UDC 628.512

DOI: 10.15372/CSD20170601

Direct Heterogeneous Catalytic Oxidation of Hydrogen Sulphide for Associated Petroleum Gas Treatment

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(Received October 01, 2017)

Abstract

Up to 1 billion nm^3 of hydrogen sulphide-containing associated petroleum gas (APG) is annually flared in Russia, which leads to the release into the atmosphere to 60 thousand t of H_2S, SO_2, SO_3, carbon black, carbon monoxide, and to 3 million t of carbon dioxide and most importantly, to loss of hundreds of millions of cubic meters of hydrocarbon raw materials. The development of environmentally safe, efficient, and compact technologies to solve this problem is a pressing issue. The paper carries out a brief analysis of existing technical solutions and the description and the main trial results for technologies of the Boreskov Institute of Catalysis SB RAS.

Keywords: hydrogen sulphide, oxidation catalysts, associated petroleum gas (APG)

INTRODUCTION

According to the data of the Ministry of Energy, 83.3 billion m^3 of associated petroleum gas (APG) was extracted in the Russian Federation in 2016, which was by 6 % higher compared to a similar indicator in 2015. The main increase is ensured due to the involvement into the fuel and energy balance of sulphurous oil, at extraction of which APG containing significant amounts of hydrogen sulphide (from 0.5 to 6 vol. %) are released. A high hydrogen sulphide content eliminates dispersion of APG in the atmosphere (the maximum permissible concentration of hydrogen sulphide in the atmosphere is 0.008 mg/m^3) or its use as hydrocarbon fuel sold to population, industrial enterprises, or used for commercial needs (process heating).

Up to 1 billion of APG containing hydrogen sulphide is flared in Russia, which leads to the atmospheric emission to 60 t of H_2S, SO_2, SO_3, carbon black, carbon monoxide, and to 3 million t of carbon dioxide and most importantly, to loss of hundreds of millions of cubic meters of hydrocarbon raw materials.

Recycling of APG is strictly regulated by Decree of RF Government No 1148 from

08.11.2012 (ed. by 17.12.2016) “On peculiarities of calculating charges for negative impact on the environment due to emissions in atmospheric air of polluting substances produced by combustion in flares and (or) dispersion of associated petroleum gas” (together with “Regulation on peculiarities of calculating charges for negative impact on the environment due to emissions in atmospheric air of polluting substances produced by combustion in flare plants and (or) dispersion of APG”).

Transportation of associated petroleum gas through pipelines to specialized sulphur-refinement plants (oil refinery and gas processing plants) would be an acceptable solution. However, APG is characterized by an exceptionally small debit (100–1000 nm^3/h) and low overpressure (to 0.5 MPa), which requires the development of a chain of powerful compressor stations, the use of specialized doped materials for pipelines and predetermines a lack of options for the development of APG treatment plants in extraction places.

On the other hand, dozens of medium-proved and low-yield fields of the Volga-Ural oil and gas province (Republic of Tatarstan, Bashkortostan, Komi Republic, Samara region, Perm Krai, *etc.*) are currently mothballed because of a lack of reliable and proven technology for the associated petroleum gas treatment.

The Vysokovskoye Oil and Gas Field discovered in 1990 and localized in Berezovsky District of Perm Krai is a typical example. Oil yield during testing wells varies from 1.66 to 43.9 t/day, on average, being 17.6 t/day, gas yield – from 34.3 to 224 thousand m^3/day, on average – 60 thousand m^3/day. The productivity coefficient is 8.28 t/(day · MPa). The main problems related to the use of hydrocarbon reserves of the field for exploitation are caused by the presence of hydrogen sulphide in the amount to 0.3 % in APG, owing to which gas flaring, liquefaction, and the use of APG in communal and household needs are eliminated.

Power generation in gas turbine power plants (GTPP) or the use of gas as raw materials for obtaining synthetic fuel by GTL technology is a cost-effective option. Each of the proposed options requires deep gas treatment until the maximum permissible norm on hydrogen sulphide content (0.02 g/m^3). To date, however, the field is found in the so-called preliminary operation, while hydrocarbon resources are not used because of a lack of a technological solution acceptable from the economic standpoint [1].

