Technical science and innovation

Volume 2024 | Issue 2 Article 2

4-17-2024

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Recommended Citation

Aripdjanov, Oybek Yusupdjanovich; Khayrullaeva, Diyora Zokhid qizi; and Abdumuminov, Jonibek Avazek ogli (2024) "MAIN PROSPECTS OF NATURAL GAS PURIFICATION TECHNOLOGIES FROM ACIDIC COMPOUNDS," *Technical science and innovation*: Vol. 2024: Iss. 2, Article 2.
DOI: https://doi.org/10.59048/2181-0400
E-ISSN: 2181-1180
.1546
Available at: https://btstu.researchcommons.org/journal/vol2024/iss2/2

UDC 677.027.622+543.422.4

MAIN PROSPECTS OF NATURAL GAS PURIFICATION TECHNOLOGIES FROM ACIDIC COMPOUNDS

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Received: January 23, 2024; Accepted: April 17, 2024; Online: July 01, 2024.

Abstract. *The article discusses the main prospects for the technology of purifying natural gas from acidic components and the problems of ensuring the purity of oil and gas products in accordance with state standards. An increase in the degree of purification from H_2S, CO_2, elemental sulfur, carbonyl sulfide, ethyl mercaptans (thiols), methyl mercaptan, carbon disulfide, sulfides, disulfides (dithioethers), thiophene, sulfoxides and sulfones is considered. Also, the physicochemical properties of the absorbent for the purification of sulfur compounds (generated during natural gas processing) are studied. Based on the study of various absorbents (ethanolamine (EA), methylethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), DGA-diglycolamine and combined absorbents), the following were identified: high sorption capacity, selective separation of no more than 20 mg/m^3, corrosive resistance to metals, low foaming, and they are often used in the production: MDEA and DEA absorbents. Thus, the processing of high-sulfur natural gases containing sulfur is an urgent and targeted task for the gas industry of the Republic of Uzbekistan, which has scientific and practical meaning (for this, research must be carefully scrutinized). This concerns the development of new absorbents, the introduction of a combined method of gas purification and increasing the efficiency of technologies for purifying natural and secondary gases from sulfur compounds.*

Keywords: *absorbtion, absorbent, alkanolamine, acid components, hydrogen sulfide, ethanolamine (EA), methylethanolamine (MEA), diethanolamine (DEA).*

Annotatsiya. *Maqolada tabiiy gazni nordon komponentlardan tozalash texnologiyasining asosiy istiqbollari va neft va gaz ishlab chiqarish mahsulotlarining davlat standartlariga muvofiq tozaligini ta'minlash muammolari ko‘rib chiqiladi. H_2S, CO_2, elementar oltingugurt, karbonil sulfid, etil merkaptanlar (tiollar), metil merkaptan, uglerod disulfidi, sulfidlar, disulfidlar (ditioefirlar), tiofen, sulfoksidlar va sulfonlardan tozalash darajasining oshishi ko‘rib chiqilib, tabiiy gazni qayta ishlash jarayonida hosil bo‘ladigan oltingugurt birikmalarini tozalash uchun qo‘llaniladigan absorbentlarning fizik-kimyoviy xususiyatlari o‘rganiladi. Turli absorbentlarni (xususan, etanolamin (EA), metiletanolamin (MEA), dietanolamin (DEA), metildietanolamin (MDEA), DGA-diglikolamin va kombinatsiyalangan absorbentlar) o‘rganish asosida quyidagilar aniqlandi: ularning yuqori sorbsiyalanish qobiliyati, 20 mg/m^3 dan ortiq bo‘lmagan miqdorda selektiv ajratish, turli metall markalariga korroziyaga chidamliligi, past darajada ko‘piklanishi va ko‘pincha MDEA va DEA absorbentlarining ishlab chiqarishda qo‘llanilishidir. Shunday qilib, tarkibida oltingugurt bolgan yuqori oltingugurtli tabiiy gazlarni qayta ishlash Ozbekiston Respublikasi gaz sanoati uchun ilmiy va amaliy ahamiyatga ega bolgan dolzarb va maqsadli vazifa hisoblanadi (bu uchun esa tadqiqotni diqqat bilan tekshirish kerak). Bu yangi absorbentlarni ishlab chiqish, gazni tozalashning kombinatsiyalangan usulini joriy etish va tabiiy va ikkilamchi gazlarni oltingugurt birikmalaridan tozalash texnologiyalari samaradorligini oshirishga tegishli ekanligini anglatadi.*

Tayanch so‘zlar*: absorbsiya, absorbent, alkonolamin, nordon birikmalar, vodorod sulfid, etanolamin (EA), metiletanolamin (MEA), dietanolamin (DEA).*

