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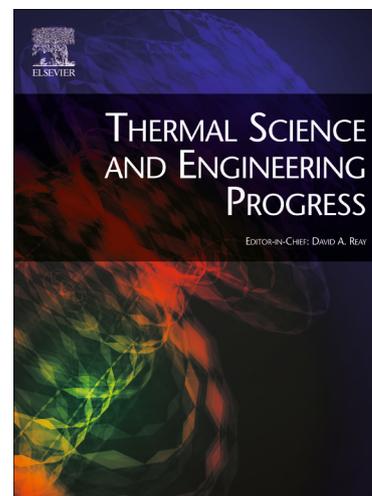
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Waste tyre pyrolysis – impact of the process and its products on the environment.

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Abstract

The constant development of the automotive industry causes a steady growth in the production of tyres, which have to be utilized properly after their lifespan. Pyrolysis is considered a promising solution, providing many advantages for the environment in comparison with traditional waste management methods. The pyrolysis of waste tyres was undertaken at three different temperatures (400, 500 and 600°C) and subsequently the products obtained were investigated in the context of their influence on environmental components such as the atmosphere, hydrosphere, soil and biosphere. Special attention was focused on the sulfur-containing compounds and heavy metals. Additionally, ultimate and proximate analyses were made and the organic composition of the liquid fraction was checked. The concentration of heavy metals in pyrolysis oils and chars were, in general, very low and this allows their further usage to be considered safe for the environment and human health. Additionally, the presence of valuable chemicals such as limonene, toluene and xylene enhance the profitability of the process as well as saving natural resources. On the other hand, the high concentration of sulfur-containing compounds in pyrolytic gas and oils makes their usability dependent on desulfurisation processes. However, the very high energy content (calorific value) in all three products encourages their industrial application.

Keywords:

heavy metals, hydrogen sulfide, mercaptans, limonene, ultimate analysis, proximate analysis, calorific value

Abbreviations:

A – ash

FC – fixed carbon

HHV – higher heating value

IR – infrared

PAH – polycyclic aromatic hydrocarbon

RT – retention time

VM – volatile matter

W – water

1. Introduction

Waste management is one of the most important issues for modern societies. In many areas more and more people endeavour to reduce the amount of waste produced. However, the number of vehicles and subsequently car waste is growing each year. The European Tyre & Rubber Manufacturers' Association (ETRMA) estimated the worldwide number of passenger and commercial vehicles as 1.3 billion in 2016 and assumed that the global number of them will exceed 1.6 billion by 2024. The annual production of tyres was as high as 4.94 million tonnes in 2016 and the recorded growth is small but stable [1]. Durability and safety, regardless of weather conditions, makes disposal of this product after lifespan very difficult.

Waste tyre dumping has been a problem in many regions worldwide, which generates not only simply unpleasant views but a lot of other implications. For example, inadequate disposal can block water channels or storm water drains, resulting in changes in flow patterns which in turn may contribute to an increased flood risk. In turn, especially in tropical and subtropical regions, piles of waste tyres represent an ideal habitat for rodents and breeding sites for mosquitoes that transmit very dangerous diseases: dengue and yellow fever [2]. Fortunately, a revision of literature data on the potential of chemicals to leach from used tyres concluded that the impact of used tyres on the soil or surface water under neutral environmental conditions was negligible with regard to groundwater and surface water quality and the aquatic environment [2].

Across the European Union there is a legal ban on waste tyre landfilling and their incineration must fulfil strict emission limits [3]. However, in Third World countries piles of scrap tyres greatly litter many towns and cities, thus often resulting in their burning by residents in order to reduce this problem [4]. This procedure is highly dangerous for the environment, human health and even life. Accidental tyre fires can burn for months, generating smoke and oil, leaching toxic contaminants that affect the soil, waterways and air. The composition of smoke emitted through the combustion of tyres is presented in Table 1. As can be seen, tyre fires in the open air emit black smoke that contains carbon dioxide (the best known greenhouse gas), carbon monoxide, nitrogen and sulfur oxides, volatile organic compounds and other hazardous pollutants, such as polycyclic aromatic hydrocarbons or heavy metals [2]. Measured concentrations of polychlorinated biphenyls and dioxins and furans were comparable to those observed in ambient air. However, it should be highlighted that measured concentrations of pollutants are in g/kg tyre burned, and they seem to be enormous, but it would be more perspicuous to use the unit mg/m³ in which emission limits are mostly defined. As analysed by Juma *et al.* [5] the combustion of waste tyres emits more PAHs and CO than coal combustion, whereas the NO_x emission level was lower.

Table 1. Composition of smoke from tyre open burning [2]

Component	Emission, g/kg of tyre burned
Carbon dioxide	1450
Carbon monoxide	35
Nitrous oxide	0.9

Nitric oxide	3.2
Sulfur oxide	15
Cyanhydric acid	4
Hydrochloric acid	not detected
Unburned organics (toluene equivalents)	23
Dust	285
Metals (total) including aluminium and zinc >99%	31.9
Polycyclic aromatic hydrocarbons	0.0633
Polychlorinated biphenyls (total)	2.66×10^{-4}
Dioxins/furans (total)	6.44×10^{-7}

Pyrolysis is one of thermochemical processes that is continuously attracting attention from the waste management sector, since it allows the mass and volume of waste to be reduced, as well as providing valuable products in the form of gaseous fuel, differentiated-composition oils and chars. Comparing with burning, pyrolysis and subsequent combustion of produced gases emits much less pollutants because the process is undergone without oxygen [6]. Pyrolysis can be considered as one of renewable sources of energy. Using them is an important social and engineering task [7]. Moreover, the oils produced can be further utilized as a source of chemicals [8,9], and chars are widely studied as activated carbon promoters [10,11]. However, the very complex composition of pyrolysis oils, and the necessity of strict process control conditions in order to obtain repeatable-quality products may deter potential investors. Many laboratory studies on waste tyre pyrolysis have been carried out worldwide [12–15], but few viable plants exist [16,17]. However, there are several companies worldwide, which produce ready-to-install relatively small pyrolysis units, for instance *Klean Industries* [18].

It is worth noting, that used tyres feature a rather stable composition regardless of the source, and they can be characterized as a homogenous type of waste. The simplified average composition of tyres is presented in Figure 1. This is a very important advantage for the pyrolysis process because the stable composition of feedstock ensures a stable composition of the products. However, the product composition repeatability is strongly related to the parameters of the process. Thus, it is very important to define optimal conditions that produce the best quality products, and then carefully control them. In that case the thermochemical processing of tyres should provide more quality-repeatable products than a similar utilization of biomass or municipal solid waste.

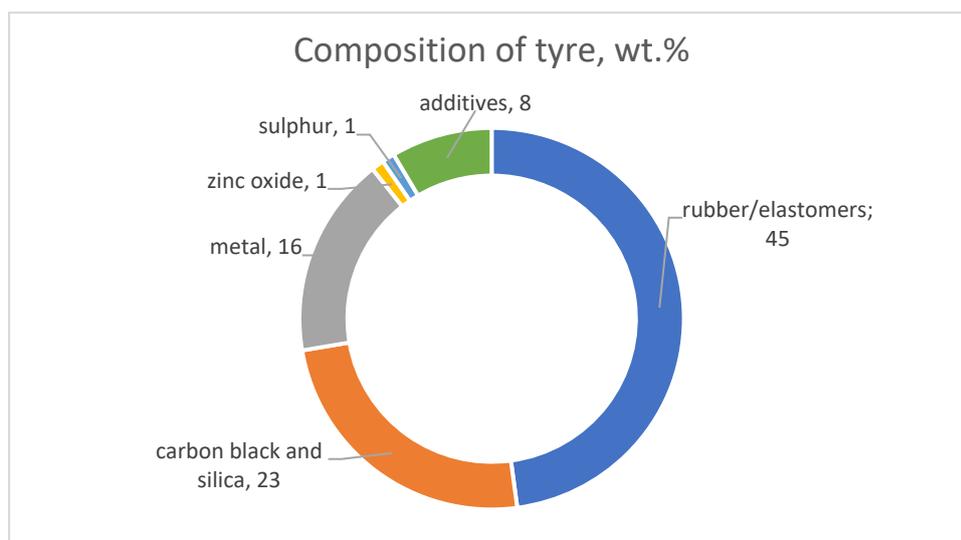


Figure 1. Composition of typical passenger car tyre [2].

On the other hand, pyrolysis can be difficult to apply and control on an industrial scale. Firstly, the process features a high energy demand. Thus, utilization of the gas produced to provide heat (except for the start-up phase) may be a key factor for ensuring the profitability of the investment [3,19]. Secondly, pyrolysis requires well-sealed tanks to prevent oxygen leaking in, and relatively advanced control systems.

Additionally, tyres feature a relatively high sulfur content (see Figure 1) which creates some difficulties with the utilization of the pyrolysis products. Sulfur is introduced in tyres in the process of rubber vulcanisation in order to achieve better stability, toughness, and heat resistance of the raw material. Long chain polymers crosslinked by sulfur bonds in vulcanised rubber provide protection by antioxidants and antiozonants resisting degradation [20]. Sulfur from tyres goes into pyrolysis products in different proportions, but it is always present in oil, char and gas. Gaseous sulfur-content compounds are especially very toxic. For instance, hydrogen sulfide and methyl mercaptan caused the death of 50 % of rats at concentrations of 444 ppm and 675 ppm, respectively [21]. Unfortunately, those compounds are also dangerous for human health and life. Methyl mercaptan attacks the central nervous system and causes death - similar to hydrogen sulfide - by respiratory paralysis. Exposure to it leads to ocular and mucous membrane irritation, headache, dizziness, staggering gait, as well as nausea and vomiting [21].

Moreover, one of the aims of investigating waste tyre pyrolysis is to produce valuable materials that may be used commercially, thus their safety also should be carefully studied. The nature of the effects that are caused by heavy metals can be toxic, neurotoxic, carcinogenic, mutagenic or teratogenic [22]. Unfortunately, little attention has been paid to the content of heavy metals in pyrolysis products so far, which is surprising given the social awareness about their content in different types of waste.

