



## PHYSICAL AND CHEMICAL ANALYSIS OF FORMALDEHYDE ABSORPTION PROCESS

K. S. Kuramshina and K. A. Pavlova

Federal State Budgetary Educational Institution of the Highest Vocational Training Kazan National Research Technological University Kazan, Russia

### ABSTRACT

This paper presents the new approach to the physical and chemical analysis of formaldehyde absorption process on which basis possibility to propose the new more cost-effective technology based on efficient use of resources and power saving occurs. According to authors, the major way of process control over formaldehyde absorption is a liquid temperature stage control that provides grounds for the further researches. The paper is devoted to research of principles of the mechanism and kinetics of the physical and chemical processes proceeding upon formaldehyde absorption in the presence of methanol with the further preconditions on development of more effective way of formaldehyde absorption.

**Keywords:** physical and chemical analysis, mathematical analysis, formaldehyde absorption, new technology.

### INTRODUCTION

Process of formaldehyde absorption by water is the material transfer process complicated by chemical reaction in a fluid phase [1]. In a general view the basic mass-transfer resistance is presented by the equation:

$$\frac{1}{K} = \frac{1}{\beta_r} + \frac{m}{\beta_{\text{ж}}} \quad (1)$$

Where: K is a mass-transfer coefficient;  
m is equilibrium constant in gas - liquid system;  
 $\beta_r$ ,  $\beta_{\text{ж}}$  are mass-transfer coefficients in a gas and a fluid phase, accordingly.

### KINETICS AND CATALYSIS OF FORMALDEHYDE ABSORPTION PROCESS

In the process of formaldehyde absorption by water with obtaining a water solution of formaldehyde the equilibrium constant value is not fixed and depends on: concentration of formaldehyde in the solution, concentration of methanol in the solution, and temperatures [2]. When concentration of formaldehyde and methanol in the solution is low (absorption by water) and temperature is relatively low the equilibrium constant value is small and comes nearer to null. In these conditions the member  $\frac{m}{\beta_{\text{ж}}}$  value comes nearer to null in the equation of the basic mass-transfer resistance, and the equation (1) takes the form:

$$\frac{1}{K} = \frac{1}{\beta_r} \quad (2)$$

Hence, in the process of formaldehyde absorption by water at rather low temperature the basic mass-transfer resistance is concentrated in a gas phase and value of a mass-transfer coefficient is equal to value of overall mass transfer coefficient in gas phase:

$$K = \beta_r \quad (3)$$

In accordance with Higbee model, value of overall mass transfer coefficient depends on a time of phase contact surface renewal according to the equation:

$$\beta = a \sqrt{\frac{D}{\tau}} \quad (4)$$

Where: a is a constant;  
D is a diffusion factor;  
 $\tau$  is a phase contact time.

It is apparent from the equation (4) that for an intensification of formaldehyde absorption by water it is necessary to increase, first of all, extent of a gas turbulization and rapidly renew an active phase contact surface. It is known that with increase in velocity of a gas flow the turbulization extent of a gas phase increases practically proportionally to gas velocity in a zone of phase contact. It is typical practically for all known mass-transfer apparatuses including packed columns, plate-type apparatuses with bubblers, plate-type apparatuses with vortex devices and even high-speed spraying Venturi tubes [3].

The generalizing equation of dependence of overall mass transfer coefficient in a gas phase on gas velocity looks like:

$$\beta_r = c \cdot w^{0,8} \quad (5)$$

Where: c is a constant  
w is a velocity of a gas flow

The equation (5) can be presented in criterial form:

$$Nu_r = A \cdot Re_r^{0,8} \quad (6)$$

Where:  $Nu_r$  is a Nusselt number;  
A is a constant;  
 $Re_r$  is a Reynolds number.

It is known that each of apparatuses stably operates within a certain range of a gas flow velocity value.



Gas velocity in packed columns routinely ranges within the limits of 0.5–1.5 m/s. Upon increase in gas velocity more than 1.5 m/s there starts a "flooding" mode at which hydraulic resistance sharply increases. Besides, drop entrainment sharply increases. For this reason, in practice, the "flooding" mode is not applied in the case of a multistage contact. In the operating three-stage packed column a gas flow velocity reaches 1.5 m/s at the inlet of a nozzle. In the case of increase in the charge of a gas flow the operating packed column transfers in a "flooding" mode and becomes inoperative. Upon that, there are occurred transformation of the three-stage apparatus into the one-stage, sharp increase in hydraulic resistance of the apparatus, increase in drop entrainment, and increase in formaldehyde losses.

