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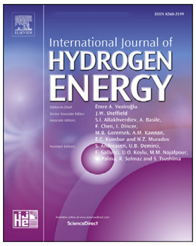

Experimental investigation of waste tyres pyrolysis gas desulfurization through absorption in alkanolamines solutions

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HIGHLIGHTS

- Pyrolysis gas is a valuable fuel, but it needs pre-treatment focused on desulfurization.
- Raw pyrolysis gas contains high concentrations of H_2S (up to 5.1%) and mercaptans.
- Solutions of alkanolamines can be applied in desulfurization of pyrolysis gas.
- DEA, MDEA and as their blends are effective in cleaning pyrolytic gas from H_2S (>97%).
- Blends of DEA/MDEA can also remove other sulfur containing compounds.

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ABSTRACT

Pyrolysis of waste tyres produces harmful hydrogen sulfide and other mercaptan compounds as by-products. The current study is concerned with the purification of hydrogen-rich pyrolysis gas from hydrogen sulfide gas that is present in a great amount (up to 5.1% mol at 420 °C), and mercaptans that are also problematic impurities. The method proposed is absorption by alkanolamines which is one of the most economical methods applied in natural gas sweetening. However, it has not been adopted in waste tyre pyrolysis gas purification yet. Two organic absorbents were tested, diethanolamine (DEA), N-methyldiethanolamine (MDEA) as well as theirs blends, at various concentrations. The application of 30 wt% DEA in water reduced H_2S emission by 98%. In turn, 40 wt% MDEA aqueous solutions reduced H_2S emission by 97%. The best results were produced when 30 wt% DEA was mixed with 40 wt% of MDEA (1:1 vol ratio) which allowed a removal of 99% of H_2S from the pyrolysis gas. Moreover, the maximum H_2S emission was 7 ppm, and a level below 5 ppm was kept for 99% of experiments duration. Finally, the application of this mixture also reduced significantly the concentrations of other sulfur-containing compounds such as methyl mercaptan and carbonyl sulfide (a minimum of 98%), ethyl mercaptan (~90%), and carbon disulphide (by more than 99%). Thus, aqueous solvent mixture of 30 wt% DEA

Abbreviations: CAS, Chemical Abstracts Service; COS, carbonyl sulfide; DEA, diethanolamine; GC, gas chromatography; K, rate constant; MDEA, N-methyldiethanolamine; PFPD, pulsed flame photometric detector; ppm, parts per million.

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with 40 wt% of MDEA (1:1 v/v) can be recommended as a potential desulfurization method for waste tyres pyrolysis gas.

Introduction

Every year, over 1.5 billion tyres lose their usefulness [1]. In line with the principle of a circular economy, they should be reprocessed into new materials or fuels, whether liquid, solid or gaseous. The importance and challenges related to the utilization of waste tyres have been discussed previously, especially in the contexts of high emission of gasses and byproducts. Available utilization methods include but are not limited to re-treading, reclaiming, combustion, grinding and pyrolysis [2]. Pyrolysis seems to be very attractive since it allows to reduce the amount of bulky waste, and at the same time to produce valuable materials such as limonene [3], diesel-like fuels [4] or energy [5]. On the other hand, the process itself is endoenergetic, so the external source of energy is needed. The most reasonable option might be to utilize the pyrolysis gas in order to heat the pyrolysis reactor (except the start-up phase when natural gas can be used instead) [6].

Pyrolysis gas features heating value around 35 MJ/kg that is comparable to natural gas [7]. It is composed mainly of hydrogen, light hydrocarbons, carbon oxides, and sulfur-containing compounds especially hydrogen sulfide and mercaptans (thiols) as a major impurities. In previous works [7,8] the authors presented the concentrations of numerous sulfur-containing compounds that feature disgusting smell and toxicity, including hydrogen sulfide and mercaptans. Hydrogen sulfide average content in pyrolysis gas was very high − 3.6 mol %, and reached even 5.1% mol at 420 °C [7], taking into consideration the fact that concentrations above 50 ppm are very dangerous for humans [9].

Pyrolysis gas from waste tyre has to be cleaned prior utilization. For instance, Abdallah et al. [10] highlighted the need of cleaning the pyrolysis gas before combustion because of the hydrogen sulphide presence, also Aylon et al. [11] mentioned that the proper gas cleaning instalation should be included in waste tyre pyrolysis plant to avoid emissions of acid gases. Removing H_2S is essential to prevent corrosion of equipment and pipelines as well as to meet fuel gas requirements. Moreover, removal of H_2S to a very low level is mandatory for environmental reasons [12]. Desulfurization of waste tyres pyrolysis gas is an important practice since according to the Industrial Emission Directive [13] pyrolysis plant, in which occurs subsequent combustion of produced gases, is treated the same as waste incineration plant. Thus, it has to fulfil very strict emission limits, that is a serious limitation for development of the waste tyres pyrolysis process However, there is an exception from above mentioned rule, namely pyrolysis plant does not have to meet the emission limits if the produced pyrogas is cleaned before combustion and cannot produce pollution worse than natural gas combustion. According to above, researchers are looking for a suitable method for pyrolysis gas desulfurization to ensure the quality of the pyrolysis gas comparable with natural gas.