The aim of this work is to investigate the composition of waste tyre pyrolysis products in order to determine their industrial potential as well as possible challenges in further applications. It is important to define advantages and disadvantages of pyrolysis as a waste tyre management solution in comparison with the simplest solutions like landfilling and burning. Across the European Union there are a very strict emission limits for industrial incineration. However, the

pyrolysis combined with subsequent combustion of its products can be excluded as long as “the gases resulting from this thermal treatment of waste are purified to such an extent that they are no longer a waste prior to their incineration and they can cause emissions no higher than those resulting from the burning of natural gas [23]”. Usually the concentration of hydrogen sulfide is measured, but we decided to carefully examine also the presence of various mercaptans in produced gas since they are also very dangerous, but generally belittled. Additionally, we have investigated the presence of heavy metals - listed in above mentioned directive - in chars and oils as well as heating value to check their safety and utilization potential. The concentration of heavy metals in flue gases from combustion of waste tyres pyrolysis gas have been reported as a very small [24], still the produced oils after relatively simple treatment also become a fuel, thus the level of metals listed in the Industrial Emission Directive also should be examined, and has not been studied extensively before.

2. Methodology

2.1. Samples preparation

Samples of ground waste tyres were provided by the company “Recykli” located in Greater Poland (Poland). Three different-size fractions were obtained, and the smallest of them with particle size of about 5 mm was chosen for pyrolysis experiments. It is worth noting that the whole of the tyres were shredded, thus the experimental results are more representative than those for rubber-only pyrolysis [25], since in a full scale pyrolysis plant usually the whole tyres are treated. Additionally, the sample was placed indoors for several days before conducting the experiments in order to reduce the moisture content, since the ground tyres were stacked outdoors.

2.2. Procedure of pyrolysis experiments

About 40 g of tyre sample was placed inside a stainless-steel reactor which in turn was heated in a tube furnace (Carbolite Gero) from room to the programmed temperature with a heating rate of 5°C/min that was controlled by internal unit of the tube. The temperature inside the furnace was also checked by an additional thermocouple (N type) and the measurements obtained were continuously saved onto an SD card. The reactor was kept at a relatively steady temperature (400°C±10°C, 500°C±10°C or 600°C±10°C) for two hours to ensure complete decomposition of the organic matter. Before the beginning of heating the reactor was flushed with nitrogen (2 l/min) for two minutes to remove the air from the chamber and then a low nitrogen flow (about 30 ml/min) was maintained during the whole experiment to avoid oxygen leaking into it. The condensable vapours released from the process were continuously cooled down and carefully collected inside an ice trap. After the experiment, the condenser was sealed to prevent evaporation of highly volatile products and weighed. In some experiments syngas was collected in Tedlar® bags using a vacuum chamber accompanied with pump and subsequently analysed in a laboratory outside the experimental set-up, whereas in the others gas was released to the atmosphere through a demineralised water scrubber. The time between gas sampling and analysis was shorter than 24 hours and transportation was conducted properly. The flow of gases released from the laboratory stand was very low, thus it is acceptable to release them without any additional treatment. Experiments at the desired temperature were repeated two or three times and the results obtained were averaged. The experimental set-up connected with the vacuum chamber is shown in Figure 2.

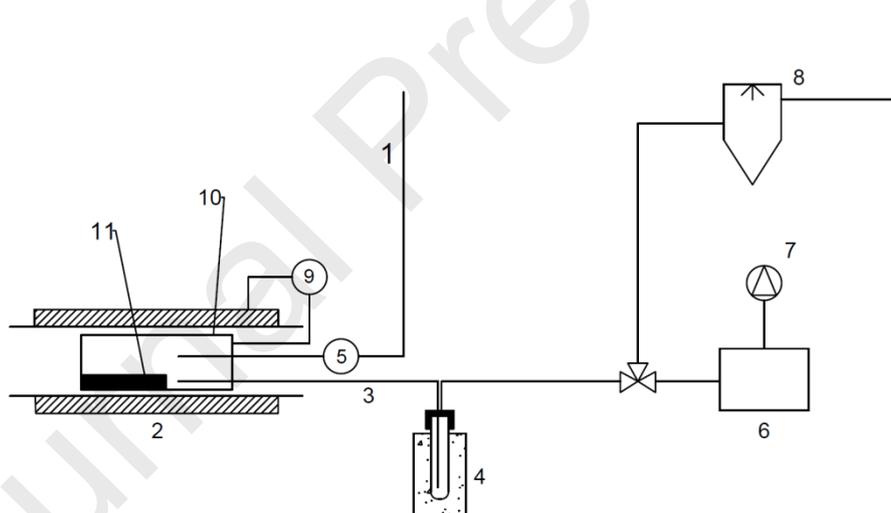
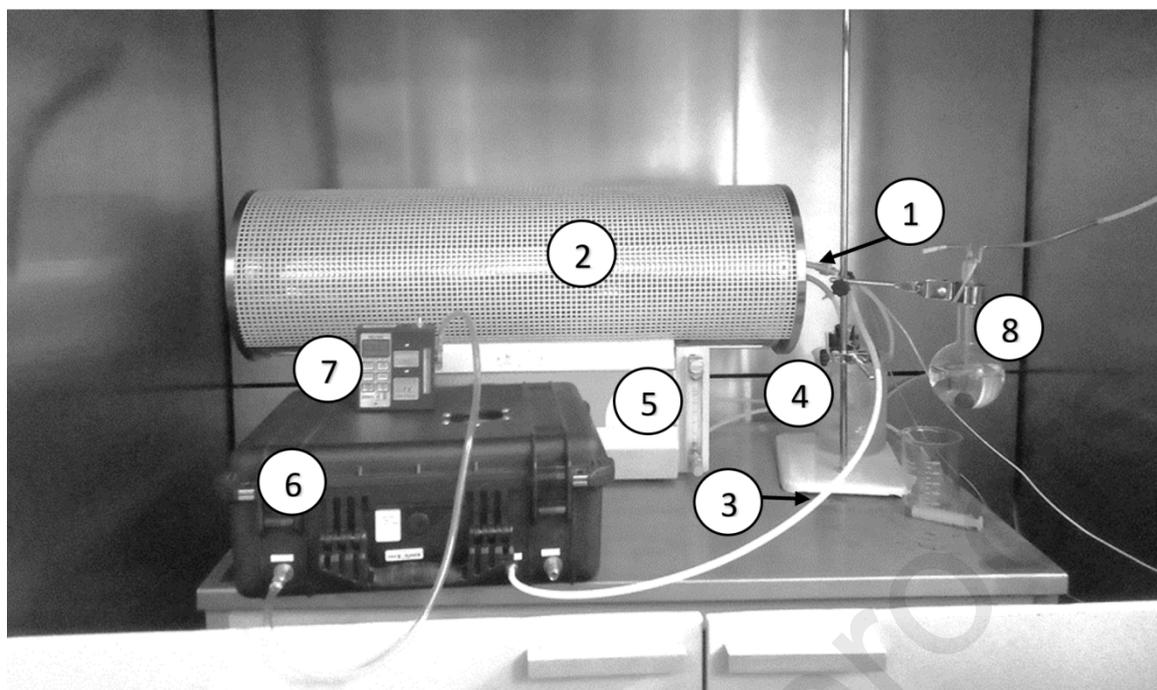


Figure 2. Waste tyre pyrolysis experimental set-up: [1] nitrogen inlet, [2] tube furnace, [3] gas and vapours outlet, [4] condensate collection, [5] gas flow meter, [6] vacuum chamber, [7] pump, [8] scrubber, [9] thermocouple, [10] reactor, [11] tyre sample.

2.3. Heavy metal content

The concentrations of particular metals in liquid and solid pyrolysis products were obtained by applying two analytical methods. In the case of mercury, it was cold vapour-atomic absorption (CVAAS) combined with the amalgamation technique. In turn, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to measured concentrations of cadmium (Cd), thallium (Tl), antimony (Sb), arsenic (As), lead (Pb), chromium (Cr), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), and vanadium (V). The results for chars were for the dry

state. Typical expanded uncertainty at $k = 2$ level combined with 95% confidence level were applied. The range and uncertainty of measurements are presented in **Error! Reference source not found.**

Table 2. The range and uncertainty of measurements of heavy metals content in the pyrolysis products

Element	Range	Uncertainty
Hg	0.01 – 20 mg/kg	30%
Cd, Pb, Cr, Co, Cu, Mn, Ni, V	> 1 mg/kg	35% for <10 mg/kg 20% for >10 mg/kg
As, Sb	> 2 mg/kg	
Tl	> 5 mg/kg	

2.4. Proximate analysis, ultimate analysis and calorific value

The chars obtained were air dried, pulverized to a size below 200 μm and homogenized, while oils were analysed on an as-received basis. The moisture content was determined according to Czajka [26] at 110°C, volatile matter at 950°C [27] and ash at 815°C [28]. The fixed carbon content and combustible matter content were calculated by difference. The uncertainty of proximate analysis is $\pm 0,2\%$.

The total content of carbon, hydrogen and nitrogen was determined in accordance with ISO 16948:2015 [29]. The sulfur content, was given a special focus and investigated in a wider range than it is required by ultimate analysis standards (in details described in the next section). The oxygen content was calculated by difference ($=100\% - \text{ash} - \text{moisture} - \text{C} - \text{H} - \text{N} - \text{S}$). The uncertainty of ultimate analysis is $\pm 0,3\%$.

The higher heating values of oil and char were analysed with IKA WERKE C2000, according to ISO 18125:2017 [30] and ASTM D4868 [31], while for syngas it was calculated by difference. The uncertainty of the higher heating value determination is $\pm 100 \text{ kJ/kg}$.

