CHEMISTRY AND CHEMICAL ENGINEERING

Volume 2023 | Number 4 Article 12

March 2024

STUDY OF KINETICS OF HYDROCARBON GAS PURIFICATION WITH COMPOSITE ABSORBENTS

Oybek ARIPDJANOV
Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan, aripdjanov81@gmail.com

Shavkat NURULLAEV
Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan, nurullaev@mail.ru

Shodiyakhon AZIMOVA
Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan, prof_azimova@mail.ru

Recommended Citation

ARIPDJANOV, Oybek; NURULLAEV, Shavkat; and AZIMOVA, Shodiyakhon (2024) "STUDY OF KINETICS OF HYDROCARBON GAS PURIFICATION WITH COMPOSITE ABSORBENTS," *CHEMISTRY AND CHEMICAL ENGINEERING*: Vol. 2023: No. 4, Article 12.
DOI: 10.34920/cce2023412
Available at: https://cce.researchcommons.org/journal/vol2023/iss4/12

STUDY OF KINETICS OF HYDROCARBON GAS PURIFICATION WITH COMPOSITE ABSORBENTS

Oybek ARIPDJANOV (aripdjanov81@gmail.com)
Shavkat NURULLAEV (nurullaev@mail.ru)
Shodiyakhon AZIMOVA (prof_azimova@mail.ru).
Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan

The aim of the work is to improve the process of natural gas purification from acidic components using a composite absorbent. To study the sorption of acidic components in the gas composition, a chromatographic analysis method was used. The kinetics and rate of corrosion of carbon steel grade st.10 when using composite absorbents MDEA +DEA + AVRP have been studied. The results of the study show that the volume of absorption increased from 0.55 mol/mol to 0.65 mol/mol, and the amount of H_2S in the purified gas decreased from 0.022 g/m^3 to 0.014 g/m^3. Corrosion of equipment has practically disappeared, the degree of corrosion of metals is 0.06 mm instead of 0.10 mm/year.

Keywords: methyldiethanolamine, diethanolamine, nitrogen-containing water-soluble polyelectrolytes, steel, corrosion

ИЗУЧЕНИЕ КИНЕТИКИ ОЧИСТКИ УГЛЕВОДОРОДНЫХ ГАЗОВ КОМПОЗИЦИОННЫМИ АБСОРБЕНТАМИ

Ойбек АРИПДЖАНОВ (aripdjanov81@gmail.com)
Шавкат НУРУЛЛАЕВ (nurullaev@mail.ru)
Шодияхан АЗИМОВА (prof_zimova@mail.ru)
Ташкентский химико-технологический институт, Ташкент, Узбекистан

Целью работы является усовершенствование процесса очистки природного газа от кислых компонентов с применением композиционного абсорбента. Для изучения сорбции кислых компонентов в составе газа был использован хроматографический метод анализа. Изучены кинетика и скорость коррозии углеродистой стали марки ст.10 при использовании композиционных абсорбентов МДЭА+ДЭА+АВРП. Результаты исследования показывают, что объем абсорбции увеличился с 0,55 моль/моль до 0,65 моль/моль, а количество H_2S в очищенном газе уменьшилось с 0,022 г/м^3 до 0,014 г/м^3. Коррозия оборудования резко снизилась – степень коррозии металлов составила 0,06 мм/год вместо 0,10 мм/год.

Ключевые слова: метилдиэтаноламин, диэтаноламин, азотосодержащие водорастворимый полиэлектролиты, сталь, коррозия

KOMPOZITSIYON ABSORBENTLAR BILAN UGLEVODOROD GAZLARINI TOZALASH JARAYONI KINETIKASINI O'RGANISH

Oybek ARIPDJANOV (aripdjanov81@gmail.com)
Shavkat NURULLAYEV (nurullaev@mail.ru)
Shodiyaxon AZIMOVA (prof_zimova@mail.ru)
Toshkent kimyo-texnologiya institute, Toshkent, O'zbekiston

Tadqiqotning maqsadi tabiiy gaz tarkibidagi nordon komponentlarni tozalash texnologiyasini kompozotsion absorbentlar bilan takomillashtirish. Gaz nordon romponentlarning sorbsiyasini o'rganish uchun xromatografik tahlil usuli ishlatilgan. MDEA+DEA+ASSEP kompozit absorbentlari bilan p.10 markali uglerodli po'latning korroziya kinetikasi va tezligi o'rganildi. Tadqiqot natijalari shuni ko'rsatadiki, yutilish hajmi, 0,55 mol/moldan 0,65 mol/molgacha ko'tarildi, tozalangan gazdagi H_2S miqdori 0,022 g/m^{3}dan 0,014 gacha kamaydi. Uskunaning korroziyasi deyarli yo'q bo'ldi, korroziyalanish yiliga 0,10 mm o'rniga 0,06 mmga kamaygan.