THE SEPARATION OF ACID COMPONENTS BY LIQUID SORBENTS (AMINE OR ALKALI TREATMENT)

Absorption gas treatment from hydrogen sulphide is carried out as follows: At the first stage, hydrogen sulphide in the absorber is washed off in contact with a solution of an absorption agent, after which the saturated absorbing solution is sent to the thermal regeneration stage. A wide range of operational parameters (pressure, temperature, and the yield of purified flows), the guaranteed degree of hydrogen sulphide extraction with reaching residual hydrogen sulphide content regulated by GOST 5542–2014 and OST PJSC Gazprom 51.40–93 are undoubted advantages of the methods. However, in accordance with the requirements of modern legislation, acting or created amine treatment plants should be equipped with hydrogen sulphide disposal unit, and flaring H_2S is prohibited [2].

The Sulfurex® technology of DMT Environmental Technology (Netherlands) is a chemisorption method for alkaline treatment of APG from hydrogen sulphide and mercaptans [3].

The principle of operation for the treatment plant of hydrocarbon streams containing acid components (hydrogen sulphide and carbon dioxide) is as follows.

Gas containing hydrogen sulphide and requiring treatment is received into the lower part of a scrubber.

A circulating alkali solution is supplied to the upper part of the scrubber and waters rising gas with counterflows. The alkali reacts with H_2S and CO_2. The reaction products are accumulated in the lower part of the scrubber and then removed from the system.

An additional feed of the circulating solution to maintain a given concentration of alkali therein is carried out from a storage tank of NaOH solution. The alkali solution is fed therefrom into a dosing monitoring system by means of a metering pump.

A solution containing sulphides and carbonates is sent for recycling *via* a method of injecting into the formation or a reservoir designed for this.

Typical disadvantages are inherent in the process with the seeming simplicity and high indicators of effectiveness. The main of them (high operational costs) is mainly related to irrevocable losses of alkali that, in addition to target consumption (binding hydrogen sulphide), is spent for the generation of carbonates.

With the standard coefficient of the ratio (M_{NaOH} /$M(_{CO_2 + H_2S})$ = 1.2), alkali consumption during treatment of low-yield APG flow with a consumption of 8 million m^3 a year will be about 200 t, or in financial equivalent – at about 10 million RUB.

THE SEPARATION OF HYDROGEN SULFIDE FROM HYDROCARBON GASES THROUGH SOLID SORBENTS (ZEOLITES)

Adsorption processes of natural gas treatment using zeolites have been carried out at Orenburg, Minnibaevsk, Sosnogorsk, Moscow, and Nizhnevartovsk gas processing plants and additionally at Messoyakha and Medvezhie fields for gas drying. The largest gas treatment plants from hydrogen sulphide and thiols using adsorption process are in operation at the Orenburg gas processing plant. Simultaneously with treatment, gas drying to a dew point of –70 °C is also performed. Despite the active utilization of adsorption processes using synthetic zeolites, there is a series of significant limitations, the main of which include the low sorption capacity, which predetermines the frequency of adsorption/regeneration cycles, and a high cost, which negatively affects the monetary measures of the final product, *i.e.* fuel gas. Additionally, adsorption (zeolite) treatment should be accompanied by the expensive regeneration procedure, during which to 10 % of purified raw materials is lost [4].

Chemisorption processes are actively used in the modern practice of natural gas desulphurization with total extraction of hydrogen sulphide of not more than 400 kg per day. The Sulphurtrap® process developed by USA Chemical Products is a typical example. Nanoscale iron (II) oxide species with a size of 5–10 nm are used as an active component. Iron (II) oxide is synthesized from natural siderite composed mainly of iron(II) carbonate [5, 6]. As it follows from the published materials of the company,the sorption capacity for hydrogen sulphide reaches 35 %. The relative cheapness of the sorbent allows sending it for processing without regeneration.