One of the promissing method can be absorption of sulfur-containing compounds in aqueous solution of alkanolamines, such as diethanolamine (DEA) and N-methyldiethanolamine (MDEA). Important advantages of the method is the low cost of removal even very high amounts of acid impurities, and the possibility of regeneration [14,15]. For the H_2S-amine-H_2O blend, the following equilibrium reactions take place in the bulk of the liquid [16–18]:

Water ionization:

$$2H_2O \overset{K_{H_2S}}{\Leftrightarrow} H_3O^+ + OH^- \tag{1}$$

Dissociation of hydrogen sulfide:

$$H_2O + H_2S \overset{K_{H_2S}}{\Leftrightarrow} H_3O^+ + HS^- \tag{2}$$

Dissociation of bisulfide:

$$H_2O + HS^- \overset{K_{HS^-}}{\Leftrightarrow} H_3O^+ + S^{2-} \tag{3}$$

Dissociation of protonated DEA:

$$H_2O + (CH_2CH_2OH)_2NH_2 + \overset{K_{DEA}}{\Leftrightarrow} H_3O^+ + (CH_2CH_2OH)_2NH \tag{4}$$

Dissociation of protonated MDEA:

$$H_2O + CH_3NH(C_2H_4OH)_2 + \overset{K_{MDEA}}{\Leftrightarrow} H_3O^+ + CH_3N(C_2H_4OH)_2 \tag{5}$$

Additionally, in the liquid film the following reactions between the gas and the absorbents occur instantaneously, which involve a proton transfer:

$$(CH_2CH_2OH)_2NH + H_2S \overset{K'_{DEA}}{\Leftrightarrow} HS^- + (CH_2CH_2OH)_2NH_2{}^+ \tag{6}$$

$$CH_3N(C_2H_4OH)_2 + H_2S \overset{K'_{MDEA}}{\Leftrightarrow} HS^- + CH_3NH(C_2H_4OH)_2{}^+ \tag{7}$$

To our best knowledge, there has been very little work that investigated the cleaning of waste tyre pyrolysis gas so far, while the problem of pyrolysis oil desulfurization is under rapid development [19]. Recently, Hu et al. [20] studied hot desulfurization of oil derived from co-pyrolysis of biomass and polymer waste. The process was based on molten carbonates (Li_2CO_3–Na_2CO_3–K_2CO_3) and conducted in 500 °C. Result showed high sulfur-containing compounds removal efficiency. Kaur *el al.* [21] underwent oxidative desulfurization of waste tyre pyrolysis oil. They developed and tested two categories of titanium-incorporated mesoporous supports with 20 wt% loaded heteropoly molybdic acid catalyst (HPMo/Ti–Al_2O_3 and HPMo/Ti-TUD-1) as well as several different oxidants. The most successful results were obtained when the second support was applied using hydrogen peroxide as an

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oxidant. Previously, Czajczyńska et al. [7] investigated the absorption and adsorption of H_2S from waste tyre pyrolysis gas by inorganic materials such as sodium hydroxide solutions at various concentrations and metal oxides. The best H_2S removal efficiency – 94% - was noticed for 0.05 M solution of NaOH.

In this study Authors investigate the possibility and effectiveness of the application of aqueous solutions of DEA and MDEA as well as their blends, on the removal of hydrogen sulfide from waste tyres pyrolysis gas. The pyrolysis of waste tyres was conducted at 500 °C under atmospheric pressure in a fixed bed. Additionally, the effectiveness of mercaptans and other sulfur-containing compounds removal was investigated for the most promising solvents solutions.

Methodology

Materials

A sample of finely ground waste tyres was collected from the Polish company *Recykl*, and then it was stacked indoors for several days before the experiment was conducted to reduce the moisture traces. The proximate and ultimate analyses of the sample were performed and presented before, the higher heating value was - 33.3 MJ/kg [8]. It is worth noting that the elemental sulfur content in the sample directed to the pyrolysis process was high (~2.2 wt%) since it is a key agent in rubber vulcanisation process [22]. The specifications and sources of the chemicals used in this work are summarized in Table 2.

