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^{2}H-Ne-He AS THE WORKING FLUID COMPONENTS IN CRYOGENIC SYSTEMS

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Abstract:

Recently with the increasing demand for isotopic materials, the development of customized refrigeration units which allows temperature stabilization, or cryostatting in the temperature range of 30…50 K became necessary. The required temperature stabilization depends on the isotope and process type and need to be performed at different temperatures. Thus, it is obvious that the development of a reliable and efficient refrigeration unit operating in the temperature range of 30…50 K is a relevant objective. This paper presents the result of a preliminary study of the cryogenic system designed for the cold production in the temperature range of 20...50 K. Structurally, the system is designed as a cascade of two refrigeration machines using a mixed refrigerant media as coolant. The Linde-Hampson refrigeration unit, which generates cold at a temperature level of about 90...100 K, is the upper high-temperature stage of the refrigeration cascade. The working fluid of the upper stage is a multicomponent zeotropic mixture of hydrocarbons. The working mixture is compressed in a hermetic lubricated compressor with a moderate compression ratio and a maximum discharge pressure of up to 30 bar.

The lower "cryogenic" stage of the system implements the Bell-Coleman cycle. A three-component zeotropic mixture ^{2}H-Ne-He is used as the working fluid of the low-temperature stage, which ensures the operability of the "cryogenic" stage of the system in the temperature range of 20...90 K.

The current paper presents the design diagrams and thermodynamic cycles of the system and its elements. The rationale for selection of the refrigerant mixture and a preliminary analysis of the system components are reported.

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1. INTRODUCTION

The proposed cryogenic system can be used in various fields of cryogenic technology and spans research, development, and manufacturing industries. The main advantage of this system is its autonomy, which makes it possible to use this system as a stand-alone. For example, this system can be proposed for the field of extraction of stable isotopes of various substances, which has become increasingly popular in recent years.

In engineering of the technological process for stable isotopes obtaining, the various problems related to both the safety of the working cycle, as well as the cryogenic cycle, in which the process of extracting the final product takes place need to be solved. There are many technological processes for the production of stable isotopes. The technological process is widely different, for example, distillation or adsorption, and can also be carried out in a wide range of temperatures levels, starting from an ambient temperature level of about 343 K to obtain ^{18}O and nitrogen isotopes from nitric acid, and up to a cryogenic temperature level of about 1...3 K during the ^{3}He isotope extraction process. The temperature level in the range of 22.4...77 K is used in the separation of various isotopic mixtures of hydrogen using rectification or adsorption, to extract, for example, tritium. The choice of the operating temperature depends on the type of the substance to be separated, its initial composition (component concentrations). Should be noted that the operating temperature also affects the separation coefficient.

Thus, the development of a cryogenic installation operating in a wide temperature range for thermal stabilization (thermostatting) and ensuring a constant temperature of the distillation process is an urgent task.

It is assumed that the use of neon as a refrigerant will be optimal for a temperature level of about 27 K.

To separate binary mixtures such as protium-deuterium, deuterium-tritium, protium-tritium, and obtain the optimal value of the separation coefficient α, the refrigerant must be able to operate at a temperature level of about 21...24 K. At this temperature level, the neon will become crystallize and cannot be used as a refrigerant component of the working mixture. Instead of using neon as a refrigerant component, it is possible to use hydrogen or helium, but cryogenic cycles with these substances as refrigerants have not very high thermodynamic efficiency and required expensive and complex equipment.

2. TERMODYNAMICAL AND PROCESS MODEL OF THE LOW-TEMPERATURE SYSTEM

A simplified process flow diagram of a cryogenic system and a conditional thermodynamic process diagram of the process are shown in Figure 1. For preliminary precooling of a three-component mixture of ^{2}H-Ne-He down to temperature level of about 90...100 K, a low-temperature mixed refrigeration Linde-Hampson cycle (MRLH) is used. As a refrigerant in the MRLH cryogenic cycle, a three-component mixture of hydrocarbons is used. The precooling is organized in a way that during the operation of the MRLH unit it is possible to change the proportion of the refrigerant flow entering the precooling stage and thereby maintain the balance of the system's cooling capacity at the required level. After preliminary cooling of the three-component ^{2}H-Ne-He mixture to a temperature level of 90...100 K, the Bell-Coleman refrigeration cycle is used. The Bell-Coleman refrigeration cycle makes possible to achieve and stably operate in the desired temperature range of 20...90 K.

