

Production of acetone by catalytic hydration of acetylene

Abdikhakim Karjavov^{1*}, *Normurot Fayzullaev*², and *Azim Baykulov*¹

¹Samarkand State Medical University, 140101, Samarkand, Republic of Uzbekistan

²Samarkand State University, 140101, Samarkand, Republic of Uzbekistan

Abstract. Among the known processes for the production of acetone, the most promising is the synthesis by hydration of acetylene in the presence of catalysts. The advantage of this method is the possibility of carrying out the process in existing acetaldehyde production plants. On the other hand, the process of simultaneous production of acetaldehyde and acetone under the action of polyfunctional catalysts and the implementation of the process using flexible technology is promising. To study the influence of various factors on the process of obtaining acetone by the catalytic hydration of acetylene and to create a technology for producing acetone. The specific surface area, crushing strength, total pore volume, and ash content of the samples were determined. Acetylene was saturated with water at a temperature of 70-80 °C and a ratio of water: and acetylene = (1:3)-(1:5), mol was passed through the catalyst bed at 360 °C with a space velocity of 180-200h⁻¹. The gas-vapour mixture leaving the reactor was cooled in a refrigerator. The reaction products were collected with water. The catalyst contains acetaldehyde, acetone, crotonaldehyde, etc. To maintain the degree of acetylene conversion not lower than 80%, the reaction temperature was raised by 10 °C every 20 hours. After 96-120 hours, the degree of acetylene conversion decreases to 75-70%. The reactions of catalytic hydration of acetylene to acetaldehyde and acetone were carried out on the selection of polyfunctional mixed catalysts. As a result, a catalyst with cadmium fluoride and chromium(III) oxide dissolved in alumina promoted with aluminium fluoride was chosen to produce acetaldehyde. Acetaldehyde is formed by the interaction of acetylene: water = 1:3–1:5 at 360-440 °C in the presence of a catalyst based on cadmium fluoride with a composition of 18% CdF₂, 2,0% AlF₃, 5% Cr₂O₃, 75% Al₂O₃. The addition of zinc oxide or fluoride to the cadmium-chromium-aluminium catalyst (Catalysts No.5) ensures the selectivity of the catalyst and directs the acetylene hydration reaction towards the formation of acetone. As the temperature rises above 450 °C, the yield of acetone formation and the selectivity of the process decrease due to the transformation of the formed acetone into other substances. In the temperature range of 360-500 °C, the relationship between the reaction yield and temperature is extreme, and at 450 °C the yield was considered to be maximum. Based on the obtained results, a technological scheme for the production of acetone by the catalytic hydration of acetylene was proposed.

* Corresponding author: fer.sapedu@gmail.com

1 Introduction

Acetone is a valuable product of the chemical industry. It can be obtained by oxidative dehydrogenation of isopropyl alcohol, propylene oxidation, decomposition of acetic acid and ethyl alcohol, cumene oxidation, etc. [1–4].

Among the known processes for the production of acetone, the most promising is the synthesis by hydration of acetylene in the presence of catalysts. The advantage of this method is the possibility of carrying out the process in existing acetaldehyde production plants. On the other hand, the process of simultaneous production of acetaldehyde and acetone under the action of polyfunctional catalysts and the implementation of the process using a flexible technology is promising [5–7].

The vapour phase hydration of acetylene with the formation of acetone on polyfunctional catalysts was studied. Process parameters have been found that ensure the production of acetone with high selectivity and acetylene conversion.

At present, acetaldehyde is mainly produced by two methods: acetylene hydration and ethylene oxidation [8–13].

The process of hydration of acetylene to acetaldehyde in the presence of catalysts has been studied quite well. Numerous catalysts have been proposed for this process [14–19]. Among the known catalysts for the hydration of acetylene to acetic aldehyde, cadmium-calcium phosphate catalyst (CCP) turned out to be the most active, which is recommended for industrial use [17–20]. However, the cadmium-calcium phosphate catalyst is not without its drawbacks. The average yield of acetaldehyde per pass of acetylene does not exceed 7.0%. The CCF catalyst is very sensitive to temperature changes; its service life before regeneration does not exceed 72–76 hours.

Hydration of acetylene in the presence of a catalyst can be carried out to obtain acetone. The advantage of this method is the possibility of carrying out the process in existing units for the production of acetaldehyde. Replacing the cadmium–calcium phosphate catalyst with a zinc-containing catalyst makes it possible to obtain acetone in good yield with minor changes in technology.

