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GAS-CHROMATOGRAPHIC DETERMINATION OF SULFUR COMPOUNDS IN THE GASOLINE FRACTIONS OF SHALE OIL AND OIL OBTAINED FROM USED TIRES

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Abstract. *The sulfur compounds content of the gasoline fractions of shale oil and oil obtained from used tires was investigated by the method of gas chromatography (GC). There was a marked difference in quantitative chromatograms estimation between the normalization method and the internal standardization method. The application of the internal standardization method proved to be preferable. In addition, the results obtained on the content of sulfur compounds in the studied gasoline fractions allow us to conclude that the co-processing of used tires with oil shale will not affect the quality of the light fraction of oil produced and thus, it enables not to change the method of purification from sulfur compounds.*

Keywords: *shale oil, used tires, gasoline fraction, sulfur, gas chromatography.*

1. Introduction

The oil shale processing industry has suffered many changes due to fluctuations in the petroleum market over the last several years. Record-breaking low prices of petroleum have hindered large investments in shale oil quality improvement [1, 2]. During this period, possibilities of oil production from different solid wastes and co-processing of oil shale with waste materials

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have been considered, thereby reducing the cost of production of the obtained liquid fuels.

One possible option to pursue could be co-processing of oil shale and pyrolysis of used tires, which has been researched previously to some extent [3–6]. The main task of co-processing is to obtain oil of quality that would meet the requirements of the market. One of the basic requirements for fuel quality is low sulfur content. The determination of sulfur quantity as well as sulfur compounds in fuels is an important task in the face of tightening requirements for sulfur content levels in fuels. Gas chromatography (GC) is one possible technique for identifying sulfur compounds. GC permits quantitative estimation of chromatograms. Three methods are used to determine sulfur concentrations in both gasoline fractions. The internal standardization method consists in analyzing a sample of unknown quantitative composition, to which a known quantity of a substance not contained in it (internal standard) is added. The response areas of each sulfur compound of interest are compared to that of the internal standard. The external standardization method draws a relationship between peak parameter (area or height) and content of the substance in a sample via the results of a series of analyses. A calibration coefficient is then determined. The response areas of each sulfur compound of interest are compared to that of the external standard. The third method is the normalization method. This method is based on a principle that the sum of areas (heights) of all peaks on the chromatogram is taken as 100%.

The aim of the present work is to study possible gas chromatographic methods for the exact determination of sulfur compounds in the 90–150 °C gasoline fractions of shale oil and oil obtained from pyrolysis of used tires.

2. Experiments

2.1. Pyrolysis

Oil shale of the Estonian deposit and rubber crumb of particle sizes of 4 mm and smaller obtained from used tires were applied as raw materials for oil production. Experiments were carried out on the laboratory retorting unit. The unit consisted of a reactor with external heating, an air condenser and a water condenser with condensation temperatures of 10–12 °C, and a gas-liquid separator. Gas was directed from the system and the liquid product bleeding from the tank was carried out manually.

A diagram of the experimental retorting unit is shown in Figure 1.

In the process of retorting, a sample was placed in the middle of the reactor and heated for 8 hours up to the final temperature of 520 °C. A precise graph of sample heating is depicted in Figure 2.

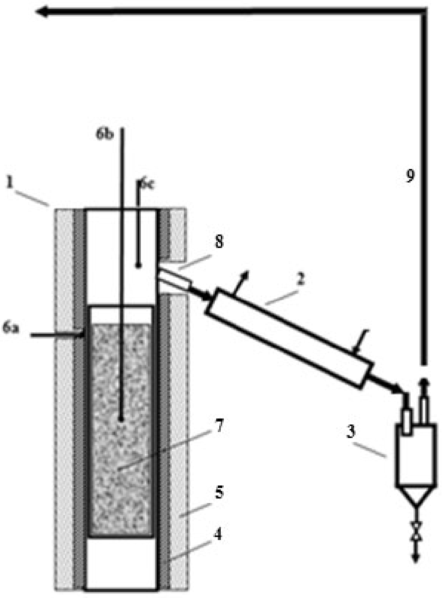

Fig. 1. Retorting unit: 1 – reactor; 2 – air condenser and water condenser; 3 – gas-liquid separator; 4 – heating element; 5 – insulation; 6 – thermocouples (6a – on the wall, 6b – in the mixture, 6c – in the vapours); 7 – initial raw material; 8 – output of steam-gas mixture; 9 – non-condensable gases.