For numerical and optimization of the thermodynamic cycle calculations of the cryogenic system and for selecting the working mixture as well, a specially developed computer program with using the Intel Fortran and the connected database modules RefProp 9.1 (NIST, 2018a) NIST SUPERTRAPP 3.2 (NIST, 2018b) and PROSIM (Prosim, 2018) was used.

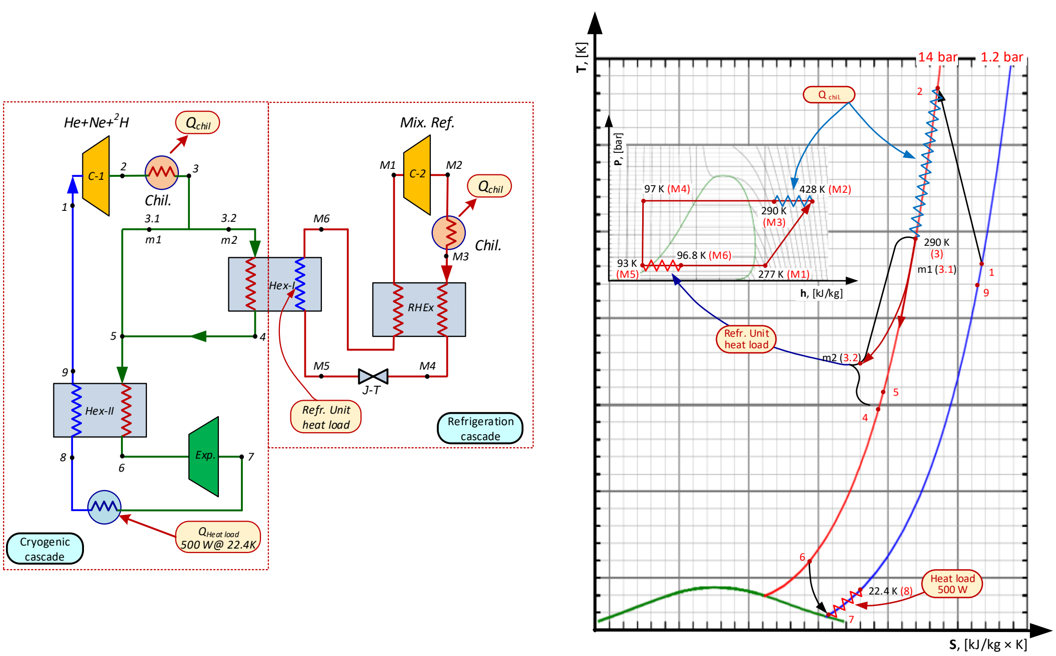
The REFPROP subroutines are based on the most accurate pure fluid and mixture models currently available. It implements three models for the thermodynamic properties of pure fluids:

- Equations of state explicit in Helmholtz energy;
- Modified Benedict-Webb-Rubin equation of state;
- Extended corresponding states (ECS) model.

Mixture calculations employ a model that applies mixing rules to the Helmholtz energy of the mixture components; it uses a departure function to account for the departure from ideal mixing. Viscosity and thermal conductivity are modelled with either fluid-specific correlations, an ECS method, or in some cases with the friction theory method.

The SUPERTRAPP subroutines calculate phase compositions with the Peng-Robinson equation of state and offers a choice of the Peng-Robinson or the NIST extended corresponding states model (EXCST) for the calculation of phase properties. The calculations of thermodynamic phase properties of hydrocarbon mixtures used the recommended (default) NIST extended corresponding states mode; to calculate vapour-liquid equilibria the Peng-Robinson model was used.

For the cryogenic cycle calculation, the multiparameter-cycle optimization method and the gradient-descent method on the rapid sparse computational grid and the dense computational grid was used. On this slide, the model of the rapid calculations on the sparse computational grid and on the dense computational grid (Dalakov et al., 2019; Randall, 1985).



a) b)

Figure 1. a) Simplified flow diagram of a cryogenic system. C-1, C-2 - circulation compressors; Exp - turbo expander; Chil. - chillers; Hex-I, Hex-II - heat exchangers, RHex - recuperative heat exchanger. b) - conditional p-h and T-s diagrams for the Linde-Hampson mixed cycle and the Bell Coleman cycle, respectively

3. MATHEMATICAL FORMULATION AND RESULTS OF PRELIMINARY CALCULATIONS

The results of preliminary calculations of the cryogenic system energy efficiency are presented in Figure 1. The cooling capacity coefficients for several operating modes of the system and a number of working mixtures of the cryogenic stage were determined as well.

