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Study of Pyrolysis Products Oil-Bitumene Rocks

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Abstract

According to estimates of the leading international economic organizations in 2020-2025 years the peak of production of traditional oil will be reached after which its recession in view of exhaustion of the main reserves of this type of energy carriers will begin. The most promising step in this direction is to attract such minerals as high-viscosity oil, natural bitumen and bitumen-bearing rocks, since the main raw materials are concentrated in their fields. Oil bitumen rocks (OBR) are an alternative raw material for obtaining various products [1, 2]. Studies of liquid and the resulting products of pyrolysis of petroleum-bituminous rocks, methods of gas-liquid chromatography (flame ionization detector) and IR spectroscopy are carried out. The gas chromatograph "The Kristall Lux 4000" (Yoshkar-Ola, Mariy-El Republic) was used. Analysis conditions: Packed column, length 1 m; Sorbent - "Chromaton NDMCS" with 5% OV-101; Carrier gas — helium, gas flow rate 30 ml / min; Hydrogen - 30 ml / min; Air - 300 ml / min; Flame Ionization Detector (FID). Temperatures: Detector - 270 °C; Evaporator - 270 °C; Column - initial temperature 40 °C; 2 minutes in isothermal mode, then heating 40 ° / min up to 260 °C; The volume of the injected sample - 3 µl. The calculation was carried out according to the method of simulation distillation ASTM-89. The pyrolysis process consists in heating the OBR without air access, which leads not only to the distillation of the petite-bituminous fraction, but also to the course of complex chemical reactions during high-temperature pyrolysis at 580-600 °C. As a result of pyrolysis, gaseous (not trapped), liquid and solid products are formed and almost all volatile products are removed. An iron retort for dry distillation was used. Liquid and solid products of OBR pyrolysis were dissolved in benzene. It is established that the products of the OBR pyrolysis mainly contain fuel oil 370-500 and diesel fuel 200-370.

Keywords: Oil bitumen rocks, pyrolysis, mechanism, IR-spectroscopy.

1. Introduction

The Republic of Kazakhstan pays great attention to the construction of modern highways that meet international standards, but for long term use in the spring and summer and especially in autumn and winter periods in multiple alternating temperature changes from -40 °C to + 40 °C and in heating Road cover 90-100 °C, roads wear out quickly, which requires annual renewal of the top layer - the asphalt [3]. Earlier thermomechanical studies showed that bitumen softens at 0 ° C, goes into a viscous-fluid state at 20 °C and 100% decomposition is achieved at 40 °C, and there is no area of highly elastic deformation [3]. In the work [4] considered the issues of improving the condition of roads subject to use at its oil Sands construction rocks , in which it is expected to obtain economic benefits from lower costs of building materials by 30-40%. The pyrolysis OBR is not fully studied. The composition of products of hydrothermal conversion of natural concentrate of tar-asphaltene substances (asphaltite) at temperatures up to 575 °C has been studied in [5]. It was found that thermal degradation takes place in the range 175–575°C, leading to the formation of gases, in particular H2S, and liquid and insoluble products (oil and carbenes-carboids, respectively). The amount of saturated and aromatic compounds in the liquid products of hydrothermal conversion is greater than in the starting sample. The ratio of benzene-extractable to alcohol-benzene-extractable resins substantially varies in favor of the latter compounds, which are enriched in oxygen-containing structural units. The relative amount of higher (>20°C) n-alkanes in the products of conversion at 175–325°C or 350–575°C is respectively higher or lower than in the virgin asphaltite. At conversion temperatures of ≥400°C, the products contain α-olefins. The paper [6] considers ecological and physicochemical aspects of the processes of thermal processing of acidic tar into road bitumen. The paper [7] investigates the transformations of resins and asphaltenes of different chemical composition of heavy oils in the primary processing of the Usinskoye (Komi Republic, Russia) and Zuunbayanskoye (Mongolia) fields. Using the data of elemental composition, molecular mass, PMR-spectroscopy the structural and group parameters of molecules of resins and asphaltenes of initial oils and oil

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residues (fuel oil), obtained by atmospheric distillation with the selection of fractions of NK-350. Changes in the average molecular structures in the process of primary oil refining were revealed and it was established that these changes depend on the chemical composition of the initial oils. In work [8] the analysis of a modern condition of problems in the field of processing of hydrocarbon-containing waste of petrochemistry and oil refining is presented. The basic methods of utilization and neutralization of hydrocarbon waste, equipment for these reactionary processes are considered. The paper [9] presents a unit for processing of bituminous wastes.

