Hydrogen sulfide removal from waste tyre pyrolysis gas by inorganics.

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Abstract

The article presents research on the purification process of pyrolysis gas from hydrogen sulfide. To our best knowledge, similar studies have not been performed yet on a real pyrolysis gas obtained from waste tyres, which contains huge amounts of hydrogen sulfide - average 3.6 % (up to 5.1 % at 420 °C). Different sorbents were tested, among them sodium hydroxide, zinc oxide, and manganese oxide. NaOH in concentration 0.05 M appeared to be the most efficient, showing ~94 % H_2S removal efficiency under the conditions studied. ZnO features a better efficiency of H_2S removal from hot gas (~55 %) than MnO. Furthermore, the combination of ZnO and a 0.05 M solution of NaOH was studied. The detailed composition of the pyrolysis gas was performed, too. The main components and sulfur-containing compounds, such as methyl mercaptan, carbonyl sulfide, and ethyl mercaptan, concentrations were measured. Predominantly, the gas consists of methane, hydrogen, ethane, ethene, carbon dioxide, iso-butane, and hydrogen sulfide. Aggregated concentrations of the above-mentioned exceed 80 % of the gas, which makes it a very promising gaseous fuel.

Keywords:

mercaptans, emissions, gas cleaning, sodium hydroxide, zinc oxide, manganese oxide

Abbreviations:

$_{(aq)}$ – water solution;

FID - flame-ionisation detector;

PFPD – pulsed flame photometric detector;

$_{(g)}$ – gas;

GC - gas chromatography;

$_{(s)}$ – solid state;

TCD - thermal conductivity detector

1. Introduction

Since a high level of industrialisation and development has been reached in many regions worldwide, environmental issues have become one of the most important parts of management in modern society. Waste management, as well as water and air protection, are urgent problems.

The growth of different types of transportation was somewhat slowed down because of the limitations caused by the SARSCOV-2 pandemic. However, the number of vehicles and subsequent car waste is growing almost each year. The latest reports released by the European Tyre & Rubber Manufacturers'Association (ETRMA) estimated that tyre production of tyres was as high as 5.1 million tonnes in 2018, while in 2016 it was 4.94 million tonnes and the growth recorded is small but relatively stable [1,2]. The utilization of waste tyres is challenging because of their bulkiness and durability. Pyrolysis is a thermochemical endoenergetic decomposition of raw material under an oxygen-free or inert atmosphere that has attracted the attention of researchers interested in tyre utilization since the late1920s [3–9] because it allows the reduction of waste as well as the production of valuable gaseous fuel, oils and chars.

Researchers are usually focused on maximizing the yields of the liquid products obtained during the pyrolysis process, which seems to be reasonable from an economic point of view, since the oil features a high heating value and properties comparable with those of liquid fuels, as well as being composed of valuable chemicals. Another promising solution is the production of good-quality activated carbons from chars [10,11]. However, the separation of chemicals from the oil, especially the predominant one - limonene (dipentene) - are problematic. Pakdel *et al.* [12–14] in a series of studies were able to produce 95 wt.% pure dipentene from waste tyre pyrolysis oil and concluded that at least two successive distillation steps, followed by additional purification, would be required to produce high purity dipentene from pyrolysis oil. On the other hand, pyrolysis gas may become the most important factor in large-scale waste tyre processing, because it can be immediately utilized as a fuel for the heating of the pyrolysis reactor (except the start-up phase) [15]. Czajczyńska *et al.* [16] analysed the potential of pyrolysis gas from waste tyres as a fuel. In general, it features a high heating value comparable to natural gas (35 – 40 MJ/m^3) [16]. It is composed of light hydrocarbons (methane, ethane, propane, butane, pentane), hydrogen, carbon oxides, and hydrogen sulfide. The yield of pyrolytic gas increases with increasing process temperature and can reach 30 wt.% [17,18]. It should be noted that the measured pyrolysis enthalpy was approximately 270 J/g and the gross heating value of the produced gas was 2900 J/g (expressed as energy per unit mass of rubber tyre). Therefore, the utilization of gas can satisfy the process requirements and can be used for other purposes [19].

However, very few studies mentioned the need for pyrolysis gas treatment before further utilization. For example, Aylon *et al.* [20] analysed emissions from the combustion of the gas phase from the pyrolysis of waste tyre. An enormous excess of SO_2 concentration in the flue gas (4780 mg/m^3) was found in comparison with the limit (50 mg/m^3) assigned in the Waste Incineration Directive [21]. This SO_2 comes mainly from the oxidation of H_2S present in the pyrolysis gas. The researchers assumed that "it should be necessary to incorporate in the pyrolysis installation a gas cleaning system to achieve the abatement of acid gases" [20]. However, it seems to be reasonable to remove H_2S from the raw pyrolysis gas (a significantly lower amount of gas for treatment) instead of SO_2 from exhaust gases [22]. Moreover, Abdallah *et al.* [23] mentioned that there is a high need to clean the pyrolysis gas before burning because of the hydrogen sulfide. Unfortunately, the exact concentration of H_2S and accurate composition of the gas was not presented. Usually, the concentrations of main components (light hydrocarbons, hydrogen and carbon oxides) are analysed and the presence of impurities is omitted [24,25]. Even Ucar *et al.* [26], who carefully measured the concentration of hydrogen sulfide in pyrolysis gas from two different types of tyres: truck and passenger cars, did not discuss the importance of cleaning the gas before use. In a previous work [27] the authors presented the concentrations of various sulfur-containing compounds that exhibit unpleasant odour and toxicity, including hydrogen sulfide and mercaptans. However, equipment limitations did not allow measurement of H_2S content. Hence, its predicted concentration was calculated on the sulphur content in the raw sample, the liquid product, and char.

Hydrogen sulphide is a very corrosive and aggressive compound, therefore some measurement methods (i.e., electrochemical) fail to define high H_2S concentrations [27]. The expected concentration of sulfur-containing compounds, mainly hydrogen sulfide, in raw pyrolysis gas is between 3.0 and 3.5 wt.% [27], which is enormous knowing that concentrations above 50 ppm are already very dangerous for humans [28]. Moreover, the momentary concentration of H_2S may even reach 5 vol % [29]. Ucar *et al.* [26] determined that the hydrogen sulphide content in the pyrolysis gas of truck tyres, and passenger car tyres was 0.94 and 4.18 wt.%, respectively. They applied lead sulfur precipitation, which is formed from the reaction between H_2S and lead nitrate in laboratory traps. Simple burning of hydrogen sulfide, which is flammable, as a component of pyrolysis gas, is not acceptable from safety and environmental considerations, since one of the combustion products is sulfur dioxide, which is also toxic and its emission limit is very strict [30,31]. Furthermore, SO_2 is subsequently oxidized to SO_3 (heterogeneous oxidation of particulate matter). Sulfur trioxide, in turn, is highly soluble in the water present in the atmosphere, which results in the formation of acid rain [32]. Thus, an appropriate method for the removal of hydrogen sulfide from the gaseous fuel obtained should be proposed.

To the best of our knowledge, there has been very little work that has studied the cleaning of waste tyre pyrolysis gas so far. However, recently Kordoghli *et al.* [29] studied different combinations of four catalysts, three solid supports, and three configurations of bed position to optimize hydrogen production. They have been able to reduce the average concentration of H_2S in the pyrolysis gas produced from 1.04 % to 0.65 % by applying a double $CaCO_3$ bed stage based on oyster shells. The lower heating value increased slightly from 31.95 MJ/m^3 (without catalyst) to 32.39 MJ/m^3. Unfortunately, the H_2 yield was not the best in this case, and even the reduced concentration of hydrogen sulfide does not allow the gas to be used as it is.

There are many methods applied in the removal of H_2S, as well as CO_2 and some other acidic contaminants from natural gas before sale. Taken together, the processes are popularly called 'gas sweetening'. The most popular options used around the world include absorption, adsorption, oxidation, and membrane permeation [33]. The absorption process driving force may be physical or chemical, the former when only physical interactions are involved and the latter in the case where a chemical reaction is present [34]. The composition of pyrolysis gas from waste tyres and natural gas is quite similar [16] thus we have decided to examine the methods of H_2S removal from natural gas on the pyrolysis gas described below.