Because of increase in concentration of formaldehyde in a liquid at a third stage of phase contact, a liquid withdrawal to a synthesis stage results in additional increase in losses of formaldehyde in a reactor. To reduce losses of formaldehyde and to increase productivity, it is necessary to increase diameter of the packed column. For example, diameter of packed columns reaches 4.6 m in foreign practice upon productivity by formaldehyde of 100 thousand tons in a year. Domestic packed columns have diameter of 3.2 m and operate with productivity of 80 thousand tons in a year [1]. Even without productivity increase the operating column operates with high drop entrainment. When trying to increase in productivity, a drop entrainment sharply has increased.

However, application of packed columns with large diameter is not in accordance with scientific foundations of intensification of formaldehyde absorption process; it has no scientific substantiation and is a brake in development of large-capacity formaldehyde production of. There are known attempts to apply multistage plate-type apparatuses with bubbling devices on plates. Plate-type apparatuses can operate at gas velocity in a column up to 2.5 m/s that is much higher than for a packed column. In the conditions of formaldehyde absorption large heat quantity (up to 15 million kcal per one ton of formaldehyde) is produced. Main quantity of heat should be withdrawn at the first two stages of phase contact using a method of liquid circulation through a heat exchanger.

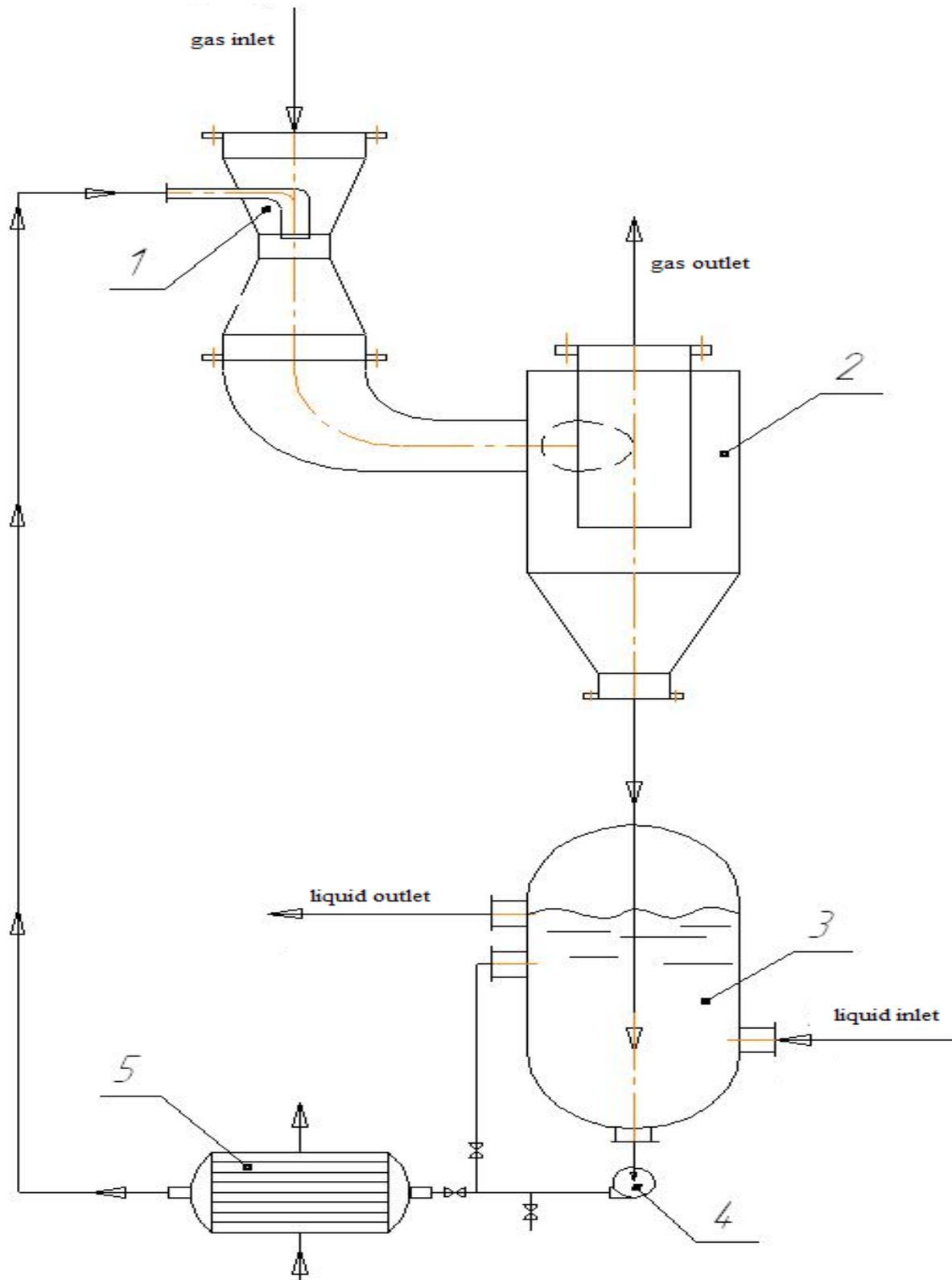
Without liquid circulation through heat exchangers the liquid starts boiling in first two stages along the gas flow. Upon that, plate-type apparatuses with hydraulic seals between plates become inoperative. It is difficult to organize effective heat exchange on a plate in practice, as there is no enough plate area. Even in the case of circulation of a considerable liquid quantity through a plate-type stage by means of the pump with an external heat exchanger on a plate with bubbling devices zones with local liquid overheat are formed, and hydraulic seals will be broken through. Therefore plate-type multistage apparatuses with bubbling devices are efficient only at small productivity [4].

