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COMPOSITION OF THE OIL FROM WASTE TIRES.
1. Fraction boiling at up to 160 °C

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Abstract. The qualitative and quantitative composition of the oil fraction of waste tires boiling at up to 160 °C was determined using capillary GC with OV-101 and SW 10 columns and GC/MS. Over a hundred components (paraffins, naphtenes, olefins, monoterpenes, aromatic hydrocarbons) representing more than 96% of the fraction were identified by means of retention indices and mass spectra. The main components in this oil fraction were aromatic hydrocarbons (27%) and dipentene (12%).

Key words: waste tires, oil, fraction boiling at up to 160 °C, composition, GC, GC/MS.

As part of our research into the utilization problems of waste tires we analysed the qualitative and quantitative composition of oil in radial tires. This paper presents the results obtained for the first fraction, which boils at up to 160 °C.

EXPERIMENTAL

Material

The oil from waste tires was obtained by thermal destruction at 520 °C of tire scraps in a laboratory retort [1]. The total yield of oil from waste tires was 41.2%. The waste tire oil was rectified on the APH-2 apparatus. The fraction boiling at up to 160 °C constituted 19.7% from the total rubber oil [1].

Analysis

The analysis of waste tire oil was performed on a Chrom-5 gas chromatograph (Laboratorni Pristroje, Prague, Czech Republic) equipped with a flame ionization detector. Helium was used as a carrier gas with a splitting ratio of about 1:150. A Hewlett-Packard Model 3390A integrator was applied for data processing. Table 1 specifies the fused silica columns with bonded stationary phases and the conditions of analyses.

Table 1. Capillary columns used and operating conditions

Parameter	Stationary phase	
	Polymethyl siloxane OV-101	Polyethylene glycol 20M SW 10
Column length, m	50	60
Column i.d., mm	0.20	0.32
Stationary phase film thickness, µm	0.50	0.25
Number of plates for *n*-decane at 90 °C	145 000	300 000
Injector temperature, °C	160	160
Helium flow rate, ml/min	0.25–0.28	0.87–1.00
Column temperature, °C	6 min at 30, then 30–100	10 min at 40, then 40–130
Programming rate, °C/min	1	2

The mass-spectrometric analyses were carried out on a Hitachi-M 80 B gas chromatograph double focussing mass-spectrometer (ionization voltage 70 eV). SPB-1 capillary column (30 m × 0.25 mm i.d.) and the temperature program 60 °C for 5 min and then programmed from 60 to 150 °C at 5°/min were used.

The individual compounds in the oil fraction were identified by comparing their retention indices (RI) determined on the temperature programming condition with authentic data that were either determined in our laboratory or obtained from the literature [2–13]. The results were confirmed by GC/MS. The reproducibility of RI expressed in terms of the standard deviation was below 2 index units.

The quantitative composition of components in the oil fraction was calculated using their peak areas without any correction for the relative response factor. The results presented are mean values of three injections.

RESULTS AND DISCUSSION

The complex nature of the oil fraction of waste tires boiling at up to 160 °C is demonstrated by the large number of peaks in the chromatogram (Fig. 1). The identified components (103 peaks) and their concentrations in the fraction are listed in Table 2.