Typical experiment conducted and equipment used

The pyrolysis process as well as health and safety precautions were described in our previous paper [7]. Therefore, we only refer to a brief summary here. About 25 g of sample was pyrolyzed in quartz reactor externally heated by tube furnace. First, the reactor was kept at 100 °C for 10 min to evaporate the moisture residues and subsequently heated up to 500 °C (heating rate:5 °C/min), and then the set temperature was held for 30 min. Nitrogen has been used for flushing the system before heating and then it was used as a carrying gas. Two rotameters manufactured by *Cache* and *SKC* were used to control the gas flow while thermocouples type K and type N measured temperatures in different points of the process. The released vapours were continuously cooled down and collected as a condensing oily phase. The pyrolysis gas after the cooler was directed to the cleaning scrubber and the concentration of H_2S was measured continuously by gas analyser *Quintox Kane 9026*. In each experiment 250 ml of liquid absorbent, with desired concentration, was bubbled during the whole experiment. The experiment with each particular absorbent/absorbent combination was replicated, the results obtained were compared, and finally averaged. The scheme of experimental set-up is shown in Fig. 1.

Additionally, for the most efficient sorbent solutions, analysis of various sulfur-containing compounds (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) in cleaned pyrolysis gas was performed. In those cases, samples of gas were collected in Tedlar® bags using a vacuum chamber. Gas have been collected during 1 min for every 5 min. Taken samples thereafter were analyzed on gas chromatograph *Brücker SCION* 436-GC equipped with a pulsed flame photometric detector (PFPD). The measurement range for all tested compounds was 0.00001–0.05%. The further presented results of the GC analysis are accompanied by an expanded uncertainty for a 95% confidence level and k = 2.

The total efficiency of hydrogen sulfide removal by different applied absorbents has been calculated. It is expressed as follows [7]:

$$\eta_{tot.} = \frac{\int_{t_0}^{t_1} C_0 - \int_{t_0}^{t_1} C_1}{\int_{t_0}^{t_1} C_0} \cdot 100\% \qquad (8)$$

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

Results and discussion

Diethanolamine (DEA) – hydrogen sulfide removal

Primary and secondary alkanolamines such as diethanolamine (DEA) are used for general deacidification. Diethanolamine was the first organic solvent investigated in this study which showed a very good hydrogen sulfide capture from the pyrolytic gas stream. Chemical formula of DEA is $(CH_2CH_2OH)_2NH$, which spatial arrangement presented in Fig. 2. Two types of hydrogen bonds S–H···N and O–H···S formed between H_2S and alkanolamines water solutions were considered to be the driving forces in the absorption process. H_2S can behave as a hydrogen bond acceptor and a donor [23].

Table 2 – Specification of used chemicals.

No.	Chemical	CAS registry number[a]	Source	Purity
1.	Nitrogen	7727-37-9	*Linde Gaz Polska*	technical (4.0)
2.	Diethanoloamine	111-42-2	*Chempur®*	analytical reagent
3.	N-methyldiethanoloamine	105-59-9	*Thermo Scientific™*	analytical reagent

[a] unique numerical identifier assigned by the Chemical Abstracts Service (CAS).

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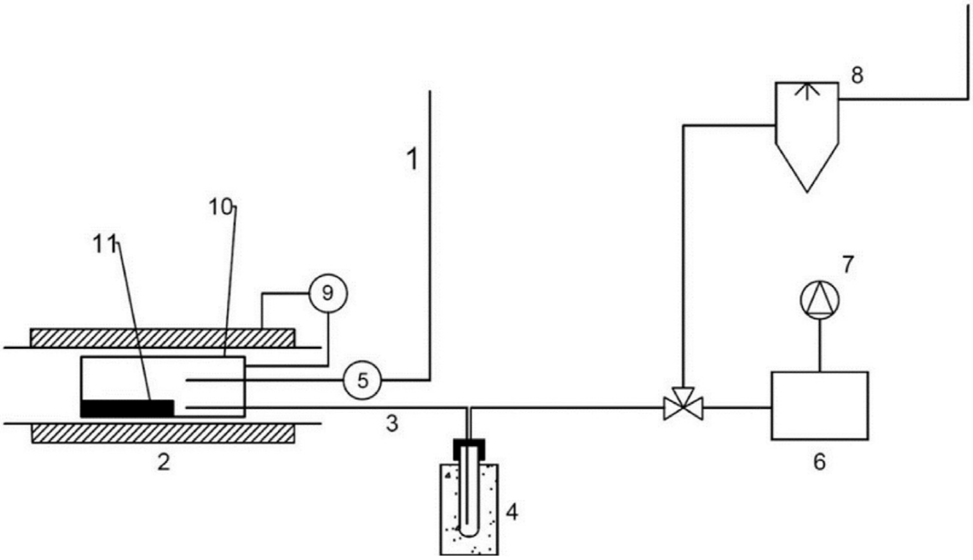

Fig. 1 – Experimental set-up for production and cleaning of pyrolysis gas: 1 – nitrogen inlet, 2 – tube furnace, 3 – gas and vapours outlet, 4 – cooler, 5 – rotameter, 6 – vacuum chamber,7 – pump, 8 – scrubber, 9 – thermocouple, 10 – quartz glass reactor, 11 - tyre sample [7].

