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COMPARATIVE CHARACTERIZATION OF SEMICOKING OILS OBTAINED FROM RUBBER WASTES AND FROM CO-PROCESSING OF KUKERSITE OIL SHALE AND RUBBER WASTES IN SOLID HEAT-CARRIER UNIT

V. VYSOTSKAYA
M. LIIV
J. KANN

Tallinn Technical University,
Institute of Chemistry
15 Akadeemia St., Tallinn
12618 Estonia

Semicoking oil was obtained from tires only and from kukersite with addition of tires in solid heat-carrier unit SHC-3000 at Estonian Power Plant in Narva. Chemical composition of these oils has been studied using thin-layer and gas-liquid chromatography. The semicoking oil obtained from tires only contains 84.8 % of hydrocarbons, 17.4 % of which are nonaromatic compounds. Treating kukersite together with tires improves oil quality, makes it lower boiling and more unsaturated, increases the content of nonaromatic compounds in oil up to 29.8 %, and so brings its composition closer to that of commercial liquid fuel.

Introduction

Utilization of tires is a serious environmental problem for they are not easily biodegradable under the action of natural factors. Tires are accumulated in huge amounts. They are flammable and produce compounds polluting surroundings intensively.

Rubber wastes have been utilized together with kukersite oil shale on the solid heat-carrier unit SHC-3000 at Estonian Power Plant [1], and this method has been patented [2]. The method enables to reduce the amounts of feed shale and to increase the yields of oil and gas.

At the Institute of Chemistry at Tallinn Technical University attempts were taken to solve this problem in another way. A series of experiments of thermal treating of tires only in a shaft furnace (SF) in semicoking conditions was carried out [3].

Table 1. **The Yield of Chemical Group Compounds of Oils, wt.% (on the Total Oil Basis)**

Group of compounds	Experiment			
	(1) Oils from semicoking of ordinary kukersite	(2) Oils from semicoking of kukersite-kerogen-90	(3) Oils from processing of kukersite and rubber waste in SHC-3000	(4) Oils from semicoking of rubber waste in shaft furnace
Hydrocarbons:				
Aliphatic and naphthenic	13.0	10.9	29.8	17.4
Alkylaromatic	5.6	2.3	8.1	16.0
Condensed aromatics	16.4	26.1	16.6	51.4
Heteroaromatic compounds:				
Neutral	14.2	27.7	18.9	7.1
Polar	17.6	10.1	13.5	4.7
Acidic (mainly phenols)	33.2	23.6	13.1	3.4

Experimental

The aim of this work was to study the chemical composition of the above-mentioned oils (amiably given by Dr. A. Elenurm and Dr. M. Marguste), and of oils obtained at semicoking both of ordinary kukersite oil shale (K-OR-oil) and enriched kukersite-kerogen-90 (K-90-oil) in an alumina retort with electroheating. Thereafter the phenols were separated from total oils by treatment with sodium hydroxide 10 % solution. Phenol-free oils were divided into groups of chemical compounds by thin-layer chromatography on silica gel using *n*-hexane as solvent. Five groups of compounds were separated (see Table 1):

(1) Nonaromatic hydrocarbons (NAHC)
(2) Alkylaromatic hydrocarbons (AAHC)
(3) Condensed aromatic hydrocarbons (CAHC)
(4) Neutral oxygen-containing compounds (NOCC)
(5) Polar oxygen-containing compounds (POCC)

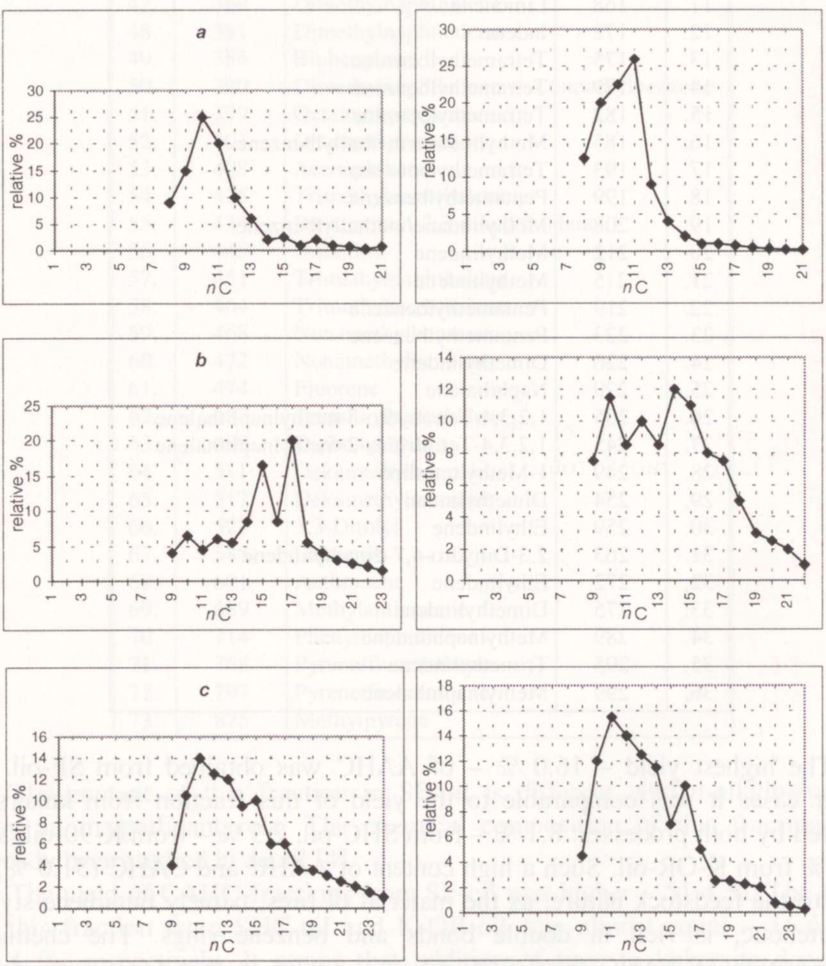
The first four groups of compounds and phenols were investigated by gas-liquid chromatography. Besides, the condensed aromatic compounds of SHC-oil were investigated by chromato-mass spectroscopy.

