REMOVAL OF HYDROGEN SULFIDE FROM NATURAL GAS, A MOTOR VEHICLE FUEL

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Compressed natural gas (CNG) is one of the fossil fuels, and is nothing other than the compressed version of the natural gas extracted by mining. CNG is mostly used for heating and the production of electricity. If used as a fuel for motor vehicles, it entails less emission of CO_2 than does the use of gasoline or diesel. Irrespective of usage, the contents of commercial natural gas are strictly regulated by laws. Besides energy density, hydrogen sulfide content for example is a critical quality parameter of natural gas, hence it is strictly regulated. Hydrogen sulfide is extremely corrosive for the pipes. When burning such gases, hydrogen sulfide is converted to sulfur dioxide (SO_2) which is harmful for the environment. We have devised a procedure for the replacement of solid adsorbents and amine-containing chemicals in hydrogen sulfide removal that can also be used with gases containing carbon dioxide. The essence of the method is that the natural gas is brought into contact with a dilute solution of NaOH in contact time of less than 1 second. At the beginning of chemisorption, hydrogen sulfide is absorbed 1-2 orders of magnitude faster than carbon dioxide. For the experiments, a laboratory Jet reactor was planned. The efficiency of purification was examined with different hydrogen sulfide containing model gas mixtures with respect to the following parameters: gas volume flow, alkali volume flow and alkali concentration.

Keywords: compressed gas, motor vehicle fuel, hydrogen sulfide, chemisortpion, selective extraction

Introduction

Natural gas is a primary raw material. The typical contents of natural gas are given in *Table 1*, but they can be different for every gas field.

The natural gas consumption of Hungary exceeds 14 billion m^3 per annum, which is 70% of the total energy consumption [1].

Table 1: Typical contents of natural gas

Component	Percentage
methane (CH_4)	97%
ethane (C_2H_6)	0.919%
propane (C_3H_8)	0.363%
butane (C_4H_{10})	0.162%
carbon dioxide (CO_2)	0.527%
oxygen (O_2)	0–0.08%
nitrogen (N_2)	0.936%
noble gases (Ar, He, Ne)	trace
other (e.g..:H_2S)	0–0.001%

There are 210 well- and/or research sites of natural gas. Most of the wellsites are in the Western Transdanubia and in Eastern Hungary. Domestic resources do not satisfy the consumption, making the country dependent on a significant import, the extent of which is nowadays 80%. Most of the import is arriving from Russia.

Fig. 1 illustrates the distribution of natural gas use. The major part of it (45%) is the residential consumption with district heating (more than 6 billion cubic meters per annum). Electricity production (21%) requires 3 billion cubic meters of natural gas per annum. Industrial consumers constitute 33%, while other uses are less than 1%.
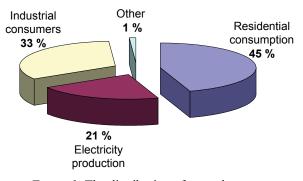

Figure 1: The distribution of natural gas use

Other uses include use as motor vehicle fuel. However, it is important do differentiate between LPG and CNG fuelled vehicles [2].

LPG (Liquefied Petroleum Gas) is a by-product of petroleum oil drilling [3]. Formerly it was usually burned off; nowadays it is sold on the market. As for its contents, it consists of a mixture of 40% propane (C_3H_8) and 60% butane (C_4H_{10}). It is used in fuel tanks at a

pressure of 6 bar in a liquefied form. There are approximately 260 LPG tank stations in Hungary.

CNG (Compressed Natural Gas) is not a by-product, but the extracted fossil gas. CNG contains 90–92% methane and is in the gaseous state even when densified. The main problem with its use can be caused by imperfect burning, causing the release of greenhouse gases into the atmosphere. This however, is not a threat with a well-set CNG motor vehicle in a good condition. When burning pure methane, one part carbon dioxide (CO_2) and two parts water (H_2O) in the form of vapor are formed. Compared to traditional fuels, the amount of carbon monoxide (CO) is lower by 60–90%, while the amount of hydrocarbons (CH_x) by 40–60%. CNG burns at a lower temperature than gasoline, reducing the amount of nitrous oxides (NO_x) by 20–40% in the exhaust gas. In contrast to diesel motor vehicles, there is no release of carcinogenic solid particles.