One of the best known methods of natural gas sweetening is absorption in alkaline solutions [35]. The direct proton transfer reaction between hydroxyl ions and hydrogen sulfide allows for its absorption into the above-mentioned:

$$H_2S_{(g)} + OH^-_{(aq)} \rightarrow HS^-_{(aq)} + H_2O_{(l)} \quad (1)$$

$$HS^-_{(aq)} + OH^-_{(aq)} \rightarrow S^{2-} + H_2O_{(l)} \quad (2)$$

The absorption of carbon dioxide by aqueous alkaline solutions is much slower than that of hydrogen sulfide, thus it is also possible additionally to attain partial selectivity [36]. Sodium hydroxide is predominantly applied in this term, because of its low price and availability. The optimal solution of NaOH for H_2S removal was presented to be 0.1 M [37]. Unfortunately, NaOH is not regenerable, so its usage is limited to the removal of small amounts of acid gases. However, Álvarez-Cruz *et al.* [37] suggested that it is possible to produce valuable sulfides in this way. Argonul *et al.* [38] were able to obtain a H_2S removal efficiency greater than 99% with two NaOH scrubbers applied followed by guard beds. The investigated gas cleaning demonstration plant was designed for coal gasification and the composition of the syngas was different from that of the pyrolysis gas since it usually contains much higher amounts of CO – approximately 50 %. Nevertheless, the results are very promising since it may be assumed that it is possible to obtain excellent hydrogen sulfide removal efficiencies when caustic scrubbers are applied.

Interestingly, it would also be desirable to test the possibility of hot gas desulfurization, which minimizes the cost of reheating gaseous fuel after the cleaning process. Usually, commercial gas desulfurization technologies operate at low temperatures (~40 to 55 °C) [39]. In the case of pyrolysis gas, it should be cooled, cleaned, and finally reheated when it is directed into a gas turbine. The use of metal sorbents to remove H_2S from gas is a common practice nowadays for the desulfurization of hot coal gas at elevated temperatures (600–850 °C). Coal is gasified at temperatures above 1000 °C to produce raw syngas (~ 850 °C) which then goes to a desulfurizer loaded with solid sorbents such as zinc oxide, copper oxide and manganese oxide based sorbents, to remove sulfur-containing compounds. Eventually, the cleaned syngas is directed to a gas turbine for electricity power generation [40]. The application of metal sorbents for H_2S removal from hot pyrolysis gas is a promising and, more importantly, a regenerative process. Sulfidation (reaction between solid state (s) metal oxide and gaseous (g) H_2S leading to the production of solid metal sulfide) and regeneration (removal of sulfur from the sulfides in an oxygen atmosphere to recover the metal oxides) processes proceed according to the reactions below:

$$\text{Sulfidation: } H_2S\,(g) + yMO(s) \rightarrow H_2O\,(g) + yMS\,(s) \tag{5}$$

$$\text{Regeneration: } yMS(\mathrm{s}) \xrightarrow{O_2} \mathrm{yMO(s)} + \mathrm{ySO_2(g)} \tag{6}$$

where

y - stoichiometry coefficient,

MO - metal oxide

MS - metal sulfide

Notice that MO and MS in the equation do not strictly refer to stoichiometric compounds, i.e., MO may stand for e.g., ZnO as well as Fe_2O_3 [41,42].

Westmoreland & Harrison examined the potential of 28 solid primarily metal oxides in high-temperature (400 - 1200 °C) desulfurization and found the 11 elements with potential as follows: barium, calcium, cobalt, copper, iron, manganese, molybdenium, strontium, tungsten, vanadium, and zinc [43]. In the case of the removal of H_2S from the waste tyre pyrolysis gas at 500 °C, barium, calcium and strontium cannot be applied since the temperature is not sufficiently high to begin the sulfidation. Widely used sorbents based on metal oxides including iron-based, manganese-based, zinc-based, calcium-based and copper-based have been recently discussed by Sadegh-Vaziri & Babler [41].

For example, ZnO shows an excellent efficiency of H_2S removal - 99.5% - in temperatures below 650 °C [39]. Marcantonio *et al.* [44] recently presented a very interesting simulation study on gasification combined with a hot gas cleaning system composed of a combination of catalyst sorbents inside the gasification reactor, catalysts in the freeboard and subsequent sorbent reactors. The researchers demonstrated that zinc oxide has been able to reach a removal of H_2S close to 100% H_2S removal for steam-containing syngas containing steam between 1.5% and 3%, which is an excellent result. Furthermore, ZnO also has the potential also to remove mercaptans from the stream of gas [45]. The chemical reactions between ZnO and H_2S that occur can be summarized as follows:

$$\text{Sulfidation: } ZnO + H_2S \rightarrow ZnS + H_2O \tag{4}$$

$$\text{Regeneration: } 2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \tag{5}$$

In turn, according to Westmoreland & Harrison [43], manganese-based sorbents also feature high effectiveness in H_2S removal from hot gases in a very wide range of temperatures. Manganese oxide presents a higher sulfidation reactivity in comparison to zinc oxide. However, the manganese sulfide produced cannot simply be regenerated at the same temperature with steam back to MnO [40,46].

In this paper, researchers have made an attempt to remove hydrogen sulfide from waste tyre pyrolysis gas produced in a fixed bed reactor under 500 °C and atmospheric pressure. Pyrolysis gas was subjected to the sorption process with the application of different NaOH solutions, which is dedicated to natural gas purification. Additionally, the sulfidation of H_2S was tested with metal oxides (ZnO and MnO) directly in the quartz reactor. To the best of our knowledge, similar studies have not been performed yet on a real pyrolysis gas obtained from waste tyres.

2. Methodology

2.1. Materials

A sample of ground mixed (car and truck) waste tyres with a particle size of about 5 mm was provided by the company *Recykl* located in Greater Poland (Poland). The size of the particles appears to be optimal from the point of view of the effectiveness of conversion [47]. It was placed indoors for several days before the experiment was conducted to reduce the moisture content since the ground tyres were stacked outdoors on the company premises. The proximate and ultimate analyses of the sample are shown in Table 1. and the higher heating value was measured as 33.3 MJ/kg [27]. The content of elemental sulfur is noticeably high (~2.2 wt.%) due to its introduction into the tyres during rubber vulcanization [48].

Table 1. Proximate and ultimate analysis of waste tyre samples [27].

Proximate analysis, % (on as received basis)		**Ultimate analysis, % (on dry ash free basis)**	
Water	2.3 ± 0.1	C	85.9 ± 0.2
Ash	7.3 ± 0.1	H	6.8 ± 0.2
Volatile Matter	66.3 ± 0.2	N	0.66 ± 0.1
Fixed Carbon by difference (=100%-W-VM-A)	24.1 ± 0.2	S	2.2 ± 0.2
		O by difference (=100%-C-H-N-S)	4.5 ± 0.2

The nitrogen (4.0) used as the carrying gas during the pyrolysis experiments was provided by *Linde*. In turn, the applied sorbents: sodium hydroxide (15% solution, AR quality) and manganese oxide (AR quality) were manufactured by *Chempur*, while zinc oxide (AR quality) was provided by *Merc*.

Furthermore, the sources of chemicals used in the quantification of bulky amounts of hydrogen sulfide using iodometric methods are presented in Table 2.

Table 2. Specification of chemicals used.