Аннотация. *В статье рассматриваются основные перспективы технологии очистки природного газа от кислых компонентов и проблемы обеспечения чистоты продуктов нефтегазового производства в соответствии с государственными стандартами. Рассматривается повышение уровня очистки от H_2S, CO_2, элементарная сера, карбонилсульфид, меркаптаны (тиолы) этилмерка, метилмеркаптан, сероуглерод, сульфиды, дисульфиды (дитиоэфиры), тиофен, сульфоксиды и сульфоны, а также изучены физико-химические свойства абсорбента для очистки сернистых соединений, образующихся при переработке природного газа. На основе изучении различных абсорбентов (этаноламин (ЭА),*

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метилэтаноламин (МЭА), диэтаноламин (ДЭА), метилдиэтаноламин (МДЭА), ДГА-дигликоламин и комбинированные абсорбенты) выявлены следующие: высокой сорбционной способностью, селективным разделением не более 20 мг/м^3, коррозионной стойкостью к маркам металлов, низким пенообразованием, и часто применяется в производстве абсорбенты МДЭА и ДЭА. Таким образом, переработка высокосернистых природных газов, содержащих серу, является актуальной и целенаправленной задачей для газовой отрасли Республики Узбекистан, которая имеет научно-практический смысл (при этом исследования должны быть тщательно изучены). Это касается разработки новых поглотителей, внедрения комбинированного метода очистки газов и повышения эффективности технологий очистки природных и вторичных газов от сернистых соединений.

***Ключевые слова**: абсорбция, абсорбент, алканоламин, кислые компоненты, сероводород, этаноламин (ЭА), метилэтаноламин (МЭА), диэтаноламин (ДЭА).*

Introduction

In refining gases, the volume of gas production and processing has increased over the next three years; now the annual volume of these indicators in the Uzbekistan is 50.0 billion. m^3. At the same time, the content of hydrogen sulfide in natural gas is also increasing; also high-sulfur gases produced in it make up a large part [1]. In addition to hydrogen sulfide, which is considered toxic and harmful for environmental protection and corrosively active, carbon dioxide, thiols, mercaptans and alkyl sulfides remain in the composition of natural gases, and their separation is required at the initial stages of processing.

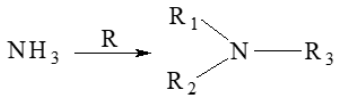
Research Methods and the Received Results

Gaseous compounds of sulfur contained in raw materials are toxic and harmful, it causes a number of problems in gas extraction, storage and refining processes, including corrosion of equipment metals, poisoning catalysts and affecting their physical, mechanical and operational properties. At the same time, sulfur compounds extracted from natural gas (ethyl mercaptans, odorants for household gases, ethyl and butyl mercaptans) are important for the production of insecticides and various detergents.

At the world level, currently, methyldiethanolamine (MDEA) solution, diethanolamine (DEA) solution are used in gas purification devices [1]. The presence of sulfur compounds (COS, R-SH, R-S-R', etc.) and chlorine ions in the gas transferred to natural and secondary gas purification devices using amines, as well as from gas drying devices using zeolites, causes the formation of stable salts in MDEA and DEA solutions used in the device. Also, such technological problems accelerate the corrosion of devices and equipment, causing them to fail, and have a significant impact on environmental protection.

The processes of cleaning natural and waste gases generated in production conditions can be divided into the following groups [2; p. 517]:

1. Chemosorption liquid processes of gas purification using absorbers with aqueous solutions



of alkanolamines: monoethanamine (MEA), diethanolamine (DEA), diglycolamine (DGA), etc. These processes are based on the chemical reaction of the components with alkanolamines, which are the active, important part of the absorbent.

where, R_1 - an alcohol radical, for example C_2H_4OH; R_2, R_3 - or an alcohol, or a hydrocarbon radical, or H^+.

2. The physical method of absorption of sour components with organic solvents. It is done with propylene carbonate, dimethyl ether of polyethylene glycol, N-methylpyrrolidone and others. These processes are based on the physical absorption of acidic components.

3. Combined processes are used to purify gases from acidic components with solvents consisting of a mixture of organic solvents and aqueous solutions of alkanolamine, for example, sulfolane, methanol, etc.

4. Irreversible rotation of absorbed hydrogen of sulfide to elementary sulfur based on oxidation processes such as Giammarco-Wetrocock or Stretford.

5. Adsorption processes. Such processes are mainly used in the deep purification of natural gases from sulfur compounds. Molecular sieves-zeolites are widely used as adsorbents in this process.

6. Membrane processes. In these processes, partial separation of gas components is carried out due to the difference in their partial pressure.

Choosing the method of natural gas purification, in most cases, is carried out depending on the composition and physical parameters of the gas raw materials, the required level of purification standards, the type and amount of available energy resources, and the standard requirements of environmental protection. Analysis of studies on natural gas purification in world practice showed that the absorption purification method is highly effective.

