Досліджено вплив вуглеводневих домішок (метану, етану, пропілену, бутанів) у пропановому холодоагенті на технологічні параметри отримання штучного холоду і на ефективність роботи холодильної установки. Встановлено, що домішки сприяють підвищенню загального тиску парів у холодильному циклі. Це негативно впливає на роботу устаткування. Збільшуються потужність, споживана компресором, та сумарне теплове навантаження на холодильне обладнання

Ключові слова: холодильна установка, холодильне устаткування, пропановий холодоагент, вуглеводневі домішки, тиск парів

Исследовано влияние углеводородных примесей (метана, этана, пропилена, бутанов) в пропановом хладагенте на технологические параметры получения искусственного холода и на эффективность работы холодильной установки. Установлено, что примеси способствуют повышению общего давления паров в холодильном цикле. Это отрицательно влияет на работу оборудования. Увеличиваются потребляемая компрессором мощность и суммарная тепловая нагрузка на холодильное оборудование

Ключевые слова: холодильная установка, холодильное оборудование, пропановый хладагент, углеводородные примеси, давление паров

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1. Introduction

Artificial cold is used to obtain low temperatures, which cannot be achieved through cooling by natural coolants (water, air).

Refrigeration unit is an actual steam compression machine that works in the Carnot reverse cycle with fluid overcooling and coolant throttling before evaporators.

Most often, ammoniac is used in cold production as a coolant, but at high performance plants, it is appropriate to use propane as a coolant. Propane does not interact with construction materials of the equipment, has less toxicity than ammoniac. However, it contains more impurities compared to other coolants.

Refrigeration department has almost no inertia and is very sensitive to inaccuracies in maintaining of the technological process. Its work is affected by many factors. Some negative factors may be eliminated during previous technological operations, the influence of the others can be reduced. Revealing "bottle necks" of the process of cold obtaining and optimization of technological parameters are very relevant, because they allow a significant increase in efficiency of using energy resources and equipment.

Composition of a coolant is one of the most influential factors, which affects stability and uninterrupted operation

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INFLUENCE OF IMPURITIES IN PROPANE COOLANT ON THE PROCESS OF OBTAINING ARTIFICIAL COLD

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of a refrigeration unit. Propane, which is used as a coolant, contains such impurities as methane, ethane, propylene, and a mixture of butanes. At evaporation temperatures, impurities form the pressure that by its value is different from the pressure of the main component. The ratios of components of a coolant are changed in the course of operation of the unit, so does the impact of specific impurities on the total pressure of vapors.

Research into influence of the quality of a cooling agent on the basic technological parameters of the cold obtaining process will make it possible to assess the impact of each separate component on total pressure in the system and technical indicators of performance of the equipment. The relevance of the work in this direction lies in the fact that obtained results will contribute to development of measures regarding reduction of undesirable influence of impurities on production.

2. Literature review and problem statement

A combined deparaffination and oil removal unit is designed for deparaffination of distilled and residual raffinates and oil removal from obtained gatch for the purpose of obtaining deparaffinated oils, paraffin and ceresin. The unit

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consists of a steam compressing refrigeration unit, which provides cooling of the mixture of raw materials.

The process of cold obtaining is influenced by such factors as composition and temperature of cooling mixtures, temperature of material flows, and ambient temperature. Composition of a coolant is one of the most influential factors, which affects stability and uninterrupted operation of the unit, performance and quality of the finished product.

Four main impacts, associated with the use of contaminated with impurities coolants, are distinguished [1]:

- changes in thermal properties of operation fluid;

chemical changes that affect inner stability of the system;

 physical changes that affect the structure of components and behavior of materials;

- consequences of toxicity at the outlet of the system.

Research into influence of impurities on the refrigeration cycle, was mostly carried out for ammoniac refrigeration systems, where the major undesirable component is the air. Technological process of cold obtaining with the use of ammoniac refrigerating machines is sufficiently studied and quite effective. However, most industrial ammoniac refrigeration units are morally and physically obsolete and require substantial renovation. The authors of paper [2] consider that the key trend of improvement of the technological process is application of the optimal level of boiling temperature in the evaporator, improvement of design and mode of operational characteristics of refrigeration units.