Today, world scientists are very interested in syntheses based on methane and acetylene. It is especially important to obtain ethylene from methane and vinyl acetate from acetylene in one step. Ethylene is obtained not only by one-stage oxycondensation of methane but also by methanol and dimethyl ether. The creation of a catalyst with high efficiency by this method is an urgent task today. At the same time, the extraction of aromatic hydrocarbons from the propane-butane fraction and associated gases is the only way to utilize the propane-butane fraction and associated gases [19,20].

Aim. To study the influence of various factors on the process of obtaining acetone by the catalytic hydration of acetylene and to create a technology for producing acetone.

2 Material and methods

Experiments on the catalytic hydration of acetylene and its derivatives in the gas phase were carried out in a reactor with a diameter of 25mm, a height of 1000mm, and made of stainless steel under stationary conditions.

The specific surface area, crushing strength, total pore volume, and ash content of the samples were determined.

The specific surface area was determined by the method of thermal desorption of nitrogen in a flow of a carrier gas, helium, at the boiling point of liquid nitrogen; the experimental data were processed according to the BET equation.

The crushing mechanical strength of the granules was measured using a Prochnomer PK-1 device designed to test the mechanical strength of granular materials under static

conditions by the compression method. The arithmetic mean of 25 individual tests was taken as the result of the analysis.

The total pore volume of the granules was calculated by the formula:

$$V = \frac{1}{p_k} - \frac{1}{p_n} \tag{1}$$

Where, p_k and p_n are the apparent and pycnometric density of granules, g/ml, respectively.

The apparent density of granules was determined by measuring their volume without taking into account internal pores. The volume of the granules was found by immersing them in a solid powder (quartz sand with a particle size of 0,063– 0,1mm).

The phase composition of the samples was determined by X-ray diffractometry, the survey was carried out on a DRON-3M diffractometer on CuK_α radiation with a Ni filter, and X-ray radiation length. $\lambda = 1,54\text{\AA}$

The specific surface area of the resulting catalyst was calculated by the BET method, and the average mesopore size was calculated by the VUA method. The dispersion properties of the catalyst were studied using a scanning electron microscope (JSM-6510LV). The catalytic activity of the obtained sample was studied in the reaction of hydration of acetylene.

Acetaldehyde and acetone were synthesized as follows. Acetylene was saturated with water at a temperature of 70-80 °C and a ratio of water: and acetylene = (1:3)-(1:5), mol was passed through the catalyst bed at 360 °C with a space velocity of 180-200 h⁻¹. The gas-vapour mixture leaving the reactor was cooled in a refrigerator. The reaction products were collected with water. The catalyst contains acetaldehyde, acetone, and crotonaldehyde. To maintain the degree of acetylene conversion not lower than 80%, the reaction temperature was raised by 10 °C every 20 hours. After 96-120 hours, the degree of acetylene conversion decreases to 75-70%.

Chromatographic analysis of the products of the catalytic reaction of acetylene hydration. For a complete analysis of the products of the catalytic reaction of acetylene hydration, the ability of several phases to separate under the same analytical conditions was studied by choosing a stationary liquid phase. Among the studied stationary liquid phases, dinonyl phthalate and Apiezon-M proved to be the most effective. It was found that the products of the catalytic acetylene hydration reaction are very well separated on Apiezon-M. Therefore, further studies were carried out in Apiezon-M. To select the optimal conditions for the analysis, the influence of various factors on the process of separation of substances was studied: the flow rate of the carrier gas, the temperature of the thermostat of the column, the length of the column, etc. range of 1-3m, column thermostat temperature in the range of 80-150 °C.

As a result of the research, the following optimal conditions for analysis were chosen.

Table 1. Chromatographically optimal conditions for the products of the catalytic reaction of acetylene hydration.