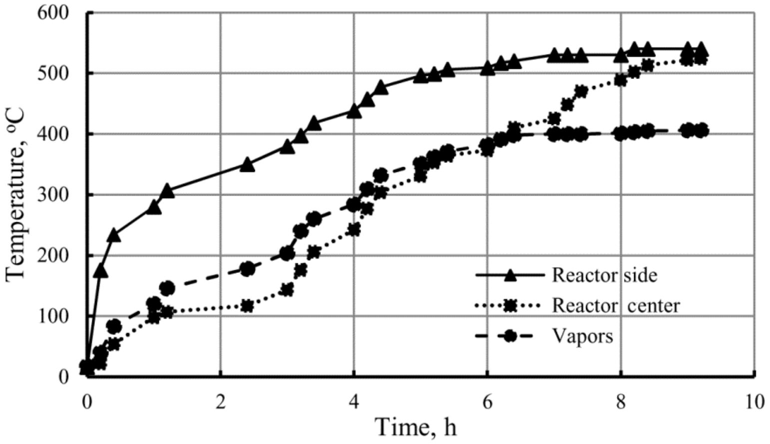

Fig. 2. The graph of temperature change in the process of retorting.

2.2. Distillation

For further research, the 90–150 °C fractions on the B/R Instrument distillation column were separated from shale oil and oil from rubber crumb at atmospheric pressure and a reflux ratio of 1. The column height was 40 cm with 200 theoretical plates. Oils characteristics are given in Table 1. As seen from the table, the density of oil obtained from used tires is higher than that of shale oil. On the other hand, the sulfur mass percent content of shale oil is twice that present in used tire oil. The iodine number is in the same range whereas the acid number is much higher for shale oil.

Table 1. Characteristics of shale oil and used tire oil (boiling range fraction 90–150 °C)

Item	Method	Shale oil	Used tire oil
Density at 15 °C, kg/m^3	EVS-EN ISO 12185	776.6	828.2
Sulfur total, S_t, %, mass	EVS-EN ISO 20846	1.04	0.50
Iodine number, gJ_2/100 g	GOST 2070	107.7	98.5
Acid number, mg KOH/g	ISO 668	3.2	0.05

2.3. Analysis of sulfur compounds

Since there are no standard methods for total sulfur determination of the gasoline fractions from both shale oil and oil from the rubber crumb of used tires, in this work, the standards for light petrochemicals were applied.

Determination of the quantitative content of total sulfur in the studied samples was carried out according to the Standard EVS EN ISO 20846 (Petroleum products – Determination of sulfur content of automotive fuels – Ultraviolet fluorescence method) [7]. EVS-EN ISO 20846 specifies an ultraviolet (UV) fluorescence test method for the determination of the sulfur content of motor gasolines containing up to 3.7 % (m/m) oxygen (including those blended with ethanol up to approximately 10 % (V/V)) and of diesel fuels, including those containing up to approximately 10% (V/V) fatty acid methylester (FAME) with sulfur contents in the range of 3–500 mg/kg. Other products can be analysed and other sulfur contents can be determined according to this test method. However, no precise data for products other than automotive fuels or for results outside the specified range have been established in EVS-EN ISO 20846 [7].

Sulfur compounds in the fractions were determined by gas chromatography according to ASTM D 5623 test, which is applied to distillates, gasoline motor fuels (including those containing oxygenates species) and other petroleum liquids with a final boiling point of approximately 230 °C or lower at atmospheric pressure. This test method covers the determination of volatile sulfur-containing compounds in light petroleum liquids [8].

Chromatographic analysis of the studied samples was implemented using the normalization and internal standardization methods. The above methods of quantitative estimation of chromatograms are also described in ASTM D 5623 test [8].

Sulfur compounds in the fractions were determined by gas chromatography employing a TRACE GC chromatograph with a flame photometric detector (FDP). The Zebron ZB-5HT Inferno column with a nonpolar phase and a length of 60 m was used for separation with a helium carrier gas.

Analysis was carried out in the programmable temperature rise mode: 40 °C (3 min), rising rate of 8 °C/min up to 250 °C (1 min hold time), then up to 280 °C (5 min hold time), and injector temperature of 280 °C.

When determining sulfur compounds by the normalization method, the sulfur content of each compound was calculated as a sulfur share of all components. Further, knowing the total sulfur content in a sample as determined by the ultraviolet fluorescence method, the contents of individual sulfur compounds were calculated.