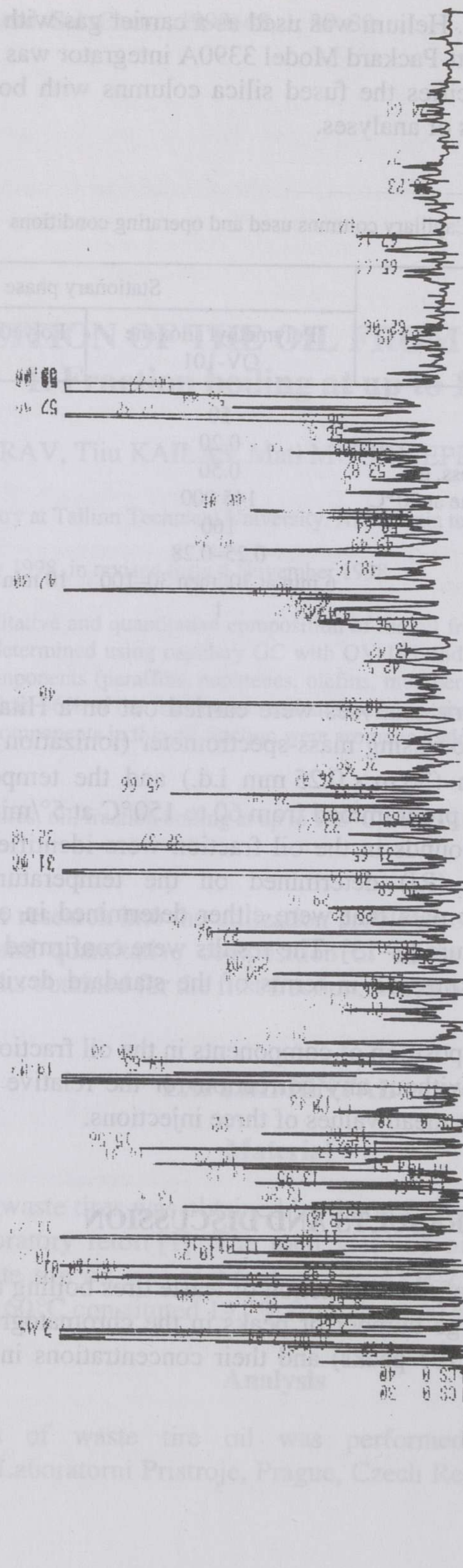

Fig. 1. Gas chromatogram of waste tire oil fraction boiling at up to 160 °C on OV-101 capillary column. For peak identification see Table 2.

Table 2. Composition of the waste tire oil fraction boiling at up to 160 °C and identification data

Peak No.	Component	RI on OV-101	Concentration, %	Identification
1.	2-Methylpropene		0.41	MS
2.	2,2-Dimethylpropane	<500	0.19	GC
3.	3-Methylbutane	<500	0.27	GC
4.	2-Methylbutane	<500	0.47	GC
5.	2-Methyl-1-butene	<500	1.53	GC
	Acetone			GC, MS
6.	*n*-Pentane	500	5.37	GC
	Isoprene			GC, MS
7.	2-Methyl-2-butene	522	4.16	GC
	2-Pentene			MS
8.	2,2-Dimethylbutane	536	0.18	GC
9.	4-Methyl-1-pentene	554	0.36	GC, MS
10.	3-Methyl-1-pentene	559	0.39	GC, MS
11.	2,3-Dimethyl-1-butene	564	0.17	GC
	Cyclopentane			GC
	2,3-Dimethylbutane			GC
12.	2-Methylpentane	571	0.67	GC
	4-Methyl-*trans*-2-pentene			GC, MS
13.	3-Methylpentane	583	0.21	GC
14.	1-Hexene	589	0.89	GC, MS
	2-Methyl-1-pentene			GC
15.	Not identified	594	0.35	
16.	*n*-Hexane	600	0.61	GC
17.	2-Methyl-2-pentene	607	0.91	GC
	2,3-Dimethyl-1,3-butadiene			GC
18.	*cis*-2-Hexene	610	0.74	GC
	3-Methyl-*cis*-2-pentene			GC, MS
	2,3-Dimethyl-2,3-butadiene			MS
19.	*trans*-3-Methyl-2-pentene	620	1.04	GC
	trans-4,4-Dimethyl-2-pentene			GC
20.	Methylcyclopentane	626	0.47	GC
	2,2-Dimethylpentane			GC, MS
21.	2,2,3-Trimethylbutane	634	0.58	GC
	1,3-Cyclohexadiene			MS
22.	2,3,3-Trimethyl-1-butene	637	0.48	GC
23.	*cis*-4,4-Dimethyl-2-pentene	643	0.24	GC
	2,4-Dimethyl-1-pentene			GC
24.	Benzene	649	3.02	GC, MS
	2,4-Dimethyl-2-pentene			GC
25.	2,3-Dimethyl-1-pentene	658	0.19	GC
	Cyclohexane			GC
26.	*trans*-4-Methyl-2-hexene	664	0.30	GC
27.	1,1-Dimethylcyclopentane	673	0.52	GC
28.	*cis*-3,4-Dimethyl-2-pentene	677	0.32	GC
	Cyclohexene			GC, MS
	3-Methylhexane			GC, MS
29.	2-Methyl-1-hexene	686	0.35	GC
	trans-1,3-Dimethylcyclopentane			GC