Results and Discussion

Comparing the data of Table 1 one can see that semicoking of tires only gives oil that contains nonaromatic compounds in an amount comparable with that present in semicoking oil of kukersite only (both kerogen-90 and ordinary kukersite) – 17.4, 10.9 and 13.0 %, respectively. The yield of

NAHC from SHC-oil is higher – 29.8 %, and this fraction is more unsaturated (the ratio olefins/paraffins is 1.395, while for SF-oil it is 0.337). The distribution of paraffins and olefins according to the length of carbon chain (Fig. 1) shows that their content and distribution in oils obtained from various processing are different and depend on the treatment conditions.

At SHC-processing the heating rate and rate of removing reaction products are so great that secondary reactions do not take place, and olefins form in large amounts. Paraffins in SHC-oil have their maximum within C_{10}-C_{11}, and this number is lower than that in semicoking oils – C_{15}-C_{17} in case of SF-oil, and C_{11}-C_{13} for K-90-oil. The differences between distribution of paraffins and olefins in semicoking oils obtained from tires only and kerogen-90 depend on the feedstock.



Distribution of *n*-alkenes (left column) and *n*-olefins-1 (right column) depending on the carbon atom number in the hydrocarbon chain: *a* - SHC-oil, *b* - SF-oil, *c* - K-90-oil; *n*C – number of carbon atoms in chain

Table 2. **The List of Components Identified in the Condensed Aromatic Fraction of SHC-Oil**

No.	Scan. no.	Name
1.	108	Hexane
2.	111	1,3-Cyclohexane
3.	117	Dimethyl sulfone
4.	123	Cresol
5.	127	Cyclopentene, 3-ethylidene-1-methyl
6.	134	Styrene
7.	141	3,5-Xylenol
8.	153	Trimethylbenzene
9.	156	Methylstyrene
10.	165	Tetramethylbenzene
11.	168	Limonene
12.	172	Indene
13.	175	Tetramethylbenzene
14.	179	Tetramethylbenzene
15.	182	Tetramethylbenzene
16.	185	Methylindane/methallylbenzene
17.	193	Tetramethylbenzene
18.	199	Pentamethylbenzene
19.	208	Methylindane/methallylbenzene
20.	212	Methylindene
21.	215	Methylindene
22.	219	Pentamethylbenzene
23.	223	Pentamethylbenzene
24.	226	Dimethylindene
25.	229	Naphthalene
26.	235	1,2,3,4-Tetrahydro-5-methylnaphthalene
27.	245	1,2,3,4-Tetrahydro-2-methylnaphthalene
28.	249	1-Methyltetraline
29.	254	Dimethylindan
30.	259	Ethylindene
31.	263	2,3-Dihydro-4,7-dimehylindene
32.	272	Ethylindene
33.	275	Dimethylindene
34.	289	Methylnaphthalene
35.	295	Trimethylindene
36.	299	Methylnaphthalene

The highest yield – 16.0 % – of AAHC was obtained from SF-oil. In other cases it was comparable to the yield of this fraction from kukersite treated by both processes: 8.1 % – from SHC-oil, 2.3 % – from K-90-oil, and 5.6 % from K-OR-oil. Such a high content of AAHC and CAHC (51.0 %) is due to the feedstock nature, as the material of tires, namely butadiene-styrol caoutchouc, is rich in double bonds and benzene rings. The chemical composition of AAHC from SHC-oil was similar to that from semicoking kukersite and consisted of a series of *n*-alkylbenzenes with the length of side chain from 2 to 10 carbon atoms (somewhat shorter than C_4-C_{16} in the case of kukersite).

