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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^3) 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 catalyst capable of functioning in boiling layer was selected subject to such demands as selectivity, mechanical and thermal strength, possibility to regeneration, low price as well as stability in aqueous medium as water takes strong inhibitory action on catalyst activity [12]. To carry out the experiments four industrial catalysts at aluminum oxide carrier recommended by specialists of Catalysis Institute of RAS SD, Novosibirsk meeting all the enumerated demands were selected, Table 1.

Table 1. *Characteristics of the researched catalysts*

Catalyst type	IK 12-74	IK 12-73	IK 12-72	IK 12-70
Active phase	FeO	Cu – Cr – Mg	Mg – Cr	Cu – Cr
Active phase content, wt. %	≤5,5	1,2...10,6...1,8	3,0...12,0	5,0...11,3
Saturated density, kg/m^3	1090	1090	1140	1100
Specific surface, m^2/g	150	127	135	123

Experimental part

To determine the possibility in principle of methanol deep oxidation in water the experiments in oxidation of methanol of different concentration were carried out at the device with pseudo-liquated layer of coated catalyst in G.K. Boreskov Catalysis Institute of RAS SD. For preliminary tests the catalyst IK 12-73 as probably the most active was selected. The experiments were carried out at temperature 450 °C.

For the final selection of catalyst, determination of process optimal parameters and investigation of chosen catalysts behavior the further experiments were carried out at continuous-flow catalytic device with catalyst static bed, Fig. 1.

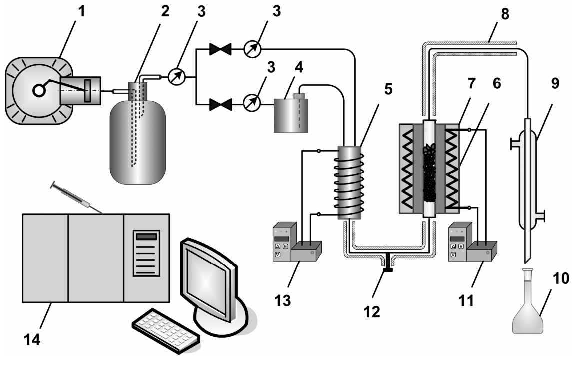

Fig. 1. *Diagram of experimental catalytic device for methanol oxidation: 1) compressor; 2) receiver; 3) manometers; 4) capacity with the original solution; 5) evaporator; 6) reactor; 7) catalyst; 8) thermal insulation; 9) cooler; 10) run-down tank; 11,13) heat controller; 12) gas simple extraction to reactor; 14) gas chromatograph «Crystal-2000M» with electronic data processing*

The experimental technique consisted in the fact that the required volume of the researched catalyst (catalyst layer height is 1...5 cm) was placed in the reactor – 6 at the lattice. Then the device was prepared for operation and for this purpose the compressor – 1 was switched on for air supplying into airline controlling its consumption and the device was heated up to the stated process temperatures. To transfer the original liquid mixture into gas-vapor mixture the temperature in the evaporator – 5 was stated equal to 250 °C, the reactor temperature was stated in the range of 250...450 °C depending on the purpose of the experiment. All the lines were heat-insulated for preventing water condensation from gas-vapor mixture. Outputting the device to the operating mode the supply of the original mixture with specified methanol concentration was switched on. At the reactor output the reaction products passed through the countercurrent cooler – 8 and divided into two phases liquid (mainly water) and gaseous (carbon dioxide and air) with residual content of methanol. Gaseous and vapor phases before and after reactor underwent gas chromatography analysis on methanol content.

To determine working temperature of oxidation process at which maximal degree of methanol oxidation was achieved the influence of reactor temperature of catalytic oxidation in the range of 250...450...250 °C with a step in 50 °C on degree of methanol oxidation was investigated. The temperature of evaporator was maintained at the level of 250 °C.

Results and their discussion

The investigations carried out at the device with pseudo-liquated catalyst layer showed (Table 2) that even at high degree of solutions dilution with air (45 mg/dm^3) oxidation occurs and methanol concentration in condensed gas-vapor phase at the reactor output amounts to 2,2±0,2 mg/dm^3 and less that is lower than MPC. However, it was stated that at methanol concentration in the mixture lower than 45 mg/dm^3 methanol «breakthrough» through the catalyst starts that influences the decrease of purification degree.