### DESCRIPTION OF APPARATUSES FOR THE INVESTIGATED PROCESS

The stage which is most simple in design represents a combination of the high-velocity atomizer of a Venturi tube type with the cyclone separator. The analysis of mass-transfer coefficient dependence on a gas velocity in various apparatuses shows that the greatest value of a mass-transfer coefficient is reached in a Venturi tube [5]. However, upon that the share of power expenses in the costs of formaldehyde production becomes commensurable with the share of depreciation expenses. However, in the example of a Venturi tube application with descending way of phase interacting, simplicity and reliability of the stage is decisively apparent. The developed design philosophy for a stage with descending way of interacting of phases is promising (Figure-1).

Figures-1, 2, 3 represent three design versions of a phase contact stage. The common feature for all stages is the descending way of interacting of phases in a mass-transfer unit and application of a centrifugal forces field for separation of phases.

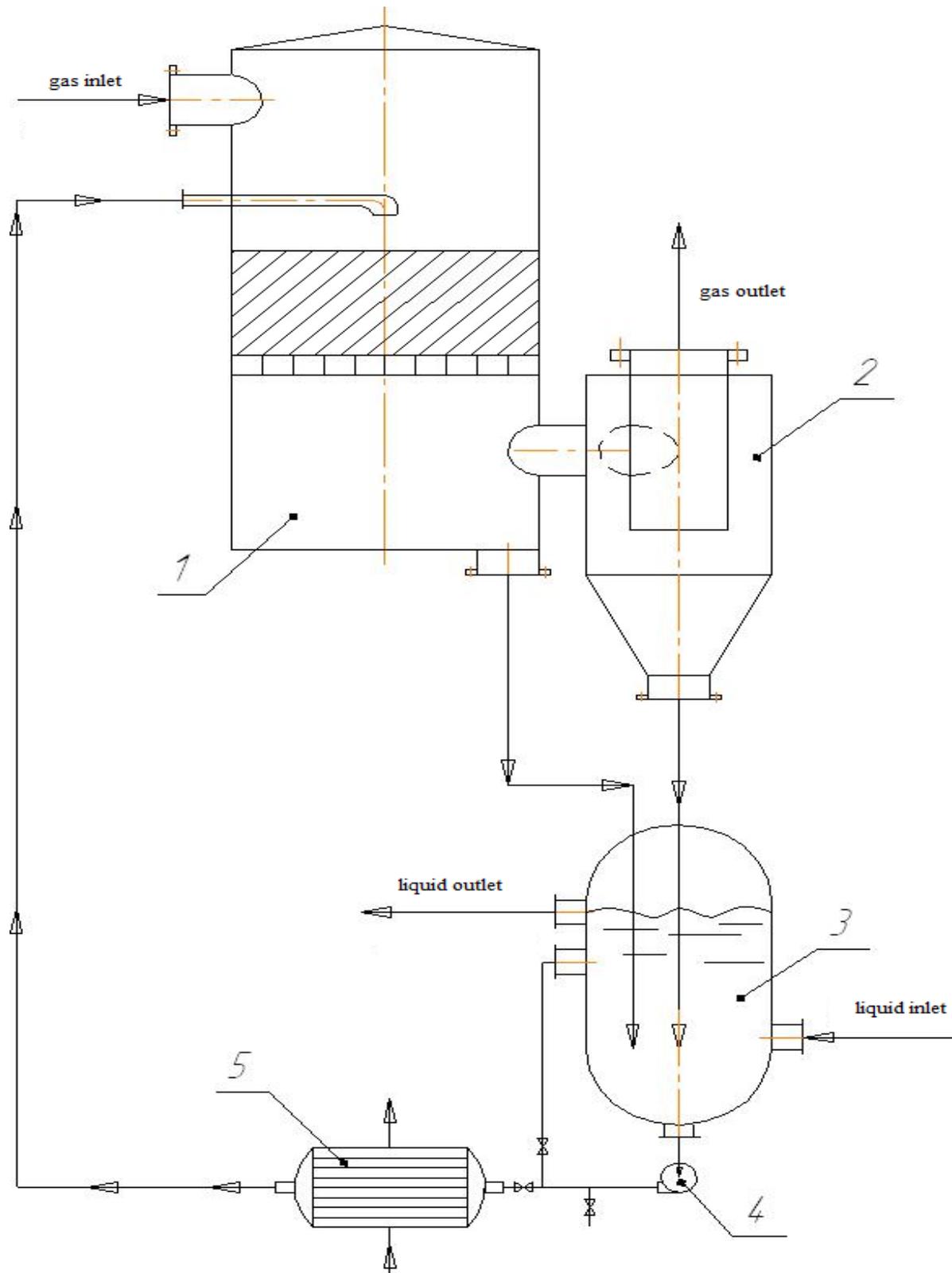
The developed principle of designing the units of the stage is based on two major steps: mixing of gas with a liquid and separation of phases. Academician V.V. Kafarov has suggested to designate such steps in the form of systems of cybernetic operators. Figure-4 represents the scheme of a phase contact stage of an absorber in the form of cybernetic operators [6].