No.	Chemical	Source	Purity
1.	Iodine	Chempur	standard volumetric solution – 0.10 mol/L
2.	Sodium thiosulfate pentahydrate	Chempur	AR quality
3.	Acetic acid – solution 80 %	Eurochem BGD Sp. z o.o.	AR quality
4.	Sulfuric(VI) acid – solution 95 %	Chempur	AR quality
5.	Cadmium acetate dihydrate	Chempur	AR quality
6.	Starch, soluble	Sigma Aldrich	ACS reagent

2.2. Typical experiment conducted and equipment used.

Approximately 25 g of the tyre sample was placed inside a manufactured quartz reactor (see Figure 1), which in turn was set in a tube furnace (*Carbolite Gero*). The reactor was kept at 100 °C for 10 minutes to evaporate moisture traces, and then heated to the programmed temperature of the furnace (500 °C ±10 °C) with a heating rate of 5 °C/min. The temperature of the quartz reactor wall was also checked by an additional thermocouple (type N), and the measurements obtained were continuously saved onto an SD card and displayed on a temporary website. The reactor was kept at a steady temperature (500 °C±10 °C) for half an hour to ensure complete decomposition of the organic matter. Measurements continued while the furnace was cooled down to 450 °C. Before the beginning of heating, the reactor was flushed with nitrogen (2 l/min) for ten minutes to remove air from the chamber. A constant flow of nitrogen was kept in the majority of the experiments, controlled by two rotameters manufactured by *Cache* and *SKC*. The flow was divided – the lower flow (approximately 200 ml/min) of nitrogen was directed into the pyrolysis reactor and the higher flow (approximately 1800 ml/min) was added to the gas stream after the completed process (just before the analysis device). The condensable vapours released from the process were continuously cooled down and carefully collected. The temperature of gases after the reactor and after the cooler, as well as the ambient temperature, were also measured by thermocouples (type K), recorded and displayed live. In some experiments, the pyrolysis gas was collected in Tedlar® bags using a vacuum chamber and thereafter analysed on two gas chromatographs: 1) *Brücker SCION 436-GC* equipped with a pulsed flame photometric detector (PFPD), and 2) *Perkin Elmer Clarus 500* with system *Arnel 1115* equipped with thermal conductivity detector (TCD) and flame-ionisation detector (FID), while in most cases the gas was directed to the cleaning scrubber and analysed continuously by the gas analyser *Quintox Kane9206*. The pH measurements have been made by pH-meter *HACH HQ440d multi*.

In each absorption experiment, 250 ml of liquid was poured into a scrubber before the experiment and bubbled throughout the whole experiment. The scrubber was not heated, thus the temperature of the sorption process was ambient. Also, the pressure was kept normal. In turn, 0.5 g of metal oxides (ZnO, MnO) used as adsorbents were settled on a high temperature resistant glass fibre and placed inside the quartz reactor together with the tyre sample before the experiment. In addition, the water scrubber (250 ml) was applied in those experiments as well. The experiment with each particular sorbent/sorbent combination was triplicated, the results obtained were compared, and finally, averaged. The experimental setup (scheme and real photograph) is shown in Figure 1.

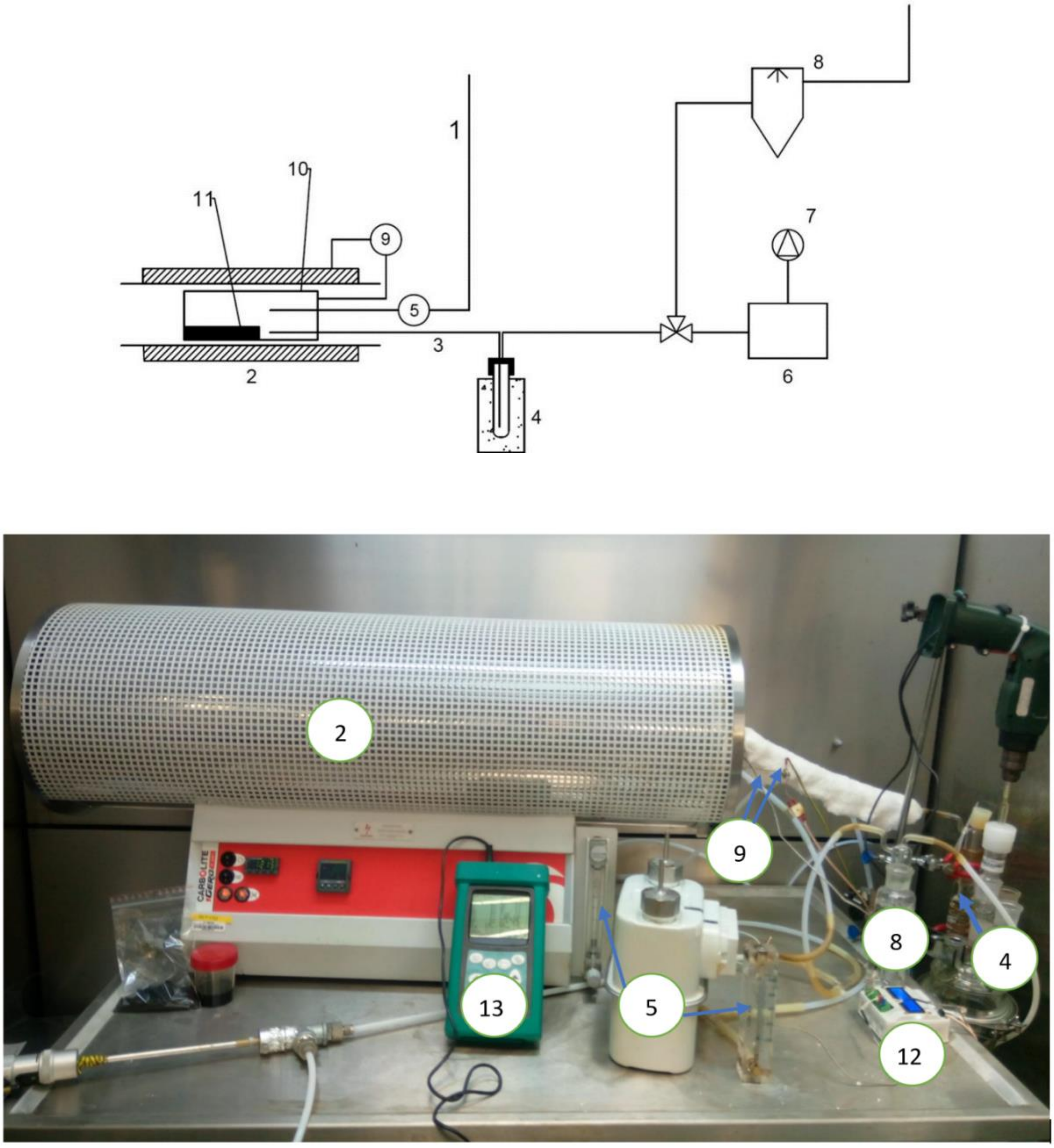


Figure 1. Experimental setup and schematic flow diagram for the production and cleaning of pyrolysis gas: 1 – nitrogen inlet , 2 – tube furnace , 3 – gas and vapors outlet, 4 – cooler, 5 – rotameter, 6 – vacuum chamber,7 – pump, 8 – scrubber, 9 – thermocouple, 10 – quartz glass reactor, 11 - tyre sample, 12 – temperature display, 13 – analyser display.

The measurement ranges for particular compounds analysed by gas chromatography are presented in Table 3. The further presented results of the GC analysis are accompanied by an expanded uncertainty for a 95% confidence level and k = 2.

The limit of quantification of the gas chromatograph *Brücker SCION 436-GC* and the gas analyser *Quintox Kane9206* are <500 ppm and <1000 ppm of H_2S, respectively. Therefore, the iodometric method was also applied according to the procedure described in BN-89 0541-03/05 [49] to estimate the real concentrations of hydrogen sulfide in the pyrolysis gas, which are expected to reach even 5 %. The detection and quantification limit for the iodometric method are 10 and $1{,}0\times10^5$ ppm respectively. The measurement range is wide in this case, however, the accuracy is relatively low and amounts to 15%. Nevertheless, it is acceptable to obtain reasonable estimates [38].

Table 3. Measurement range for particular compounds analysed by GC.