Table 2 continued

Peak No.	Component	RI on OV-101	Concentration, %	Identification
30.	1-Heptene	689	0.53	GC, MS
	2,2,4-Trimethylpentane			GC
	cis-3-Methyl-3-hexene			GC
31.	2-Methyl-2-hexene	697	0.70	GC, MS
	cis-3-Heptene			GC
32.	*n*-Heptane	700	1.17	GC, MS
	cis-3-Methyl-2-hexene			GC
33.	*trans*-2-Heptene	708	1.03	GC
	2,3-Dimethyl-2-pentene			GC
	2,5-Norbornadiene			GC
	Diisobutylene			MS
34.	*cis*-2-Heptene	713	0.21	GC
	2,4,4-Trimethyl-1-pentene			GC, MS
35.	Methylcyclohexane	717	0.81	GC
	cis-1,2-Dimethylcyclopentane			GC
36.	Ethylcyclopentane	727	0.37	GC
	2,4,4-Trimethyl-2-pentene			GC, MS
	2-Norbornene			GC
37.	2,5-Dimethylhexane	732	0.53	GC
	Dimethylsulphone			MS
38.	2,4-Dimethylhexane	732	0.48	GC
	2,2,3-Trimethylpentane			GC
39.	4-Methylcyclohexene	734	0.12	GC, MS
	2,5-Heptadiene			MS
40.	2,3-Dimethyl-1-hexene	751	3.09	GC
	trans-2-Methyl-3-heptene			GC
	2-Methyl-2,4-hexadiene			MS
41.	Toluene	754	6.80	GC, MS
42.	2,3,3-Trimethylpentane	756	0.97	GC, MS
43.	2-Methyl,3-ethylpentane	759	0.20	GC
	2,5-Dimethyl-2-hexene			GC
	1,1,2-Trimethylcyclopentane			GC
	2-Methyl,3-ethylpentane			GC
	2,3-Dimethylhexane			GC
	trans-4-Methyl-2-heptene			GC
44.	3,5,5-Trimethyl-1-hexene	763	0.94	GC
	1-Methylcyclohexene			GC, MS
45.	3,4-Dimethylhexane	767	0.49	GC
	3,5,5-Trimethyl-1-hexene			GC
46.	3-Methyl-3-ethylpentane	770	0.17	GC
	cis-1,2,*trans*-2,4-Tetramethylcyclopentane			GC
	2,2,4,4-Tetramethylcyclopentane			GC
47.	2,3,4-Trimethyl-2-pentene	773	0.81	GC
	1,*cis*-3-Dimethylcyclopentane			GC
	3-Methylheptane			GC
	3-Ethylhexane			GC
	trans-1,4-Dimethylcyclohexane			GC
48.	2,2,5-Trimethylhexane	784	0.18	GC
	2-Methyl-1-heptene			GC

