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Characterization of Lubricating Base Oil by Chromatographic method

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ABSTRACT

Today's market trend is to make high quality, high performance lubricating oil, which incorporates high dose of additive. This has made refiner more quality conscious of the base oil. The quality of base lubricating oil should be controlled by its generic chemical fractions in addition to physical tests. There are four chemical fractions which control the inherent (generic) properties of base oil. The four generic fractions are saturates (paraffinic and cycloparaffinic), naphthene aromatics, polar aromatics and asphaltenes. Saturates are normally considered good as lubricating oil whereas last two mentioned fractions deteriorate the lubricating oil properties. The present work evaluates the quality of the oil on the basis of these four generic fractions. A method, based on chromatography has been adopted for this purpose.

INTRODUCTION

The petroleum fraction used as lubricating oil consists of 18 or more carbon atoms per molecule. The fraction is a complex mixture of paraffinic, cycloparaffinic (naphthenic) and aromatic compounds, together with heterocylic compounds containing sulphur, nitrogen and oxygen. Engine lubricating oil consists of two major components, namely lubricating base oil and additive package. The quality of finished lubricating oil depends on these two components. In refinery the quality of lubricating base oil is controlled by physical and some chemical tests (Allinson, 1975). These traditional test methods are now being replaced by instrumental techniques based on physico-chemcial methods which include infra red, ultra violet and emission spectroscopy, x-ray absorption, chromatography and fluorescence methods (Hersh et al, 1948; Smith, 1952). The detailed individual component analysis is obtained by mass spectroscopy (Furby and Ku, 1973).

This report deals with the characterization of lubricating base oil by selective-adsorption and desorption chromatography (Corbett, 1969). The selective adsorption and desorption procedure separates oil into four well defined fractions and has been accepted as a standard ASTM procedure for separation of the four fractions of heavy petroleum product (ASTM, 1984). The four generic fractions are saturates, naphthene aromatics, polar aromatics and asphaltenes.

Lubricating oil manufactured as a result of vacuum distillation of crude petroleum, is a dark coloured liquid. It is further refined by furfural extraction method (Nelson, 1958). The extract contains most of the coloured material consisting of aromatic and olefinic hydrocarbons. It is called carbon oil. The raffinate is clear light coloured transparent liquid. It consists of predominantly saturated hydrocarbons, with small amount of unsaturated and aromatic hydrocarbon. It is the efficiency of the furfural extraction unit which determines the quality of lubricating base oil. Virtually this unit removes the asphaltene, aromatic and unsaturated hydrocarbons from the distillate lubricating oil and improves the quality of the oil. Appreciable amount of sulphur, nitrogen and oxygen compounds are also removed accordingly.

EXPERIMENTAL

Lubricating base oils and extracts were supplied by National Refinery Limited. Physical and chemical properties of the oils normally used in specifications were obtained by standard ASTM methods. Oxidation stability of the oil was determined by bubbling air through the oil at 100°C for 24 hours in presence of copper and separating the sludge formed. The acidity of the oil was estimated by titration according to IP Method 307.

Adsorption-desorption chromatography was carried out as follows. A sample of lubricating oil was first separated into n-heptane insolube asphaltenes and n-heptane soluble petrolenes. Petrolene was further fractionated into saturates, naphthene aromatics and polar aromatics in a chromatographic column.

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Apparatus

All the experiments reported were performed with standard laboratory equipments except for chromatographic column. The column, 1000 mm long, 31 mm inside diameter, was made of borosilicate glass tubing having a 2 mm teflon stop-cock. A graduated 500 ml equal pressure funnel was fitted at each end, to facilitate the addition and withdrawal of sample from the column.

Reagents and Materials

Alumina, F-20 chromatographic grade 80-200 mesh, supplied by Sigma Chemical Company, was calcined at 415°C for 16 hours, prior to use.

Solvents used for elution i.e. n-heptane, methanol, toluene and trichloroethylene were of extra pure quality.