2.5. Sulfur compound distribution

The pyrolysis products were carefully checked by sulfur content, since the presence of sulfur-containing compounds possibly is the most challenging task to solve in order to use them commercially. In the case of chars and oils, high-temperature burning accompanied with IR detection according to PN G-04584:2001 [32] was applied to determine sulfur concentration. In turn, to determine concentrations of hydrogen sulfide and other sulfur-containing compounds in gaseous pyrolysis products, Gas Chromatography with Pulsed Flame Photometric Detector (GC PFPD) according to ISO 19739:2004 [33] was used. The range of measurements was from 0.1 to 500 ppm and the accuracy was 0.01 ppm.

2.6. Organic composition of oils

Three oil samples collected from pyrolysis at different temperatures were checked for organic compound content according to the following procedure. A 10 mg of sample was weighed into a 20 ml headspace vial and 10 ml of deionized water was added. The vial was closed with a teflon-butyl membrane cap and inserted into the headspace autosampler (HS-20, Shimadzu). Before analysis the vial was incubated for 30 minutes at 80°C and subsequently 1 ml of the volatile fraction was taken automatically and injected into a ZB-5 chromatography column

(30m x 0.25 ID x 0.25 film, Phenomenex, USA). The analysis was conducted by the GC / MS QP-2010 Ultra system (Shimadzu) in scan mode (40-600 amu).

3. Results and discussion

3.1. Heavy metal content

The concentrations of heavy metals in liquid and solid samples derived at temperatures of 400°C, 500°C and 600°C are presented in Table 3.

Table 3. Concentration (ppm) of heavy metals in waste tyre pyrolysis products

Metal	Char (400°C)	Char (500°C)	Char (600°C)	Oil (400°C)	Oil (500°C)	Oil (600°C)
arsenic (As)	2±0.7	7±2.5	3±1.1	<2	<2	<2
cadmium (Cd)	2±0.7	4±1.4	3±1.1	<1	<1	<1
cobalt (Co)	164±33	257±51	194±39	<1	<1	<1
chromium (Cr)	12±2.4	12±2.4	8±2.8	<1	<1	<1
copper (Cu)	276±55	264±53	250±50	<1	<1	<1
mercury (Hg)	0.01±0.003	<0.01	<0.01	0.01±0.003	0.01±0.003	0.02±0.006
manganese (Mn)	32±6.4	28±5.6	27±5.4	<1	<1	<1
nickel (Ni)	14±2.8	17±3.4	11±2.2	<1	<1	<1
lead (Pb)	1629±325	446±89	249±50	<1	<1	<1
antimony (Sb)	8±2.8	6±2.1	5±1.8	<2	<2	<2
thallium (Tl)	<5	<5	<5	<5	<5	<5
vanadium (V)	4±1.4	5±1.8	6±2.1	<1	<1	<1

The overall concentration of heavy metals in liquid samples is very low – in most cases below the equipment's limit of detection. Only concentrations of mercury were detectable in oils. It is possible to conclude that oils produced through scrap tyre pyrolysis are essentially free of heavy metals which is very promising since usually oils are the most desirable products in waste tyre pyrolysis plants.

However, the presence of all the metals analysed (except thallium) in the solid samples was proven. In char produced in a 400°C process there was a detectable amount of mercury – 0,01 mg/kg and at higher temperatures Hg was no longer detectable.

A – ash

FC – fixed carbon

HHV – higher heating value

IR – infrared

PAH – polycyclic aromatic hydrocarbon

RT – retention time

VM – volatile matter

W – water

Nevertheless, there was still a very low level of mercury in all the products, which is desirable. In the case of arsenic, cadmium, antimony, chromium, nickel and vanadium the tested concentrations were generally very low and mostly below the Polish limits for grounds [34], thus their concentrations in chars can be considered safe and do not need any further action. Slightly higher concentrations of manganese may have appeared due to the steel used in tyre production, which is enriched by Mn, and small pieces of metal were present in the pyrolysed sample.

In contrast, the measured concentrations of cobalt and copper were higher. Additionally, Cu levels slightly decreased with increasing temperature, but the differences in concentration of Co and Cu in different char samples are within uncertainty limits. It can be said that the observed levels of both elements are acceptable.

On the other hand, the measured concentrations of lead in the solid residue can cause serious concern, especially in the case of char produced at 400°C. There was 1629 mg of lead per kg of analysed char (dry basis). It is definitely much higher than the acceptable level for grounds. However, there is hardly any lead in a new tyre. Moreover, the lead concentration in analysed samples of waste tyres was also very low – 20 ppm. This brings us to the conclusion, that the tyres can be contaminated with Pb during tyre lifespan or treatment in scrap car plants. In particular, the common use of lead-acid batteries seems to be a very possible source of contamination. An interesting situation was discovered at the end of 2008 in the USA. It was found that the lead concentration in the rubber turf used in the soccer field in East Harlem (NY) dramatically exceeded the limit for grounds - 400 ppm. After that, a massive survey in about 100 sport fields was made, but a similar concentration of Pb was not detected elsewhere [35]. Those results may confirm the conclusion that rubber from waste tyres in general has a safe low level of heavy metals, but secondary pollution occasionally occurs. To ensure the safety of ground rubber the United States Environmental Protection Agency (EPA) decided in 2016 to conduct wide studies in this area, which are currently under review [36].

Since the lead concentration in solid samples (especially in the one collected after pyrolysis in 400°C) was a bit alarming, an analysis of the content of additional metals was done. The results obtained are presented in Table 4.

Table 4. Concentration (ppm) of heavy metals in the waste tyre and in pyrolysis chars

Metal	Waste tyre sample	Char (400°C), sample 1	Char (400°C), sample 2	Char (400°C), sample 3	Char (400°C), sample 4	Char (500°C), sample 1	Char (600°C), sample 1
arsenic (As)	<2	2±0.7	3±1.1	3±1.1	10±3.5	2±0.7	11±2.2
cadmium (Cd)	1±0.4	2±0.7	2±0.7	2±0.7	3±1.1	3±1.1	4±1.4
cobalt (Co)	67±13	125±25	175±35	209±42	317±63	307±61	263±53

chromium (Cr)	13±2.6	6±2.1	5±1.8	7±2.5	8±2.8	7±2.5	8±2.8
copper (Cu)	73±15	141±28	216±43	214±43	253±51	270±54	323±65
mercury (Hg)	0.12±0.036	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
manganese (Mn)	12±2.4	20±4.0	24±4.8	24±4.8	31±6.2	31±6.2	34±6.8
nickel (Ni)	5±1.8	14±2.8	12±2.4	10±3.5	13±2.6	14±2.8	41±8.2
lead (Pb)	20±4.0	38±7.6	45±9.0	62±12	52±10	62±12	87±17
antimony (Sb)	<2	13±2.6	8±2.8	9±3.2	17±3.4	12±2.4	14±2.8
thallium (Tl)	<5	<5	<5	<5	<5	<5	<5
vanadium (V)	1±0.4	5±1.8	4±1.4	5±1.8	5±1.8	5±1.8	6±2.1

As can be observed in all examined samples (four collected for 400°C and one each for 500 and 600°C) the concentration of lead did not exceed 100 ppm any longer. Thus, it can be assumed that the previous results could be individual cases, which are difficult to explain or justify. Additionally, the concentrations of heavy metals in raw samples of shredded tyres were examined. Measured levels of particular elements were low and safe. Moreover, it can be observed that metal content was proportionally higher in chars than in raw samples (except for the case of chromium) which strongly suggests that volatilization of them did not occur. Analysis of heavy metal presence in the liquid from gas scrubber also was made, and the results are available as a supplementary material. The concentrations of analysed elements in the liquids was very low, thus it is possible to assume that evaporation did not occur in significant amounts. This information is very important because it is then possible to assume that the pyrolysis gas is almost free of heavy metals and there is no need to monitor the gaseous emission of them. In general, comparing Tables 2 and 3 allows the observation that concentrations of all the other metals are quite similar, safe for the environment and for human health. Finally, this work provides sufficient results – in our opinion - to conclude that the concentration of heavy metals in waste tyre pyrolysis products is acceptable. However, the occasional check is still recommended, since tyre producers may change the composition of their products.

3.2. Proximate analysis, ultimate analysis and calorific value

Table 5 and Figure 3 show properties of oils and chars derived during the pyrolysis of waste tyres (proximate analysis results presented in this chapter are given on an as-received basis, while ultimate analysis is on a dry ash-free basis). The content of moisture in chars was 0.7%, 1.1% and 1.1% for samples obtained at 400°C, 500°C and 600°C, respectively. Similar values have been reported in the literature, for example Cunliffe & Williams [37] determined a moisture content of 0.5% (at 450°C), Li *et al.* [38] 1.3% (at 550°C) and Galvagno *et al.* [39] 1.4% (at 680°C). In the case of oils, the content of water was 4.2%, 2.0% and 2.1%. These values were higher than in papers [38] (0.5%-1.3%) and [40] (0.3%-1.6%), but similar or even lower than in [25] (2.8-4.6%) and [41] (4.6%). The presence of water in oils was an effect of dehydration reactions, enhanced by the low heating rate (5°C·min⁻¹), long residence time (2 hours) and relatively high oxygen content in primary fuel (4.5%). The hygroscopic nature of rubber-formed tyres affected the content of moisture in gaseous products, while moisture in char

resulted from water absorption from ambient air during sampling. The drop in moisture content in oil, observed for higher temperatures (500 and 600°C), may indicate enhanced evaporation of water. Nevertheless, the evolution of H₂O should favour steam gasification of solid char and increase the yield of gaseous products [42], which has not been observed.