Compound	**Method**	**Measurement range, % mol/mol**
methane, ethane, ethene, propane, propene, butanes, butenes, 1,3-butadien	GC TCD/FID	0.001 – 100
pentanes	GC TCD/FID	0.001 – 0.5
C_{6+}	GC TCD/FID	0.001 – 5
nitrogen, carbon dioxide, helium, hydrogen, oxygen, carbon monoxide	GC TCD/FID	0.005 – 100
hydrogen sulphide	GC PFPD	0.00001 – 0.05
methyl mercaptan, ethyl mercaptan, propyl mercaptan, butyl mercaptan, carbonyl sulfide, carbon disulphide, dimethyl sulfide, dimethyl disulphide, methyl ethyl sulfide, diethyl sulfide, diethyl disulphide, dipropyl sulfide	GC PFPD	0.00001 – 0.05

2.3. Health and safety precautions

As mentioned in the Introduction, hydrogen sulfide is a dangerous and toxic compound, thus it was necessary to implement several solutions that ensure the health and safety of the laboratory work. First, the experimental setup was completely placed inside a very efficient fume hood with an exhaust gas flow of 1500 m^3/h. The main body and the handset of the *Quintox Kane9206* analyser also were most of the time under the fume hood, while the data was collected via Bluetooth connection. The analyser was taken outside the fume hood only during the flushing time. Secondly, next to the experimental setup was settled a data acquisition station. To ensure the safety of the research team, an additional H_2S sensor Dräger Pac 6000 was placed on the station (desk). The alarm (light, sound, and vibration) levels was programmed at 5 and 10 ppm. Finally, to avoid the unexpected explosion of flammable gases, the pyrolysis gas has been diluted with an inert one – nitrogen.

During gas collection experiments, only official disposable Tedlar® bags were used, and the vacuum chamber was applied to avoid pump damage and elevation of gas pressure. The sampling process was obviously conducted under the fume hood. All samples were then placed inside the expanded polystyrene box, sealed with special tape, and immediately transported to the GC analysis.

3. Results and discussion

3.1. Pyrolysis gas composition

Pyrolysis of waste tyres produced approximately 39 % of char, 44 % of oil and 17 % of gas, which is comparable to previous studies [50–54]. Table 4 presents yields of products from pyrolysis of waste tyres carried out in fixed bed reactors at 500 °C.

Table 4. Comparison of products yields from waste tyre pyrolysis in 500 °C.

Gas (wt%)	Oil (wt%)	Char (wt%)	Ref.
6.1	55.8	38.1	[50,51]
14	48	38	[52]
11.92	51.98	36.09	[53]
29	38	33	[54]
17	44	39	this work

In one experiment it was possible to obtain about 17 % of the gas which corresponds to nearly 4 l. The inert gas was used to flush the setup before heating, and then the whole gas produced during the experiment was collected in Tedlar® bags and the composition was tested for the main components and sulfur-containing compounds. The concentration of numerous 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 – has been investigated in a previous paper [27]. However, the gas obtained during the pyrolysis was divided into three portions. In this paper, the analysis of the gaseous mixture collected during the whole process has been investigated, so the averaged composition of the pyrolysis gas is presented in Table 5. Nitrogen from the flushing of the reactor was still a major component of the analysed gas and was excluded in the following analysis [55]. Additionally, in further experiments, the hydrogen sulfide concentration was measured while its emission was the highest, at a temperature above 380 °C.

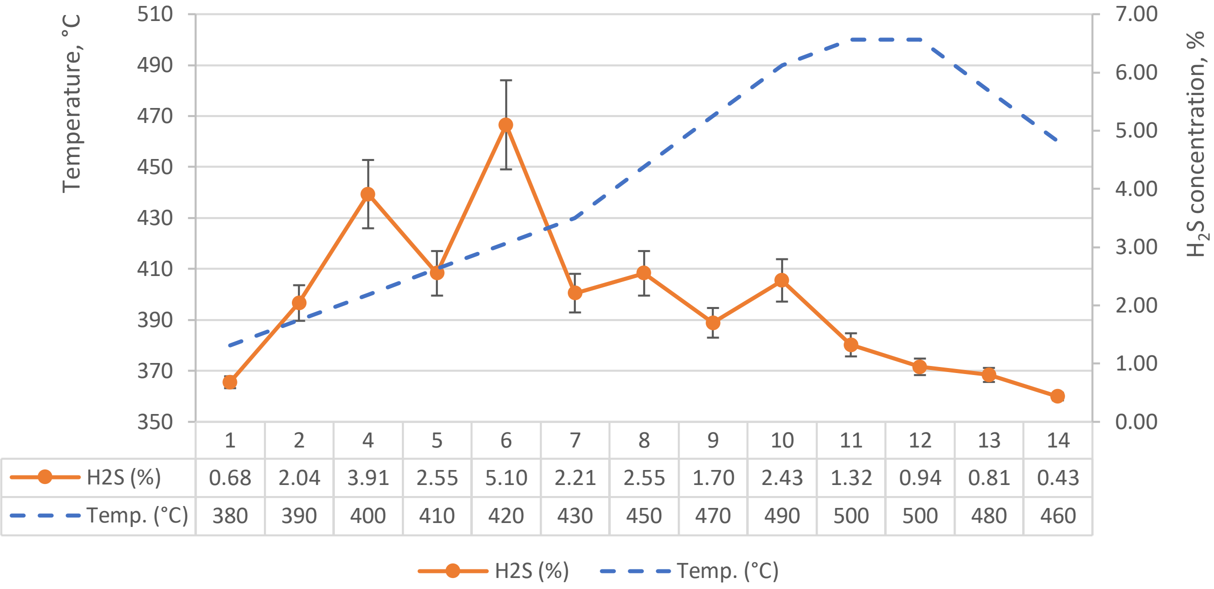
Table 5. Composition of pyrolysis gas from waste tyres.

No.	Compound	Concentration		Unit
1.	methane	24.458	±0.415	% mol/mol
2.	hydrogen	20.524	±0.839	% mol/mol
3.	ethane	9.877	±0.374	% mol/mol
4.	carbon dioxide	8.728	±0.217	% mol/mol
5.	iso-butene	7.074	±0.190	% mol/mol
6.	ethene	6.535	±0.248	% mol/mol
7.	propane	4.846	±0.261	% mol/mol
8.	propene	4.402	±0.237	% mol/mol
9.	hydrogen sulphide	3.635	±0.543	% mol/mol
10.	carbon monoxide	3.227	±0.025	% mol/mol
11.	oxygen	2.022	±0.189	% mol/mol

12.	i-butane	1.125	±0.133	% mol/mol
13.	1-butene	0.405	±0.048	% mol/mol
14.	C_{6+}	0.263	±0.027	% mol/mol
15.	T-2-butene	0.250	±0.030	% mol/mol
16.	1,3-butadiene	0.166	±0.019	% mol/mol
17.	C-2-butene	0.127	±0.009	% mol/mol
Sum: ~98				% mol/mol
18.	methyl mercaptan	> 500		$\times 10^{-4}$ %mol/mol
19.	carbonyl sulfide COS	> 500		$\times 10^{-4}$ %mol/mol
20.	ethyl mercaptan	106.87	±19.66	$\times 10^{-4}$ %mol/mol
21.	carbon disulphide CS_2	18.72	±3.14	$\times 10^{-4}$ %mol/mol
22.	n-propyl mercaptan	8.28	±1.47	$\times 10^{-4}$ %mol/mol
23.	i-propyl mercaptan	6.65	±1.18	$\times 10^{-4}$ %mol/mol
24.	dimethyl sulfide	4.18	±0.74	$\times 10^{-4}$ %mol/mol
25.	i-butyl mercaptan	1.47	±0.26	$\times 10^{-4}$ %mol/mol
26.	n-butyl mercaptan	1.13	±0.20	$\times 10^{-4}$ %mol/mol
27.	methyl ethyl sulfide	1.12	±0.20	$\times 10^{-4}$ %mol/mol
28.	s-butyl mercaptan	1.08	±0.19	$\times 10^{-4}$ %mol/mol
29.	tert-butyl mercaptan	0.74	±0.13	$\times 10^{-4}$ %mol/mol
30.	diethyl sulfide	0.46	±0.08	$\times 10^{-4}$ %mol/mol
31.	dipropyl sulfide	0.38	±0.07	$\times 10^{-4}$ %mol/mol
32.	diethyl disulphide	0.37	±0.07	$\times 10^{-4}$ %mol/mol
33.	dimethyl disulphide	0.18	±0.03	$\times 10^{-4}$ %mol/mol

