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Short communication

Viscosity properties of mineral paraffinic base oils as a key factor in their primary biodegradability

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Abstract

The primary biodegradability of two types of paraffinic base oils (solvent and catalytically dewaxed oils) and their blends was evaluated using the CEC L-33-A-93 test. The biodegradability values varied between 10% and 75%. Base oil mixtures displayed varying contents in aromatic and polar compounds and a wide range of kinematic viscosity (KV) values, from roughly 10 to 600 cSt (at 40 °C), while their viscosity indices were almost constant (90-100). The biodegradability of oils was closely related to their content in polycyclic aromatic hydrocarbons and was also decreasing with kinematic viscosity. For the two types of base oils, a linear relationship could be set between the biodegradation percentages and the logarithms of KV values. These results show that, beside overall chemical features such as the contents in aromatic compounds, KV may be a prominent parameter for assessing the primary biodegradability of mineral base oils.

Abbreviations: B – biodegradability, CDW – catalytically dewaxed, KV – kinematic viscosity, PAHs – polycyclic aromatic hydrocarbons, SDW – solvent dewaxed, VI – viscosity index

Introduction

Significant amounts of lubricants are lost in the environment, particularly in environmentally sensitive applications, such as forestry and mining (Van Donkelaar 1990) or through engine losses (Völtz et al. 1995). Lubricants are essentially composed of one or more base oils which represent at least 85 percent of the formulation. These base oils are in general of mineral origin, i.e., they are produced from petroleum crude by various processing steps.

Biodegradation is the main process by which oil products are removed from soil and water compartments (Leahy & Colwell 1990; Cornish et al. 1993). Therefore, there is a growing concern in improving the biodegradability of lubricants to minimize their environmental side effects. Although the low biodegradability of mineral base oils is well known, data on this biodegradability are relatively scarce (Basu et al. 1998; Battersby et al. 1992; Battersby & Morgan 1997; Novick et al. 1996; Völtz et al. 1995). The relations between oil (physical and chemical) properties and their biodegradability have also been little studied. Among the physico-chemical characteristics of lubricants, however, viscosity is known to have an important impact on biodegradability (Amund & Adebiyi 1991; Carpenter 1994; Willing 1999), which is attributable to bioavailability effects and structural factors, but this impact has never been quantified.

In the present study, we have investigated the primary biodegradability of two types of mineral (paraffinic) base oils and their blends. The biodegradability test used was CEC L-33-A-93 test (CEC 1995), initially developed for two-stroke outboard engine lubricants but subsequently applied to a large variety of oil products. The biodegradability values of the tested base oils and oil mixtures have then been compared to their viscosity parameters.

Materials and methods

Oils

Mineral base oils were obtained from Mobil Oil Corporation. They included solvent dewaxed base oils (SDW oils), i.e., solvent extracted and solvent dewaxed vacuum distillates, and catalytically dewaxed base oils (CDW oils), i.e., solvent extracted and catalytically dewaxed vacuum distillates. Blends of oils belonging to the same family were carried out to obtain a wide range of viscosities.

Determination of the physical properties of base oils

Kinematic viscosities (KV) were determined at 40 °C and 100 °C according to the ASTM standard D 445 (ASTM 1997) using a Cannon Automatic Viscometer CAV3. The time was measured for a fixed volume of liquid to flow under gravity through a capillary. KV values were obtained by multiplying the measured flow time by the calibration constant of the viscometer. Viscosity indices (VI) were calculated from KV values at 40 °C and 100 °C as specified in the ASTM standard D 2270 (ASTM 1993). Briefly, calculations involved the KV values at 40 °C of two reference oils having (arbitrary) VI values of 0 and 100, respectively, and the same KV value at 100 °C as the tested oil (Moore et al. 1997).

CEC L-33-A-93 biodegradability test

The primary biodegradability of oils was obtained using CEC L-33-A-93 test (CEC 1995). In this test, biodegradability is assessed by monitoring the loss of infrared absorbance at a wavelength of 2930 cm^{-1} (CH_2–CH_3 band) in solvent extracts from inoculated flasks and that occurring in uninoculated poisoned controls. The absorption values are used to calculate the residual oil contents of the poisoned and test flasks. Biodegradability is expressed in % as the difference in residual oil contents between the poisoned flasks and the respective test flasks.

