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Canola-based Motor Oils

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MOTOR OILS

Motor oils have been utilized since the development of steam engines as a buffer between moving and static engine components. The basic jobs of the lubricant are to prevent metal-to-metal contact and to transfer heat from friction away from the contact point. During the time of steam power, one of the best lubricants available was derived from rapeseed oil. With the development of internal combustion engines, petroleum fuels became popular and a byproduct, the heavier components of refining, became available for lubrication. Early petroleum motor oils were highly ineffective. These oils were composed of basically three hydrocarbon types: naphthalene, paraffin, and aromatics. None of these structures are chemically functional and petroleum chemists quickly found the addition of phosphates and sulfur improved the lubrication ability of petroleum. By chemically functional, the components of petroleum are considered inert materials and basically function as carriers of metallic salts that provide the basic lubrication needs of modern internal combustion engines. Today, numerous chemicals are added to provide functionality to the base oil, many of which result in the product becoming toxic and carcinogenic. One of the most notable being zinc di-phosphate (ZDP).

Vegetable oils, however, are excellent in terms of functionality without chemical modification. Vegetable oils, however, tend to loose functionality when exposed to environments where heat, pressure, and metal catalysts are present. This is the environment of a modern, high compression engine. Vegetable oils also tend to become solids (crystalline) at temperatures at/or slightly below freezing (0° to –12°C) and would provide no lubrication on cold days. Consequently, a study was initiated in 1996 to develop a vegetable-based motor oil which maintains its natural lubricity yet performs like a petroleum product in terms of oxidation resistance (a chemical restructuring of the base molecule at high temperatures in excess of 100°C) and resists turning to a crystalline structure at low temperatures (–32°C).

ENVIRONMENTAL MARKETS FOR BIO-BASED LUBRICANTS

The stimulus for the use of environmentally benign chemicals has been increasing for the past decade. In Europe, for example, Lubrizol Corporation has illustrated the potential for environmentally friendly lubricants (Table 1). The use of motor oils, hydraulic oils, greases, bar-chain oils, and similar products illustrate the wide diversity of markets available to concerned consumers. In hydraulic oils, Lubrizol points to a world market of 610,000 tonnes of oil used per annum. Of this volume, Europe consumes 20,000 t of biodegradable hydraulic oil while the potential European market is 250,000 t annually. The current under-utilization of bio-based products is typically based upon poor performance, cost, and lack of availability.

Manufacturers also limited the stimulus for further development of bio-based products. In 1994, 60% of the US base lubricant market as owned by five major petroleum oil companies. Eight petroleum companies essentially produced finished oil products. The lack of competition and low incentive to develop bio-based products has limited development and market acceptance of these products.

To produce a marketable product, Frost and Sullivan (1999) suggest that: (1) marketers must improve price/performance ratios to leverage sales against traditional lubricants; and (2) market research indicates strong market growth as participants become aware of application uses and biodegradable merits. Based upon these principles, Frost and Sullivan have evaluated the probability of market acceptance in the United States (Table 2). Grow-

Table 1. European markets for bio-based oils. Source: IENICA 2001.

Oil use	World market (1,000 t)	European markets (1,000 t)	
		Current	Potential
Hydraulic	610	20	250
Grease	90	0.6	35
Two cycle	70	1	3
Chain oil	40	10	40
Mould release	40	2.5	30
Anti-corrosion	25	0.6	7.5
Other	0	0.6	3

ing environmental awareness and stringent government regulations have stimulated interest in bio-based products. Other aspects reported by the Industrial Agricultural Products Center (1994) include performance becoming more important than price in this market and the government's greater efforts to subject non-point sources of pollution to liability.

While market size comparisons are similar for both the US and Europe, there has been a far greater acceptance of bio-based products in the European marketplace (IENICA 2001). Europeans have shown more concern for both functionality and environmental support. Cost of product is of less concern to Europeans. US markets are dominated by cheap petroleum and little or no governmental incentives to convert to bio-based resources. Consequently market entry is limited and bio-based products must compete in a market defined by petroleum.

