Making biogas desulphurisation more effective by using surfactants

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This work, studying three surfactants, has proved that if they are added in an amount below 0.1 wt. % to the washing solution of the Fe-EDTA complex capturing hydrogen sulphide from biogas, it is possible to reduce the required amount of oxidation air regenerating washing solution up to four times. This can also lead to a significant reduction in the volumes of technological apparatuses, the washing medium, costs of chemical substances. The aim of this research is to make the desulphurisation process more effective, reducing the costs of chemical solvents make the process quicker, reduce the volume of reaction reactors and reduce the energy requirements.

Key words*: biogas, desulphurisation, surfactants, EDTA, complex chelate*

Introduction

The desulphurisation of biogases produced during the fermentation of biomaterials, excrements from large-scale cattle and pig fattening farms or during waste-water purification is performed using various dry, wet, adsorption or absorption methods [1–4]. The applied redox methods capturing the undesirable hydrogen sulphide include the chelating method, where the complex chelate bond of a polyvalent metal in an absorbing aqueous solution enables its easy reversible oxidation–reduction transition between individual ion states [5,6].

Chelating method

The chelating process, using complexed iron in biogas desulphurisation, has been applied to various modifications and with diverse apparatus arrangements, optimising both the possibilities of chemical reactions and the working conditions and economic costs [7–12].

The actual, relatively simple, washing is done using an aqueous solution in reactors, in pulse columns or using washers. The speed, efficiency and economy of the processes are determined by the concentration and stability of the chelate, its price, the pH buffering of the washing solution, the temperature of the solution, etc. The speed and demands of oxidation play an important role here as well.

A certain disadvantage of this procedure is the fact that the oxidation of the reduced form into an active oxidised form is slow. For re-oxidation, it is necessary to blow a large amount of gas containing oxygen into the washing solution and ensure its dispersion. Oxygen solubility at a pressure of 1 bar at 25°C is $2.5 \cdot 10^{-4}$ mol/l of the solution and its dissolution is the slowest process of regeneration oxidation. This also entails a high consumption of electrical energy for the compression of the oxidising gas. In order to ensure the proper functioning of the desulphurisation technology, it is necessary to work with large volumes of the washing liquid. This requires a large volume of the oxidation tank as well.

The most frequently applied chelation agents in practice are nitrilotriacetic acid (NTA, labelled as Syntron A in industry), ethylenediaminetetraacetic acid (EDTA, Syntron B) and 2- hydroxyethyenediaminetriacetic acid (HEDTA), less often diethylenetriaminepentaacetic acid (DTPA), 1,2-cyclohexylenedinitrilotetraacetic (CDTA), the mixtures EDTA-HEDTA, EDTA-NTA and the alkali metal salts of these acids.

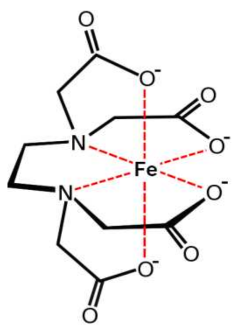

Fig. 1. Fe-EDTA sandwich complex.

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The process of the capture of hydrogen sulphide from biogas can be divided into several phases. In the first one, it is absorbed in an alkali aqueous solution while yielding ions HS^- ions. In the second phase, this is followed by a reaction between Fe^{3+} ion bound in the form of a sandwich complex of an amino acid – e.g. EDTA – Fig. 1 – with a HS^- ion according to the equation

$$2\,[Fe^{3+}EDTA^{4-}]^- + HS^- + H_2O \rightarrow 2\,[Fe^{2+}EDTA^{4-}]^{2-} + S + H_3O^+ \qquad (1)$$

The individual reactions take place practically immediately after the biogas containing hydrogen sulphide comes into contact with a washing solution.

For the conversion of the washing solution back into an active form, oxidation by atmospheric oxygen is used

$$4\,[Fe^{2+}EDTA^{4-}]^{2-} + 4\,H_3O^+ + O_2 \rightarrow 4\,[Fe^{3+}EDTA^{4-}]^- + 6\,H_2O \qquad (2)$$

The washing solution captures hydrogen sulphide until the oxidation capacity is exhausted. That is manifested e.g. by a decrease in pH, visually by a gradual change of a dark red colour first into light red and then to undesirable green and yellow.

In order to ensure the proper functioning of the washing process and to minimise the costs associated with the loss of washing solution efficiency, it is necessary to maintain some of its basic parameters at an optimum value.

