

While modeling the influence of the main perturbation actions (fluoride concentration and gas consumption) and possible control actions (raw material loading, heat removal intensity and heating) on stationary and transient conditions in the device was estimated.

The developed mathematical model implemented in the package MATLAB 7.0 will be used for synthesizing modernized control algorithm of DCR. Improvement of algorithm is in automated stabilization of the required tempera-

ture distribution profile in the device retort by changing raw material loading in the device. Control algorithm will be implemented at modern software with software support at high-level object-oriented programming language. The model may be also used for studying other control objects in radiochemical technology of counterflow and uniflow devices with gas and disperse fluxes (for example, flame reactors for obtaining UHF, counterflow devices for processing product unreacted in fluoridation reactor etc.).

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## MATHEMATICAL SIMULATION OF WATER AND METHANOL SEGREGATION PROCESSES AT FIELD PREPARATION OF GAS CONDENSATE

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*Calculation modulus for water and methanol segregation processes from gas condensate has been developed. Applying the developed technological system the influence of process variables on segregation processes of water and methanol is studied. Modes of operation of liquid separators at which the most efficient segregation of water-methanol solution from unstable condensate occurs are recommended.*

When producing and preparing gas condensate for transportation the supply of raised concentration methanol to the system is provided. When mixing hydrocarbon condensate with water methanol solution the mixture which should be divided is formed. Indistinctness of division of water-methanol and hydrocarbon phases results in considerable losses of methanol with unstable condensate and tank gas.

Applying methods of mathematical modeling and using computer analogues (A) allows solving these problems and many other ones rather efficiently.

On the basis of experience in developing analogues for various technologies we developed the mathematical models [1–4] of the processes of commercial treating of oil, gas and gas condensate on the basis of which the technological analogue (TA) for computing material balances and on-line analysis of operating practices of complex gas treatment device (CGTD) was developed.

The main blocks of the developed TA of complex gas and gas condensate treatment technology are modulus of computing processes of separation, tip leakage, liquid separation, throttling and heat exchange.

Constants of phase equilibrium were calculated by the technique proposed in papers [5, 6] on the basis of which there is the main Gofman-Kramp equation. For calculating constants of phase equilibrium of methanol and water the equation of Teck-Still was chosen [7].

The given correlation differs in high accuracy at calculating vapor pressures of polar substances and substances with hydrogen bonds at low temperatures. The equation of Teck-Still for calculating saturated vapor pressure of chemical substances has the following form [7]:

$$\ln P_{VP} = A \left( 1,14893 - \frac{1}{T_r} - 0,11719 \cdot T_r - \right. \\ \left. - 0,03174 \cdot T_r^2 - 0,375 \cdot \ln T_r \right) + \\ + (1,042\alpha_c - 0,46284A) \times \\ \times \left[ \frac{T_r^{5,2691+2,0753 \cdot A-3,1738 \cdot h} - 1}{5,2691+2,0753 \cdot A-3,1738 \cdot h} + \right. \\ \left. + 0,040 \cdot \left( \frac{1}{T_r} - 1 \right) \right], \quad (1)$$

where  $A = \frac{\Delta H_{ub}}{RT_c \cdot (1 - T_{br})^{0.375}}$ ,  $h = T_{br} \frac{\ln P_c}{1 - T_{br}}$ ,  $T_r = \frac{T}{T_c}$ ,  $T_{br} = \frac{T_b}{T_c}$

are the reduced temperatures;  $T_c$ ,  $T_b$  are the critical and normal boiling temperatures of the component;  $P_c$  is the critical pressure;  $\alpha_c$  is searched by the formula (1) from the condition:  $P_{Vr} = 1/P_c$  and  $T_r = T_{br}$ .

Comparison of values of saturated vapor pressures of methanol and water calculated by the technique given above and scientific literature data showed their satisfactory convergence [8, 9].

