

WASTE TIRES AS A SOURCE OF VALUABLE CHEMICALS

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Abstract

The aim of the study was to determine the possibility of the isolation of valuable chemical compounds from pyrolysis oil obtained from the pyrolyzed waste car tires. Produced pyrolysis oil were subjected to a distillation process to isolate medium naphtha fraction average naphtha that contains limonene, which according to the literature data, can be used as an environmental friendly solvent in a number of cleaning agents. Considering the boiling point of limonene (176°C), the medium fraction of the separated oil was re-distilled to isolate compounds with temperature of boiling point between 174-177°C. The prepared sample was analysed by gas chromatography coupled with mass spectroscopy. Based on the chromatographic analysis, it was found that in a separate sample of pyrolysis oil the highest share constituted toluene, and then cyclobutane, benzene derivatives, which is essential in the chemical industry. The share of limonene was low (approx. 1%), what is explained by too high temperature of the pyrolytic process. The results of analysis and literature allow unequivocally state that in order to separate specific compounds from pyrolytic oil, parameters of this process should be first determined in pilot studies. In conclusion, it is believed that the pyrolysis of tires is suitable method of disposing of the waste, thereby obtaining products containing valuable compounds for the fuel and chemical industries.

Keywords: waste tyres, pyrolysis, pyrolytic oil, chemical composition

1. Introduction

It is estimated that approx. 2% of the total amount of waste produced in the world constitute the tires. It would seem that it is a small amount, but the adverse impact to the environment, as well as a large fire hazard in case of disposed of it in landfills result in growing interest in recycling of waste tyres [4]. One of the most popular methods of processing waste rubber is pyrolysis. Pyrolysis is a process during which organic materials are thermally decomposed into simpler constituent compounds when subjected to high heat, under an atmosphere oxygen free [7]. The tyres are composed of natural rubber (NR), styrene butadiene rubber (SBR), polybutadiene and butyl rubber, with small amounts of organic and inorganic additives. Main of those compounds are consists of long-chain hydrocarbons, which during reprocessing are converted to another valuable hydrocarbons useful for energy and chemical feedstock production such as benzene, xylene, limonene [11, 14, 16]. It is worth noting the fact that the chemical composition of pyrolysis oil is conditioned mainly by the temperature and pressure of the pyrolysis process, as well as vapour resistance time in the reactor and sample size [1-3, 5, 6, 8, 9, 12, 13]. Laresgoiti et al. analysing liquid fraction obtained from pyrolysis of tyres in 5 different temperatures (300, 400,

500, 600 and 700°C) reported that major components were limonene, methyl- and ethyl benzene (toluene and styrene) and dimethylcyclohexane [3]. Limonene is a dipentene that is derived from the thermal decomposition of polyisoprene [8-9]. Roy et al. investigating the impact of the vacuum pressure on pyrolytic oil composition found that with the increase of pressure content of limonene decreased [13]. On the other hand, López et al. analysing the impact of the pyrolysis temperature on L- limonene and D-limonene found that in the highest temperature 600°C the content of those components was significantly lower (0.21 and 0.73 wt.%) than at 425°C (1.10 and 19.30 wt.%) [6]. Similar results obtained Cunliffe and Williams [1]. Cited authors found that at 450°C a maximum yield of limonene was 3.1 wt.% of total pyrolytic oil, while during increasing of temperature to 600°C the content of this compound decreased to 2.5 wt.% of total oil. Li et al. carrying out the pyrolysis of scrap tires in a continuous rotary kiln reactor also observed decrease in the limonene content with increasing temperature (from 5.4% at 450°C to 0.07% at 650°C) [5]. Pakdel et al. found that a temperature of the pyrolysis higher than 500°C tends to the degradation of the limonene molecules to trimethylbenzene, m-cymene and indane, which have boiling points similar to dl-limonene [8]. Production of the limonene based on the pyrolytic oil is important alternative for using one of the product of tires pyrolysis. This isolated compound could be used in the formulation of industrial solvents, resins and adhesives, and as a dispersing agent for pigments. Limonene can be also used as a feedstock for fragrances and flavourings production, such as hand cleaners, water-based degreasers and replacements for chlorofluorocarbon solvents to clean electronic circuit boards [1]. However, as was indicated by the other authors, pyrolysis oil can also be a valuable source of compounds such as toluene and benzene [3, 15]. The boiling point of limonene is 176°C [14], however, in order to reach highest degree of extraction of this compound the distillation should be carried out gradually. During this operation, the ranges of temperature should be gradually narrowed. This method let to achieve a final step of the desired boiling point. The separated fraction can be characterized by other compounds, which may also be used in the production of feedstock. Accordingly, the objective of this study was to determine the composition of the fraction of pyrolysis oil separated at a temperature in range of 174-178°C.