In works [10-12] bitumen-containing sands are heated up and provide manufacture of transport fuel. Volatility products of two-stage (400, 650 °C) flash pyrolysis of asphaltite of Ivanovskoye deposit of the Orenburg region, its asphaltenes, oils, benzene and ethanol-benzene resins are characterized by the method of chromatomass spectrometry (CMS) [13, 14] in the on-line mode. At both temperatures, the products are dominated by an "indissoluble complex mixture" of unidentified compounds. The composition of the identified compounds in the products obtained at 400 and 650 °C is significantly different, especially for resins and asphaltenes. At 650 °C, products for all samples are characterized by the same set of compounds, including homologues of alkanes, -olefins, cyclohexanes, pregnanes and sterans, heilantans and hopans, hopenes, mono-, bi- and tricyclic aromatic hydrocarbons, benzo and dibenzothiophenes. This confirms the presence of most of these compounds in the "bound" form as structural fragments of molecules of resinous asphaltene components of natural asphaltites. The procedures for obtaining fuels are described in detail, and the use of non-conventional and renewable energy sources on a global scale is predicted [15]. In [16] bituminous sandstones are extracted with a mixture of α-olefins obtained from polyethylene waste and boiling in the temperature range of 70-435 °C. The extract is used to disperse the fraction of a-olefin mixture boiling in the temperature range of 70-300 °C. As a result, bitumen oil is produced. Ultra-high-performance Bitumen compaund Warming Method is used in the work [17] The article [18] summarizes the information on the main directions of using the process of aqua-thermolysis of oil in the conditions of supercritical state of water at alternative sources of traditional oil. In [19] bitumen cracking in the presence of 10% microspheres at a cracking temperature of 450 °C leads to an increase in the yield of fractions at 360 °C by 10% wt. compared with the original bitumen. The results of structural group analysis of resins and asphaltenes indicate a significant destruction of molecules of high-molecular components of bitumen during cracking, initiated by ozone and microspheres.

In the article [20] an idea of natural bitumens is given, deposits of natural bitumens and heavy oils and methods of their extraction and processing are considered.

The cracking of bitumen in the Beke field has been found to lead to a deterioration of the fractional and component composition of liquid products. The quality of liquid products of Munailu Mola bitumen cracking improves due to the destruction of both resinous and asphaltene components [21].

2. Experiment

Oil bitumen rocks (OBR) after pyrolysis in an airless environment were studied: solid F1 and liquid products: F3, F4, F5, No. 4.

Gas-liquid chromatography.

Gas-liquid chromatography is one of the most promising methods of analysis. The widespread and promising use of GC methods is due to the fact that they allow the separation and quantification of substances in a complex mixture, even in cases where they are similar in chemical properties, and the boiling point differs by tenths of a degree. Very small amounts of the substance are required for analysis, and the determination time is usually calculated in minutes. We studied the products of pyrolysis of oil Sands rocks by gas-liquid chromatography (flame ionization detector). In this investigation, we used a gas chromatograph "Crystal Suite 4000" production (Yoshkar-Ola, Mari-El). Assay conditions: packed column, length 1 m Sorbent - "Chromaton NDMCS» c 5% OV-101; Carrier gas - helium gas flow rate of 30 ml / min hydrogen - 30 ml / min air - 300 ml / min; flame ionization detector (FID). Temperatures Detector - about 270; Evaporator - about 270; Column - initial temperature of 40, and 2 minutes in the isothermal mode, and then heating the 4 o / min to 260 of Volume of the sample injection - 3 l. The calculation was performed by the method of simulation of distillation ASTM-89 [22].

