RESEARCH ON SYNTHESIS OF ADSORBENT BASED ON MONOETHANOLAMINE AND ACETIC ALDEHYDE

[1]Janayev M., [2]Adilov R., [3]Alimukhamedov M.
[1]Namangan Institute of Engineering and Technology
[2.3]Tashkent Institute of Chemical Technology
https://doi.org/10.5281/zenodo.11171204

Abstract. *In this study, the processes of monoethanolamine (MEA) with acetaldehyde (SA) acedolization were investigated. As a result of the study, it was found that the increase in the molar ratio of acetic aldehyde to monoethanolamine decreased the nitrogen mass fraction (%) and hydroxyl number (mgKON/g) in the final product, and increased the molecular mass (MM). Our obtained samples were studied using IR spectra.*
Keywords: *acetic aldehyde, monoethanolamine .*

Introduction. Currently, the increase in demand for oil and gas in the world has a significant impact on the rapid development of this industry. This, in turn, requires the synthesis and practical application of effective absorbents for the production of quality products, purification of natural gases from various sour additives.

In recent years, the scientists of the world and our country have achieved certain results in order to improve the quality of oil and gas products, synthesis of various composite absorbents for cleaning them from sour additives, and improvement of cleaning technologies. This article:

In the Action Strategy for further development of the Republic of Uzbekistan

"Raising the industry to a new level in terms of quality, deep sources of local raw materials processing, acceleration of production of finished products, new types of products and

the tasks of mastering technologies" are defined. In this regard, scientific research aimed at creating new composite absorbents with different functional groups and tending to purify gases released from sour components in natural gas processing and chemical production is of great importance. It contributes to a certain extent to the decision of President Shavkat Mirziyoyev on March 9, 2017 "On approval of the Program for increasing the extraction of hydrocarbon raw materials in 2017-2021" [1].

Literature analysis

The most widely used absorbents in industry as absorbents for cleaning natural and gases from sour components such as carbon dioxide (SO2), hydrogen sulfide (H2S), mercaptans (RSH) are ethanolamines: monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA) are listed. Usually, MEA is used only in the treatment of small amounts of CO 2 storage gases in oil refineries. MEA solutions can cause significant corrosion when cleaning gases from CO 2. Due to the many inherent disadvantages of MEA, this amine is not currently used in the design of new facilities, and most of the existing plants are being transferred to MDEA [2]. In large gas processing plants of the gas industry, DEA is considered the base absorbent used on a project basis for the non-selective desalination of gases from sour components. Currently, in gas processing plants in our country, aqueous solutions of DEA up to 40% are used for gas purification. This process allows required purification of gases from H 2 S and CO 2. However, the increase in heat costs during absorbent regeneration is a disadvantage of DEA. Destructive decomposition of DEA occurs in gas treatment plants due to high amine saturation and temperature rise, and its destructive decomposition rate is about 7% per year, which in turn requires periodic replacement of the solution and its vacuum specifies the necessity of purification from impurities by distillation. In the purification of hydrocarbon gas raw materials from sour components, in the presence of CO 2, in the selective purification of H 2 S (for example, in the transfer of gas to gas pipelines without deep processing), tertiary amine - MDEA is used. Compared to MEA, MDEA solutions are characterized by their corrosion activity, tendency to thermodestructive decomposition, and low energy required for regeneration and high saturation with sour components in use [3-4]. For this reason, in the research conducted, in order to increase the efficiency of gas cleaning while keeping the corrosion attack of absorbents to a minimum value, absorbent compositions with methyl ethers of polyethylene glycols (PGME) of MDEA/DEA mixture were prepared. For the experiment, by adding different amounts of PGME to the MDEA/DEA mixture in different ratios, the absorption properties of the resulting composition were analyzed. The use of the proposed composite absorbent made it possible to increase the selectivity in gas purification compared to the pure MDEA solution, increasing from 20-25% to 35-40% of the total amount of CO 2 remaining in the purified gas. The difference in the rate of reaction of H2S and SO2 with amines means that the mass transfer resistance in the absorption of H2S with amines is concentrated in the gas phase, while in the absorption of SO2 it is absorbed in the liquid. The difference in reaction rates of MDEA with H2S (instant reaction) and SO2 (slow reaction) is very fast compared to secondary amines. The effect of a fast reaction with hydrogen sulfide and a slow reaction with SO2 is used in the selective removal of hydrogen sulfide from the mixture with SO2 methyldiethanolamine [5]. In this case, the absorber must be sized to provide a gas contact time sufficient to effectively absorb all of the hydrogen sulfide, but not enough to remove a practical amount of carbon dioxide. The selectivity of the process for hydrogen sulfide increases with decreasing gas-liquid contact time. MDEA provides the ability to selectively remove H2S in the presence of SO2, thereby increasing the proportion of H2S in the sour gas. The advantage of MDEA is shown as a selective absorber in the treatment of low-sulfur gases, where the ratio of H2S to SO2 is less than 1 [6]. Factors affecting the efficiency of amine cleaning and methods of carrying out the cleaning process One of the main disadvantages of amine cleaning technology is the high regeneration temperature of amine solutions and their decomposition in the presence of oxygen. In addition, cations of alkanolamine form a heat-resistant salt (ICHT) as a result of interaction with anions of organic (amine degradation products) and inorganic acids. ICHT is stable and does not degrade under typical conditions for solvent regeneration. Accumulation of ICHT in the absorption system leads to operational problems, i.e., reduction of absorption properties of CO2 and reduction of its physicochemical properties, such as increased corrosion activity, clogging and erosion of equipment. causes. ICHTs can be removed from amine solvents by distillation (ion exchange) or electrodialysis (YED). But both approaches lead to the removal of charged particles along with the ICHTs components, and additional treatment may be required to remove the degraded neutral products, such as sand filter and activated carbon. ICHT is formed due to the presence of some acidic components in the process gas and liquid, that is, it leads to irreversible reactions with the formation of ICHT with amine. These contaminants include chloride, sulfate, formate, acetate, oxalate, thiocinate, and thiosulfate. The formed salts have a relatively strong chemical bond, which leads to the slow accumulation of ICHTs in the circulation circuit of amine, when the amount of ICHTs exceeds the permissible limit, a number of problems appear in operation and maintenance [7]. Along with hydrocarbons, natural gases contain sour gases, carbon dioxide (SO2), hydrogen sulfide (H2S), mercaptans (RSH) and others, which complicates the process of transportation and use of gases under specific conditions. In order to prevent possible complications in processing, transportation and use, a plan of necessary measures aimed at achieving the established regulatory indicators for the composition of unnecessary components in natural gas will be developed in advance. Taking this into account, the main criteria in the selection of technologies for gas cleaning processes and absorbers are to remove "unnecessary" components with a specified depth are considered to be achievable and to produce the desired products from them.

