Section 6. Technical science in general

STUDY OF THE PROCESS OF DRYING NATURAL GAS USING GLYCOLS USING MULTIFUNCTIONAL ADDITIVES AND AZEOTROPIC SOLVENTS

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Abstract

This article presents experimental results on the effect of azeotropic solvents and poly-functional additives in the drying of natural gas with glycols. The addition of hydrocarbon azeotropic solvents to the glycol recovery system increases the TEG concentration and reduces the moisture content of the glycol. The addition of azeotropic solvents to the glycol recovery system increases the concentration of TEG and reduces the viscosity of the glycol. A regeneration scheme has been developed by adding 0.10–0.30 kg of petroleum ether per 1 kg of glycol to a desorber in an absorption drying apparatus for natural and satellite gases.

Keywords: *gas dehydration, gas, glycol, triethylene glycol (TEG), diethylene glycol (DEG), azeotrope, azeotropic distillation*

Introduction

In the gas industry, the process of drying moisture contained in gases using liquid absorbents (glycols) is widely used. This process consists of absorbing moisture with glycol, desorbing the regenerated glycol, and recycling. The depth of gas drying largely depends on the residual concentration of water in the glycol at the desorber outlet (Yuan, B., Sun, H., Wang, T., Xu, Y., Li, P., Kong, Y., Niu Q.J., 2016).

To increase the depth of recovery of glycol, the following methods are used: in-creasing the temperature, decreasing the pressure, cleaning with dry gas and introducing a substance that forms an azeotropic mixture with water.

The main disadvantages of absorption drying (Maddox Rand, 2008; Manovyan, A. K. 2001):

- insufficient depth of water desorption, which reduces absorption efficiency;
- in the absorber of glycol foaming;
- acids formed as a result of degradation of glycols corrode devices;

- desorption during of glycol water steam with to disappear.

The purpose of this work is to improve the deep drying process of natural gas with glycols using an azeotrope forming agent and surfactants.

In our country, DEG is mainly used in the processes of drying hydrocarbon gases, while TEG is used in many countries of the world. TEG has several advantages over DEG in gas drying processes: its total loss rate is 2––3 times lower, TEG has relatively higher dew point depression, and less acid formation as a result of its regeneration (CY Pan AIChE Journal 19 9 8.– #34). However, adapting the DEG regeneration device to the TEG is difficult due to the fact that their regeneration temperatures differ by 30–40 °C and requires considerable economic costs. We know that azeotropes lower the boiling point of solutions. Therefore, the use of these substances to adapt DEG to TEG in gas absorption dryers provides a significant cost reduction.

We calculated the boiling point of some hydrocarbon mixtures with water according to Antoine's equation. Since the mutual solubility of hydrocarbons and water is less than 0.2%, an immiscible component model was used for the calculation. The results are presented in Table 1.

As shown below, the boiling point of the hydrocarbon-water mixture is almost identical to the experimental results of the boiling temperature of the hydrocarbon-water-TEG mixture. Consequently, the boiling temperature of the hydrocarbon-water mixture is almost unaffected by TEG. As can be seen from the results of Table 1, the calculated temperature of the hydrocarbon-water mixture exceeds 100 °C for some components. For example, this indicator for decan exceeds 132.7 °C.

Our experiments have shown that, in fact, the boiling point of the n-decane-water mixture is in the range of 97–100 °C. Thus, the results of the study showed that the effect of glycol in the presence of TE EG in the calculation of the boiling phase equilibrium of azeotropic hydrocarbon-water mixtures is not significant.