The Boreskov Institute of Catalysis SB RAS (BIC) in cooperation with All-Russian Scientific Research Institute of Hydrocarbon Raw Material (VINIIUS) JSC have developed a formula and methods for preparation of granular samples based on iron-manganese nodules of offshore fields of the Gulf of Finland with different types of binders, such as aluminium oxide, methylcellulose, nitric acid, and magnesium oxide. Adsorption properties of the materials developed during the removal of sulphur compounds from gas flows modelling real hydrocarbon gases and a procedure for regeneration of adsorbents have been explored. The effective capacity of sorbents is 12–15 g H_2S/SO_2 per 100 g adsorbent [7, 8].

HOMOGENEOUS OXIDATION OF HYDROGEN SULPHIDE IN THE LIQUID PHASE (RED-OX PROCESSES)

One of the areas of hydrogen sulphide processing in the composition of various gases is its oxidation by oxygen to elemental sulphur in solutions of metal complexes with wide variation in pH of the medium in accordance with the reaction:

$$H_2S + 1/2O_2 \rightarrow S + H_2O + Q \quad (1)$$

The SulFerox® process developed by The Shell uses a reagent of The Dow Chemical Company characterized by elevated stability and low capital and operating costs. The latter only for reagents are 80–100 dollars per 1 t of hydrogen sulphide. Up to 80 % of methyl mercaptan and to 60 % of carbonyl sulphide is removed alongside with hydrogen sulphide during gas treatment, as demonstrated. The SulFerox® process is characterized by the use of new complexon composition that is similar to ethylenediamine tetraacetate (EDTA), however, the concentration of iron compounds is considerably higher (up to 3 mass %) than in the competitive process of the same type, Lo-Cat (to 0.5 mass %) [9]. The most powerful plant was launched in the city of Denver in 1992 (Texas). This plant is used for the treatment of the flow of carbon dioxide containing 1500 ppm hydrogen sulphide at a pressure of 2.0 MPa, the treated gas at the plant outlet contains not more than 20 ppm H_2S. Currently, the SulFerox® process is developing especially dynamically. From 1990 to 2010, The Shell designed and built more than 50 plants for treatment of various process gases.

The Volga Research Institute of hydrocarbon raw materials (VINIIUS JSC, Kazan) developed the Serox-Gas-2 process for treatment of gas flows from hydrogen sulphide by solutions of iron complexonate with obtaining elemental sulphur. The process is similar to Lo-Cat, and its main distinguishing characteristic is the composition of a sorbent that has low corrosive activity in relation to carbon steel and high stability under gas treating conditions. It is implemented *via* the standard two-stage scheme with filtration of sulphur foam and ensures hydrocarbon gas treatment to the residual H_2S content of not more than 20 mg/m^3 (GOST 5542–87) [10–12].

As demonstrated by the more than 30 year experience of VINIIUS JSC, the gas-treating process from hydrogen sulphide by chelate complexes (iron salts with EDTA) has a number of disadvantages that limit its use for gases with hydrogen sulphide content of not more than 1–2 g/m^3 (0.07–0.15 vol. %):

1. Due to the need to use a working solution, the pH of which should not exceed 8.5–9.0 units, the capacity of this solution for hydrogen sulphide is low, which leads to the requirement to increase its circulation rate through an absorber (in other words, energy costs for pumping-over increase).

2. The generation of a side product of hydrogen sulphide oxidation, *i.e.* thiosulphate, which leads to the irreversible consumption of reagents including EDTA.

3. The separation of sulphur from the resulting pulp is a significant technological problem. Despite the fact that automatic filter machines of FPAK type (automatic chamber filter press, drum vacuum filter) have been developed to date, the complexity of their operation and high costs make the treatment process economically expensive.

4. A low quality of elemental sulphur makes it difficult to use it as a chemical product.

DIRECT OXIDATION FOR HYDROGEN SULPHIDE REMOVAL FROM GAS FLOWS

As demonstrated by the presented analysis of literature sources, all the methods listed are characterized by significant drawbacks, general of which are insufficient flexibility and consequently, low environmental safety. Methods based on direct heterogeneous oxidation of H_2S, when reaction (1) is carried out in a layer of a special solid catalyst that ensures hydrogen sulphide conversion into elemental sulphur with high selectivity, are largely free from these disadvantages.