To determine sulfur compounds by the internal standardization method, the chromatograph was calibrated. Since the response of the device detector is not linear, a calibrating linear equation in a narrow range of concentrations was determined for each compound. Shale oil and oil from the rubber crumb of used tires are mixtures containing dozens of different sulfur compounds. In the internal standardization method, it is necessary to apply reference substances. It is practically impossible to identify each individual component in the samples with such complex compositions. When determining calibration linear equations for unidentified sulfur compounds, the equations of nearby identified individual components were applied.

The chromatograms of sulfur compounds of the studied samples are shown in Figures 3 and 4.

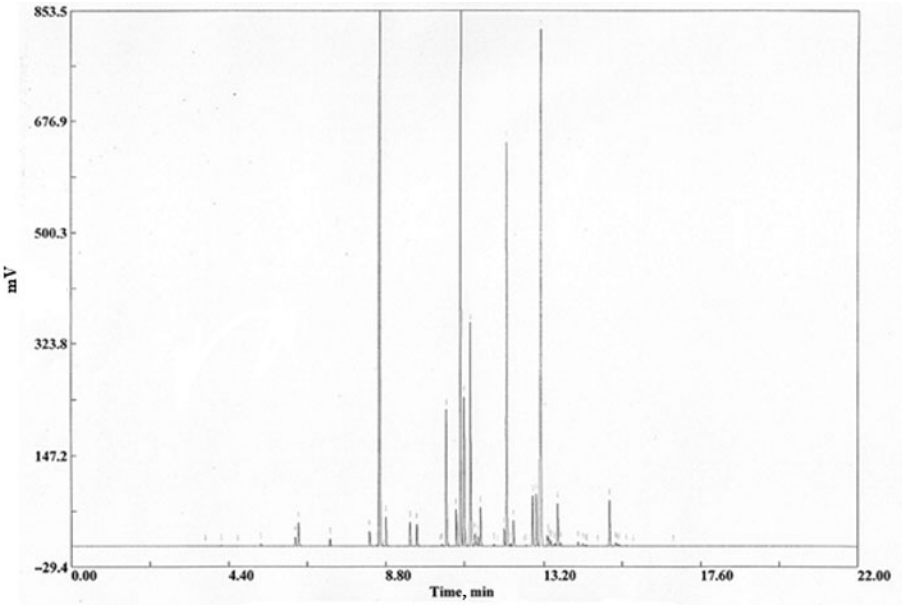

Fig. 3. Chromatogram of the fraction of shale oil (boiling point range 90–150 °C).

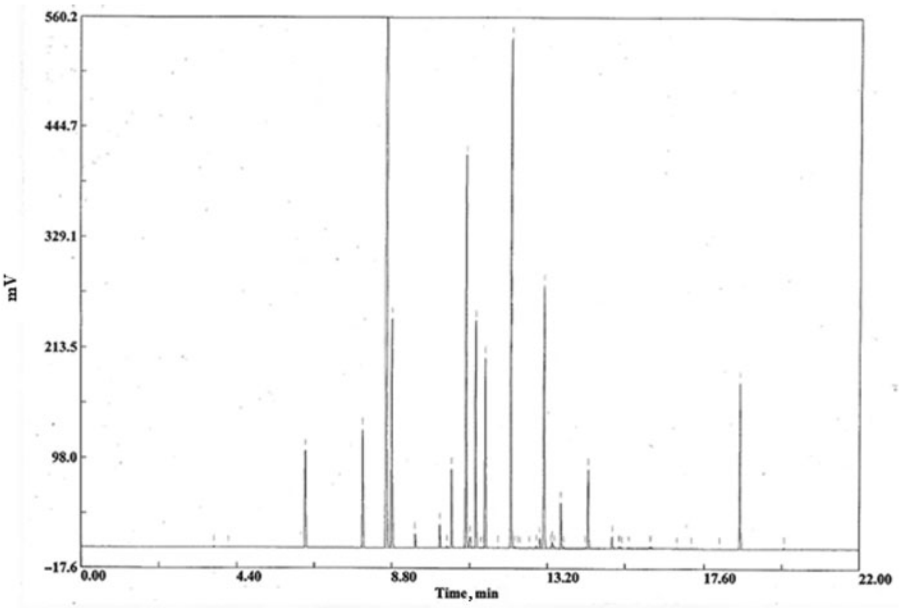

Fig. 4. Chromatogram of oil obtained from used tires (boiling point range 90–150 °C).

3. Results and discussion

Data on quantitative sulfur content in the gasoline fractions of shale oil and oil obtained from the rubber crumb of used tires by different methods are presented in Table 2.