	<i>Quantities</i>	<i>Conditions for separating products</i>	
		Acetaldehyde	Acetone
1	Column length, m	2	2
2	Column thermostat temperature, °C	100	100
3	Amount of stationary liquid phase, %	15	15
4	Carrier gas (nitrogen) consumption, ml/min	Thirty	Thirty
5	Evaporator temperature, °C	180	180
6	Constancy of analysis, min	4	5

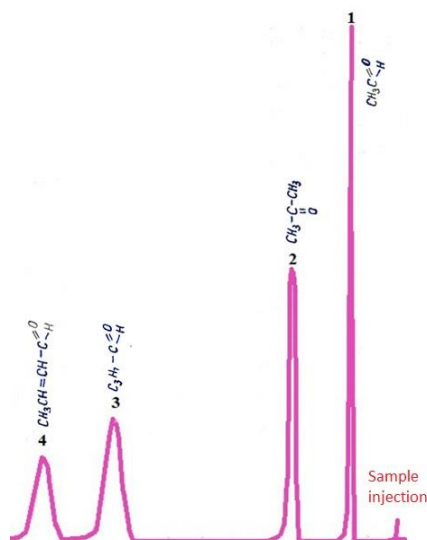


Fig. 1. Chromatogram of products of acetylene catalytic hydration reaction.

The qualitative and quantitative composition of the reaction products was studied by gas-liquid chromatography under the following optimal conditions. Stationary phase - 15% Apiezon-M in Tsvetohrom, column oven temperature – 80 °C, gaseous nitrogen flow - 40 ml/min, detector - DIP. Quantitative analysis was carried out by the method of internal standards.

According to the chromatogram obtained under selected optimal conditions, the reaction products contain acetaldehyde, acetone, crotonaldehyde, and butyric aldehyde.

The quantitative composition of reaction products was determined by the following formula.

$$C = \frac{K_i S_i}{\sum_{i=1}^n K_i S_i} \quad (2)$$

K_i is the correction factor, S_i is the peak surface of the detected components in mm².

3 Results and discussion

Oxides and salts of various metals, including phosphates, tungstates, vanadates, molybdates, and chromates, were tested as catalysts for this process. Among all the tested catalysts for the reaction of catalytic hydration of acetylene to acetaldehyde, the acidic cadmium-calcium phosphate catalyst with $\text{CdHPO}_4 \cdot \text{Ca}_3(\text{PO}_4)_2$, created by Yu.A. Gorin and S.M. Momozon, showed high activity and stability. This catalyst is active at 350-400 °C and is regenerated with air and steam at 400-450 °C. The process is carried out under conditions of volume ratio of water vapour: acetylene 7-10:1. At this time, the conversion of acetylene is 45-50%, the yield of acetaldehyde is 89%, crotonaldehyde is 6-7%. This process also produces acetic acid (0,5-1,0%), acetone (0,3%) and various additives. The activity of the catalyst is reduced due to the formation of resinous products and carbon (coke). Therefore, after the operation of the catalyst for 70-100 hours, the temperature is raised to 400-410 °C. After that, the catalyst is regenerated. Catalyst performance 140-216 kg/(m³·cat.h) for acetaldehyde.

The disadvantages of this catalyst are rapid loss of activity, low selectivity, low product yield, thermally unstable, etc.

Based on the foregoing, we have chosen a catalyst with high activity, selectivity and productivity, high selectivity and thermal stability based on local raw materials.

The reactions of catalytic hydration of acetylene to acetaldehyde and acetone were carried out on the selection of polyfunctional mixed catalysts. As a result, a catalyst with cadmium fluoride and chromium(III) oxide dissolved in alumina promoted with aluminium fluoride was chosen to produce acetaldehyde.

The composition and properties of the synthesized catalysts are given in Table 1. 2.

Table 2. Properties and composition of synthesized catalysts.

№	Composition, mass %	Comparati ve surface, m ² /g	Operating time before regeneration, h	Expected product yield, %	
				CH ₃ CHO	aceto ne
1	ZnO – 20; AlF ₃ – 3; Al ₂ O ₃ – 77	138	75	12	83
2	CdF ₂ -20; Al ₂ O ₃ -80	188	98	78	6
3	CdF ₂ – 18; AlF ₃ – 3; Al ₂ O ₃ – 79	218	99	84	4
4	CdF ₂ – 18; AlF ₃ – 2; Cr ₂ O ₃ -5; Al ₂ O ₃ -75	225	120	85	2,5
5	ZnO – 18; CdF ₂ – 2; Cr ₂ O ₃ -5; Al ₂ O ₃ -75	169	120	4	87

As a result of the acetylene hydration reaction under the same conditions, depending on the composition and nature of the catalyst used, acetaldehyde or acetone is formed.

In particular, acetaldehyde is formed during the interaction of acetylene: water = 1:3–1:5 at 360-440 °C in the presence of a catalyst based on cadmium fluoride with a composition of 18% CdF₂, 2.0% AlF₃, 5 % Cr₂O₃.75% Al₂O₃.