Table 5. Physicochemical properties of analysed samples

	W	A	VM	FC ¹	C	H	N	S	O ²	HHV ³
	% (on as received basis)				% (on dry ash free basis)					
Waste tyres	2.3±0.1	7.3±0.1	66.3±0.2	24.1±0.2	85.9±0.2	6.8±0.2	0.66±0.1	2.2±0.2	4.5±0.2	33.3±0.1
Char 400°C	0.70±0.1	16.4±0.2	42.8±0.2	40.1±0.2	84.1±0.3	1.3±0.2	0.33±0.1	2.5±0.2	11.8±0.1	35.5±0.1
Char 500°C	1.1±0.1	17.7±0.2	6.1±0.1	75.1±0.2	84.5±0.2	0.67±0.1	0.41±0.1	2.8±0.2	11.6±0.1	28.7±0.1
Char 600°C	1.1±0.1	18.1±0.2	4.9±0.1	75.9±0.2	86.6±0.3	0.45±0.1	0.44±0.1	2.9±0.3	9.6±0.1	27.4±0.1
Oil 400°C	3.2±0.2	<0.01		96.8±0.2 ⁴	85.5±0.3	8.5±0.2	1.5±0.2	1.2±0.1	3.3±0.2	34.7±0.1
Oil 500°C	2.4±0.2	<0.01		97.6±0.2 ⁴	86.3±0.3	8.3±0.2	1.3±0.1	1.2±0.1	2.9±0.2	42.7±0.1
Oil 600°C	2.5±0.2	<0.01		97.5±0.2 ⁴	87.1±0.3	7.8±0.2	1.2±0.2	1.3±0.1	2.6±0.2	42.2±0.1

¹by difference (=100%-W-VM-A); ²by difference (=100%-C-H-N-S); ³on as received basis; ⁴combustible matter (=VM+FC)

The concentration of ash determined in chars was 16.4% (at 400°C), 17.7% (at 500°C) and 18.1% (at 600°C), which is in quite good accordance with values resulting from ash balance, equal to, respectively, 17.5%, 19.5% and 19.4%. The slight content of ash in oils (<0.01%) proved that it was not getting through the filter, thus the difference between measured and simulated ash content in chars should rather be attributed to the liberation of heavy metals such as mercury, the uncertainty in measurements or ash sticking to the reactor walls. The amount of ash was high compared to data presented in the literature, for example in [37] authors reported values of 11.6-12.4%, in [38] 12.3-14.6% and in [39] 11.6-14.8%, but it was not surprising, considering that the supplier shreds whole tyres, including steel belts and beads. Furthermore, results from the determination of heavy metal content, in details presented in the next chapter, confirmed that shredding whole tyres results in metals such as manganese, cobalt and copper remaining in the ash. In combustion appliances, the content of ash and moisture is often classified as a ballast decreasing energy conversion efficiency, thus it is recommended to keep these parameters at relatively low levels [43].

Volatiles are liberated in the form of gas and vapour (exclusive of moisture), at high temperature, under the oxygen-free atmosphere. The total amount of them and their composition is not a particular property of the fuel, but depends on the reactor used and heating conditions such as the heating rate, the residence time and the final temperature. The chars derived at 400°C, 500°C and 600°C contained 42.8%, 6.1% and 4.9% of volatiles. The content of volatile matter determined for samples at 500°C and 600°C was similar to that reported in the literature, while the value determined for a sample derived at 400°C was significantly higher. According to results presented by Cunliffe & Williams [37] chars obtained by means of a fixed bed batch reactor, at 450°C, 500°C and 600°, contained from 3.0% to 2.3% of volatiles. In paper [38], solid products of pyrolysis obtained in the pilot-scale continuous rotary kiln

reactor were reported to have from 16.6% to 5.9% content of volatiles (at a temperature range 450-600°C). Results provided in [39] indicated that chars from a pilot-scale externally heated rotary kiln reactor were characterized by the content of volatiles from 12.3% to 5.2% (at a temperature range 550-680°C). The extraordinary high content of volatiles measured in chars obtained at 400°C can be attributed to an incomplete degradation of rubber. According to Chen & Qian [44], at temperatures below 420°C, plasticizer, additives and natural rubber tend to decompose, while butadiene rubber and carbon black remain unreacted. The decomposition of mainly natural rubber was confirmed in this study by the predominant presence of D-Limonene in oil derived at 400°C (see Table 5). Furthermore, at temperatures of 500°C and 600°C the yield of D-Limonene decreased and aromatic hydrocarbons increased which indicated degradation of butadiene rubber.

Fixed carbon is considered as the residue after the volatile matter test, thus its content is interrelated with the content of volatiles. Values determined during tests were close to data given in the literature (for example in [38]), with the exception of results measured for 400°C (as explained above). Fixed carbon along with volatiles constitute combustible matter (CM), which from an industrial point of view is important due to its high combustion efficiency. The content of combustible matter for the oils obtained was higher than for chars, respectively 95.8%-97.5% compared to 82.9%-80.8%. It is worth noting that in case of chars, a higher temperature of the pyrolysis process led to a lower amount of combustible matter. The opposite tendency was reported in [39], while in [37,38] authors did not observe any correlation.

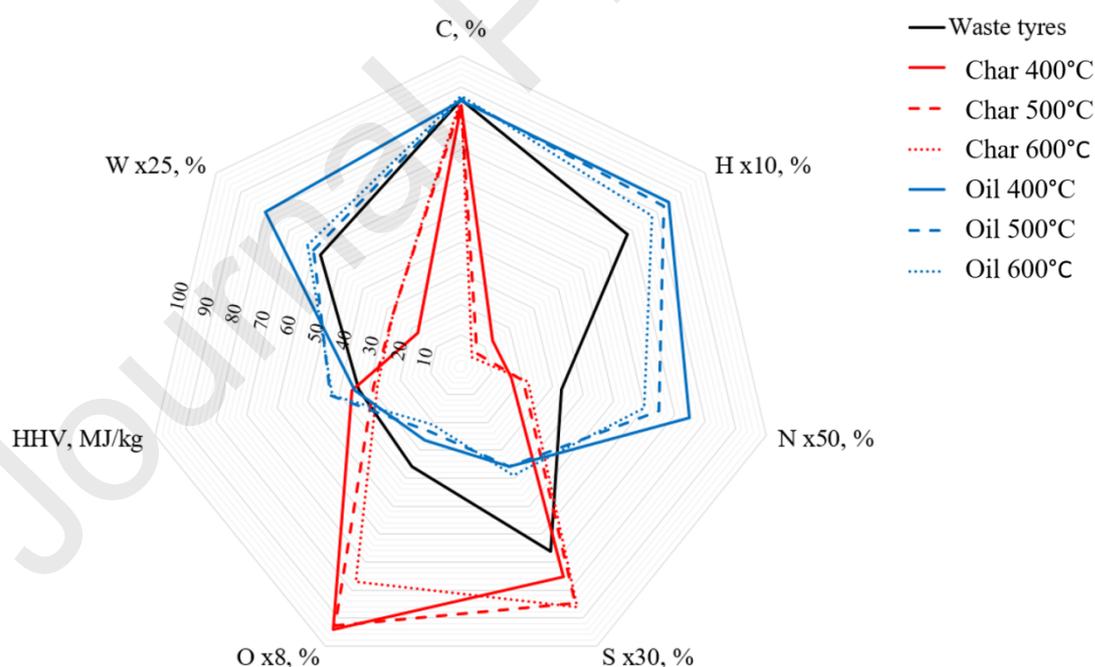


Figure 3. Comparison of chosen properties of raw fuel and chars/oils derived from it

The yield of combustible matter was to some extent related to their composition, manifesting in a higher heating value (HHV). The HHV for chars were reported to be 35.5 MJ/kg, 28.7 MJ/kg and 27.4 MJ/kg (on average 30.5 MJ/kg), similar to results given in [37] (mean value about 30.4 MJ/kg) and [39] (mean value about 30.1 MJ/kg). The HHV of obtained oils varied from 34.7 MJ/kg (at 400°C) to 42.2-42.7 MJ/kg (at 600°C and 500°C). Results obtained for higher temperatures were very similar to data given by many researchers, for example [12,25,38,40,41], while the HHV characterizing oil derived at 400°C was significantly lower than values reported in the literature, possibly due to a high concentration of water in analysed sample. The HHV calculated from a balance for gaseous products was 34.5 MJ/kg (at 400°C), 13.0 MJ/kg (at 500°C) and 11.9 MJ/kg (at 600°C). Assuming a density of syngas as 0.95 kg/m³ [45], the values obtained were in accordance with data provided for example by Gonzalez *et al.* [13] (12.6 MJ/kg), Zhang *et al.* [14] (18.2 MJ/kg) and Bianchi *et al.* [46] (42.6 MJ/kg). Moreover, the tendency indicating that syngas obtained at lower temperatures has a higher HHV than that obtained at higher temperature is similar to the observation of Laresgoiti *et al.* [47]. According to that paper, the trend observed should be attributed to the fact that evolution of CO and CO₂ increased with temperature and that the proportion of longer hydrocarbons, which have the greatest calorific values, dropped.

The content of organic carbon is often identified as a measure of the degree of carbonization [48]. The ultimate analysis performed confirmed the fundamental knowledge that at higher temperatures of pyrolysis the content of organic carbon rises in liquid and solid products. The content of organic carbon in chars and oils was respectively equal to 84.1%, 84.5%, 86.6% and 85.5%, 86.3%, 87.1%. The results obtained are in agreement with data provided by other authors, for example in [38] (chars: 80.8%-82.2%, oils: 84.3-88.0%), [39] (chars: 85.2%-85.6%) and [25] (oils: 84.6%-87.9%). Interestingly, the content of organic carbon in chars from waste tyre pyrolysis was significantly higher than in pyrolysis products from biomass (62.9%-76.4% [49]) and municipal waste (57.3% [50]) and close to that formed from coal (87.1%-88.7% [51]), which may be beneficial for the combustion/co-combustion purposes.

