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Identification and Characterization of Aromatic Compounds in RASCO Light Gas Oil

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التعرف على المركبات الأروماتية ووصفها في وقود الديزل المنتج في راس لانوف

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زيت الوقود الخفيف (وقود الديزل) المستخدم لمحركات الديزل يحتوي على العديد من المركبات الأروماتية (أحاديه، ثنائيه وعديدة الحلقات الأروماتيه). إن وجود هذه المركبات بنسبة عالية يؤثر سلبا على مواصفاته القياسية. تم فصل هذه المركبات الأروماتية الى عدة قطفات بواسطة السيليكا جيل المحفزة وباستعمال بعض المذيبات العضوية . وتم التعرف على هذه المركبات الأروماتية باستخدام كلا من الأشعة تحت الحمراء وكروماتوغرافيا ومطياف الكتلة وجهاز الرنين المغناطيسي.

تشير النتائج أن وقود الزيت الخفيف المنتج في راس لانوف يحتوي على نسبة قليلة من المركبات الأروماتية، (حوالي 9.27%). وأن المركبات الأروماتية عديدة الحلقات ومشتقاتها توجد بنسبة أقل مقارنة بالأحادية وبثنائية الحلقات.

Abstract: *Light gas oil (LGO) as fuel for diesel engines contains numerous aromatic hydrocarbon (mono, di and poly) compounds. High contents of these compounds negatively influence the LGO standard specification. The LGO aromatic compounds were separated into several subfractions by active silica gel and different organic solvents. FT-IR, NMR and Gas chromatography/Mass spectrometry (GC-MS) techniques were used to identify and characterize these aromatic compounds. The results indicated that the RASCO LGO contains low aromatic compounds (9.27%). The polyaromatic compounds and alkyl / substituents (C1 to C5) exit in a trace concentration while the di and alkyl aromatic compounds are dominant in RASCO LGO.*

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INTRODUCTION

The type and quantity of aromatic compounds negatively influence LGO standard specification, quality and combustion properties. The aromatic hydrocarbons are mono-, di- and poly aromatic compounds and may contain a heteroatom. The LGO mono aromatic hydrocarbon compounds are: aliphatic chains and/or rings, side-substituents attached to one benzene ring (alkyl benzene), while the LGO di- and polyaromatic compounds are naphthalene, biphenyl, fluorine, anthracene, phenanthrene and their alkyl analogue and alkyl benz anthracene and benz phenanthrene (the alkyl either chains and/or rings), the ring either fused or attached alkyl substituents.

The increasing demand for diesel fuel has resulted in an increase in the number of blend streams, including cracked components from secondary processes using mostly heavy crude of different origins[1]. So diesel engines will increasingly be favoured by motorists, because of their greater fuel savings[2]. The superior fuel economy is of great environmental significance because of increased

awareness of the products of hydrocarbon combustion such as carbon dioxide[3]. Diesels produce smaller quantities of regulated gaseous emission, namely carbon monoxide and unburned hydrocarbons, than do similarly powered petrol engines[4].

The major drawback of diesel fuel combustion is the emission of the fine carbonaceous particulate matter on which organic compounds, from the exhaust stream, can be adsorbed and condense[5]. These compounds include polyaromatic hydrocarbon compounds – (PAHC), many of which have been shown to be genotoxic [6],[7]. Because of that a number of countries, have decided that diesel fuel aromatics content is an important property and have included it in their diesel fuel specifications.

There are various methodologies available for determination of aromatics content in petroleum products. Aniline point (ASTM-D 611-98) is most often used to provide an estimate of the aromatic hydrocarbon content of diesel fuels; high aromatic contents exhibit a low aniline point and low aromatic contents exhibit a high aniline point[8]. The PAHC exhaust emissions arise in two main ways. One is by survival from a combination of diesel fuel PAHC[9],[10] and PAHC accumulated in lubricating oil;[11] the other is by generation and emission of PAHC from pyrolysis of diesel fuel or oil component during combustion [12],[13]. Survival of diesel fuel PAHC (unburned) has been postulated as the dominant route[10].

In the present paper the isolation and identification of aromatic compounds in RASCO light gas oil was studied using Nuclear magnetic resonance (NMR),FT-IR and gas chromatography mass spectrometry (GC-MS).