Table 2. *Indices of methanol oxidation in pseudo-liquated layer of catalyst IK 12-73*

Methanol concentration (subject to dilution with air), ±0,2 mg/dm^3		Purification degree (subject to dilution with water), %
In the reactor	In condensate at the device output	
120	0,5 0,3 0,3 0,4	99,6 99,7 99,7 99,6
71	0,2 0,2 0,2 0,2	99,6 99,6 99,6 99,6
54	0,1 0,1 0,6 0,3	99,7 99,7 99,8 99,7
45	0,2 0,2 0,4 0,4 0,4	99,6 99,6 99,8 98,8 99,8
30	5,3 6,0 6,8 5,9	82,3 80,0 77,3 80,3

Note: Methanol was not observed in gaseous mixture

The results obtained during the process of deep oxidation of methanol at the device with fixed bed of catalyst are presented in Table 3. It follows from Table 3 that maximal purification degree from methanol in water is achieved using catalysts IK 12-73 and IK 12-72 at temperature 450 °C. Such high temperature of the process may indicate the difficulty of opening the bound methanol-water. At temperatures lower than 400 °C methanol molecules are introduced into water structure forming branching networks with hydrogen bounds «alcohol – water» [13] with the result that methanol molecules «slip» through the catalyst and oxidation does not occur. Thus, for achieving deep oxidation of methanol it is necessary either to rise temperature of the process (that is expensive) or increase mixture contact time with catalyst or raise methanol concentration in the original solution. However, the fulfillment of the last condition is inappropriate due to methanol losses as an agent.

Table 3. *Dependence of purification degree on process temperature of fur various catalysts*

Temperature, °C	Methanol concentration at liquid phase output, mg/dm^3 / Purification degree from methanol, %			
	IK 12-74	IK 12-73	IK 12-72	IK 12-70
250	5559,6 / 38,5	11672,1 / 27,4	11081,9 / 31,1	4216,4 / 53,4
300	988,8 / 89,1	3921,6 / 75,6	1991,1 / 87,6	371,4 / 95,9
350	67,4 / 99,3	869,8 / 94,6	1608,9 / 90,0	21,5 / 99,8
400	151,5 / 98,3	77,2 / 99,5	232,8 / 98,6	7,6 / 99,9
450	52,3 / 99,4	0,9 / 99,9	0,7 / 99,9	2,9 / 99,9

Note: 1. Original concentration of methanol amounted to less than 2 wt. %; 2. Methanol was not revealed in gaseous phase at temperature higher than 400 °C

It should be also taken into account that methanol oxidation may result in formation of different intermediate products the appearance of which depends on catalyst type, amount of oxygen taking part in the reaction, process temperature, pressure. It was stated [12, 14] that the main products of methanol partial oxidation are formaldehydes CH_2O, formic acid HCOOH, dimethyl ether CH_3OCH_3, methyl formate $HCOOCH_3$, methylal $(CH_3O)_2CH_2$. The possible ways of methanol oxidation which are divided into two principle groups are given in Fig. 2: reactions occurring with oxygen (molecular or supplied by the catalyst) at the formation of final products – carbon dioxide and water; and reactions the occurrence of which is possible in anoxic environment. In the given paper methanol oxidation process was fulfilled at oxygen excess. Stoichiometric calculations subject to the conditions of oxidation process carrying out showed that air oxygen is enough at process carrying out in optimal conditions for methanol deep purification up to carbon dioxide and water.

Dependence of purification degree on contact time of working mixture with catalyst layer was studied at constant temperature 450 °C for catalysts IK 12-72 and IK 12-73. The obtained results are presented in Fig. 3.

It is seen that at τ=0,9 with methanol oxidation at IK 12-73 and IK 12-72 is practically equal 100 % that in terms of concentration amounts to 0,9 and 0,8 mg/dm^3 respectively. MPC by methanol in condensate is achieved for both catalysts; however, activity of catalyst IK 12-73 is higher than of IK 12-72. In gaseous phase methanol is not revealed in both cases that is its content was lower than detection limits of gas chromatograph (≤0,1 mg/dm^3).