Paper [3] presented the data on refrigeration systems operating on natural gas, which in addition to methane, contains harmful impurities. Impurities negatively influence efficiency of technological equipment. The authors of the article propose to clear natural gas from acidic impurities (H_2S , CO_2), water vapor, sulfur, mercury and heavy metals before using it in refrigeration equipment. In addition, to minimize the impact of undesirable components on the technological parameters of the process, it is proposed to apply the operation of blowing off a part (3–5 %) of low-pressure gas flow. The authors of the paper indicate the negative effect of impurities on operation of the refrigeration cycle. But the studies, cited in the article, regard the use of methane with hydrogen sulfide impurities, carbon dioxide, sulfur and others as a coolant.

In article [4], the authors made thermodynamic analysis of various cooling cycles that use mixtures of substances as coolants. It was shown that it is possible to increase productivity of a refrigeration plant by applying gas mixtures with a large share of high-boiling components. At the same time, the article does not contain any information about the quality of mixtures of raw materials.

Papers [5, 6] contain results of research into cascade refrigeration systems, in which carbon dioxide (R744) is used as coolant in low temperature circuits and ammoniac (R717) is used in high temperature circuits [5], as well as a new binary mixture of carbon dioxide (R744) and propane (R290) [6]. The study was carried out to determine thermodynamic and technological characteristics of the system. The data on the influence of impurities on operation of the refrigeration cycle are not cited in the paper.

Physical and chemical characteristics of the mixture of R290, R600a and R290/R600a were explored in [7]. Surface tension of such coolant as propane, isobutene and the propane-isobutene mixture in the temperature range between

253 K and the critical temperature was determined. The article does not examine the influence of impurities on physical and chemical properties of coolants, including propane.

Article [8] presents the results of research into equilibrium of the steam-fluid system for propane coolant with addition of 1,1,1,3,3,3-hexafluoridepropane (R236fa) at temperature of (283.13, 303.19 and 323.26) K. The authors point out existence and negative impact of hydrocarbon impurities (n-butane and isobutene) in the propane coolant on the equilibrium condition of substances. Experimental data indicate existence of azeotropic composition at high concentrations of propane and significant deviation of the raw material mix from the Raoul law. The paper does not explore existence of ethane, methane, propylene in the raw material mixture and their impact on characteristics of the coolant.

The research into dependence of pressure in the refrigeration cycle was presented in paper [9]. It was shown that impurities have a negative impact on energy consumption of the refrigeration equipment. However, there is no information about the impact of each separate impurity component on indicators of the process of obtaining of low temperatures.

The above details allow us to assert that the issue of the influence of hydrocarbon impurities (ethylene, methane, propylene, butanes) in the propane coolant on technological parameters of refrigeration cycle was not actually explored in the literature. The authors examined either pure raw mixtures, or the systems with impurities, but different from the impurities that exist in the propane coolant of industrial refrigeration units.

3. The aim and objectives of the study

The aim of present research was to determine the influence of inert impurities on technological parameters of obtaining of artificial cold and, as a result, the efficiency of the cooling unit.

To accomplish the set goal, the following tasks were to be fulfilled:

 to determine the impact of quality of propane on the total vapor pressure of the coolant in the process of condensation and evaporation;

– to determine the impact of separate impurities, contained in the coolant, on operation of equipment in the refrigeration department.

4. Materials and methods of research into the influence of propane quality on total pressure of vapors of cooling agent

4.1. Equipment and materials used in the experiment

The research was carried out in the refrigeration department of the industrial combined unit of raffinate deparaffination and oil removal from obtained gatch [9]. The refrigeration unit consisted of propane crystallizers and evaporators, fluid separators, turbochargers, the propane supercooler, refrigerators-condensers, and the receiver.

The influence of the composition of the coolant on total pressure in the receiving reservoir and in the turbochargers' injection reservoir was studied. The methodology of the experiment was based on the fact that analysis of the composition of the gas mix was performed at the same parameters of the process. Analysis of obtained results was conducted for the data that met the following technological conditions:

- raw material consumption - 22 m³/h;

- multiplicity of dilution of raw material with the solvent - 1:2;

 ratio of components of a solvent (methyl ethyl ketone: toluene) – 45:55;

- temperature of solvent - 35 °C;

– temperature of the raw material mix at the inlet into the pipe space of propane crystallizers – 12 °C;

 temperature of cooled raw material mix at the outlet from the pipe space of propane crystallizers – minus 12 °C;

– temperature of return water flow, fed to water condensers – 24 $^{\circ}\mathrm{C};$

- consumption of return water - 490 m³/h;

– average daily temperature of the air, that comes to air refrigerators – condensers for cooling – 10 °C.

