COMPARISON OF YIELD OF TIRES PYROLYSIS IN LABORATORY AND PILOT SCALES

POROVNÁNÍ VÝTĚŽNOSTI PRODUKTŮ Z PYROLÝZY PNEUMATIK V LABORATORNÍM A POLOPROVOZNÍM MĚŘÍTKU

Adéla ČÍŽKOVÁ[1], *Dagmar* JUCHELKOVÁ[2]

[1] *Ing., Institute of Environmental Engineering, Faculty of Mining and Geology,*
VSB-Technical University of Ostrava, 17. listopadu 15, 708 33 Ostrava, Czech Republic
e-mail:adela.cizkova.st@vsb.cz

[2] *Prof. Ing. Ph.D, Department of Energy Engineering, Faculty of Mechanical Engineering,*
VSB-Technical University of Ostrava, 17. listopadu 15, 708 33 Ostrava, Czech Republic
e-mail:dagmar.juchelkova@vsb.cz

Abstract

The contribution deals with the pyrolysis of waste tires of passenger vehicles and trucks. During the pyrolysis pyrolytic char, oil and gas occur. Within the research a yield of individual fractions determined according to ČSN ISO 647 and a pilot scale test was performed, in order to carry out basic physical and chemical characteristics of pyrolytic char. During the test according to ČSN ISO 647 about 39 % of pyrolytic char, 44 % of tar occurred and by 16 % the gaseous phase was represented. During the pilot scale test the material was pyrolyzed up to the temperature of 600 °C, heating rate was set to 2.7 °C/min and residence time was 60 min. Under the given conditions the tire pyrolysis passes over at temperatures from 175 to 500 °C. We obtained 51.74 % of organic liquid, 39.16 % of char, 8.94 % of gas and 1.16 % of orogenic water. A problem of further use of the pyrolytic char may be a high content of zinc and other ballast inorganic substances.

Abstrakt

Příspěvek se zabývá pyrolýzou směsi odpadních pneumatik osobních a nákladních aut. Při pyrolýze pneumatik vzniká pyrolytický koks, olej a plyn. V rámci výzkumu bylo provedeno stanovení výtěžnosti jednotlivých frakcí dle ČSN ISO 647 a poloprovozní pokus za účelem provedení základní fyzikálně-chemické charakteristiky pyrolytického koksu. Při zkoušce provedené dle ČSN ISO 647 vzniklo okolo 39 % pyrolytického koksu, 44 % dehtu a 16 % byla zastoupena plynná fáze. Při poloprovozním testu byl materiál pyrolyzován až do teploty 600 °C, rychlost ohřevu byla nastavena 2.7 °C/min a doba zdržení byla 60 min. Při daných podmínkách probíhá štěpení pneumatik při teplotách od 175 do 500 °C. Bylo získáno 51.74 % organické kapaliny, 39.16 % koksu, 8.94 % plynu a 1.16 % orogenetické vody. Problémem dalšího použití pyrolýzního koksu může být vysoký obsah zinku a jiných balastních anorganických látek.

Key words: pyrolysis, tires, pyrolytic char, pyrolytic oil, pyrolytic gas

1 INTRODUCTION

As a result of rapidly growing number of car owners, among others, also the production of used tires increases. Most of the used tires accumulates in landfills, they are bulky and do not degrade. Currently, it is preferable to reduce filling the landfills and focus on recycling methods, the use of tires as a valuable source of energy and chemical substances [1]. The pyrolysis is one of the conventional methods, however in the field of processing of used tires is a relatively new technology. This is the decomposition of organic material at high temperatures in an inert atmosphere (or vacuum). The pyrolysis of waste tires represents an alternative environmentally-friendly processing and at the same time enables you to gain useful products. As a rule, during the pyrolytic process 33-38 wt. % of pyrolytic char occur, 38 -55 wt. % of pyrolytic oil and 10-30 wt. % of gases.