In both Europe and in the United States, consumer acceptance is based upon three principles:

1. It must function equal to or better than the product they are currently using. This becomes especially critical when it involves a major capital expense such as a motor vehicle. The motor oil should have properties such as a low phosphorus content to preserve catalytic converters in the exhaust system, a low viscosity (to meet future ILSAC standards for fuel economy), and provide for reduced friction.
2. The cost should be similar to those of the product they are currently using. These costs may include extraneous costs such as disposal, pollution, or safety. Costs of the product, at the retail level, should be no more than 50% above current product cost. In Europe, product cost to the consumer is less an issue than in the United States.
3. It should be environmentally friendly. Motor oils are, by their very nature, unfriendly. They are contributors to air pollution by their association with internal combustion engines. They contribute to soil pollution by leakage or spillage. They contribute to water pollution by contaminating water supplies through rain-borne runoff or deep hydraulic percolation. The best that can be said for a bio-based motor oil is that it is environmentally benign. It should be nontoxic to fish and mammals. It should be biodegradable. It would be beneficial if it were recyclable to reduce disposal costs.

Table 2. US potential markets for bio-based lubricants. Summarized from NPRA 1998.

Oil use	US market (1,000 t)	Probable % market acceptance of bio-based
Crankcase	3900	24
Hydraulic	721.5	60
Marine	189.3	75
Natural gas	147.8	23
Turbine	144	20
Two cycle	68.2	20
Drip oil	48.8	65
Metal cutting	12.4	30
Bar chain	8.1	60
Wire rope	6.5	70
Rail flange	3.2	55
Dust control	3.2	30

Technical research on general environmental safety and road trials have been summarized by Johnson (1998, 1999). Lacking general acceptance of bio-based products has required a direct comparison of these products with their current competitive products using technologies acceptable to the petroleum industry of functionality and performance

THE BIO-BASED MOTOR OIL PROJECT: BENCH TESTS

The canola-based motor oil project was initiated in 1996 in response to a need for a motor oil compatible with, and nontoxic to, fragile ecosystems. The oils are composed primarily of high oleic canola as the base oil. This oil is combined with sources of hydroxy fatty acids and wax esters or estilides. Additional modifications include the inclusion of bio-based pour-point depressants and supplemental antioxidants. The components and formulations are available in US Patent No. 5,888,947 (1999).

Several bench tests utilized and recognized by the petroleum industry were used to preliminarily evaluate the formulated oil. A primary tool to determine frictional load was the "steel-on-steel frictional analysis" provided by the Falen pin and vee block (ASTM D 3233). This test is used to determine wear properties of the lubricant, its high-pressure performance and provides frictional data related to fuel economy. The oils will tend to "break" where pressure and heat fracture the oil, allowing metal to metal contact.

Additional bench tests include an engine deposit test to determine ash deposition. Two tests are recognized: (1) the US Environmental Protection Agency recognizes a PSMO analysis; and (2) the automotive industry recognizes a more strenuous TEOST-M33 analysis.

Acids are generated through breakdown of the oils in use. Acids, in turn, etch metal creating wear surfaces in the engine. It would be desirable to minimize the acid production of the oil to minimize engine wear. Using KOH titration of used motor oils is an accepted means of determining acid production in used oils.

Longevity of motor oil can be calculated using the Rotating Bomb Oxidation Test (RBOT). In an RBOT analysis, oils are subjected to high heat and pressure conditions to determine time until the oils polymerize and become solid. An RBOT value in excess of 200 minutes is preferred.

A final analysis of the motor oil involves the production of volatile organic compounds or VOCs. Accepted US and International analysis include use of a NOACK protocol for volatility loss.

Pin-and-vee analysis conducted by Rhodes Consulting show significantly less friction and a reduced friction for a prolonged period of time when compared to a conventional 5W30 motor oil (Fig. 1a). Comparisons of the oil with a synthetic 10W50 show the bio-based oils also outperform synthetic oils (Fig. 1b). Expectations are that the oil should increase fuel economy of vehicles using bio-based oils over conventional oils by 5%. Fuel economy should increase by 1.5% over use of synthetic oils. In addition, the vegetable motor oils can withstand far higher temperatures before oil breakdown than either the conventional or synthetic oils. In conventional oil comparisons, petroleum oils failed at 400 psi while the canola-based oils failed at 1050 psi.

In comparisons to synthetic oils, the synthetic oils began to fail at 400 psi failure of the bio-based oils did not occur until 825 psi (Fig. 1b). Rather surprisingly, the vegetable motor oils outperformed the synthetic oil in most applications.

Results of the engine deposit test (Fig. 2) show that in both the EPA and Automotive methods, the bio-oils produced significantly less ash buildup. Ash is associated with loss of engine power and incomplete combustion.

