Methanol Solution Recuperation at Gas Distillate Production

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Abstract – Two-stage scheme is represented for purify industrial wastewater from methanol:

– industrial wastewater separation in the vacuum evaporator to the condensate fluid with methanol concentration of 80–90% and vat residue with concentration of 4–6%;

– after treatment of vat residue by electric-discharge method down to the maximum permissible concentration level.

The solution separated effectiveness is characterized by the following energy inputs: 2.16 kJ/l (first stage) and 2.18 kJ/g (second stage).

The gas raw material proceeded from the bore represents a mixture of liquid and gaseous hydrocarbons with water. The raw material is supplied to the technological platform to separate it to fractions and to purify the hydrocarbon fractions from admixtures. The mixture pressure at the treatment achieves 200 atm. In the treatment process the mixture content, temperature and pressure change. At that, in the areas of sharp pressure decrease the formation of hydrates – ice plugs which change the treatment mode is possible. To prevent the formation of hydrates the methanol is introduced to the raw material. The water and methanol separated from hydrocarbon raw material represent an industrial wastewater. The methanol content in the wastewater can be 40%, this means that 1 m^3 of wastewater can contain more than 300 kg of methanol.

The methanol is a very toxic substance which influences on nervous and cardiovascular system of human organism. According to the sanitary standard requirements [1] the maximum permissible concentration of methanol is 3 mg/dm^3. The methanol extraction out of industrial wastewater, its recuperation to the technological process, wastewater purification down to the safe level represent a very important task.

To purify industrial wastewater the two-stage scheme is offered:

– industrial wastewater separation in the vacuum evaporator to the condensate fluid with methanol concentration of 80–90% and vat residue with concentration of 4–6%;

– after treatment of vat residue by electric-discharge method down to the maximum permissible concentration level.

The first stage. The distillation and rectification are the most wide-spread methods of liquid uniform mixtures separation which consist of two or more volatile components. The processes of distillation and rectification are based on the different volatility of mixture components at one and the same temperature. The volatile components boil at a less temperature than persistent components. At the end of the distillation or rectification the initial mixture is divided to distillate saturated by volatile components and vat residue saturated by persistent components.

The vacuum evaporators carry out the division of liquids according to the components. Moreover, they permit to organize energy recuperation. At that, the energy inputs for the distillation process decrease and the deep product separation is provided.

The installation scheme on industrial wastewater is presented in Fig. 1.

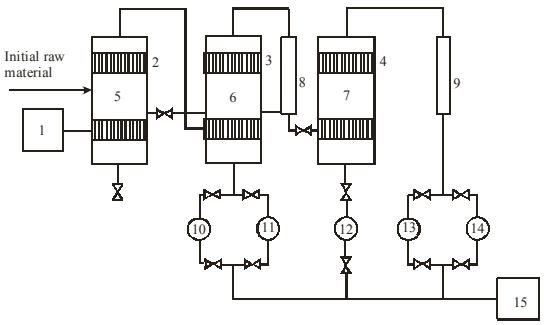

Fig. 1. The vacuum installation scheme for industrial wastewater separation. *1* – heat-generator; *2–4* – dephlegmator; *5*, *6* – reactor; *7* – dresser; *8*, *9* – condenser; *10–14* – receiving capacitor; *15* – vacuum pump

The initial raw material proceeds to the vacuum reactor *5* and begins to boil. The vapors leaving the reactor are directed to the dephlegmator *2* where partially are condensed. At the partial condensation the phlegm saturated by water forms. The phlegm is poured back to the reactor *5* and interconnects to the vapors going out of the reactor. The vapors passed through the dephlegmator goes to the dresser *6* through the heat-generator *6* and condenser *8*. The vapors with volatile components of the second stage go to the dresser *7* through the dephlegmator *3* and condenser *8*. In the dresser the additional separation of the raw material into methanol and vat residue takes place. The condensate saturated by methanol up to the concentration of 80–90% goes to the collectors *13*, *14*. The vat residue of the first stage goes to the second stage where additionally the methanol separation takes place. The vat residue from the second stage with con-

centration of 4–6% goes to the vat residue collectors *10*, *11*. The condensate with methanol concentration of 90% can be repeatedly used to prevent hydrates formation.