The tire pyrolysis research run using laboratory and pilot plant equipment; also operational units were developed (e.g. the pyrolytic equipment of the company Metso Minerals Industries, Inc. with a capacity of 100 kg/hour). Basic physical, chemical properties and adsorption properties of pyrolytic char from tires are presented by Helleur [2]. The pyrolytic char must be further carbonized to remove undesirable odours and traces of pyrolytic oil. The carbonized char has an excellent adsorption capacity for phenol and metals (e.g. lead) from solutions. By steam activation (900 °C, 3 hours) of char activated carbon occurs, which has a good specific surface area (302 $m^2 \cdot g^{-1}$), excellent adsorption property for phenol and methylene blue, however this treatment did not increase the adsorption property for capturing metals.

In order to determine optimum conditions of pyrolysis in terms of the production of pyrolytic char and oil Barbooti [3] studied effects of temperature (400-460°C), nitrogen flow rate (0.2-0.5 $m^3 \cdot h^{-1}$) and particle size of tires (2-20 mm). Optimum conditions related to the yield of pyrolytic char and oil were set to 430 °C, 0.35 $m^3 \cdot h^{-1}$ and particle size to 10 mm. Under these conditions 32.5 % of pyrolytic char and 51.0 % of pyrolytic oil were gained. The effects of temperature and heating rate on the composition of pyrolytic products in a static-bed batch reactor were studied by Williams [4]. The experiments ran at temperatures between 300 to 720 °C, heating rate was set to 5-80 $°C \cdot min^{-1}$. Maximum conversion of the material ran over at the temperature below 600 °C (about 55 % of oil, 10 % of gas and 35 % of char). The effects of temperature and residence time on the quantity and composition of pyrolytic gas were investigated by Leung [5]. At temperatures between 500-1000 °C the pyrolytic gas yield varies from 5 % to 23 %, maximum value is achieved at 900 °C. The ratio of gas, tar and char is 21:44:35 at 800 °C.

The paper is focused on the experimental determination of the yield of pyrolysis products of tire mixture, comparison of results with the literature data and carrying out the basic physical and chemical characteristics of pyrolytic char.

2 METHODS AND MATERIALS

To compare the results of pilot tests with real technological possibilities of material the yields of tar, water, gas and char residue were determined in laboratories of the Brown Coal Research Institute at low-temperature distillation according to ČSN ISO 647 "Brown Coal and Lignite. Determination of yield of tar, water, gas and char residue at low-temperature distillation". Tires and pyrolysis products were further analyzed according to ČN ISO 1171, ČSN ISO 441375 and ČSN P CEN/TS 15104. In order to determine trace elements a non-standardized method of X-ray- fluorescent analysis was applied.

Gas concentrations were determined by the method of gas chromatography with a thermal conductivity detector. Gases were analyzed using the gas chromatograph LABIO – C 82TT. Two 2-meter long columns with a diameter of 3.2 mm were used: a molecular sieve 5A., 60/80 MESH, as a carrier gas argon was used - 22 ml/min, Porapak Q column, 80/100 MESH, as a carrier gas helium was used - 29 ml/min.

As an initial material for determining physical and chemical properties a mixture of tires for passenger cars and trucks was used. Pieces of metal and textile were taken away from rubber slices, then the slices were shredded using the IKA WERKE MF Basic shredder into particles of 1 mm particle size. Tires consist of synthetic rubber (27 %), natural rubber (14 %), sulfur and sulfur-containing components, silicon, phenolic resins, oils (aromatic, naphthenic and paraffinic), fibers (polyester, nylon), waxes, pigments (ZnO – 1.52 %, TiO_2), carbon black (28%), the rest are fatty acids, inert material, steel bracing. A controversial parameter is chlorine, whose content is in tires 2-5 times higher than in coal, an average of 0.15 % [6].

3 RESULTS

The following Table 1 gives the results of tests performed according to ČSN ISO 647. The content of pyrolytic char in dry matter is 38.50 %, tar phase is 44 % and gases is 16.79 %.