EXPERIMENTAL

Strait run LGO samples, used in this study, were obtained from Ras Lanauf Oil and Gas Processing Company (RASCO) refinery. All samples were filtered through cotton before analysis. Sulfur content was determined by x-ray fluorescence (ASTM D 4294), naphthalene and alkyl naphthalene according to (ASTM-D 1840-96) and aniline point was analyzed by (ASTM-D 611-98). The total aromatic content of LGO and NMR spectrum (Fig. 1) were carried out by Bruker AC/100MHz superconducting spectrometer, the sample is prepared by mixing 0.2 ml with 2 ml of deuterchloroform as solvent and 1% tetramethysilane as internal stander; number of scans (NS) 64; spectral width (SW) 16K; pulse width (PW) 3.0; inter pulse delay 10s; the spectral integration was carried out after the baseline correction.

LGO sample was fractionated chromatographically by using active silica gel in a glass column (Elution Chromatography). The LGO separated in two main fractions saturated and aromatic using several organic solvents[16] and applying different solvents ratios. A 12g silica gel 60-120 mesh, particle size 0.13-0.25 mm was activated at 155ºC in an oven for 7 hours, and then wet packed in a glass column of 1m length and 1cm diameter. The height of the silica gel in the glass column was about 25cm. A 5ml (4.10g), LGO sample boiling range (211-335ºC) was charged to the column. The saturated compounds were eluted with 150-ml n-hexane.

The aromatic hydrocarbon of LGO was separated and collected in 5 subfractions. The first 3 subfractions were eluted with mixed solvent of benzene in n-hexane as the following; the first aromatic subfraction I, eluted with 25 ml mixed solvent (2% benzene in n-hexane). The second aromatic subfraction eluted with 3 times of 25 ml mixed solvent (10% benzene in n-hexane) and the collected subfraction assigned as IIa, IIb and IIc.

The third aromatic sub-fraction (III) eluted with 25 ml mixed solvent (50% benzene in n-hexane). The 4th sub-fraction (IV) eluted with 50 ml pure benzene. The 5ft sub-fraction eluted with 50 ml mixed solvent of 60% methanol in benzene and assigned as sub-

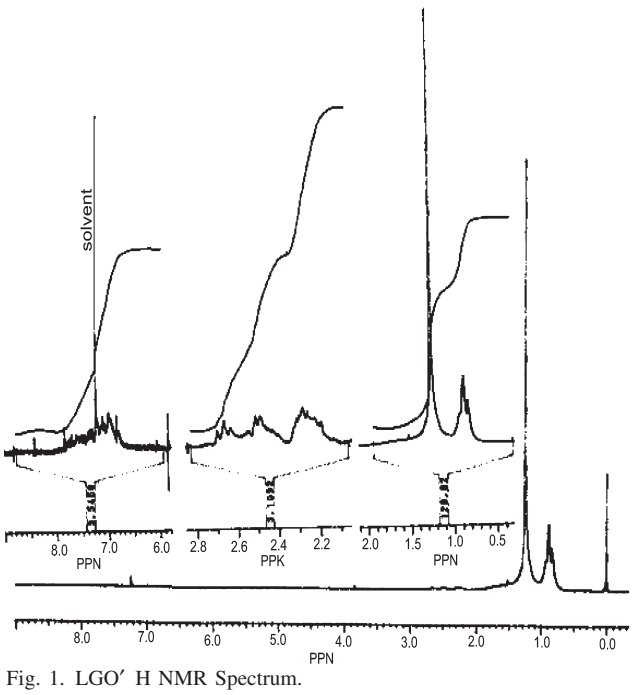


Fig. 1. LGO′ H NMR Spectrum.

fraction V. The elution solvent of each aromatic sub-fraction was evaporated, using a warm water bath, under a gentle stream of nitrogen gas, reducing the volume to about 1ml.

FT-IR spectrum of LGO sample (Fig. 2) was obtained by squeezing a drop of LGO sample between two sodium chloride plates.

The aromatic compounds of LGO were identified by Trace GC-MS / DSQ from Thermo Finnigan, consisting of a capillary colums (30 meter long Rtx-5MS. Crossbond 5% diphenyl. 95% dimethyl polysiloxane. 0.25 mm in diameter, film coated 0.25 u df) running in split mode at 70 eV inter-phased with a data system. The mass spectra recorded over a range 40-450 u. Gas chromatography operating temperature-programmed, as follows initial temperature at 50ºC isothermal for 2 minutes, rate 2ºC /minute, up to 300ºC isothermal for 10 minutes. Injected volume was 0.5µL. Both the injector and the inter-phase temperature were 300ºC. Carrier gas was helium. A computerized library search (NIST-MS).