The preliminary tests on methanol separation from water were carried out at the installation with productivity of 10 l/hour. The methanol concentration in water was 40%, the treated solution volume was 5 liters. The solution separation effectiveness is characterized by the following coefficients:

– final vat residue concentration – 6%;

– distillate concentration – 80%;

– energy inputs ~ 0.6 kW · h/l (2.16 kJ/l).

The second stage. The vat residue of the second stage reduces to the maximum permissible concentration level by electric-discharge method. At the second stage the methanol solution with concentration of 10% was treated. It was the following 5 l of distillated water and 0.5 l of methanol. The solution from the tank was supplied by the pump to the water-stream sprayer. At the output from the water-stream sprayer the stream of small drops of solution and air was formed. The solution expense through the sprayer was 0.4 m^3/h, air expense was 3 m^3/h. This stream was treated in the electrode system by voltage pulses. The treated by discharge drops flew down to the tank. From the tank the solution was again supplied to the sprayer for treatment. The electrode system represented two sets of wires which were placed at the 2 cm distance. The typical drop diameter was 0.1–1.0 mm, the time of treatment of respiratory mixture in the discharge gap was 1–2 ms. The voltage at electrodes was 35 kV, pulse duration was $2 \cdot 10^{-7}$ s, pulse energy 0.25 J, the pulse repetitive rate was 10^3 s^{-1}. The plasma of such a pulsed discharge is characterized by the essential increase of electron temperature over the atom and molecule temperature. In the discharge plasma the hydrogen peroxide, ozone and radicals OH, H, O are formed. The electrons and UV-radiation influence the stream. Under the influence of these factors the methanol destruction and decomposition take place.

The solution stated above was treated for 50 min. After that the sample splitting for analysis was carried out. To the left solution 5 g of $KMnO_4$ was added and the treatment by discharges was continued for 20 min. To estimate the decomposition effectiveness the analysis of the residual concentration of methanol in water was carried out. The analysis results are given in the table1. After 50 min of solution treatment 82.5 g of methanol from 396 g of initial one was destructed. The energy inputs for methanol decomposition by electric discharges were 91.8 kJ/mole what increased the energy of 1 mole of methanol formation by 1.22 times.

The $KMnO_4$ addition to the solution and its subsequent treatment for 20 min leaded to decomposition of 137.5 g of CH_3OH. In this case 10 g of methanol was oxidized in the reaction with $KMnO_4$ and 127.5 g of methanol was destructed in the discharge plasma with the catalysis presence – MnO_2. In this case the input for decomposition of 137.5 g of methanol is 300 kJ and formation energy of 137.7 g of methanol is 1024 kJ. So the energy input for methanol decomposition in this experiment was 3.41 times lower than theoretical energy input.

The evaluations show that two-stage installation with productivity of 1 m^3/h for recuperation and decomposition of methanol in the industrial wastewater will have the flowing parameters:

– vacuum evaporative stage with power capacity of 600 kW, weight – 1000 kg;

– electric-discharge stage of purification of 5% industrial wastewater with power capacity 50 kW, weight about 700 kg.

– total power of two stages is 650 kW, weight 1700 kg.

For one hour of work up to 227 kg of methanol can be recuperated from 1 m^3 of industrial wastewater with volume concentration of 30% to the industrial process. The price of methanol recuperated to the industrial process is 1135 rubles (the wholesale price of 1 kg of methanol is 5 rubles). The energy inputs in the process of separation is 650 kW · h, expense price is 780 rubles (the price of 1 kW · h is 1.2 ruble). The methanol concentration in the industrial wastewater after treatment is at the level of maximum permissible concentration. The following ways of process effectiveness increase and energy inputs decrease exist:

– increase of system efficiency of high-voltage generator – reactor;

– choice of discharge type and its parameters optimization;

Table 1

#	Treated mixture content	Treatment time, min	Energy spent for treatment, J	Methanol residual concentration in solution, g/l	Energy imputs for methanol decomposition, kJ/g
1	5l H_2O + 0.5l CH_3OH + 2.5 m^3 air	50	$75 \cdot 10^4$	57	9.1
2	5 l H_2O + 0.5 l CH_3OH + + 1m^3 air + 5 г $KMnO_4$	20	$30 \cdot 10^4$	32	2.18

– application of effective, cheap catalyses;

– the search of conditions that could initiate the exothermal reaction in the wastewater purification process from methanol.

References

[1] *Control of Chemical and Biological parameter of the Environment*, Ed. by Prof. L.K. Isaev, St. Peterburg, 1998, p. 112, 210.