**Figure-1.** Circuit design of the stage consisting of a Venturi tube with descending way of interacting of phases and the cyclone separator. 1 – Venturi tube, 2 – cyclone separator, 3 – container, 4 – pump, 5 – heat exchanger.



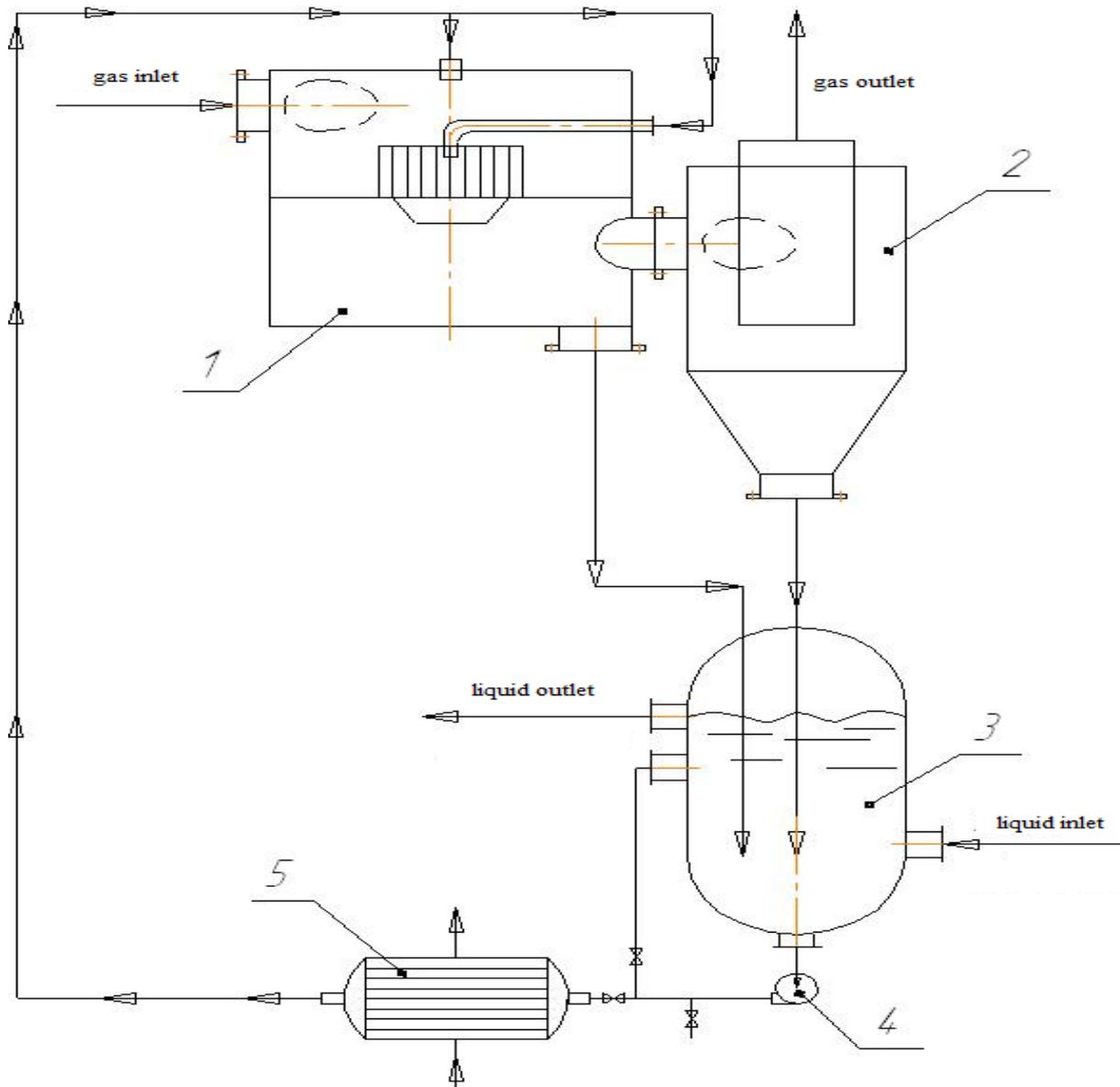
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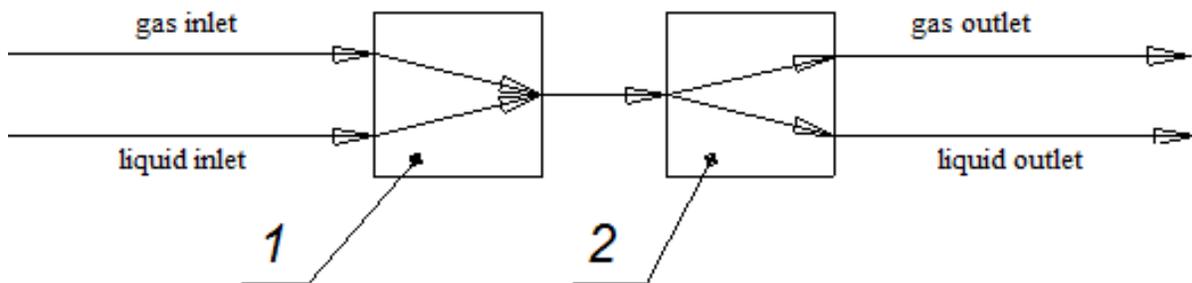
**Figure-2.** Circuit design of the stage consisting of the packed column with descending way of interacting of phases and the cyclone separator. 1 - packed stage, 2 - cyclone separator, 3 - container, 4 - pump, 5 - heat exchanger.