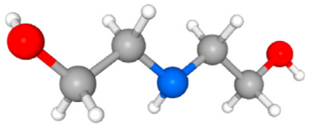

Fig. 2 – Diethanolamine – 3D model [24].

Based on literature data [25–27] 25, 30 and 35 wt% solutions of DEA in distilled water have been chosen for experiment and tested. The lower concentrations produced poor results of lower H_2S removal efficiency, while the very high concentration did not provide sufficiently aqueous environment which is necessary for the reactions described in Equation 1.-7. Obtained results are presented in Figs. 3 and 4. As can be seen from Fig. 3., the emission of hydrogen sulfide when the purification was applied, was very low (below 20 ppm) in comparison with the test without any treatment. Maximum concentration of H_2S in the raw diluted gas was as high as 675 ppm. The highest emission range of H_2S from the pyrolysis without gas cleaning applied – from 350 ppm up to 675 ppm – has been observed between 65 and 95 min of the experiment. This period of time corresponds the temperature range 365–450 °C inside the pyrolysis reactor. This is in good agreement with previously done thermogravimetric analysis in which temperature range between 350 and 500 °C featured the most rapid evolution of volatiles – gases and vapours [28]. More detailed information about H_2S emission from waste tyre pyrolysis conducted at 500 °C can be found elsewhere [7]. In further figures the "no-treatment" curve was omitted to make the graphs more readable.

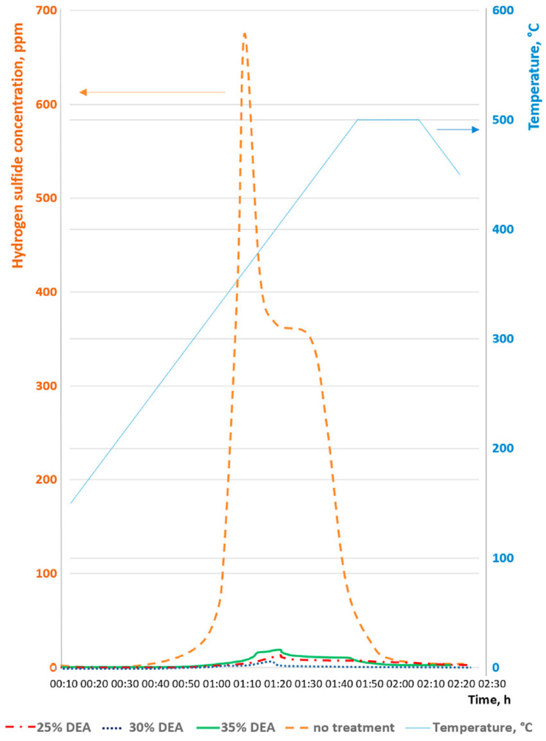

Fig. 3 – Hydrogen sulfide emission from the pyrolysis with or without cleaning process.

As presented, in each case the maximum H_2S concentration has not exceeded 20 ppm. Application of 30 wt% DEA water solution allowed to obtain the most successful hydrogen sulfide removal, and the maximum concentration equalled 11 ppm. Moreover, a concentration below 5 ppm has been kept for 95% of the experiment duration, and the total H_2S removal efficiency was as high as 98%. Hydrogen sulfide dissociates to form a weak acid, while the alkanolamines are weak organic bases. When the raw pyrolytic gas containing H_2S is contacted counter-currently with alkanolamine water solution, the acid and the amine base produce salts in the

