

Method for Purification of Oil and Gas Condensate from Hydrogen Sulfide and Mercaptans

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ABSTRACT: Hydrogen sulfide and mercaptans contained in oil or gas condensate after treatment with an aqueous solution containing formaldehyde, nitrogen-containing organic bases (primary and secondary amines, alkanolamines and urea), ammonia and caustic soda and / or sodium carbonate, with the formation of less toxic compounds. 0.8 - 10.0 mol of formaldehyde, 0.3 - 5.0 mol of a nitrogen-containing base, urea, ammonia or mixtures thereof and 0.001 - 0.05 wt. % NaOH and/or Na₂CO₃. The reagents were introduced in the form of aqueous solutions or as a pre-prepared mixture. To speed up the process, up to 1 mol of elemental sulfur per 1 mol of RSH and up to 0.1 nm³ of air per 1 mol of hydrogen sulfide and mercaptan sulfur were added.

This method made it possible to reduce the consumption of reagents with a high degree of purification of raw materials and energy costs. We used a more watered solution of reagents, the amount of this solution is much higher than the amount of a more concentrated solution, which led to an increase in the contact surface between the organic and aqueous phases in the emulsion; water-soluble, low molecular weight mercaptans and hydrogen sulfide to a greater extent pass into the aqueous phase, where they quickly react with formaldehyde. The combination of these factors made it possible to drastically reduce the required mixing time (the volume of the reactor decreases), reduce the reaction temperature and the cost of heating the feedstock, and carry out a deeper purification of the feedstock at the same reagent consumption or reduce the consumption of reagents.

KEYWORD: oil, gas condensate, reagent cleaning, ethanalamines, mercaptan, formaldehyde.

Introduction

Oils containing hydrogen sulfide are cleaned using chemical and physical methods. The use of chemical methods leads to a deterioration in the quality of oil, since the reaction products partially or completely enter the commercial oil. When using physical methods, hydrogen sulfide is converted into a gaseous state together with other light fractions of hydrocarbons, which makes it possible to combine the process of cleaning oil from hydrogen sulfide with stabilization aimed at obtaining oil with a given saturation vapor pressure. In view of the foregoing, it is preferable to physically clean oil from hydrogen sulfide by removing this component, which is aggressive and dangerous to humans and the environment, and then disposes of it. To date, many technologies have been proposed and

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there are many patents on the issue of cleaning oil from hydrogen sulfide, incl. combining physical and chemical methods.

We propose a new method for the reagent purification of oil and gas condensate from hydrogen sulfide and mercaptans. Hydrogen sulfide and mercaptans contained in oil or gas condensate were treated with an aqueous solution containing formaldehyde, nitrogen-containing organic bases (primary and secondary amines, alkanolamines, and urea), ammonia, and sodium hydroxide and/or sodium carbonate to form less toxic compounds. 0.8 - 10.0 mol of formaldehyde, 0.3 - 5.0 mol of a nitrogen-containing base, urea, ammonia or mixtures thereof and 0.001 - 0.05 wt. % NaOH and/or Na₂CO₃. The reagents were introduced in the form of aqueous solutions or as a pre-prepared mixture. Waste aqueous solution was used instead of water. The concentration of amines in relation to water was 3 - 35%. The reaction proceeds at 0 - 60°C. To speed up the process, up to 1 mol of elemental sulfur per 1 mol of RSH and up to 0.1 nm³ of air per 1 mol of hydrogen sulfide and mercaptan sulfur were added. This method allows to reduce the consumption of reagents with a high degree of purification of raw materials and energy costs. The purpose of this method is to simplify the technological process, reduce the consumption of expensive amine, increase the efficiency of the process of cleaning raw materials from H₂S and light mercaptans C₁-C₃ and reduce toxic waste (wastewater). In our method, the goal is achieved by carrying out the process at a concentration of nitrogen-containing organic base 3 -35 wt.% with respect to water in the reaction mixture and additional introduction of 0.001-0.05 wt.% sodium hydroxide or soda into the raw material in the form of solutions in water, an aqueous solution of a nitrogen-containing organic base or a spent aqueous solution of reagents. To speed up the process, elemental sulfur was additionally added to the raw material in an amount of up to 1 mol per 1 mol of mercaptans and air in an amount of up to 0.1 nm³ per 1 mol of mercaptan and hydrogen sulfide sulfur. As a nitrogen-containing organic base, along with those specified in the known method (prototype) amines and ammonia used methanol-, ethanolamines and urea. Distinctive features of the proposed method are the additional processing of raw materials with solutions of NaOH or Na₂CO₃ and the reaction of mercaptans and hydrogen sulfide with formaldehyde and a nitrogen-containing organic base at an optimal concentration of the latter in water of 3 - 35%. These distinguishing features of the technical solution determine its novelty and inventiveness in comparison with the prior art, since the process of cleaning oil and gas condensate using formaldehyde and 3 - 35% aqueous solutions of amines and urea in the presence of NaOH or NaCO₃, improves efficiency process; reduce the necessary time for mixing raw materials with reagents; reduce the consumption of expensive amine; carry out the process at a temperature of 0-25°C, i.e. reduce energy costs for heating raw materials and reduce the amount and toxicity of waste water. NaOH or Na₂CO₃ reacts primarily with naphthenic acids and phenols. The resulting sodium naphthenates are good emulsifiers and contribute to the formation of more stable emulsions of solutions of formaldehyde and nitrogen-containing organic base with raw materials than emulsions formed in the absence of sodium naphthenates. In this case, short-term (1–5 min) stirring is sufficient to form an emulsion, then the reaction between H₂S and RSH with reagents (CH₂O and RNH₂) can continue in any vessel equipment, i. in the main pipeline or in a tank for storing purified raw materials, which simplifies the hardware design of the process (reduces the volume and number of reactors). In the absence of NaOH or Na₂CO₃, naphthenic acids bind part of the amine, forming RCOO-+NH₃R. Neutralization of these acids with alkalis reduces the consumption of amine. Elongation of the reaction time due to more efficient emulsification, for example, up to 3 hours, allows for either a deeper purification of the raw material, or the same purification, but with a lower consumption of amines and formaldehyde. With the introduction of less than 0.001% NaOH into the raw material, its emulsifying effect becomes little noticeable, insignificant.