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**Figure-3.** Circuit design of the stage consisting of a vortex absorber with descending way of interacting of phases and the cyclone separator. 1 - vortex absorber, 2 - cyclone separator, 3 - container, 4 - pump, 5 - heat exchanger.

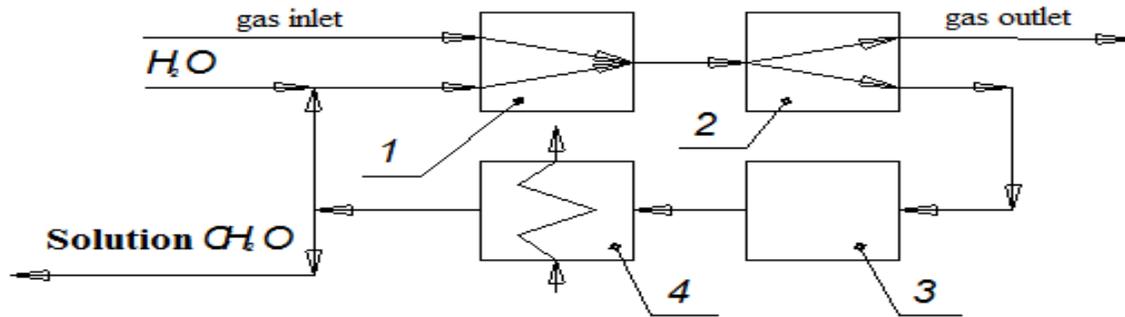


**Figure-4.** - The scheme of a phase contact stage in the form of two consistently connected cybernetic operators: 1 – mixing operator, 2 – separation operator.



It is necessary to cool a liquid at each stage in specific conditions of formaldehyde absorption. Cooling is carried out through a heat exchanger on the basis of circulation of a liquid by means of the pump. In these

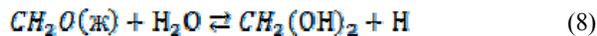
conditions the cybernetic schema of the phase contact stage looks as follows (Figure-5).



**Figure-5.** Cybernetic scheme of a stage of formaldehyde vapors absorption with liquid circulation: 1 - mixing of phases, 2 - phase separation, 3 - compression of a liquid by the pump, 4 - liquid cooling in a heat exchanger.