Procedure

About 10 gram of lubricating oil sample was taken in a 1-litre Erlenmeyer flask. The flask was cooled and n-heptane solvent in the ratio of 50 ml of solvent per gram of oil was added in the flask. The flask was heated and the temperature was maintained near boiling point of heptane with moderate stirring. The digestion period was 0.5 hour. After the digestion, the flask was kept overnight to settle the precipitates of asphaltenes. Clear heptane-petrolene solution was decanted into 1-litre separating funnel. The solution was filtered through Whatman No. 540 filter paper using Buchner funnel fitted with 1-litre suction flask. After the filtering of petrolene, the entire content remaining in the Erlenmeyer flask was transferred to the Buchner funnel using fresh heptane from a squeeze bottle. The asphaltene was repeatedly washed with heptane until the filterate became colourless. The asphaltene on the filter paper was dried to constant weight at 105°C. Filterate containing petrolene was concentrated to about 50 ml on a rotary vacuum evaporator.

Separation of petrolene.__ The chromatographic column was prepared by filling it with 450 g alumina (F20) and gently tapping it. The column was prewet with 50 ml n-heptane. Immediately concentrated petrolene solution was transferred to the column with minimum amount of heptane. 200 ml of heptane eluant from the top of equal pressure funnel was added to the column at a drip rate of about 5 ml/min and simultaneously eluate was collected at the same rate in the receiving funnel. More solvent was added and received according to the separation scheme shown in Table 1. Each eluate was taken into a beaker and evaporated to dryness till constant weight.

Table 1. Separation Scheme.

Eluate feed	Eluate ml	Fraction recovered
n-Heptane	200	Saturates
Toluene	100	Saturates
Tolene	300	Naphthene aromatics
Methanol-Toluene	300	Naphthene aromatics
Trichlorethylene	500	Polar aromatics
Trichloroethylene	hold-up	Polar aromatics

Cut point of fraction.__ The first yellow drop of naphthene aromatic was taken as the cut point between saturate and naphthene aromatic. The cut point between naphthene aromatic and polar aromatic fraction was the black descending ring in the column. Polar aromatic fraction was the last to be separated from the column. The hold up in the column was due to solvent collected by gravity draining, which was colourless.

RESULTS AND DISCUSSION

Six lubricating base oils obtained as raffinate from furfural extraction unit of refinery and three carbon oils, termed as extracts from the same unit, were evaluated. Properties of these oils are given in Tables 2 and 3, whereas chemical composition as determined by adsorption and desorption chromatography is shown in Tables 4 and 5.

Properties given in Tables 2 and 3 depend on the relative distribution of chemical compounds shown in Tables 4 and 5. For a given molecular size or grade, the paraffinic or saturated base oil has relatively low density, low ASTM colour, low viscosity, high viscosity index, low conradson carbon and low refractive index as compared to aromatic hydrocarbon oil. Aromatic base oil is characterized by high density, darker colour and rapid change of viscosity with temperature (low viscosity index). Naphthenic base oil has properties that are

Table 2. Properties of lubricating base oil (furfural raffinate).

	HVI-100	MVI–100	HVI-400	MVI-650	HVI Br/st
Density @ 15°C	0.8740	0.8924	0.8879	0.9213	0.9065
ASTM Colour	L 1.5	L 2.5	L 3.0	L 6.5	L 5.0
Kin. Viscosity @100°C (c St)	3. 97	4. 20	9.74	11.20	32.55
Kin. Viscosity @40°C (c St)	19.43	22.78	81.55	115.7	498.3
Viscosity Index	97	76	97	78	97
Flash Point (°C)	198	208	254	244	302
Pour Point (°C)	-6	-6	-6	-3	Zero
Sulphur Content (Wt. %)	1.30	1.70	1.34	2.40	1.43
Conradson Carbon (Wt. %)	0.02	0.04	0.02	0.10	0.43
Total Ash (Wt. %)	0.003	0.006	0.01	0.01	0.02
Refractive Index	1.4803	1.4923	1.4868	1.5097	1.4960
Oxidation Stability					
Acidity (mg KOH/g)	0.20	0.30	0.40	0.70	0.38

Table 3. Properties of carbon oil (furfural extract).