IR spectroscopy

For information about the processes by mixing oil-bitumene rocks with polymeric binders were held infrared spectroscopic studies of the respective samples. Infrared absorption spectra of bitumen, OBR and polymer compositions were obtained on an automatic dual-beam spectrometer UR-20 in the absorption interval of 400-4000 cm^{-1}.

Pyrolysis held various fields oil-bitumene rocks of western Kazakhstan and the method of gas-liquid chromatography investigated liquid and solid products of decomposition. Previously there have been studied methods modified OBR electron paramagnetic resonance (PMR) [7]. The pyrolysis process comprises heating OBR without access of air, which leads not only to oil-bitumene distillation fraction to flow but of complex chemical reactions at high temperature pyrolysis at 580-600 ^{0}C. As a result, the pyrolysis gas produced (not caught) liquids and solids are removed, and almost all of the volatile products. To carry out distillation was used iron retort. Liquid and solid pyrolysis products OBR was dissolved in benzene.

3. Results and discussion

The research methods of pyrolysis products OBR gas-liquid chromatography (flame ionization detector).

Pyrolysis of various deposits held oil-bitumene rocks (OBR) in Western Kazakhstan and by gas-liquid chromatography investigated liquid and solid products of decomposition. It was found that the pyrolysis products contain mainly masut 370-500 and diesel 200-370.

Fig. 1 and 2 show the chromatograms and the content of the pyrolysis products OBR number 4 of the lower and upper layers, respectively. From Figure 1 it follows that in the products of pyrolysis gasoline fraction and no tar. The

pyrolysis products are diesel and fuel oil fraction. Diesel 200-370 is present in an amount of 65.18%, and oil 370-500 - in an amount of 34.82%.

From Fig. 2 shows that the top of the content of the gasoline fraction pyrolysate minor - 0.12%, diesel fuel - 41.75% oil - 58.13%. From a comparison of data content of diesel fuel and fuel oil OBR number 4 in the top and bottom fractions (Fig. 1 and Fig. 2, respectively) that during the transition from the bottom to the top of the diesel fuel fraction falls to 23.43%, and amount of fuel oil increased by 23.31%. Apparently, the depolymerization reactions occur and degradation oil-bitumene rocks.

Of particular interest are the IR spectroscopic studies of the OBR. For figures 3-6 the results of IR spectroscopic analysis of samples: F-1, F-3, F-4 and F-5 after pyrolysis are presented.

From Fig. 3 it follows that The F-1 sample has high peaks intense peaks: at 2952.7 cm^{-1}, 2925.1, 2888.1 cm^{-1}, related to the valence fluctuations of the methylene and terminal methyl groups, caused mainly by cycloalkanes and aliphatic heterocompounds, and not by n-alkanes and isoprenes [23]. Nadirov N.K., Brawn A.E., Trokhymenko M.S. and others, Oil bitumen rocks of Kazakhstan: problems and prospects, Alma-Ata, Nauka, 1985. P. 376.], a small peak at 2726.7 and small peaks: at 1708,2 1604,4 1456,9 1376,6 1300,8 1031,2 965,3 814,6 747,8 562,2 cm^{-1}.

From Fig. 4 it is seen that the F-3 summer has the same high peaks intense peaks at 2953.9 2926.8 2923.8 2867.3 2855.4 cm^{-1} as the F-1 sample. However, the F-3 sample has a low but wide peak at 3417.0 cm^{-1}, which corresponds to the valence fluctuations of the bonds -OH and -NH groups and small absorption bands at 2727.3 1706.5 1641.1 cm^{-1}, medium intensity: at 1456.3 1376.4 and small peaks: at 1303.2 1158.2 1032.3 964.8 975.7 813.2 745.8 and 561.6 cm^{-1}.