Table 2 continued

Peak No.	Component	RI on OV-101	Concentration, %	Identification
49.	2-Methyl-2-heptene	786	0.20	GC
50.	1-Octene	788	0.35	GC, MS
51.	2,3-Dimethyl-2-hexene	796	0.38	GC
	cis-4-Octene			GC, MS
	trans-3-Octene			GC, MS
52.	*n*-Octane	800	0.58	GC, MS
53.	*trans*-2-Octene	804	0.85	GC
	2,6-Dimethyl-2,4-hexadiene			MS
54.	*cis*-2-Octene	811	0.15	GC
	2,4-Octadiene			MS
	Alkyl imidazol		tr.	MS
	Ethyl phenol		tr.	MS
	Dimethyl phenol		tr.	MS
55.	2,2-Dimethylheptane	818	1.16	GC
	2,2,3,4-Tetramethylpentane			GC
56.	2,4-Dimethylheptane	823	0.85	GC
57.	4,4-Dimethylheptane	826	0.54	GC
	2,6-Dimethylheptane			GC, MS
58.	Ethylcyclohexane	834	0.44	GC
	3,3-Dimethylheptane			GC
59.	2,3-Dimethyl-1-heptene	842	0.30	GC
60.	Ethylbenzene	847	4.24	GC
61.	*cis*-4-Methyl-2-octene	850	0.16	GC, MS
62.	1,3-Dimethylbenzene	857	5.46	GC, MS
	1,4-Dimethylbenzene			GC, MS
	trans-4-Methyl-2-octene			GC
63.	2-Methyloctane	862	0.40	GC
64.	3-Methyloctane	867	0.46	GC, MS
65.	2-Methyl-2-octene	873	0.56	GC, MS
66.	Styrene	875	0.19	GC, MS
67.	1,2-Dimethylbenzene	877	0.97	GC, MS
	2,3-Dimethyl-2-heptene			GC
68.	2-Methyl-1-octene	880	0.64	GC
69.	Not identified	883	0.36	
70.	3,5-Dimethylbenzenemethanol	885	0.32	MS
71.	1-Nonene	890	0.25	GC
72.	*trans*-4-Nonene	894	0.19	GC
	cis-3-Nonene			GC
73.	*n*-Nonane	900	0.55	GC
74.	*trans*-2-Nonene	903	0.35	GC
75.	Isopropylbenzene	908	1.74	GC
	2,2-Dimethyloctane			GC
	cis-2-Nonene			GC
76.	2,2-Dimethyloctane	918	0.18	GC
77.	3,5-Dimethyloctane	924	0.38	GC
78.	1,2-Dimethyl-1-octene	929	0.37	GC
79.	*n*-Propylbenzene	939	0.36	GC, MS
	3,3-Dimethyloctane			GC

Table 2 continued

Peak No.	Component	RI on OV-101	Concentration, %	Identification
80.	Propylcyclohexane	944	0.71	GC, MS
	cis-4-Methyl-2-nonene			GC
81.	1-Methyl,3-ethylbenzene	947	0.48	GC, MS
82.	1-Methyl,4-ethylbenzene	949	2.78	GC
83.	1,3,5-Trimethylbenzene	954	0.28	GC, MS
	trans-4-Methyl-2-nonene			GC
84.	2,3-Dimethyl-2-octene	961	0.09	GC
85.	2-Methylnonane	963	0.25	GC
86.	1-Methyl,2-ethylbenzene	964	1.41	GC
	2-Methyl-2-nonene			GC
	α-Methylstyrene			GC
87.	3-Methylnonane	970	0.25	GC
88.	Not identified	973	0.24	
89.	*tert*-Butylbenzene	975	0.33	GC
	2-Butyl-1-hexene			GC
90.	1,2,4-Trimethylbenzene	976	0.94	GC, MS
	Alkyltiophene			MS
	2-Methylstyrene			GC
	3-Methylstyrene			GC
	2-Methyl-1-nonene			GC
91.	4-Methylstyrene	982	0.43	GC
92.	2-Ethyl-1-octene	987	0.22	MS
93.	1-Decene	988	0.25	GC, MS
94.	*cis*-5-Decene	990	0.19	GC
95.	*trans*-4-Decene	992	0.27	GC
	cis-4-Decene			GC
	trans-5-Decene			GC
96.	*cis*-3-Decene	993	0.26	GC
97.	*trans*-3-Decene	995	0.51	GC
98.	*n*-Decane	1000	0.30	GC, MS
	1,2,3-Trimethylbenzene			GC, MS
99.	*trans*-2-Decene	1003	0.46	GC
	1-Methyl,3-isopropylbenzene			GC
100.	1-Methyl,4-isopropylbenzene	1005	3.42	GC, MS
101.	Terpinene	1008	0.64	GC, MS
	cis-2-Decene			GC
102.	Dipentene*	1018	12.60	GC, MS
103.	1-Methyl,2-isopropylbenzene	1024	0.22	GC
	Indene			GC, MS
	Alkyltiophene			MS
104.	1,3-Dimethyl,4-ethylbenzene	1063	0.23	GC
	2-Methyldecane			GC
105.	1,2-Dimethyl,4-ethylbenzene	1070	0.46	GC
	3-Methyldecane			GC
106.	1,3-Dimethyl,2-ethylbenzene	1075	0.41	GC
	Terpinolene			GC, MS
	Total		97.55	