There is no need to introduce more than 0.05% Na₂CO₃ into the raw material. In the proposed method, the concentration of amine in relation to water in the reaction mixture was taken in the range of 3-35%. The concentration of amine in relation to water in the mixture is:

$$\frac{1}{1+0,63} \dots \frac{1}{1+2 \cdot 0,63} 100 = 61 \dots 44\% .$$

The use of dilute (3-35%) amine solutions also made it possible to more efficiently extract low-molecular, most toxic C₁-C₃mercaptans from raw materials. In the aqueous phase of the emulsion, where the concentration of aldehyde and amine is much higher than in the organic phase, water-soluble C₁-C₃mercaptans react rapidly with the reagents. Thus, the use of 3-35% amine solutions made it possible to increase the selectivity of the demercaptanization process, i.e. the selectivity of the process with respect to C₁-C₃ mercaptans, and also increased the reaction rate by increasing the amount of the aqueous phase. The increase in the reaction rate and the possibility of lengthening the reaction time due to the formation of a more stable emulsion ultimately made it possible to carry out the process at a lower (0-25°C) temperature than in known methods (30-80°C), there is no need to heat the raw material before deodorization, i.e. simplifies the process.

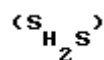
The method provides for the possibility of reusing part of the spent aqueous solution of reagents for diluting the original amine, which made it possible to save expensive amine and reduce the amount of toxic waste water. When using solutions with an amine concentration of less than 3%, the rate of the demercaptanization reaction decreases due to the dilution of formaldehyde. With an increase in the concentration of amine above 35%, the selectivity (selectivity) of the process in relation to mercaptans C₁-C₃ decreases. Aqueous solutions of formaldehyde (technical formalin or paraformaldehyde), amines, alkaline agents and waste water solution are introduced into the raw materials separately or in the form of pre-prepared mixtures. The additional introduction of elemental sulfur somewhat speeds up the process, since sulfur with mercaptans forms hydropolysulfides: RSH + S = RSnH, which are more reactive than mercaptans. Sulfur was introduced by preliminary dissolving it in the original amine, sulfur was also dissolved to 1-1.5% in the raw material, then this solution was introduced into the raw material being purified. Additional introduction of oxygen (air) at a pressure of 0.1-1.0 MPa also accelerates the process, since oxygen dissolved in the raw material in the presence of an amine oxidizes hydrogen sulfide and partially mercaptans to elemental sulfur and disulfides. Pressure to dissolve air in the raw material; at 1.0 MPa, about 1 nm₃ of air was dissolved in oils, which made it possible to oxidize up to 10 moles of hydrogen sulfide. This makes it possible to save formaldehyde. Up to 10% methyl alcohol was added to commercial technical formalin in order to prevent freezing in winter. The presence of methanol does not affect the demercaptanization process. To lower the freezing point of formalin, acetone can be added instead of methanol. The presence of acetone in the process, unlike methanol, accelerates the process of neutralization of mercaptans, i.e. gives an additional positive effect.