The addition of zinc oxide or fluoride to the cadmium-chromium-aluminium catalyst (Catalysts No. 5) ensures the selectivity of the catalyst and directs the acetylene hydration reaction towards the formation of acetone.

The effect of temperature, catalyst size, and reactor parameters on the technological parameters of the process has been studied.

As can be seen from Table 2, the production rate of acetone in the presence of Catalyst No. 5 is 87% and the run time to regeneration is 120 hours. This indicates that among the selected catalysts, the most optimal is a catalyst containing zinc oxide, cadmium fluoride, and chromium (III) oxide. Therefore, we investigated the effect of temperature on the yield of acetone in the presence of this catalyst. The effect of temperature on the yield of acetone and the conversion of acetylene is presented in Fig. 2.

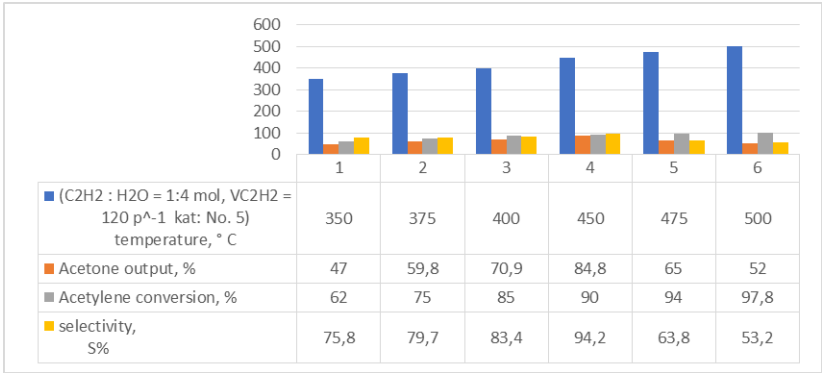


Fig. 2. Effect of Temperature on Acetone Yield and Acetylene Conversion.

As can be seen from the table, the productivity of the formation of acetone, the selectivity increases up to 450 °C. As the temperature rises above 450 °C, the yield of acetone formation and the selectivity of the process decrease due to the transformation of the formed acetone into other substances.

It is known from the literature that cadmium and its compounds adversely affect the human body. Cadmium compounds are highly toxic (MAC 0.1 mg/m³) substances.

Therefore, we investigated the catalytic activity of cadmium-free compounds in acetylene hydration reactions.

Influence of the catalyst composition on the yield of the catalytic reaction of acetylene hydration. The effect of various factors (temperature, space velocity, acetylene: water ratio, catalyst content, etc.) on the product yield and process selectivity in the reaction of catalytic hydration of acetylene was studied. Table 3 shows the effect of the active components of the catalyst on the reaction products.

Table 3. Influence of the catalyst composition on the yield of reaction products (T=450 °C; $V_{C_2H_2} = 120_{h^{-1}}$)

№.	Catalyst composition. mass %	Acetylene conversion. %	Catalyst composition. mass %	
			Acetaldehyde	Acetone
1	ZnO-15.0; NiO-5.0; Al ₂ O ₃ -80.0	89.2	12.0	78.6
2	ZnO-10.0; CoO-5.0; Al ₂ O ₃ -85.0	88.6	10.8	67.8
3	ZnO-15.0; Fe ₂ O ₃ -5.0; Al ₂ O ₃ -80.0	84.8	10.4	72.0
4	ZnO-10.0; NiO-5.0; Fe ₂ O ₃ -5.0 Al ₂ O ₃ -80.0	94.8	10.5	81.8
5	ZnO-10.0; CoO-5.0; Fe ₂ O ₃ -5.0 Al ₂ O ₃ -80.0	82.4	9.2	61.8

As can be seen from the table, in the presence of catalyst No. 4 containing iron, zinc and nickel oxides, the yield of acetone formation is 81.8%, and the conversion of acetylene is 94.8%.

Effect of temperature on the reaction yield. When studying the effect of temperature on the yield of acetone in the presence of catalyst no. 4 with high activity and productivity, it was found that the optimum temperature for carrying out the acetylene hydration reaction is 450 °C (Fig. 3).

