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Development of a new high-capacity formaldehyde absorption unit for environmental problems solving and resource saving in formalin production

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Abstract. Ways of further intensification of formaldehyde absorption process and new constructions of more compact apparatuses have been developed on the basis of generalization of results of experimental study of regularities of mechanism and kinetics of formaldehyde absorption in conditions of formalin production. The most effective and for intensification of formaldehyde absorption process are vortex apparatuses in the form of a cascade of one-stage vortex apparatuses, or in the form of a vortex column including three vortex phase contact stages. A new splash trap with bag filtering elements was developed for effective fog catching.

Formaldehyde is one of the most important half-products of organic synthesis and has been produced on an industrial scale since 1889. Formaldehyde is the main raw material in various branches of the chemical industry: synthesis of industrial resins (melamine formaldehyde, urea formaldehyde and phenol formaldehyde), polymers, paints. Due to the use of formaldehyde derivatives in woodworking and furniture production, carpeting and textiles, as well as in the production of building materials, formaldehyde is rightfully considered one of the most important compounds in the world economy [1]. Nevertheless, not many studies have been devoted to the study of the production of this economically important product. Enterprises producing formaldehyde and polymers based on it steadily increase the production capacity of this most valuable semi-product. Therefore, the issue of intensification of formaldehyde production process becomes acute. However, at present the task is not only to increase formaldehyde production capacity, but also to reduce toxic gas emissions into the atmosphere, since their number is growing in proportion to the increase in productivity.

Among the urgent environmental problems of the Republic of Tatarstan is the atmospheric air pollution by formaldehyde, which has carcinogenic and mutagenic properties. During 2018 in Kazan there were 171 cases of formaldehyde exceeding MPCm.r. [2].

Formaldehyde has manifold toxic effects on living organisms. The danger of formaldehyde as a mutagen lies in the fact that it not only induces somatic mutations dangerous to the life of the organism, but also that these mutations accumulate, are transmitted to offspring and appear on the next generations. In addition to its general toxic effects, it has been found to have carcinogenic properties [3].

The current environmental problem of the Republic of Tatarstan is the atmospheric air pollution by formaldehyde, which has carcinogenic and mutagenic properties. During 2018 in Kazan there were 171 cases of formaldehyde exceeding threshold limit value – short-term exposure limit (TLV- STEL) [2]. Formaldehyde has multiple toxic effects on living organisms. The danger of formaldehyde as a mutagen
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Today, the main method of producing formaldehyde is the absorption of formaldehyde-containing reaction gases. These gases are formed as a result of the interaction of methanol with air oxygen, in the presence of water vapor, in the contact apparatus, in a catalyst bed heated to a certain temperature

Absorption is carried out by water with obtaining methanol formalin solution [4]. However, formaldehyde absorption stage is still carried out in obsolete packed columns.

Analyzing the data on the dependence of the equilibrium vapor pressure of formaldehyde on the concentration of formaldehyde in aqueous solution at different temperatures shows that the equilibrium vapor pressure of formaldehyde increases with increasing formaldehyde concentration in solution and with increasing solution temperature. Therefore, to avoid undesirable emissions at the stage of formaldehyde absorption it is necessary to reduce the temperature at the last stages of absorption [5].

It is determined experimentally that the formaldehyde absorption process is a mass-transfer process with a rapid chemical reaction in the liquid. The chemisorption process is instantaneous and accompanied by heat release. The liquid surface heats up considerably, which reduces the driving force of the formaldehyde vapor absorption. Therefore, it is necessary to rapidly and effectively remove heat from the phase contact surface. Consequently, to intensify the formaldehyde absorption process, effective heat exchange with rapid active renewal of the phase contact surface is essential, which is only possible due to a high degree of turbulization of both gas and liquid. However, as the temperature decreases, the probability of formation of a solid formaldehyde polymer - paraform - inside the absorber increases, which can make the absorber inoperable.

In addition, it should be noted that in the process of formaldehyde absorption a fog can be formed [5]. The size of the fog particles depends on the degree of oversaturation of the gas. The value of critical oversaturation of gas by formaldehyde vapor is not yet known to science. A specific requirement of ecology of formaldehyde absorption process is the need to prevent the phenomenon of formation of fine fog particles. It is known that fine fog is poorly trapped by the liquid, even with a high value of the phase contact surface. In order to reduce gas oversaturation, it is necessary that the gas first comes into contact with the hot solution, over which the equilibrium vapor elasticity is greater. The latter makes it possible to control both the degree of gas supersaturation and the degree of formaldehyde absorption in the fog-free mode. It should be noted that formaldehyde vapors in the gas at the inlet to the absorber comes not only in the form of pure formaldehyde, but also in the form of hydrates CH₂O - H₂O; CH₂O-2H₂O; CH₂O - 3H₂O, etc.

Effective formaldehyde fog catching and complete elimination of liquid splashback cannot be achieved with a packed spray trap. There is an obvious question about the reliability of the filters. It becomes clear that a specific feature of the formaldehyde absorption process is the formation of polymeric formaldehyde mist particles in the gas, which are formed by the condensation mechanism [6]. The study showed that dissolution of polymeric formaldehyde particles in water proceeds relatively quickly. Therefore, on water-wetted filters formaldehyde dissolution rate is high and accumulation of formaldehyde in the form of a layer of sediment does not occur. Aqueous formaldehyde solutions of low concentration with formaldehyde concentration less than 20 % do not tend to solidify. In practice, however, an accidental temporary shutdown of the pump to circulate liquid through the first phase contact stage along the gas path is possible. In this case, the gas flow can enter the second stage with a relatively high concentration of formaldehyde vapor. Research has shown that bag filter elements made of fibrous materials are the most effective for catching spatter [7]. In order to prevent secondary splashing of liquid from the filter surface the filtering material has to be made multi-layer. At that, between the layers with dense packing of fibers there must be a looser drainage layer. The maximum efficiency of particle catching is provided by relatively dense filter media made on the basis of parallel packing of fibers. If the fiber material is slightly irrigated, the fog-catching efficiency of the filter increases. However, the filter should not be heavily irrigated. If the
filter is heavily irrigated, the hydraulic resistance increases and secondary splashing begins. Therefore, to limit the irrigation density of the filters, an effective spray head must be placed in front of the bag filters. Therefore, a vortex device and bag filter elements must be an integral part of an effective splash trap and an effective formaldehyde absorption unit. However, there is no such splash trap in the current technology yet.

In a new advanced high-performance technology of formaldehyde absorption in a cascade of single-stage vortex apparatuses (figure 1) should be laid three vortex phase contact stage for formaldehyde absorption and one sanitary stage for waste gas purification.

![Figure 1. Scheme of high-capacity formaldehyde absorption unit in vortex apparatus cascade for capacity of 100 thousand tons per year of formaldehyde. I- first vortex formaldehyde absorption stage; II- second vortex formaldehyde absorption stage. III- third vortex formaldehyde absorption stage; IV-sanitary stage of flue gas purification.](image)

Formaldehyde vortex absorption stage is a set of two apparatuses connected in series: a vortex absorber and a spray head. The splash trapped in the splash trap flows as a liquid into the vortex absorber. The sanitary stage consists of a sprayed gas duct and a splash trap. Purification of waste gases in the splash trap is carried out by bag filtering elements. The captured formaldehyde mist in the form of liquid from the splash trap flows to the vortex absorber. Pumps for liquid circulation are provided at each phase contact stage.

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