CEC L-33-A-93 tests were performed in triplicate. The inoculum was a coarse-filtered secondary (final) effluent from Notre-Dame de Gravenchon (France) sewage treatment plant. Infra-red spectroscopic grade 1,1,2-trichloro-1,1,2-trifluoroethane (Merck) was used as the solvent for test and reference materials and as the extractant. The maximum absorption of CH_2– and CH_3– bonds was measured using a Perkin Elmer 1760 FTIR spectrometer.

Contents in aromatics and polars

Oil contents in total aromatics, polycyclic aromatic hydrocarbons (PAHs) and polar compounds were determined by UV spectrometry following a proprietary procedure developed by the Mobil Oil Co.

Results and discussion

The primary biodegradability values of mineral base oils and their blends were between 10% and 75% (Table 1), i.e., below the commonly accepted European standard of 80% required for environmentally acceptable lubricants (Battersby & Héry 1998).

For the two types of base oils, biodegradability decreased as the oil content in PAHs and polar compounds increased. This relationship was quasi linear in the case of PAHs (Figure 1). The low biodegradability of aromatic and polar compounds is well documented (Cerneglia 1993; Gibson & Subramanian 1984; Riis et al. 1996). The correlation did not hold for monoaromatics, i.e., total aromatics minus PAHs in Table 1 (SDW oils, $r^2 = 0.15$; CDW oils, $r^2 = 0.72$). Monoaromatics are known to be more susceptible to microbial attack than PAHs (Walker et al. 1975).

Mineral base oils and their blends displayed a wide range of KV values, from roughly 10 to 600 cSt, while VI values were almost constant, ranging between 90 and 100 (Table 1). The biodegradability of mineral base oils was decreasing with kinematic viscosity. A linear relationship could be set between the biodegradation percentages and the logarithms of KV values (Figure 2).

Viscosity is among the most important characteristics of a lubricating oil. KV values must be high enough to provide proper lubricating films while avoiding excessive friction losses. VI is an arbitrary number that reflects the temperature-dependence of viscosity: the higher the VI the less the viscosity of an oil is affected by temperature. Viscosity of a macromolecular solution is strongly dependent on the size (e.g., molecular weight) and shape (e.g., chain branching and inter-chain entanglements) of the solute. In order to facilitate the design of new or improved lubricants, a number of studies have been recently undertaken to try to predict the dependence of the rheological properties of lubricants, more particularly viscosity, on their molecular-level details

Table 1. Biodegradability of mineral base oils and their overall chemical composition, kinematic viscosity and viscosity index

Sample	KV at 40 °C (cSt)	VI	Total aromatics (mmol kg^{-1})	PAHs (mmol kg^{-1})	Polars (mmol kg^{-1})	Biodegradability
SDW1	8.72	100.0	n.d.	n.d.	n.d.	72
SDW2	9.32	97.7	370.13	69.34	48.37	70
SDW3	19.84	97.0	458.00	87.00	62.75	63
SDW4	30.61	101.3	559.36	143.62	74.55	51
SDW5	30.91	98.2	515.62	116.07	70.71	60
Blend1	54.08	n.d.	597.66	175.39	80.78	47
SDW6	61.74	96.6	465.20	117.80	61.23	55
Blend2	108.60	n.d.	512.67	152.49	67.16	42
Blend3	161.70	94.6	558.26	190.69	73.11	37
SDW7	163.60	94.9	554.20	180.10	71.30	40
Blend4	205.80	n.d.	569.81	197.16	74.28	30
Blend5	264.20	92.5	669.67	266.94	88.34	23
Blend6	299.20	94.1	604.26	226.56	78.62	26
Blend7	353.40	n.d.	697.50	287.72	91.94	33
Blend8	405.90	93.5	626.20	245.75	81.43	17
Blend9	452.90	94.1	712.18	299.85	93.89	16
Blend10	525.70	92.3	635.54	256.60	82.41	12
SDW8	567.00	94.6	654.68	274.44	84.63	20
CDW1	9.38	91.2	345.31	57.98	44.65	64
Blend1	102.00	97.1	635.70	220.82	84.45	30
CDW2	165.49	90.7	686.57	247.91	91.34	34
Blend2	200.60	91.3	692.66	257.41	92.07	22.5
Blend3	257.80	95.1	677.28	267.07	89.90	16
Blend4	297.80	93.7	703.37	275.12	93.14	14
Blend5	418.80	92.0	718.98	291.81	95.01	12
CDW3	501.70	94.7	732.80	306.76	96.44	15

n.d.: not determined.

(Kioupis & Maginn 1999). These computer-based molecular simulations have been limited so far to linear or branched alkanes and their binary blends, i.e., much simpler formulations than the complex mixtures found in lubricants.

