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## MODELING OF A TWO-FLOW GAS PURIFICATION FROM CARBON OXIDES (IV) BY METHYLDIETHANOLAMINE SOLUTION

The object of research is the stage of purification of process gas of ammonia production with a capacity of 1360–1500 t/day in a two-section plate absorber. The paper substantiates the possibility to replace the monoethanolamine (MEA) absorbent solution with the activated solution of methyl diethanolamine (aMDEA) on the example of the Ukrainian multi-tonnage production, working under the two-flow purification scheme. One of the most problematic areas is the lack of a mathematical model for the absorption of carbon monoxide (IV) by a new absorbent for two-flow purification schemes. In the course of the study, the method of compiling the material balance was used, which takes into account the peculiarities of the interaction of the aMDEA components with CO<sub>2</sub>, and numerical integration to calculate the number of plates.

An algorithm for calculating material and heat balances for finely and roughly regenerated solutions has been developed and implemented in Excel. The algorithm and the program provide for multivariate calculations with varying concentration parameters for gas and solution and their temperature. Thermal calculations take into account the adiabatic heating due to the exothermic absorption reaction and determine the temperature of the solutions at the outlet of each part of the absorber. Analysis of the material balance calculations in comparison with the data on the MEA solution shows a decrease in the solution consumption by 5.5 % when using aMDEA, which will help to reduce the energy costs for pumping and regeneration. By kinetic calculation, the number of plates for the absorber was determined to be 13. With the number of 15 in a standard absorber, the calculated number of plates allows the gas to be purified to a content of 0.01 % CO<sub>2</sub>. An increase in the temperature of the solutions at the inlet to both sections by 10 degrees does not significantly affect the number of plates. Thus, mathematical modeling of a two-section plate absorber showed a real possibility of replacing an 18 % MEA solution with a 40 % aMDEA solution. It is proposed to implement this on existing equipment without changing the technological scheme.

**Keywords:** process gas, carbon monoxide (IV), methyldiethanolamine, piperazine, two-section plate absorber, numerical integration.

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### 1. Introduction

Purification of process gas from carbon monoxide (IV) in the production of ammonia is traditionally carried out by chemisorption methods, first of all, with a solution of monoethanolamine (MEA) or a hot solution of potash K<sub>2</sub>CO<sub>3</sub>, activated with diethanolamine. The chemistry of purification by these methods is provided in [1]. Tech-

nological schemes, apparatus designs are considered by the authors of works [2, 3]. A comparative analysis of purification methods is provided in [4, 5].

In the XXI century, a purification method was proposed using a solution of methyldiethanolamine (aMDEA) with a concentration of up to 50 %, activated with piperazine C<sub>4</sub>H<sub>10</sub>N<sub>2</sub> (diethylenediamine) with a concentration of up to 5 % [6]. The advantage of MDEA is easy regeneration

with a slight decrease in heat consumption, but, accordingly, the depth of absorption worsens. That is why the piperazine activator is used. In addition, MDEA is characterized by lower corrosion rate and solution degradation.

Chem-Engineering Services (USA) has developed a typical single-flow technological scheme for CO<sub>2</sub> removal with an ammonia capacity of 1550 t/day [7]. The Russian company «GazSerf» presented its version of Amines purification with an ammonia capacity of 1000 t/day [8]. In [9], the simulation of single-stream gas purification from CO<sub>2</sub> with aMDEA solution for a packed absorber with an ammonia capacity of 600 t/day is carried out. The undoubted promise of purification process gas with aMDEA solution determines in-depth attention to the calculation aspects when introducing this method, especially for large-scale production. Therefore, it is urgent to develop and implement a mathematical model of precisely two-stream CO<sub>2</sub> absorption. Thus, *the object of research* is the stage of purification of process gas of ammonia production with a capacity of 1360–1500 t/day in a two-section plate absorber. And *the aim of research* is to substantiate the possibility of replacing an absorbent solution of monoethanolamine (MEA) with an activated solution of methyldiethanolamine (aMDEA) at multi-tonnage plants operating according to a two-line purification scheme.

## 2. Methods of research

The algorithm of material and heat balances of purification with MEA solution [10] was revised for corresponding calculations using aMDEA solution and implemented in Excel. In the course of the study, the method of compiling the material balance was used, taking into account the peculiarities of the interaction of the aMDEA components with CO<sub>2</sub>, and numerical integration to calculate the number of plates for the absorber. At the same time, it is taken into account that the two-stream process gas purification provides for the supply of a finely regenerated solution to the upper part of the absorption column and a coarsely regenerated solution to the lower part. The temperature of the solutions at the outlet of each part is determined by adiabatic heating due to the exothermic absorption reaction.