Its advantage compared to LPG is that it is a volatile gas that does not set close to the ground [4].

Several car manufacturers have their own CNG models in Hungary, e.g. Opel (Zafira and Combo), Ford (Focus) and Volvo (S60, S80 and V70). The only setback for CNG fueled vehicles to become widespread is the scarcity of the tank stations.

Irrespective of usage, the contents of commercial natural gas are strictly regulated by laws. Besides energy density, hydrogen sulfide content for example is a critical quality parameter of natural gas, hence it is strictly regulated.

The amount of hydrogen sulfide can be different for different wellsites, in Hungarian wells, it ranges from 50 to 3000 ppm. The amount of hydrogen sulfide in commercial natural gas, however, cannot exceed 5 ppm.

Removal of hydrogen sulfide from natural gases

There are several indications for the removal of hydrogen sulfide. The most important is environmental protection, because by burning hydrogen sulfide, sulfur dioxide (SO_2) is formed, which is harmful for the environment. The operational indication is that hydrogen sulfide is extremely corrosive for pipes. Since pure natural gas has a higher price, there is also an economical reason.

There are several methods for the removal of hydrogen sulfide, such as adsorption, absorption, membrane technology and biological removal. These methods are compared in the followings.

For the adsorption methods, the following adsorbents can be used: activated carbon [5, 6], zeolite [7, 8], metal-based (Fe, Ti, Cr, Zn, Al) adsorbents [9, 10] and composites [11, 12]. These adsorbents are efficient at absorbing sulfur, but they have to be regenerated. Most adsorbents can only be regenerated 2 or 3 times consecutively, after this the packing needs to be replaced and disposed of.

Membrane separation methods are characterized by ease of installation and use. Membranes are used for hydrogen sulfide removal [13] but their efficiency is not good enough on their own. Because of this, they are used in combined methods [14].

Hydrogen sulfide can be selectively removed by biological ways. However, these systems are hard to control [15].

The absorption techniques use for example alkanol-amines [16, 17]. Their advantage is that they have a high yield and they are regenerable; their disadvantage is that they foam and they are not environmentally friendly. Sodium hydroxide is also used as an absorbent. These techniques can be utilized for the removal of hydrogen sulfide with good efficiency in traditional chemisorption devices [18]. However, with the use of NaOH solution, the selective removal of hydrogen sulfide can be realized for gases containing carbon dioxide as well. The technique based on competitive chemisorption has been known for 55 years now [19].

There are different techniques for the realization of chemisorption. The essence of all of them is that the contact time has to be very short (below 1 sec) and the contact has to be very intensive. This is because (depending on pressure) hydrogen sulfide is absorbed orders of magnitudes faster than carbon dioxide at the beginning of chemisorption [20]. The reaction is exothermic and strongly pH dependent [21]. The above cannot be realized with chemisorbers of classical construction.

For alkali consumption, the range of HS^- formation is the optimal. For efficiency, a higher, 12-13 pH range is better. Optimization is required of course to determine whether an excess of alkali or several steps are required for the best separation [22, 23].

The intensive contact can be realized by parallel static mixing reactors [24] or by counterflow vaporization [22].
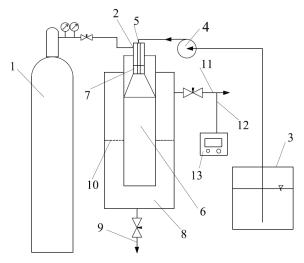
Experimental

The natural gas that had to be purified contained 20–100 ppm hydrogen sulfide and 10 (V/V)% carbon dioxide. The aim of the research is the selective removal of hydrogen sulfide. The chosen method is chemisorption with an aqueous solution of sodium hydroxide. Quick and intensive contact is provided by vaporization in the already known process; while the construction enables efficient and fast phase separation to take place.

Experimental device

Fig. 2 illustrates the experimental device built at the Department of Chemical Engineering at the University of Pannonia.