The results presented in Table 2 show that sulfur compounds contents determined by the normalization method differ considerably from those obtained by the internal standardization method. In most cases, the contents of sulfur compounds determined by the former method are lower for the components with minor content. Sulfur compounds of higher content in the samples are, on the contrary, overestimated. The total quantity of identified mercaptans in the gasoline fraction of shale oil determined by the internal standardization method is 440 ppm, and by the normalization method, 101 ppm. For the gasoline fraction of oil from the rubber crumb of used car tires, the respective values are 29 ppm and 2 ppm. There is an opposite tendency in the identification of thiophenes. The sulfur quantity in the gasoline fraction of shale oil determined by the internal standardization method is 2795 ppm, being 4135 ppm by the normalization method. In the gasoline fraction of oil from the rubber crumb, the quantities are 2203 ppm and 4260 ppm, respectively. In the total amount of identified and unidentified compounds, the difference between the results obtained by the methods of internal standardization and normalization is 972 ppm and 1460 ppm, respectively, for the shale gasoline fraction, and respectively 817 ppm and 1638 ppm for the gasoline fraction from the rubber crumb.

Table 2. Quantitative sulfur content in the gasoline fractions of shale oil and oil from the rubber crumb of used tires

Sulfur compound	Retention time, min	Sulfur in shale oil, mg S/kg		Sulfur in used tire oil, mg S/kg	
		Internal standardization method	Normalization method	Internal standardization method	Normalization method
Methyl mercaptan	3.74	24.19	0.62	14.95	1.27
Ethyl mercaptan	4.16	29.97	1.87	14.12	0.58
2-Propanethiol	4.63	13.11	1.34	–	–
Ethyl methyl sulfide	5,39	35.72	6.13	–	–
1-Methyl1-propanrthiol	6.26	157.53	24.18	–	–
Thiophene	6.35	236.22	59.73	145.48	106.76
1-Butanethiol	7.23	68.58	18.29	–	–
DMDS	7.98	–	–	534.29	141.25
Unidentified	8.35	110.03	39.72	–	–
Unidentified	8.55	72.71	4.44	–	–
2-Methylthiophene	8.62	1716.66	3398.03	1566.00	3601.67
3-Methylthiophene	8.80	147.60	76.11	262.82	278.21
Unidentified	9.48	132.74	61.86	48.28	16.67
1-Pentathiol	9.66	146.59	55.11	–	–
Unidentified	10.15	–	–	57.00	27.19
Unidentified	10.30	69.24	1.56	–	–
Unidentified	10.36	72.71	4.92	36.07	2.07
Unidentified	10.49	447.67	364.20	119.20	100.86
Unidentified	10.77	162.09	89.87	–	–
Unidentified	10.89	1567.67	2663.79	431.40	479.51
Unidentified	10.99	56230	474.28	–	–
Unidentified	11.03	–	–	52.18	25.09
3-Ethylthiophene	11.17	694.53	601.05	215.47	273.16
Unidentified	11.30	101.03	31.23	41.01	0.57
Unidentified	11.33	76.20	7.86	41.50	1.05
Unidentified	11.39	95.24	25.73	41.04	0.43
Unidentified	11.44	174.20	101.73	198.38	260.83
Unidentified	11.83–13.00	1024.93	391.25	299.05	23.00
Unidentified	13.12	1174.28	1498.95	277.12	417.88
Unidentified	13.28–16.84	1773.78	395.93	746.57	216.19
Benzothiophene	18.05	–	–	13.02	0.45
Unidentified	18.63–19.87	–	–	176.30	217.00
Unidentified	18.63	–	–	42.04	1.74
∑unidentified, mg S/kg		7617	6157	2766	4404
∑identified, mg S/kg		3271	4243	2607	1790
Total, mg S/kg		10888		5373	
∑gas chromatography method, mass %		1.09		0.54	
∑ultraviolet fluorescence method, mass %		1.04		0.62	

Since the total sulfur content calculated by the internal standardization method is close to the result determined by method of ultraviolet fluorescence, it can be deduced that the obtained results for the quantitative sulfur compounds are reliable.

4. Conclusions

In this research paper, the sulfur compounds determined quantitatively by the normalization method are considerably different from those obtained by the internal standardization method.

It is shown that for precise determination of sulfur compounds content in gasoline fractions by gas chromatography, the use of the internal standardization method is more appropriate than the normalization method.

The sulfur content in the gasoline fraction determined in the used tire oil is lower than the sulfur content of the shale gasoline. The sulfur compounds in both fractions are similar. As a result, the use of the rubber crumb in co-processing with oil shale does not negatively influence the quality of the final product.

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