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REGENERATION OF ALKANOLAMINES USED IN NATURAL GAS PURIFICATION

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ABSTRACT

The paper reports data referring to the alkanolamines treatment of natural gas and their subsequent regeneration. The physico-chemical properties (density, refractive index and aqueous solutions concentration) of alkanolamines, are determined in correspondence with the state standards, whereas their molecule sizes are calculated with the application of the Brigleba-Stewart model. Comparative data are presented concerning the behavior of original DEA, wasted after usage at Uchkyr gas processing plant as well as the regenerated DEA at the same plant. The composition of the wasted and regenerated DEA is identified by gas-liquid chromatography. Activated carbons based on local wasted material - fruit seeds (apricots, peaches, cherries), were obtained. The sorption capacity for benzene at dynamic conditions of the liquid phase ranges from 0.22 to 1.26 g/100 g adsorbent. These adsorbents were tested for obtaining a high purity cyclohexane. Activated carbon produced from apricot pits shows the best result (cyclohexane 99.50 %) for cleaning the wasted DEA.

Keywords: *natural gas, acidic components, adsorbents, alkanolamines, regeneration.*

INTRODUCTION

The earth of Uzbekistan possesses big stocks of hydrocarbon raw materials. About 60 % of the republic's territory has the potential of containing oil and gas deposits. Uzbekistan has 171 oil and gas fields. Oil production proceeds on 51 fields, gas is obtained on 27, whereas condensate is produced on 17 [1]. More than 50 % of the deposits are in a process of exploitation, 35 % of them are prepared for development, and the rest are in a course of provision.

The rise in prices for gas fuel and deficiency of the reconnoitered deposits of natural gases without sulphureted impurities put abreast the major problems its clearing from sour impurity (in particular, from sulphureted hydrogen), doing such gases impossible for using them as fuel, and, as well as causing environmental contamination, corrosion of the equipment process and destruction of building designs.

At the same time there are explored and conserved a lot of gas, oil, condensate sulfur-containing deposits on the territory of Uzbekistan. However, their development without ensuring their efficient desulphurization equipment may cause serious environmental complications. Environmental hazard of hydrogen sulphide is largely defined by product of its combustion (sulfur dioxide), which has an active anthropogenic impact on the environment, national economic and natural objects. Except for hydrocarbon gases, there may be other sulfur compounds in hydrogen sulphide such as mercaptans of the general formula R-SH and carbonyl sulfide (COS), carbon disulfide (CS_2). This makes it extremely important to find the ways for reducing the volume of sulfur emissions and their neutralization. Selection process of gas purification from sulfur compounds is defined by economics and depends on many factors. Various methods are used for purification of the natural gas from H_2S, CO_2 and other impurities using [2 - 4]:

- chemisorption ones, based on chemical interaction of impurities with liquid-absorbent;

- physic absorption, in which the impurities are selectively absorbed by an organic solvent;

- combined ones using simultaneously both chemical and physical absorption;

- oxidizing ones based on irreversible transformations of impurities into elemental sulfur and other substances;

- adsorption ones, in which the impurities are selectively absorbed on the surface of solids - activated coal, aluminum silicate, etc.;

- cleaning methods of alkali;

- non regeneration methods of cleaning.

Processes with application of amines are widely used for natural gas purification. Monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA), diisopropanolamine (DIPA), methyldiethanolamine (MDEA) are well-known ethanolamines used in gas purification from H_2S and CO_2. Monoethanolamine and diethanolamine have obtained the greatest practical application. The use of DEA is particularly advantageous in those cases where COS and CS_2 are contained in the feed gas along with H_2S and CO_2, which irreversibly reacting with MEA, cause significant its losses. A tertiary amine - ethyldiethanolamine is used for selective extraction of H_2S in the presence of CO_2.

Hitherto, monoethanolamine (MEA) and diethanolamine (DEA) are mainly used as an absorbent for cleaning the acid gases in industry installations. Analysis of world practice shows that there is a tendency for replacing the IEA by a more efficient absorbent, namely, by methyldiethanolamine (MDEA) [5].

Methyldiethanolamine (tertiary amine) is less corrosive as compared to MEA (primary amine), which allows the use of more concentrated solutions of MDEA (30 - 50 mass %), in comparison with MEA (12 - 18 %).

The properties of some alkanolamines identified under generally accepted government standards are shown in Table 1. The calculated size of these molecules according to Brigleba-Stewart models are presented, too.

As a rule, alkanolamines are used in the form of aqueous solutions. The concentration of amine may vary widely, chosen on the basis of experience, and taking into consideration the equipment corrosion (Table 2).

Alkanolamines, being alkali, react easily with acid gases H_2S and CO_2, forming water soluble salts.

The interaction of amines with hydrogen sulphide is defined by their alkalinity. Their dissociation constants at 20°C are: for MEA - $5 \cdot 10^{-5}$; for DEA - $6 \cdot 10^{-6}$; for TEA - $3 \cdot 10^{-7}$.