Kalit so'zlar: metildietanolamin, dietanolamin, azot saqlovchi suvda eriydigan polielektrolitlar, po'lat, korroziya faollik

DOI: 10.34920/cce2023412

Introduction

Recently, in the Republic of Uzbekistan, in the industrial enterprises of oil and gas processing, the main focus is on the search for methods for the purification of natural and waste gases of production from organic sulfur compounds, mercaptans, carbonyl sulfide (COS), carbon disulfide (CS_2) and sulfides (RSR), as well as the creation of new types of highly efficient composite absorbents for gas purification. The Action Strategy for the Further Development of the Republic of Uzbekistan provides for the tasks: "Raising the industry by transferring it to a qualitatively new level, to further intensify the production of finished products on the basis of deep processing of local raw materials, mastering the production of new types of products and technologies." In this regard, research on the creation of composite absorbents and the development of highly efficient composite absorbents in various functional groups are important, increasing the degree of cleaning of acidic components of natural and exhaust gas emissions [1-2].

At the same time, scientific research is underway to obtain new effective additives based on secondary resources and production waste for the synthesis of composite sorbents, as well as the use of these additives to improve the anti-corrosiveness of equipment having a high absorption volume, low absorption and desorption temperature, low foaming, low consumption of absorbents, providing longer service life and studying technological, practical, environmental and economic aspects of the new diethanolamine and methyl diethanolamine composite sorbents [3-6].

Absorption and adsorption methods [6]. When RSH mercaptans react with alkalis in the presence of O_2 and CO_2, which are always, albeit in small amounts, in gases, di- and polysulfides are formed, which are poorly soluble in the absorbent. Carbon sulfide neutral in nature, organic sulfides of RSR '(and a number of other compounds) dissolve in these absorbents, although their sorption capacity is significantly less than that of RSH. The presence of CO_2 in gases above 0.1-0.3% leads to its preferential dissolution, significantly reducing the absorption of RSH. Natural gases tend to have a CO_2 content above 0.7%, making it difficult to use these methods for fine cleaning. The methods are also ineffective for purifying thiophene from C_4H_4S and its derivatives.

Mono- and diethanolamine solutions with various activating additives, such as N-methylpyrrolidone-2, Di propanolamine, etc., are also widely used for purification from acidic sulfuric substances.

Adsorption methods have become significantly widespread. They are based on selective absorption (adsorption) of sulfur compounds by solid sorbents. As a rule, adsorption is carried out at a temperature of 20-50 ° C and increased pressure, and regeneration (desorption) of adsorbent saturated with sulfur substances is carried out at a low pressure and temperature of 100-350 °C. For regeneration, any inert gases, low-sulfur natural or petroleum gas, water vapor, etc. are passed through the adsorbent bed [11-13].

In some cases, catalytic reactions occur simultaneously with adsorption, whereby sulfurous substances are converted into elemental sulfur, which is recovered during regeneration and then used.

Molecular sieves (zeolites) of grades CaA and, especially, NaX have been widely used as adsorbents to purify multi-grained natural and petroleum gases. Their adsorption capacity depends to a large extent on the content of H_2O, CO_2 and higher hydrocarbons in the gases, operating conditions and the degree of purification and ranges from 2 to 18%.

