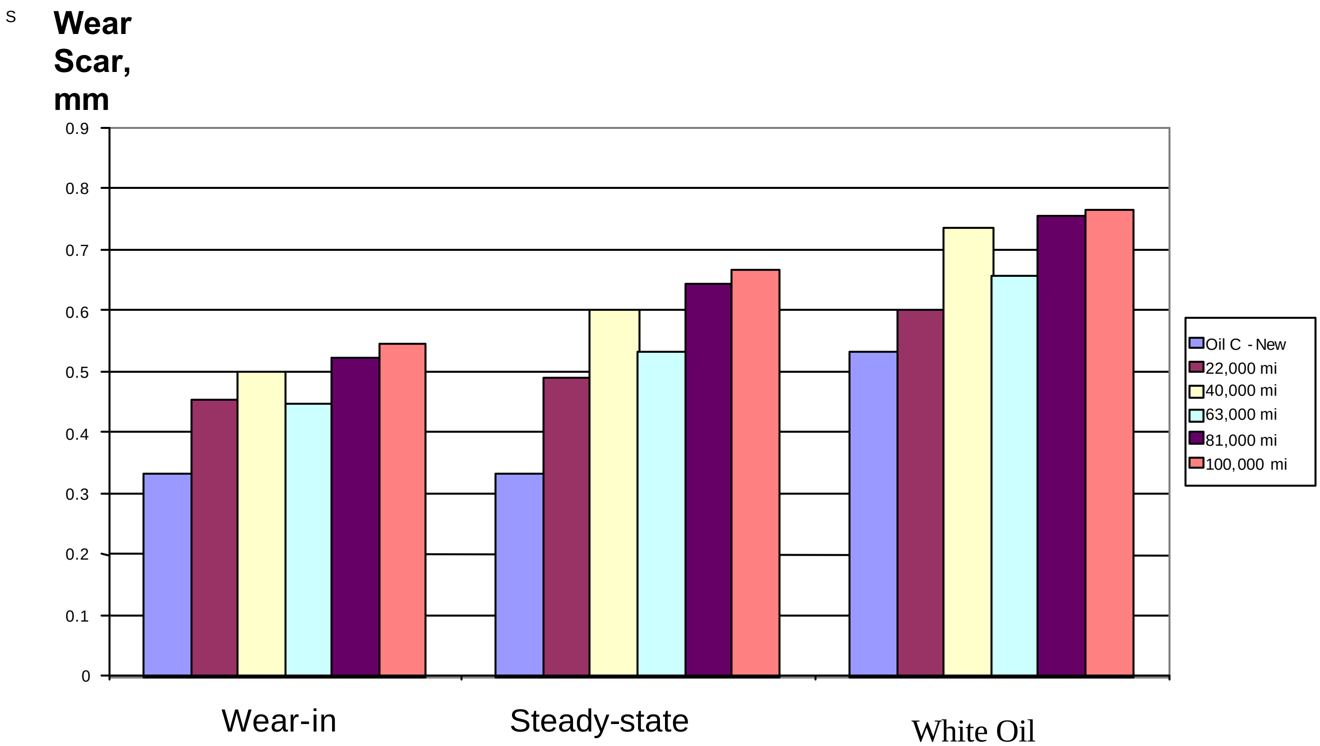

Fig. 10. Sequential Wear Tests – Increase in Wear With Miles., Oil C

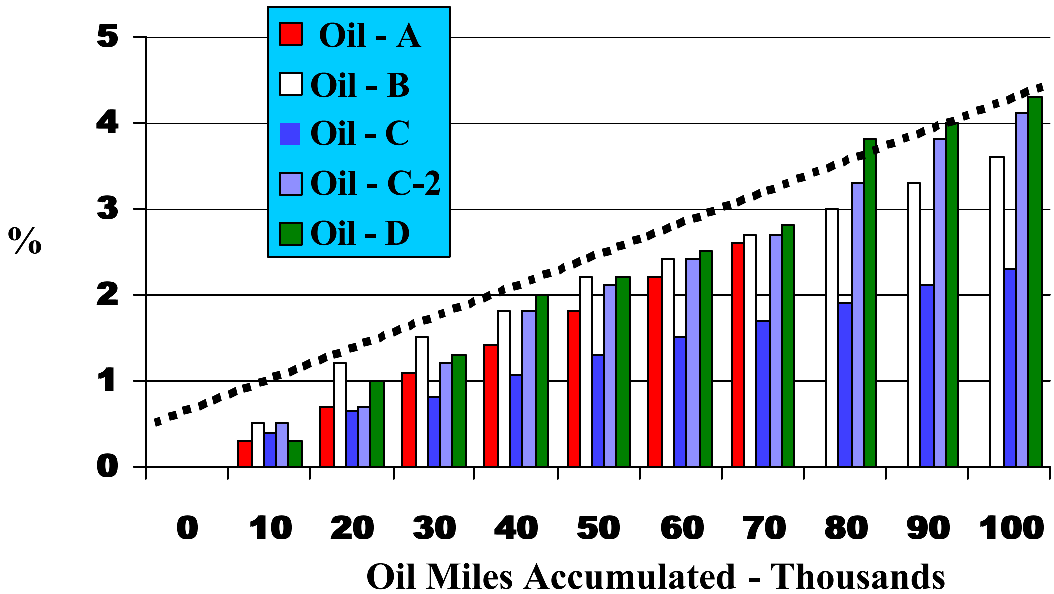

Fig.11. Soot Accumulation With Mileage –5 Trucks