Acid numbers were determined using a potassium hydroxide titration method. Results (Fig. 3) show the acids generated after 6,500 km in a 2000 Ford Ranger truck were half those of the petroleum standard. These low acids show mechanical fracturing of the oils do not induce a reduction in pH. The low acid numbers indicate less potential etching of metal contact surfaces by the oil.

Oxidative stability analysis (RBOT) was able to demonstrate that bio-based motor oils were more chemically stabile than 10W30 petroleum oils under extreme heat and pressure (Johnson 1999). In addition, volatility losses were significantly less than conventional oils and comparable to synthetic oils (Fig. 4). The low VOCs implied in Fig. 4 for synthetic and bio-based oils mean that by 2003, they will be the only oils meeting new US and international standards for air quality.

BIO-BASED MOTOR OILS: IN-FIELD TESTS

Oil analysis using laboratory protocols provides an acceptable level for most engineering applications. However, some tests are better conducted using field or automotive systems. There were concerns that high levels of toxic metals were recovered during early engine oil drains after conversion from conventional to bio-based motor oils. The concern was whether the metals were from existing sludge buildup within the engine or

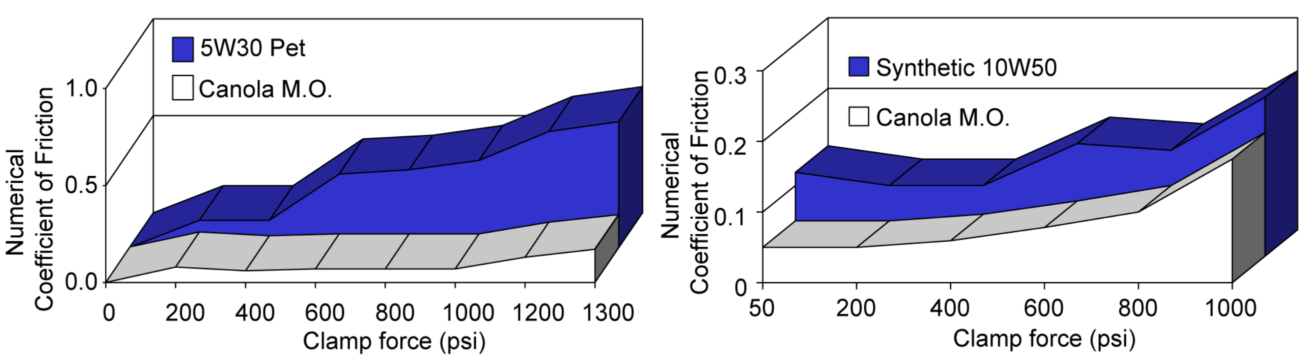

Fig. 1. A) Friction and load analysis with conventional oils. B) Comparison of pin and vee using bio- and synthetic oils.

actual wear induced by the oils on engine parts.

Working in conjunction with the United States Postal Service, delivery vehicles were monitored through a period of six oil drain intervals. The used oils were analyzed using atomic absorption for zinc, lead, copper, and tin. Zinc is commonly found as an oil additive. Lead, copper, and tin are typically components of bearings. Decreases in all metals after the initial conversion (drains 1,2…6) from petroleum (drain 0) show the heavy metals were derived from engine sludge rather than from wear induced by the bio-oil (Fig. 5).

Oil changes from petroleum to bio-based oils also show very significant reductions in tailpipe exhaust emissions (Fig. 6). In a petroleum to petroleum cycle (Pet-pet), hydrocarbons (HC), carbon monoxide (CO), and nitrous oxides (NOx) all show increases over the 6,500 km test period. Conversion from petroleum to a bio-based motor oil (pet-can) has an immediate and dramatic decrease in exhaust emissions. Continued use of the bio-oil continued to decrease HC production while giving no additional losses to the already depressed CO and NOx production.

Utilizing the postal data illustrated in Fig. 6, a new EA85 Ford Explorer provided by the US Postal Service was evaluated for non-methane hydrocarbons (NMHC) or VOCs, carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons (HC), and nitrous oxides (NOx). Comparisons were made using the manufacturers' recommended 5W30 conventional oil and a bio-oil. Results show a very highly significant reduction in NMHC, CO, HC, and NOx and significant reduction in CO_2 (Fig. 7). Reductions from the petroleum standard were NMHC: 25%; CO: 48%; HC: 32%; NOx: 80%, and CO_2: 1%.