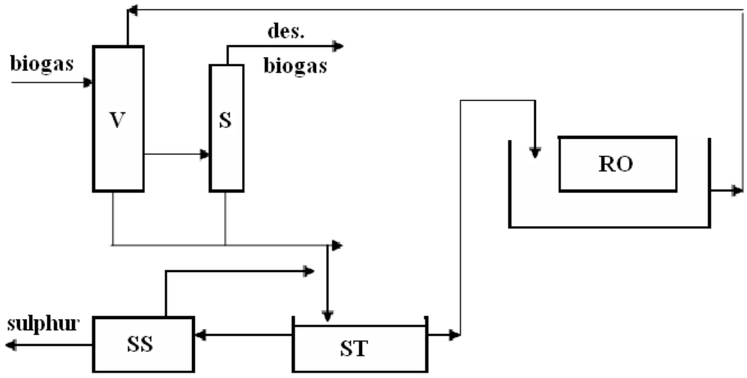
First and foremost, the concentration of EDTA must be maintained in tenths of mol/l and the concentration of iron slightly below the stoichiometric concentration. Moreover, the pH value must be kept at ca 9 in the initial phase by means of buffering agents and the temperature of the solution at the lowest possible level by cooling in oxidizers. Acidic solutions have low reaction rates while those that are too alkaline, i.e. at pH 10–11, are no longer selective and also wash carbon dioxide out of the biogas. This is no longer desirable when desulphurised biogas is utilised in CHP engines with respect to the decreasing relative density of the gas.

The effectiveness of the regeneration of the redox washing solution may be increased by adding a surfactant to the washing desulphurisation solution, by raising its temperature up to 85°C [13] or by using regeneration gas preferably containing 30–80 vol. % of oxygen to act on the washing solution; the gas emerging from the regeneration may be used in subsequent energetics [14]. Another way to increase the effectiveness of the process discussed, mainly the separation of the sulphur formed, is to add cupric salt into the washing solution in an amount of up to 5 g/l or aldehydes with 1–3 carbons in a molecule in an amount below 50 g/l [15].

The apparatus installed in the biogas station in a large-scale pig fattening farm, depicted in Fig. 2, desulphurised for many years biogas from the process of the fermentation of pig slurry, in which the concentration of hydrogen sulphide was around 0.3 vol. %. The desulphurised biogas with a calorific value of ca 22 MJ/m^3 was operationally used for the production of electrical energy, for the heating of fermenters and for the preparation of the warm utility water necessary to run the pig farm. The biogas was developed in two concrete fermentation tanks of a volume of 3,000 m^3 heated by desulphurised biogas to 40°C. Its production from the slurry treated reached 450 l/kg of dry matter.

EDTA was used in the concentration of 0.12 mol/l, $NaHCO_3$ of ca 60 g/l (to maintain pH at ca 9) and Fe of 0.09 mol/l. During normal operation, the concentration of hydrogen sulphide was in the range of 40–50 mg/m^3.

In the process, the complicated character of the regeneration was resolved i.a. by the oxidation of the washing solution using rotating discs covered with materials having a large spongy surface. Nevertheless, the forming methane, dissolved in the washing solution, may create an explosive environment. (Yet this problem must be taken into account in other arrangements of the oxidation of chelating solutions by compressed air as well.)



V – Venturi washer, S – biogas separator, ST – sedimentation tank, SS – sulphur separation, RO – rotation oxidiser

Fig. 2. A diagram of the desulphurisation of the biogas from the fermentation of pig slurry.

Experimental

The aim of the work was to verify whether an addition of a surfactant increases the effectiveness of the washing solution oxidation process and thus reduces the costs of desulphurisation technology along with the amount of waste gases from the oxidizer, the volume of the washing liquid, the volume of the corresponding technological containers, or energies.

The Solutions Studied

Since the addition of surfactants reduces the surface tension of the aqueous solutions of the complexes, which facilitates the transfer of oxygen from the surrounding gas into an aqueous phase, we performed experimental tests focused on monitoring the effectiveness of the oxidisability of the reduced washing solution by air after an addition of a surfactant. On the basis of preliminary laboratory tests and long-term experience, we selected the substances whose characteristics are listed in Tab. 1.

Tab. 1. The surfactants studied.

Surfactant	Characteristics
Slovamin SK-7	Alkylamino polyethylene glycol with 18 carbon atoms in alkyl and 7 moles of bound ethylene oxide, foamy
Slovamin SM-20	Alkylamino polyethylene glycol with 18 carbon atoms in alkyl and 20 moles of bound ethylene oxide, foamy
Slovanik T-610	Copolymer of ethylene oxide and propylene oxide containing a polypropylene part of a molecular weight of 1 500–2 000 and 7–15 wt. % of bound ethylene oxide, non-foamy

For the assessment of the influence of surfactants, the first phase monitored the reduction of the surface tension (γ) of the washing solution after their addition. This effect was measured when the selected surfactants studied were added in the amount of 0.55 g/l to the basic washing solution, one litre of which contained 103.36 mmol of EDTA, 100.80 mmol of Fe and 40 g of Na_2CO_3.