The hydrogen content in the chars obtained was from 1.3% (at 400°C) to 0.45% (at 600°C), while in oils it diverged from 8.5% (at 400°C) to 7.8% (at 600°C). These results are similar to values reported in the literature [25,38,41,52]. In the case of oxygen concentration, the results obtained were in range 9.6-11.8% (for chars) and 2.6-3.3% (for oils). It is worth noting, that the content of oxygen in chars may seem high compared to results provided in [37] and [52], however it is similar to data given by Li *et al.* [38] and Galvagno *et al.* [39]. For both hydrogen and oxygen elements, it was observed that higher temperatures of pyrolysis led to a drop in oxygen and hydrogen in chars and oils. The observed trend should be attributed to enhanced liberation of more reactive compounds containing hydrogen (for example via dehydrogenation) and oxygen (through condensation) at higher temperatures. To some extent similar tendencies may be observed in papers of Galvagno *et al.* [39] (concerning the content of hydrogen in chars) and Roy *et al.* [40] (concerning the content of oxygen in oils). Nevertheless, it has to be mentioned that drawing conclusions from the results for oxygen is hindered due to uncertainty associated with indirect measurement of its content, and should be supported by further investigation.

Scrap tyres contain only limited amounts of nitrogen (0.61%), which may be attributed mainly to the presence of proteins in natural rubber and acrylonitrile in nitrile-butadiene rubber [53]. It may also come from the vulcanization process [54], however such a technique is not commonly

in use nowadays. The content of nitrogen in chars and oils obtained was respectively about 0.39% and 1.3%. The special attention brings relatively high concentration of nitrogen in oils, which is rarely seen in the literature, but present (for example in [12] - 2.1%). Investigation of the distribution of nitrogen compounds between char and oil revealed that less than 20% of them remained in the char. The result is surprising, especially compared to results known for coal [55], where up to 80% of elemental nitrogen was embodied in char. The high reactivity of nitrogen compounds present in waste tyres may result in high emissions of fuel NO_x during combustion, which has recently been reported in the literature [56]. Nevertheless, it has to be remembered that the overall NO_x emission cannot be estimated only based on fuel properties, because the formation mechanism involves also formation of thermal and prompt nitrogen oxides, whose concentrations depend on combustion conditions (e.g. temperatures, oxygen availability, etc).

3.3. Sulfur compounds distribution

Sulfur is one of the most important ingredients used in tyre production, thus the concentration of several specific, problematic sulfur-content compounds in pyrolysis gas was investigated. The results are presented in Table 6. The proportions of sulfur as an element in all oils and chars obtained were examined, and the results are depicted in Figure 4.

Table 6. Selected sulfur-containing compounds in pyrolysis gas collected in different temperature ranges

Compound	260 – 355°C	365 – 450°C	460 – 600°C
	Concentration, ×10 ⁻⁴ % mol/mol	Concentration, ×10 ⁻⁴ % mol/mol	Concentration, ×10 ⁻⁴ % mol/mol
hydrogen sulfide	23.6±3.2	>500	>500
carbonyl sulfide	115.0±20.0	>500	>500
methyl mercaptan	62.6±8.4	>500	>500
ethyl mercaptan	6.68±1.19	322.2±59.3	268.1±49.3
dimethyl sulfide	0.60±0.11	6.68±1.19	4.83±0.86
carbon disulfide	56.0±9.4	55.7±9.4	28.8±4.8
i-propyl mercaptan	0.88±0.16	7.33±1.31	7.50±1.34
tert-butyl mercaptan	0.53±0.09	0.61±0.11	0.63±0.11
n-propyl mercaptan	0.62±0.11	10.96±1.95	11.19±1.99
methyl ethyl sulfide	<0.1	1.64±0.29	2.14±0.38
s-butyl mercaptan	0.90±0.16	1.62±0.29	1.57±0.28
i-butyl mercaptan	0.23±0.04	1.97±0.35	1.47±0.26
diethyl sulfide	<0.1	0.31±0.05	0.35±0.06
n-butyl mercaptan	0.27±0.05	1.13±0.20	1.67±0.30
dimethyl disulfide	0.15±0.03	0.30±0.05	0.11±0.02

dipropyl sulfide	0.20±0.03	0.44±0.08	0.38±0.07
diethyl disulfide	<0.1	<0.1	<0.1

Pyrolysis gas samples collected into Tedlar ® Bags were tested for the following sulfur compounds that feature unpleasant smell and toxicity: hydrogen sulfide, methyl mercaptan, ethyl mercaptan, propyl mercaptan, butyl mercaptan, carbonyl sulfide, carbon disulfide, dimethyl sulfide, dimethyl disulfide, methyl ethyl sulfide, diethyl sulfide, diethyl disulfide and dipropyl sulfide. It is worth noting that almost all the compounds investigated occur in pyrolytic gas in concentrations above $0.1\% \times 10^{-4}$ mol/mol. Furthermore, at temperatures above 365°C, concentrations of hydrogen sulfide, carbonyl sulfide and methyl mercaptan exceed 0.05 % mol/mol. In addition to the three compounds mentioned above, a high content of ethyl mercaptan and carbon disulfide in the syngas analysed was also observed. The highest total concentration of sulfur compounds was recorded for the sample taken at 365 - 450°C. Moreover, this temperature range was characterized by the most intensive production of pyrolytic gas. This could be seen by the filling level of the bags (each with a nominal volume of 1000 ml), which was the highest for the second sample despite the fact that it covered the range only about 115 degrees. On the other hand, overall production of pyrolysis gas was the highest for the process conducted at 400°C, which was reported before elsewhere [19]. Hydrogen sulfide is a very corrosive and aggressive compound, thus many measurement methods (i.e. electrochemical) fail to define high H₂S concentrations. In order to assay it, lead sulfur precipitate can be applied, which is formed from the reaction between H₂S and lead nitrate in laboratory traps. Ucar *et al.* [57] determined this way the hydrogen sulfide content in the gaseous products of truck tyre and passenger car tyre pyrolysis which was 0.94 and 4.18 wt.%, respectively. It is expected that the H₂S concentration in the waste tyre sample analysed in this work is around 1 – 4 wt.%, since the sample is a mixture of different types of scrap tyres. This expectation corresponds with calculated concentrations of sulfur-content compounds in pyrolysis gas presented below. However, accurate measurements should be made in order to verify it.

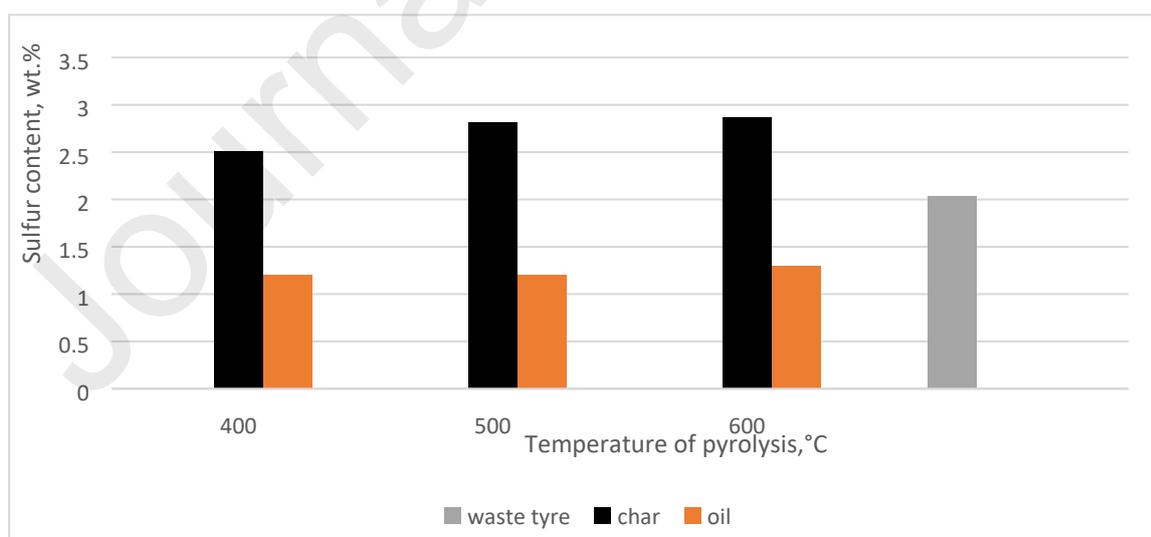


Figure 4. Sulfur content in the waste tyre sample and in the pyrolysis products depending on the process temperature

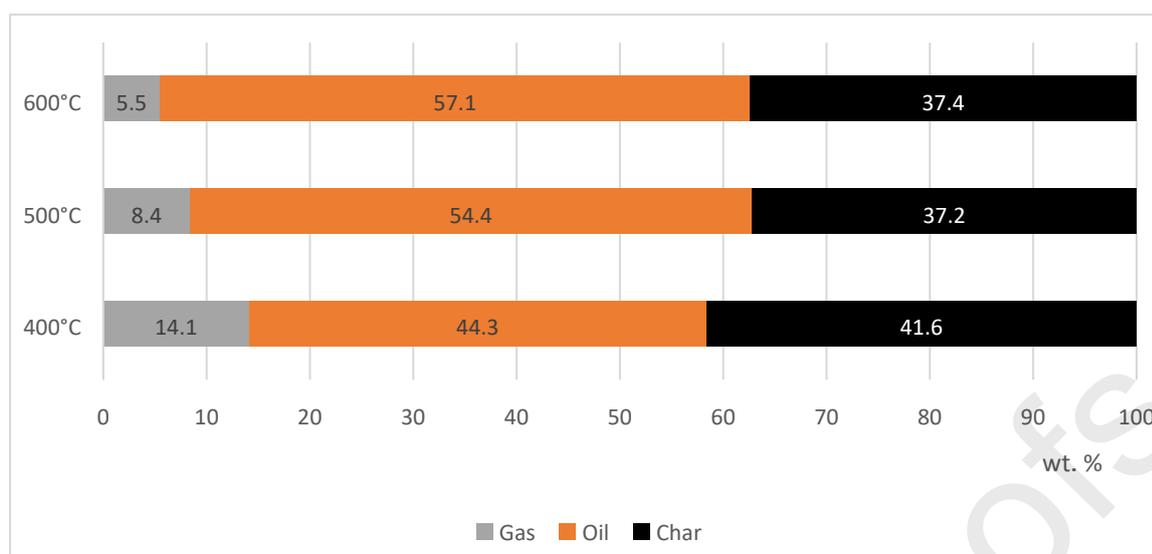


Figure 5. Pyrolysis product proportions obtained at different process temperatures