The Environmental Protection Agency of the United States estimates the average automobile user will generate 16.7 kg of hydrocarbons, 123.8 kg of carbon monoxide, and 8.7 kg of nitrous oxides per vehicle per

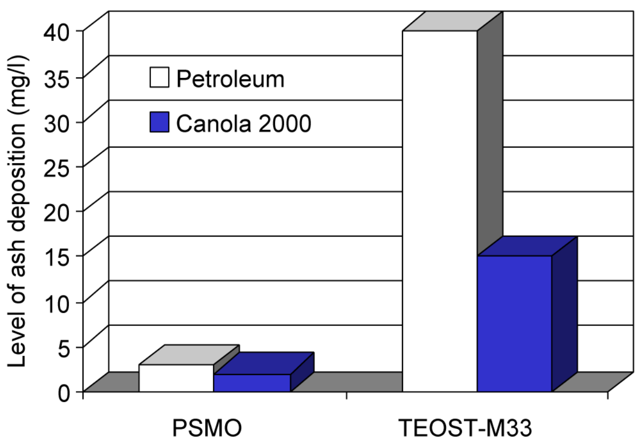

Fig. 2. Engine ash deposition test. Left axis indicates levels of deposition of the ash in mg/l.

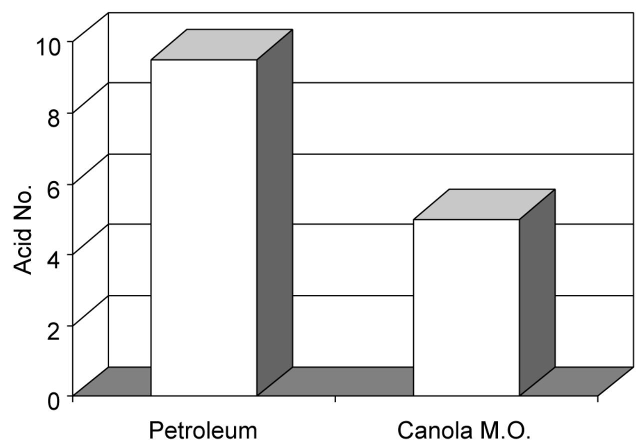

Fig. 3. Acid titration values in used, 6500 km motor oil.

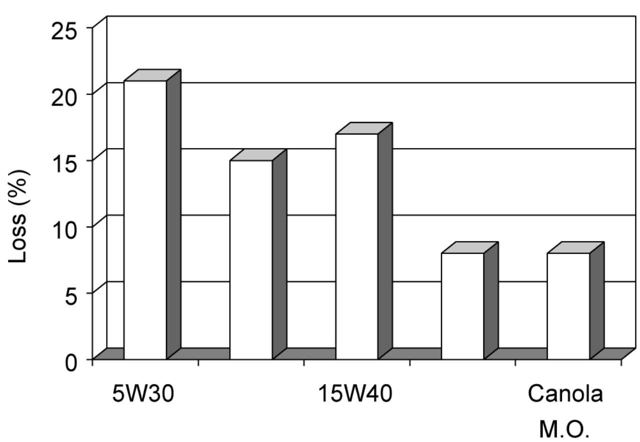

Fig. 4. NOACK oil volatility test.

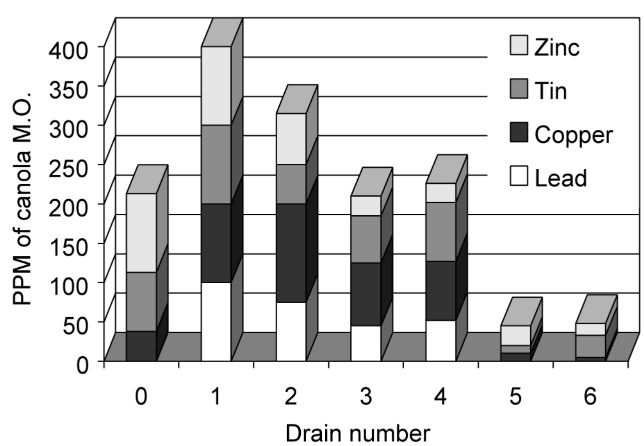

Fig. 5. Metal content of drain oil over time.