This process has a number of significant advantages, the main of which are the following:

The single-step character and continuity;

"Soft" conditions (T = 220–280 °C) through the use of highly active catalysts, which allows for oxidation of hydrogen sulphide directly in the composition of hydrocarbon gases.

There were attempts made to develop techniques of selective treatment of gas hydrocarbon streams based on the process of direct oxidation of hydrogen sulphide. For instance, the results of pilot tests of catalysts based on natural bauxites from the Turgai field during treatment of natural gas from the Mubarek field (the Republic of Uzbekistan) are presented in [11]. A fundamental opportunity for single-stage treatment of initial gas from hydrogen sulphide to the norms determined by GOST 5542–87 (20 mg/m^3 H_2S) has been demonstrated.

The M-I Swaco developed the SulfaTreat® DO process [13, 14] for APG treatment from hydrogen sulphide by direct oxidation. The process is carried out at a temperature of 175 °C, a pressure of 65 bar and allows carrying out treatment of gases containing to 3 % of H_2S. A catalyst is a mixture of transition metal oxides promoted with alkali metal oxides. The concentration of H_2S in purified gas does not exceed 950 ppm, as demonstrated by the test results of a pilot plant. The degree of sulphur extraction, in this case, was more than 88 % with a minor conversion of hydrocarbon fraction.

The leading positions in the study area of the process for direct heterogeneous catalytic oxidation of hydrogen sulphide with obtaining elemental sulphur and the development of complete technologies for industrial use belong to BIC SB RAS.

The technology modification is carrying out direct oxidation of hydrogen sulphide in a reactor with a fluidized bed of spherical catalyst granules with simultaneous heat removal from the reaction zone. Treatment objects in this case are sour gases, gases of hydrotreating (hydrogen sulphide concentration in the source gas of 5–95 vol. %), formed resulting from amine treatment of initial hydrocarbon gas, high-sulphur natural gases [15–33].

There are also issues for treatment of energy carriers, such as APG that have low overpressure, tail and vent gas of various chemical industries.

To solve these tasks it was proposed to carry out direct oxidation in a reactor with a monolithic or granular catalyst or catalyst with honeycomb structure [32–40].

Field tests of the technology were carried out for the first time at Astrakhan gas condensate field (AGCF), the main characteristic of which is high hydrogen sulphide content in natural gas (to 28 vol. %).

Figure 1 gives the technological scheme for the pilot plant, the main element of which is a fluidized bed reactor. As demonstrated by the test results, the degree of treatment was no less than 96.6 % during the whole operating time, moreover, hydrocarbon fraction composition remained quantitatively.

INDUSTRIAL PLANTS FOR ASSOCIATED PETROLEUM GAS TREATMENT BY THE TECHNOLOGY FOR DIRECT CATALYTIC OXIDATION OF HYDROGEN SULPHIDE OF THE BORESKOV INSTITUTE OF CATALYSIS SB RAS

Industrial plant for direct oxidation of hydrogen sulphide at the Bavlinskii desulphurization plant of Tatneftegazpererabotka Administration of Tatneft PJSC

A sulphur removal facility was created in 1975 to purify APG of the Romashkinskoye field and includes as the main node amine treatment to separate hydrogen sulphide that was flared. During operation, to 200 000 t hydrogen sulphide, sulphur dioxide, and sulphuric acid, to 1000 t carbon monoxide and to 1000 t cancerogenic carbon black compounds were