Tab. 1 : Results of laboratory tests – the yields of individual fractions

(% wt)		Contents in dry matter (% wt)				Contents in combustible (% wt)			
W^a	A^d	T_{SK}	$_{SK}$	W_{SK}	G_{SK}	T_{SK}	$_{SKC}$	W_{SK}	G_{SK}
0.56	5.29	44.46	38.51	0.24	16.79	57.50	35.07	0.25	7.18

Legend: W^a - water analytical, A^d – ash in a dry state, $_{SK}$ – semi-char, W_{SK} – pyrogenetic water, G_{SK} – gas, T_{SK} – tar

In Tables 2 and 3 the results of laboratory analysis are showed – determination of elemental composition in an anhydrous tire sample and semi-char and in combustible. The analyses were performed in the Brown Coal

Research Institute. The coefficient of enrichment with carbon in semi-char, which was calculated as the ratio of carbon content in semi-char and in the input material in dry matter, is 1.03.

Tab. 2 : Results of laboratory tests - the elemental composition in an anhydrous sample

	W^a	A^d	C^d	H^d	N^d	O^d	S^d
	(%)						
Semi-char	0.53	12.78	85.27	0.33	0.26	0	2.33
Input material - tires	-	0.01	82.64	6.77	0.38	5.37	0.83

Tab. 3 : Results of laboratory tests - the elemental composition in combustible

	C^{daf}	H^{daf}	N^{daf}	O^{daf}	S^{daf}
	(%)				
Semi-char	97.76	0.38	0.30	0	2.67
Input material - tires	82.65	6.77	0.38	5.37	0.83

4 PILOT-SCALE PYROLYSIS

After evaluating the pyrolysis tests in compliance with the standard a pilot scale test was carried out in laboratories of the Brown Coal Research Institute Most, a.s., as the pyrolysis of tires for the purpose of further characterization of the chemical composition of condensate, gas and properties of pyrolytic char. The pyrolysis pilot scale test was performed in a retort furnace with a capacity of 2 l. The diagram of the equipment as shown in Fig. 1.

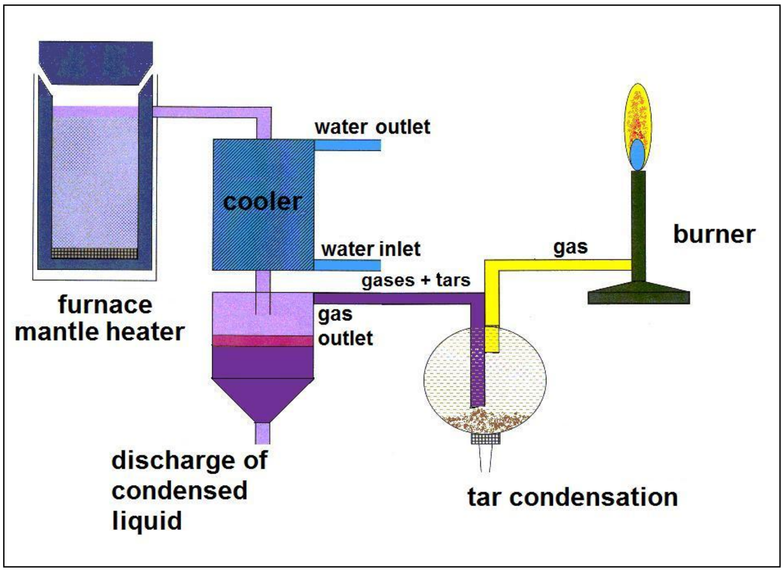

Fig. 1: Diagram of pyrolysis equipment of the Brown Coal Research Institute Most, a.s.

The pilot test was performed with a sample tires shredded below 5 mm in a weight of 500 g, the initial temperature was 25 °C, heating rate was set to 2.7 °C / min and the final furnace temperature to 600 °C, residence time 60 minutes. The expected yield of the liquid phase was 50%. Table 4 and Fig. 2 show the course of pyrolysis.