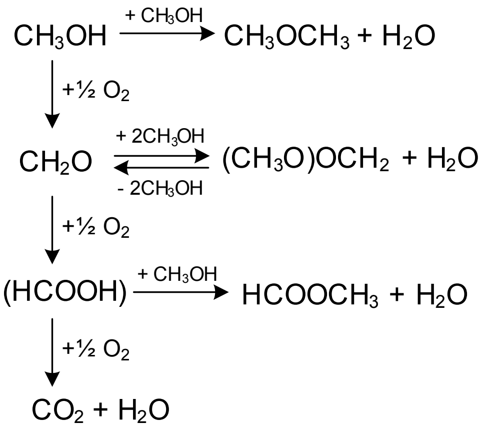

Fig. 2. *Possible ways of occurring methanol oxidation reaction*

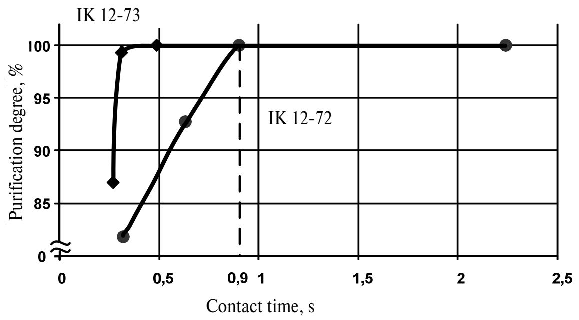

Fig. 3. *Dependence of purification degree on contact time*

Life tests of selected catalysts IK 12-72 and IK 12-73 showed catalyst stability in aqueous medium at temperature 450 °C and high activity unchanging during 100 h of continuous work (Fig. 4, 5).

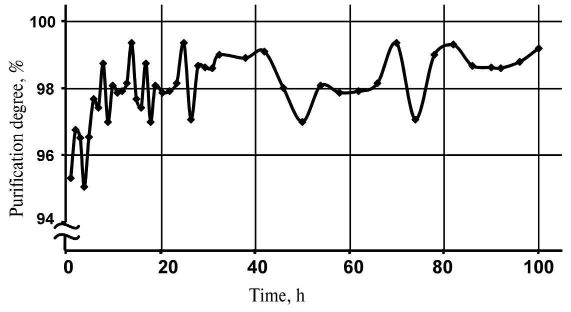

Fig. 4. *Life tests of IK 12-72*

Scanning electron micrographs of the surface of new and dead catalyst IK 12-73 are given in Fig. 6 and 7. It follows from them that catalyst surface is inhomogeneous and porous before life tests and after continuous interaction with water catalyst surface becomes more homogeneous, pores are less marked, there are no cakes.

Elemental analysis of both catalysts carried out with microanalyzer EDAX ECON IV showed that at catalyst surface before tests active components are distributed inhomogeneously while at the reverse catalyst at each point of the surface similar composition is observed. It was shown that catalyst surface area, composition and content of active components of dead catalysts had not practically changed. It indicates that the selected catalysts are capable of continuous service in water which does not take (or takes in a minor degree) inhibitory action and catalyst activity during all tests at similar conditions remain unchangeable.

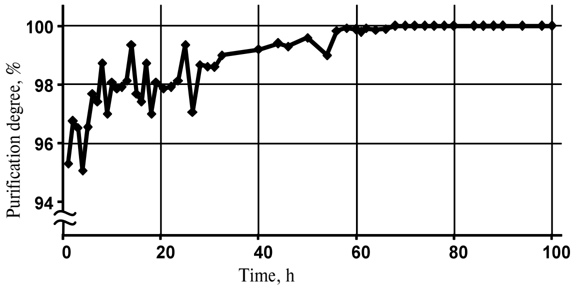

Fig. 5. *Life tests of IK 12-73*

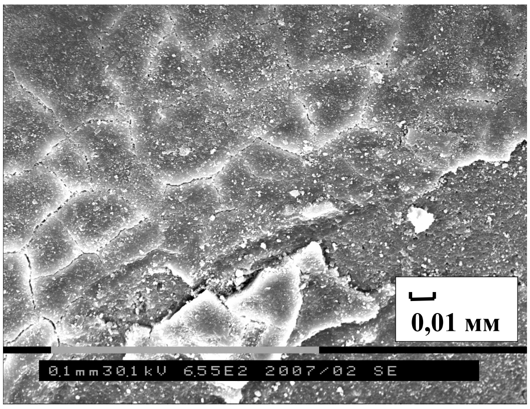

Fig. 6. *Scanning electron micrograph of catalyst IK 12-73 surface before life tests*

Fig. 7. *Scanning electron micrograph of catalyst IK 12-73 surface after life tests*

On the basis of the obtained data the basic and instrument-technological diagrams of closed technological cycle of methanol extraction from GCF wastes and development of its concentration in industrial wastes up to MPC might be suggested (Fig. 8, 9).