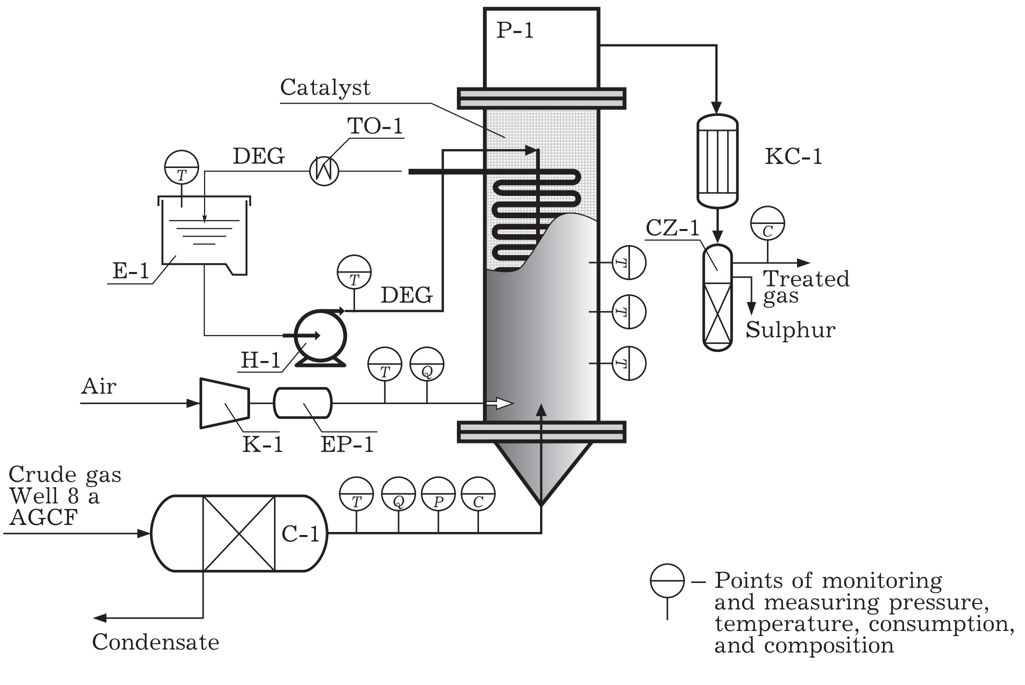

Fig. 1. Functional diagram of the pilot plant for gas treatment from hydrogen sulphide in the Astrakhan gas condensate field. A fluidized bed reactor, capacity up to 50 nm^3/h; hydrogen sulphide content in the source gas up to 27 vol. %; hydrocarbon fraction composition: methane – 95 %, C_{2+} hydrocarbons – rest.

emitted to the atmosphere. Boreskov Institute of Catalysis in cooperation with Tatneft PJSC and VINIIUS JSC created and put in operation an industrial fluidized bed plant for disposal of hydrogen sulphide in 2011. Table 1 and Fig. 2 give the major parameters and the appearance of the plant.

The main outcomes of plant operation in the Bavlinskii gas shop from May of 2011 until now are listed below:

i) There has been produced 650 million m^3 of treated gas for supply to customers;

ii) There has been recycled 3500 tons of hydrogen sulphide to elemental sulphur;

iii) Emissions of 7000 t of sulphur dioxide and sulphuric acid have been prevented.

iv) Environmental damage for the sum of about 2 billion rubles has been averted.

TABLE 1

Main parameters of the unit for direct oxidation of hydrogen sulphide at Bavlinskii sulphur removal facility of Tatneftegazpererabotka Administration of Tatneft PJSC

Parameters	Value
Yield of associated petroleum gas entering amine treatment, nm^3/h	Up to 8000
Yield of acid gas after installation of amine treatment at direct oxidation unit, nm^3/h	Up to 250
H_2S concentration in acid gas, vol. %	25–65
Fluidized bed reactor diameter, m	0.55
Catalyst loading, kg	200
Sulphur yield, t/h	Up to 0.1

Industrial plant for direct oxidation of hydrogen sulphide in the oil treatment unit at the booster pump station (BPS) 3010 of SMP-Neftegaz JSC

Sulphur-containing associated petroleum gas with hydrogen sulphide content of 1–3 vol. % is released in the amount up to 600 nm^3/h during oil separation in BPS. Earlier, these gases have been flared leading to irrecoverable losses each year to 10 000 t of hydrocarbon raw materials and release to 500 t of sulphurous compounds to the atmosphere.