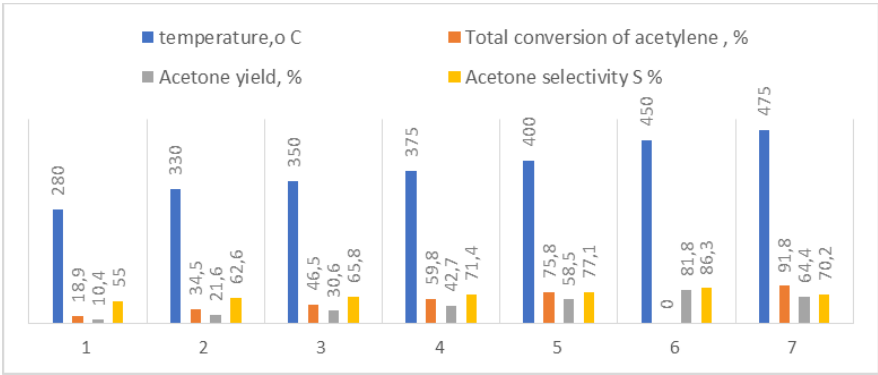


Fig. 3. The effect of temperature on the conversion of acetylene to the yield of acetone and the selectivity of the process (catalyst No. 4).

As can be seen from the table, when the temperature reaches 450 °C, the yield of acetone is 81,8%, and the selectivity of the process for acetone is 86,3%.

Influence of space velocity on acetylene conversion and acetone yield. The effect of space velocity on acetone yield and acetylene conversion was also investigated, and the experimental results are presented in Fig. 4.

Fig. 4 shows that the overall conversion of acetylene decreases with an increasing space velocity of acetylene.

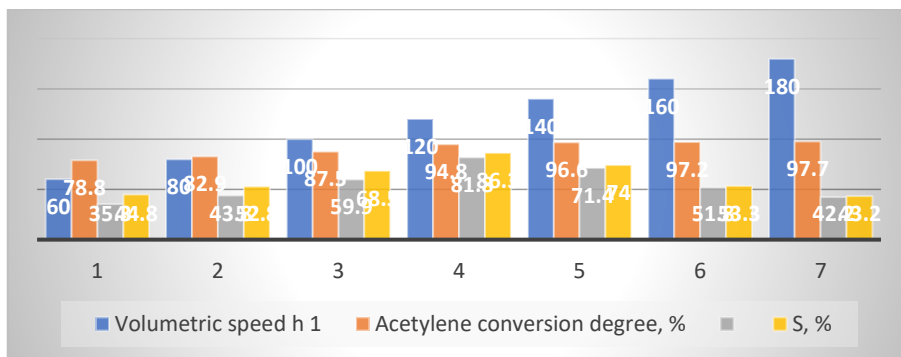


Fig. 4. Effect of space velocity on acetaldehyde yield and acetylene conversion (cat. 4; $T = 450\text{ }^{\circ}\text{C}$)

Influence of molar ratios of reagents on acetylene conversion and acetone yield. In addition, the influence of the molar ratio $\text{C}_2\text{H}_2:\text{H}_2\text{O}$ on the yield of acetone and the conversion of acetylene was studied. The results of the experiment are presented in Fig. 5.

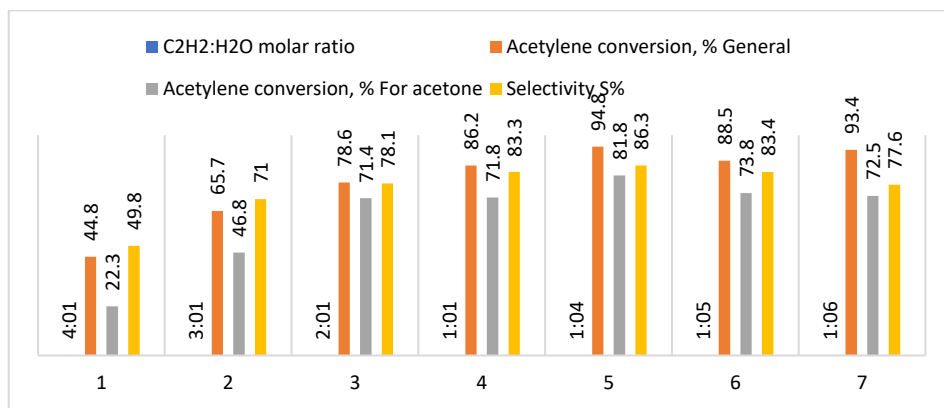


Fig. 5. Influence of molar ratios $\text{C}_2\text{H}_2:\text{H}_2\text{O}$ to the output of acetone ($T = 450\text{ }^{\circ}\text{C}$, catalyst No. 4; $V_{\text{C}_2\text{H}_2} = 120\text{ h}^{-1}$)