Figure 3 illustrated the total mass spectra of LGO by GC-MS. While the sub-fractions aromatic compounds of LGO I-V are shown in Figures 4-10. The identified aromatic compounds of RASCO / LGO are listed in Table 1.

RESULT AND DISCUSSION

Figure 1 shows a ^{1}H NMR (CDC13) spectrum of LGO. Each chemical shift region has been assigned to one or more structural groups. The region in the range 6.5-8.0 ppm is characteristic of the aromatic compounds.The signals appearing in the region 2.5-2.8 ppm and 2.05-2.5 ppm were due to a-substituent group of the aromatic, and related to CH/ CH2 and CH3 protons[17], respectively.

The FT-IR spectrum; of LGO (Fig. 2) indicates absorbance of a small peak at 1600 cm^{-1} which is evident in the spectrum, this small absorbance peak is due to the aromatic compounds of the LGO; the size of the peak is related to the aromatic content of the sample. LGO total aromatic content is 9.27 m%, naphthalene and 4.8 m% alkyl naphthalene. Total sulfur is 0.045 m% and the aniline point was 81ºC.

The GC-MS chromatogram (Fig. 3) of LGO represents the total aliphatic and aromatic compounds. The numbers associated with the peaks refer to the retention time of the compounds. The LGO chromatogram obtained by GC-MS, can not be used to identify the whole aromatic compounds in LGO due to big size chromatogram peaks of the LGO aliphatic compounds, which represent 90.73 m% of the total LGO compounds, and that can either overlap

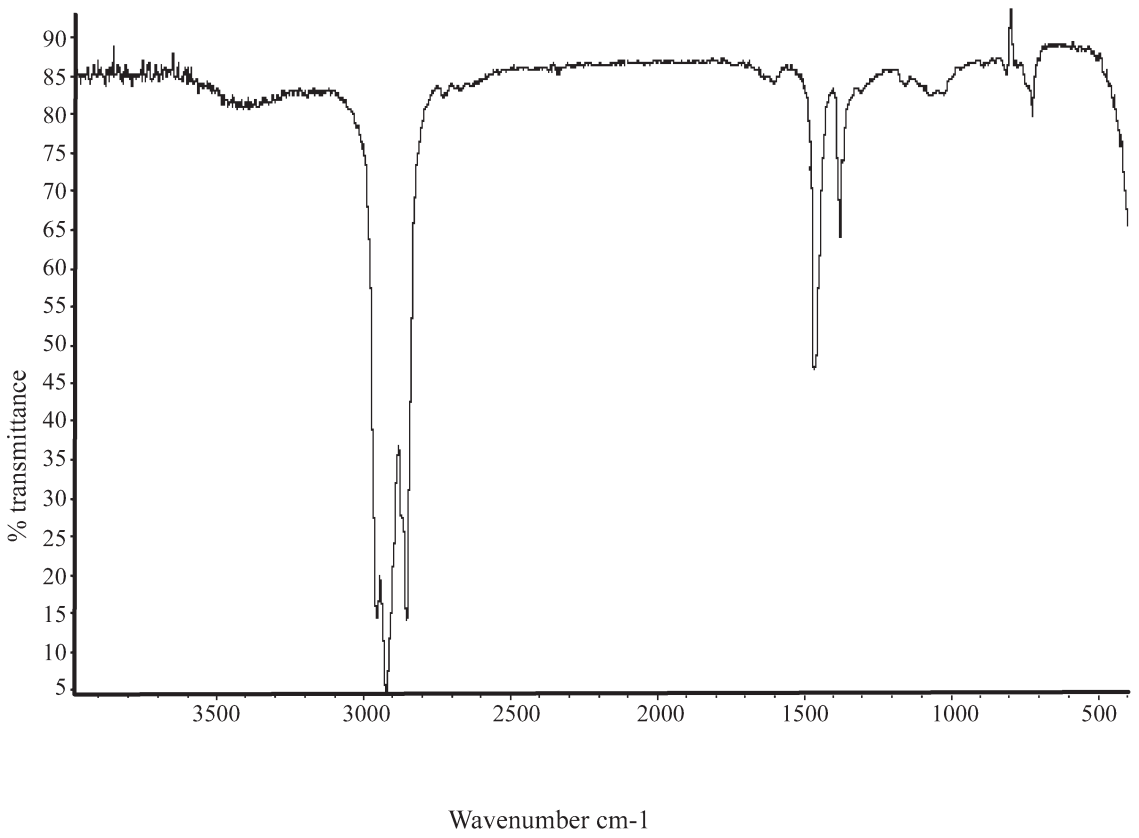


Fig. 2. FT-IR LGO spectrum.