As can be seen in Table 5, the pyrolysis gas produced consisted mainly of methane, hydrogen, ethane, carbon dioxide, iso-butene, hydrogen sulfide, propane and propene. Complete analysis is available as an *Appendix 1*. The aggregate concentrations of the above listed exceeded 80 % of the gas. Light hydrocarbons came mainly from the rupture of polybutadiene–styrene (one of the major components of rubber), which forms short aliphatic chains, as well as from secondary cracking reactions that are favoured by the high temperatures [56]. In this work, the pyrolysis gas obtained contained almost 25 % mol/mol of methane and more than 16 % mol/mol of C_2 gaseous hydrocarbons, among C_4 predominant iso-butene. In turn, hydrogen production slightly exceeded 20 % mol/mol, which is relatively high. The aromatization and cyclization reactions contributed to its production [56]. It was reported that, while the temperature of the process is increasing, the production of hydrogen increases, too. Li *et al.* [25] studied the pyrolysis of waste tyre rubber at 800 °C, and obtained up to 34.03 vol.% of hydrogen in the gas released without catalyst application. Carbon oxides (CO and CO_2) are about 12 % mol/mol of the pyrolysis gas. The researchers suggested that CO_X presence in pyrolysis gas is due to decarbonilation, decarboxilation reactions and char secondary reactions as well as the decomposition of inorganic compounds present in the tyres such as $CaSiO_4$, $CaCO_3$ or ZnO [56–59].

In turn, sulfur-containing pollutants in the pyrolysis gas probably came from −SH radicals from the decomposition of sulfur-containing compounds in tyres. The radicals react with −H and $-CH_3$ derived from the decomposition of polymers and result in the evolution of H_2S and methyl mercaptan (CH_3SH) [60]. These processes lead to the production of pyrolysis gas that contains significant amounts of hydrogen sulfide accompanied by mercaptans. The gradual evolution of H_2S during pyrolysis was measured using the iodometric method. The results are shown in Figure 2. As can be noticed, the highest concentrations were 5.1 %, 3.9 % and 2.6 % when inside the pyrolysis reactor it was 420 °C, 400 °C and 410 °C, respectively. An additional experiment was performed to measure the average concentration of H_2S in the pyrolysis gas collected throughout the entire experiment and it was 3.6 %. Since that point all recalled temperatures refer to the pyrolysis process conditions (inside the reactor), to make presented results easier to compare. Cheng *et al.*[60] also found the highest emission of H_2S at 420 °C, but their heating rate was 20 °C/min. Additionally, they showed that a higher heating rate promotes higher emission peaks of sulfur-containing pollutants. When the heating rate is low, the emissions seem to be more stable, which can be important from the point of view of industrial applications.



	1	2	4	5	6	7	8	9	10	11	12	13	14
H2S (%)	0.68	2.04	3.91	2.55	5.10	2.21	2.55	1.70	2.43	1.32	0.94	0.81	0.43
Temp. (°C)	380	390	400	410	420	430	450	470	490	500	500	480	460

Figure 2. Highest hydrogen sulfide emissions from pyrolysis of waste tyres.

Based on the composition of the main components of the pyrolysis gas, the average heating value was calculated and was about 30 MJ/kg, equivalent to approximately 34 MJ/m^3. The results are comparable to those obtained before [58,61,62]. However, the reported heating value of the pyrolysis gas from waste tyres varied from 12 MJ/m^3 up to 80 MJ/m^3 [16].

3.2. Purification of the pyrolysis gas from hydrogen sulfide – water scrubber (blank test)

Hydrogen sulfide is quite well dissolved in water (0.5 g/100 ml at 20 °C[63]), but water is not considered a commercial absorbent for H_2S removal. Nevertheless, in this work a distilled water scrubber has been applied as a blank test to obtain data for comparison with the effectiveness of different sorbents. In Figure 3, the measured hydrogen sulfide emissions from the pyrolysis of the waste tyres without any treatment as well as with the application of a water scrubber are shown. It must be highlighted that those measurements came from the *Quintox Kane9206* and the pyrolysis gas was diluted so that the concentration would not exceed 1000 ppm to prevent sensor destruction.

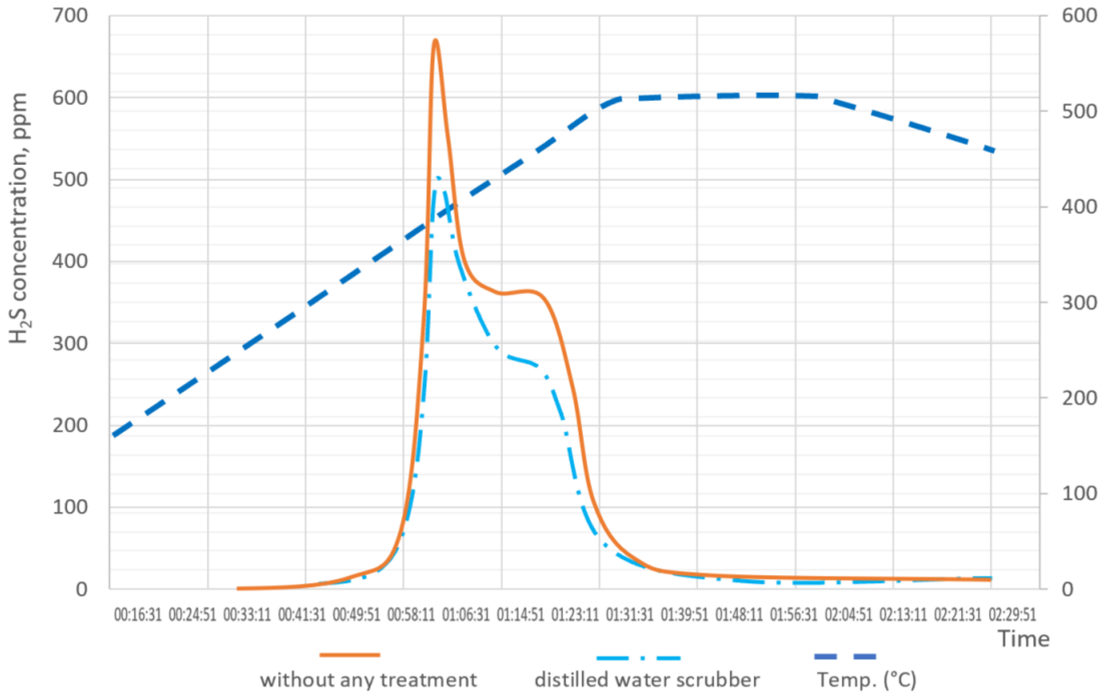


Figure 3. Hydrogen sulfide concentrations in pyrolysis gas without any treatment and with water scrubber.

As can be seen in Figure 3, the highest measured concentration of H_2S without any treatment was 675 ppm, while with a H_2O scrubber application it was 500 ppm. Emissions began at 260 °C reaching maxima at 385 °C. It is worth mentioning that the researchers found a difference in temperature for the highest emission of H_2S measured by the iodometric method – 420 °C (see Figure 2) – and by the automatic analyser – 385 °C (see Figure 3), which may be due to the time required for sampling the gas during the first method. The results obtained from the analyser are in better agreement with the study by Cheng *et al.* [60]. They found the highest hydrogen sulfide emission at ~ 380 °C, when the heating rate was the same as in this work - 5°C/min. The H_2S concentration was very high to around 460 °C and then quite rapidly decreased to the level of 50 ppm. After that, the amount of hydrogen sulfide gradually decreased to several ppm at 450 °C, when the measurements were completed. The distilled water scrubber removed moderate amounts of hydrogen sulfide emitted. Nevertheless, this efficiency - below 30 % - is definitely too low to apply it commercially.

