Preliminary purification of biogas from hydrogen sulfide in biomethane production

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Abstract - The prospects of biogas and biomethane technologies are shown. The technology of preliminary purification of biogas from hydrogen sulfide by the quinhydrone method in the production of biomethane is described.

Keywords - biomethane, production, biogas, purification, hydrogen sulfide, quinhydrone oxidation system.

Introduction

Biogas is an environmentally friendly fuel and one of the most promising sources of energy in the world. It is obtained during anaerobic decomposition by microorganisms of various types of organic raw materials. During this process, organic fertilizer is also obtained - digestate.

The resulting biogas contains mainly methane (50... 70%) and carbon dioxide (45... 30%). Depending on the type of raw material for its production, biogas may be contaminated with impurities of ammonia NH_3 , hydrogen sulfide H_2S , nitrogen NH_3 , siloxanes, and oxygen O_2 .

Biogas is mainly used for combustion and electricity production. However, it can also be purified from CO_2 , enriched with CH_4 content, and biomethane, which is an analog of natural gas, can be obtained. It is expected that the production of biomethane, as a more valuable chemical product and fuel, will exceed the production of biogas. Thus, in 2020, 15 billion m³ of biogas and 3 billion m³ of biomethane were produced in EU countries. It is planned to produce 7 billion m³ of biogas and 35 billion m³ of biomethane in 2030 [1].

Ukraine, unlike the EU countries, is just beginning its journey toward the use of biomethane. Recent NERC Resolution No. 847 dated 02.08.2022. "Amendments to the Code of the Gas Transmission System and the Code of Gas Distribution Systems" removed restrictions on the oxygen content of biomethane, which limited its supply to gas networks and, in general, the growth of the biomethane industry in Ukraine. As a result, the agricultural company "Gals Agro" launched in the Chernihiv region the first in Ukraine biomethane installation on the basis of one of the company's six biogas plants with a total capacity of 6.9 MW of electric energy. 600 m³/h of crude biogas is supplied for enrichment, which is produced mainly from corn silage, from which is produced 330 m³/h biomethane (equivalent to 1.3 MW). Upgrading of biogas to biomethane takes place in the membrane installation of the company BRIGHT BIOMETHANE (Netherlands).

In world practice, there are many methods of purification of biogas from CO_2 and the production of biomethane (physical, adsorption, absorption, chemisorption, etc.). Membrane technologies are widely used in the EU. But for almost all methods of biogas production, as a rule, preliminary purification of biogas from hydrogen sulfide is necessary. Hydrogen sulfide is known to be a toxic and chemically active substance that causes environmental pollution, catalyst poisoning, equipment corrosion, etc. in the processes of processing and use of biogas.

The work aimed to provide information on the quinhydrone method of gas purification from hydrogen sulfide, which can be successfully used at the stage of preliminary purification of biogas from hydrogen sulfide.

Lviv Polytechnic National University has developed a quinhydrone method for purifying gases from H_2S . The method has experience in industrial applications for ventilation gas purification from H_2S at Yavoriv State Mining and Chemical Enterprise "Sirka" (Lviv region) [2].

The method consists of the chemisorption of H_2S from gases with an absorption solution based on sodium carbonate, oxidation of H_2S to S by a quinhydrone oxidizing system (QOS) and regeneration of the reducing form of QOS with air oxygen:

$$Na_2CO_{3(L)} + H_2S_{(G)} = NaHS_{(L)} + NaHCO_{3(L)}$$

$$(1)$$

 $NaHS_{(L)} + NaHCO_{3(L)} + \{Q\}_{(L)} = Na_2CO_{3(L)} + \{Q\}H_{2(L)} + S_{(S)}$ (2)

$$Q H_{2(L)} + 1/2 O_{2(G)} = \{Q\}_{(L)} + H_2 O_{(L)}.$$
(3)

where $\{Q\}$ and $\{Q\}H_2$ are the "quinone" and "hydroquinone" forms of QOS.

For preliminary purification of biogas to a hydrogen sulfide content of less than 0.006 g/m^3 , we have developed a method with chemical regeneration of QOS (Figure).

Biogas is fed for purification from hydrogen sulfide to the absorber HABD - a horizontal absorber with bucket dispersants (2). The absorber is irrigated with an absorption solution with component concentrations, kg/m³: Na₂CO₃ 10...20; Na₂S₂O₃ 250...350; quinhydrone 5. The process temperature 25....35 °C. Purified biogas is sent for further purification from CO₂ and biomethane production.

Regeneration of the absorption solution is also carried out in the absorber HABD (4) with a temperature 35... 45 °C. The exhaust air after the drip trap (3) is emitted into the atmosphere. After its regeneration, the sulfur paste is separated from the absorption solution in a sump (5) and a drum vacuum filter (8). The clarified solution from the sump and the filtrate from the vacuum filter is collected, adjusted in composition, and returned for biogas purification to the absorber (2).

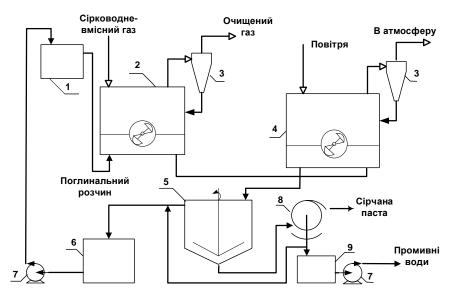


Figure - Technological scheme of biogas purification from H2S in absorbers HABD: 1 -hydraulic pressure tank; 2 -absorber HABD; 3 -drip trap; 4 -solution regenerator; 5 -sump; 6 -tank for a regenerated solution; 7 -pumps; 8 -vacuum filter, 9 -tank for sulfur washing water.

A paste of fine sulfur can be used as an additive to the digestate or as a raw material for the production of a valuable sulfur fungicide.

References

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