2. Material and methods

The research material was a sample of pyrolysis oil obtained from the plant "Eko-Top", located in the Ryki village in Lublin province, in Poland. Pyrolysis of scrap tires was conducted at 500-550°C for approx. 8 h with limited oxygen access. By the thermal decomposition of tires pyrolysis oil, pyrolysis gas, charred residue and steel wire were obtained.

The course of the distillation of pyrolytic oil sample

Supplied sample of pyrolysis oil were subjected to distillation in a laboratory kit, equipped with a heater, three-necked flask (fitted with a mercury thermometer and thermocouple), the spherical radiator and receiver. Initially, sample was heated to 169°C. Then the temperature was increased by 2°C to 171°C, and gradually by 1°C to 173°C. Then, in order to collect compounds with boiling point between 174-178°C the temperature was set to 177°C, and after that was increased by 1°C. Isolated fraction of compounds was subjected to analysis with using gas chromatography coupled with mass spectroscopy.

The gas chromatograph coupled with mass spectrometer (trace GC Ultra-DSQII Thermo Scientific) and flame ionization detector (FID) by MS-FID Splitter (SGE Analytical Sciences) was used. The analysis was performed on a capillary column Rxi1-ms (length 60 m, internal diameter 0.25 mm, thickness of stationary phase film 0.25 µm). The correction factor for the FID detector was determined using solutions of limonene (97%, Sigma-Aldrich) and addition of decane (> 99%, Sigma-Aldrich) as internal standard. To the weighed on an analytical balance (Radwag AS220 / X) sample of 1g of pyrolysis oil 500 µl of decane (at a concentration of 20 mg / 1 ml) was added using a microsyringe (SGE Analytical Science). Analyses were performed in triplicate. The given value is the mean value.

3. Results and discussion

Based on the chromatographic analysis it was showed that the distilled fractions of pyrolytic oil was characterized by 114 compounds, including 74 of them accounted for < 0.05% (Tab. 1). Share of the other 18 compounds: tetrahyrofuran, 3-methyl-2-pentene, methylcyclopentane, 5-methyl-1 3-cyclopentadiene, 2 4-dimethyl-2-pentene, 5-methyl-1-hexyne, ethylcyclopentane, 3-methylthiophene, + cis-1 3-trans-1 4-dimethylcyclohexane, tetrahydrothiophene, 1-octene, 4-etenylocykloheksen, 3 5-dimethyl-1-cyclohexen, 1 6-dimethylcyclohexene, ethylbenzene, m-xylene + p-xylene, 1 2-dimethylcyclohexene, o-xylene, isopropylbenzene, p-cymene was in the range of 0.50 to 1.00% (Tab. 1). Among all share of 14 compounds accounted for from 1.00 to 3.00%. These compounds included 1-metylo-cyklopenten, benzene, 2-metyloheksan + 2 5-dimetylofuran, 2 2 4-trimethylpentane + 1-heptane, 3-methyl-2-hexene, 4-methyl-2-pentanone + methylcyclohexane, 2 4 4-trimethyl-2-pentene, 4-methylcyclohexene, 1-etylocyklopenten, cyclopentanone, octane, 3-ethyl-1,4-hexadiene + 2 3 3-trimethyl-1,4-pentadiene, 1 3-dimethyl-1-cyclohexen, limonene. The other 8 compounds constituted the largest share in distilled fractions of pyrolysis oil. Among them, toluene is most abundant (12.63%). Also, cyclobutane accounted for a significant share 6.00%. Moreover, the total share of m-xylene + p-xylene was 4.05%, ethylbenzene 3.99%, heptane + 2 4-dimethyl-1 3-pentadiene 3.72%, 1 5-dimethylcyclopentene 3.60% and cyclohexene 3.16%. The remaining 7.36% of compounds was not possible to identify.