The change in the surface tension was measured using the drop weighing method. It was utilised as a relative method – a comparison was made between the same volumes of a liquid with a surfactant and liquid with a known surface tension and without a surfactant addition – in our case distilled water. The results of the measurements carried out at 20 °C after equilibration (20 minutes) are summarised in Tab. 2.

Tab. 2. The surface tension and densities of the washing solutions at 20 °C.

Substance	Density – ρ [kg/m^3]	Surface tension – γ [N/m]
Distilled water	998.2	0.06597
A washing solution without a surfactant	1089.8	0.0662
Slovamin SK-7	1084.0	0.0464
Slovamin SM-20	1087.8	0.0479
Slovanik T-610	1095.4	0.0360

As arises from Tab. 2, surfactants are intensively involved in the reduction of the surface tension of a washing solution. The addition of the surfactant Slovanik T-610 reduced the surface tension almost twice (in comparison with the surface tension of a washing liquid without a surfactant). The surfactants Slovanik SK-7 and Slovamin SM-20 had approximately the same effect.

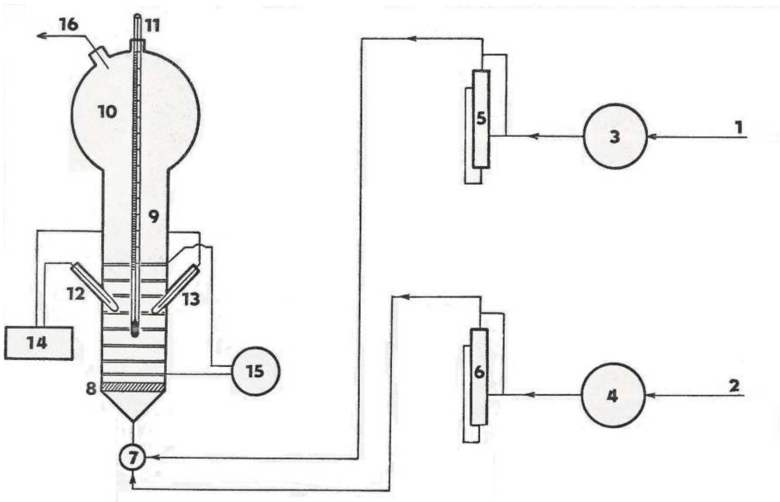
The Description of the Apparatus

The model apparatus utilised to monitor the effect of the surfactants, shown in Fig. 3, was operated in the following way. The model gas (nitrogen) containing hydrogen sulphide was fed into the reactor with the washing liquid studied at a flow rate of 0.2 l/min. That the correct flow rate was maintained was monitored by a gasometer along with the total amount of gas flowing through the reactor. Once the required volume had passed through the reactor with the washing liquid, the gas inlet was closed and the air inlet was opened. Its flow rate was 0.75 l/min.

The volume of the washing liquid was always 400 ml; the volume of the model gas (nitrogen) containing hydrogen sulphide in one cycle was 5 l. The concentration of hydrogen sulphide in it was 90 mg/l. One cycle represented one reduction and one oxidation. Each series of measurements was conducted ten times and these were repeated at least three times, which proved to be sufficient to assess the reproducibility of the process.

The measurement process was monitored by measuring pH values through an electromotive force at selected electrodes. We used a glass electrode as an indication and calomel electrode as a reference. The ratios of the amount of the added surfactant to the amount of the washing liquid were selected as 1:1 000 (i.e. 0.45 g to 450 g of the washing liquid), 1:2 000 (0.22 g) and 1:4 000 (0.11 g).

The effectiveness of the surfactants was compared at 20°C; the influence of the temperature was monitored by increasing the temperature of the washing solution to 50°C.



1 – hydrogen sulphide inlet, 2 – regeneration air inlet, 3,4 – gasometers, 5,6 – flowmeters, 7 – three-way valve, 8 – frit, 9 – quartz reactor, 10 – foam trap, 11 – thermometer, 12 – glass electrode, 13 – calomel electrode, 14 – acidimeter, 15 – heating regulator, 16 – gas outlet

Fig. 3. A diagram of the model apparatus.

Results and discussion

By repeating the processes of the washing and re-oxidation of the basic solution (103.36 mmol of EDTA/l, 100.80 mmol of Fe/l, 40 g of Na_2CO_3/l), which did not contain a surfactant, it was determined that for the regeneration of the solution after the passage of 5 l of the standard, i.e. 450 mg of hydrogen sulphide, 40 l of air are required at 20°C. First, these basic data were compared with the follow-up data on the effects of the surfactants studied and their amount at 20°C. The information obtained may be summarised as follows.