	Carbon Oil-A	Carbon Oil-B	Carbon Oil-C
ASTM Colour	Brownish Black Double D/L. L.40	Brownish Black Double D/L. L5.0	Brownish Black Double D/L.L5.0
Density @ 15°C	1.041	1.071	1.092
Kin. Viscosity @100°C (c St)	18.01	35.86	39.90
Kin. Viscosity @40°C (c St)	750.0	3995.0	6286.0
Viscosity Index	-	-	-
Flash Point (°C)	220	242	242
Pour Point (°C)	+6	+27	+27
Sulphur Content (Wt. %)	5.1	5.6	5.9
Conradson Carbon (Wt. %)	2.2	6.0	7.4
Total Ash (Wt. %)	0.01	0.03	0.03
Oxidation Stability			
Acidity (mg KOH/g)	1.3	1.8	2.2
Sludge (Wt.%)	5.0	7.2	9.8

Table 4. Chemical composition of lubricating base oil (furfural raffinate).

	HVI-100	MVI–100	HVI-400	MVI-650	HVI Br/st	MVI Br/st
Saturates (Wt.%)	81.6	67.0	76	48.6	62.0	32.9
Naphthene Aromatics (Wt.%)	18.0	32.0	22.5	46.2	35.2	55.2
Polar Aromatics	0.4	1.0	1.5	5.1	2.7	11.7

Table 5. Chemical composition of carbon oil (furfural extract).

	Carbon Oil - A	Carbon Oil - B	Carbon Oil - C
Saturates (Wt.%)	15.8	16.9	12.3
Naphthene Aromatics (Wt.%)	66.8	67.9	73.2
Polar Aromatics	17.5	15.4	14.3
Asphaltenes (Wt.%)	0.1	0.2	0.2

intermediate to those of paraffinic and aromatic oils (Kirk and Othmer, 1980).

The data shown in the Tables 2 and 3 are normally used for quality control of the lubricating base oil. Kinematic viscosity and flash point are controlled by distillation unit, whereas other properties, such as viscosity index, conradson carbon, colour and pour point are governed by furfural extraction unit. Furfural extraction unit preferentially removes the asphaltene, aromatic and olefinic hydrocarbon fractions from a given lubricating oil, depending upon the conditions of the unit. Under severe conditions of the extraction unit, high viscosity index (95) oil is produced, having less aromatic fractions. Mild conditions of extraction produces oil of more aromatic fractions and comparatively lower viscosity index (MVI). Refinery should be encouraged to produce HVI oil.

Asphaltenes and polar aromatics are totally undesirable in lubricating oil. Most of the hetero atoms such as sulphur, nitrogen and oxygen are present in these fractions. These hetero atoms on oxidation or in service produce acidic chemicals which cause corrosion and rusting. Paraffinic oil has high oxidation stability and little tendency for sludge formation compared to the oil with high aromatic contents. Aromatic base oils are of two types. One in which aromatic nuclei are fused to multi saturated rings called naphthenic hydrocarbons, the other in which aromatic nuclei are attached to hetero atoms called polar aromatics. Polar aromatics are the most reactive (low oxidation stability) and form on oxidation, in addition to acidic material, polymeric substance called sludge or asphaltenes. The data indicate that as the amount of polar aromatic and asphaltenes reduces, the quality of the lubricating base oil improves. Response of additive is also better in paraffinic base oil than the aromatic hydrocarbons (Hobson and Pohl, 1973).

Thus it may be concluded that all the specification properties mentioned in Tables 2 and 3 are related to the four generic fractions of the base oil and these should be included in the specification of the base oil. Additionally with known chemical composition, the performance of lubricating oil can also be predicted.

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