### THE CHEMISTRY OF FORMALDEHYDE ABSORPTION PROCESS

It is apparent that there are simultaneously some processes at one stage of phase contact. Physical processes consist of some steps: mixing of phases, phase separation, compression and cooling of the circulating liquid. Besides, in the course of absorption there is a concurrent chemical reaction of a formaldehyde hydrolysis:



Chemical reaction (8) proceeds rapidly. The reaction equilibrium constant looks like:

$$K = \frac{[\text{CH}_2\text{O}]}{[\text{CH}_2(\text{OH})_2]} \quad (9)$$

Dependence of an equilibrium constant on temperature is presented by the equation.

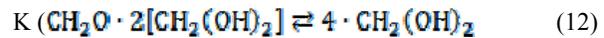
$$\lg K = 2,9602 - \frac{8544}{4,575 \cdot T} \quad (10)$$

From the equation (10) it follows that in equilibrium conditions there are no practically any dissolved formaldehyde in a liquid. All dissolved formaldehyde presents in a liquid in the form of methylene glycol  $\text{CH}_2(\text{OH})_2$ . Hence, both at formaldehyde desorption, and at its absorption the curve of dependence of equilibrium formaldehyde vapor pressure over a solution on concentration of formaldehyde in a solution will not be a straight line, but the convex curve which equation looks like:

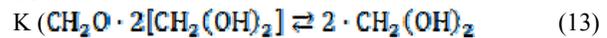
$$P = k[\text{CH}_2\text{O}]^{0,75} \quad (11)$$

From the equation it is possible to draw a conclusion that in a gas phase there are available not only

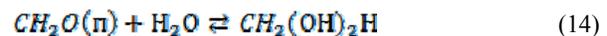
formaldehyde vapors, but also its hydrated compounds with water. In the equation (11) the index of power near the concentration of formaldehyde in a liquid is equal to  $\frac{3}{4}$ . It is possible to say that there are three parts of formaldehyde in gas for four parts of formaldehyde in a liquid



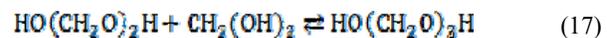
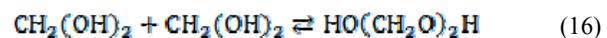
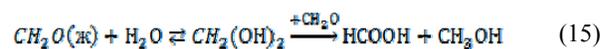
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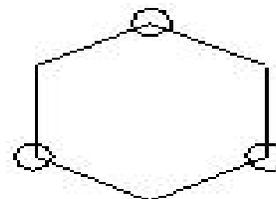
Hence, upon increase in concentration of formaldehyde in a solution there is a polymerization process which simultaneously proceeds also in a gas phase. It is accepted to write in the literature reaction in a gas phase in the following form:



It is accepted to write in the literature reaction in a fluid phase in the following form:

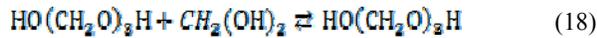


Upon that, some part of substance  $\text{HO}(\text{CH}_2\text{O})_3\text{H}$  can have structure of the following form:

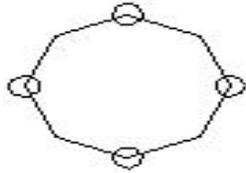




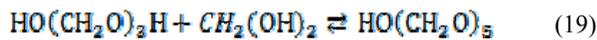
Further, polymerization reaction proceeds:



Upon that, some part of substance  $\text{HO}(\text{CH}_2\text{O})_3\text{H}$  can have equilibrium structure of the following form:



Further, polymerization reaction proceeds:



Polymerization reaction does not stop at this step. There is a further growth of a polymer chain.

#### PHYSICAL AND CHEMICAL GROUNDS OF FORMALDEHYDE ABSORPTION TECHNOLOGY

Understanding of physical sense and relationships of condensation processes of formaldehyde, water and methanol vapors is of paramount importance for an intensification of formaldehyde absorption process. This is due to that condensation processes may be the basic ones and proceed simultaneously with absorption. This is testified by the following facts. The fluid phase can be formed in all stages of phase contact due to condensation of a circulating liquid on the cooled surface. Therefore condensation process can be carried out on a heat exchange surface in the gas / solid wall system of a heat exchanger even without application of the pump for liquid

circulation. In the example presented the absorptive stages can be replaced with the condensing ones. However, in the presence of liquid circulation the value of phase contact surface area is much greater and a phase contact surface is more reactive [7].