The values of total pressure and temperature in the receiving reservoir and the injection reservoir were selected from mode sheets of the unit under above mentioned conditions.

In the course of research, the equipment was not switched over, additional processes, which could influence the obtained results, were not performed.

In the experiment, technical propane with the content of the main component of 91-96 % by weight was used as a coolant, the rest were hydrocarbon impurities.

4.2. Methods for determining the composition of a cooling agent

To determine the composition of the coolant, chromatographic method for separation of hydrocarbons was used. Specially prepared modified aluminum oxide was used as an absorber, mixture of aluminum oxide and Vaseline oil was used as solvent.

To determine specific kept volume of gases, aluminum oxide was loaded in the chromatographic column. The column was installed in the chromatograph and activated in the flow of gas-carrier at 250 °C for two hours without connection to the detector. Then the column was cooled to room temperature, and connected to the detector.

The mix of propane and the air in the ratio of 1:2 was injected with a syringe to the chromatographer through the sampler, and time of components' keeping was determined by a stopwatch. Specific kept volume of propane $\left(V_g^{\tau}\right)$ was calculated from the formula:

$$V_{g}^{\tau} = \frac{V_{R}^{1}}{m_{1}}; \quad V_{R}^{1} = (t_{R} - t_{0}) \cdot V_{\alpha}, \tag{1}$$

where V_R^1 is the reduced kept volume of propane, cm³; t_R is the time of keeping propane, s; t_0 is the time of keeping the air, s; V_a is the velocity of gas-carrier, cm³/s; m_1 is the weight of aluminum oxide, g.

The data were obtained in the form of a chromatogram.

Hydrocarbon composition of liquefied gas was determined by relative kept volumes. Relative volume of keeping (V_{e}) was calculated from the formula:

$$V_g = \frac{l_n}{l_{n-butane}},\tag{2}$$

where l_n is the distance from the first peak to the maximum peak of correspondent hydrocarbon, mm; $l_{n-butane}$ is the distance from the first peak to the peak of n-butane, mm.

Mass fraction of separate hydrocarbon in gas (X) in per cent was determined from formula:

$$X_i = \frac{S_i \cdot 100}{\sum S_i},\tag{3}$$

where S_i is the reduced area of the peak of this hydrocarbon, mm²; $\sum S_i$ is the sum of reduced areas of peaks of all hydrocarbons, mm².

Reduced area of the peak of carbohydrates (S_i) in mm^2 was calculated from the formula:

$$S_i = h \cdot a \cdot k \cdot b, \tag{4}$$

where *a* is the width of the measured peak in the middle of its height, mm; *b* is the scale of the recorder; *h* is the height of the peak, mm; *k* is the mass coefficient of sensitivity.

5. Results of research into influence of propane quality on the operation of a refrigerator compartment

5. 1. Results of research into influence of gas mixture components on total vapor pressure of the coolant

To determine the influence of quality of a propane coolant on total pressure, we selected indicators of pressure and temperature in the reception reservoir and the turbocharger injection reservoir from operation mode sheets of the refrigeration unit under fixed conditions. The samples of the coolant mixture, taken under the same conditions, were analyzed for the contents of propane and hydrocarbon impurities (Table 1).