The absorption band at 1708.2 cm^{-1} (sample F-1) and 1706.5 cm^{-1} (sample F-3) characterizes the presence of oxygen compounds, carbonyl-containing groups: saturated aldehydes, ketones, aliphatic esters, etc. the bulk is represented by fatty acids and their esters.

For figures 5 and 6 represent the IR spectra of the F-4 and F-5 samples. A comparison of figures 5 and 6 shows that the highest intense and broad peak at 3427.0 cm^{-1}, (sample F-4) and 3418.3 cm^{-1} (sample F-5) corresponds to the valence fluctuations of the –OH and –NH groups.

The F-4 summer has a small peak at 2957.1 cm^{-1} at 2073.0 cm^{-1}, an average peak at 1639.5 cm^{-1}, small peaks at 1536.2, 1452.5 1317.1 and 1075.5 cm^{-1}.

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The F-5 sample has very high intense peaks at 2953.1, 2924.2, 2867.9 cm^{-1}, small peaks at 2723.3 and 2088.1, medium intensity at 1704.3, 1642.6, 1455.6, 1376.5, small peak at 1302.9, medium intensity at 724.9 and 561.8 cm^{-1}.

The absorption bands at 2951-2953 cm^{-1} and 1455.6-1456.3 cm^{-1} belong to methylene groups groups in cycloalkanes and heterounits, which indicate in favor of the hydrocarbon base of bitumens.

The absorption bands in the long-wave infrared region are 724.9 and 745.8 $cm^{-1}$and correspond to the deformation fluctuations of the methylene groups R - (CH2)n-CH3 in paraffin chains.

Thus, the GC- and IR-spectroscopic studies performed on the original sample of oil bitumen (sample K-1) and the compositions obtained on its basis prove that new chemical compounds were formed in them, for example, polymer bitumen, which corresponds to the brands of road construction.

4. Conclusions

1. It was found that pyrolysis in an airless environment is accompanied by the formation of diesel fuel 200-370 and fuel oil 370-500.
2. It was found that Oil bitumen rocks (OBR) # 4 in the upper part of the pyrolysis of gasoline - 0.12%, while in the lower part of the gasoline fraction is absent.
3. It was found that the studied samples are characterized by the presence of F-1 methylene groups with absorption bands does not have an absorption band at 3000-3200 cm^{-1}, whereas the F-3 sample has a small peak at 3417.0 cm^{-1}, and the F-4 and F-5 samples have wide intensive absorption bands, respectively, at 2953.9 2926.8 2923.8 2867.3 2855.4 cm^{-1}, which belong to methylene groups in cycloalkanes and heterounits.
4. It was found that the absorption bands at 3427.0 cm^{-1} and 3418.3 cm^{-1} cause valence fluctuations of the –OH and –NH groups.

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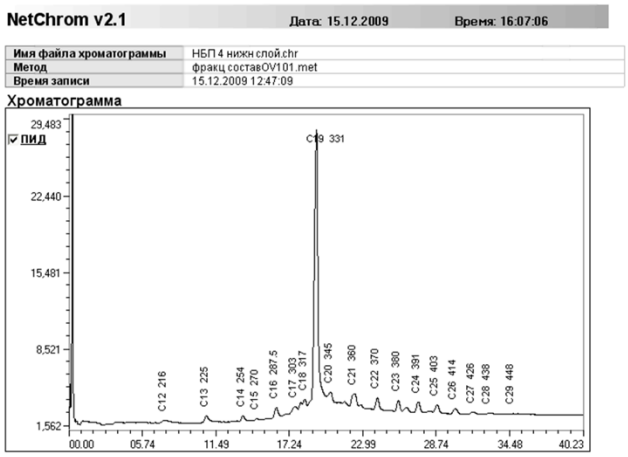
Appendix