3.3. Purification of the pyrolysis gas from hydrogen sulfide – NaOH solutions

The first absorbent, which was chosen to remove hydrogen sulfide from the pyrolysis gas, was sodium hydroxide. Álvarez-Cruz *et al.* [37] decided to analyse the absorption efficiency of several different NaOH solutions as follows: 0.01, 0.1, 0.5, 1 and 2 M. They observed that at the lowest initial NaOH concentration the H_2S absorption and neutralization was completed in less than 5 minutes and after this time the NaOH concentration remained constant. Similar behaviour was measured for the 0.1 and 0.5 M samples, but the time for maximum neutralization was 20 and 40 minutes, respectively. Furthermore, hydrogen sulfide consumed 92% of the initial NaOH from the 0.1 M solution, while in others it was 20, 77.6, 48, and 30 for the 0.01, 0.5, 1 and 2 M solutions, respectively. It was explained that at high NaOH concentrations, H_2S dissolves only slightly due to acid-base equilibria. Thus, the dissolution of large amounts of H_2S requires longer reaction times and becomes less effective. 0.1 M NaOH solution was suggested as the best way to obtain sulfides when H_2S is absorbed under the presented conditions.

In this work 0.01, 0.05 M, 0.1 M and 0.2 M NaOH solutions were tested. Additionally, a 15 % NaOH solution was checked since it is also often used in mercaptans removal [45]. To the best of our knowledge, similar studies have not been performed yet on a real pyrolysis gas from waste tyres. As can be seen in Figure 4, there is a small measured hydrogen sulfide emission in 0.2 M NaOH solution around 300 °C and then continuous emission began at 425, 455, and 450 °C when 0.2, 0.1 and 0.05 M solutions were applied, respectively. In turn, the peaks of H_2S concentration – 24 ppm, 17 ppm and 12 ppm – were noticed at 475, 500, and 495 °C, which is presented in Table 6. After about 10 minutes at 500 °C the concentration of H_2S tended to several ppm and became steady until the end of the measurements. Additionally, the total efficiency of hydrogen sulfide removal has been calculated. It is expressed as follows:

$$\eta_{tot.} = \frac{\int_{t_0}^{t_1} C_0 - \int_{t_0}^{t_1} C_1}{\int_{t_0}^{t_1} C_0} \cdot 100\% \qquad (7)$$

where:
$\eta_{tot.}$ - total efficiency, %
C_0 – concentration without treatment, ppm
C_1 – concentration after treatment, ppm
t_0 – beginning of the measurements, s
t_1 – end of the measurements, s

The best total efficiency in H_2S removal reached application of 0.05 M NaOH solution and it was about 94 % compared to the measured emission without any treatment. Moreover, the difference between the initial and final pH of the scrubber was the highest, which may indicate the most efficient process of the neutralization reaction between the OH^- and H^+ ions. Argonul *et al.* [38] were able to obtain a H_2S removal efficiency greater than 99% with two NaOH scrubbers applied. However, the demonstration plant was designed for coal gasification and the composition of the gas was different from that presented in this work. Nevertheless, the results are promising because it may be assumed that it is possible to obtain even higher hydrogen sulfide removal efficiencies, when suitable technical solutions are applied.

Table 6. Comparison of NaOH solutions in H_2S removal

NaOH solution	**Highest H_2S concentration, ppm/ Temperature, °C**	**Removal efficiency, %**	**Initial pH**	**Final pH**
0.05 M	12/495	94	12.65	11.44
0.1 M	17/500	93	12.80	12.46
0.2 M	24/475	90	12.92	12.59

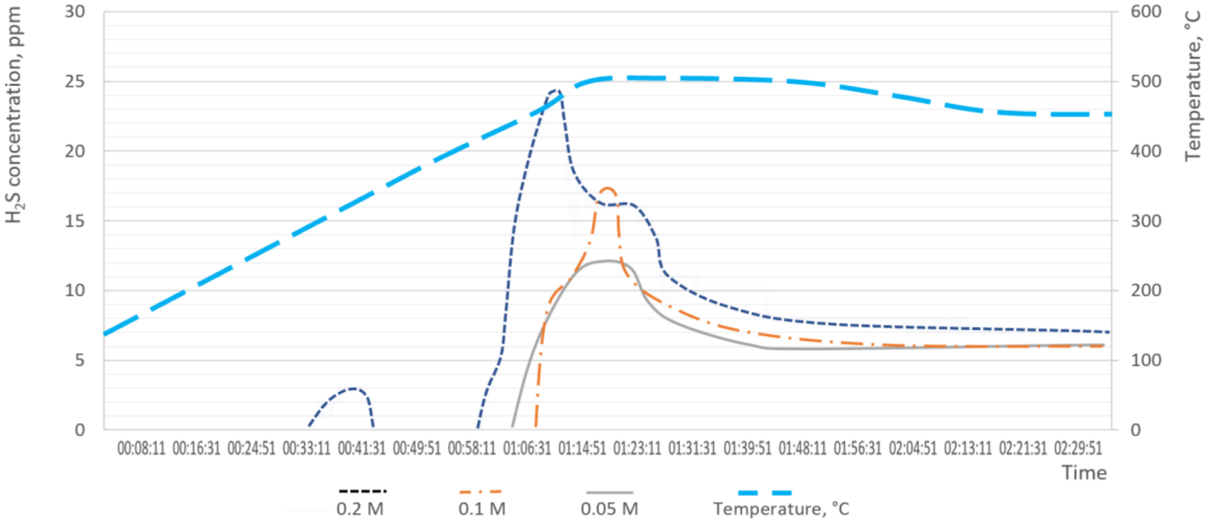


Figure 4. Measurements of H_2S concentration in dependence on the applied NaOH solution.

The effectiveness of H_2S removal is presented in Figure 5. The curves show the temporary efficiency, and were obtained through application of Equation 6.

$$\eta_{temp.} = \frac{C_0 - C_1}{C_0} \cdot 100\% \tag{6}$$

where:
$\eta_{temp.}$ - temporary efficiency, %
C_0 – concentration without treatment, ppm
C_1 – concentration after treatment, ppm

The initial periods without hydrogen sulfide emission as well as the final ones after exhaustion of sorption capacity were removed from the figure to make them more understandable and effortless in comparison. It can be seen that the curves for 0.1 M and 0.05 M of the NaOH solutions are quite similar. However, the minimum that corresponds with the highest measured concentration of H_2S in each experiment is deeper in the case of 0.1 M of NaOH. In the case of 0.2 M of NaOH solution there are two minima, due to the presence of emission around 300 °C and then continuous emission from 425 °C, and the second one is much deeper (the removal efficiency dropped to around 40 %) than the corresponding ones in 0.1 M and 0.05 M.