## 3. Research results and discussion

The output has the following parameters. The absorber operates under pressure  $P_{abs}=28$  atm. The composition of the original aMDEA: MDEA  $C_{MDEA}=35$  % wt., Piperazine  $C_{PZ}=5$  % wt. The carbonization degree of the AMDEA solution: at the entrance to the stage of «fine» purification  $\alpha_{2B}=0.1$ ; at the exit from the stage  $\alpha_{2H}=0.35$ ; at the entrance to the stage of «rough» purification  $\alpha_{1B}=0.35$ ; at the exit  $\alpha_{1H}=0.67$ . CO<sub>2</sub> content at the outlet of the absorber  $c(\text{CO}_2)_2=0.01$  % vol. The peculiarity of the algorithm is to search for the value of CO<sub>2</sub> concentration at the exit from the stage of «rough» purification  $c(\text{CO}_2)_1$  equal to 5.65 % vol. This value is selected by material calculation, provided that the flow rates of finely and roughly regenerated solutions are equal to the regenerator-recuperator. The composition of the outlet gas is as follows (Table 1).

The calculation results are shown in Table 2–6, taking into account the physical absorption of gas components in water. A mixture of 549670.82 kg/h of solution after fine

purification and 529653.48 kg/h of coarsely regenerated solution from the regenerator-recuperator enters the stage of «rough» purification. The gas leaving the absorber is wet and contains 465 kg/h of water vapor.

**Table 1**

Output dry converted gas parameters

Component	nm <sup>3</sup> /h	% w.	kg/h	% wt
H <sub>2</sub>	126978.4	61.64	11301.1	8.34
N <sub>2</sub>	41097	19.95	51371.3	37.90
CO <sub>2</sub>	35761.6	17.36	70235.8	51.81
CO	1030	0.5	1287.5	0.950
Ar	515	0.25	919.3	0.678
CH <sub>4</sub>	618	0.3	441.2	0.326
Total	206000	100	135556.2	100

Analysis of the Tables 4–6 in comparison with similar data on the monoethanolamine solution [10] shows a decrease in the solution consumption by 5.5 % when using aMDEA, which will help to reduce the energy costs for pumping and regeneration. The developed algorithm and its implementation in Excel make it possible to carry out multivariate calculations with varying concentration parameters for gas and solution, and their temperature.

**Table 2**

Dry gas parameters after the «rough» purification stage

Component	m <sup>3</sup> /h	% w.	kg/h	% wt
H <sub>2</sub>	126808.7	70.36	11285.9	13.24
N <sub>2</sub>	41062.7	22.78	51328.3	60.19
CO <sub>2</sub>	10190.6	5.65	20014.4	23.47
CO	1028.6	0.57	1285.8	1.51
Ar	513.9	0.29	917.4	1.08
CH <sub>4</sub>	616.6	0.34	440.3	0.52
Total	180221.1	100.00	85272.1	100.00

**Table 3**

Dry gas parameters after the «fine» purification stage

Component	m <sup>3</sup> /h	% w.	kg/h	% wt
H <sub>2</sub>	126710.0	74.57	11277.2	17.28
N <sub>2</sub>	41042.7	24.15	51303.4	78.62
CO <sub>2</sub>	17.0	0.01	33.4	0.05
CO	1027.8	0.60	1284.7	1.97
Ar	513.3	0.30	916.2	1.40
CH <sub>4</sub>	615.9	0.36	439.7	0.67
Total	169926.7	100.00	65254.6	100.00

**Table 4**  
Consolidated material balance of the purification process according to aMDEA

aMDEA input			aMDEA consumption		
Component	kg/h	%	Component	kg/h	%
Thinly regenerated solution including	529653.5	50.00	aMDEA	409743.3	36.29
aMDEA	208664.4	39.40	H <sub>2</sub> O	614149.9	54.39
H <sub>2</sub> O	312996.7	59.09	CO <sub>2</sub>	105151.1	9.31
CO <sub>2</sub>	7992.4	1.51	H <sub>2</sub>	23.9	0.0021
Thinly regenerated solution including	529653.5	50.00	N <sub>2</sub>	67.9	0.0060
aMDEA	201078.8	37.96	CO	2.7	0.0002
H <sub>2</sub> O	301618.3	56.95	Ar	3.0	0.0003
CO <sub>2</sub>	26956.4	5.09	CH <sub>4</sub>	1.5	0.0001
Total	1059306.0	100	Total	1129143.1	100

**Table 5**  
Material balance for finely regenerated solution

Solution, including	aMDEA input		aMDEA consumption	
	kg/h	%	kg/h	%
	529653.5	100.00	549670.6	100
aMDEA	208664.4	39.40	208664.4	37.9617
H <sub>2</sub> O	312996.7	59.09	312996.7	56.9426
CO <sub>2</sub>	7992.4	1.51	27973.3	5.0891
H <sub>2</sub>	–	–	8.8	0.0016
N <sub>2</sub>	–	–	24.9	0.0045
CO	–	–	1.0	0.0002
Ar	–	–	1.1	0.0002
CH <sub>4</sub>	–	–	0.6	0.0001

**Table 6**  
Material balance for coarsely regenerated solution

Solution, including	aMDEA input		aMDEA consumption	
	kg/h	%	kg/h	%
	1079324.3	100.00	1129143.1	100
aMDEA	409743.3	37.96	409743.3	36.29
H <sub>2</sub> O	614614.9	56.94	614149.9	54.39
CO <sub>2</sub>	54929.7	5.09	105151.1	9.31
H <sub>2</sub>	8.8	0.00081	23.8	0.0021
N <sub>2</sub>	24.9	0.00231	67.8	0.0060
CO	1.0	0.00009	2.7	0.0002
Ar	1.1	0.00010	3.0	0.0003
CH <sub>4</sub>	0.6	0.00005	1.5	0.0001

The number of theoretical absorber plates is found by numerical integration of the expression:

$$N = \int \frac{dP}{(P - P^*)}$$

where  $P$ ,  $P^*$  – working and equilibrium CO<sub>2</sub> pressure, respectively, Pa.