Table 2. The List of Components Identified in the Condensed Aromatic Fraction of SHC-Oil (end)

No.	Scan. No.	Name
37.	304	Heptamethylbenzene
38.	310	Unknown cyclic
39.	316	Heptamethylbenzene
40.	323	Heptamethylbenzene
41.	330	Heptamethylbenzene
42.	334	Heptamethylbenzene
43.	338	Biphenyl
44.	343	Trimethylindene
45.	350	Ethylnaphthalene
46.	359	Dimethylnaphthalene
47.	369	Dimethylnaphthalene
48.	381	Dimethylnaphthalene
49.	385	Biphenylene
50.	390	Dimethylnaphthalene + octamethylbenzene
51.	399	Octamethylbenzene
52.	401	Octamethylbenzene
53.	408	Acenaphthene
54.	425	Trimethylnaphthalene
55.	434	Pentamethyl-2,3-dihydroindene
56.	445	Unknown
57.	451	Trimethylnaphthalene
58.	464	Trimethylnaphthalene
59.	468	Nonamethylbenzene
60.	472	Nonamethylbenzene
61.	474	Fluorene
62.	487	Trimethylnaphthalene
63.	499	Diphenylethane
64.	511	Dekamethylbenzene
65.	517	Dekamethylbenzene
66.	523	3,3-Ditolyl
67.	585	Unknown
68.	601	Anthracene
69.	689	Methylanthracene
70.	714	Phenylnaphthalene
71.	768	Pyrene/fluoranthene
72.	797	Pyrene/fluoranthene
73.	875	Methylpyrene

The content of this fraction in SF-oil is different, and *n*-alkylbenzenes play an insignificant role. The chemical composition of this fraction has already been studied in detail [4].

The yield of CAHC-fractions from SF-oil was higher – 51.4 %. The yield of this fraction from SHC-oil and K-OR-oil was almost equal – 16.6 and 16.4 %, respectively. It seems that addition of tires to kukersite does not increase the yield of CAHC. However, the yield of this fraction from K-90-oil was 26.1 %. It is possible that the yield of this fraction was influenced by the carbonate matter of kukersite when K-OR and K-OR with tires were processed in the unit with solid heat carrier. Chemical composition of this fraction from SHC-oil was investigated by chromato-mass spectroscopy and the results are given in Table 2.

CAHC from SHC-oil compared to CAHC from SF-oil contain more low-boiling compounds (approx. 50 % of the fraction), which boil at lower temperatures than naphthalene. It was found that during thermal decomposition a great amount of limonene was formed [5]. Limonene was found also in CAHC fraction of SHC-oil but in smaller amounts (see Table 2) due to smaller amounts of added tires. CAHC fraction from K-90-oil compared to CAHC fraction from SHC-oil contains more low-boiling compounds, and the reason is also the addition of tires. Commonly, SF-oil contains 84.8 % of hydrocarbons (NAHC, AAHC, CAHC together), SHC-oil – 54.5 %, K-90-oil – 39.3 % and K-OR-oil – 35.0 %. Limonene (1,8-menthadiene) forms more probably through cyclization of butadiene and migration of the double bond than through hydrogenation of the benzene ring. The yield of limonene from SF-oil is significant (approx. 10 % per fraction boiling at 160-180 °C into which limonene belongs as its boiling temperature is 174 °C [5]). In industry, limonene is obtained by treating £-terpene. Thermal treatment of tires may be an alternative way of getting limonene.

The share of oxygen-containing compounds (OC-fraction) in oils formed from kukersite during processing in retort and SHC-unit is following: 31.8 % – K-OR-, 37.8 % – K-90-, and 32.4 % – SHC-oil. In SF-oil the content of OC-fraction is 11.8 %, and it is logical, as tires contain no oxygen. Very likely, oxygen for formation of these compounds is taken from the air and moisture present in the semicoking unit. The chemical composition of this fraction is similar to that of oil obtained from kukersite. It consists of two series of ketones – symmetrical ketones with the double bond in the chain centre, and methylketones-1 with the chain length C_9-C_{24}.

It is observed that methylketones-1 predominate up to C_{13}, and after that symmetrical ones predominate. OC-fraction from SF-oil contains symmetrical ketones with the maximum C_{17}-C_{21}. These ketones have evidently been formed at oxygenation of the last double bond of the butadiene chain.

The information given above completely concerns the yield as well as the chemical composition of the phenols separated from these oils.

Thus, the oil obtained at SHC-unit is unsaturated, and the oil obtained during SF-processing of tires only has a low flash point: +5 °C [3] and cannot be used as a fuel without an additional treatment. It is reasonable to treat the tires with addition of the ordinary kukersite in SF-processing; carbonate matter of kukersite should bind the sulfur of tires, and oil would be enriched with hydrocarbons and phenols.

Acknowledgements

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