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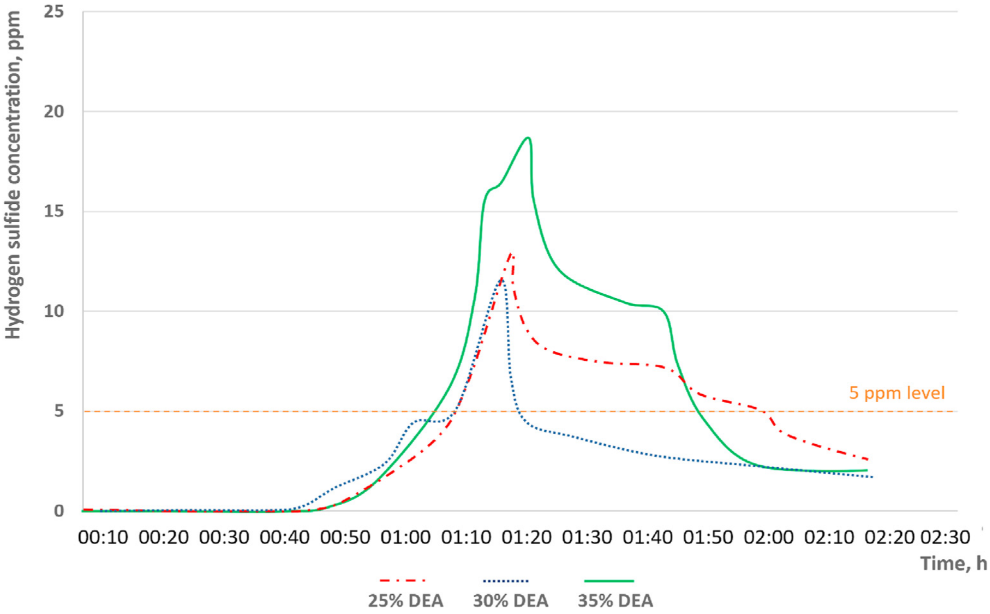

Fig. 4 – Hydrogen sulfide emission from waste tyre pyrolysis after gas purification with different diethanolamine solutions applied.

form of acid-base complex. This complex can be shattered by steam stripping, releasing back the H_2S and regenerating the amine solution for reuse. Released stream of concentrated hydrogen sulfide can be further treated for elemental sulfur [14] or even hydrogen production [29]. It can be observed that the rapid release of greater amounts of pyrolysis gas with very high H_2S load (about 1 h after the beginning of the test) led to exceeding the sorption capacity of the liquid organic sorbents. Nevertheless, majority of the hydrogen sulfide was removed. Therefore, total removal efficiencies were very satisfying. In order to avoid exceeding the 5 ppm level, it would be recommended to introduce additional operation improving the mass transfer or prolonging the contact time. However, it was also reported that the absorption of H_2S using alkanolamines goes forward at the condition when the pressure is high and the temperature is low, while it goes in the opposite direction when the pressure is low and the temperature is high [23]. In this work both temperature and pressure were kept low. Thus, the highest flow rate when the most intensive gas evolution takes place can make the reversible reaction shift to the forward direction and lowered the H_2S removal efficiency.

25 wt% DEA aqueous solution also produced good results. The maximum measured concentration of H_2S was slightly higher - 13 ppm. However, the level below 5 ppm was only for 73% of the experiment duration, which made this option less favourable. The least satisfactory hydrogen sulfide removal efficiency (95%) among three tested solutions produced when applying 35 wt% of DEA. It is worth noting that increasing the concentration of DEA above 30 wt%, did not improve the H_2S removal efficiency. This is probably due to the hindered occurrence of dissociation reactions in the aqueous solution, which are necessary for subsequent reactions between DEA and H_2S (see Equation (6).). Nevertheless, the effectiveness of hydrogen sulfide removal by tested DEA solutions was very high.

N-methyldiethanolamine (MDEA) - hydrogen sulfide removal

Second investigated compound is N-methyldiethanolamine. Tertiary amines, such as MDEA, are used for selective H_2S removal [30,31]. In Fig. 5 three-dimensional model of the MDEA ($CH_3N(C_2H_4OH)_2$ is presented. Important advantage of MDEA in comparison to other organic solvents is lower cost of regeneration energy [32]. However, it reacts slowly with carbon dioxide and carbonyl sulfide, which can be beneficial for selective hydrogen sulfide removal, or unfavourable when general gas purification is desirable [33].

According to data presented in Fig. 6, application of 30 wt% and 40 wt% water solution of MDEA produced quite comparable results. Total H_2S removal efficiency was 97% in both cases, and a concentration below 5 ppm has been kept about 81% duration of experiments. However, it is worth noting that when 40 wt% MDEA has been tested the measured H_2S concentration did not exceed 10 ppm – the maximum was 8 ppm (in the 70th minute of the test) - which is highly desirable. Sidi-Boumedine et al. [35] studied hydrogen sulfide loading capacity in aqueous alkanolamine solutions at 313 and 373 K and pressures up to about 1.3 MPa, which conditions are different from presented in this study. They reported that loading capacity of H_2S in water solution of DEA is higher than in MDEA solution. Elevated temperature and high pressure speed up the reaction rate, but the features of particular compound

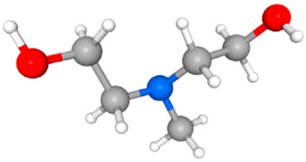

Fig. 5 – *N-methyldiethanolamine – 3D model* [34].