*The upper part of the absorber.* Additional output data: based on the results of thermal calculation: the temperature of the aMDEA solution at the inlet to the upper part of the absorber  $T_1=318$  K, at the outlet  $T_2=331.62$  K.

The calculation algorithm is given in [10]. The equilibrium CO<sub>2</sub> pressure over the MDEA solution, depending on the degree of carbonization and temperature, is determined by the equation, Pa:

$$P_0^* = 10^3 \cdot e^{(2567+3.0495 \ln \alpha - 6395.69/T)}$$

The decrease in the equilibrium CO<sub>2</sub> pressure over the activated solution of aMDEA in comparison with MDEA is corrected by the correction factor  $K_{cor}$ . Its dependence on the carbonization degree  $\alpha$  for absorption conditions at a temperature of 50 °C has the form:

$$K_{cor} = -94.167 \cdot \alpha^3 + 131.09 \cdot \alpha^2 - 64.32 \cdot \alpha + 12.998$$

Equilibrium CO<sub>2</sub> pressure over aMDEA solution taking into account  $K_{cor}$ , Pa:

$$P^* = P_0^* / K_{cor}$$

The implementation of the algorithm is presented in Table 7. The number of theoretical plates is 4.41. Taking into account the efficiency of the plate  $\eta_p=0.5$ , 8.82 plates are required.

**Table 7**  
Determination of the number of theoretical plates of the upper part (fragment)

No.	$\alpha$	$T$	$P_0^*$	$K_{cor}$	$P^*$	$P$	$N$
0	0.100	318.000	231.317	7.783	29.722	280.000	–
1	0.105	318.272	273.086	7.581	36.024	3440.315	0.928
2	0.110	318.545	320.163	7.384	43.361	6600.631	0.482
3	0.115	318.817	372.986	7.192	51.864	9760.946	0.326
48	0.340	331.074	21373.492	2.582	8277.677	151975.135	0.022
49	0.345	331.346	22704.206	2.544	8925.490	155135.450	0.022
50	0.350	331.619	24101.697	2.507	9613.320	158295.765	0.021
Number of theoretical plates							4.41

*The lower part of the absorber.* Additional output data: according to the results of the thermal calculation, the temperature of the aMDEA solution at the inlet  $T_1=324.8$  K, at the outlet  $T_2=341.6$  K. The correction factor  $K_{cor}$  is higher than the value of the carbonization degree  $\alpha=0.47$  is calculated by the equation:

$$K_{cor} = -57.501 \cdot \alpha^3 + 85.52 \cdot \alpha^2 - 42.472 \cdot \alpha + 9.0416$$

The number of theoretical plates is 1.935 (Table 8). Taking into account the efficiency of the plate  $\eta_p=0.5$ , 3.87 plates are required. The total number of plates in the absorber is  $\approx 13$ , which is close to the industrial absorber, in which 15 plates are located [11].

Calculations at the temperature of the solutions for irrigation of the upper and lower sections increased by 10 degrees gave the number of plates less than 14. This indicates the possibility of carrying out absorption at slightly elevated temperatures.

Table 8

Determination of the number of theoretical plates  
of the lower part (fragment)

No.	$\alpha$	$T$	$P_0^*$	$K_{car}$	$P^*$	$P$	$N$
0	0.350	324.819	16095.93	2.507	6420.10	89600.0	–
1	0.356	325.155	17360.00	2.463	7049.56	97529.6	0.088
2	0.363	325.491	18704.15	2.421	7727.38	105459.2	0.081
3	0.369	325.827	20132.41	2.381	8456.20	113388.8	0.076
48	0.657	340.945	278994.78	1.744	159946.39	470220.8	0.026
49	0.664	341.281	292718.68	1.714	170791.57	478150.4	0.026
50	0.670	341.617	307019.41	1.681	182628.47	481310.7	0.027
Number of theoretical plates							1.935

#### 4. Conclusions

Analysis of material balance calculations in comparison with the data on the MEA solution shows a decrease in the consumption of solutions by 5.5 % when using aMDEA, which will help to reduce energy costs for pumping and regeneration. The number of absorber plates, calculated by numerical integration, corresponds to the parameters of a standard absorber and allows purification the gas to a content of 0.01 % CO<sub>2</sub>. An increase in the temperature of the solutions by 10 degrees at the entrance to each section does not significantly affect the number of plates. Thus, the mathematical modeling of a two-section absorber shows a real possibility of replacing an 18 % MEA solution with a 40 % aMDEA solution. This should be implemented on existing equipment and will not require a change in the technological scheme.

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