A large number of methods and technologies are used in the manufacturing industry, which include cleaning agents (absorbers), indicators for cleaning acidic components and rediffers in terms of volumes of processed raw materials. The interaction of H2S and SO2 with amines occurs depending on the type of amines. The presence of a substituent on the nitrogen atom depends on the reactivity of the amine. Compared with MDEA (tertiary amine) MEA and DEA, the removal of hydrogen sulfide is more selective in minostat, that is, it is usually characterized by the amount of unabsorbed carbon dioxide [8-13].

The widespread use of monoethanolamine as an absorbent is determined by its high reactivity, simplicity of regeneration of saturated solutions, the possibility of achieving a high level of H_2S purification, and low cost. Its disadvantage is high vapor pressure. And this is its large losses both with the purified gas and in the regeneration of the saturated solution. MEA reacts irreversibly with COS and CS_2, and much more heat is spent on regeneration of MEA and more energy is required to decompose the compounds formed.

Based on the conducted corrosion studies, this fact was explained by the transition of the surface sulphide film of the metal with a crystalline structure to an amorphous structure, as well as the loss of its mechanical strength and blurring in the areas of increased flow rate [14].

Research object and methods.

The following substances were used in the research: monoethanolamine (GOST 2768-84, produced in the Russian Federation) content of the main substance - 99.3%, density 1.012 g/cm ^{3}, acetic aldehyde (GOST (TU) 2633-51) content of the main substance - 99%, boiling point 20-22 ^{0}C.

The acidolysis process was carried out in a four-necked flask equipped with a thermometer, a capillary and a separatory funnel under an inert nitrogen atmosphere. 44 g of SA (acetaldehyde) and 61 g of MEA (monoethanolamine) were slowly added to the flask using a separatory funnel. The stirrer was then turned on and nitrogen was continuously passed through the reaction mass.

In this case, the temperature should not exceed 15°C. After the end of monoethanolamine dripping, the reaction mass was slowly raised to 30°C and the process was carried out for 4-5 hours. The system temperature was then further increased to 50 °C and stirred for 30 min. The reaction produced a dark cherry colored product 1 image.

Then, water was extracted from the composition of the acidolysis product under a vacuum at a pressure of -1 MPa. 40°C water started to separate.