Efficiency of methanolic water segregation in liquid separators depends to a considerable extent on drop size formed at material flow movement through the supply pipe-line. Therefore, the stage of dispersed phase tip leakage should precede the process of methanolic water precipitation in the device. Tip leakage occurs in the flow at mixture movement through the supply pipe-line, in branch pipes of liquid separators and capacities. The size of formed drops is taken into account at calculating sedimentation process [1, 2] therefore it is important to estimate the influence of technological conditions for gas condensate preparation for the process of tip leakage and further segregation of methanolic water.

Calculation of tip leakage and sedimentation processes was fulfilled similarly to the techniques given in the paper [4] size of drop diameter was calculated by the formula suggested in [10].

Modeling processes of commercial preparation of oil, gas and gas condensates the calculation of water and water-methanol solution sedimentation process is of considerable difficulty. In the TA applied at the present the phase equilibriums are mainly calculated in the system: hydrocarbons-methanol-water. According to the physical entity two processes are considered in liquid separators: gas separation from liquid phase and separation of water-methanol solution from condensate owing to sedimentation processes.

Thus, mathematical model of liquid separator includes the model of separation process and the model of sedimentation process.

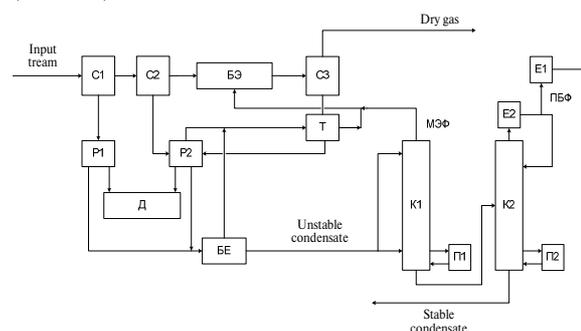
The technological analogue developed by us in the foundation of which there are mathematical models of the main processes of gas condensate preparation allows computing device material balances, compositions of product flows subject to the consumption, water content in supply steam, methanol supply and a number of constructive peculiarities of the devices such as device volume, sedimentation zone volume, height of water-methanol layer and diameter of inlet branch.

In general, TA allows predicting the influence of thermobaric conditions, composition of stratal mixture, consumptions and constructive peculiarities of the devices applied in the given technological diagram for the processes of commercial preparation of gas condensate including separation processes of water-methanol solutions.

For increasing efficiency of CGTD operation and quality of the obtained commercial output the optimal

technological conditions supporting the best water and methanol segregation from the unstable condensate should be selected. Using TA the influence technological parameters on processes of commercial preparation of gas condensate was investigated.

Liquid separators and capacitors of different technological purposes are provided in technological diagram (Fig. 1) of the device for complex preparation of gas condensate [3] for water and methanol separation (Table. 1).

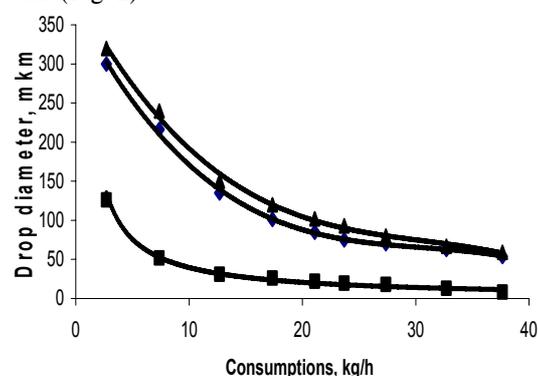


**Fig. 1.** Principle flow diagram of gas and gas condensate preparation: C1, C2, C3 are the separators; БЭ is the ejector block; Т is the heat exchanger; P1, P2 are the three-phase separators; Д is the degasifier; БЕ is the block of raw material capacities; K1, K2 are the rectifying columns; П1, П2 are the furnaces; E1 is the capacity of condensed gas gathering; E2 is the irrigation capacity; ПБФ is the propane-butane fraction; МЭФ is the methane-ethane fraction

**Table 1.** Technological conditions of operation of liquid and capacity separators

Parameters	Devices		
	Separator P1	Separator P2	Capacities БЕ
Time of mixture being in the device, h	0,7	0,5	1,1
Diameter of device inlet fitting, m	0,15	0,08	0,15
Temperature, °C	19,0	3,0	22,5
Pressure, MPa	3,8	3,2	2,4

The influence of technological parameters: pressure, temperature and mixture consumption on water drop formation (water-methanol solution) in carbon condensate was studied by the model of tip leakage process (Fig. 2).