The presence of heavy hydrocarbon vapors in the gas has a significant impact on the zeolite capacity of sulfur compounds. By the degree of sorbability on zeolites, the compounds included in the composition of natural gas can be arranged in a row:

$$H_2O>RSH>H_2S>COS>CO_2$$

The main problem of adsorption purification of gas on zeolites from hydrogen sulfide in the presence of CO_2 is that the adsorption of CO_2 and H_2S produces the formation of carbon sulfoxide (COS) by the reaction:

$$CO_2 + H_2S = COS + H_2O$$

Although the equilibrium constant of this reaction is small and is $6{,}6 \cdot 10^{-6}$ at 298 K, however, the almost complete removal of H_2O vapors in the frontal layer of the zeolite shifts the equilibrium to the right, and this leads to the formation of significant concentrations of COS. Zeolite regeneration is carried out by nitrogen, low-sulfur natural or petroleum gas, and in regeneration gases (regenerates) the content of sulfurous substances increases by 5-10 times compared to the initial one. In addition to coal, zeolites, alumina, bauxites, aluminosilicates, etc., are also used in the purification process. The advantage of adsorption methods is the ability to carry out the process at low temperatures, as well as the fine purification of gases not only from hydrogen sulfide, mercaptans, organic sulfides, but also from substances difficult to remove by other methods such as thiophene and its derivatives.

This method also has a number of significant drawbacks. Almost all gases have a certain number of vapors of H_2O, CO_2, higher hydrocarbons, well adsorbed by coals and zeolites, which reduces the sulfur capacity of adsorbents. The periodic purification process requires the installation of several parallel operating columns: on some, sulfur substances are absorbed (adsorption stage), and on others, adsorbents are regenerated.

Materials and methods

The study of sulfur absorption kinetics was carried out by changing the electrical conductivity of the absorber solution. For measurement, a freshly prepared absorber solution was used - a sample (AWSP) diluted with water in a ratio of 1:3, and a sample of ozone-containing algae-soluble polyelectrolyte used at gas processing plants before the breakthrough of hydrogen sulfide into a Drexel control flask with $CdCl_2$. The mixing table of the

Table 1

Mixing of Stock and Waste Solutions (1:3) AWSP sample

Type of mixture	Mass content, %					
Content of the AWSP stock sample in the mixture, %	100	80	60	40	20	0
Content of spent sample 4 in the mixture, %	0	20	40	60	80	100
Mixture resistance, Ohm	6780	689	568	543	502	489

two samples is given below (Table 1).

In Figure 1. the dependence of resistivity of the AWSP sample solution (1:3) is given depending on the fraction of spent solution in the initial one.

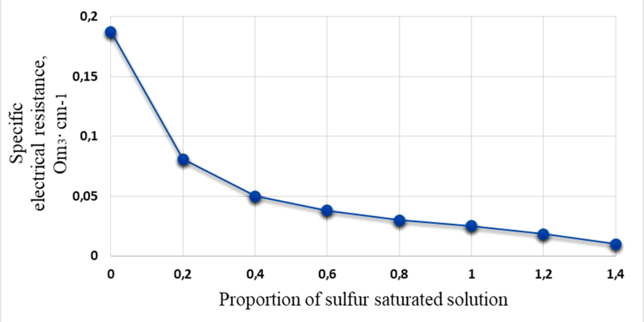

Figure 1. Dependence of resistivity of sample solution AWSP (1:3) of the fraction of saturation of the gray solution.

As it follows from the given data, the resistivity of the aqueous solution of AWSP decreases sharply when the spent solution appears in the initial reagent. After the fraction of waste solution in the starting reagent exceeds 20%, the resistivity decreases more smoothly. In this regard, the resistivity index of the solution can serve as an indicator of the treatment of the starting reagent during gas sulfurization [14-16].

Based on the study of the sulfur absorption kinetics of the composite absorbent, experimental development of the technology of the sulfur treatment process using AWSP was carried out at small plants of gas processing plants. The reagent was tested during gas purification from sulfur compounds both at the inlet of these plants and at the outlet of the plant in order to determine the effectiveness of natural gas after treatment. When conducting tests on experimental plants, the flow rate of purified gas and the content of sulfur compounds in it were monitored, and the effectiveness of using the synthesized reagent in the process of sulfur treatment of natural gas and the selection of optimal operating parameters was also determined [15].