TABLE 2

Main parameters of the unit for direct oxidation of hydrogen sulphide at the installation of oil treatment at the booster pump station (BPS) 3010 of SMP-Neftegaz JSC

Parameters	Value
Yield of associated petroleum gas, nm^3/h	Up to 600
H_2S concentration in APG, vol. %	1–3
Catalytic reactor diameter, m	0.9
Catalyst loading, t	0.9
Sulphur yield, t/year	180
Expected degree of H_2S removal from gas , %	>95

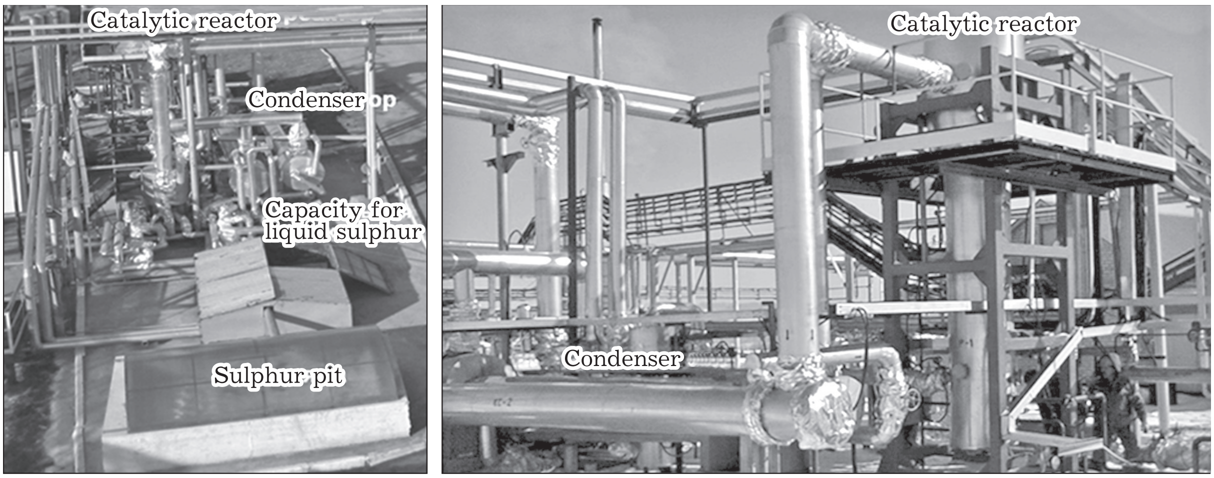

Fig. 2. Appearance of an industrial plant for hydrogen sulphide disposal at the Bavlinskii desulphurization facility of Tatneftegazpererabotka Administration of Tatneft PJSC. A fluidized bed reactor, productivity for acid gas of amine treatment up to 250 nm^3/h; hydrogen sulphide content of 25–65 vol. %.