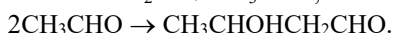
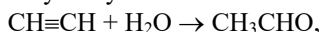
Acetone production technology. Acetaldehyde and acetone were synthesized as follows. Acetylene was saturated with water at a temperature of $70\text{--}80\text{ }^{\circ}\text{C}$ and at a ratio of water: acetylene = (1:3)–(1:5), mol was passed through the catalyst bed at $360\text{ }^{\circ}\text{C}$ with a space velocity of $180\text{--}200\text{ h}^{-1}$. The gas-vapour mixture leaving the reactor was cooled in a refrigerator. The reaction products were collected with water. The catalyst contains acetaldehyde, acetone, crotonaldehyde, paraldehyde, etc. To maintain the degree of acetylene conversion not lower than 80%, the reaction temperature was raised by $10\text{ }^{\circ}\text{C}$ every 20 hours. After 96–120 hours, the degree of acetylene conversion decreases to 75–70%. Then the reaction was stopped and the catalyst was regenerated.

Subsequently, the influence of various parameters (temperature, space velocity, acetylene-water ratio) on the conversion of acetylene and the yield of acetone was studied.

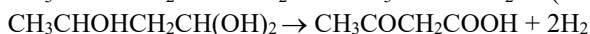
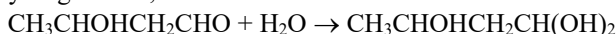
As a result of studying the effect of temperature on the yield of acetone, it was found that in the temperature range of 360-500 °C, the dependence between the reaction yield and temperature is extreme, and at 450 °C, the yield was considered to be maximum.

Based on the results of the qualitative and quantitative composition of the reaction products on this catalyst, we propose the following mechanism for the formation of acetone:

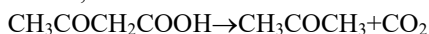
3-hydroxy butanal is formed as a result of an aldol condensation.



Upon hydration of 3-hydroxy butanal, a trihydric alcohol is formed, and upon further dehydrogenation, acetoacetic acid is formed:



In turn, acetoacetic acid under these conditions is decarboxylated and acetone is formed.



The above method of obtaining acetone is promising for Uzbekistan.

Based on the obtained results, the existing technology of acetylene hydration at OAO “NAVOIYAZOT” was improved. The technological scheme for the production of acetaldehyde, acetone (or mixtures thereof) is shown in fig. 6.

According to the scheme, water is dosed into the heat exchanger using a pump and heated to a temperature of 80-85 °C. Acetylene is supplied to heat exchanger 3 from the gas holder 2 at a pressure of 0.12-0.15 MPa. Acetylene saturated with water vapour in the form of a gas-vapour mixture enters the upper part of the reactor, where the catalyst is located, heated to a temperature of 360 °C. (The reactor is a basket, multi-sectional). The reaction is exothermic. Acetaldehyde, acetone and other reaction products are separated from the gas stream by washing with water. The gas-vapour mixture enters after the reactor into heat exchanger 5, where part of the catalyst is condensed. The uncondensed part enters column 7 for absorption by water. The condensed part of the catalyst from the heat exchanger and the column enters tank 6 and then goes to rectification. In the distillation column, acetaldehyde is first isolated, then acetone. VAT residue, consisting of crotonaldehyde, paraldehyde, water, etc. is sent for processing. The unreacted part of acetylene (up to 20% on average) is mixed with hydrogen and carbon dioxide after the column is recycled.

Based on the research, a technology for producing acetone was created (Fig. 5, 6). According to the scheme, the required amount of water vapour is heated to 353-358 °K and mixed with acetylene at a pressure of 0.12-0.15 MPa and sent to the reactor (1).

The reaction is exothermic. Acetone, acetaldehyde and other reaction products are separated from gaseous substances by washing with water. The gas-vapour mixture leaving the reactor is fed into the heat exchanger (2), where the catalyst condenses. The non-condensable part is sent to the absorption column (3). The condensed part of the catalyst from the heat exchanger and the column enters a special container (6) for the catalyst, and from there it is sent to the distillation column (4).