Table 1

Composition of coolant over the period of studies

| No. of entry | Mass fraction of components, % | | | | | | | |
|-----------------|--------------------------------|---|---|----------------------|----------------------------------|-----------------------------------|--|--|
| | methane (CH ₄) | $^{\text{ethane}}_{(\mathrm{C}_{2}\mathrm{H}_{6})}$ | propane (C ₃ H ₈) | propylene (C_3H_6) | isobutene $(_{i}C_{4}H_{10})$ | n-butane ($_{n}C_{4}H_{10}$) | | |
| 1 | 0.03 | 6.08 | 91.75 | 0.99 | 1.02 | 0.13 | | |
| 2 | 0.03 | 6.92 | 90.72 | 1.12 | 1.07 | 0.15 | | |
| 3 | 0.02 | 6.07 | 92.11 | 0.65 | 1.03 | 0.13 | | |
| 4 | 0.01 | 3.36 | 94.88 | 0.58 | 1.06 | 0.12 | | |
| 5 | 0.01 | 5.31 | 93.01 | 0.67 | 0.90 | 0.10 | | |
| 6 | 0.01 | 4.75 | 94.00 | 0.40 | 0.74 | 0.08 | | |
| 7 | 0 | 3.67 | 95.30 | 0.30 | 0.70 | 0.03 | | |
| 8 | 0.02 | 1.74 | 95.82 | 1.40 | 0.90 | 0.09 | | |
| 9 | 0.03 | 4.61 | 93.58 | 1.00 | 0.64 | 0.10 | | |
| 10 | 0.02 | 5.04 | 93.18 | 0.99 | 0.68 | 0.11 | | |

Dependence of temperature on pressure of saturated vapor of the coolant in evaporators is shown in Fig. 1, in condensers – in Fig. 2. These dependences were plotted based on the experimental data, obtained as a result of research.

Dependence of vapor pressure of coolant in condensers and evaporators on propane quality is shown in Fig. 3.

The curves, presented in Fig. 3, were plotted based on experimental data.

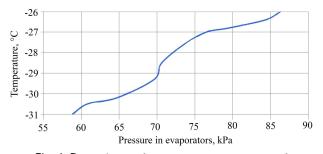


Fig. 1. Dependence of temperature on pressure of saturated vapor of coolant, used in evaporators

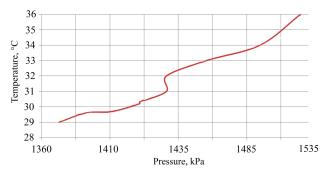


Fig. 2. Dependence of temperature in condensers on pressure of saturated vapor of coolant

By polynomial approximation of experimental data for cooling process in the condensers in the explored range of values, the following analytical dependence was obtained:

$$P = 88389X^3 - 242297X^2 + 220898X - 66903.$$
(6)

Approximation reliability coefficient in this case was $R^2=0.9617$.

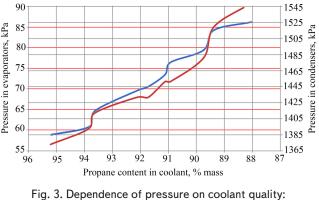
It is known that total pressure P of the mixture of ideal gases is equal to the sum of partial pressures P_i of the components in the mix [10]:

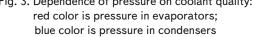
$$P = P_1 + P_2 + \dots + P_n \tag{7}$$

or

$$P_m = \sum_{K=1}^{K=N} P_K,\tag{8}$$

where P_m is the pressure of the mix; P_k is the partial pressure of the *k*-th component; *N* is the number of separate gases that make the gas mix.





It follows from formula (8) that partial pressure of each component of the gas mix is equal to the product of mole share of a component by total pressure of the mixture:

$$P_{K} = N_{K} \cdot P_{m}, \tag{9}$$

where N_{K} is the molar share of the *k*-th component.

Impact of each component of the gas mixture on total pressure is calculated from formula (9). Results of calculations of pressure in the receiving reservoir are shown in Table 2, calculations of pressure in the injection reservoir are shown in Table 3.

Amount of separate impurities in coolant is different. And such will be a contribution of each component in the total pressure in the studied systems.