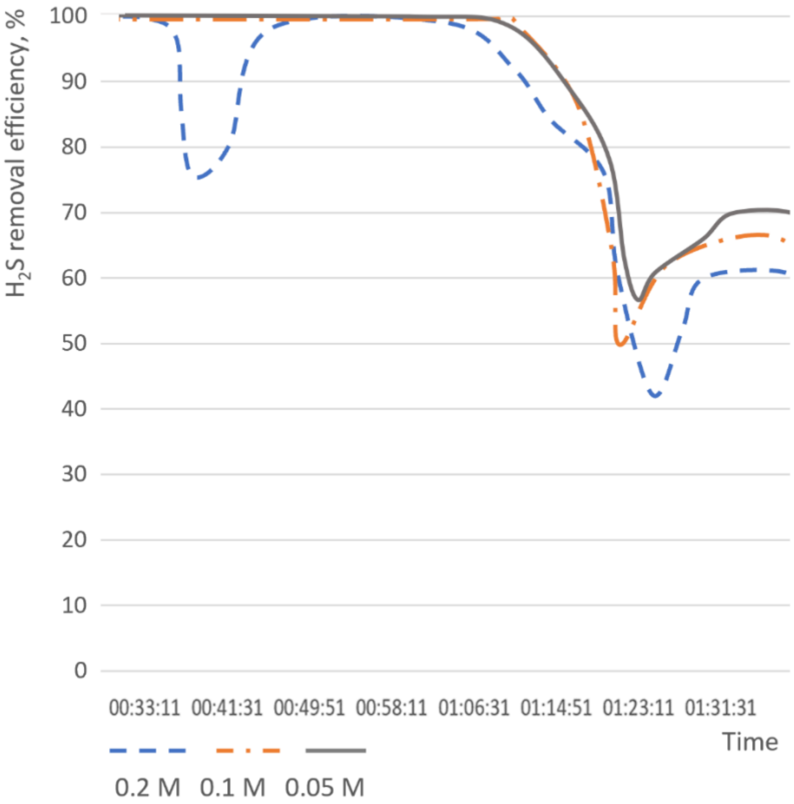


Figure 5. Temporary removal efficiency of hydrogen sulfide during the process – different NaOH solutions applied.

After conducting the experiments described above, two additional series have been done. Since the least concentrated solution appeared to be optimal, we decided to check for an even lower concentration of NaOH – 0.01 M. This solution contains too small amounts of available –OH ions for effective removal of H_2S. The sorption capacity ran out quickly – H_2S appeared at 420 °C and easily reached 143 ppm at 500 °C. A series of experiments with concentrated 15 % NaOH was also conducted. It effectively removed hydrogen sulfide with the highest measured concentration of 13 ppm at 495 °C, which is comparable to the 0.05 M solution. Obviously, application of a less concentrated compound means lower costs, and thus the second option is recommended. The successful application of such a low concentration of NaOH in the removal of hydrogen sulfide from pyrolysis gas seems to be a very promising solution because of the very low cost of caustic soda diluted in water. The spent sorbent contains sulphides, considered as potentially valuable products [37], and has a high pH that possibly can be reduced when recirculation combined with gradual exchange of a spent sorbent into a fresh one is applied.

3.4. Hydrogen sulfide removal – metal oxides

The chosen adsorbents for the removal of hydrogen sulfide from the pyrolysis gas were two metal oxides, ZnO and MnO. Adsorption is a process by which a solid, the adsorbent, holds molecules of a gas or liquid, unlike absorption where the sorption process takes place in the entire volume of the liquid absorbent [64]. Both zinc and manganese oxides are solid state in a form of fine powder, white and dark grey in colour, respectively. Zinc oxide is considered the most favourable for hydrogen sulfide removal from hot gases among all 11 elements with potential [43,65], while manganese oxide features a very good stability and effectiveness in a wide range of temperatures [66]. Figure 6 presents the results of ‘hot gas desulfurization’ experiments with the application of the oxides mentioned above. Zinc oxide reduced the H_2S concentration by more than half, which reached a peak of 155 ppm at 450 °C, while the highest measured level of hydrogen sulfide when the manganese oxide was applied – 265 ppm – was found at 475 °C. In both cases, the level of H_2S rapidly decreased just after the maximum, subsequently stabilized at several ppm after approximately 20 minutes at 500 °C.

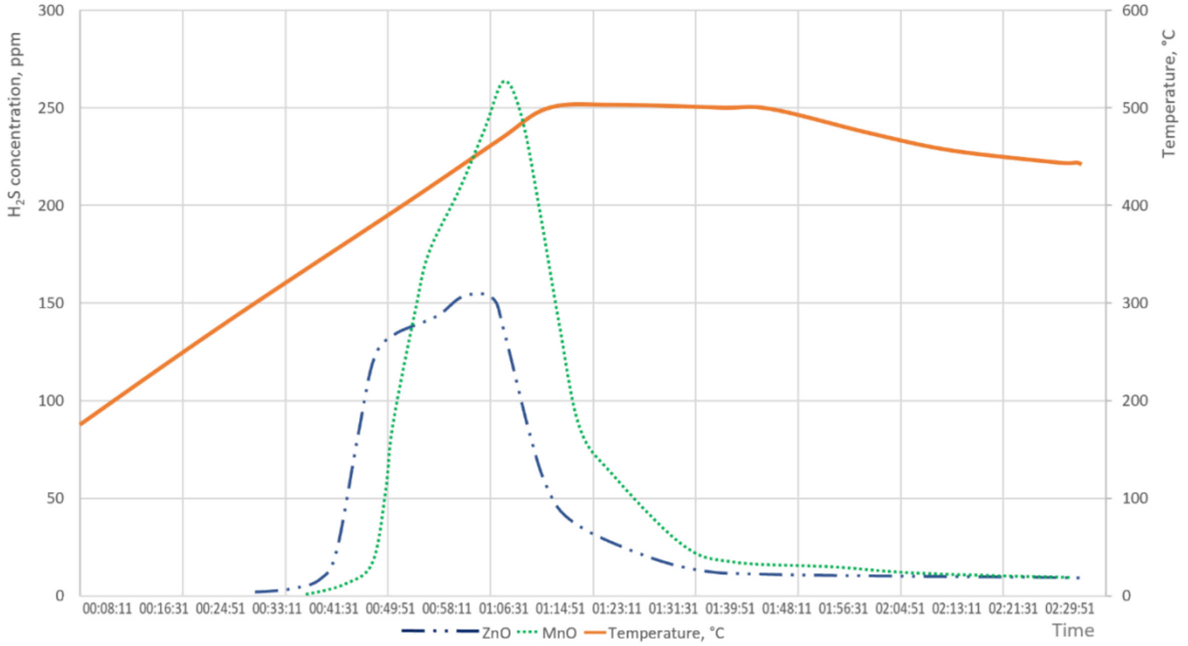


Figure 6. Measurements of H_2S concentration in dependence on the applied metal oxide.

As can be seen in Figure 7, ZnO presents a better effectiveness of H_2S removal (~ 55%) than MnO (~ 38%). However, these results are much lower than those reported in a modelling study [44], where the H_2S removal efficiency from syngas was called even ‘quasi-total’, almost 100%. In turn, Mandilas *et al.* [67] presented an innovative device for hot flue gas cleaning – a monolithic reactor coated with ZnO/CuO. The analysed gas stream was simulated and consists of H_2, H_2O, CO_2, CO, N_2 and H_2S (25 ppm). The average H_2S removal efficiency increased with temperature from ~96% at 160 °C to ~99.9% at 250 °C and remained at the level 99.9% for the remainder of the temperature range, up to 400 °C.

In the case of ZnO, the reduction of effectiveness is more gradual and slower. Moreover, the minimum is visible, but soon after that the removal efficiency quickly reached 0%, which means that the measured concentration of H_2S was not less than at the analogical time during the process without the purification applied – the sorption capacity ran out. In the case of MnO, the removal efficiency went down rapidly and reached 0 % even before the minimum was visible. However, even the better one is not sufficient to ensure the proper quality of the pyrolysis gas for utilization as a fuel. Thus, additional operations for extending the sorption capacity of metal oxides are highly desirable. There are several options for improving the efficiency of the hot gas desulfurization process, e.g. adding second metal elements to ZnO or MnO that boosts its mechanical strength and stability, using spinel or perovskite oxides, application of metal oxides on mesoporous support, etc. [40]. On the other hand, a combination of different sorbents may contribute to an improvement in H_2S removal, too.