* 1-Methyl-4-isopropenyl-1-cyclohexene.

The GC and GC/MS identification showed that the light fraction of tire waste oil contained various groups of hydrocarbons (paraffins, olefins, naphthenes, terpenoic and aromatic hydrocarbons) and some oxygen and sulphuric compounds. The main group of components in this fraction consisted of aromatic hydrocarbons (Table 3). The total amount of unsaturated hydrocarbons (monoterpenes, alkadienes, isoalkenes, *n*-alkenes, cycloalkenes, and cycloalkadienes) was very high (45%), isoalkanes made up 9%, while *n*-alkanes and cyclanes occurred only in small quantities (<3%) in the light fraction of tire oil.

Table 3. Group content of the rubber waste oil fraction boiling at up to 160 °C

Group of components	Concentration, %	
	OV-101	SW 10
n-Alkanes	2.9	
Isoalkanes	9.0	
n-Alkenes	8.6	
Isoalkenes	11.7	
Alkadienes	9.6	
Cyclanes	2.7	
Cycloalkenes and cycloalkadienes	1.5	
Monoterpenes	13.6	12.5
Arenes	34.3	26.6
Oxygen compounds	1.9	
Sulphyric compounds	0.8	
Total	96.6	

To control the concentration of aromatic hydrocarbons in the oil fraction a SW 10 capillary column was used. On the polar SW 10 stationary phase the retention times of arenes, which are the most polar compounds, are much higher than those of the other hydrocarbon groups compared with nonpolar OV-101 phase, where the peaks of arenes and other hydrocarbon groups can overlap. For that reason the amount of arenes in the fraction boiling at up to 160°C calculated on the SW 10 column was somewhat smaller (27%) than the sum on the OV-101 column (34%).

The major constituent in the fraction studied was dipentene, which formed 12% of the oil fraction. Isoprene, 2-pentene, benzene, toluene, 2-methyl-2,4-hexadiene, ethylbenzene, dimethylbenzenes, and *p*-cumene (1-methyl-4-isopropylbenzene) were found in quantities over 3%.

CONCLUSIONS

The oil fraction boiling at up to 160°C constitutes about 20% of the total waste tire oil. It is a very complicated mixture of hydrocarbons. The main groups of components of this fraction are aromatic and unsaturated hydrocarbons. The major individual component in this mixture is dipentene.

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SÕIDUAUTO KASUTATUD RADIAALKUMMI ÕLI KOOSTIS
1. Kuni 160 °C juures keev fraktsioon

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Kapillaargaasikromatograafia ja massispektromeetria meetoditega on määratud sõiduauto kasutatud radiaalkummi termilisel lagundamisel saadud õli kuni 160 °C juures keeva fraktsiooni kvalitatiivne ja kvantitatiivne koostis. Kummiõli kerges fraktsioonis identifitseeriti üle saja komponendi, mis kokku moodustasid 96% õli koostisest. Kõige rohkem oli aromaatseid ja küllastumata süsivesinikke. Tsüklilisi süsivesinikke (sealhulgas monoterpeene) sisaldas õli 18%, *n*-alkaane oli alla 3%. Enam kui 5% leidus uuritud fraktsioonis dipenteeni, isopreeni ja tolueeni.