Пики

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1	7,51	C12 216	0,5610
2	10,77	C13 225	1,0024
3	13,61	C14 254	0,4063
4	14,73	C15 270	0,3564
5	16,21	C16 287.5	1,8317
6	17,67	C17 303	2,9573
7	18,44	C18 317	4,7592
8	19,36	C19 331	34,3398
9	20,45	C20 345	9,6762
10	22,31	C21 360	9,6574
11	24,11	C22 370	9,2102
12	25,75	C23 380	6,8562
13	27,30	C24 391	6,8165
14	28,77	C25 403	4,8157
15	30,19	C26 414	2,7352
16	31,58	C27 426	1,5503
17	32,83	C28 438	1,2985
18	34,70	C29 448	1,1698
			100,0000

Группы

№	Группа	Детектор	Концентрация, % об.
1	бензин-200	ПИД	0,000000
2	дизель топ-200-370	ПИД	65,179222
3	мазут-370-500	ПИД	34,820778
4	гудрон выше- 500	ПИД	0,000000

Fig. 1. "The chromatogram OBR No. 4 (bottom layer)" – a brown liquid

NetChrom v2.1 Дата: 15.12.2009 Время: 16:14:27

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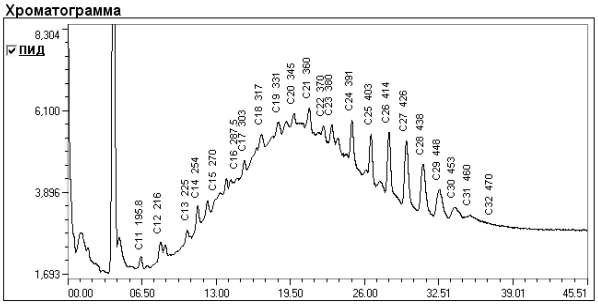
Время записи	14.12.2009 12:03:22

Хроматограмма



Пики

№	Время, мин	Компонент	Площадь,%
1	6,48	C11 195.8	0,1068
2	8,10	C12 216	0,8014
3	10,47	C13 225	0,9833
4	11,36	C14 254	2,5874
5	12,89	C15 270	2,5538
6	14,77	C16 287.5	3,2289
7	15,47	C17 303	3,4481
8	16,97	C18 317	6,7151
9	18,47	C19 331	6,7127
10	19,78	C20 345	8,1542
11	21,15	C21 360	8,1506
12	22,38	C22 370	8,7435
13	23,11	C23 380	10,5871
14	24,88	C24 391	8,2703
15	26,54	C25 403	7,0532
16	28,11	C26 414	6,7822
17	29,63	C27 426	5,3233
18	31,10	C28 438	3,7812
19	32,53	C29 448	2,6182
20	33,84	C30 453	1,6541
21	35,18	C31 460	1,2163
22	37,09	C32 470	0,5282
			100,0000

Группы

№	Группа	Детектор	Концентрация, % об.
1	бензин-200	ПИД	0,120521
2	дизель топ-200-370	ПИД	41,749981
3	мазут-370-500	ПИД	58,129494
4	гудрон выше- 500	ПИД	0,000000