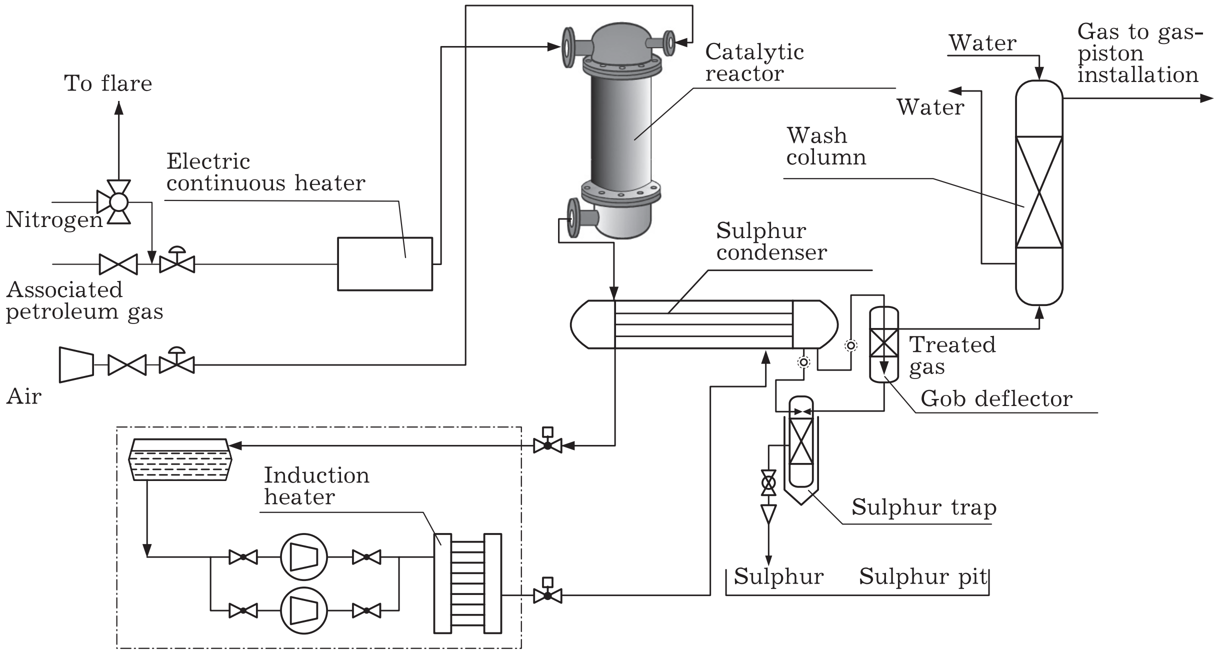

Fig. 3. Functional diagram of an industrial plant for associated petroleum gas treatment using direct catalytic oxidation. A fluidized bed reactor, APG productivity up to 600 nm^3/h; hydrogen sulphide content up to 3 vol. %.

In 2016, using the oil treatment unit of BPS 3010 of the SMP-Neftegaz JSC, BIC in collaboration with specialists from TATNIINEPHTEMASS JCS and VINIIUS JSC developed an industrial unit for the selective removal of hydrogen sulphide directly in the composition of APG in accordance with the direct oxidation reaction (1). [41, 42] Table 2 and Fig. 3 and 4 give the main parameters and the appearance of the plant.

The selectivity against the hydrocarbon fraction of the treated gas is the most important process indicator. In this regard, a method has been developed and the studies of gas hydrocarbon fraction composition accompanied by exact identification of individual components have been carried out.

Fig. 4. Appearance of an industrial plant for treatment of associated petroleum gas (APG) using direct catalytic oxidation.

TABLE 3

Composition of the initial and treated gas by the technique for direct catalytic oxidation of hydrogen sulphide from associated petroleum gas

Components	Concentration, vol. %	
	Raw gas	Treated gas
Hydrogen sulphide	1.50	<50 ppm
Water	0.69	2.03
Helium	0.05	0.04
Hydrogen	0.006	0.004
Oxygen	0.04	0.92
Carbon dioxide	4.70	4.56
Nitrogen	39.82	41.00
Ethane	9.60	9.60
Methane	25.60	24.22
Propane	9.96	9.8
Isobutane	2.02	1.96
n-Butane	3.45	3.34
Isopentane	1.23	1.19
n-Pentane	0.85	0.81
Hexanes	0.32	0.31
Heptanes	0.07	0.065
Octanes	0.10	0.09

Table 3 gives the research results. As can be seen from the data given, hydrocarbon components are quantitatively preserved, and the treated gas may be used for the generation of heat and electric energy with the minimum impact on the environment.

CONCLUSION

Based on fundamental research, single-stage techniques of associated petroleum gas treatment from hydrogen sulphide have been developed. They have been industrially realized.

An associated petroleum gas treatment plant has been developed and operated at the Bavlinskii gas shop of Tatneftegazpererabotka Administration of Tatneft PJSC.

A plant for selective catalytic treatment of associated petroleum gas from hydrogen sulphide in its composition has been developed (oil treatment unit in BPS 3010, Zainsky District, Republic of Tatarstan).

The technique of direct catalytic oxidation of hydrogen sulphide combined with amine treatment ensures:

Production of fuel gas and sulphur in accordance with the requirements of GOST (fuel gas – GOST 5542–87, technical sulphur – GOST 127.1–93).

Operation range expansion compared to the Claus process.

Reducing capital and operating costs compared to the Claus process.

A significant improvement of environmental indicators.

The payback period for the plants is 1–2 years.

An opportunity to use the proposed technical solutions for the direct efficient removal of hydrogen sulphide from gas hydrocarbon streams has been demonstrated on an industrial level.

Acknowledgement

The work was performed in the frame of budget funding of Boreskov Institute of Catalysis (project No. 0303-2016-0014).

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