Along with the use of technical formalin, the proposed method provides for the possibility of using polymeric formaldehyde (paraform, paraformaldehyde), which is more convenient for transportation to oil fields remote from roads. In the method, waste water containing amines and formaldehyde is released from purified raw materials during settling. The most effective way to neutralize wastewater from formaldehyde is its condensation by treatment with alkalis. At the same time, alkali (NaOH or Na₂CO₃) is already contained in this water, i.e. there is no need for additional alkalization of wastewater.

Cleaning oil and gas condensate is easy to implement and can be implemented in oil fields as a temporary measure until the creation of industrial plants for cleaning raw materials from H₂S and

RSH or in fields with a small amount of oil production. This method has been tested in the laboratory. Below are examples and results of the experiments.

№1. In 100 ml of oil or gas condensate, we add the calculated amounts of 37% formalin containing 4% methanol, and a solution of monoethanolamine (MEA) and soda in water. The mixture in a closed flask under an argon atmosphere at 0-60[deg.]C was stirred with a magnetic stirrer for 3-30 minutes, then allowed to stand without stirring at the same temperature. After 0.5; 1 and 3 hours take samples for analysis (Table 1). In table. 1 shows the content of light mercaptans C₁-C₃ in terms of sulfur in the original and purified raw materials. The consumption of reagents CH₂O and MEA are given in moles per 1 mole of hydrogen sulfide



and sulfur mercaptan C₁-C₃ (RSH), the consumption of Na₂CO₃ and H₂O - as a percentage of the feedstock. When calculating the H₂O content, the water content in the initial formalin (59%), monoethanolamine (5%) and in the raw material (0.016%) was taken into account. First, a 10% solution of soda in water was prepared, then this solution was mixed with monoethanolamine, and the missing amount of water was added to the mixture. During the separation in the table. 1, the settling time of 50% of the total amount of aqueous solutions of reagents introduced into the raw material is taken.

Table 1. As a result of cleaning gas condensate and oil from hydrogen sulfide and mercaptans with solutions CH₂O, H₂NCH₂CH₂OH, Na₂CO₃ and NaOH.

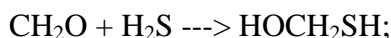
| № | reagentcosts | | | | Con cent ration MEA in water % | Tem pera ture, °C | mixi ngti me, min | Sepa ratio n time τ,mi n | testresults, ppm | | | | | |
|---|---|--------------|--|------------------------|---|----------------------------|----------------------------|---|------------------|----------|----------------------|----------|----------------------|----------|
| | CH ₂ O, mol | MEA, mol | Na ₂ CO ₃ , % | H ₂ O, % | | | | | 0.5 hour | | 1 hour | | 3 hour | |
| | | | | | | | | | | SRS H | SH ₂ S | SRS H | SH ₂ S | SRS H |
| Known method experiments. Raw material - a mixture of the Kukdumalak field (10:1) S _{H₂S} =172 ppm; S _{RSH} =930 ppm | | | | | | | | | | | | | | |
| 1 | 1.0 | 0.6 | Is abs. | 0.032 | 38.2 | 40 | 5 | 3 | 68 | 998 | 47 | 972 | 28 | 950 |
| 2 | 3.0 | 2.0 | Is abs. | 0.061 | 47.3 | 40 | 5 | 2 | 22 | 908 | 12 | 807 | Is abs. | 610 |
| 3 | 3.0 | 2.0 | Is abs. | 0.061 | 47.3 | 40 | 30 | 2.5 | Is abs | 710 | Is abs | 569 | Is abs. | 446 |
| 4 | 3.0 | 2.0 | Is abs. | 0.061 | 47.3 | 15 | 30 | 4.5 | 90 | 1116 | 46 | 980 | 21 | 888 |
| | Experiments on the proposed method: 1) using the above raw materials | | | | | | | | | | | | | |
| 5 | 1.0 | 0.6 | 0.03 | 0.31 | 5.8 | 40 | 5 | 60 | Is abs | 1160 | Is abs | 740 | Is abs | 380 |
| 6 | 3.0 | 2.0 | 0.006 | 0.118 | 30 | 40 | 5 | >180 | Is abs | 670 | Is abs | 280 | Is abs | 170 |
| 7 | 3.0 | 2.0 | 0.006 | 0.118 | 30 | 5 | 5 | >180 | 52 | 860 | 12 | 418 | Is abs | 280 |
| 8 | 3.0 | 2.0 | 0.006 | 0.118 | 4.5 | 5 | 5 | >180 | 18 | 688 | Is abs | 342 | Is abs | 260 |
| 9 | 8.0Para forms | 2.0 | 0.01 | 0.10 | 10 | 55 | 5 | >180 | 75 | 900 | 26 | 630 | Is abs | 202 |
| 10 | 5.0 | 5.0- Urea | 0.002 NaOH | 0.6 | 20- Urea | 30 | 5 | 60 | 56 | 980 | 16 | 890 | 12 | 900 |
| | 2) Raw materials - carboxylic oil containing S _{H₂S} =320 ppm; S _{H₂S} = 72 ppm | | | | | | | | | | | | | |
| 11 | 0.8 | 0.5 | 0.01 | 0.12 | 12 | 20 | 3 | >180 | 216 | 168 | 106 | 124 | 80 | 75 |