Table 1. Mass spectral data for the provisionally identified aromatic compounds in LGO sample.

compounds	*Formula*	*mlz*	*Main identifiying masses(%)*
Toluene	C_7H_8	92	92 (59%), 65(10%)
O, m and p-xylene	C_8H_{10}	106	106(57%), 77(12%), 57(55%)
Cumene (1-methyl-ethylbenzene)	C_9H_{12}	120	120(30%),105(100%),77(15%)
1-ethyl-4-methylbenzene	*C_9H_{12}*	*120*	*120(40%), 105(100%), 71(30%),57(69%)*
1,2,4-trimethylbenzene	*C_9H_{12}*	*120*	*120(51%),105(100%), 77(10%)*
Naphthalene	$C_{10}H_8$	128	128(100%),102(25%),51(15%)
1-methyl-4-propylbenzene	*$C_{10}H_{14}$*	*134*	*134(34%),105(100%)*
p-methylcumene:1-methyl-4-(1-methyl-ethylbenzene)	*$C_{10}H_{14}$*	*134*	*134(35%), 119(95%),71(100%),57(74%)*
Isodurene (1,2,3,5-tetramethylbenzene)	*$C_{10}H_{14}$*	*134*	*134(48%), 119(100%)*
1-ethyl-dimethylbenzene	*$C_{10}H_{14}$*	*134*	*134(36%), 119(100%) 71(64%)*
Methylnaphthalene	$C_{11}H_{10}$	142	142(100%), 141(76%), 115(52%)
1,2-dimethyl-propylbenzene	*$C_{11}H_{16}$*	*148*	*148(12%), 106(39%), 105(100%)*
1,1-dimethyl-propylbenzene	*$C_{11}H_{16}$*	*148*	*148(23%), 119(100%), 97(33%)*
Pentamethylbenzene	*$C_{11}H_{16}$*	*148*	*148(38%), 133(100%)*
Biphenyl	$C_{12}H_{10}$	154	154(100%), 153(58%), 152(33%),77(16%),76(26%)
Ethylnaphthalene	$C_{12}H_{12}$	156	156(39%0, 141(100%), 115(93%)
Dimethylnaphthalene	$C_{12}H_{12}$	156	156(100%),141(84%),128(29%), 115(24%), 77(43%)
Fluorene	$C_{13}H_{10}$	166	166(100%), 115(54%), 76(80%)
Methylbiphenyl	*$C_{13}H_{12}$*	*168*	*168(100%), 167(86%), 165(34%), 152(24%)*
Diphenylmethane	$C_{13}H_{12}$	168	168(100%), 167(75%) 151(17%), 51(25%)
1-propylnaphthalene	*$C_{13}H_{14}$*	*170*	*170(44%), 141(100%), 115(80)*
Iso-propylnaphthalene	$C_{13}H_{14}$	170	170(40%), 155(100%), 128(25%), 77(16%)
Trimethylnaphthalene	$C_{13}H_{14}$	170	170(79%), 155(100%),128(22%)115(21%), 76(17%)
Phenanthrene	$C_{14}H_{10}$	178	178(100%), 176(24%),89(28%),76(32%)
Anthracene	*$C_{14}H_{10}$*	*178*	*178(100%),176(24%),89(28%),76(33%)*
Methylfluorene	$C_{14}H_{12}$	180	180(67%), 165(100%),88(30%),76(31%)
Ethylbiphenyl	$C_{14}H_{14}$	182	182(23%),167(100%),152(41%),91(39%), 86(38%)
Dimethylbiphenyl	$C_{14}H_{14}$	182	182(100%),167(89%),152(33%),82(37%)
1-Methyl-3-(phenyl methyl)benzene	$C_{14}H_{14}$	182	182(75%),167(100%),166(47%),91((38%)
1,2,3,4-tetramethylnaphthalene	*$C_{14}H_{16}$*	*184*	*184(45%),169(100%), 152(29%), 77(36%)*
Tert-butylnaphthalene	$C_{14}H_{16}$	184	184(85%),169(100%), 153(31%),128(30%)
1,4,5,8-tetramethylnaphthalene	*$C_{14}H_{16}$*	*184*	*184(100%),169(60%), 165(48%), 128(56%)*
Methylphenanthrene	$C_{15}H_{12}$	192	192(100%),191(75%), 189(39%),95(34%),82(43%)
Methylanthracene	$C_{15}H_{12}$	192	192(100%), 191(50%), 94(33%)
Dimethylfluoren	$C_{15}H_{14}$	194	194(56%),179(100%),178(59%), 152(26%),89(46%)
Methyl-9, 10-dihydrophenanthrene	$C_{15}H_{14}$	194	194(43%), 178(100%), 163(70%), 76(77%)
Methyl-9, 10-dihydroanthracene	$C_{15}H_{14}$	194	194(40%), 179(100%), 178(89%), 82(59%)
1,2-dimethyl-4(phenyl methyl)benzene	*$C_{15}H_{16}$*	*196*	*196(100),195(61%), 181(43%),166(56%),115(54%)*
Dimethylphenanthrene	*$C_{16}H_{14}$*	*206*	*206(100%), 189(48%), 89(77%)*
Dimethylanthracene	$C_{16}H_{14}$	206	206(100%), 191(70%), 89(86%)
4,5,9,10-tetrahydropyrene	$C_{16}H_{14}$	206	206(99%),203(65%),106(79)%),102(100%),88(79%)
9,10-dimethyl-9, 10-dihydroanthracene	*$C_{16}H_{16}$*	*208*	*208(30%), 193(100%), 178(20%),96(31%)*
Trimethylphenanthrene	$C_{17}H_{16}$	220	220(100%), 205(95%), 178(39%),89(50%)
Benz(Anthracene-7-methyl)	*$C_{19}H_{14}$*	*242*	*242(100%), 241(53%), 120(57%)*
Benz(Phenanthrene-6-methyl)	*$C_{19}H_{14}$*	*242*	*242(100%),241(68%), 119(75%)*
Dibenzothiophene	$C_{12}H_8S$	184	184(100%),152(31%),139(36%),92(29%)