Table 1. *Calculation of boiling temperature of "Hydrocarbon – Water" and "Hydrocarbon – Water – TEG" mixtures and comparison of experimental results*

| Hydrocarbon | Boiling temperature, °C | | |
	"Hydrocarbon – Water-TEG" mixture calculation	"Hydrocarbon – Calculation of water" mixture	"Hydrocarbon – Results in literature for water" azeotrope mixture (Bekirov T.M., Lanchakov G.A. 1999)
Pentane	35.9	34.5	34. 4
Hexane	66.9	61.6	61.6
Heptane	91.9	79.2	79.2–79.6
Octane	11.2	89.4	89.4–89.6
Dean	133.0	97.6	97.3
Isooctane	93.0	79.4	78.9
Cyclohexane	78.1	69.4	69.4
Benzene	77.2	70. 0	69. 4
Toluene	100.9	84.5	84.1–81.5
Ethylbenzene	117.2	92.0	89.0–92.0

A comparative analysis of the amount of azeotropic solvents needed to distill the same amount of water is of practical interest. The results of such calculations are summarized in Table 2.

We know from literature sources that C+ hydrocarbons form azeotropic mixtures with TEG at atmospheric pressure, and the more carbon atoms in the hydrocarbon, the greater the concentration of TEG in the azeotrope. Thus, it can be concluded that during azeo-

tropic distillation of hydrocarbon-water-glycol mixtures, the use of low molecular weight hydrocarbons with a number of carbon atoms not exceeding $C_7 - C_8$ is the most beneficial, as this reduces glycol losses. However, Table 2 shows that the more carbon atoms in a hydrocarbon, the less water is required for complete distillation. Therefore, it is possible to use hexane-heptane fraction or petroleum ether boiling fractions in the temperature range of 70–100 °C as an alternative azeotropic agent in the regeneration process (Carroll, D. 2007).

Table 2. *Calculation of the hydrocarbon mass of the "Hydrocarbon – Water" azeotropic mixture*

| Hydrocarbon | Calculation results | | Results of water concentration in the azeotropic mixture in the literature,% mass (Echt W. I., Dortmundt, D. D. and Malino, H. M.) |
	Concentration of water in the azeotropic mixture,% mass	The ratio of 1 kg of hydrocarbon to 1 kg of water in an azeotropic mixture	
Pentane	1.5	70.5	1.5
Hexane	5.4	18.1	5.5
Heptane	13.0	7.0	12.9
Octane	24.9	3.2	25.5
Dean	58.5	0.6	51.0
Isooctane	11.7	7.8	10.9
Cyclohexane	8.5	11.0	8.4
Benzene	8.9	10.5	8.8
Toluene	19.8	4.3	13.5–20.2
Ethylbenzene	33.2	2. 1	30.6–33.0

The effect of azeotropic hydrocarbon scavengers on TEG drying rate and its regeneration was investigated using a Dina-Stark extraction-distillation laboratory unit and simple atmospheric distillation.

From the label, the following were selected as additives that increase the degree of water blowing: n-heptane, n-decane, isooctane, cyclohexane, toluene, petroleum ether (40–70), petroleum ether (70–100), nitrogen. The selection of these hydrocarbons is related to the task of testing the behavior of each of the hydrocarbon classes (n-alkanes, isoalkanes, cycloalkanes and aromatic hydrocarbons) for the degree of water distillation from triethylene glycol.

The research carried out by us consisted of checking the correctness of the developed theoretical concepts and calculations, namely: testing petroleum ether (70–100) as an alternative hydrocarbon solvent that forms an azeotrope forming a mixture with water in solution with TEG and 1 kg of glycol at a temperature of 165 ° C for (70–100) is to determine the optimal concentrations of petroleum ether.

A gas-adsorption chromatography method was used to determine the amount of water in low concentrations in TEG.

Table 3 presents the results of atmospheric distillation studies of water-TEG mixture in Dina-Stark device by adding different hydrocarbon agents. Each study was conducted for 1 hour at temperatures between 160–180 °C.