Firstly, from the chart it can be seen that the raw sample of waste tyres contains 2.04 wt.% of sulfur (dry basis). This result is comparable with results obtained by Januszewicz *et al.* [58], Singh *et al.* [59], Gu *et al.* [60], Galvagno *et al.* [61] and many other researchers. However, the sulfur content in waste tyres reported in the literature data mentioned varies from approximately 1 to above 2 wt.%. Secondly, the sulfur content in oils produced at different temperatures of the process slightly increases from 1.2 to 1.3 wt.%, while in chars it rises from 2.5 to 2.9 wt.%. This phenomenon can be explained by hydrogen liberation and an increase in the importance of sulfur. Finally, taking into account the proportions of different pyrolysis products (see Figure 5) it is possible to prepare simplified sulfur distribution graphs (Figure 6) that allow the calculation of the approximate concentrations of sulfur in the pyrolysis gas. These concentrations were as follows: 3.0, 3.5, and 3.2 wt.% for 400°C, 500°C, and 600°C, respectively. Susa & Haydary [62] investigated the sulfur distribution in the products of waste tyre pyrolysis depending on the residence time (88.6 s, 80.2 s, and 73.9 s) and process temperature (600 – 800°C). In the liquid, sulfur content varied from 1.1 wt.% to 1.3 wt.%, while in the solid phase it was from 2.4 wt.% to 2.6 wt.%. At 600°C (RT: 80.2 s) the proportions of sulfur in char, oil and gas were 70.47 wt.%, 18.23 wt.%, and 11.31 wt.%, respectively [62]. Ucar *et al.* [57] also analysed sulfur distribution in tyre pyrolysis products based on a sulfur mass balance. They found sulfur contents as follows: 39.2 wt.% and 16.6 wt.% in gas, 37.4 wt.% and 31.3 wt.% in liquid, 23.4 wt.% and 52.1 wt.% in solid residue, for passenger car tyre and truck tyre pyrolysis, respectively. In turn, Rodriguez *et al.* [63] reported that more than 50 wt.% of the initial sulfur remains in the char, when the pyrolysis was conducted above 500°C.

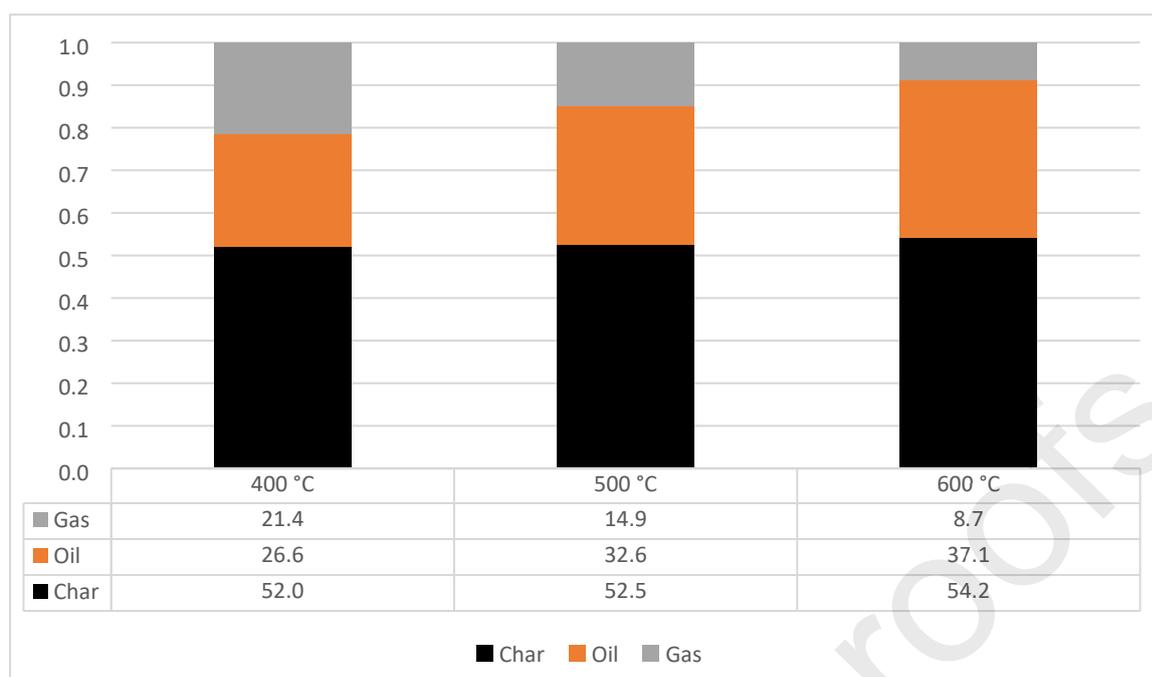


Figure 6. Sulfur distribution in pyrolysis products [wt.%] depending on process temperature

3.4. Oil composition

Many investors focus on the production of valuable organic compounds from pyrolysis oil, thus it was reasonable to check the composition of those obtained in conditions proposed in this work. The results of chromatography analysis are presented in chromatograms (see Figure 7 - Figure 9). Tables contained lists of all identified compounds are available as a supplementary data.

As can be seen the liquids obtained are predominantly composed of d-Limonene, o-cymene, o-xylene/p-xylene, toluene and ethylbenzene. Altogether they represent about 40wt.% of the oils obtained at 400°C and slightly less than 30wt.% in liquid phase produced in 500 and 600°C. However, the total amount of oil produced at different temperatures increased with increasing temperature from 44.3wt.% at 400°C to 57.1wt.% at 600°C [19].

Overall, the investor focused on oil production probably will choose the higher process temperature, because the aggregated production from a defined amount of waste tyres (yields of oil × concentration of particular chemicals) is beneficial, and it allows the avoidance of a much higher by-production of char. Moreover, 600°C was described as an optimal waste tyre pyrolysis temperature according to the kinetics of the process [64].

Limonene is the compound which is attracting the most attention of potential investors because of its wide use in many applications combined with high proportion of the pyrolysis oil [65]. The concentration of limonene in pyrolysis oils decreased with increasing temperature from almost 22 wt.% to about 9 wt.%. This phenomenon has been reported before and it is caused by its propounded degradation and aromatization at higher temperatures. D-limonene decomposes to isoprene along with many other compounds [9,66]. The highest yields of d-limonene were reported at 400°C [67], 425°C [68] or 450°C [69]. Limonene is mainly used as an industrial solvent, for cleaning electrical circuit boards, as a pigment dispersing agent or in

pesticides, and the production of mosquito repellents. Moreover, d-limonene smells like oranges thus it is applied in fragrances and the manufacture of flavourings [9].

Cunliffe & Williams [25] conducted pyrolysis of shredded scrap tyres at temperatures between 450 and 600°C. They identified limonene as a major component of the oils. However, it represented only 3.1 wt.% at 450°C falling to 2.5 wt.% of the total oil at 600°C. Other aromatics such as benzene, toluene, xylene and styrene were also found in significant amounts. The aromatic content of the oils increased with increasing temperature, while the aliphatic content went down [25]. Also, Kyari *et al.* [70] analysed products from the pyrolysis of different brands of tyres conducted at 500°C. In general, the oil was a very complex mixture, consisting of single ring and polycyclic aromatic compounds as well as their alkylated derivatives. The compounds identified included, inter alia, toluene, ethylbenzene, styrene, indene, and biphenyl. The predominant component of the oils obtained was limonene, and its concentration varied from 2.82 to 4.76 wt.% depending on the tyre brand. Several alkanes and higher molecular weight compounds appeared, too. Finally, sulfur-containing compounds and nitrogen-containing compounds were also identified. It is concluded that all of the oils were very similar in the range of chemical compounds identified but varied in the concentration of each individual compound depending on the tyre brand [70].

Also, other compounds identified in significant amounts in the liquid produced from the pyrolysis have promising industrial potential. For instance, toluene is one of the most popular solvents. It is used in the production of other chemicals, medicines, perfumes, detergents or even explosives [71]. O-xylene is the second largest of xylene isomers. It is mainly consumed in the production of phthalic anhydride, which is subsequently used in polyvinyl chloride resins, unsaturated polyesters for glass-reinforced thermoset applications, and alkyd resins for surface coatings. Recently o-xylene is also applied in the manufacture of polyethylene naphthalate polymer, which allows high performance film and rigid packaging to be obtained [72]. In turn, ethylbenzene is an intermediate in the production of styrene monomer, which is well known as a source for polystyrene and the production of many other plastics. [73]. O-cymene – like other cymenes – can be used as a solvent, in synthetic-resin manufacture, as metal polish, or in an organic synthesis [74].

A variety of valuable organic compounds present in waste tyre pyrolysis oil can be quite easily utilized in the chemical industry. This way of applying products from waste processing features several advantages in comparison with traditional waste management processes. Firstly, the atmosphere is protected from emissions from uncontrolled burning of tyres, and resources are preserved. The soil and hydrosphere also are saved since dangerous leaks from waste dumping is avoided, too. The presence of valuable chemicals in pyrolysis oil is very promising from the point of view of the preservation of environmental resources. There is a clear global trend into renewable materials and energy sources. Unfortunately, there is no competitive option for pneumatic tyres, thus they still must be produced. However, applying waste tyre pyrolysis oil in the chemical industry can be considered as a very promising case of material recycling. The possibility of utilizing the liquid products obtained allows the saving of significant amounts of crude oil that contains from 2 to 20 wt.% of aromatics [75]. If only 10 wt.% of the waste tyres produced worldwide annually would be processed through pyrolysis, it would be possible to save about 200,000 tonnes of crude oil which is now directed into chemical synthesis.