Boiling was carried out up to 70°C to remove water and other substances.

We then raised the temperature to 110°C at a pressure of -1 MPa to isolate the target product. In this case, a dark orange colored oligomer was isolated Fig. 2.

Figure 1. Acedolysis product.

Figure 2. Acedolysis product after water removal.

The obtained products were determined: the composition of hydroxyl groups - GOST 25261-82, the number of amine groups, the average molecular mass [15], the IR spectra were obtained on the IR spectrum "IRAffinity-1".

Discussion of the obtained results .

In order to study the composition and structure of the products formed by the reaction of monoethanolamine and acetic aldehyde, the properties of the target products synthesized in different proportions were studied (Table 1).

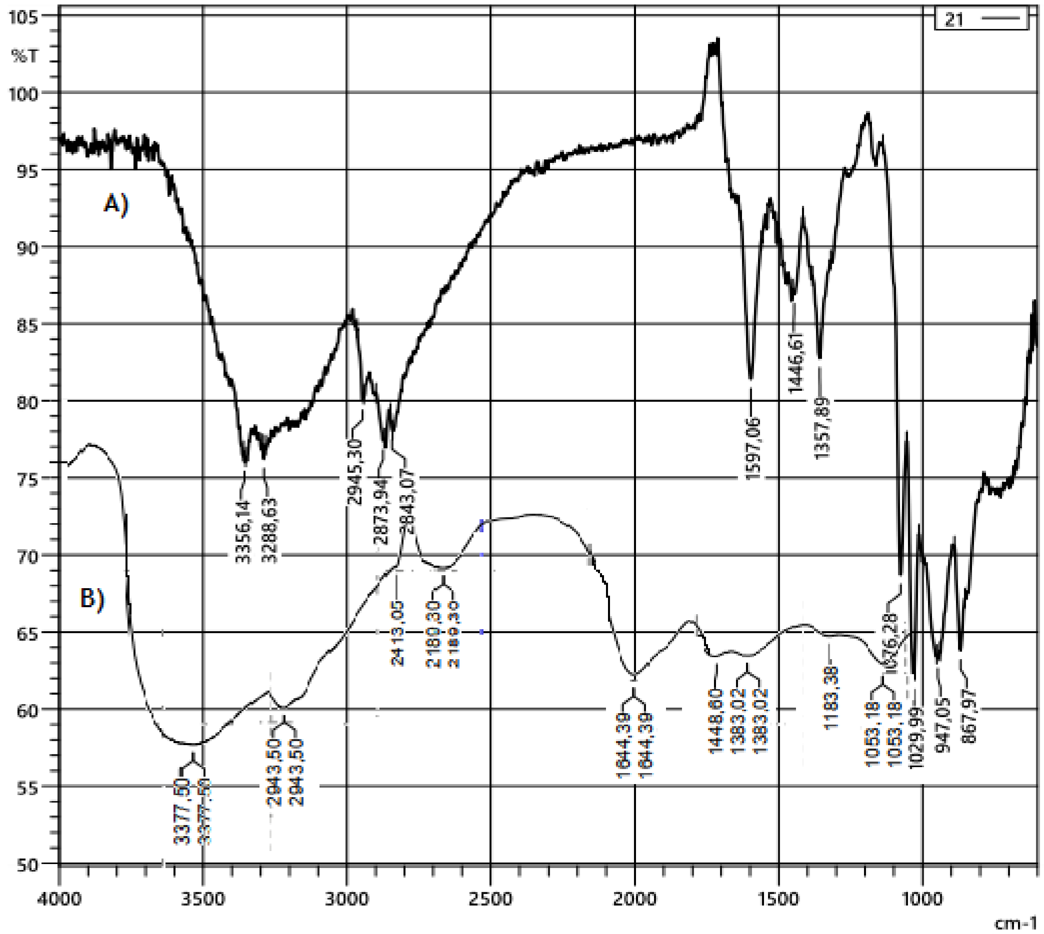
MEA : SA (mol:mol)	Mass fraction of nitrogen (%)	Amount of hydroxyl groups, mgKON/g	Molecular mass (MM)
1:0.5	16.3	417.78	94.75
1:1	12.8	337.65	163.3
1:2	7.0	246.23	260.7

Table 1. Physical and chemical properties of target products obtained in different proportions .

As can be seen from Table 1, with an increase in the mole ratio of acetic aldehyde to monoethanolamine, it was determined that the nitrogen mass fraction (%) and the amount of hydroxyl groups in the final product decreased, and the molecular mass (MM) [15] increased.