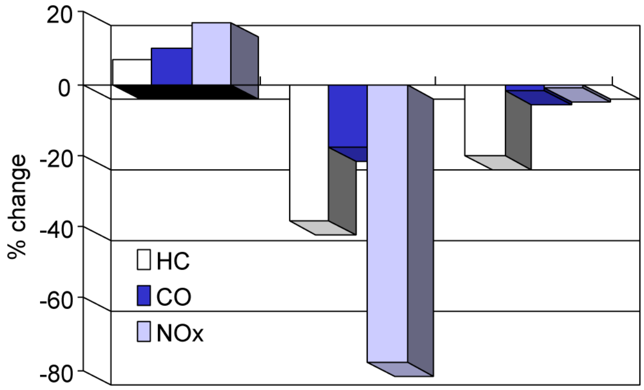

Fig. 6. Emissions from new petroleum-used petroleum (6,500 km) (left); used petroleum to used bio-oil (6,500 km) (center) and new bio-oil to used bio-oil (6,500 km) (right). Oil changes were made in sequence within vehicles.

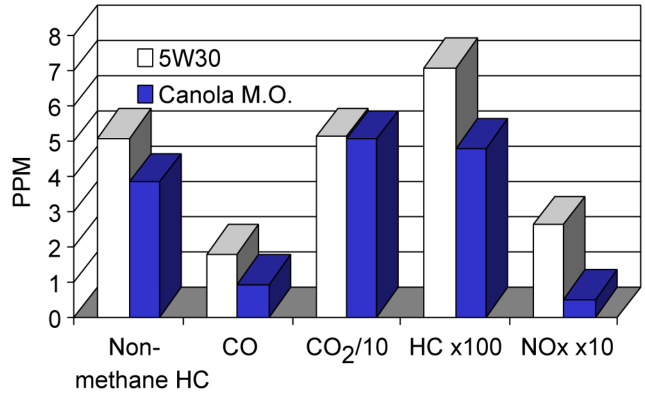

Fig. 7. Emissions reductions in a 2001 USPS Ford Explorer (data from left to right: NMHC, CO, CO_2, HC and NOx).

year (based on the average number of miles driven per vehicle). By conversion of one million vehicles to a bio-based motor oil, the United States could annually reduce hydrocarbons by 1,214.8 t, carbon monoxide by 96,444 t, and nitrous oxides by 1,561.1 t. The value of Emission Reduction Credits currently in the United States is $7,300/ton for NOx, $7,000/t for NMHC, and $2,000/t for carbon sources. In effect, a fleet of vehicles has the ability to repay itself for the use of a bio-oil as a motor lubricant.

SUMMARY

Canola-based motor oils have rapidly evolved into a competitive product. In terms of pricing, they are highly competitive with synthetic motor oils. They are also the most “environmentally friendly” of the motor oils available maintaining properties of non-toxicity and biodegradability. In terms of functionality, they have exceeded expectations by surpassing both conventional and synthetic oils in the tests conducted. As a low friction fluid, these tests indicate vegetable motor oils, or bio-oils, are a competitive product in modern engine applications.

A pleasant surprise has been the response of engines in terms of tailpipe and manifold gas emissions. The reductions in nitrous oxides, carbon monoxide, non-methane hydrocarbons, and hydrocarbons provide an easy and effective way to reduce air pollution. The value of these exhaust emissions has now become established and, in effect, may have more value than the oil itself. The impact of conversion to a bio-based motor oil for each million automobiles driven 18,590,000,000 km per year (17,699 km per vehicle) would be staggering. Hydrocarbons from automotive exhaust would be reduced annually by 1,101 t; carbon monoxide would be reduced by 87,475 t; and nitrous oxides would be reduced by 1,416 t.

REFERENCES

Anon. 1994. The industrial agricultural products center. agproducts.unl.edu/soyoil.html

Frost, M. and J. Sullivan. 1999. U.S. biodegradable lubricants markets. Consultative Report New York.

IENICA. 2001. Summary report for European Union: Oil crops. www.csl.gov.uk/ienica/national%20reports/BIG%20oils.pdf

Johnson, D.L. 1998. Update on the soybean engine oil project. Lubricants and Fluids: Technical Advisory Panel Meeting Report. Omni Tech Int., Ltd.

Johnson, D.L. 1999. High performance 4-cycle lubricants from canola. p. 247–251. In: J. Janick (ed.), Perspectives on new crops and new uses. ASHS Press, Alexandria, VA.

National Petroleum Refiners Association. 1998. Report on U.S. lubricating oil sales. Washington, DC. National Petroleum Refiners Association.