| | | | | | | | | | | | | | | |
|--|-----|-----|-------|------|----|----|----|------|------|-----|------|-----|------|-----|
| 12 | 3.0 | 0.5 | 0.01 | 0.15 | 12 | 20 | 3 | >180 | 85 | 150 | 28 | 98 | 14 | 66 |
| Experiments using spent reagent solution. Raw material - gas condensate: S _{H₂S} = 156 ppm; S _{RSH} = 398 ppm | | | | | | | | | | | | | | |
| 13 | 2.5 | 1.2 | 0.004 | 0.03 | 20 | 50 | 30 | 2 | 24 | 480 | 6 | 206 | отс. | 142 |
| 14 | 2.5 | 1.0 | 0.004 | 0.05 | 4 | 50 | 30 | 2 | отс. | 320 | отс. | 48 | отс. | 116 |

As can be seen from Table. 1, with the same consumption of CH₂O and MEA, the proposed method achieves a much more efficient purification of raw materials from H₂S and C₁-C₃ mercaptans. This is due to two factors:

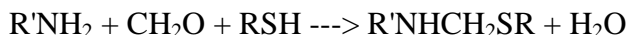
1. In the proposed method, due to the presence of alkali or soda, which form sodium naphthenates (emulsifiers) with naphthenic acids, more stable emulsions are formed; lengthening the contact time.
2. In the proposed method, a more watered solution of reagents was used, the amount of this solution is much higher than the amount of a more concentrated solution, which leads to an increase in the contact surface between the organic and aqueous phases in the emulsion; water-soluble, low molecular weight mercaptans and hydrogen sulfide to a greater extent pass into the aqueous phase, where they quickly react with formaldehyde. The combination of these factors made it possible to drastically reduce the required mixing time (the volume of the reactor decreases), to reduce the reaction temperature and the cost of heating the feedstock, and to carry out a deeper purification of the feedstock at the same reagent consumption (experiments №1 and 5; 2 and 3; 6 and 8) or reduce the consumption of reagents (experiments 3 and 5). Reducing the consumption of reagents, of course, leads to a decrease in their amount in waste - in waste water.

In experiment №14, MEA was diluted with waste water formed in experiment №13. With the same consumption of fresh reagents in these experiments, a deeper purification was achieved in experiment №14. Reuse of waste water containing amines, urea and unreacted formaldehyde reduces the consumption of reagents and the amount of waste water. The increase in the amount of mercaptans during the first 30 minutes of the reaction is explained by the formation of mercaptomethanol and its derivatives from hydrogen sulfide according to the reactions:

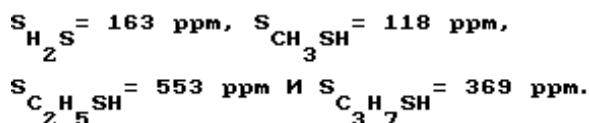


Mercaptans, including mercaptomethanol, react with formaldehyde more slowly than hydrogen sulfide;