Additionally, the noticeable concentrations of volatile hydrocarbons present in the oils can significantly enhance the profitability of the investment in waste tyre pyrolysis. It is worth noting that plants which utilize tyres can be paid for by tyre producers or sellers across the European Union countries according to the polluter-pays principle. They are obligated to “manage the waste in a way that guarantees a high level of protection of the environment and human health” [76]. However, pyrolysis is an energy-intensive process, thus it can consume the money from taxes. Therefore, the profitability of the investment is dependent on product quality and outlet. For example, effectively separated limonene obtained from processing ten tonnes of waste tyres is worth about 1500 US\$.

On the other hand, operating plants – such as Reoil Sp. z o.o. in Bukowno (Poland) - are focused on production and distillation of oil combined with refining, micronisation and granulation of carbon black instead of fractioning of oil to particular valuable compounds. This technologies are already relatively cheap and easy to apply providing products with quality comparable with commercial liquid fuels or carbon black [16]. It seems like trying to obtain for example pure limonene from the oil are still too complicated and expensive. Several studies have been conducted to produce various fractions of pyrolysis oil in order to the end use as a fuel or fuel additive, through distillation [40,77], or selective condensation [78]. Those processes resulted production of limonene-enriched fraction. However, pure limonene is not possible to obtain this way. Pakdel *et al.* [79–81] in the series of research were able to produce 95wt% pure dipentene, and concluded that at least two consecutive distillation steps, followed by a purification step, would be required to produce high purity dipentene from pyrolysis oil. However, the methods used are not easily applicable in a larger scale. Additionally, concentrated limonene samples featured unpleasant odour, which make them in practise useless in manufacture of fragrances or flavourings. It is possible to conclude that production of liquid fuels of commercial quality is possible and profitable for investor who would like to set-up a pyrolysis plant. However, composition of oils may be promising option for the future when reuse od hydrocarbon become a necessity.

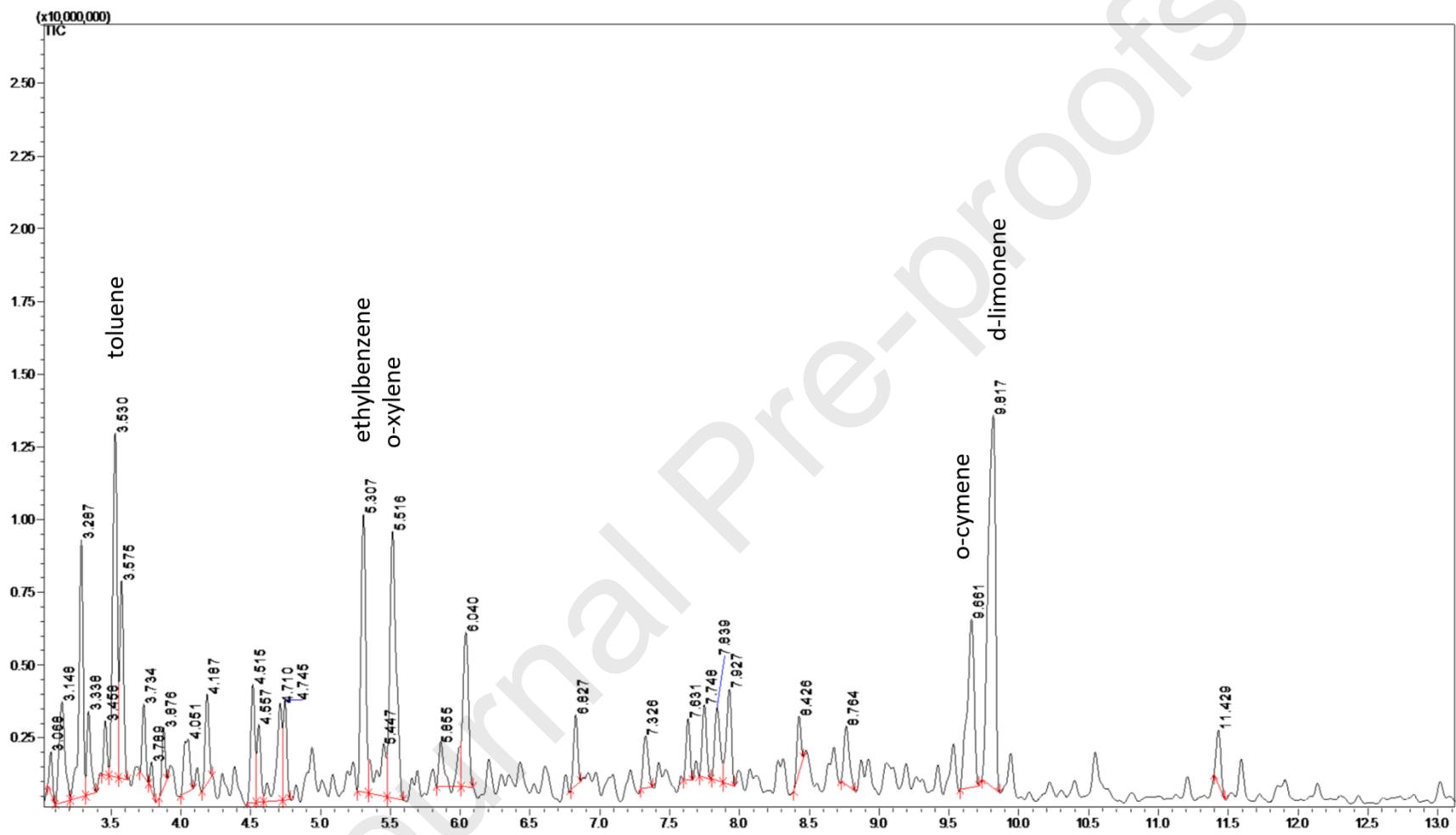


Figure 7. The chromatogram produced for 400°C pyrolysis oil.

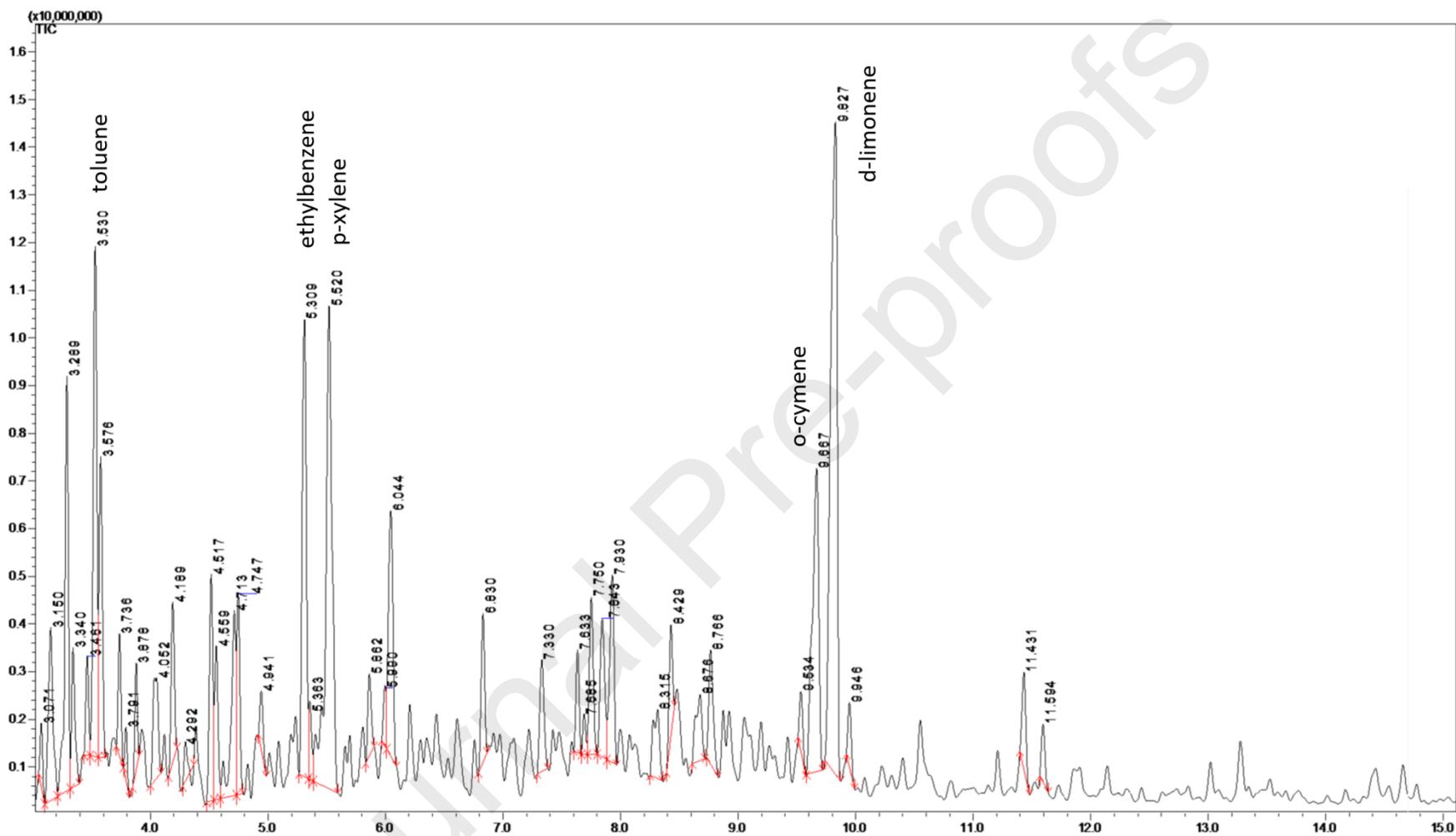


Figure 8. The chromatogram produced for 500°C pyrolysis oil.

