Basic technologies of direct catalytic oxidation of H2S to sulfur

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Abstract. A brief analysis of the existing technical solutions for the purification of gases from hydrogen sulfide is carried out. The huge volume of such emissions and the lack of ready-made solutions for mini-gas processing plants and mini-refineries determine the relevance of the development of environmentally reliable, efficient and compact technologies to solve this problem. The main results of tests of technologies and installations developed at the Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk) based on the direct catalytic oxidation of hydrogen sulfide are presented.

1. Introduction

More than 40% or > 70\cdot10^{12} \text{nm}^3 of the world’s hydrocarbon gas reserves are hydrogen sulfide containing natural and oil-associated gases. This feedstock is a significant resource for energetics and chemical synthesis. However, high content of hydrogen sulfide (1-30 vol.%) excludes the direct application of these gases as fuels or raw materials for downstream production. The currently used flame combustion of such gases leads to air pollution with toxic sulfur di- and trioxide, sulfuric acid, products of incomplete combustion of hydrocarbons, and carcinogenic soot, amount of which attains one million tons a year.

2. Results and discussion

The available worldwide experience in the utilization of hydrogen sulfide is based mainly on the Claus process. The Claus method [1-6], which consists of several stages, is a classic multi-tonnage process for processing gases highly concentrated in hydrogen sulfide. The feed gas for the Claus process is acidic gases. The term “acid gases” is used to denote gases obtained after sorption purification processes of hydrocarbon raw materials. As a rule, sour gases formed during the hydrotreating of oil fractions are characterized by a significantly lower flow rate (<1000 nm3 / h) and a high content of hydrogen sulfide, the concentration of which, depending on the efficiency of the primary treatment plant, usually exceeds 90% compared to sour gases generated at the GPP (for example, the capacity of only one technological line at the Astrakhan GPP is over 15,000 nm3 / hour).

Also, for the disposal of hydrogen sulfide, processes of the WSA type, developed by the Danish company Haldor Topsø [7], are actively used (Fig. 1).
The gas is combusted to sulfur dioxide in the waste heat boiler burner. If the feed gas contains no combustible gas contamination, combustion support is required if the feed gas contains less than 25% H₂S. A gas is formed, containing, as a rule, 5-6% SO₂ and all the water from the combustion of H₂S and other combustible substances. Gas leaves the waste heat boiler at a temperature of about 400°C. After that, the gas enters the SO₂ reactor for contacting, which has 2 or 3 shelves with a catalyst, depending on the actual process conditions and the desired degree of conversion. Because the reaction is exothermic, the gas is cooled between the catalyst shelves along the line of optimum temperatures. After the last stage of conversion, the gas is cooled, most of the SO₃ reacts with water vapor, and gaseous sulfuric acid is formed. Then the gas is directed to the WSA condenser, where the final hydration and condensation of the acid takes place. The WSA condenser has a tubular structure, where the tubes are made of special borosilicate glass, resistant to temperature extremes and acid. The gas moves through tubes that are cooled from the outside by the counterflow of air. Sulfuric acid is concentrated in the stream by the hot process gas. The gas containing sulfuric acid vapors passes inside the pipes and is cooled to 100°C by heat exchange with air at ambient temperature. The acid is condensed, concentrated and cooled before being pumped into storage. The cooling air leaves the condenser at a temperature of 200-250°C. Part of the hot air is used as air for combustion of hydrogen sulfide, and the rest can be used for preheating boilers. The excess heat of reaction can be used to generate steam. The saturated steam taken from the steam drum is then used to cool the SO₂ reactor shelves and exits as superheated steam, its temperature is usually more than 400°C, or it can be given the desired properties. The required steam pressure is determined by the SO₃ and water content in the process gas so that the entire surface temperature is well above the acid dew point.
An alternative to the Claus process can be biological treatment [8-10]. For example, UOP LLC, Shell Global Solutions B.V. and Paques Bio System B.V. the THIOPAQ process has been developed for the selective biological treatment of gaseous hydrocarbon streams of H₂S and light mercaptans, which are converted into elemental sulfur or sulfate [8].

The Thiopaq process combines three stages: absorption (removal of H₂S from the gas), bioreactor (s) and sulfur recovery.

A key element of the process is a specially designed bioreactor. In a reactor with air-lift circulation in the presence of microorganisms and under controlled conditions, sulfide ion (HS⁻) is oxidized to elemental sulfur in the presence of aerobic microorganisms (bacteria). Bacteria use the energy released during sulfide oxidation for metabolism. The resulting elemental sulfur is hydrophilic in nature and is separated from the aqueous phase in a three-phase separator.

The stage of absorption of H₂S from gas is integrated into the general scheme of the Thiopaq process; the used absorbent is subjected to regeneration. Regeneration is carried out due to the fact that in the process of oxidation of sulphide to elemental sulfur, alkali is regenerated, which was consumed for the absorption of H₂S. The bioreactor is operated at atmospheric pressure and a temperature of 30-35°C.

At Boreskov Institute of Catalysis, new processes based on direct catalytic oxidation of hydrogen sulfide were developed. Main advantages of this method are: a single catalytic reactor providing H₂S conversion of up to 99%, mild reaction conditions (T=220-280°C), selective oxidation of H₂S in the presence of hydrocarbons and possibility to build and operate units of small and medium size.

Two versions of the technology have been developed: in the reactor with a fluidized bed of catalyst and in the reactor with honeycomb monolithic catalyst. Nowadays this technology was successfully tested in the pilot and industrial scale on the largest sour gas fields, refineries and gas processing plants in Russia, such as Astrakhan and Orenburg sour gas fields and Ufa refineries.