On the other hand, a decrease in biodegradability with increasing viscosity has been reported in several investigations concerning different oil products such as synthetic polyalphaolefin fluids (Carpenter 1994), complex oleochemical esters derived from renewable resources (Willing 1999) and natural crude oil (Sugiura et al. 1997). In these studies, however, the number of tested samples remained limited. Basu et al. (1998) have reported a number of data on biodegradability of various commercially available base oils that were characterized by their overall chemical composition, kinematic viscosity and viscosity index. If the general tendency of a decrease in biodegradability with increasing viscosity can be observed, the broad range of oils tested does not allow to sort out the specific impact of individual parameters, e.g., KV, on oil biodegradability. From the foregoing, it seems unlikely that the effect of viscosity on biodegradability mainly reflects simple molecular features of base oils such as their contents in isoparaffins.

Conclusions

The present results show that, beside chemical features such as the contents in polar and aromatic compounds, KV may be a prominent parameter for assessing the primary biodegradability of mineral base oils. Viscosity-biodegradability relationships are particularly interesting from a practical point of view since viscosity is considered the most significant prop-

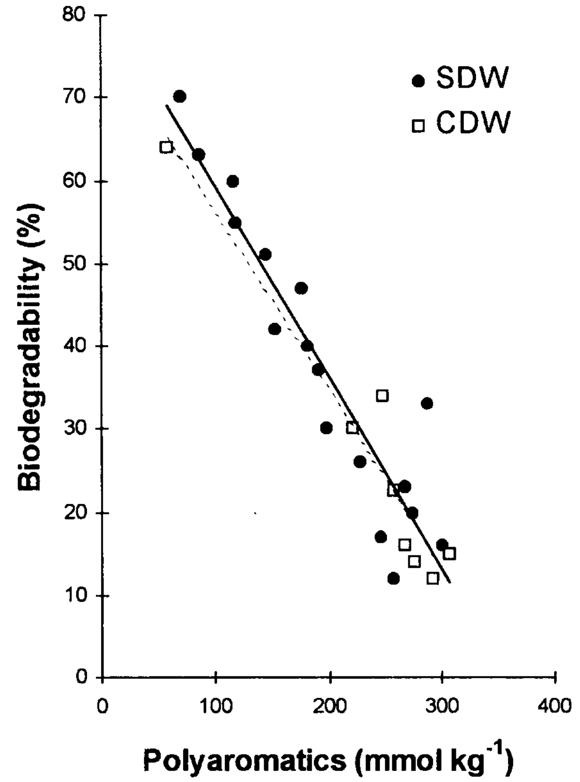

Figure 1. Biodegradability of mineral oils as a function of their content in PAHs. Correlation lines: solid, SDW oils (r^2 = 0.87); dotted, CDW oils (r^2 = 0.93).

erty of a lubricant and is systematically measured. We are currently investigating by multiple regression analysis the relationships between the primary biodegradability of a number of base oils and several other physical parameters such as the VI, pour point and refraction index. The goal is to develop a predictive model of mineral base oil biodegradability based on simple macroscopic characteristics that are used routinely to evaluate the lubricant performance. The first results seem to confirm the good correlation between KV and biodegradability for the tested base oils while the correlation between oil biodegradability and their content in PAHs is less well verified (Haus et al., in preparation).

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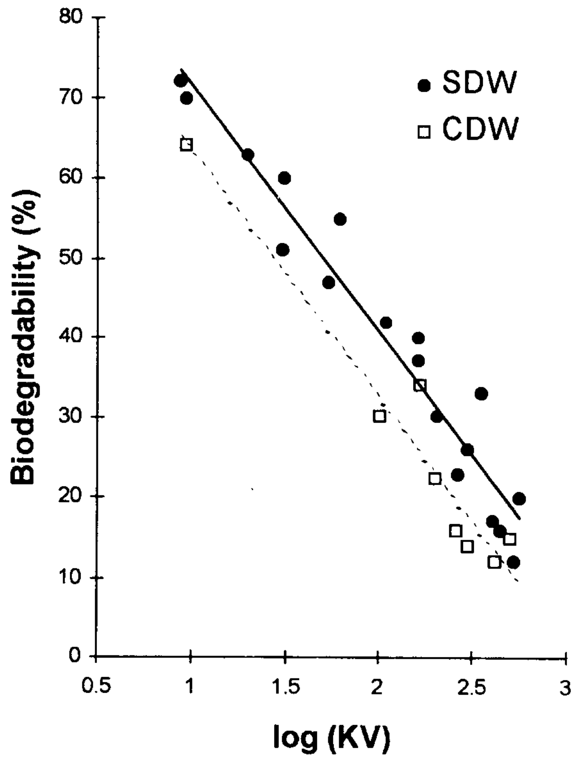

Figure 2. Biodegradability of mineral base oils as a function of the logarithm of their kinematic viscosity. Correlation lines: solid, SDW oils (r^2 = 0.94); dotted, CDW oils (r^2 = 0.94).