**Fig. 2.** Dependence of drop diameter of methanolic water on stream consumption

**Table 2.** Studying technological parameters influence on water and menthol segregation processes in liquid separators P1 and P2

Parameters	Calculation variant											
	1		2		3		4		5		6	
	P1	P2	P1	P2	P1	P2	P1	P2	P1	P2	P1	P2
Temperature, °C	18,9	3,0	10,0	3,0	18,9	15,0	10,0	15,0	18,9	3,0	18,9	15,0
Pressure, MPa	3,8	3,2	3,8	3,2	3,8	2,6	3,5	2,6	3,8	3,2	3,8	2,6
Methanolic water content in liquid phase at separator input, wt. %	2,54	1,61	2,54	3,18	2,54	3,08	2,54	3,19	2,47	3,11	2,46	3,10
Methanol and water content in unstable condensate from liquid separators, kg/h												
Water	16,4	8,7	17,2	8,1	16,4	6,6	17,5	6,6	17,6	5,7	17,7	4,3
Methanol	0,0	15,0	0,0	14,5	0,0	11,3	0,0	11,2	0,0	13,3	0,0	10,0
Σ	16,4	23,7	17,2	22,6	16,4	17,9	17,5	17,8	17,6	19,0	17,7	14,3
Methanolic water content, wt. %	0,11	0,20	0,11	0,19	0,11	0,16	0,12	0,16	0,11	0,17	0,11	0,14
Methanol and water content in unstable condensate, kg/h												
Water	25,1	25,5	23,7	23,0	24,0	23,4						
Methanol	15,0	14,5	12,6	11,3	11,2	13,3						
Σ	40,1	40,0	36,3	34,3	35,2	36,7						
Methanolic water content, wt. %	0,15	0,14	0,14	0,13	0,13	0,14						
Methanol and water content in commercial gas, kg/h												
Water	0,4	0,4	0,4	0,5	0,5	0,4						
Methanol	17,6	17,6	17,5	17,5	17,6	18,8						
Σ	18,0	18,0	17,9	18,0	18,1	19,2						

The investigations showed that such parameters as temperature and pressure influence weakly the drop diameter value.

And at the same time, as calculations showed, diameters of supply pipe-lines and branch pipes in liquid separators as well as mixture consumption influence greatly the size of forming drop. The influence of material flow consumptions on liquid drop size was studied (Fig. 2). It follows from calculations that, for example, changing consumptions in the range of 7,4...37,4 t/h (P1) drop diameter decreased from 68 to 36 mkm and in P2 changing consumption from 2,7 to 32,7 t/h drop diameter decreased from 126 to 15 mkm.

Applying technological analog the processes of gas condensate commercial preparation at various technological conditions of CGTD operation were studied.

As the results of calculations showed 0,023 wt. % of methanolic water enters commercial gas and 0,15 wt. % is removed with unstable condensate.

The results of studying the influence of technological parameters on water and methanol segregation processes at CGTD are given in Table 2. The analysis of the obtained results showed that temperature increase in P2 at simultaneous pressure decrease promotes reduction of methanolic water content in unstable condensate. Temperature decrease in the first separator also promotes reduction of water and methanol content in condensate.

The results of calculation of water and methanol segregation processes in capacities at CGTD and studying the influence of technological parameters on the indices of the process are given in Table 3.

Pressure variation in the range from 1,5 to 3,5 MPa results in insignificant changes in quantity of segregated water phase (Table 3). Temperature at its change from 3

to 30 °C influences similarly. Residual condensate watering changes from 0,009 to 0,011 wt. %.