For comparison, Figure-6 represents lines of dependence on temperature of an equilibrium pressure of formaldehyde vapors and water vapor. It is apparent from the curves that dependences mentioned above have similar character. Besides, it is apparent that an equilibrium pressure of water vapor over formaldehyde solution is always higher than an equilibrium pressure of formaldehyde vapors. For example, at temperature 70-80°C and concentration of formaldehyde in a solution of 37-38 % an equilibrium pressure of water vapor over production formaldehyde solution is 6 times higher than the equilibrium pressure of formaldehyde vapors over the solution. When cooling to 50 °C an equilibrium pressure of water vapor is 8 times higher than an equilibrium pressure of formaldehyde vapors. Dependence of an equilibrium pressure of formaldehyde vapors on its concentration in liquids is presented in figure 7. It is apparent the following from curves in Figure-7: rate of curves remains similar within a wide range of temperature; influence of formaldehyde concentration in a solution on equilibrium pressure of water vapor is less essential than temperature effect. For example, in the case of twofold increase in concentration of formaldehyde an equilibrium pressure of formaldehyde vapors in gas increases less than twice. However, in the case if temperature increases in 2 times, for example, from 40 °C to 80°C an equilibrium pressure of formaldehyde vapors increases in 12 times. Figure-5 shows dependence of an equilibrium pressure of water vapor on concentration of formaldehyde in a solution at various temperatures.

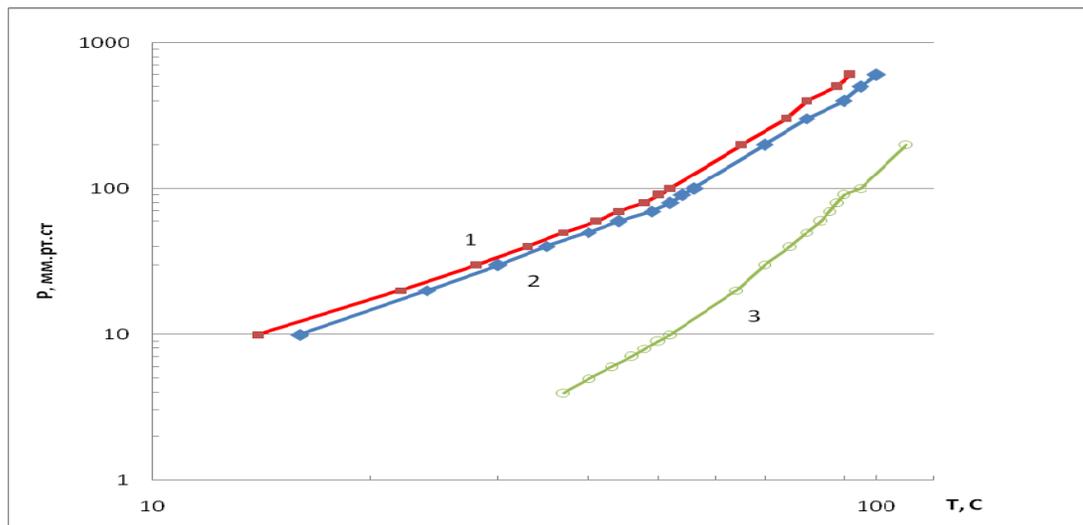


Figure-6. Dependence of equilibrium pressure of water vapor and formaldehyde vapors on temperature: MM.pt.ct. - mm Hg.



The curve 1 - Dependence of equilibrium pressure of water vapor over water; the curve 2 - Dependence of equilibrium pressure of water vapor over formaldehyde solution upon concentration of formaldehyde in a solution

of 40 %; the curve 3 - Dependence of equilibrium pressure of formaldehyde vapors over a solution in the case of formaldehyde concentration in a solution of 40 %.