Fig. 2. "The chromatogram OBR No. 4 (top layer)" – a light-brown oil

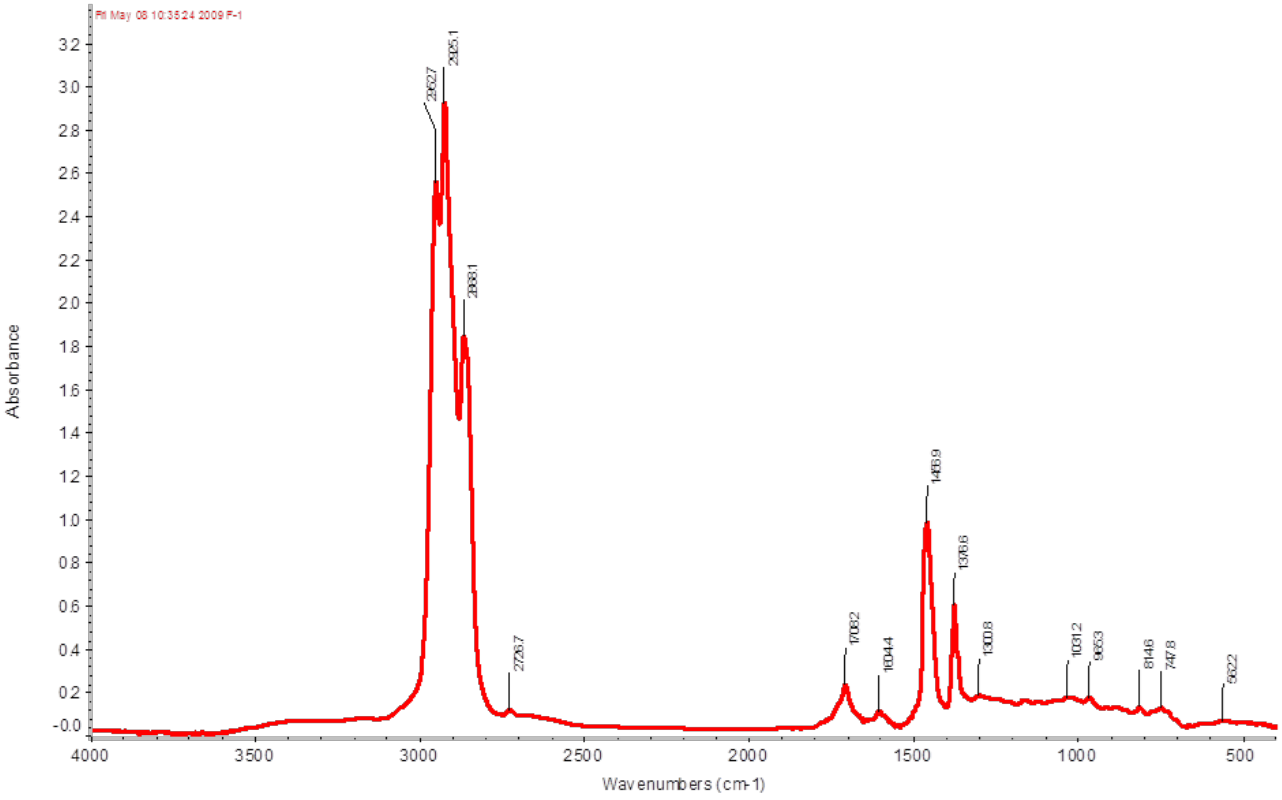


Fig. 3. IR spectra F-1 sample – a dark solid residue

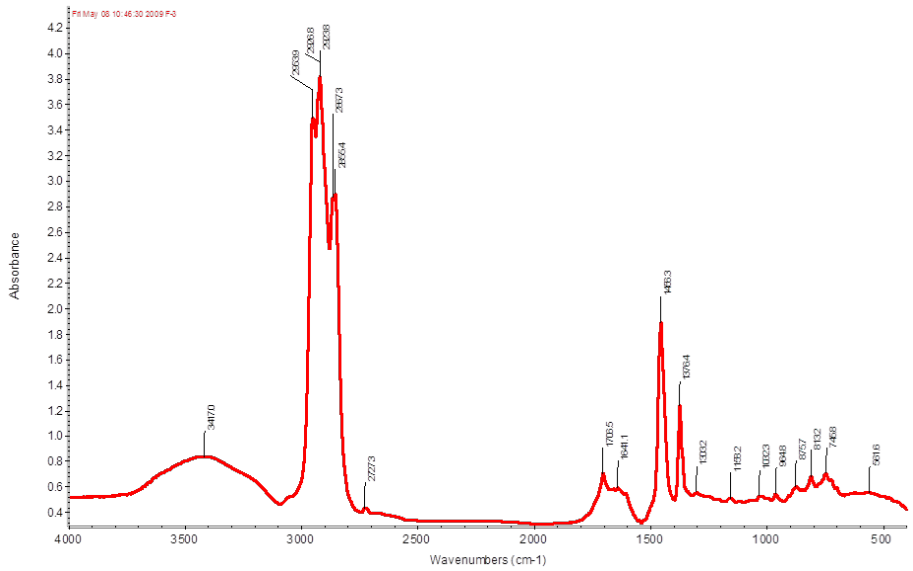