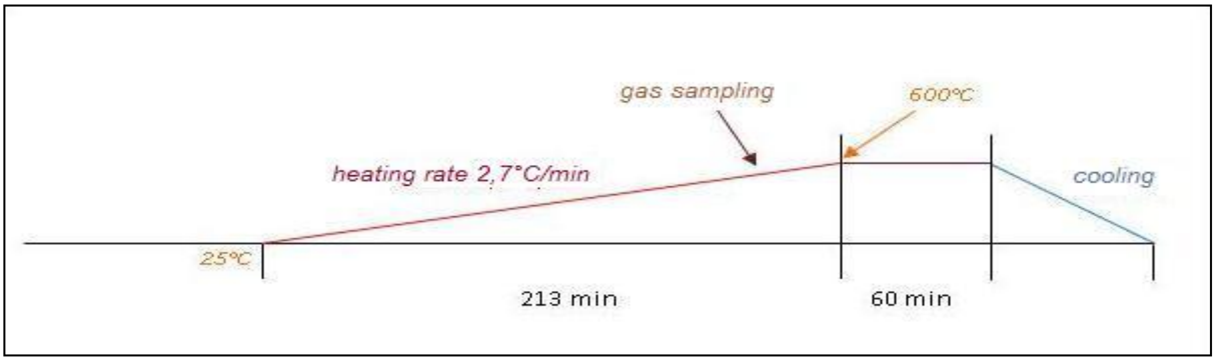

Fig. 2: Temperature experiment program

Tab. 4 : Course of pyrolysis test

Time (min)	Furnace temperature (°C)	Temperature in retort (°C)	Process
0	25	25	start of experiment
70	212.8	119	no water
85	251.4	152	first water drops
95	277.5	175	start of decomposition - carbonization
130	377.3	274	spontaneous decomposition - carbonization
180	507.6	461	gas sampling for analysis
193	544.3	500	end of decomposition
213	600	563	end of experiment

The amount of products after pyrolysis, while reaching the final temperature of 600°C (in retort 563°C), is shown in Table 5. The table below provides the yield of pyrolysis products from the laboratory tests according to ČSN ISO 647, the pilot scale test and literature. The results of laboratory test according to ČSN ISO 647 are in full compliance with the data published by Boxioing [7]. Percentage of products of the pilot tests corresponds to the results published by Kaminsky [8]. The reason for the increased oil production at the expense of gas in the pilot tests in comparison with the results of tests according to ČSN ISO 647, can be the higher final temperature of pyrolysis in the pilot experiment. In general, the increase in pyrolysis temperature should on the contrary result in an increase in the share of gas [9].

Tab. 5: Comparison of yields of individual fractions

	Temperature	Heating rate	Char	Oil	Gas	Water
	(°C)	(°C·min^{-1})	(%)			
ČSN ISO 647	520	1.5 - 9	38.51	44.46	16.79	0.24
Pilot plant	600	2.7	39.16	51.74	7.94	1.16
Barbooti [3]	460	-	34.1	53.0	12.9	-
Kaminsky [8]	600	-	40	51	9.1	0.24
Williams [4]	600	5-80	35	55	10	-
Boxioing [7]	500	10	37.59	45.9	16.5	-

Islam [10] shows that the increase in temperature supports secondary reactions that give rise to a larger amount of gas product at the expense of liquid components, the amount of pyrolytic char remains constant. According to Roy [11], even the increase in temperature over 420°C does not affect the yield of oil, gas or char, because the decomposition of elastomer in tires is complete at this temperature. On the contrary, Arabiourrutia

[12] shows that the temperature has a fundamental impact on the production of individual fractions, the gas production will increase sharply from 425 to 500 °C and then slightly decreases, which corresponds to the above comparison. The pilot test carried out shows that the tire decomposition takes place until the temperatures are over 500 °C (see Table 4). The yields of individual fractions are also affected by other process parameters, such as particle size [3] and the amount of initial material [10], residence time [10], heating rate (according to [4] it has little influence), design concept of pyrolysis equipment [12], carrier gas [3]. The yields of pyrolysis products are then given by a combination of all these effects.

4.1 Gas

The gas concentrations were determined using gas chromatography. In the mixture the following gases were detected: Methane, ethane, ethylene, propene, sulfane, nitrogen, hydrogen, carbon dioxide, carbon monoxide, oxygen. The concentrations of these gases, whose sampling took place at the furnace temperature of 507.6 °C and the retort temperature 461 °C, are shown in Table 6, During the pyrolysis of tires gas occurs, which has a sufficient calorific value, can be used to produce energy.