The first two experiences were conducted using Drexel slips as contactors. At the same time, a bactericidal additive was used as a sulfur-absorbing reagent, designed to suppress sulfate-reducing bacteria during oil and gas production. The AWSP content in the bactericidal additive did not exceed 25%. The experiments carried out confirmed the high efficiency of AWSP in the sulfurization of natural gas and the ability of the reagent to purify the gas to the complete absence of sulfurous compounds. The sulfur absorption experiments were performed in a vertical glass contactor with a diameter of 25 mm. As a nozzle in a glass contactor, wood chips impregnated as a sulfur-absorbing reagent DEA (diethanolamine)+AWSP, MDEA (methyl diethanolamine) +AWSP and DEA+MDEA+AWSP were used. Gas for purification was taken from the MHPP overhead separator and from the end separator after treatment. The hydrogen sulfide content of the feed gas varied during runs from 0.0113 g/nm^3 to 0.44 g/nm^3. For the experiments, a concentrated sample of AWSP was used with a content of the main sulfur-absorbing substance of up to 80% by weight.

Results and discussion

Based on these experiments, it has become apparent that the main factors influencing the value of the specific flow factor are parameters contributing to an increase in the phase contact surface of the gas and the reactant, such as the viscosity of the AWSP, the height of the reaction zone, the volume and linear velocities of the gas, and the residence time of the gas in the reaction zone.

In connection with the planned pilot tests of the composite absorbent DEA +MDEA+AWSP, their corrosiveness was investigated.

The experiments were carried out in glass ampoules and autoclaves according to the procedure. The use of ampoules made it possible to obtain preliminary information with limited time and reagents, and autoclaves - information close to real conditions.

The results of the studies are shown in Figure 2, 3 and Table 2 (ampoule experiments), as

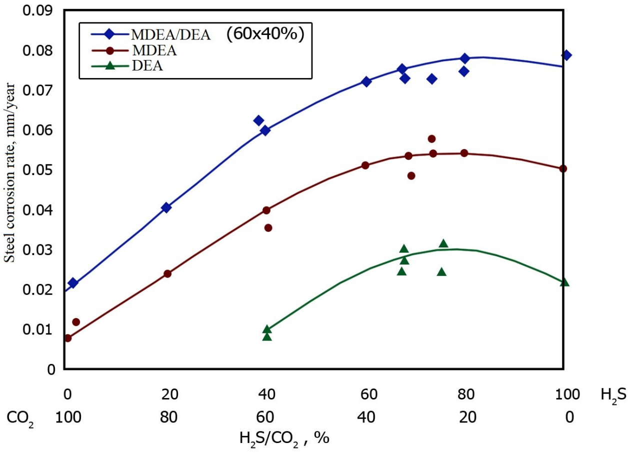

Figure 2. Effect of H_2S/CO_2 ratio on carbon steel corrosion rate (S.10; t=80 °C; α=0,6 mol/mol; τ=100 hour).

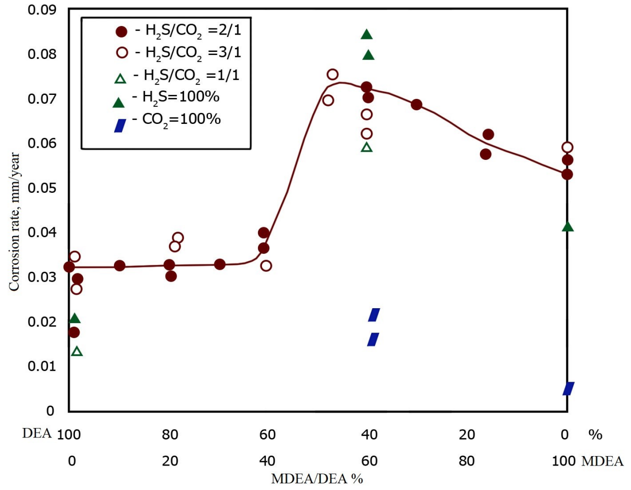

Figure 3. Effect of MDEA/DEA/ H_2S/CO_2 ratio on carbon steel corrosion rate
(t=80 °C, α=0.6 mol/mol, τ=100 hour).

well as in Table 3 and Figure 4 (autoclave experiments). Analysis of the data obtained in the ampoules shows that the corrosion rate S.10 in DEA+MDEA, MDEA+DEA absorbents is higher if the absorbent is saturated with one H_2S than in the case of saturation with one CO_2 (Figure 2, 3). In the presence of H_2S and CO_2, the maximum corrosion rate began to be observed at a ratio of H_2S/CO_2= (1.5-4):1.