For this reason, amines may interact with carbon dioxide to form carbonates. The following reactions take place in the absorption of acid gases:

$$HOCH_2CH_2NH_2 + H_2S \leftrightarrow (HOCH_2CH_2NH_3)^+HS^-$$
$$HOCH_2CH_2NH_2 + H_2O + CO_2 \leftrightarrow (HOCH2CH_2NH_2)^+HCO_3^-$$
$$CO_2 + H_2O \leftrightarrow H_2CO_3 \text{ (slow)}$$
$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \text{ (fast)}$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^- \text{ (fast)}$$

Formation of di-substituted sulfides is possible, too:

$$HOCH_2CH_2NH_2 + H_2S \leftrightarrow (HOCH_2CH_2NH_3)_2^+S^{2-}$$

At low temperatures (10 - 40°C) and pressure up to 1.0 MPa, the reaction equilibrium is shifted towards the formation of sulfides and hydrosulfides. At temperatures of 100 - 190°C they are destroyed, that results in segregation of acid gases and the regeneration of the amine.

Consumption of amines is one of the most important indicators of work in gas cleaning plants, as the cost of absorbents is high and expenses constitute a significant part of absorbent operating ones.

The main components of the loss of amines in plants are gas entrainment, thermochemical degradation of amines, mechanical losses [6].

The quantity of amine loss during normal operation of default settings is 20 - 30 mg m^{-3} of gas and it is increased to 100 mg m^{-3} while foaming solution [7].

Thermal decomposition of the amines without carbon dioxide occurs in a small degree, and rises with increasing the temperature and the degree of saturation of the amines with CO_2 [8].

Mechanical losses occur from spills and leaks through cracks in the system equipment storage and transferring solution by a pump. Other losses are caused by a chemical reaction of an amine with other gas components (COS, CS_2, RSH, etc.), air oxygen.

The primary method for reducing the losses of amines as a result of thermochemical decomposition is the removal of the degradation products from the system by filtration and adsorption (activated carbonl,

Table 1. Properties of alkanolamines used for natural gas purification from CO_2 and H_2S.

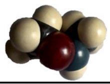
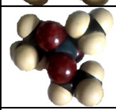
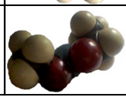
Names of amines	Molecular mass	Empirical Formula	Molecules	Indicators of properties											
				Molecular size according to Stewart-Brigleba models, nm			*T* boiling at 0,1 Pa, °C	*T* freezing, °C	Density at t=20°C, g/cm³	Viscosity, Pa•s	Vapor pressure at 40°C, kPa	Index of refraction	Solubility, grams per 100 grams of heptane (25°C)	*T.* ignition, °C	*T* freezing solution, °C
				d (critical diameter)	*l* (length)	*h* (height)									
MEA	61	Monoethanolamine $HOCH_2CH_2NH_2$		0.49	0.71	0.36	172	10.5	1.015	$24.1 \cdot 10^{-3}$ (20)*	7.4	1.4541	0.6	93	-17 (15%)
DEA	105	Diethanolamine $(HOCH_2CH_2)_2NH_2$		0.48	0.83	0.37	268	27.5	1.096	$38 \cdot 10^{-2}$ (30)	7.4	1.4776	0.1	148.9	-16 (30%)
TEA	149	Triethanolamine $(HOCH_2CH_2)_3N$		0.79	0.80	0.39	360	21.2	1.124	$10.13 \cdot 10^{-4}$ (20)	-	1.4852	0.2	179	-13 (30%)
MDEA	119	Methyldiethanol-amine $CH_3N(CH_2CH_2OH)_2$		0.48	0.70	0.41	250	-21	1.018	$10.1 \cdot 10^{-2}$ (20)	7.4	1.4668	0.15	-	-

Table 2. Properties of the aqueous solutions of amines.

Amine	Concentration		T boiling at 180 kPa, °C	T freezing, °C	Viscosity at 0°C, 10^3 Pa•s	Pressure steam at 40°C, kPa
	Kmol m^{-3}					
MEA	2.5	15	118	-5	1.0	7.4
DGA	6	63	124	-50	6.5	4.0
DEA	2	21	118	-5	1.3	7.4
DIPA	2	27	118	-5	1.06	7.4
MDEA	2	24	118	-6	1.06	7.4
TEA	2	30	118	-	-	-

Table 3. Characteristics of DEA samples.

Samples of DEA	Concentration of the aqueous solution of DEA, %	Density at 20°C, mg m^{-3}	Refractive indices n_D^{20}
Original	30	1.1062	1.4595
Wasted	22	1.0611	1.3690
Regenerated	20	1.0290	1.3630

zeolites, etc.). Maintaining the temperature not higher than 130°C of the saturated amine at regeneration, is of great importance, too.

EXPERIMENTAL

The adsorption method is chosen for alkanolamine regeneration used in the process of cleaning the natural gas and free acid components, as it is simple, accessible and cost-effective.

