Comparative Analysis of Gas Purification Processes from Acidic Components

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A B S T R A C T
The article discusses methods for cleaning hydrocarbon gases by absorption, adsorption, catalysis, membrane technologies and directions for their development. A comparative evaluation of the effectiveness of each method for the removal of carbon dioxide and organic sulfur compounds has been carried out.

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Against the background of the globalization of the world economy, there is an increase in competition in the world energy markets, which leads to quantitative and qualitative changes in their structure, the development of exchange trading and the liberalization of pricing models.

Based on the results of studies by domestic and foreign authors, as well as reports from energy organizations, the following trends in the transformation of energy markets in general and the gas industry in particular have been identified: an increase in the share of gas in the global energy balance, an increase in world trade in natural gas, the development of LNG and the displacement of pipeline supplies by it, demonopolization regional gas markets and changing gas pricing mechanisms.

Of all the energy carriers in the world, natural gas consumption has grown at the fastest rate in recent decades. In this connection, experts predicted a significant increase in demand for gas, which will exceed the growth in demand for other energy sources. However, the coronavirus pandemic has made its own adjustments to the forecasts for the development of the global gas market.

The capacity of gas processing enterprises in the world in recent years, according to OGJ, has increased significantly (1,1%). The development of the gas processing industry also demonstrates positive dynamics in terms of key indicators such as growth in gas production and an increase in its efficiency. A significant part of the increase in productivity was obtained through the construction of new facilities, the rest - due to the expansion of production at existing enterprises.

It should be noted the influence of the gas composition on the complexity of its preparation and processing. Hydrocarbon gases contain a significant amount of acid gas components, water vapor, mechanical impurities, salts, small amounts of oil and hydrocarbon condensate.

The moisture content in gases adversely affects the processes of their processing, the main technical and economic indicators (TEI) of the installation and transportation worsen, where the precipitation of water condensate in the pipes will lead to the formation of crystalline hydrates. In the presence of acidic components, water vapor contributes to the occurrence of active corrosion processes. Usually, heavy hydrocarbon gases under the same conditions contain less water vapor than light ones. The presence of hydrogen sulfide (H_2S) and carbon dioxide (CO_2) in the composition of the gas increases the content of water vapor, the presence of nitrogen (N_2) reduces them.

Liquid inclusions of condensate in gases impede the operation of drying and low-temperature gas processing plants, have shock effects on the moving parts of gas compressors, which subsequently leads to their premature wear.

Thus, one of the important stages of gas processing is its preliminary preparation.

Purification of hydrocarbon gases from acid components and inert gases, as well as water vapors that impede processing processes, is carried out using:

- adsorption;
- absorption;
- catalytic methods;
- membrane technology.

Adsorption processes based on the absorption of acidic components by solid absorbers of cleaning are divided into chemical and physical. The main difference between the two types of adsorption is determined by the energy characteristics of the bonds. Absorption is based either on the chemical binding of acid gases and sulfur compounds - chemisorption, or on the solubility of acidic components - physical absorption, as well as their combination.

During physical adsorption (physisorption), no change in the electronic structure of atoms or molecules is observed. Physical adsorption is caused by van der Waals forces of interaction between adsorbate and adsorbent molecules. These forces are small, since there is no activation barrier, and therefore the heat of physical adsorption is $\sim 10 - 30\ kJ/mol$. Physical sorption is characterized by reversibility (regeneration of the adsorbent), multilayer adsorption. In addition, the process proceeds only at relatively low temperatures.

Physical adsorption can proceed on active carbons, on silica gels and alumina gels. However, their low capacity due to the coadsorption of heavy hydrocarbons makes them unpromising, and synthetic zeolites, which are selective to polar molecules and have a high absorption capacity, are mainly used for purification in industry. CO_2 and H_2S are successfully absorbed by CaA, NaX and NaA grade molecular sieves. The desorption stage is carried out by heating the adsorbent, vacuuming, purging with an inert gas and requires significant energy consumption.

chemical bonds that arise between the adsorbate and the adsorbent, in which surface compounds are formed. The chemisorption process is of an activation nature, the heat of chemisorption is $\sim 100 - 400\ kJ/mol$. The adsorbate and adsorbent molecules must have an energy that exceeds the threshold value of the activation energy.

Iron and zinc oxides have found industrial application among chemical methods. But these processes are less widespread due to low manufacturability, non-recoverability and the need to dispose of the spent sorbent.

Due to the availability and low cost, it would be promising to use methanol and water as an absorbent, but there are a number of disadvantages such as low carbon dioxide absorption capacity and low selectivity.