the minor aromatic compounds small peaks or diminish and render them undetectable peak that appear as the baseline range. The following mono aromatic compounds are identified directly from the GC-MS chromatogram of the LGO because they have a low retention time and a rather detectable concentration. These are: toluene, o, m, and p-xylenes, cumene (1-methyl-ethyl benzene), 1-ethyl-4-methyle-benzene, 1,2,4-trimethyl benzene, 1-methyl-4-proply benzene, p-methyl cumene (1-methyl-4-(1-methyl-ethylbenzene), isodurene (1,2,3,5-tetramethyl benzene), 1-ethyl-dimethyl benzene, 1,2-dimethyl propyl benzene , tert-pentyl benzene (1,1-dimethyl-propyl benzene), as well as some of the aromatic compounds that have an appreciable detectable concentration in the LGO sample as the biphenyl and the methylbiphenyl aromatic compounds and some of the diaromatic compounds such as methylnaphthalene, di- and trimethylnaphtalene and some of the polyaromatic compounds such as phenanthrene, anthracene and their alkyl analogues and 9.10-dimethyl-9,10-dihydroanthracene. All of these aromatic compounds were identified directly from the GC-MS chromatogram (Fig. 3), while the other aromatic compounds that have a low concentration or even exist as trace aromatic compounds in the LGO are easily identified from the GC-MS chromatograms of the aromatic subfractions I-V, shown in Figures 4-10. The GC-MS chromatograms of these sub-fractions show a good resolution, because they are completely free of the aliphatic compounds. Table 1 shows the total identified aromatic compounds from the GC-MS chromatogram of LGO and the GC-MS chromatogram of aromatic subfractions. The identified LGO aromatic compounds are mono, di and polyaromatic compounds. Diaromatic compounds and alkyl mono and diaromatic compounds are major aromatic