Slovamin SK-7

With the ratios 1:1,000 and 1:2 000, the washing solution was repeatedly sufficiently regenerated by 10 l of air. In the third case (1:4 000), it was determined that 15 l of air are necessary to regenerate the washing liquid perfectly. It arises from a comparison with the data ascertained during the washing of hydrogen sulphide in the process without a surfactant that the use of an addition of 0.45 and 0.22 g /l reduces the necessary volume of the regeneration air four times, the use of 0.11 g /l 2.7 times.

Slovamin SM 20

The surfactant Slovamin SM-20 is basically analogous to the surfactant Slovamin SK-7. It is also alkylamino polyethylene glycol with 18 carbon atoms in alkyl; unlike the surfactant Slovamin SK-7; however, it has 20 atoms of bound ethylene oxide in its molecule.

The ratio of the surfactant to the washing liquid was selected as 1:2 000. The amount of the air necessary for the regeneration was the same as in the case of Slovamin SK-7.

Slovanik T- 610

Like in the preceding cases, the measurements were conducted with the additions of 0.450 g, 0.220 g and 0.110 g to 400 ml of the washing liquid. In all the cases, the regeneration of the washing liquid was done by 10 l of air. The measurements proved that this volume is sufficient for the perfect reproducibility of the process. If we compare the results of this process with the process without a surfactant, it is evident that the addition of Slovanik T-610 reduces the amount of air for the regeneration of the washing liquid up to four times. This surfactant had the best results. Its advantage also lies in the fact that even with the lowest addition (0.110 g/400 ml), it is enough for the regeneration of 10 l of air.

Combinations of surfactants

Operationally, it is not suitable to apply foamy surfactants. Therefore, for the reduction of the amount of air necessary for the regeneration of the washing liquid, the combination of the foamy surfactant Slovamin SK-7 with the non-foamy Slovanik T-610 was tested as well. This combination turned out to be the best because Slovanik T-610 suppresses the foamy properties of Slovamin SK-7. Two measurements were carried out – with the total charge of the surfactants being 0.220 and 0.110 g always to 400 ml of the washing liquid. The surfactant weight ratio was always 1:1. It arose from a comparison with the measurement without a surfactant that in the case of the 0.220 g charge, the regeneration is four times less demanding on the amount of air – 2.7 times in the case of the 0.110 g charge.

Temperature Increase

Since an increase in the temperature generally accelerates the regeneration of the washing solution containing complexed iron, measurements were carried out at a temperature of 50°C as well. The surfactant used was Slovanik T-610 because it had the best results in the preceding measurements at laboratory temperature. The measurements were performed with the addition of the surfactant in the ratios 1:2 000 and 1:8 000. The measurement process monitored based on changes in pH values, which are summarised in Tab. 3, documents that 5 l of air suffice for the perfect regeneration in this case. A significant finding is that the addition of the surfactant may be reduced to a half without any negative impact. Its importance is increased by the fact that in numerous cases the use of biogas for energy, despite being economical, is limited by the use of waste heat, mainly in the summer months. This is precisely one of the possibilities for its application.

It is necessary to realise that there is potential for further optimisation, which would take into account the actual industrial situation arising from other possibilities of the contact of air with the washing liquid. In our case, we did not observe a process that would thoroughly correspond to the smallest volume of air necessary for the perfect regeneration.

Tab. 3. The pH values measured at 50 °C.

Cycle	**1:2 000 addition**		**1:8 000 addition**	
	oxidation	**reduction**	**oxidation**	**reduction**
1	8.9	8.95	8.85	8.9
10	8.7	8.85	8.8	8.9
20	8.6	8.80	8.8	9.05
30	8.7	8.9	9.0	9.05
40	8.8	9.0	8.95	9.0
50	9.0	9.1	8.9	8.95
60	8.95	9.1	8.9	8.95
70	8.85	9.0	8.95	8.9
80	8.85	9.0	8.85	8.95
90	8.95	9.0	8.8	9.0
100	8.9	8.95	8.95	8.95

Note: washing – 5 l of the standard with hydrogen sulphide, oxidation – 5 l of air

Conclusion

Research highlighted in this article proves that the addition of monitored surfactants Slovamin SK 7 and Slovanik T-610 to the scrubbed solution in concentrations of from 0.2 to 0.5 g / l allows reducing the volume of scrubbing liquid to one-third. This enables to reduce the cost of preparing up to 50% - i.e. the quantity of needed EDTA, Fe, soda, respectively costs associated with the construction and size of the apparatus and the cost of operating energy media. A forthy finding is also a reduction in the volume of regeneration and waste gas from the regeneration process. This gas reduction leads to a reduction in costs of gas waste management up to a quarter.

It was also verified that the addition of surfactants is preferred for suppressing foaming of a surfactant with foaming properties.

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