



Technical and Economic Level, Justification of Basic Technological Solutions of Formalin Production in Navoyazot, Selecting the Optimal Production Method

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ABSTRACT: Formaldehyde is a very active chemical compound that easily reacts with other substances to form a large class of new compounds, many of which have important properties. Due to its reactivity, formaldehyde in a relatively short period of time has become one of the indispensable semi-products of large-tonnage organic synthesis.

KEYWORDS: Formaldehyde, methanol, conversion, poorly soluble varnishes, coatings, adhesives, laminated plastics.

INTRODUCTION

Formaldehyde is used industrially as a raw material for the production of synthetic resins, plastics, new organic dyes, surfactants, varnishes, pharmaceuticals and explosives. In agriculture for seed treatment, in the leather industry for tanning leather, in medicine as an antiseptic and in animal husbandry. The range of applications for formaldehyde is growing from year to year. In this regard, its production is also growing.

Currently, the main consumer of formaldehyde is the synthetic resin industry: production of phenol-formaldehyde, urea-formaldehyde resins; resins modified by formaldehyde treatment; poorly soluble varnishes, coatings, adhesives, laminated plastics.

MATERIALS AND METHODS

The most widespread product is a product containing 35 % formaldehyde and 6 % methanol called formalin. Formalin recipe was formed historically, under the influence of the following factors. First, methanol and water accompany formaldehyde at the stage of its production by the most common method (methanol is a raw material, water is a by-product and an absorbent). Secondly, a solution of the specified composition at positive temperatures is quite stable to polymer precipitation and can be stored or transported for an indefinite period of time. In - Thirdly, in the form of an aqueous formaldehyde-methanol solution can be used in most industrial synthesis, as well as the ultimate user. and, finally, fourthly, it is formalin that is obtained during the oxidative conversion of methanol in the presence of metal catalysts for the absorption of a contact gas; as a rule, no additional operations for imparting marketable properties to the product (concentration, purification, etc.) are required. [16 pp 4]

In the city of Navai, at the Navoiyazot plant, there is an operating formalin production facility (Navoiyazot) with a capacity of 12-15 thousand tons per year.

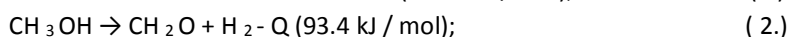
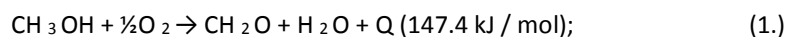
The main goal of the project is to determine the possibility of expanding this production using the example of a formaldehyde synthesis unit. An important point is to establish the possibility of providing new, increased productivity with existing equipment. It is also necessary to consider issues related to technological control, labor protection and ecology in the changed operating conditions.

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Formaldehyde is obtained from methanol, dimethyl ether, natural and associated gases (gas of coke production and oil refining). Commercially mastered methods of obtaining formaldehyde:

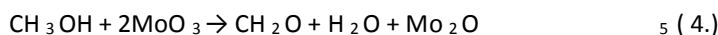
1.) Catalytic oxidation of methanol on metal catalysts.
2.) Catalytic oxidation of methanol on oxide catalysts.
3.) Oxidation of natural gas and lower paraffins.

In the first case, silver is most often the catalyst (gold or platinum can be used); in order to save methanol, silver is uniformly applied to an inert carrier, for example, pumice. The essence of the method consists in the vapor-phase oxidation of methanol hydrogenation with atmospheric oxygen in an adiabatic reactor, followed by the absorption of the reaction products by water. In the process, a methanol-air mixture is supplied with a composition above the upper explosive limit (36.4% - volume fractions) and with oxygen deficiencies according to the chemical equation for the oxidation of methanol to formaldehyde, since catalyst - oxidation-dehydrogenation:



At the same time, side reactions occur, which reduces the formaldehyde yield and increases the consumption of methanol. Formaldehyde yield reaches 80-5% at a degree of conversion of methanol was 85-%. Since the oxidative dehydrogenation is carried out with a lack of oxygen, the deep oxidation process does not receive significant development. At the same time, the dehydrogenation itself, initiated by oxygen, proceeds faster; therefore, the percentage of side reactions is not large. This method can be used to obtain formalin of two grades: FM-% with a methanol content of up to 10% and FMB-% with a methanol content of less than 1%. Formalin FM brand is subject to transportation and storage, because methanol stabilizes it.