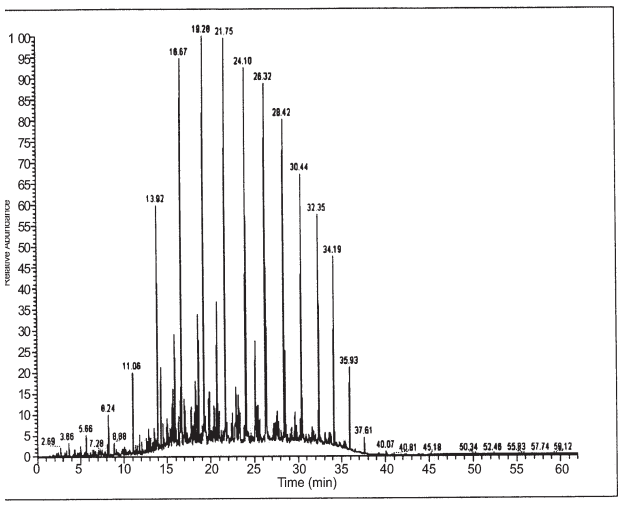


Fig. 3. GC-MS Chromatogram of L.G.O.

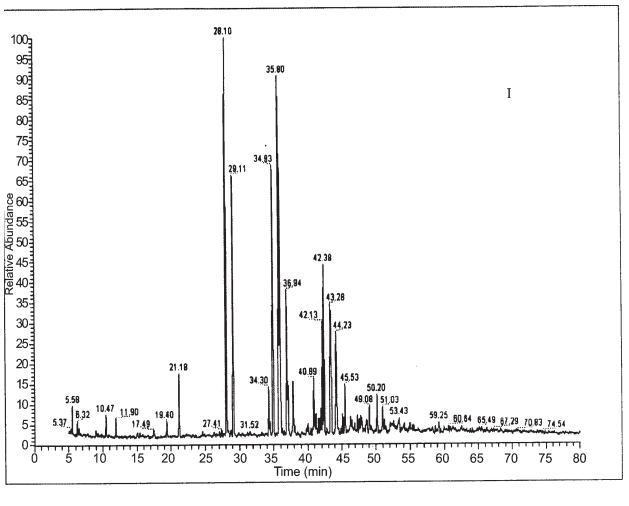


Fig. 4. LGO subfraction I.

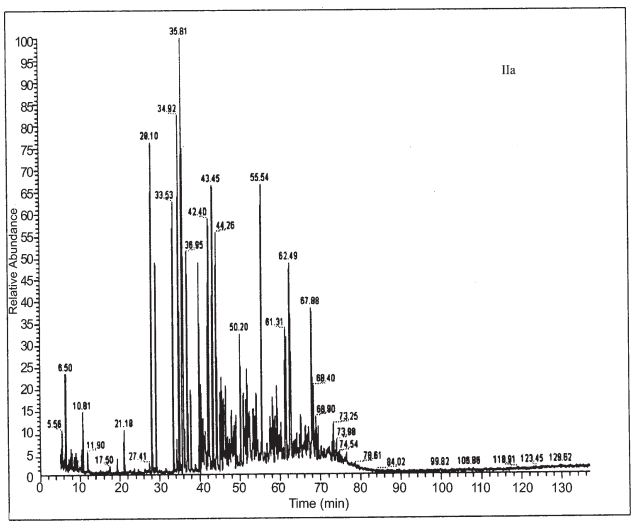


Fig. 5. LGO subfraction II a.

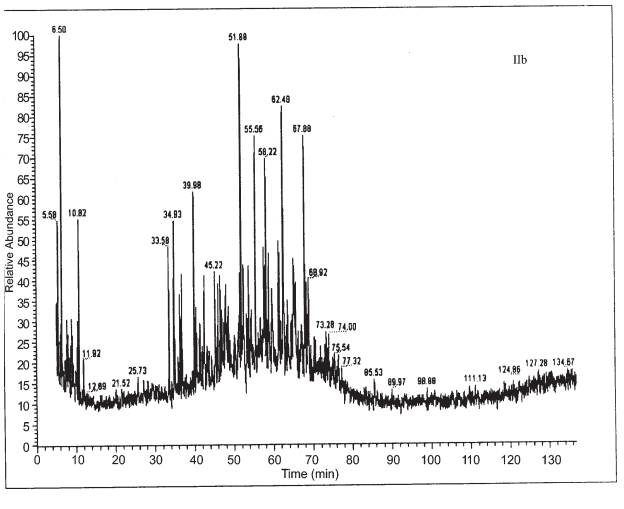


Fig. 6. LGO subfraction II b.