Tab. 6: Gas concentrations during the pilot-scale pyrolysis

Reaction gases	**% vol**
Hydrocarbons+ H_2S+….	37.86
Methane	26.73
Nitrogen	15.05
Hydrogen	14.87
Carbon dioxide	2.45
Carbon monoxide	1.73
Oxygen	1.31

4.2 Char

An important property of pyrolytic char is its morphological similarity with natural carbon black. The high ash content reduces their recycling and use in the manufacture of tires, but can be used in the manufacture of rubber [2]. A fundamental difference between the commercially sold carbon black and pyrolytic carbon black is the content of inorganic component (ZnO, S), as well as SiO_2 and Al_2O_3. With increasing temperature of pyrolysis a reaction between ZnO and S occurs to form ZnS, consisted of individual particles with a density higher than of pyrolytic char and the particles can be further separated [11]. Even in our case, the zinc content in pyrolytic char determined by the X-ray fluorescence was very high, up to 7.6% of ZnO; Ba, Cr, Fe etc. occurred to 1%. The character of pyrolytic char with a porous structure is evident from the following photo documentation (Fig. 3).

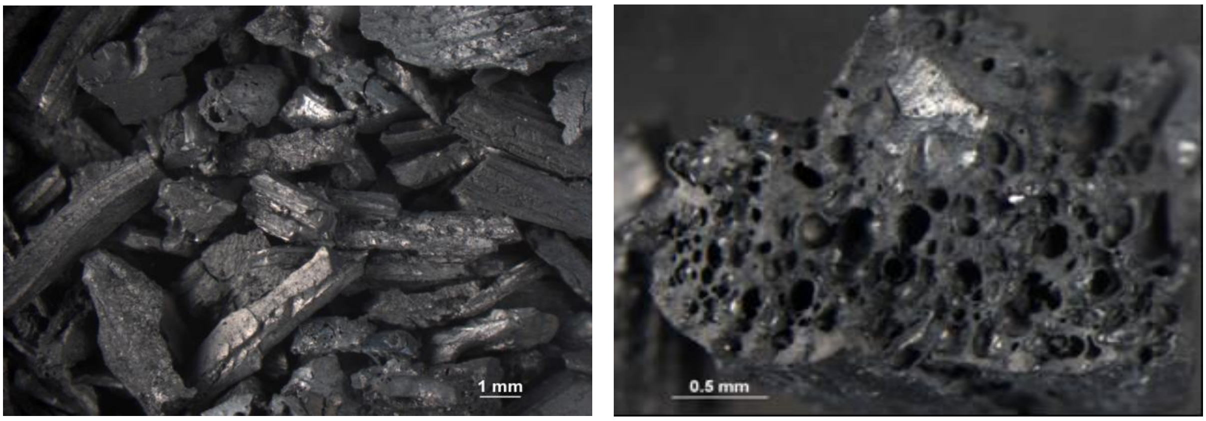

Fig. 3: Surface and structure of pyrolytic char from pyrolysis of tires

5 CONCLUSION

The laboratory test of the yield of individual fractions and the pilot-scale test proved the compliance with the literature data. During the test according to ČSN ISO 647 about 39 % of pyrolytic char, 44 % of tar phase and 16 % of gaseous phase occurred. The pyrolysis results show that under the given conditions the tire degradation takes place at temperatures from 175 to 500 °C. Upon reaching the final pyrolysis temperature 51.74 % of organic liquid, 39.16 % of char, 8.94 % of gas and 1.16 % of pyrogenetic water were obtained.

Oils obtained by pyrolysis can be used directly as a fuel or as an admixture to products of petrochemical industry, as well as be a source of chemicals. Gases can also be used as a fuel. Char can be used either as a smokeless fuel, carbon black or activated carbon, or can be gasified to obtain gaseous fuels. A problem of further utilization of pyrolytic char may be a high content of zinc and other ballast inorganic substances.

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