For the experiments, a model gas mixture (1) was produced in a acid-proof gas mixing bridge. The alkali was fed from the alkali vessel (3) with a feeder pump (4), whose volume flow can be regulated. The alkali is vaporized into the reaction space by the gas to be purified (6) through a nozzle (7). The intensively contacted gas and liquid get from the reactor space to the separation space (8). The wastewater (9) can be removed from the

separation space, and, after a drop catcher (10), the purified gas (11).There is sampling at both the gas inlet and outlet (12). The hydrogen sulfide and carbon dioxide percentage of the gas is measured by a Dräger X-am 7000 gas analyzer (13). A computer can be attached to the device. With the help of a program, the alkali and gas volume flows can be precisely set. The measured data (temperature, pressure, pressure drop, gas velocity, alkali velocity, gas concentration) can be recorded.
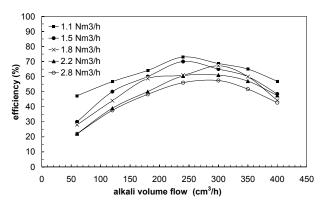

Figure 2: Experimental device.
1. gas cylinder, 2. gas inlet, 3. alkali vessel,
4. chemical feeder pump, 5. alkali inlet, 6. reactor space,
7. nozzle, 8. separation space, 9. wastewater removal,
10. drop catcher, 11. outlet of purified gas,
12. gas sampling, 13. gas analyzer

The effect of parameters on the efficiency of purification

The carbon dioxide concentration of the natural gas was a constant 10 (V/V)% for all experiments, as was the operational pressure of 30 bar. The aim of the experiments is to determine if the incidental fluctuation of the amount of gas or its concentration has any effect on the efficiency of the purification. This is important, because the gas parameters can change when opening or closing a well at a wellsite. The aim is to prove that the procedure can be operated stably, safely and with a near constant efficiency in a given range. The efficiency of the gas purification was examined by changing the following parameters: gas velocity, alkali velocity and alkali concentration.
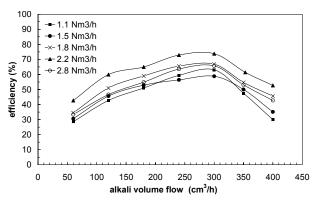
Figs 3 and *4* show the effect of the change of the amount of the gas to be purified. The experiments were carried out with two nozzles: one marked with "a" (Fig. 3) and one marked with "b" (Fig. 4). The velocity of the gas changes in accord with the amount of gas, thus affecting the efficiency of vaporization. Because of this, the nozzles can only be loaded in a given interval without significant changes in efficiency. Nozzle "a" is most efficient at 1100 Nm^3/h.

Figure 3: Change in efficiency as a function of the amount of alkali and gas with nozzle "a".

Fig. 4 illustrates the experiments with nozzle "b". Nozzle "b" is most efficient at 2200 Nm^3/h.

As for the experiments of Figures 3 and 4, it can be stated that the decrease of efficiency can be compensated by properly adjusting the velocity of the alkali. With a proper alkali velocity in the range of 1000–3000 Nm^3/h, the efficiency of purification changes by ±10%. The adjustment of the amount of alkali to the actual amount of gas can be solved easily.

Figure 4: Change in efficiency as a function of the amount of alkali and gas with nozzle "b".

Figs 3 and 4 also show the effect of the volume flow of the alkali on the purification efficiencies. As it can be seen, increasing the amount of alkali only increases the efficiency to a certain level. By increasing the amount of the inlet alkali even further, the efficiency is affected negatively. This is due to factors in vaporization. For a given gas velocity, an increasing amount of liquid decreases the efficiency of vaporization. Because of this no intensive contact takes place, also causing the efficiency of purification to decrease.

In order to get good efficiency, it is important to choose the appropriate size of nozzles for the given volume flow of the gas, and to set the appropriate alkali velocity as well.

Fig. 5 shows the effect of alkali concentration on the efficiency of purification. Only little improvement of efficiency can be achieved by increasing the concentration of the alkali. As long as pH favors the formation of HS, the rate of reaction is minimally dependent on concentration.