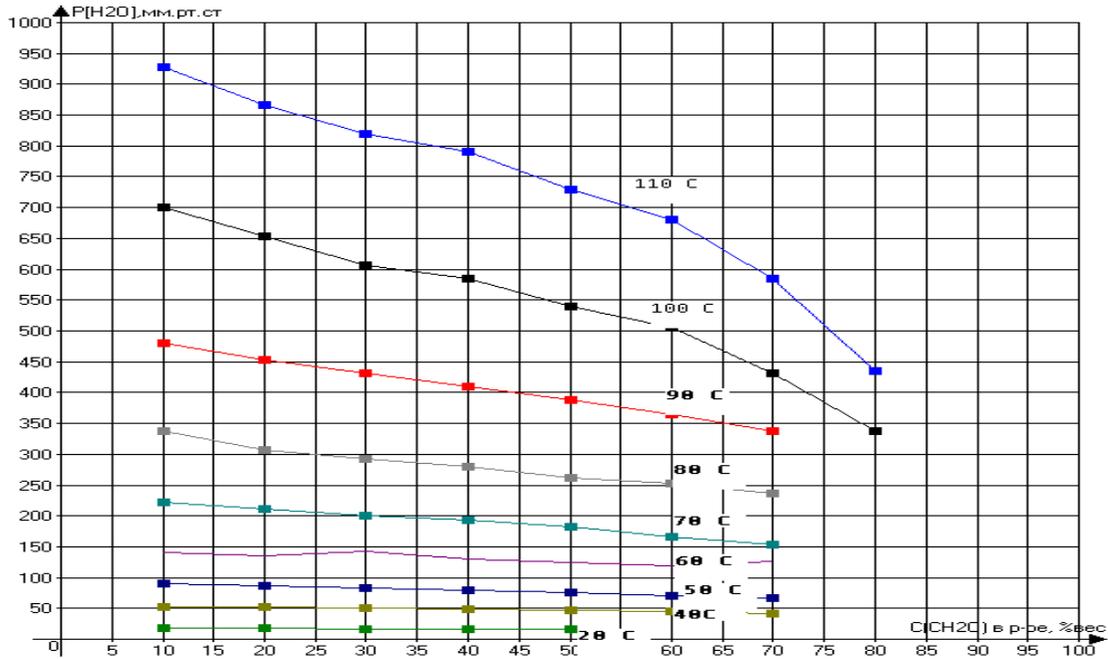


Figure-7. Dependence of an equilibrium pressure of water vapor on concentration of formaldehyde in a solution at various temperatures.

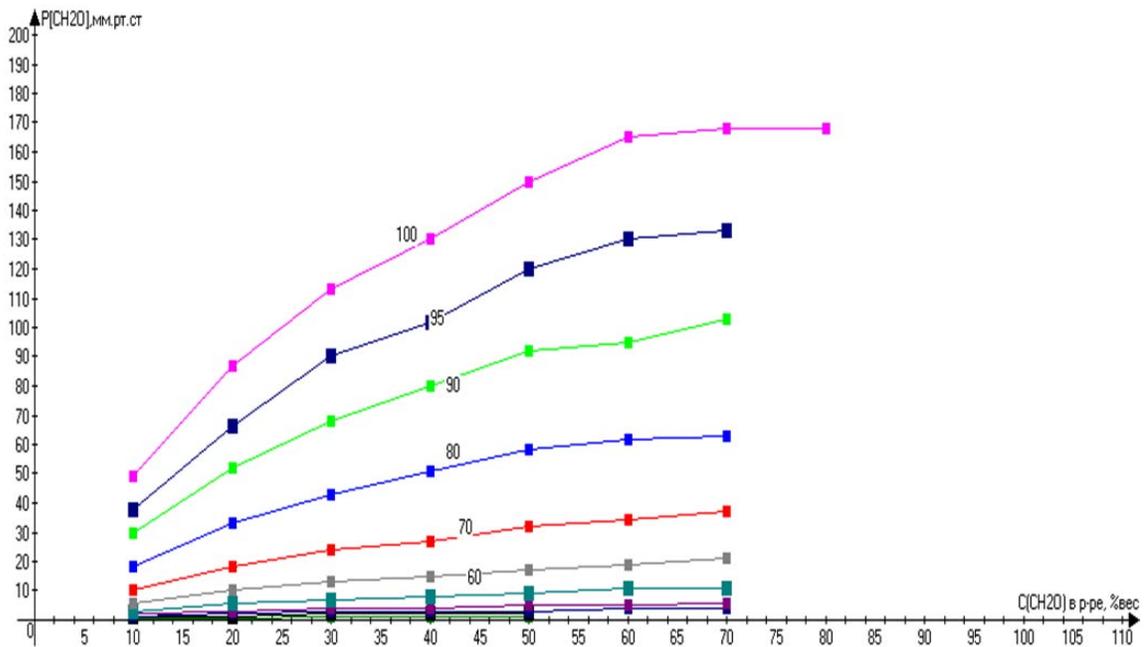


Figure-8. Dependence of an equilibrium pressure of formaldehyde vapors on its concentration in a liquid. в р-ре, % в.с. - in a solution, % w/w.



## CONCLUSIONS

Curves in Figures-7 and 8 confirm once again that an equilibrium pressure of water vapor is considerably higher than an equilibrium pressure of formaldehyde vapors. It is possible to draw the important conclusion from curves of figure 5 that the equilibrium concentration of water vapor over a liquid on the second and the third stage practically does not depend on concentration of formaldehyde in a solution and depends only on temperature. Upon that, an equilibrium pressure of water vapor over a solution practically comes nearer to value of an equilibrium pressure of water vapor over water alone.

The analysis of curves presented in Figures-6, 7, 8 shows that the major way of formaldehyde absorption process control is control over a liquid temperature on all stages that provides grounds for the further researches.

## COMPETITIVE INTERESTS

The authors affirm that the introduced data do not contain the competitive interests.

## ACKNOWLEDGEMENTS

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