**Table 3.** Research of technological parameters influence on water and methanol segregation processes in capacities

Parameters	Calculation variants			
	1	2	3	4 (2 BE)
	T=10 °C P=2,4 MPa	T=22,5 °C P=2,4 MPa	T=30 °C P=2,4 MPa	T=22,5 °C P=2,4 MPa
Input content, kg/h				
Water	25,1			
Methanol	15,0			
Watering, wt. %	0,15			
Output content, kg/h				
Water	1,7	1,5	1,4	0,7
Methanol	1,0	0,9	0,9	0,4
Watering, wt. %	0,011	0,009	0,009	0,0043

Processes of segregating water and methanol small quantities causes rather complicated. As the researches showed the time of mixture being in the device has the main influence. Increasing this time twice (that is switching on the second capacity, variant 4, Table 3) results in decreasing residual water and methanol content approximately two times as well. That is, a good segregation of water-methanol solution from unstable condensate is observed in the studied range of temperature and pressure variation. Therefore, at efficient operation of the capacity (BE) the condensate containing approximately 0,01 wt.% of water and methanol may enter the CCW that should not influence greatly the technological conditions of the device operation.

Thus, modeling the processes of gas condensate commercial preparation applying TA allows estimating optimal technological modes of the device operation and determining water and methanol quantity in all flows of commercial device.

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## THE DEVELOPMENT OF PURIFYING TECHNOLOGY OF PROCESS WATERS OF GAS CONDENSATE FIELD FROM METHANOL

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*The possibility in principle of methanol deep catalytic oxidation in water up to MPC has been confirmed by gas chromatography method. Oxidation process of methanol contained in vat residue after regeneration stage in concentrations of 1, 5 wt. % and less, at metal oxide catalysts at  $Al_2O_3$  is considered. The basic flow diagram of closed technological cycle of methanol extraction from process waters of gas condensate fields is proposed. It consists in methanol regeneration with further deep catalytic oxidation of methanol residue quantity.*

Methanol use in gas dewatering system and as an inhibitor of hydrator formation is the main technological approach of its applying in gas and oil branches. Methanol content in industrial solutions formed after its application varied at the average in the range of 30...50 wt. %. Absence of regeneration methods of such solutions in some cases and further deep purification of process waste waters from methanol is rather expensive both in terms of money and in the fact of deterioration of ecological situation around this deposition. Methanol delivery to the Extreme North fields at least redoubles its cost. Methodical discharge or burning industrial wastes containing methanol into environment may cause serious stress for ecosystem of the given region. Therefore, technologies intended both for methanol regeneration and further purification stage from it attract attention.

In this connection works aimed at the development of methanol extraction technology from wastes of gas-condensate fields and return of methanol main part into technological cycle with further reducing methanol residual concentration in discharged industrial wastes to maximum permissible concentration (3 mg/dm<sup>3</sup>) are rather actual.

Methanol may be regenerated by rectification as the most reliable and efficient technology allowing extracting from industrial wastes up to 99 wt. % of methanol with residual concentration in vat waters about 1 wt. % and more [1–4]. The most perspective destructive method of industrial waste purification among the existing ones is the method of deep catalytic oxidation [5, 6]. However, the method is expensive due to applying catalysts of noble metals and their rapid poisoning. Therefore, in contrast to the less efficient technologies existing at the present time [7–10] the technology providing rectification with further methanol oxidation in vat residual in the device with boiling catalyst layer is proposed. Using pseudo-liquated layer the methanol oxidation process should be more efficient [11] as the pseudo-liquated catalyst layer is capable of continuous functioning with mixtures where impurity concentration is low.

Taking into account low methanol concentration (15 wt. % and lower) and high water content after rectification stage in vat residual it was necessary to state the possibility in principle of deep catalytic methanol oxidation up to carbon dioxide and water and select the catalyst being capable of operating in these conditions. The