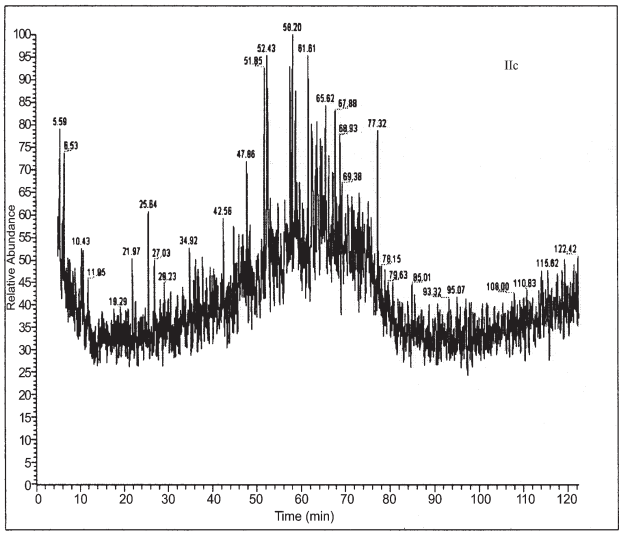


Fig. 7. LGO subfraction II c

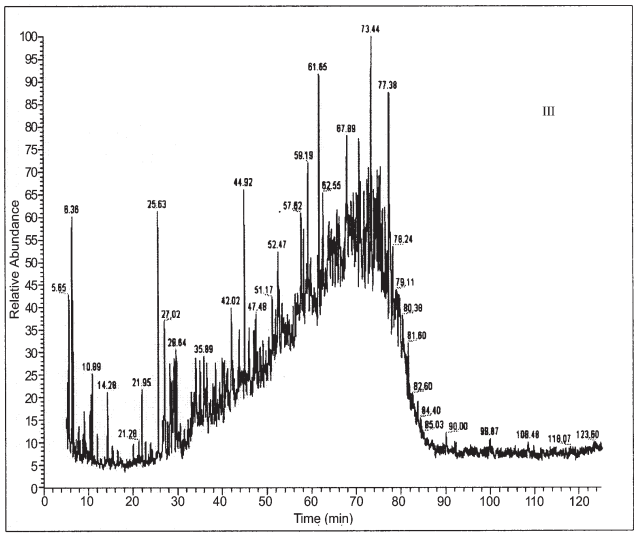


Fig. 8. LGO subfraction III

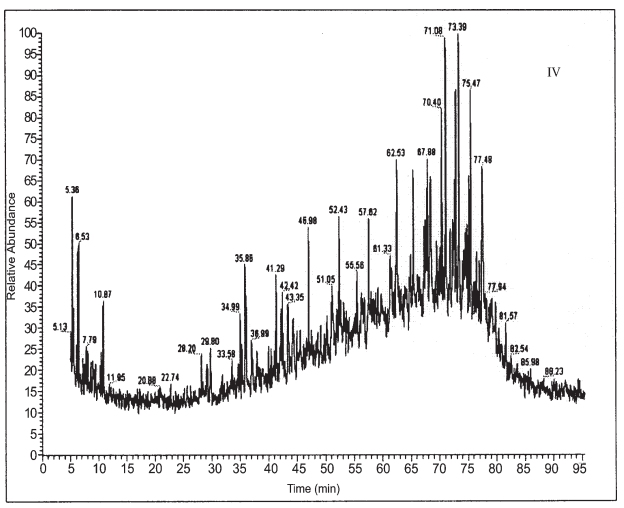


Fig. 9. LGO subfraction IV

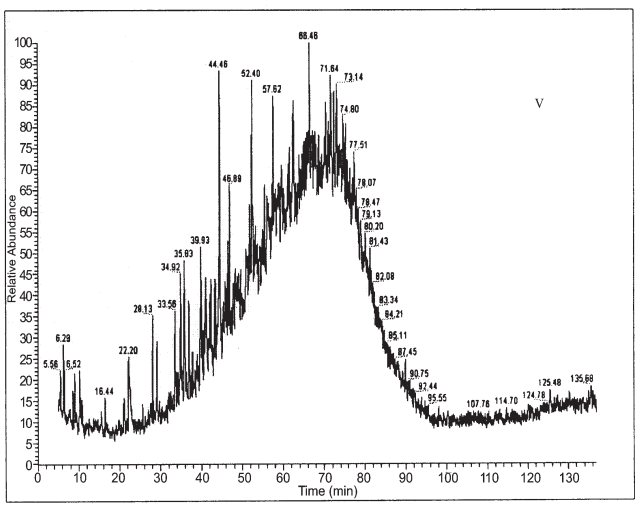


Fig. 10. LGO subfraction V

content. While the polyaromatic compounds and their alkyl analogues and benzothiophene are minor aromatic compounds in LGO.