Table 2

Partial pressure of components of coolant in the receiving reservoir, kPa

| No. of entry | methane | ethane | propane | propylene | isobutene | n-butane | Total pressure |
|--------------|---------|--------|---------|-----------|-----------|----------|----------------|
| 1 | 0.069 | 8.501 | 75.970 | 0.984 | 0.682 | 0.095 | 86.30 |
| 2 | 0.067 | 7.329 | 75.375 | 0.860 | 0.633 | 0.076 | 84.34 |
| 3 | 0.040 | 6.903 | 71.297 | 0.524 | 0.604 | 0.071 | 79.44 |
| 4 | 0.023 | 5.821 | 69.552 | 0.528 | 0.512 | 0.054 | 76.49 |
| 5 | 0.037 | 5.325 | 67.019 | 0.743 | 0.368 | 0.059 | 73.55 |
| 6 | 0.056 | 4.681 | 64.763 | 0.727 | 0.332 | 0.049 | 70.61 |
| 7 | 0.021 | 4.756 | 64.143 | 0.285 | 0.383 | 0.042 | 69.63 |
| 8 | 0.019 | 3.146 | 60.607 | 0.388 | 0.511 | 0.058 | 64.73 |
| 9 | 0.000 | 3.222 | 57.061 | 0.188 | 0.316 | 0.012 | 60.80 |
| 10 | 0.029 | 1.489 | 56.022 | 0.859 | 0.400 | 0.041 | 58.84 |

| No. of entry | methane | ethane | propane | propylene | isobutene | n-butane | Total pressure |
|--------------|---------|---------|-----------|-----------|-----------|----------|----------------|
| 1 | 1.240 | 152.627 | 1,364.034 | 17.664 | 12.241 | 1.704 | 1,549.51 |
| 2 | 1.216 | 132.095 | 1,358.495 | 15.505 | 11.401 | 1.368 | 1,520.08 |
| 3 | 0.740 | 128.687 | 1,329.072 | 9.774 | 11.255 | 1.333 | 1,480.86 |
| 4 | 0.435 | 110.455 | 1,319.794 | 10.015 | 9.725 | 1.016 | 1,451.44 |
| 5 | 0.726 | 105.084 | 1,322.552 | 14.660 | 7.257 | 1.161 | 1,451.44 |
| 6 | 1.145 | 94.930 | 1,313.265 | 14.748 | 6.730 | 1.002 | 1,431.82 |
| 7 | 0.430 | 97.793 | 1,318.993 | 5.870 | 7.875 | 0.859 | 1,431.82 |
| 8 | 0.424 | 68.633 | 1,322.252 | 8.473 | 11.156 | 1.271 | 1,412.21 |
| 9 | 0.000 | 73.807 | 1,306.946 | 4.317 | 7.241 | 0.279 | 1,392.59 |
| 10 | 0.686 | 34.736 | 1,307.214 | 20.046 | 9.336 | 0.961 | 1,372.98 |

Partial pressure of components of coolant in injection reservoir, kPa

5.2. Analysis of influence of composition of coolant on operation of equipment of refrigeration department

To describe behavior of gas hydrocarbon mixture, we used Peng-Robinson equations of state, which unite major thermodynamic parameters of real gas by introducing additional cubic trinomial that takes into account intermolecular interaction in real gas [11].

The standard form of Peng-Robinson equation of state is as follows:

$$P = \frac{R \cdot T}{V - b} - \frac{a}{V \cdot (V + b) + b \cdot (V - b)},\tag{10}$$

where *P* is the pressure, MPa; *T* is the temperature, K; *V* is the molar volume, $m^3/kmol$; *R* is the universal gas constant.

Coefficients of equation (10) for pure substances were determined based on condition that in dependence P=P(V), critical point is a point of inflection:

$$\frac{\partial P}{\partial V} = 0 \\ \frac{\partial^2 P}{\partial^2 V} = 0 \\ \end{bmatrix} V = V_C, \quad P = P_C, \quad T = T_C,$$
(11)

where P_c is the critical pressure, MPa; T_c is the critical temperature, K.

It follows form condition (11) that coefficients in equation (10) are equal to:

$$a = a_C \cdot \phi(T), \tag{12}$$

$$a_c = 0,457235 \cdot \frac{R^2 \cdot T_c^2}{P_c},$$
 (13)

$$b = b_c = 0,077796 \cdot \frac{RT_c}{P_c}.$$
 (14)

To improve description of behavior of pure substances, temperature amendment $\varphi(T)$ was introduced:

$$\phi = \left[1 + \psi \left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2,\tag{15}$$

 $\psi = 0,37464 + 1,5422\omega - 0,26992\omega^2,$

(16)

where ω is the acentric factor of substance.

To calculate the influence of the coolant of different composition on the processes of compression, we applied the software complex Hyprotech Ltd HYSYS of 3.2 version, which is used for engineering calculations in design of equipment for chemical, oil and gas extracting, oil and gas refining, as well as petrochemical industries.