In a simplified form, the reaction can be written as:



Urea enters into this reaction weakly, but it can be used to purify raw materials from hydrogen sulfide (experiment №10).The Kukdumalak gas condensate (Kashkadarya region of Uzbekistan) was used as a raw material, containing:



A 12% soda solution was prepared in water. Calculated amounts of MEA or urea were introduced into this solution or water. The calculated amount of the resulting solution was placed in a 100 ml round-bottom flask, the air was blown out of the flask with argon. 50 g of raw material and the calculated amount of formaldehyde (formalin) solution were introduced into the flask, closed with a cork, and vigorously stirred by shaking for 3 min. Temperature 18°C. Then they gave exposure at the

same temperature without stirring. After a certain time, samples were taken from the middle zone of the solution for chromatographic analysis of H₂S and mercaptans CH₃SH, C₂H₅SH, and C₃H₇SH. The results of the experiments are given in table. 2.

Table 2. Purification of gas condensate from H₂S and mercaptans C₁ – C₃

| № | Amount of reagents added | | | | Concentration of RNH ₂ in water % | Air consumption nm ³ /tonn | Sulfur consumption mol | Reaction time min | Sulfur compounds in refined raw materials, ppm | | | |
|----|--------------------------|---------|---------------------------------------|-----------------------------------|--|---------------------------------------|------------------------|-------------------|--|---------------------|------------------------------------|-----------------------------------|
| | CH ₂ O mol | MEA mol | CO(NH ₂) ₂ mol | Na ₂ CO ₃ % | | | | | SH ₂ S | SCH ₃ SH | SC ₃ H ₅ S H | SC ₃ H ₇ SH |
| 1 | 0.82 | 0.5 | - | - | 5.2 | - | - | 100 | 18 | 73 | 450 | 289 |
| 2 | 0.82 | 0.5 | - | 0.002 | 5.2 | - | - | 30 | 25 | 31 | 236 | 171 |
| 3 | 1.32 | 0.5 | - | 0.001 | 3.3 | - | - | 40 | 7 | 86 | 471 | 301 |
| 4 | 1.32 | 0.5 | - | 0.005 | 3.3 | - | - | 40 | 16 | 25 | 156 | 117 |
| 5 | 1.32 | 0.96 | - | 0.002 | 18.0 | - | - | 40 | Otc | 4 | 205 | 300 |
| 6 | 1.84 | 0.2 | 0.5 | 0.002 | 3.3 | - | - | 40 | Otc | 62 | 460 | 297 |
| 7 | 1.84 | 0.5 | - | 0.002 | 3.3 | - | 0.8 | 40 | Otc | 12 | 186 | 202 |
| 8 | 1.84 | 0.5 | - | 0.002 | 3.3 | 0.5 | - | 20-40 | Otcotc | Otcotc | 160-120 | 252-230 |
| 9 | 1.84 | 0.1 | 2.0 | 0.005 | 8.8 | - | - | 40-120 | 11-otc | 82-68 | 472-446 | 344-340 |
| 10 | 1.32 | 0.96 | - | - | 46.7 | - | - | 40 | 8 | 46 | 225 | 292 |
| 11 | 5.0 – paraforms | 1.0 | - | 0.005 | 35.0 | - | - | 30 | 21 | 35 | 372 | 280 |

Since at high flow rates of formaldehyde (more than 2 mol per 1 mol of RSH) and MEA, hydrogen sulfide and methyl mercaptan quickly disappear, in order to check the selectivity of the method with respect to various mercaptans, the experiments were carried out with low consumption of reagents at room temperature. As follows from Table. 2, the presence of soda noticeably improves the process (experiments №1 and 2), but it has little effect on the selectivity of the reaction with respect to mercaptans (experiments No. 3 and 4). An increase in MEA consumption leads, first of all, to a decrease in the content of H₂S and CH₃SH (experiment №5). In the presence of urea, only hydrogen sulfide mainly reacts (experiment №9). Increasing the amine concentration above 35% with respect to water in the reaction mixture (experiment №10) leads to a clear decrease in the selectivity of the process. The presence of sulfur (sulfur was previously dissolved in the raw material) and the introduction of air significantly accelerated the process. Formaldehyde in the form of polymers (paraforms) reacts with H₂S and RSH much weaker than formalin (experiment №11). However, the transportation of powdered paraform to remote oil fields and its storage, especially in winter, in practice may be more convenient than the use of formalin.

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