In recent years, for the purification of natural gas with a low content of heavy hydrocarbons, the Rektisol process is used, based on the absorption of CO_2 and H_2S by cold methanol (-60 ÷ -70 0C). The Fluor process is used to purify natural gas with a high CO_2 content and a low H_2S /CO_2 ratio using poly- or ethylene carbonate. Among the physical processes, the most widely used is the "Seleksol" process, where seleksol, dimethyl ether of polyethylene glycol, is used as an absorbent. The advantages of selexol are:

extraction of all acidic components and organosulfurs, H_2S selectivity in the presence of CO_2, non-corrosive. However, its use is limited by the content of heavy hydrocarbons (HC). Without preliminary extraction of heavy hydrocarbons, it can only be used to clean dry gases. Physical absorbents have found application in the Purizol processes, based on the use of N-methylpyrrolidone, Estasolvat - tributyl phosphate is used.

During chemisorption, the interaction of acid gases with the active components of the absorbent leads to the formation of chemical compounds, which, when the temperature rises, easily decompose into the original components.

Among chemical absorbents, alkanolamines have found wide industrial use: amines interact with acidic gas components to form sulfides/hydrosulfides and carbonates/bicarbonates.

Among chemical sorbents, ethanolamine purification processes are most widely used in domestic gas processing. The most widely used absorbents are monoethanolamine (MEA) and diethanolamine (DEA).

There is a tendency to replace the previous ones with the most effective absorbent, methyldiethanolamine ($MDEA$), which is used as an absorbent when there is no need for a high purity of the product. To increase the efficiency of the process, imidazole is added to the $MDEA$ solution.

Diisopropanolamine ($DIPA$) is also used as a chemisorbent in the form of an aqueous solution with a concentration of up to 40 %. $DIPA$ provides fine gas purification from H_2S - up to 1,5 mg/m^3 and CO_2 - up to 200 mg/m^3 (up to 0,01 %) with low solubility of hydrocarbons in it. At the same time, up to 50 % of COS and RSH are extracted. $DIPA$ with CO_2, COS and RSH forms easily regenerated compounds. Losses of $DIPA$ during regeneration are approximately half that of MEA.

The experience of using these processes made it possible to identify the advantages and disadvantages of each (Table 1).

The common disadvantages of these processes are:

- high energy consumption (about 70 %) for absorbent regeneration and heat generation;
- corrosive activity of alkanoamines.

The solution to these problems is the addition of corrosion inhibitors to the ethanolamine solution within the protective concentration, which makes it possible to reduce the circulation of the absorbent, that is, to reduce energy costs for pumping, increase the productivity of the installation, and reduce the corrosion rate of equipment.

The maximum allowable absorption capacity of the absorbent is limited by the allowable corrosion of the apparatus and the maximum allowable heat of chemisorption.

The Econamine process is also used to purify gases, in which a solution of diglycolamine (DGA) is used as an absorbent. The use of DHA instead of MEA makes it possible to reduce the consumption of the absorbent and heat and power costs, but the disadvantage is the high solubility of propane in it.

When the gas contains a significant amount of H_2S and CO_2, purification is carried out using diethylene glycol (DEG) and triethylene glycol (TEG), which simplifies the purification technology, since water vapor is also absorbed along with acidic components.

In relation to acidic components, both from H_2S and CO_2, chemical absorption processes are characterized by high selectivity and a high degree of purification.

When using alkali solutions, fine purification of gas from organosulfur compounds is achieved. This method is used to clean gases with a low content of H_2S and CO_2. For these purposes, alkali solutions ($KOH, NaOH$) or arsenic-alkaline absorbers are used.

Table 1 - Comparative characteristics of amine absorbents

Process advantage	Process Disadvantages
Monoethanolamine method	
1. Fine purification from CO_2 and H_2S; 2. Poorly absorbs hydrocarbons; 3. High reactivity; 4. Availability, low price.	1. Large losses from evaporation; 2. Low efficiency of extraction of mercaptans; 3. Lack of selectivity to H_2S at CO_2; 4. Low saturation of the solution.
Diethanolamine method	
1. High degree of saturation; 2. More chemically stable; 3. Ease of regeneration; 4. Achieving fine gas purification from CO_2 and H_2S in the presence of COS and CS_2.	1. The absorption capacity is lower; 2. High cost; 3. High absorbent costs and operating costs; 4. Low extraction of mercaptans, etc.; 5. Formation of non-regenerating compounds with CO_2.
Diisopropanolamine method	
1. Ability to simultaneously purify gas from H_2S, CO_2, COS, RSR 2. Forms easily regenerated compounds 3. Wide operating range 4. Selectivity towards H_2S in the presence of CO_2 5. Non-corrosive	

One of the first processes for removing sulfur compounds is cleaning with an iron hydroxide solution. But the resulting iron sulfide (FeS) is difficult to regenerate and increases corrosion. To date, the process has been technologically improved and makes it possible to obtain pure sulfur as a commercial product.