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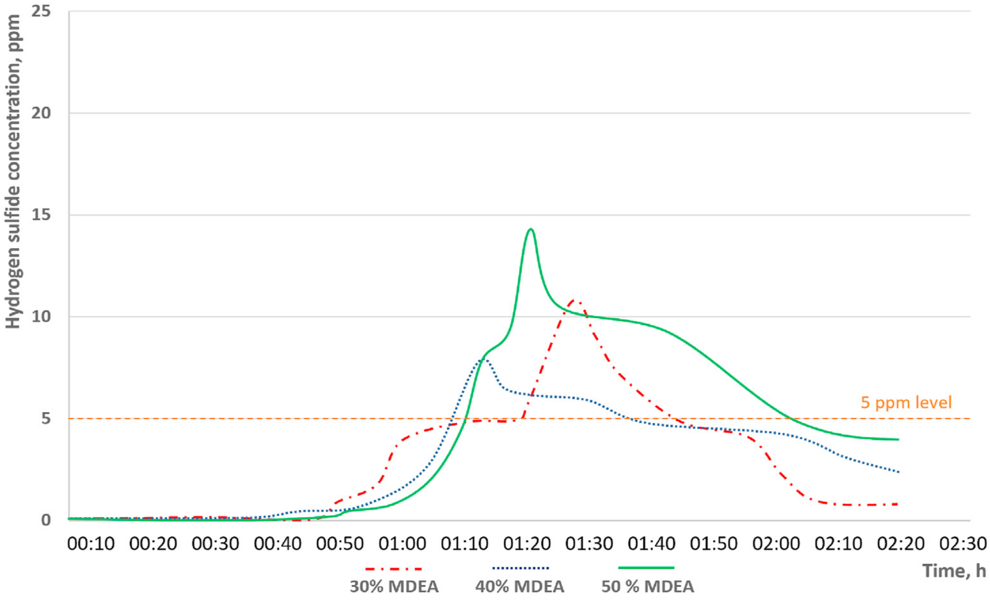

Fig. 6 – Hydrogen sulfide emission from waste tyre pyrolysis after gas purification with different N-methyldiethanolamine solutions applied.

should remain stable in quite a wide range. Results obtained by Sidi-Boumedine et al. [35] and this study demonstrate that the loading capacity of H_2S in water solution of DEA is higher than in MDEA solution regardless applied conditions. Total hydrogen sulfide removal efficiency was slightly higher for the best DEA water solution than for the best MDEA water solution, which is even more clear when the concentrations of both alkanolamines are taking account. Observed better removal efficiency of DEA confirms its higher loading capacity of H_2S. Furthermore, H_2S concentration below 5 ppm has been about 9% longer. In turn, 50 wt% water solution of MDEA application produced worse results. Maximum hydrogen sulfide emission was as high as 14 ppm, and the level of 5 ppm has been exceeded during 35% of the experiment time. This is probably due to, as mentioned earlier, unsatisfied balance between water and the alkanolamine amounts in the solution, which can impede the dissociation. In addition, absorption of the same quantity of hydrogen sulfide in a more concentrated DEA water solution results greater increase in temperature because of reaction heat releasing (exothermic reaction), and subsequent increased acid-gas vapor pressure above the solution [14].

DEA&MDEA blends – hydrogen sulfide removal

The mixed amine systems have been suggested as an improvement in gas purification processes that allows to combine higher equilibrium capacity of tertiary amines represent by MDEA with the higher reaction rate of the primary or secondary amine such as DEA [30,31]. Moreover, amines blends also offered benefit in reducing pipeline corrosion [36]. Thus, previously pointed the most effective organic sorbents solutions have been tested as 1:1 vol ratio blend, which composition are presented in a simple Table 3. Results are plotted in Fig. 7.

It is clear from Fig. 7 that the best proposed DEA/MDEA blends is mixture of 30 wt% water solution of DEA with 40 wt% water solution of MDEA (blend no. 1). The highest measured H_2S concentration was only 7 ppm. Importantly, 99% of the experiment duration provided pyrolysis gas containing less than 5 ppm, and the total removal efficiency was also 99%. Those results made blend no. 1 the most effective sorbent for hydrogen sulfide removal from all tested. Since 30 wt% water solution of DEA was the most effective H_2S absorbent among tested DEA solutions as well as 40 wt% water solution of MDEA among tested MDEA solutions, it is possible to conclude that the combination of their favourable features has been boosted by blending them together. However, the difference in H_2S removal efficiency by DEA 30 wt% and blend 1 was small. This suggests that DEA has more important role in H_2S removal efficiency in the blends. Considering lower price of DEA, it seems to be a better choice for pyrolytic gas desulfurization. On the other hand, additional benefits from the application of DEA/MDEA blends should be considered including reduced corrosion, high resistant to degradation and operating cost savings due to easier regeneration of MDEA [14]. Additionally, two more blends were investigated, but results were not that satisfactory as for blend 1, but comparable to DEA 30 wt% water solution applied singly. The most relevant data about H_2S removal from waste tyre pyrolysis gas with the use of organic absorbents are summarized in Table 4.