Examples of technologies implementation

The use of associated petroleum gases is strictly regulated by the decree of the government of the Russian Federation of 11/08/2012 N 1148 (as amended on 12/17/2016) "On the specifics of calculating fees for the negative impact on the environment when pollutants are released into the air, generated during combustion in flares and (or) dispersion of associated petroleum gas.

Along with this, APG is a significant source for the production of propane-butane fraction for the petrochemical enterprises of the Russian Federation, which are experiencing a serious shortage of this kind of feedstock. To solve the problem of primary treatment, amine treatment units with the release of hydrogen sulfide are created in the places where associated petroleum gas is collected, and hydrocarbon components are transported to the places of further processing. However, in this case, the problem is only partially solved, since the released hydrogen sulfide is burned in a flare.

Typical examples of the implementation of this approach are the Bavlinsky Gas Workshop of PJSC TATNEFT, the Shkapovsky and Tuimazinsky Gas Processing Plants of PJSC ANK Bashneft.

In 2011, the Boreskov Institute of Catalysis, together with specialists from PJSC TATneft and JSC VNIIUS, created and put into operation an industrial unit with a fluidized catalyst bed for the utilization of hydrogen sulfide from acid gases of amine purification of APG. (Fig.2)

The main results of the operation of an industrial plant in the Bavlinsky gas workshop are given below.

1. Produced 1000 million m³ of purified gas for delivery to consumers.
2. 5000 tons of hydrogen sulfide processed into elemental sulfur (Fig. 3).
3. Prevented emission of 10000 tons of sulfur dioxide and sulfuric acid into the atmosphere (400 railroad tanks).
4. Prevented environmental damage in the amount of up to RUB 2.5 rubles billion (to be specified)
Since 2002, the Russian Federation has had stringent restrictions on the content of hydrogen sulfide in oil for pipeline transport. In this case, the mass fraction of hydrogen sulfide is limited to a value in the range of 20-100 ppm (GOST R 51858-2002. Oil. General specifications, INTERSTATE STANDARD. GOST 31378-2009. Oil. General specifications). When refining 200 tons of oil per hour, up to 0.1 tons of hydrogen sulfide per hour or 800 tons of H₂S on an annualized basis are formed. This direction is all the more relevant in connection with the transition in the near future (2019-2020) to the norms determined by the Technical Regulations of the Eurasian Economic Union "On the safety of oil prepared for transportation and (or) use" (TR EAEU 045/2017), limiting the content of hydrogen sulfide to a value of 20 ppm.

To solve this problem, the Boreskov Institute of Catalysis, together with specialists from LLC "SHESHMAOIL" and JSC "VNIIUS", created an industrial installation (see the Fig.4)
Figure 4. Flow-sheet diagram of oil stripping gas purification unit at LLC "SHESHMAOIL"

Unit for direct oxidation of hydrogen sulfide in the composition of associated petroleum gases
Another area of using sulphurous APG is the use of marginal flows with a capacity of up to 1000 nm³/hour. On the one hand, such flows are a source of environmental pollution, and on the other hand, they can be used in the presence of a compact cleaning method for autonomous generation of heat and electric energy for travel heaters, power supply of gas turbine units, etc.
In 2016, at the oil treatment unit at JSC SMP-Neftegaz, the Institute of Catalysis of the SB RAS, together with specialists from JSC TatNIIneftemash and JSC VNIIUS, created an industrial unit for selective removal of hydrogen sulfide directly as part of APG [11] (Fig. 5). The unit has passed a full cycle of industrial tests and is ready for continuous operation.

Figure 5. Industrial unit for direct oxidation of hydrogen sulfide in the composition of associated petroleum gases

At present a plant for utilization of hydrogen sulfide formed in the hydrocracking process is being created at Ust-Luga Complex of PAO NOVATEK. The technology was selected as a result of sealed bids because it proved to be the most optimum one in comparison with technologies proposed by foreign companies: WSA of Haldor Topsoe, THIOPAQ of UOP LLC, Shell Global Solutions B.V. and Paques B.V.
Main ready-to-assembly sub-unit of the desulfurization plant for PJSC NOVATEK are shown at Fig. 6-7.
3. Conclusion

1. A simple one-stage technology for the purification of oil-associated gases from H₂S was developed.
2. Industrial facility in the Bavlinskiy gas shop of Tatneftegazpererabotka of PJSC Tatneft has been created and is operated continuously.
3. The following facilities have been developed and constructed and now are being in the state of starting and adjustment:
   3.1. The installation for the purification of the blow-off gases of high-sulfur crude oil. «Kutema» Cheremshansky Region. Republic of Tatarstan.
   3.2. The installation for the direct oxidation of hydrogen sulfide in the composition of oil-associated gases. DNS 3010. Zainsk Region. Republic of Tatarstan.
   3.3. The installation for the direct oxidation of hydrogen sulfide for the replacement of Claus Process. MTU-0.5 (mini oil processing plant). Republic of Kazakhstan.
   3.4. The installation for the direct oxidation of hydrogen sulfide in the composition of oil-associated gases. The unit for the oil preparation at DNS 3010 Zainsk Region. Republic of Tatarstan.
4. The technology in combination with amine treatment provides:
   4.1. The production of commercial products that correspond to Technical Standards: fuel gas (GOST 5542-87) and sulfur (GOST 127.1-93).
   4.2. Extended operational range by H₂S content in comparison with Claus units.
   4.3. Reduction of the capital and operation costs in comparison with Claus units.
   4.4. The substantial improvement of environmental situation due to excluding of hazardous emissions and wastes.

The payback period for the direct oxidation units is 1-2 years.

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