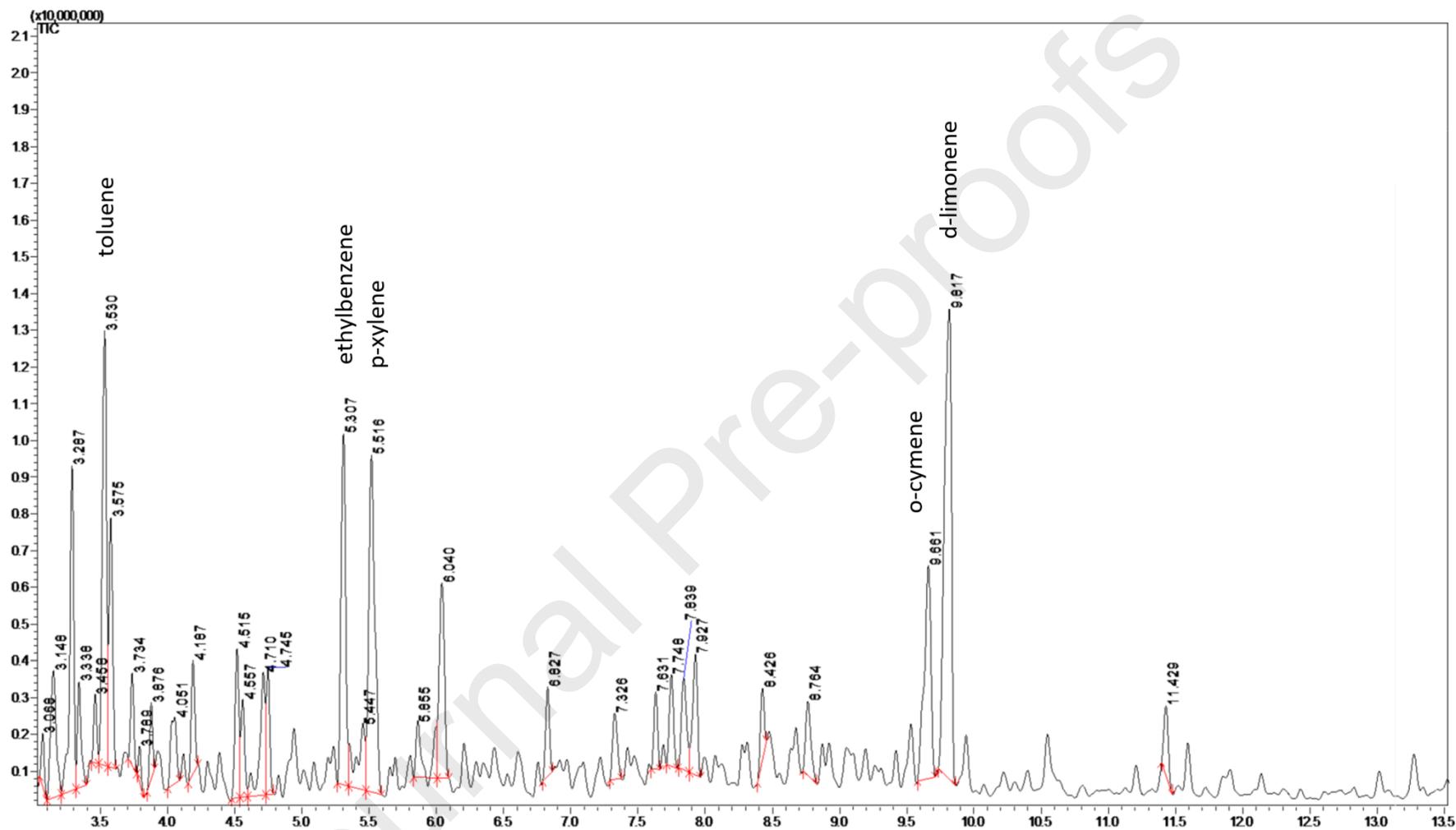


Figure 9. The chromatogram produced for 600°C pyrolysis oil.

4. Conclusion

This paper presents a wide investigation of scrap tyre pyrolysis products in the context of their influence on the environment and human health. This thermochemical utilization can provide an alternative solution to the serious problem of increasing waste tyre numbers.

In comparison with combustion, the composition of pyrolysis gas is safer, because the oxygen-free atmosphere avoids the formation of many pollutants. Pyrolysis gas features a high heating value which was 34.5 MJ/kg at 400°C but decreases with increasing temperature, and this gas can be applied directly in the plant to cover the energy-demand of the process. This solution enhances the profitability of the investment. However, high concentrations of dangerous sulfur-containing compounds enforce the addition of a gas-purification system. Special attention is focused on H₂S, for which the measured concentration was above the 500 ppm detection limit for the applied methodology and is expected to be as high as 3.8 wt% (based on the sulfur distribution in pyrolysis products). On the other hand, it should be highlighted that sulfur removal can be cheaper and more effective in this case than from the exhaust gases produced after combustion because of a much lower volume of the processed gas. Oil is a source of renewable energy as well as valuable chemicals. The HHV exceeds 42 MJ/kg for oils produced at temperatures above 500°C, which is comparable with heating oil and slightly lower than Diesel oil. It is possible to conclude that it is also heavy metal-free. However, the sulfur concentration must be lower before applying the oil for heat and energy production. Additionally, high amounts of d-Limonene, o-cymene, o-xylene, toluene and ethylbenzene in the oils make them very promising as raw materials in chemical industry. Altogether they represent 41.02 wt.%, 27.88 wt.%, 29.42 wt.% of the oils obtained at 400, 500 and 600°C, respectively. A proper treatment of raw oils may possibly save noticeable amounts of crude oil without harming the environment and human health. The chars obtained are also of a high energy density (up to 35.5 MJ/kg at 400°C). In general, the levels of heavy metals are acceptably low. Additional analysis focused on lead concentrations confirmed that char is a safe raw material for further industrial purposes.

It can be concluded that pyrolysis and its products can contribute to the preservation of environment resources since they are desirable for energy recovery or in the chemical industry. The low concentration of heavy metals allows them to be applied without harm for the biosphere. However, sulfur should be removed from the products especially when in the gaseous form, otherwise the products are toxic. When pyrolysis products are applied in energy recovery, the desulfurisation must be implemented either before or after incineration.

Acknowledgements

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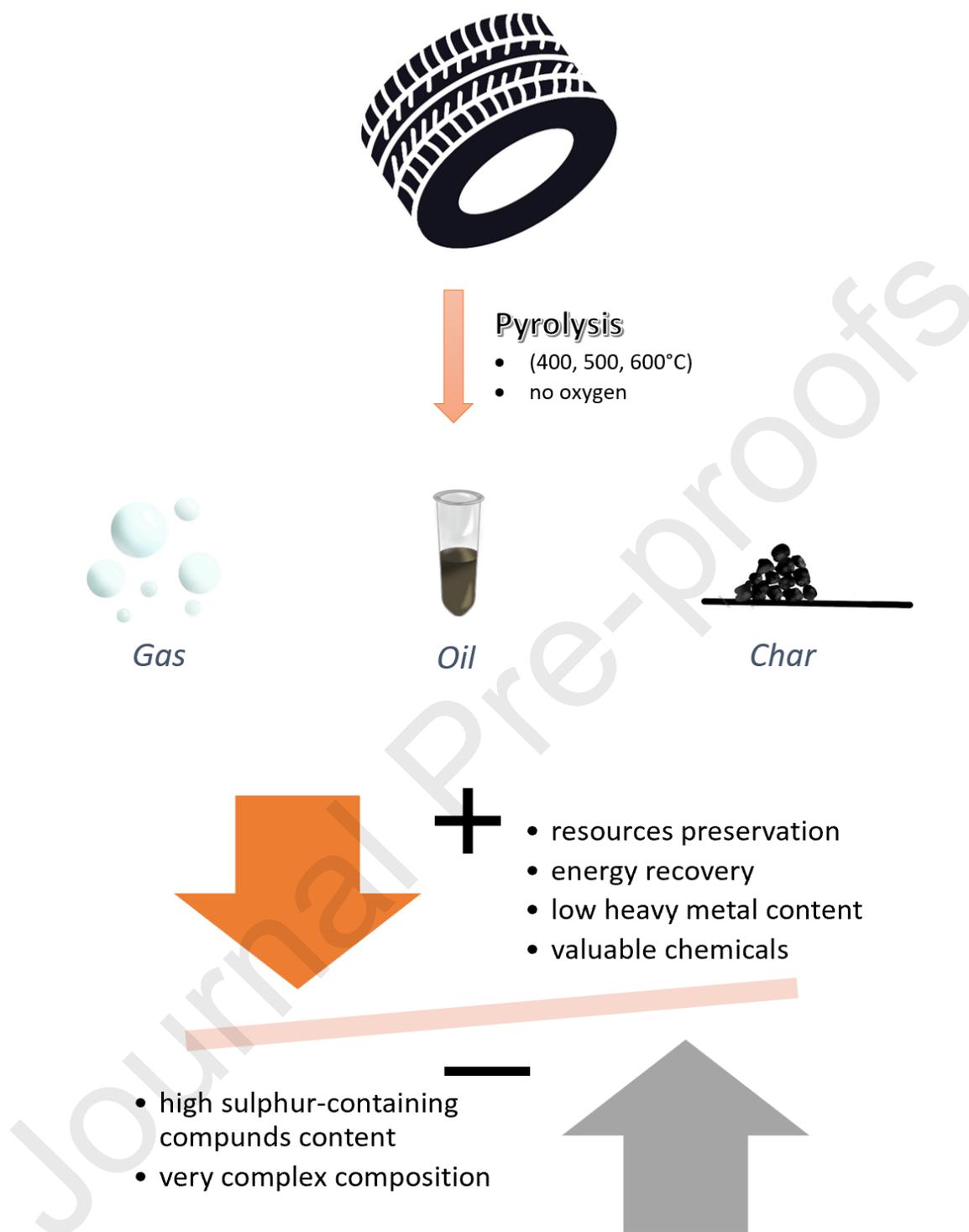
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Highlights:

- Pyrolysis of waste tyres provides products that features high calorific value – up to 42.7 MJ/kg.
- Heavy metal concentrations are below environmental limits and are mainly found in char.
- The presence of various mercaptans were detected in pyrolytic gas.
- Limonene, cymene, xylene, toluene and ethylbenzene represent about 30 - 40wt.% of the oils.
- Desulfurisation of the products is recommended - sulfur content reached 3.5wt.% in the gas.

Journal Pre-proofs