Based on calculation results, the diagram of dependence of power consumption of the compressor on the content of propane in the coolant was plotted (Fig. 4).

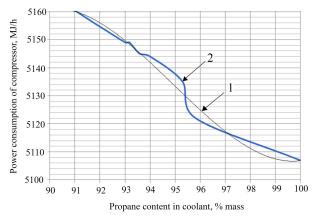


Fig. 4. Dependence of power consumption of compressor on content of propane in coolant: 1 – approximation curve, 2 – calculation data, R²=0.9812

By the polynomial approximation of calculation data (Fig. 4), the following analytical dependence with approximation reliability level of $R^2=0.9812$ was obtained in the studied range of values:

$$N = 126,32X^3 - 35978X^2 + 3 \cdot 10^6 X - 10^8, \tag{17}$$

where *N* is the power consumption of the compressor, MJ/h, *X* is the propane content in the coolant, %.

Dependence of thermal load of the condenser, the refrigerator, and the supercooler on the quality of the coolant was calculated by a similar method with the use of software complex Hyprotech Ltd HYSYS. Fig. 5 shows the curves of dependence of thermal load of refrigeration equipment on content of propane in the coolant, plotted based on calculation data.

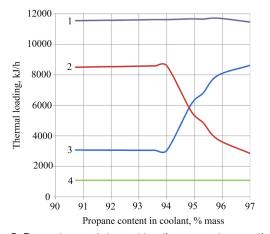


Fig. 5. Dependence of thermal loading on coolant quality: loading 1 – on cooler, 2 – on refrigerator, 3 – on condenser, 4 – total thermal load of condenser and refrigerator

6. Discussion of results of research into influence of propane quality on operation of refrigeration department

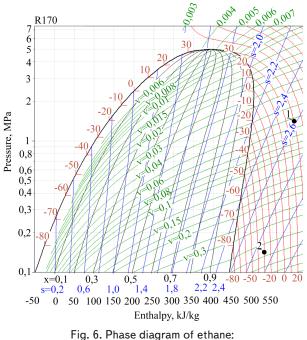
In the process of studying the impact of propane quality on operation of refrigeration department, the dependence of temperature and total pressure in the receiving reservoir and the injection reservoir of compressors was established. Pressure in the receiving reservoir of turbochargers corresponds to pressure in evaporators, and pressure in the injection reservoir of compressors corresponds to pressure in the condensation system.

At an increase in total pressure, temperature of evaporation (Fig. 1) and of condensation (Fig. 2) increases. The smaller the propane proportion in the coolant and the more impurities, the higher pressure is formed in the system of condensation and evaporation (Fig. 3). An increase in total pressure as a result of deterioration of the coolant quality in the cold obtaining technology is a negative factor and it leads to unplanned equipment stops.

Propane coolant is a gas mixture of the main component – propane and hydrocarbon impurities. Total pressure in the refrigeration system consists of partial pressures of separate gases

Impurities affect total pressure differently, as their amount in the coolant is different. In addition, each of the components of a gas mixture has its own thermodynamic properties that should be considered when determining the impact of impurities on the process of cold obtaining. In the processes of coolant condensation and vaporization, it is not temperature or pressure of a substance that changes, but its state and degree of vapor saturation. During evaporation, the state of the substance gradually transfers from liquid to wet vapor of varying degrees of saturation, and subsequently – to dry steam. The opposite process takes place during condensation. Dry superheated vapor is converted into wet vapor of various saturation degrees. This affects contribution of each separate component of the coolant to total pressure in the studied section of the system. To analyze the impact of each component of the gas mixture on the refrigeration process, phase diagrams in P-I coordinates were used [12]. From phase diagrams, the state of the component at the studied temperature and pressure was found for each component of the gas mixture.

Table 1 shows that ethane makes up the largest part in the coolant, it is 1.74–6.92 % by weight. Its impact on total pressure is the greatest. Fig. 6 shows phase diagram of ethane.



point 1 — indicators of ethane under conditions of condensation; point 2 — indicators of ethane under conditions of evaporation

Enthalpy indicators (kJ/kg) are marked on X-axis, absolute pressure (MPa) is marked on Y-axis. The wet vapor area of different degree of saturation is limited by the curve of red color. To the left of the boundary curve, there is the zone, in which the substance is in a liquid state, to the left, there is the zone of superheated vapor. In this zone, the substance is in gaseous state. On the diagram, isotherms (*t*=const, °C), are shown in red color, adiabates (*s*=const, kJ/kg·K) are shown in blue color, specific volume of substance (m^3/kg) is shown in green color. In the area of wet vapor, the isotherms go horizontally and coincide with the horizontals (*p*=const), in the zone of liquid and superheated vapor – almost vertically.