The mass spectra of all alkyl benzene show fragmentation ion peaks at m/z 91, 92. 105, 106, 119, 120, 133, 134, 147 and 148. These m/z fragmentation ion peaks appear in the spectra of these compounds, and are a clear evidence of the alkyl benzene of LGO aromatic compounds.

The mass spectra of naphthalene and alkyl naphthalene (fragmentation on peaks at m/z 127, 128, 141, 142, 155, 156, 169, 170, 183 and 184) are a clear evidence of the LGO naphthalene and alkyl naphthalene aromatic compounds. The molecular ion peak at m/z 128, 142, 156, 170 and 184 refer to naphthalene methylnaphthalene, ethyl and dimethyl naphthalene, 1-propyl-, Isopropyl- and trimethyl-naphthalene, and 1,2,3,4-tetramethyl, 1,4,5,8-tetramethyl and tert-butyl naphthalene respectively.

The mass spectra of the biphenyl and the diphenyl methane and their alkyl analogues beside the aromatic compounds with the general formula C_nH_{2n-14}, having mass spectra of fragmentation ions peaks at m/z 153, 154, 167, 168, 181, 182, 195 and 196.

The molecular ion peak of biphenyl appears at m/z 154, while the molecular ion peaks of both methylbiphenyl and diphenylmethane appears at 168. The molecular ion peaks of ethyl and dimethyl biphenyl and 1-methyl-3- (phenyl methyl) benzene appear at m/z 182. The 1, 2-dimethyl-4-(phenyl methyl) benzene appear at molecular ion peak m/z 196.

The mass spectra of fluorene, alkyl fluorene and the aromatic compounds with the general formula C_nH_{2n-16} show fragmentation ion peaks at m/z 165, 166, 179, 180, 193, 194, 207 and 208 which represent a clear evidence of these types of aromatic compounds. Fluorene molecular ion peak appears at

m/z 166, the methyl fluorene molecular ion peak appears at m/z 180. The dimpethyl fluorene, methyl-9, 10-dihydrophenanthrene and methyl-9. 10-dihydroanthracene appear at molecular ion peaks m/z 194 while the molecular ion peak of 9, 10-dimethyl-9, 10-dihydroanthracene appears at m/z 208.

Tricyclic aromatic compounds and the aromatic compounds with the general formula C_nH_{2n-18} having the following m/z ions peaks in their mass spectra 177, 178, 191, 192, 205, 206, 219 and 220. The mass spectra of both phenanthrene and anthracene show the molecular ion peaks at m/z 178. Methyl phenanthrene and methyl anthracene spectra show the molecular ion peak at m/z 192. The dimethyl analogues of both phenanthrene and anthracene as well as 4,,5,9,10-tetrahydropyrene mass spectra show the molecular ion peak at m/z 220.

The mass spectra of benz (phenanthrene-6-methyl) and benz (Anthracene-7-methyl) have the general formula C_nH_{2n-24} indicate molecular ion peaks at m/z 242. The dibenzothiophene with the general formula $C_nH_{2n-16}S$[18] has the molecular ion peak at m/z 184[19] . The ions CHS+ and CH_2S^+ have fragment ion peaks appearing at m/z 45 and 46 respectively. The fragment ion peaks are a clear evidence of the dibenzothiophene aromatic compound with a heteroation.

CONCLUSION

- The study indicates that RASCO light gas oil is low in aromatic compounds (9.27,%).
- The GC-MS results (naphthalene and alkyl naphthalene content) indicate that, the di and alkyl aromatic compounds are dominant in RASCO LGO.
- The alkyl substituents ranging from C1 to C5, and the polyaromatic compounds and their alkyl analogues have existed only in a trac concentration.
- Fractionation of the LGO sample into several sub-fraction facilitates the identification and characterization of different types of aromatic compounds.
- GC-MS is one of the useful techniques used to obtain detailed information about amounts and types of aromatic compounds in LGO.

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