A small share of limonene identified in the analysed sample was probably a result of too drastic (as for this compound) temperature of pyrolysis (500-600°C), what indicates the necessity of reducing the value of this parameter. According to the López et al., increase of pyrolysis temperature from 425 to 500°C decreased the share of limonene from 19.30 to 9.13% [6]. By contrast, process conducted at the highest temperature – 600°C, resulted in the decrease in the content of the compound 0.73%. In turn, shares of other compounds, such as benzene and toluene were higher with increasing temperature of pyrolysis. A similar correlation was presented by Laresgoiti et al. [3]. Cited authors found that pyrolysis oil obtained during pyrolysis carried out at 300°C was characterized by approx. 21% share limonene, whereas the sample obtained at 400°C contained 8.22% of the compound. In addition, the further attempts of tire pyrolysis conducted in 500 and 600°C allowed to receive samples that were characterized by a much lower share of limonene (respectively 5.12 and 3.19%). On the other hand, results of research conducted by Laresgoiti et al. presented an ambiguous impact of temperature increase on benzene and toluene content [3].

The issue of the tires pyrolysis, including the use of products derived from this process is the current research problem that is more frequently undertaken. Overall, however, it is concluded that the most valuable compounds present in the pyrolytic oil are benzene, toluene, xylenes and limonene. Williams and Brindle reported that these compounds might be used to produce various compounds and chemicals [15]. As mentioned earlier limonene is widely used as an environmental friendly solvent in a number of cleaning agents, such as degreasers, release agents, part washers and dip baths [17]. It is known that benzene can be used for the production of derivatives such as ethylbenzene, cyclohexane and cumene. It should be noted that the share of two mentioned benzene derivatives in the analysed sample was, respectively, 3.99 and 3.16%, which was higher than the share of benzene (2.52%). Park et al. indicated that these compounds could be used as materials for the production of plastics, resins, fibres, surfactants, dyestuffs and pharmaceuticals, and long chain alkylbenzenes that are commonly used as feedstock in the manufacture of surfactants. One the other hand, toluene can be used for the production of benzoic acid (a food preservative or plasticizer), phenol, and caprolactam (nylon), while xylene is widely used as a chemical raw material. For example o-xylene, together with naphthalene, may be used for the production of phthalic anhydride (plasticizer and dye), whilst p-xylene is an essential compound in the manufacture of polyester (specifically PET) [10].