Figure 5: Change of efficiency
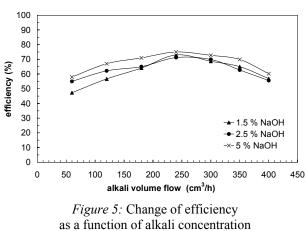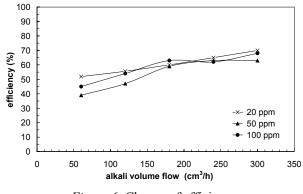as a function of alkali concentration

Fig. 6 illustrates the effect of the concentration of hydrogen sulfide on efficiency. As it can be clearly seen, the concentration of hydrogen sulfide between 20 and 100 ppm does not have an effect on the efficiency of purification (gas volume flow: 1800 Nm^3/h). This is of practical importance. If the hydrogen sulfide content of the gas at a given wellsite is fluctuating between the given limits, there is no need to change the technological parameters. The procedure operates with practically the same efficiency throughout.
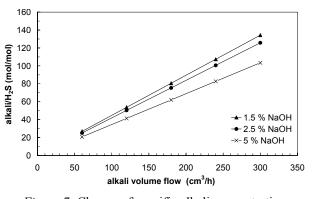

Figure 6: Change of efficiency
as a function of the hydrogen sulfide content of the gas
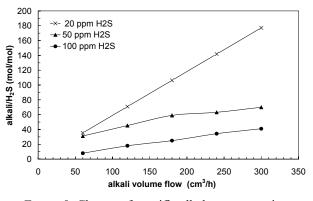
The value of specific alkali concentration

In addition to the efficiency of purification, the value of the specific alkali concentration (alkali/H_2S) is also important. The specific alkali concentration is the proportion of the used alkali and the removed hydrogen sulfide. It gives information about how much more alkali has been used compared to the amount that is required by the chemical reaction. The specific alkali concentration can be decisive when determining the volume flow and concentration of the alkali.

Fig. 7 illustrates the values of the specific alkali concentration (with the same gas velocity and 20 ppm hydrogen sulfide content) at different alkali concentrations. As it can be seen, increasing the concentration of the alkali only minimally increases the efficiency. This, however, is enough for the specific alkali concentration to be lower at higher concentrations. The difference is insignificant at lower alkali velocities. At higher alkali

velocities, the efficiency decreases, significantly increasing the specific alkali concentration.

Figure 7: Change of specific alkali concentration
as a function of alkali concentration

Fig. 8 illustrates the effect of hydrogen sulfide concentration on the specific alkali concentration (using the same amount of gas and 2.5 (m/m)% alkali). As we have already seen, the concentration of hydrogen sulfide between 20 and 100 ppm does not have an effect on the efficiency of the purification. However, the specific alkali concentration contains the amount of removed hydrogen sulfide. Hence, the higher the hydrogen sulfide concentration of the gas (in the given range), the lower the specific alkali concentration will be.

Figure 8: Change of specific alkaly concentration
as a function of the hydrogen sulfide content of the gas

Summary

We have devised a procedure for the replacement of solid adsorbents and amine-containing chemicals in hydrogen sulfide removal that can also be used with gases containing carbon dioxide. The essence of the method is that the natural gas is brought into contact with a dilute solution of NaOH in a contact time of less than 1 second. For the experiments, a laboratory Jet reactor was planned. The efficiency of purification was examined by changing the following parameters: gas volume flow, alkali volume flow and alkali concentration. It has been concluded, that for a good efficiency, a nozzle of proper size has to be selected for the given gas volume flow. Also, a proper alkali flow has to be set. The efficiency of purification changes between ±10% at the proper

alkali velocity (in the range of 1000–3000 Nm³/h). The concentration of the hydrogen sulfide gas has no effect on the efficiency of the purification between 20 and 100 ppm. Only minimal improvement in efficiency can be achieved by increasing the concentration of the alkali. These observations are of great practical value. The procedure can be operated stably and safely with almost the same efficiency if the parameters fluctuate in the above ranges.

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