Table 3 – Composition of tested alkanolamines sorbents blends.

No. of blend	DEA solution, wt%	MDEA solution, wt%
1	30	40
2	30	30
3	25	40

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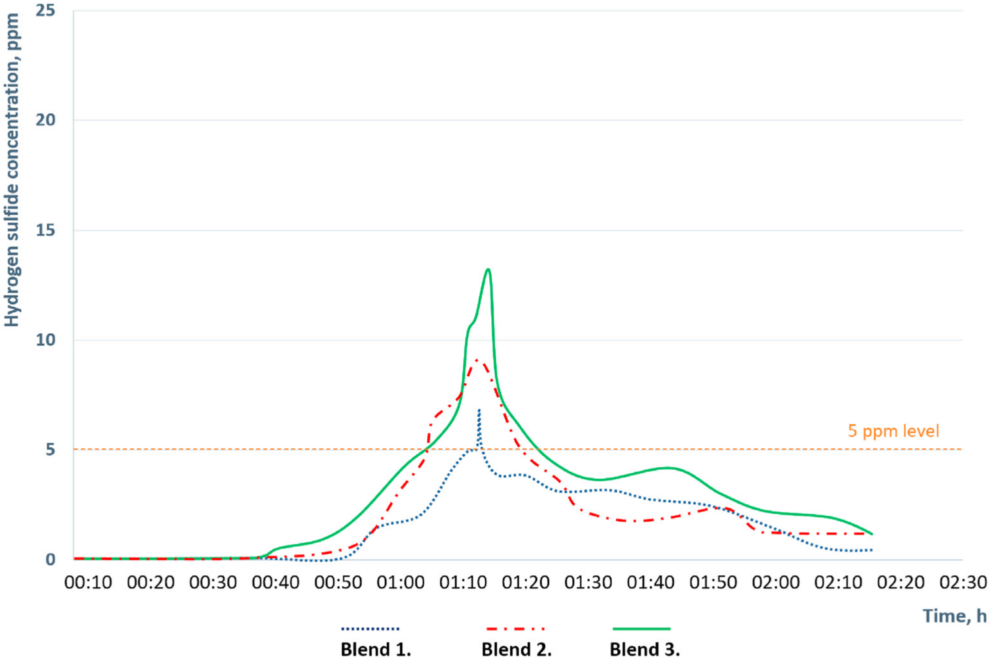

Fig. 7 – Hydrogen sulfide emission from waste tyre pyrolysis after gas purification with different DEA/MDEA blends solutions applied.

Other sulfur-containing compounds removal from pyrolysis gas

As previously examined [7] pyrolysis gas from waste tyres contains, apart from hydrogen sulfide, also significant amounts of other sulfur-containing compounds, including but not limiting to methyl mercaptan, carbonyl sulfide, ethyl mercaptan, dimethyl sulfide, carbon disulfide, propyl and butyl mercaptans. Hydrogen sulfide removal seems to be the key factor in the pyrolytic gas purification, although the mercaptans are also problematic because of their unpleasant smell and toxicity [8]. Mercaptans are much weaker acids than H_2S, but they can similarly react with amines to form mercaptide salts. This mechanism has been described by Bedell & Miller [37]. As reported by Abbas et al. [38] DEA reacts with carbonyl sulfide and carbon disulfide. Moreover, the product can be regenerated, which is very promising. In this work the removal effectiveness of various sulfur-containing compounds was evaluated using the two solutions that gave the best H_2S removal, namely 30 wt% DEA, and 30 wt% DEA with 40 wt% MDEA blend. The levels of sulfur compounds in raw waste tyre pyrolysis gas and gas treated with absorbents are presented in Table 5.