Tab. 1. List of compounds identified in fraction of pyrolytic oil

1	methantioł	0.00	58	3-methylthiophene	0.67
2	ethantioł	0.03	59	cyclopentanone	1.51
3	2-methylbutane-1 3-dien	0.05	60	1 2 3 4-tetrametylocyklobuten	0.29
4	1 2-dimethyl cyclopropane	0.04	61	1 1 2-trimetylocyklopentan	0.44
5	1 3-cyclopentadiene	0.06	62	2-metyloheptan + 1-methylcyclohexane	2.37
6	1-cyclopentane + 3-methyl-1-pentene	0.07	63	4-metyloheptan	0.23
7	2 3-dimethyl-but-1-ene	0.13	64	3 + 3 metyloencykloheksen etyloheksan	2.07
8	2-butanone	0.02	65	cis-1 3- +trans-1 4-dimetylocykloheksan	0.64
9	3-methylpentane	0.04	66	2 3 4-trimethyl-2-pentene + tetrahydrothiophene	0.22
10	1-hexene + 2-methyl-1-pentene	0.27	67	3 4-dimethyl-2 4-hexadiene	0.06
11	2-methylfuran	0.03	68	6-methyl-2-heptene + 2 3-dihydrothiophen	0.46
12	hexane	0.35	69	tetrahydrothiophene	0.63
13	2-hexene + 3-hexene	0.11	70	1-octene	0.68
14	2-methyl-2-pentene	0.40	71	trans-1-ethyl-3-methylcyclopentene	0.18
15	2-ethyl-1 3-butadiene	0.43	72	5 5-dimetyloheksadien	0.29
16	tetrahydrofuran	0.66	73	1-ethyl-5-methylcyclopentene	0.25
17	3-methyl-2-pentene	0.64	74	octane	1.21
18	methylcyclopentane	0.51	75	trans-1 3-dimethylcyclohexane	0.31
19	2 2-dimethylpentan + 2 4- dimetylomentan	0.35	76	3-ethyl-1 4-hexadiene + 2 3 3-trimethyl-1 4-pentadiene	1.12
20	2-methyl-1 3-pentadiene	0.34	77	2-metylotetrahydrotiofen	0.26
21	5-methyl-1 3-cyclopentadiene	0.73	78	1 3-dimethyl-1-cyclohexen	1.13
22	1-methyl-1 3-cyclopentadiene	0.39	79	3 5-dimethyl-1-cyclohexen	0.74
23	3-methyl-1 3-pentadiene	0.21	80	1 4-dimethyl-1-cyclohexen	0.21
24	2 4-dimethyl-1-penten + thiophen	0.49	81	4-etenylocykloheksen	0.61
25	1-methyl-cyclopentene	2.02	82	1 2 5 5-terametylo-1 3-cyclopentadiene	0.24
26	benzene	2.52	83	ethylcyclohexane	0.40
27	2 4-dimethyl-2-pentene	0.99	84	1 6-dimethylcyclohexene	0.54
28	cyclohexane + 2 4-hexadiene	0.40	85	1 1 3-trimethylcycloheksan	0.12
29	5-methyl-1-hexyne	0.55	86	3-metylotetrahydrotiofen	0.27
30	2-methyl-hexane + 2 5 dimetylomuran	1.01	87	ethylbenzene	3.99
31	2 3-dimethylpentan	0.23	88	m-xylene + p-xylene	4.05
32	cyclohexene	3.16	89	1 2-dimethylcyclohexene	0.58
33	5-methyl-2-hexene	0.07	90	2 5- tetrahydrothiophene	0.34
34	1 3-dimethyl-cyclopentane	0.13	91	styrene	0.41
35	1 2-dimethyl-cyclopentane	0.46	92	o-xylene	0.50
36	2 2 4-trimethylpentane + 1-heptane	2.65	93	1- (furan-2-yl) ethanol	0.30
37	3-methyl-3-hexene	0.26	94	2 3- tetrahydrothiophene	0.20
38	heptane + 2 4-dimethyl-1 3-pentadiene	3.72	95	1-nonene	0.18
39	3-methyl-2-hexene	1.51	96	nonane	0.32
40	2-heptene	0.32	97	isopropylbenzene	0.72
41	3-methyl-2 4-hexadiene	0.12	98	propylbenzene	0.36
42	2-methyl-2-hexene	0.41	99	1-ethyl-3-methylbenzene	0.32
43	1 5-dimethylcyclopentene	3.60	100	1-ethyl-4-methylbenzene	0.38
44	4 4-dimethylcyclopentene	0.16	101	4-ethenyl-1 4-dimethylcyclohexene	0.30
45	3-etylocyklopenten	0.40	102	1 3 5-trimethylbenzene	0.31
46	4-methyl-2-pentanone methylcyclohexane +	2.82	103	decan	0.11
47	2 4 4-trimethyl-2-pentene	1.13	104	1 2 3-trimethylbenzene	0.22
48	ethylcyclopentane	0.57	105	2-karen	0.18
49	4-methylcyclohexene	1.71	106	p-cymene	0.98
50	5 5-dimethyl-1 4-cyclopentadiene	0.16	107	Propylenobenzen + 1-p-menthane-1-ene	0.26
51	3-ethenyl-cyclopenten	0.16	108	limonene	1.15
52	1 2-dimethyl-1 3-cyclopentadiene	0.17	109	1 4-dithiane	0.04
53	3-ethyl-4-methyl-2-pentene	0.05	110	2 2 4 6 6-pentamethyl-3-heptene	0.10
54	2-metylotiofen	0.19	111	1 3 8-mentatrien	0.05
55	(1-methylethylidene) cyclobutane	6.00	112	2 5-dimethylstyrene + 3-etylostyren	0.03
56	1-etylocyklopenten	1.40	113	2 6-dimethylstyrene	0.03
57	toluene	12.63	114	terpinolene	0.05

Conclusions

It is believed that the pyrolysis of tires is suitable method of disposing of the waste, thereby obtaining products containing valuable compounds for the fuel and chemical industries. Moreover, use of analysed waste product apart from benefits for the specified industry branches, would also have a positive impact on the ecological aspect through efficient wastes processing, that are persistent for the environment.