In the second method, the catalyst is a mixture of iron and molybdenum oxides. Oxidation of methanol on oxide catalysts proceeds according to the redox mechanism:



The process is carried out in an excess of air at (350-) ^{about} C and normal pressure, otherwise, under the action of methanol and formaldehyde, the catalyst is rapidly reduced. The reaction proceeds when the ratio of methanol and air is below the explosive limit (7% - volume fractions).

The process is distinguished by a high degree of methanol conversion-%, as well as a strong exothermicity, which makes the use of cooled tubular reactors. This method allows you to obtain formalin-% with a methanol content of no more than 0.5%. The use of technologies with an oxide catalyst deserves some preference when the required productivity is not higher than 8 thousand. tons / year. Third way. From the point of view of the availability and cheapness of raw materials, as well as the simplicity of the technology (obtaining formaldehyde by direct oxidation of natural gas, consisting mainly of methanol, with atmospheric oxygen), it deserves preference over the relatively complex and multi-stage synthesis through methanol (according to the scheme):



RESULT AND DISCUSSION

However, in practice, a number of difficulties arise that are associated with insufficient stability of formaldehyde under the reaction conditions. Methanol oxidation occurs at 600^{to} C at the same time the thermal decomposition of formaldehyde is observed even at 400^{of} S. formaldehyde yield does not exceed 3% with a selectivity of 10-%. Therefore, the considered method occupies a very modest place in the balance of formalin production, and only in the future new technological methods of oxidation are used (taking into account the increasing scarcity of methanol and the comparative availability of natural gas).

Therefore, the first two methods deserve attention in choosing a method for the production of formalin. Let's consider them in comparison and choose the right one for ourselves.

Comparative characteristics of formalin production methods in table 1.

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Table 1. - Comparative characteristics of formalin production methods

Method	Benefits	disadvantages
1. Oxidation on a silver catalyst	a) there are practically no restrictions on the unit capacity of the installation b) simplicity of the design of the reactor c) low metal and energy consumption d) high performance	a) high consumption ratio for raw materials b) expensive catalyst congestion c) the presence of methanol in formalin up to 5 -%
2. Oxidation on an oxide catalyst	a) low consumption coefficient for raw materials b) the presence of methanol in formalin no more than 0.6 -, 0% and the presence of HCOOH no more than 0.02%	a) increased consumption of energy and air b) restriction unit capacity of the installation c) complexity in operation and repair d) increased metal consumption

Comparing economic and production costs, as well as the volume of production and (we need at least 3 thousand tons / year) for the needs of formalin-consuming production - urea resins (volume - thousand tons / year), we choose a production method for oxidative dehydrogenation of methanol for silver catalyst.

The choice of catalyst and its characteristics: In Uzbekistan, at all industrial plants for the production of formaldehyde from methanol, silver tribrach contacts such as silver on pumice are used. Characteristics of this catalyst:

Appearance - gray shiny grains of irregular shape.

Grain size, mm –5.

Mass fractional composition: %

Sifting through a sieve 2 2 mm, no more than 2.0;

Sieve residue 5 5 mm, not more than 5.0;

Specific surface, m^2 / h 0.5 - 0.

Most foreign formalin production uses metallic silver without a carrier (nets, crystals, spongy silver, etc.). In terms of the selectivity of formaldehyde formation, the contact and tribrach catalysts are practically equivalent. The main differences between friction and contact catalysts relate to their performance characteristics. The benefits of tribrach contacts include the following:

1. resistance to overheating;
2. reduced requirements for the purity of raw materials;
3. less one-time loading of raw materials.

The main disadvantage of this catalyst is the short duration of the inter-regeneration cycle of operation (3 months).

The use of contact (unapplied) silver has the following advantages:

1. elimination of a set of issues related to the receipt and preparation of the media;
2. "Reagent-free" catalyst preparation system;
3. practical absence of silver losses due to abrasion and contact grinding.

When choosing one form or another of a silver catalyst, such factors as experience and tradition are of decisive importance .

The technology for preparing a silver tribrach includes the main stages:

1. impregnation or deposition on the surface of the carrier salt containing silver;
2. reduction of the silver cation to a free metallic state.

In practice, the silver content of the SNP catalyst is about 40%. Catalysts with lower silver content lose activity more quickly and require "reapplication".