The wasted DEA was taken from Uchkyr gas processing plant for the investigation.

RESULTS AND DISCUSSION

The concentration of the aqueous solutions, the density (d_4^{20}) and indices of refractions (n_D^{20}) for 3 samples DEA (original, wasted, regenerated) are defined. The data are summarized in Table 3.

The composition of the wasted and regenerated DEA was determined using gas-liquid chromatography. The composition of the wasted and recovered diethanolamine is shown in Table 4.

The data for the composition of the wasted diethanolamine solution after purification from acid gas components, show that the amount of di-substituted sulfide ($(HOCH_2CH_2NH_3)_2S$) is 10.67 mass % and of foaming agents - 3.63 %, while in the regenerated solution their amounts are 5.40 and 3.55 mass %, respectively. These data suggest that DEA regeneration has not been carried out completely and it, therefore, may not be reused for the removal of acid gas components.

The technology for producing the best activated carbons based on local waste material – fruit pits (apricots, peaches, cherries) has been developed and the conditions of preparation defined. Their benzene adsorption capacity is set in dynamic conditions of the liquid phase (Table 5) [9], as well as these adsorbents were tested for

Table 4. Composition of wasted and recovered diethanolamine.

No	Components	mass % Q	
		in the wasted DEA	in the regenerated DEA
1.	$HOCH_2CH_2NH_2$	85.70	91.05
2.	$(HOCH_2CH_2NH_3)_2S$	10.67	5.40
3.	foaming agents	3.63	3.55

Table 5. Sorption capacity for benzene of developed adsorbents.

Name of fruit pits	Conditions for obtaining activated carbon		Dynamic capacity for benzene (full) g/100g	The results of treatment of cyclohexane (t_c = 3,0ºC)	
	time, h	temperature heat treatment, °C		Temperature of crystallization, t_c, °C	Degree of purity, %
Pits of apricots	3	100 - 150	0.34	3.70	98.50
		150 - 250	0.62	3.80	98.90
		250 - 350	1.26	4.45	99.50
Pits of peach	3	100 - 150	0.24	3.68	98.30
		150 - 250	0.52	3.75	98.70
		250 - 350	1.18	4.20	99.20
Pits of cherry	3	100 - 150	0.22	3.60	98.03
		150 - 250	0.45	3.62	98.20
		250 - 350	0.93	3.65	98.35

Table 6. Characteristics of DEA.

Samples of DEA	Concentration of the aqueous solution of DEA, %	Density at 20°C, g cm^{-3}	Refractive indices n_D^{20}
Original	30	1.1062	1.4595
Wasted	22	1.0611	1.3690
Regenerated	26	1.0945	1.4575

preparation of high purity cyclohexane, which is widely used as an object of petrochemical synthesis, solvent, especially in the cryoscopic studies [10].

It is necessary to have cyclohexane with high purity crystallization temperature close to 6.54ºC for the cryoscopic analyses which does not change its indicators during processing by highly active adsorbents [11].

The highest benzene adsorption capacity of the activated carbon derived from apricot pits at 250 - 350ºC is 1.26 g/100 g and the best result for cyclohexane purification is 99.50 %. These data suggest that the activated carbon from apricot pits is a suitable sorbent for the regeneration of the spent aqueous DEA. The results obtained after cleaning the spent DEA using this activated carbon are listed in Table 6.

The composition of the wasted and regenerated diethanolamine by proposed method is shown in Table 7.

CONCLUSIONS

The regeneration of alkanolamines used in the purification of natural gas from acidic sulfur components was investigated.

In accordance with generally accepted standards of the State, the physico-chemical properties of alkanolamines were determined, and the sizes of these molecules by model Brigleba-Stewart were calculated.

The density, refractive index and concentration of aqueous solutions of 3 samples DEA (original, wasted, regenerated) for Uchkyr gas processing plant were determined.

Table 7. Composition of wasted and regenerated diethanolamine.

No	Components	mass %	
		in the wasted	in the regenerated
1.	$HOCH_2CH_2NH_2$	85.70	99.05
2.	$(HOCH_2CH_2NH_3)_2S$	10.67	0.40
3.	foaming agents	3.63	0.55

The composition of the wasted and regenerated DEA by gas-liquid chromatography was also identified. The amount of disubstituted sulfide ($(HOCH_2CH_2NH_3)_2S$) is 10.67 mass % and of the foaming agent is 3.63 %, while in the regenerated solution they are 5.40 and 3.55 mass %, respectively. These data suggest that the regeneration of DEA is not complite.

Activated carbons based on local waste material - pitted fruits (apricots, peaches, cherries) were produced. The benzene sorption capacity at dynamic conditions of the liquid phase ranges from 0.22 to 1.26 g/100 g adsorbent.

These adsorbents are used for the preparation of high purity reactants, such as cyclohexane, which is widely used in petrochemical synthesis, and as a solvent, especially in studies of the freezing point depression.

Activated carbon produced from apricot pits is the best for cleaning the wasted DEA.

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