Table 3. *Results of hydrocarbon mass calculation in hydrocarbon-water azeotrope mixture*

Naming	Boiling temperature of hydrocarbon, °C	Boiling temperature of the mixture, °C	Amount of remaining moisture in TEG,% ma s s.
Without carbohydrates	–	100–105	2.85

Naming	Boiling temperature of hydrocarbon, °C	Boiling temperature of the mixture, °C	Amount of remaining moisture in TEG,% ma s s.
Petroleum ether i (40–70)	40–70	3 5–66	0.74
Cyclohexane	81.0 _	70.0 _	0.48
n – Heptane	98,2 _	79.0 _	0.14
Isooctane	99	79,1 _	0.12
Petroleum ether i (70–100)	71–100	75–94	0.12
Toluene	112	85	0.51
n – Dean	175	98	1.11

As can be seen from Table 3, all hydrocarbons form azeotropic mixtures with water, and when heated, more moisture can be extracted from the glycol without the addition of solvents.

The minimum water content in TEG was obtained using isooctane and petroleum ether fraction 70–100. With the addition of these hydrocarbon solvents, residual concentrations as low as 0.1% by weight of water can be achieved by azeotropic rectification of TEG. Although toluene gives good results, it is not advisable to use this class of hydrocarbons as an azeotroping agent because TEG is highly soluble in aromatic hydrocarbons.

Based on the data in Table 3, it showed that hydrocarbons boiling at temperatures of 70 and 100 °C give positive results. Since petroleum ether is cheaper than individual hydrocarbons, its use in the glycol recovery process is the most economically feasible.

To determine alternative concentrations of petroleum ether (70–100) as an azeotroping agent, we conducted a series of driving experiments with petroleum ether–water–TEG mixtures in a Dina–Stark laboratory setup. The results of experiments are presented in Table 4.

Table 4. *Effect of different concentrations of petroleum ether on azeotropic driving of water-TEG solutions*

TEG mass, g	Water mass, g	(70–100) mass of petroleum ether, g	Amount of petroleum ether		The amount of water remaining in TEG after driving,% mass
			Saturated TEG kg/kg	Water kg/kg	
90	10	10	0.08	1.0	0.1 4
50	5	6	0.15	2.0	0.12
50	5	12	0.28	6.0	0.16
50	5	18	0.50	12.0	0.25

Table 4 shows that the addition of 0.08–0.28 kg (70–100) of petroleum ether to saturated glycol, 1 kg of absorbent, is 0.14––0.16% by mass in the regenerated absorbent. ensures water retention.

It has been proved by the authors of a scientific study (Carroll, D., 2007) that it is possible to achieve a residual concentration of up to 2.8% by weight of water by simple distillation of a water-TEG mixture under laboratory conditions (Carroll, D., 2007). Results in a scientific study confirmed that the maximum limit of water evaporated from TEG that can be achieved by heating temperature and atmospheric distillation is a concentration in the range of 1.3–2.0% by weight of TEG.

We also conducted experiments on the simple distillation of water – TEG mixtures with the addition of nitrogen and petro-

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leum ether (70–100). The results obtained with distillation in the presence of nitrogen showed a residual water content of 0.79% by weight, and with nitrogen distillation and the addition of petroleum ether it was 70–100– – 0.56% by weight.

These obtained results proved the principle that the addition of inert gas in the driving has a positive effect on the TEG composition than driving water under normal atmospheric conditions. Nevertheless, the amount of residual water in the glycol remains higher than using azeotropes and without nitrogen addition. This can be explained by the fact that in normal distillation there is no constant return of petroleum ether (cold water) to the flask. The circulation of the azeotropic solvent in the Dina-Stark laboratory apparatus is the same as in the rectification column. This provides multiple mass exchanges between the hydrocarbon and water-TEG mixture and, accordingly, gives a low residual concentration of water in the mixture.

Thus, as a result of the conducted research, the following conclusions can be made: an alternative azeotrope-forming hydrocarbon solvent (70–100) that increases the depth of water desorption in TEG regeneration plants is petroleum ether. The use of this substance allows lowering the reboiler temperature in the desorption unit to 165–175 ^{o}C, and at the same time increases the evaporation of water from the mixture to 0.1% by weigh[t.] This, in turn, enables the conversion of gas drying plants from DEG to TEG, resulting in significant savings in operating costs.

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