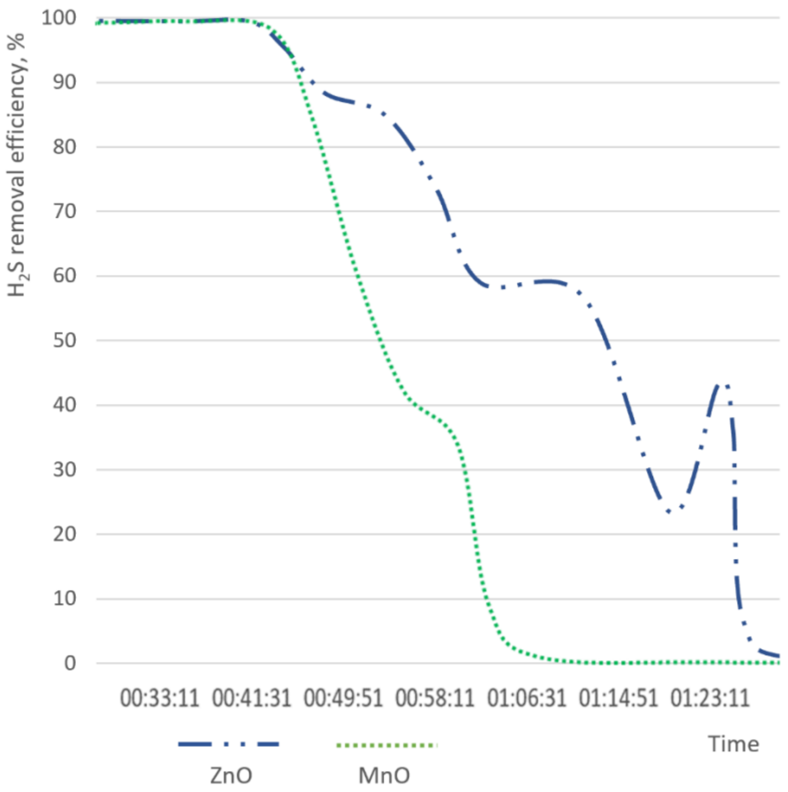


Figure 7. Hydrogen sulfide temporary removal efficiency during the process: metal oxides applied.

3.5. Hydrogen sulfide removal – 0.05 M NaOH solution combined with ZnO

After conducting all the experiments described above, better metal oxide – zinc oxide - and the best solution of NaOH – 0.05 M - were applied together, as it was expected to obtain complete removal of hydrogen sulfide from the pyrolysis gas. It was assumed that the zinc oxide present inside the reactor would decrease the concentration of hydrogen sulfide by binding the sulfur in the form of solid zinc sulfide [41]. The gas released from the reactor should have a reduced concentration of H_2S, possibly to be fully removed by the NaOH solution. The results of these experiments are shown in Figure 8 in comparison with the previous effectiveness of the NaOH solution and ZnO used separately. Surprisingly, the concentration of H_2S measured when the NaOH solution was adopted together with ZnO was higher than it was when applied singly. To be sure of this effect reliably, the experiment was performed five times. The H_2S removal efficiency of the sorbent combination was approximately 90 % while 0.05 M NaOH solution alone was able to provide almost 94 %.

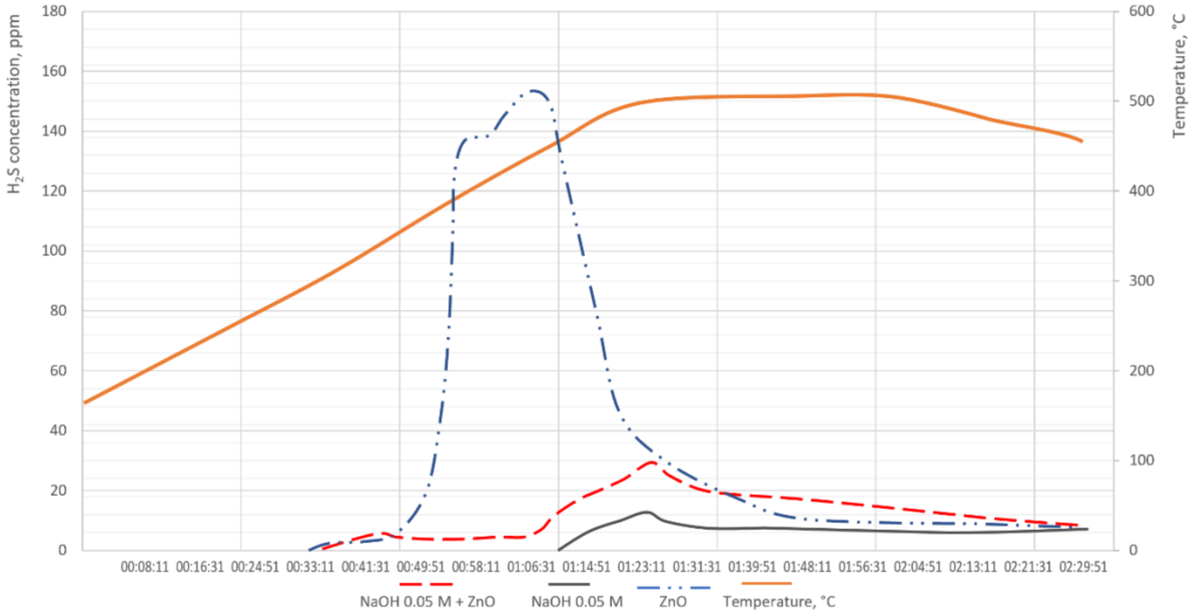


Figure 8. Measurements of H_2S concentration in dependence on the applied sorbent/sorbents.

A possible explanation for this phenomenon may be the reaction between ZnO and NaOH. It is highly possible that some particles of zinc oxide were transferred with the gas stream to the scrubber. In the water scrubber applied with ZnO adsorption, several little droplets of oil have appeared, and their formation was probably due to oxide particles behaving like condensation nuclei. From our point of view, this was not favourable since there is a likelihood of the following reaction due to the amphoteric nature of zinc oxide:

$$ZnO + 2NaOH \rightarrow H_2O + Na_2[Zn(OH)_4] \quad (5)$$

This reaction may have contributed to the reduction in the H_2S sorption capacity of sodium hydroxide.

4. Conclusion

The paper presents an investigation of the pyrolysis gas obtained from waste tyres. First, the gas has a high heating value - approximately 34 MJ/m^3, since it contains significant amounts of hydrocarbons and hydrogen. Second, the gas features high concentrations of sulfur-containing compounds which are predominantly hydrogen sulfide (average concentration measured by iodometric method – 3.6 %), methyl mercaptan (>500 ppm) and carbonyl sulfide (>500 ppm). According to those facts, the pyrolysis gas can be considered as a valuable gaseous fuel, but it needs pre-treatment focused on desulfurization.

Special attention was given to the removal of hydrogen sulfide in order to prepare the pyrolysis gas for further utilization as a source of energy comparable to that of natural gas. Sodium hydroxide has the best potential for hydrogen sulfide removal of the proposed sorbents, while the most effective concentration is 0.05 M, which reduces the concentration of H_2S in diluted gas to 12 ppm, reaching a total removal efficiency of about 94 %. However, increasing the amount of solution used in the cleaning process did not allow a complete removal of H_2S. Therefore, we recommend a gradual exchanging of the solution with a fresh one either just after the appearance of the first traces of H_2S in the analysed gas, which is around 450 °C, or continuously from the beginning of the process. Furthermore, the combination of ZnO inside the pyrolysis reactor with the NaOH scrubber was investigated, since it was expected that ZnO would lower the H_2S level before the gas reached the scrubber, and then the 0.05 M NaOH solution might be able to remove all hydrogen sulfide. Surprisingly, this combination did not improve the overall efficiency of H_2S removal, probably due to the amphoteric nature of zinc oxide. On the other hand, depending on the pyrolysis gas utilization method applied in a commercial plant, it may be favourable to use hot gas cleaning with either zinc or manganese oxide, but the sorption capacity should be improved first by available methods.

Nevertheless, the proposed cleaning methods make the gas more useful as a gaseous fuel and safer for the environment. Reaching a quality of waste tyres pyrolysis gas comparable to that of natural gas seems to be possible.

The paper was financially supported by the Department of Air Conditioning, Heating, Gas Engineering and Air Protection; Wroclaw University of Science and Technology (No. 821110416 N_PODST_BAD_EXP_BAM).

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