In the processes of physico-chemical absorption, a mixture of a physical absorbent with a chemical one is used, the so-called combined absorbents. The different nature of the influence of each absorbent makes it possible to achieve fine purification of gas not only from hydrogen sulfide and carbon dioxide, but also from organosulfur compounds. One of the most widely used combined industrial absorbents is sulfinol, which is a mixture of diisopropanolamine ($30-45\%$), sulfolane (tetrahydrothiophene dioxide $40-60\%$) and water ($5-15\%$). Shell offers a technological improvement of the Sulfinol process by connecting it to a $SCOT$ (Shell Claus off-gas treating) unit.

Also, recently, an absorbent has been widely introduced, which makes it possible to selectively purify gas from hydrogen sulfide and from organosulfur compounds in the presence of CO_2 – Ucarsol (the domestic analogue of Ecosorb).

In addition to these methods of gas purification from acid components, there are also catalytic methods based on the oxidation and reduction of acid gases in the presence of nickel, cobalt, and other catalysts. This method is used in cases where the gas contains compounds that are not completely removed with liquid absorbents or adsorbents (carbon disulfide, carbon sulphide, sulfides, disulfides, thiophene).

Reduction reactions proceed under the influence of hydrogen (hydrogenation) or water vapor (hydrolysis) when using catalysts of cobalt oxide, nickel, molybdenum oxide on aluminum oxide, the initial compounds decompose into hydrogen sulfide and compounds that do not contain sulfur.

Oxidative methods have found application in industry, consisting in the oxidation of hydrogen sulfide to elemental sulfur or mercaptides to disulfides (Merox process) on active alumina. The advantage of the process is selectivity, in the absence of the need to extract CO_2. The disadvantage is the occurrence of side reactions, which leads to increased consumption of reagents, deposits on the walls of equipment and corrosion.

Processes based on the oxidative method are also known:

- "Perox", using ammonia or soda solution as an absorber and hydroquinone catalyst;
- "Townsend", where DEG is used with sulfur dioxide dissolved in it;

- "Haynes", with regeneration of H_2S accumulated on membranes under hot SO_2, with the formation of sulfur;
- "Ferox", with the use of water-alkaline slurry of iron hydroxide and subsequent regeneration of the formed product to $FeS(OH)_3$ and sulfur;
- Strentford, where anthraquinone disulfonic acid and an aqueous alkaline solution of vanadium salts are used;
- "$Lo - Cat$" using iron as a reactant and catalyst and ethylenediaminetetraacetic acid as a chelating agent, which makes iron soluble in water.

There are combined gas purification methods, where the catalytic method is combined with the absorption method. $SCOT$ is an advanced process for removing sulfur compounds from tail gases. This process is divided into three sections:

1. Reduction reactor in which all sulfur compounds present in the off-gas are converted to hydrogen sulfide.
2. Quench section, in which the off-gas from the reactor is cooled and water is condensed.
3. Absorption section, in which H_2S is selectively absorbed by the amine solution. The loaded solvent is regenerated, and the released acid gas is returned to the inlet of the plant.

In modern production for the purification of hydrocarbon gases, the technology of absorption ethanolamine purification is the most widely used. Therefore, when evaluating the economic efficiency of the use of other technologies in certain conditions, a comparison is made with the technology of absorption by ethanolamines.

As parameters influencing the choice of technology, we can distinguish:

- the presence of water vapor and hydrogen sulfide in the composition of the raw hydrocarbon gas;

is the volatility of the absorbent;

is the strength of the adsorbent;

- selectivity, complexity of regeneration;
- cost and service life.

In addition, when comparing membranes, the permeability, flow rate and pressure of the feed stream are taken into account.

Feasibility studies of the effectiveness of using membrane, absorption or combined technologies for gas purification from acidic components for various gas compositions and production scales come down to the following conclusions:

- absorption technology of cleaning with ethanolamines is beneficial for large volumes of processed gas and low concentrations of CO_2 and H_2S;
- membrane treatment technology has advantages with a high content of CO_2 in the feed stream and relatively low production volumes;
- combined technology is more cost-effective in the area of high CO_2 concentrations and high flow rates.

The location factor is of great importance. Membrane technology is particularly attractive for offshore projects due to its small size and lower costs for meeting safety requirements.

The advantage of the combined separation scheme is the high flexibility of the process in relation to the composition and parameters of the feed stream.

According to statistics, at present, the volume of global gas processing using membranes has reached 5%, a significant share is accounted for by amine treatment $- 62\%$, other technologies account for 10%, and the rest - for the share of raw gas.

Depending on the degree of purification, the most efficient method of purification of hydrocarbon gases is chosen based on the volume and composition of the processed gas, taking into account the location of the installation and the cost of its maintenance. However, technical and economic indicators for the use of a particular method remain the determining factor.

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