Fig. 4. IR spectra F-3 sample - a dark oily liquid

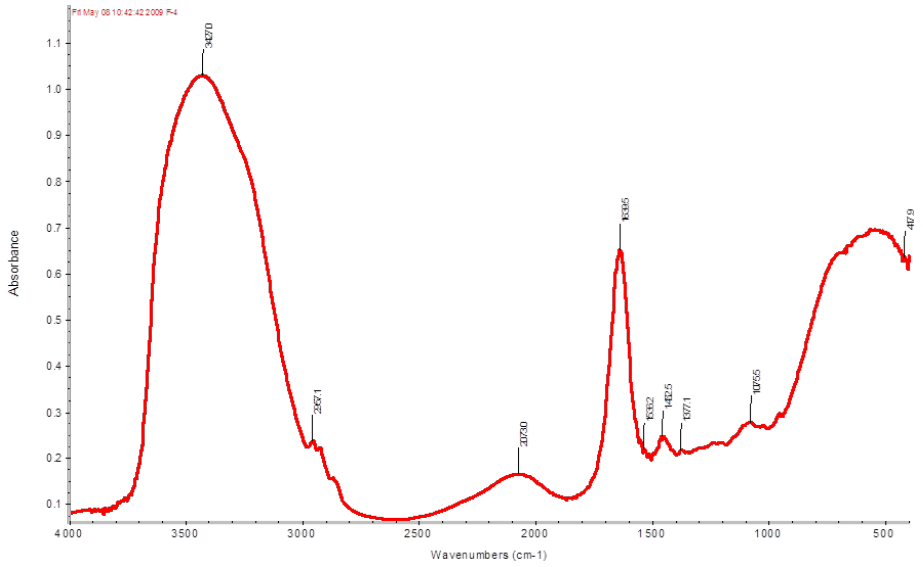


Fig. 5. IR spectra F-5 sample - a clear liquid

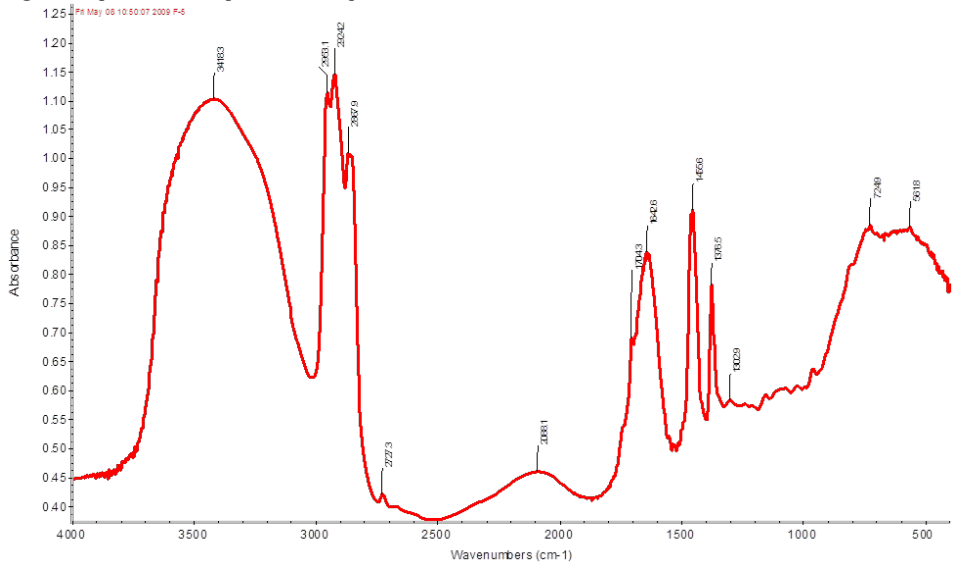


Fig. 6. IR spectra F-5 sample – a dark oily liquid