Alkanolamines easily react with sour gases H_2S, CO_2 and form water-soluble salts, due to which

gases are purified. As a result of boiling a saturated solution of the resulting salts, they are easily decomposed and the following reactions occur [3; p. 472]:

$$H_2S + [Amine] \rightleftarrows [\ Amine \cdot H]^+ + HC^- \text{ (quickly);}$$

$$CO_2 + 2\cdot[Amine] \rightleftarrows [Amine \cdot H]^+ + [Amine \cdot COO]^- \text{ (quickly);}$$

$$CO_2 + H_2S \rightleftarrows H_2CO_3 \text{ (slowly);}$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \text{ (quickly);}$$

$$HCO_3^- \rightleftarrows H^+ + CO_3 \text{ (quickly);}$$

$$[Amine] + H^+ \rightleftarrows [Amine \cdot H]^+ + HS^-.$$

The reaction with hydrogen sulfide and carbon dioxide in the presence of MEA is expressed as follows:

$$2RNH_2 + H_2S \rightleftarrows (RNH_3)_2;$$

$$(RNH_3)_2 + H_2S \rightleftarrows 2RNH_3HS;$$

Cleaning of gases contained carbonate anhydride in the presence of water goes by following reaction:

$$2RNH_2 + CO_2 \rightleftarrows (RNH_3)_2CO_3;$$

$$(RNH_3)_2CO_3 + CO_2 + H_2O \rightleftarrows 2RNH_3HCO_3;$$

$$2RNH_2 + CO_2 \rightleftarrows RNHCOONH_3R;$$

where, R- radical group $HO\text{-}CH_2\text{-}CH_2\text{-}$.

Every amines react homogeneously with H_2S to form amine hydrosulfide or sulfide, and the reaction is considered to be fast reaction. Primary and secondary amines by reacting with CO_2 form carbamates (carbamine acid salts: -amine-COO^-, H^+), which belongs to the class of fast reactions. In addition, carbonates and bicarbonates of amines are formed with CO_2, but before that there will be a reaction of slow dissolution of H_2CO_3 and CO_2 in water. Amine carbamates are unstable compounds. In a low-alkaline environment, they decompose slowly with the formation of bicarbonate, that is:

$$R_2NCOOR_2NH_2+H_2O \rightleftarrows R_2NH+R_2NH_2HCO_3,$$

where, $R - HOCH_2CH_{\overline{2}}$.

By using amines, gas purification from hydrogen sulfide and CO_2 in the initial raw materials at different working pressures and concentrations is provided to a certain degree. The solubility of hydrocarbons in these absorbents is not great, and the technological and equipment forms of the processes differ in their simplicity and reliability. Table 1 shows the recommended concentration of alkanolamines in the absorbent and their saturation level with H_2S, CO_2 [4; p. 283].

Table 1

Recommended concentration of alkanolamines and their saturation degree with H_2S, CO_2 [4; p. 283]

Alkanolamines	Concentration of alkanolamines in solution, % mass.	Proportion of H_2S va CO_2, mol/mol	
		At saturated absorbent	When regenerated
MEA-monoethanolamine $H_2N—CH_2—CH_2—OH$	15-20	0,30-0,35	0,10-0,15
DEA-diethanolamine $HN(CH_2—CH_2—OH)_2$	25-35	0,35-0,40	0,05-0,07
MDEA-methyldiethanolamine $CH_3N(CH_2—CH_2—OH)_2$	30-50	0,45-0,50	0,004-0,01
DGA-diglycolamine $HOCH_2CH_2OCH_2CH_2NH_2$	40-60	0,35-0,40	0,02-0,10

It seems that better way to improve the efficiency of the cleaning process by amine is to use new absorbents that are superior to them in all respects, where the main absorbents are MEA, DEA and MDEA.

Conclusion

Based on the aspects mentioned above, it can be concluded that absorbents used in the gas

purification processes from acidic compounds also should have:

- high absorption capacity for aggressive components of natural gas;
- high selectivity to acidic components;
- low saturated vapor pressure for minimal loss in the absorption process;
- low solubility of hydrocarbons;
- reaction inertness according to the properties of the gas to be cleaned;
- the standard level of purification (no more than 20 mg/m^3 of gas);
- no corrosive activity on metal;
- inhibitors used in gas extraction and mine processing should be neutral in relation to hydrocarbons;
- required to be stable to foaming.

Taking this into account, the processing of sour natural gases containing sulfur in the composition is a purposeful and urgent task of the gas industry of the Republic of Uzbekistan, which has a scientific and practical nature. Research aimed at introducing a combined method of gas purification, synthesis of new absorbents, and improving the efficiency of the technology of processes for purifying natural and secondary gases from sulfur compounds has not been thoroughly studied.

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