In order to clarify the formation of the target products, n samples were studied using IR spectrum analysis. (Figure 3)

When we analyzed our product using the infrared spectrum, we obtained the following results: bonded valence OH – 3356, 1076, 1029, 947 cm $^{-1}$, bonded valence – NH – 3288, 1357 cm $^{-1}$, methine, methyl, methylene groups 2945, respectively and 867 . according to the data, our synthesized substance is an amino alcohol with a linear structure, tertiary nitrogen in the form of azomethine (1597 cm $^{-1}$), and hydroxyl groups.



3. The obtained product IR spectra i A); MEA:SA=1:1 mol/mol, B); MEA:SA=1: 2 mol/mol ratio)

Summary.

Thus, the influence of the conditions of acedolysis in different mole ratios of acetic aldehyde with monoethanolamine was studied. We found out that the mass fraction of nitrogen in the final product changes, the amount of hydroxyl groups and molecular masses (MM). We confirmed the presence of azomethine group in the final product using IR spectroscopy.
our further research on the use of the obtained product as an adsorbent .

REFERENCES

1. Decision of the President of the Republic of Uzbekistan dated March 9, 2017 No. PQ-2282 "On approval of the Program for increasing the extraction of hydrocarbon raw materials in 2017-2021"
2. Effect of various additives on absorption, regeneration, corrosion and selectivity properties of alkanolamines. Sabina Alisher's daughter Fayziyeva. Saidjon Abdusalimovich Gaybullayev "Science and Education" Scientific Journal / www.openscience.uz June 2023 / Volume 4 Issue 6. p 387-396
3. Nilufar Saidyakhayevna Makhmudova, Saidjon Abdusalimovich G'Aibullayev Classification of methods for cleaning natural gases from hydrogen sulfide // Scientific progress. 2021. No. 5.

4. Abdulazizov WITH . WITH . Ў ., Sharipov M. S. , Gaybullaev WITH . A . My Fractionalarining kimyoviy tarkibi va rheologist hossalari //Science and Education. – 2021. – T. 2. – No. 3.
5. Yuldashev TR, Makhmudov MJ, Ametova DM Purification of industrial gases from dispersed particles - Science and Education in Karakalpakstan. No. 3/1 (26) 2022. ISSN 2181-9203-79-90 reg.
6. Yuldashev TR, Makhmudov MJ, // Purification of natural gases from sour components. UN. Science and technology development scientific-technical journal. 2022. – #2 – pages 82-95.
7. The effectiveness of using amine solutions with high selectivity in cleaning natural gas from sour components is tryuldashev. Digital technologies in industry are digital technology c promyshlennosti digital technologies in industry. Id: 37094 volume 1, No. 1 September 2023. Doi: https://doi.org/10.5281/zenodo.8377015
8. Korenchenko ABOUT . V. , Kharlamova M. D. Efficiency applications methyldiethanolamine in the process of amine gas purification // Chemical Sciences. - 2017. - No. 2 (56). - P. 94-98.
9. New materials for cleaning ethanolamine solutions / A.Yu. Adzhiev, Yu.N. Borushko-Gornyak, N.V. Monakhov, V.V. Melchin // Gas industry. - 2003. - No. 12. - P. 60-62.
10. Yuldashev TR, Makhmudov MJ // Technology of purification of natural gas from acidic components by absorption methods. Monograph. Against - "INTELLECT" publishing house - 2022. - 210 pages.
11. Yuldashev TR, Makhmudov MJ, // Purification of natural gases from sour components BMTI. Science and technology development scientific-technical journal. 2022. – #2 – pages 82-95.
12. Yuldashev TR, Makhmudov MJ, Ametova DM Purification of industrial gases from dispersed particles - Science and Education in Karakalpakstan. No. 3/1 (26) 2022 ISSN 2181-9203-79-90 reg.
13. Yuldashev TR, Makhmudov M, J. Cleaning of Natural from Sobe Component. Journal of Siberian Federal University. Engineeng & Technologies 2023, 16(3): 296-306/ Journal of Siberian Federal University.
14. Behruz To'Ymurodovich Salomatov, Murodillo Zoirovich Komilov, & Saidjon Abdusalimovich G'Aybullayev (2022). Nitrogen components in hydrocarbon gases and their effect on gasification properties. Scientific progress, 3 (1), 71-78.
15. Toroptseva A.M., Belegorodskaya K.V., Bondorenko. V.M. . "Laboratory workshop on chemistry and technology of high molecular compounds" Leningrad publishing house "Chemistry" Leningrad department. 1972 St. 12 3 .