The results also show that the degree of saturation of the H_2S absorbent, CO_2 and temperature significantly determine its corrosive properties. Stainless steel is practically free from corrosion. Additive 1wt% hexamethylenediamine to MDEA+DEA absorbent (60x40%), which showed the highest corrosion rate of steel grade 12 GF-1,0 mm/year, reduces it to 0.11-0.12 mm/year. This fact requires additional special research.

Table 2

Corrosion rate St. 10 in MDEA+DEA absorbent in depending on the composition of the absorbent (T=130°C, absorbent saturation 0.6 mol (H_2S and CO_2)/mol, F=100 h, concentration of amines in absorbent 40% wt)

Absorbents and their composition	Corrosion rate S.10, mm/year	
	H_2S/CO_2=3:1	H_2S/CO_2=2:1
MDEA	0,059 0,057	0,054 0,052
DEA	0,035 0,030	0,031 0,032
20% MDEA+80% DEA	0,035 0,038	0,028 0,029
40% MDEA+60% DEA	0,041 0,042	0,035 0,033
50% MDEA+50% DEA	0,070 0,075	0,065 0,067
60% MDEA+40% DEA	0,073 0,078	0,075 0,073
70% MDEA+30% DEA	0,069 0,068	0,060 0,058
80% MDEA+20% DEA	0,060 0,065	0,057 0,056

Table 3

Corrosion rate of carbon steel grade 12 GOR in absorbent MDEA+DEA+AWSP (autoclave experiments) (amine concentration 40% masses.; temperature 90 °C; amine saturation ~1,0 mol/mol; H_2S/CO_2+2;1, P_w~5 MPa; F=360 hour)

Absorbent	**Corrosion rate, steel, mm/year**
DEA	0,09
MDEA	0,51
MDEA+DEA (20x80%)	0,09
MDEA+DEA (30x70%)	0,10
MDEA+DEA (50x50%)	0,25
MDEA+DEA (60x40%)	1,05
MDEA+DEA (70x30%)	0,90
MDEA+DEA (90x10%)	0,65
MDEA+DEA (50x50%)+10% AWSP	0,10
MDEA+DEA (50x50%)+20% AWSP	0,06
MDEA+DEA (60x40%)+1% Hexamethylenediamine	0,11

It has been experimentally determined that the corrosion rate of steel also depends on the MDEA/DEA ratio in the composite absorbent. Maximum aggressiveness was observed in the MDEA/DEA ratio

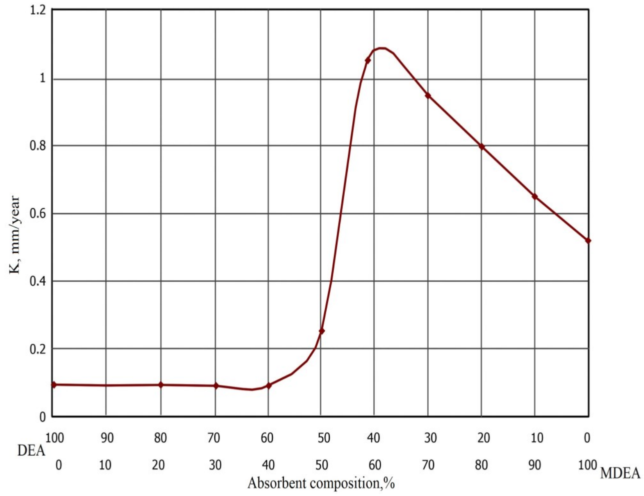

Figure 4. Corrosion rate (K) of 12GF grade carbon steel in MDEA/DEA absorbent (α~1,0 mol/mol; t =90 ^{O}C; P =5 MPa; H_2S/CO_2=2:1).

interval=(40x60%) - (80x20%). This relationship can be traced both f$_o$r the mixture of H_2S, CO_2, and individual gases - H_2S and CO_2 (Figure 3).

The results of autoclave experiments are presented in Table 2, Figure 3 and confirm an abnormal increase in the corrosion aggressiveness of MDEA + DEA solutions containing more than 40% MDEA. The addition of 10% AWSP to this absorbent reduces the corrosion rate of steel by 2 times, and the addition of 20% ~ by 3 times (Table 3).