Table 5 shows a reducing of the measured concentration of investigated sulfur-containing compounds. For example, methyl mercaptan and carbonyl sulfide (COS) concentrations dropped from above 500 ppm to around 10 ppm, which means at least 98% lowering. Interestingly, application of DEA allowed for a better carbonyl sulfide removal, while concentrations of the rest of investigated compounds were lowered more by amines contained in blend no. 1. In turn, ethyl mercaptan concentration has been reduced by approximately 90%. The rest investigated sulfur-containing compounds were present in significantly smaller amounts even in raw pyrolysis gas. Nonetheless, the emission of all above-mentioned components has been significantly reduced with the lowest removal efficiency noticed for n-propyl mercaptan, namely about 82%. Similar results in relation to COS were obtained by Palma et al. [39]. They analyzed carbonyl sulfide solubility in different alkanolamines including DEA and MDEA. They observed that DEA featured the best COS removal efficiency, while removal with MDEA was the worst. Additionally, it was proven that COS has to dissolve in water before the reaction with DEA occur [39]. Therefore, the very high concentrations of applied alkanolamines can lower the carbonyl sulfide removal efficiency.

Table 4 – Summary of H_2S removal effects from pyrolysis gas by organic solvents.

Absorbent	Solution, wt%	Maximum H_2S, ppm	H_2S removal efficiency, %	H_2S level <5 ppm, % of time
DEA	25	13	96	66
DEA	30	11	98	95
DEA	35	19	95	73
MDEA	30	11	97	81
MDEA	40	8	97	81
MDEA	50	14	96	65
DEA	25	9	98	92
MDEA	40			
DEA	30	7	99	99
MDEA	40			
DEA	30	13	98	93
MDEA	30			

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Table 5 – Comparison of sulfur-containing compounds concentrations in × 10^{-4}% mol before and after gas purification.

Name of the compound	Raw gas [7]	30 wt% DEA	Removal efficiency 30 wt% DEA, %	Blend 1	Removal efficiency Blend 1, %
methyl mercaptan	>500	10.87 ± 1.93	>98	7.48 ± 1.33	>99
carbonyl sulfide	>500	6.98 ± 1.24	>99	10.38 ± 1.85	>98
ethyl mercaptan	106.87 ± 19.66	11.98 ± 2.13	89	9.18 ± 1.63	91
dimethyl sulfide	4.18 ± 0.74	0.12 ± 0.02	>97	<0.1	>98
carbon disulphide	18.72 ± 3.14	0.11 ± 0.02	>99	<0.1	>99
i-propyl mercaptan	6.65 ± 1.18	0.35 ± 0.06	95	0.18 ± 0.03	97
tert-butyl mercaptan	0.74 ± 0.13	<0.1	>86	<0.1	>86
n-propyl mercaptan	8.28 ± 1.47	1.46 ± 0.26	82	0.78 ± 0.14	91
methyl ethyl sulfide	1.12 ± 0.20	<0.1	>91	<0.1	>91
s-butyl mercaptan	1.08 ± 0.19	0.17 ± 0.03	84	0.14 ± 0.02	87
i-butyl mercaptan	1.47 ± 0.26	0.19 ± 0.03	87	0.13 ± 0.02	91
diethyl sulfide	0.46 ± 0.08	<0.1	>78	<0.1	>78
n-butyl mercaptan	1.13 ± 0.20	0.17 ± 0.03	85	0.11 ± 0.02	90
diethyl disulphide	0.37 ± 0.07	<0.1	>73	<0.1	>73
dipropyl sulfide	0.38 ± 0.07	<0.1	>74	0.12 ± 0.02	>68

The uncertainty for the lower limit of quantification is 0.1 ± 0.02 × 10^{-4}% mol.

Conclusion and recommendation

The paper presents an investigation of hydrogen sulfide removal from waste tyre pyrolysis gas by the application of organic solvents namely DEA and MDEA as well as their blends. The concentration of H_2S in the gas must be reduced to the level of several ppm prior to their application as a gaseous fuel for reactor heating in the pyrolysis plant to ensure emission limit fulfilment The best proposed organic absorbents solutions found in this study is 30 wt% of DEA, 40 wt% of MDEA and their 1:1 vol ratio blend – allowed to fulfil those requirements during 81, 95 and 99% of experiments time, respectively. It is possible to conclude that hydrogen sulfide is effectively removed by DEA and MDEA from the gas obtained from pyrolysis of waste tyres. The total H_2S removal efficiency of each tested solution exceeded 95%, reaching 99% for blend no. 1. Moreover, application of DEA or DEA/MDEA blend efficiently removed also other sulfur-containing compounds such as methyl mercaptan, ethyl mercaptan, carbonyl sulfide, dimethyl sulfide, etc. To conclude, the proposed cleaning methods make the waste tyre pyrolysis gas applicable as a gaseous fuel relatively safe for the environment. Additionally, it is recommended to introduce these alkanolamines solutions in future designing of specific solutions that will fit for particular waste tyre pyrolysis plants. Continuation of research on cleaning of waste tyre pyrolysis gas from other impurities present even at lower amounts than sulfur-containing compounds is also recommended.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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