Fig. 6 shows that under conditions of the experiment, ethane is not transformed to a liquid and is in a gaseous state. This creates unwanted excess pressure in compression process and leads to an increase in condensation temperature. At evaporation temperatures, partial pressure of ethane is 1,489–8,501 kPa (Table 2), at condensation temperatures (Table 3), it is 34,736–152,627 kPa. After getting to vaporizers, ethane forms a gas "cushion" above the level of liquid coolant. This leads to slowing down of evaporation and heat exchange processes.

Similarly, the aggregate state of each component of the gas mixture under conditions of the experiment and their possible impact on the process were determined.

Propane is the major component of the coolant, according to which this refrigeration cycle is designed. The propane content under conditions of the experiment changed from 90.72 to 95.82 %. Partial pressure of pure propane at evaporation temperatures was 56.022–75.970 kPa (Table 2), at condensation temperatures it was 1,307.214–1,364.034 kPa (Table 3).

Propylene under conditions of the refrigeration cycle behaves as a coolant. Content of propylene ranged within 0.30–1.40 %. Partial pressure of propylene at evaporation temperatures was 0.188–0.984 kPa, at condensation temperature it was 4.317–20.046 kPa (Table 2, 3). Excess pressure, which is formed as a result of existence of propylene in the coolant, negatively affects the process.

Methane under condition of the process was in the supecritical state. At temperature of above minus 83 °C, it was only in the gaseous state irrespective of pressure. Partial pressure of methane in the receiving reservoir was 0.019-0.069 kPa, in the injection reservoir – up to 1.240 kPa. Methane's contribution to total pressure was insignificant due to its small concentration in the gas mixture and made up 0.01-0.04 % (Table 1).

The isobutene content in the cooler was 0.64–1.07 %, n-butane content of 0.03-0.15 %. Partial pressure of n-butane at evaporation temperatures was 0.012-0.095 kPa, at condensation temperatures it was 0.279-1.704 kPa. Partial pressure of isobutene at evaporation temperatures was within 0.316-0.682 kPa, at condensation temperatures it was 6.73-12.241 kPa. Isobutene and n-butane under conditions of the refrigeration cycle almost always are in the liquid state. The negative impact of butanes lies in the fact that in evaporators and condensers they formed a liquid film on heat exchange surfaces. In this case, propane vapors penetrated to the pipes' walls only by diffusion. With an increase in thickness of a fluid layer, propane penetration to the walls became complicated. This led to a gradual increase in pressure in the refrigeration system and deterioration of the processes of raw mix cooling and condensation of compressed coolant.

Calculations showed that the impurities have a negative impact on operation of the equipment of the refrigeration cycle. With a decrease in propane content in the cooler, power consumption of the compressor increases from 5,109 MJ/kg at 100 % propane content to 5,160 MJ/kg at 91 % propane content in the gas mixture (Fig. 4). This leads to deterioration of compression process and an increase in electricity consumption.

Dependence of power consumption of the compressor on propane content in the cooler is clear and unambiguously negative. The influence of the coolant quality on thermal loading of other equipment is ambiguous (Fig. 5). Thermal loading on the condenser and the refrigerator at propane content in the coolant from 90.5 to 93.9 % undergoes minor changes and is the following: loading on the condenser is 3,071–3,048 MJ/h, loading on the refrigerator is 8,486-8,578 MJ/h. Upon further increase in propane content, loading on the condenser increases dramatically and at propane content in the cooler of 97 %, it is 8,635 MJ/h. Thermal loading on the refrigerator in this case drops from 8,578 to 3,000 MJ/h. For a refined determining of the influence of propane quality on operation of refrigeration equipment, we calculated total thermal loading on the condenser and on the refrigerator, which at propane content in the coolant of 90.72-95.3 % was 11,557-11,661 MJ/h. At an increase in propane content in the gas mixture up to 97 %, total thermal load on the condenser and the refrigerator decreased to 11,467 MJ/h.

