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Thermal, spectral, oxidation stability and antioxidant behavior on Group II base oils

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HIGHLIGHTS

- A decrease in average chain length among the paraffinic oils increases the viscosity index (VI).
- Lower naphthenic (C_n) carbon content increases the oxidation stability.
- Increase in iso-paraffinic (C_{ip}) carbon content increases the thermal stability.
- Addition of antioxidant remarkably enhances the oxidation stability of the base oils.

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ABSTRACT

Due to constant increase in the demand for highly saturated Group II and Group III base oils and their application in use as special lubricants, it is a must to have a clear picture of structural distribution of base oils. In this study, pressure differential scanning calorimetry (PDSC), rotary pressure vessel oxidation test (RPVOT), kinematic viscosity (KV), Noack volatility and elemental analysis as physico-chemical tests are studied for Group II base oils. The inferences derived from these analyses established the relationship between the chemical structure and selection of the base oils to meet future product specifications. ^{1}H and ^{13}C NMR (Nuclear Magnetic Resonance) data had also been used to generate average structural profile and it was used to account for the oxidation stability of the selected base oils.

1. Introduction

Group II base oils are common in mineral oil based motor oils currently available in the market. They have fair to good performance in properties such as volatility, oxidative stability and flash/fire points. Lubricating oils are expected to operate at higher temperature and pressure there by oils are required to have thermal stability, oxidative stability, excellent temperature viscosity characteristics [1,2]. Some studies have been carried out on effect of aromatics and iso-alkanes on the pour point of different types of lube oils obtained from Indian refineries [3–5]. Structural characterization studies were also carried out using NMR spectroscopy [6,7].

A quantitative indication of the degree and severity of refining of base oils can be obtained from compositional and structural data. The use of catalytic hydro-cracking/iso-dewaxing/hydrofinishing technology provides an opportunity to improve the properties of less expensive mineral base stocks.

Hydro processing technologies provide an opportunity to modify the chemistry of hydrocarbons to improve the properties of petroleum base oils. Quantitative ^{1}H and ^{13}C NMR data has been used to generate average structural profile for a variety of base oil samples. These structural parameters could be related to the composite bulk properties of the lubricating base oils [8–10]. The NMR studies have also been used for monitoring the degree of refining of base oils [11,12].

During the hydro-cracking, many chemical reactions can occur including ring-opening, cyclization and isomerization. This resulted in nearly total removal of heteroatom which leads to saturated molecules, thermodynamically stable products [13–18]. Decomposition of different types of base oils (all-natural, fully synthetic and semi-synthetic) has been investigated by using TGA (thermo gravimetric analysis) and DSC (differential scanning calorimetry) [19–21]. Though the literature survey reveals that this type of work is appeared in several papers but it lacks in selection of base oils obtained from different technologies. To fulfill the

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lacunae the present investigation has been carried out in an elaborate manner.

In this study, base oils such as M1 and M2 (samples obtained from hydro cracking/iso-dewaxing/hydro finishing technology) and H1 and H2 (samples obtained from Extraction and catalytic iso-dewaxing technology) have been selected for physical and chemical characterization. The thermo-oxidative stability of these samples has been assessed using RPVOT and PDSC. The effect of heating with respect to kinematic viscosity has also been studied. The chemical structure of these samples was obtained in terms of average structural parameters obtained using quantitative ^{1}H and ^{13}C NMR experiments.

The cumulative data collected have been used to develop a better understanding of relationships between chemical structures and physical properties of base oils.

2. Experiment details

2.1. Base oil samples description

Group II base oils manufactured from reputed refineries using two different technologies are used for this study and are designated as M1, M2, H1 and H2. M1 and M2 samples are manufactured in hydro cracking with iso-dewaxing and hydro finishing type of technology whereas H1 and H2 samples are in solvent extraction with catalytic iso-dewaxing type of technology.

2.2. Pour point (D97), flash point (D92)

After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3 °C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point.

Approximately 70 ml of test specimen is filled into a test cup. The temperature of the test specimen is increased rapidly at first and then at a slower constant rate as the flash point is approached. At specified intervals a test flame is passed across the cup. The flash point is the lowest liquid temperature at which application of the test flame causes the vapors of the test specimen of the sample to ignite.