The top two catalyst layers are crystals 0.8–1.0 mm in size, the bottom layer is silver in the form of thin filaments.

Another firm proposed to divide the silver catalyst into 4 layers with a total height of 20–30 mm, and the silver ring around the reactor perimeter serves as the 5th layer. A characteristic feature is the use of bidispersed silver granules. So, in the lower part of the layer, it is recommended to place granules with a size of less than 0.3 mm, the amount of which is 1/8 of the

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total amount of silver. Another part of the catalyst in the form of granules up to 1-3 mm in size is poured over the fine particles. The molar yield of formaldehyde is 88%.

The use of a two-layer catalyst makes it possible to carry out the process with methanol conversion up to 97.4% at a molar selectivity of 89 -%. [

Comparing the foreign experience in the production of formalin on catalysts in a very thin layer, in the form of metal sieves (silver nets), it is proposed to switch to a similar type of catalyst.

Characteristics of the silver catalyst (sieve):

wire TU 48 —;

wire thickness, mm - 22;

the number of cells per 1 cm² -;

Excessive cost of a catalyst - 3000 sum.

The transition to silver mesh will reduce the number of workers in the catalyst department (by simplifying the preparation of the catalyst), and therefore increase labor productivity. Due to the longer service life (1 year) of the catalyst, the effective fund of working time increases, and the capacity will increase.

Processes of formaldehyde chemisorption by water : Extraction of formaldehyde and methanol from reaction products by absorption of cooled water is carried out in column-type absorption systems of various designs and is discussed in detail in the article by A. Sh. Arifzhanov and MR Pulotova., [7, P.48]. The commonality of all industrial developments is that pre-cooled gases flow down the absorber, and cooled water is supplied to the upper part of the apparatus, which, after passing through the absorber and absorbing formaldehyde and methanol, is excreted as commercial formalin with a formaldehyde content of 37-50 wt%. and methanol 0.5-1.5% of the mass. "The amount of absorbent supplied for irrigation depends on the specified concentration of formaldehyde in formalin. From the top of the absorber, waste gas leaves, containing, among other products, about 1.5% (vol.) Of carbon monoxide. 70-75% (vol.) Of offgas is returned back to the process, the rest of the offgas is emitted into the atmosphere, or sent to catalytic afterburning ". The main purpose of the latter is to neutralize carbon monoxide and formaldehyde.

Virtually on all formalin plants has place adiabatic fractionating solutions of formaldehyde at a predetermined pressure, which is accompanied by the formation of azeotropes. The composition of the latter is determined by the parameters of the process. At atmospheric pressure, the azeotrope contains approximately 20% formaldehyde, while at a pressure of 0.5 MPa from 50 to 70% of the mass. The kinetic reactions of solvation and polymerization occurring in an aqueous solution of formaldehyde determine the results of the rectification process, and equilibrium is achieved very rarely.

50% formaldehyde solution with a small amount of methanol, not containing stabilizing additives may remain unchanged to within approximately 25 days at 60° C.

For this reason, strong formalin is not transported over long distances, but rather to be processed on site.

The dependence of the duration of storage of formalin on the content therein of formaldehyde and methanol is very important for the manufacturers of this product and is presented in Table 1.

Table 1 . - Minimum temperature storage formalin in dependence on the contents in it of formaldehyde and methanol

Formaldehyde concentration , % masses.	thirty	37	37	37	37	43	fifty
Methanol content , % wt.	one	one	7	ten	12	one	one
Minimum storage temperature , °C	7	thirty	21	7	6	55	65

"In aqueous solutions containing more than 40% (mass.) Formaldehyde, in the process of boiling, the distillation temperature gradually rises.

It varies from 103 ° C for 50% formalin to approximately 113 ° C for 80% formalin. The latter solidifies upon cooling in the form of a thick paste, consisting of polyoxymethylene glycols, which is difficult to dispose of " [1].