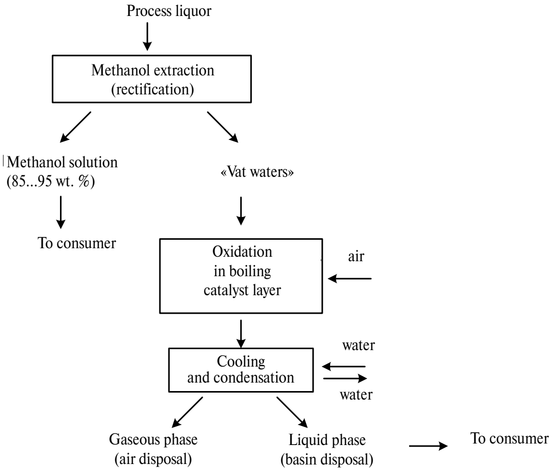

Fig. 8. *Basic diagram of utilization and purification of industrial wastes of GCF from methanol*

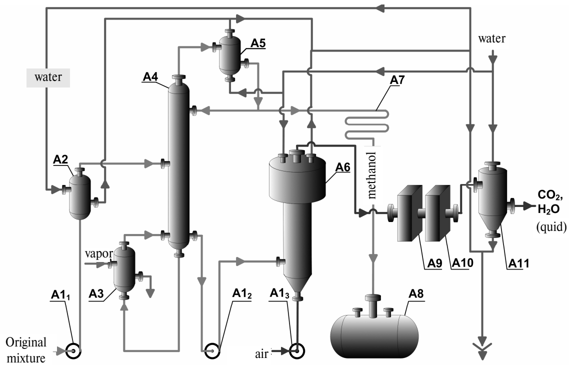

Fig. 9. *Instrument- process diagram of purifying industrial wastes of GCF from methanol: A1) pumps; A2) exchanger-preheater; A3) boiler; A4) rectifying column; A5) dephlegmator; A6) catalytic reactor; A7) distillate cooler; A8) capacity for distillate collection; A9, A10) filters (collector of catalyst entrained particles); A11) cooler of escaping gas-vapor mixture*

Original solution of methyl alcohol enters exchanger-preheater and then into plate rectifying column having 24 steps where methanol and water are divided. Distillate is cooled and enters collection capacity where methyl alcohol may be returned into technological cycle. Methanol concentration in distillate achieves 90...99 wt. %. Vat residual containing methanol (1...10 wt. %) is supplied into catalytic reactor with catalyst IK 12-73 heated up to 450 °C. Heated air which not only creates and heats pseudo-liquated catalyst layer but also promotes methanol oxidation due to the oxygen containing in it is supplied there.

The entrained catalyst particles are caught at filters or in collector/cyclone set at reactor outlet. Relatively safe gaseous oxidation products may be discharged into atmosphere and condensate discharged into the pond or used in technological cycle as circulating water.

The peculiarity of the suggested process diagram consists in the fact that it is a base for wastes purification from methanol at different gas condensate deposits. The given process diagram, and mainly its key device – catalytic oxidation reactor with pseudo-liquated catalyst layer allows solving the problem of discharging industrial wastes containing methanol into environment. Besides, the economic problem is also solved as the most part of methyl alcohol returns into technological cycle.

Conclusions

1. Possibility in principle of deep catalytic oxidation of methanol in water up to MPC was confirmed by the method of gaseous chromatography.
2. 100 % methanol oxidation is achieved using copper-chrome-magnesium (IK 12-73) and chrome-magnesium (IK 12-72) catalysts at the carrier of aluminum oxide.
3. Optimal conditions of methanol deep oxidation process in water were determined: mixture contact time with catalyst is not less than 0,9 s, process temperature is less than
4. The diagram of methanol extraction from industrial wastes of gas condensate deposits with their further purification including regeneration stage of methanol by rectification and purification stage of wastes (vat residual after rectification) from residual quantities of methanol (1,5 wt. %) by catalytic oxidation was suggested.

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