References

- [1] Cunliffe, A. M., Williams, P. T., *Composition of oils derived from the batch pyrolysis of tyres*, Journal of Analytical and Applied Pyrolysis, Vol. 44, pp. 131-152, 1998.
- [2] Jitkarnka, S., Chusaksri, B., Supaphol, P., Magaraphan, R., *Influences of thermal aging on properties and pyrolysis products of tire tread compound*, Journal of Analytical and Applied Pyrolysis, Vol. 80, pp. 269-276, 2007.
- [3] Laresgoiti, M. F., Caballero, B. M., de Marco, I., Torres, A., Cabrero, M. A., Chomón, M. J., *Characterization of the liquid products obtained in tyre pyrolysis*, Journal of Analytical and Applied Pyrolysis, Vol. 71, pp. 917-934, 2004.
- [4] Larsen, M. B., Schultz, L., Glarborg, P., Skaarup-Jensen, L., Dam-Johanes, K., Frandsen F., Herriksen U., *Devolatilization characteristics of large particles of tyre rubber under combustion conditions*, Fuel, Vol. 85, pp. 1335-1345, 2006.
- [5] Li, S.Q., Yao, Q., Chi, Y., Yan, J. H., Cen, K. F., *Pilot-scale pyrolysis of scrap tires in a continous rotary kiln reactor*, Industrial & Engineering Chemistry Research, Vol. 43, pp. 5133-5145, 2004.
- [6] López, G., Olazar, M., Aguado, R., Bilbao, J., *Continuous pyrolysis of waste tyres in a conical spouted bed reactor*, Fuel, Vol. 89, pp. 1946-1952, 2010.
- [7] Mui, E. L. K., Ko, D. C. K., McKay, G., *Production of active carbons from waste tyres – a review*, Carbon, Vol. 42, pp. 2789-2805, 2004.
- [8] Pakdel, H., Pantea, D. M., Roy, C., *Production of DL-limonene by vacuum pyrolysis of used tires*, Journal of Analytical and Applied Pyrolysis, Vol. 57, pp. 91-107, 2001.
- [9] Pakdel, H., Roy, C., Aubin, H., Jean, G., Coulombe, S., *Formation of dl-limonene in used tire vacuum pyrolysis oils*, Environmental Science & Technology, Vol. 25, pp. 1646-1649, 1991.
- [10] Park, H. J., Dong, J. I., Jeon, J. K., Yoo, K. S., Yim, J. H., Sohn, J. M., Park, Y.K., *Conversion of the pyrolytic vapor of radiata pine over zeolites*, Journal of Industrial and Engineering Chemistry, Vol. 13, pp. 182-189, 2007.
- [11] Quek, A., Balasubramanian, R., *Liquefaction of waste tries by pyrolysis for oil and chemicals – a review*, Journal of Analytical and Applied Pyrolysis, Vol. 101, pp. 1-16, 2013.
- [12] Roy, C., Chaala, H., Darmstad, H., *The vacuum pyrolysis of used tires End-uses for oil and carbon black products*, Journal of Analytical and Applied Pyrolysis, Vol. 51, pp. 201-221, 1999.
- [13] Roy, C., Darmstad, H., Benallal, B., Amen-Chen, C., *Characterization of naphtha and carbon black obtained by vacuum pyrolysis of polyisoprene rubber*, Fuel Processing Technology, Vol. 50; pp. 87-103, 1997.
- [14] Stanciulescu, M., Ikura, M., *Limonene ethers from tire pyrolysis oil. Bart 1: Batch experiments*. Journal of Analytical and Applied Pyrolysis, Vol. 75, pp. 217-225, 2006.
- [15] Williams, P. T., Brindle, A. J., *Aromatic chemicals from the catalytic pyrolysis of scrap tyres*, Journal of Analytical and Applied Pyrolysis, Vol. 67, 143-164, 2003.
- [16] Wojtowicz, M. A., Serio, M. A., *Pyrolysis of scrap tires: can it be profitable?* Chemical Technology, Vol. 26, pp. 48-53, 1996.
- [17] Zhou, W., Widmer, W., Grohmann, K., *Economic analysis of ethanol production from citrus peel waste*, Proc. of the Florida State Horticultural Society, Vol. 120, pp. 310-315, 2007.