References

Amund OO & Adebiyi AG (1991) Effect of viscosity on the biodegradability of automotive lubricating oils. Tribol. Int. 24: 235–237

ASTM Committee D2 on petroleum products and lubricants, standard D 445, current edition, American Society for Testing Materials, Philadelphia, Dec 10, 1997

ASTM Committee D2 on petroleum products and lubricants, standard D 2270, current edition, American Society for Testing Materials, Philadelphia, March 15, 1993

Basu B, Singh MP, Kapur GS, Ali N, Sastry MIS, Jain SK, Srivastana SP & Bhatnagar AK (1998) Prediction of biodegradability of mineral base oils from chemical composition using artificial neural networks. Tribol. Int. 31: 159–168

Battersby NS & Hery C (1998) Development and applications of environmentally acceptable hydraulic fluids. SAE Technical Paper Series 981493, Earthmoving Industry Conference and Exposition, April 1998, Peoria, Illinois

Battersby NS & Morgan P (1997) A note on the use of the CEC L-33-A-93 test to predict the potential biodegradation of mineral oil based lubricants in soil. Chemosphere 35: 1773–1779

Battersby NS, Pack SE & Watkinson RJ (1992) A correlation between the biodegradability of oils products in the CEC L-33-T-82 and modified Sturm tests. Chemosphere 24: 1989–2000

Carpenter JF (1994) Biodegradability of polyalphaolefin (PAO) basestocks. Lubr. Eng. 50: 359–362

CEC, Co-ordinating European Council for the development of performance tests for transportation fuels, lubricants and other fluids (1995) Biodegradability of Two-Stroke Cycle Outboard Engine Oils in Water, approved test method CEC L-33-A-93

Cerniglia CE (1993) Biodegradation of polycyclic aromatic hydrocarbons. Curr. Opin. Biotechnol. 4: 331–338

Cornish A, Battersby NS & Watkinson RJ (1993) Environmental fate of mineral, vegetable and transesterified vegetable oils. Pestic. Sci. 37: 173–178

Gibson DT & Subramanian V (1984) Microbial degradation of aromatic hydrocarbons. In: Gibson DT (Ed) Microbial Degradation of Organic Compounds (pp 181–252). Marcel Dekker, New York

Kioupis LI & Maginn EJ (1999) Rheology, dynamics, and structure of hydrocarbon blends: a molecular dynamics study of n-hexane/n-hexadecane mixtures. Chem. Eng. J. 74: 129–146

Leahy JG & Colwell RR (1990) Microbial degradation of hydrocarbons in the environment. Microbiol. Rev. 54: 305–315

Moore JD, Cui ST, Cummings PT & Cochran HD (1997) Lubricant characterization by molecular simulation. AIChE J. 43: 3260–3263.

Novick NJ, Mehta PG & McGoldrick PB (1996) Assessment of the biodegradability of mineral oil and synthetic ester base stocks, using CO_2 ultimate biodegradability tests and CEC-L-33-T-82. J. Synth. Lubr. 13: 19–30

Riis V, Miethe D & Möder M (1996) Analytical characterization of the persistent residues after microbial degradation of mineral oils. Fresen. J. Anal. Chem. 356: 378–384

Sugiura K, Ishihara M, Shimauchi T & Harayama S (1997) Physicochemical properties and biodegradability of crude oil. Environ. Sci. Technol. 31: 45–51

Van Donkelaar P (1990) Environmental effects of crankcase and mixed lubrication. Sci. Total Environ. 92: 165–179

Völtz M, Yates NC & Gegner E (1995) Biodegradability of lubricant base stocks and fully formulated products. J. Synth. Lubr. 12: 215–230

Walker JD, Colwell RR & Petrakis L (1975) Microbial petroleum degradation: application of computerized mass spectrometry. Can. J. Microbiol. 21: 1760–1767

Willing A (1999) Oleochemical esters – environmentally compatible raw materials for oils and lubricants from renewable resources. Fett/Lipid 6: 192–198