2.3. Sulfur and nitrogen (ASTM D 5762and D5453)

Nitrogen and sulfur was analyzed using TN/TS 3000 nitrogen analyzer manufactured by Thermo Electron Corporation. 30 μL diluted sample was injected into the sample tube along with pure Argon carrier gas and the furnace was heated up to the temperature of 1000 ± 25 °C. The analytical performance of this combustion UV (ultraviolet) and chemiluminescence detector system starts at 10 ppb and goes up to percentage level for a wide range of applications. The sample and boat are advanced into a high-temperature combustion tube where the nitrogen is oxidized to nitric oxide (NO) in an oxygen atmosphere. The NO contacts ozone and is converted to excited nitrogen dioxide (NO_2). The light emitted as the excited NO_2 decays is detected by a photomultiplier tube, and the resulting signal is a measure of the nitrogen contained in the sample. Similarly, the sample or boat, or both, is inserted into a high temperature combustion tube where the sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen rich atmosphere. Water produced during the sample combustion is removed and the sample combustion gases are next exposed to ultraviolet (UV) light. The SO_2 absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO_2^*). The fluorescence emitted from the excited SO_2^* as it returns to a stable state SO_2 is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the sample. Enhanced combustion technology assures optimum conversion of the samples. Two high-end thermo scientific fluorescence and chemiluminescence detectors are used for simultaneous sulfur and nitrogen detection. The nitrogen and sulfur content was measured for all the samples.

The physio-chemical properties of the base oils and the general test results are presented in Table 1.

2.4. Rotary pressure vessel oxidation test (RPVOT) ASTM D 2272

RPVOT measures the oxidation stability of oil. 50 g of sample was weighed in a glass container with copper wire as catalyst (55.6 g) and was added 5 ml of reagent water as per the method and kept in the vessel. The sample was exposed to oxygen at moderate pressure and at a test temperature until the oxygen destroyed the oxidation resistance of the oil.

2.5. Pressurized differential scanning calorimetry (PDSC, ASTM D 6186)

This experiments were carried out using a PC controlled DSC Q1000, TA instruments. This equipment is ideal for Tg (glass transition) and Cp (material heat capacity) measurements. 3.0 mg of oil was weighed into a new sample pan and the sample was heated at a rate of 100 °C/min maintained in oxygen pressure 3.5 MPa. The cell was held at a regulated temperature and pressure until an exothermic reaction occurred. The extrapolated onset time was measured and reported as the oxidation induction time for the base oil at the specified test temperature. RPVOT and PDSC test results are given in Table 1.

2.6. NMR analysis

Quantitative ^{1}H and ^{13}C NMR spectra of all the samples were recorded on a Bruker AV III 500 MHz *NMR* spectrometer at room temperature. Chemical shifts were measured with respect to tetramethylsilane (TMS) as an internal standard. For ^{13}C NMR, an inverse gated decoupling scheme was used to suppress unwanted nuclear overhauser enhancement. 50% (W/W) sample solution was prepared in deuterated chloroform solvent containing ~0.1 M tris (acetylacetonato) chromium (III) as relaxation agent to induce the spin–lattice relaxation time. Structural parameters on these oils were computed [9,10] from the data obtained from ^{1}H and ^{13}C NMR measurements and are given in Table 2. All spectrums are given in Figs. 1a–8b.

Table 1
Physiochemical properties and Oxidation data of base oils.

Tests	M1	M2	H1	H2
Density (g/ml)	0.8401	0.8525	0.8521	0.8644
KV@40 °C	31.0	90.2	32.56	88.00
KV@100 °C	5.483	10.80	5.398	10.76
VI	119	108	105	106
Pour point (°C)	−12	−12	−15	−15
Flash point (°C)	220	230	215	230
Sulfur (ppm)	16	19	79	36
Nitrogen (ppm)	Traces	Traces	Traces	Traces
Aniline point (°C)	116	124	111	114
RPVOT (min)	41	57	42	42
RPVOT (min) (with 0.2% antioxidant)	285	204	284	216
PDSC	4.46	5.06	3.68	3.30
Sulfur (ppm)	16	79	19	36

KV = Kinematic viscosity, VI = viscosity index, RPVOT = rotary pressure vessel oxidation test, and PDSC = pressure differential scanning calorimetry.