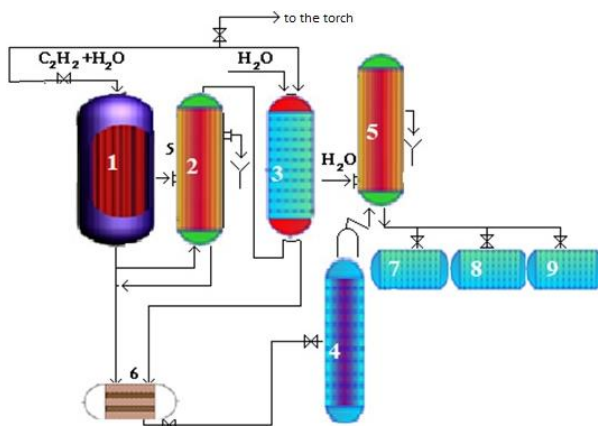


Fig. 6. Process flow diagram of the acetylene hydration reaction. 1 - reactor; 2 - heat exchanger; 3 - absorption column; 4 - distillation column; 5 - heat exchanger; 6 - container for catalyst; 7 - container for acetaldehyde; 8 - container for acetone; 9 - capacity for VAT residue.

In a distillation column, acetaldehyde is first separated, then acetone. Croton is sent for processing if it is preserved in aldehyde, paraldehyde, water and other substances. Unreacted acetylene is fed back to the reactor.

4 Conclusions

Thus, the influence of various factors (temperature, space velocity, acetylene: water ratio, catalyst content, etc.) on the product yield and process selectivity in the reaction of catalytic hydration of acetylene was studied. ZnO-10.0 containing iron, zinc and nickel oxides; NiO-5.0; In the presence of the $\text{Fe}_2\text{O}_3\text{-}5.0\cdot\text{Al}_2\text{O}_3\text{-}80.0$ catalyst, the yield of acetone formation is 81.8%, the conversion of acetylene is 94.8%. Subsequently, the influence of various parameters (temperature, space velocity, acetylene-water ratio) on the conversion of acetylene and the yield of acetone was studied.

As a result of studying the effect of temperature on the yield of acetone, it was found that in the temperature range of 360-500 °C, the relationship between the reaction yield and temperature is extreme, and at 450 °C, the yield was considered maximum. Based on the results obtained, a technological scheme for the production of acetone by the catalytic hydration of acetylene was proposed.

References

1. O.N. Temkin, *Soros Educational Journal* **7(6)**, 32-41 (2001)
2. N.S. Tangyarikov, et.al., *Chemical and chemical engineering* **58(9)**, 68-69 (2015)
3. B.A. Trofimov, A.V. Ivanov, *Vestnik SPbGU. Ser. 4*, **1(59)**, 558-566 (2014)
4. B.M. Mixalichko, et.al., *Uspexi ximii* 69(11), 1042-1070 (2014)
5. B.D. Yusupov, et.al., *Sbornik trudov Resp. nauch.texn. konf. TKTI*, pp.94-96 (2008)
6. S.M. Turabdjanyov, et.al., *International Journal of the Humanities and Natural Sciences* **11-5**, 130-133 (2022)
7. N.S. Tangyarikov, *Chemical and chemical engineering* **53(5)**, 56-58 (2010)
8. G. Abbiati, et.al., *Top. Organomet. Chem.* **43**, 231 (2013)

9. H. Schobert, Chem. Rev. **114**(3), 1743 (2014)
10. S. Quintero-Duque, et.al., Tetrahedron Lett. **56**(21), 2634 (2015)
11. V.P. Ananikov, ACS Catal. **5**, 1964 (2015)
12. D.B. Huple, et.al., Adv. Synth. Catal. **358**, 1348 (2016)
13. V.V. Voronin, et.al., Molecules **23**, 2442 (2018)
14. G.C. Midya, et.al., Org. Biomol. Chem. **12**, 1812 (2014)
15. O. Rivada-Wheelahan, et.al., Angew. Chem. Int. Ed. **55**, 6942 (2016)
16. M. Bhunia, et.al., Organometallics **35**, 3775 (2016)
17. Q. Liang, et.al., Angew. Chem. Int. Ed. V. **56**(1), 217 (2017)
18. I. Bauer, H.-J. Knölker, Chem. Rev. **115**, 3170 (2015)
19. N.I. Fayzullaev, et.al., Journal of Critical Reviews 7(7), 917–920 (2020)
20. I.I. Mamadoliev, et.al., International Journal of Control and Automation **13**(2), 703–709 (2020)