These facts are in good agreement with the data presented in Table 2. It illustrates the relationship between the boiling point of formaldehyde solutions and the value of the partial pressure.[6 pp 6]

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Table 2. - Low boiling solutions of formaldehyde and of the partial pressure

The approximate (average) concentration of the CH ₂ O solution, %	Fluctuation of concentration during distillation, %	P total, mm Hg (kPa)	Temperature in a cube, °C (K)	Concentration of CH ₂ O in distillate, %	Formaldehyde pressure, mm Hg. Art. (kPa)
one	2	3	four	five	6
20	19.3-19.4 19.4-19.4 20	756 (100.0) 756.5 (100.6) 760 (101.3)	100.9 (373.9) 100.9 (373.9) 100.9 (373.9)	17.9 18.2 18.0	90 (12.0)
40	37.9-38.7 38.7-39.4 40	759 (101.2) 759 (101.2) 760 (101.3)	101.6 (374.6) 102.0 (375.0) 101.8 (374.8)	27.6 27.7 28.0	142 (18.9)
fifty	49.9-51.2 51.2-51.6 fifty	745 (99.3) 745 (99.3) 760 (101.3)	102.7 (375.7) 102.9 (375.9) 103.2 (378.2)	34.0 34.5 34.0	175 (23.3)
60	59.3-60.2 60.2-6 60	739 (98.5) 739 (98.5) 760 (101.3)	103.2 (378.2) 103.1 (378.1) 103.9 (379.9)	38.1 38.2 38.0	203 (27.0)
70	68.3-69.9 69.9-70.2 70	748 (99.7) 748 (99.7) 760 (101.3)	107.0 (380.0) 107.3 (380.3) 107.5 (380.5)	41.5 42.4 42.0	229 (30.5)
80	81.5-82.5 82.5-83.0 80	742 (98.9) 742 (98.9) 760 (101.3)	113.0 (386.0) 114.5 (387.5) 112.5 (385.5)	48.1 49.6 48.0	267 (35.5)

The difference extracting process formaldehyde and methanol from the product of the reaction obtained on metal oxide catalysts, as compared to metallic catalysts consists in the fact that in the first case the concentration of formaldehyde and methanol is considerably lower, and the water vapor is much greater. This is due to the fact that the hydrogen released during the oxidation of methanol is converted into water, and in the method with metal catalysts - about half.

The own content of formaldehyde and methanol and the high concentration of water vapor makes it difficult to absorb and obtain concentrated formalin, however, it makes it possible to obtain a product with an improved complex of properties. [7 pp 244] "The first industrial production of formaldehyde from methanol with the use of metal catalysts has

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been organized almost simultaneously in several countries in the 1955-60 years. By this time the chemical technology has reached the level of development of a large and manufactured equipment allowed the floor Nosta automate pozharovzryvo dangerous technological process[3].

CONCLUSION

All current installations for obtaining formalin, as far as the publications in the literature can be judged, are quite close to each other in terms of schemes and hardware design. Basically, they differ in the methods of cooling the reaction products and the use of the exothermic heat of the chemical process, as well as the methods of obtaining the working mixture and the instrumentation of the individual stages.

According to the composition produced by formalin and specific costs of methanol and energy big difference between well installations there. The composition schemes technological process of preparation of formalin with using the metal catalyst includes three basic steps: - obtaining an air-off-gas methanol - containing working mixture;

- catalytic conversion of methanol to formaldehyde;

- absorption of the formed formaldehyde and unreacted methanol from the reaction products .

There are installations where the extraction of formaldehyde is carried out simultaneously with water and an aqueous solution of urea to obtain formalin and urea-formaldehyde concentrate.

Different developers offer different methods for the implementation of the main and additional stages of the formalin production technology and different hardware design.

In particular, obtaining a working alcohol-air mixture can be achieved by evaporating methanol and mixing its vapors with a heated mixture of air with offgas, adiabatic evaporation of methanol in scrubber-type devices, or by injecting methanol into a heated air - offgas mixture with mechanical nozzles. Cooling of the reaction products is carried out in a shell-and-tube heat exchanger with water with its evaporation or with a mixture of air with exhaust gas, and then with a working mixture. Cooling of the catalyst in a tubular reactor in most cases is carried out by a liquid or an evaporating coolant. There are other modifications of this stage of the process.

As stated previously, the technological process of producing formaldehyde from methanol on metal oxide catalysts carried on continuously operating plants in the three types of reactors ideal displacement:

1) tubular with cooling of the catalyst in tubes;

multilayer of Multi, many sectional bulky apparatus with cooled product of the reaction between layers of the catalyst;

2) combined with a shortened tubular part and one catalyst bed located in a bulk reactor. [20 pp 277]

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