Since the heat exchange surface of the condenser and the fridge is constant, thermal loading affects only the flow rate of return water and the air, which are fed to the equipment. The more the thermal load, the greater the flow rate of cooling substances.

Thermal load of the supercooler under conditions of the experiment almost never depended on composition of the coolant.

Research and calculations have shown that separate impurities differently influence the refrigerator cycle, however, the total impact is negative.

In the course of operation of industrial refrigeration units, impurities are periodically removed in order to lower the level to an acceptable one and reduce the risk of unplanned equipment stops. This leads to great losses of propane and pollution of the environment.

Solution of the above-mentioned problems is possible by increasing propane quality and improving the operation of the refrigeration department. It is possible to improve the quality of the coolant by lowering evaporation pressure of the coolant. This can be done by:

- creating a vacuum of the forming system;

 using a dual-circuit cooling system, when cooling of raw material mixture is first performed in propane crystallizers, then in ethane crystallizers;

 using additional equipment, in particular the de-ethanation column.

The results, presented in the article, were obtained for a separate industrial refrigeration unit. However, they can be useful for better understanding of the technological process of cooling and its improvement.

7. Conclusions

1. The influence of propane quality on total pressure of vapors of the coolant in the processes of condensation and evaporation was studied. Propane coolant is a gas mixture of the main component – propane and hydrocarbon impurities. Total pressure in the refrigeration system consists of partial pressures of separate gases.

It was found that the smaller the propane proportion in the coolant and the more impurities, the more pressure is formed in the refrigeration cycle. A decrease in propane content in the coolant from 95 % to 89 % by weight leads to an increase in pressure in evaporators from 57 to 86 kPa, in condensers – from 1,385 to 1,524 kPa.

An increase in pressure occurs, firstly, due to accumulation of impurities in the system, which creates additional pressure; secondly, due to deterioration of conditions of thermal and mass exchange. Impurities that get to the system with propane, gradually accumulate and form a liquid layer on the surfaces of heat exchange equipment. In the presence of the liquid layer, propane vapor penetrates to heat exchange surfaces only by diffusion, overcoming significant resistance. As a result, pressure in the system gradually increases.

An increase in total pressure causes an increase in temperature of evaporation and condensation processes. At an increase in pressure in evaporators from 60 kPa to 85 kPa, temperature increases from minus 30,5 °C to minus 26 °C. An increase in pressure in condensers from 1,385 kPa to 1,510 kPa causes an increase in temperature from 29.5 °C to 35.0 °C. A temperature increase occurs as a result of deterioration of heat exchange conditions due to formation of a liquid film on heat exchange surfaces. Deterioration of propane quality causes an increase in power, consumed by the compressor, i.e. it worsens the process of compression and increases electricity consumption.

Calculations showed that an increase in propane content in the raw material mixture from 95 % to 97 % leads to a decrease in total thermal loading on the condenser and the refrigerator by 1.7 %. The lower thermal loading on the equipment, the less consumption of cooling substances. An increase in total thermal loading causes additional material and energy consumption in the cold production.

2. The influence of separate hydrocarbon impurities on operation of refrigeration department was determined. Based on experimental and calculation data, the contribution of each separate impurity to total pressure of saturated vapor of the coolant in evaporators and condensers was determined. It was shown that separate impurities differently affect the equipment, however, on the whole, this impact is negative. The most harmful impurities are ethane and butane. Ethane and methane under conditions of cold obtaining process do not transfer to a liquid state and are in a gaseous state. Partial pressure of pure ethane and methane is higher than partial pressure of pure propane under the same conditions. Ethane and methane increase total pressure in the refrigeration cycle. The content of methane in the raw material mixture does not exceed 0.03 % by weight, which is why its impact on total pressure is much lower than the impact of ethane, the content of which is 7 %.

Butanes, forming a liquid film on heat exchange surfaces, worsen heat exchange processes in refrigeration equipment. Existence of a liquid film prevents propane vapor from penetrating to the walls of the tubes. The process is carried out only by diffusion, which helps increase the total pressure in the system.

Propylene acts in the system as a coolant and its impact on total pressure is negligible.

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