Conclusion

The results of autoclave experiments confirm an abnormal increase in the corrosiveness of MDEA+DEA solutions containing more than 40% MDEA. The addition of 10% AWSP to this absorbent reduces the corrosion rate of steel by 2 times, and the addition of 20% ~by 3 times. This study shows that the absorption volume, mol/mol, increased from 0.55 to 0.65, and the amount of H_2S in the purified gas, g/m 3 , increased from 0.022 to 0.014 and practically no corrosion of equipment, metal corrosion is 0.06 mm instead of 0.10 mm/year.

REFERENCES

1. *O'zbekiston neft, gaz va energetikasi -2020*. Available at: https://neftegaz.uz. (accessed 23.08.2023).
2. Newman S.A. *Acid and Sour Gas Treating Processes: Latest date and methods for designing and operating today's gas Treating Facilities*. Houston, USA, Gulf Pub. Co., 2021, 820.
3. Antonov V.G., Korneev A.E., Soloviev S.A., Alekseev S.Z., Afanasyev A.I. Carbon steel corrosion mechanism in MDEA absorbent/DEA. *Gas industry*, 2000, 10, 58-59.
4. Meisen A., Kennard M.L. DEA begradation mechanism. *Hydrocarbon Processing*, 2000, October, 105-107.
5. Musayev M.N. *Neft - va gaz sohasi ekologiyasi* [Ecology of the oil and gas sector]. Toshkent, Navro'z Publ., 2018, 272.
6. Afanasyev S.V., Sadovnikov A.A., Hartman V.L., Obysov A.V., Dulnev A.V. *Industrial catalysis in gas chemistry*. Monograph under the ed. Doctor of Technical Sciences. Samara, Ed. SNC RAS Publ., 2018, 160.
7. Fenouil L.A., Towler G.P., Linn S. Removal of H_2S from coal gas using limestone: kinetic considerations. *Ind. Eng. Chem. Res*., 1994, 33, 2, 265–272.
8. Danzig M.L, Turcheninova E.V, Danzig G.A, Sobolevsky V.S, Menshov V.N, Zhavoronkov V.V, Kondrashchenko T.A, Yermina Z.E. Development of industrial technology for the production of active zinc oxide for the production of sulfur-purification masses. *Chemical industry*, 1980, 8, 30-32.
9. Ikonnikov V.G., Titelman L.I., Danzig G.A., Obysov A.V., Danzig M.L. Experience in the Preparation and Industrial Exploitation-Tation of Zinc Oxide Molded Sulphur Scavengers. *Chemical Industry*, 1983, 9, 25-28.
10. Bahadori, A., S. Mokhatab, eds. Rapidly estimating natural gas compressibility factor. *Journal of Natural Gas Chemistry*, 2007, 16, 4, 349-353
11. Al-Juaied, M. A. (May 2004). *Carbon dioxide removal from natural gas by membranes in the presence of heavy hydrocarbons and by Aqueous Diglycolamine*. PhD diss., The University of Texas at Austin, Texas, 424.
12. Bhide, B. D., A. Voskericyan, eds. Hybrid processes for the removal of acid gases from natural gas. *Journal of Membrane Science*, 1998, 140, 1, 27-49.
13. Bord, N., G. Cretier, et al. Determination of diethanolamine or N-methyldiethanolamine in high ammonium concentration matrices by capillary electrophoresis with indirect UV detection: application to the analysis of refinery process waters. *Analytical and Bioanalytical Chem*istry, 2004, 380, 2, 325-332.
14. Aripdjanov O.Yu., Nurullaev Sh.P. Increasing and intensification of the technology of purification of natural gas by composite absorbents. *Advanced Materials Research*. Switzerland. Trans Tech Publications Ltd., 2017, 11(44), 31-37.
15. Liu G., Zhu L., Cao W., Liu H., He Y. new technique integrating hydrate-based gas separation and chemical absorption for the sweetening of natural gas with high H_2S and CO_2 contents. *ACS Omega,* 2021, 6, 26180–26190.
16. Fazaeli R., Razavi S.M.R., Najafabadi M.S., eds. Computational simulation of CO_2 removal from gas mixtures by chemical absorbents in porous membranes. *RSC Adv.,* 2015, 5, 36787–36797.