By definition, the cooling coefficient of performance (refrigeration capacity) of the system shown in Figure 1a:

$$\varepsilon_{sys} = \frac{Q_{o\_cryo}}{W_{cryo} - W_{det} + W_{ref}}, \tag{1}$$

were: Q_{o_cryo} – refrigeration capacity of the cryogenic stage of the system; W_{cryo} , W_{ref} , W_{det} - compressors' performance for cryogenic and refrigeration stages and the expander performance, respectively.

The refrigerating coefficients of each of the stages of the cascade are written as follows:

- for cryogenic stage:

$$\varepsilon_{cryo} = \frac{Q_{o\_cryo}}{W_{cryo} - W_{det}}, \tag{2}$$

- for refrigeration stage:

$$\varepsilon_{ref} = \frac{Q_{o\_ref}}{W_{ref}}, \tag{3}$$

were: Q_{o_ref} – refrigeration capacity of the refrigeration stage. The energy parameters of the cooling stages are interdependent and interconnected by the following expression:

$$Q_{o\_ref} = Q_{o\_cryo} + W_{cryo} - W_{det} , \tag{4}$$

Taking into account equations (2)-(4) the expression for the cooling coefficient of the system ε_{sys} through the refrigeration coefficients of the cooling stages ε_{cryo} and ε_{ref} will be as follows:

$$\varepsilon_{sys} = \frac{\varepsilon_{cryo} \cdot \varepsilon_{ref}}{\varepsilon_{cryo} + \varepsilon_{ref} + 1}, \tag{5}$$

The maximum possible value of the refrigeration coefficient of performance for a given system (are not refrigeration coefficient of performance ε_{C_sys}) will be:

$$\varepsilon_{C\_sys} = \frac{T_8}{T_{amb} - T_8}, \tag{6}$$

were: T_{amb} - ambient temperature (290 K); T_8 - set temperature at the outlet of the cryogenic stage of low-temperature heat exchanger.

To evaluate the thermodynamic efficiency of the system the values of ε_{cryo} and ε_{ref} considering irreversible losses in cycles were calculated. In this case, the energy parameters of the cycles were calculated using the following equations:

$$Q_{cryo} = \dot{m}_{cryo}\left(h\left(T_8, p_8, C_{cryo\_i=1..n}\right) - h\left(T_7, p_7, C_{cryo\_i=1..n}\right)\right); \tag{7}$$

$$W_{\det} = \dot{m}_{cryo}\eta_{\det}\left(h\left(s_6, p_6, C_{cryo\_i=1..n}\right) - h\left(s_6, p_7, C_{cryo\_i=1..n}\right)\right) = \dot{m}_{cryo}\left(h\left(s_6, p_6, C_{cryo\_i=1..n}\right) - h\left(s_7, p_7, C_{cryo\_i=1..n}\right)\right); \quad (8)$$

$$W_{cryo} = \dot{m}_{cryo}\eta_{compr\_cryo}\left(h\left(s_1, p_2, C_{cryo\_i=1..n}\right) - h\left(s_1, p_1, C_{cryo\_i=1..n}\right)\right) = \dot{m}_{cryo}\left(h\left(s_2, p_2, C_{cryo\_i=1..n}\right) - h\left(s_1, p_1, C_{cryo\_i=1..n}\right)\right); \quad (9)$$

$$Q_{ref} = \dot{m}_{ref}\left(h\left(T_{M6}, p_{M6}, C_{ref\_i=1..n}\right) - h\left(T_{M5}, p_{M5}, C_{ref\_i=1..n}\right)\right); \quad (10)$$

$$W_{ref} = \dot{m}_{ref}\eta_{compr\_ref}\left(h\left(s_{M1}, p_{M2}, C_{ref\_i=1..n}\right) - h\left(s_{M1}, p_{M1}, C_{ref\_i=1..n}\right)\right) = \dot{m}_{ref}\left(h\left(s_{M2}, p_{M2}, C_{ref\_i=1..n}\right) - h\left(s_{M1}, p_{M1}, C_{ref\_i=1..n}\right)\right), \quad (11)$$

where: T, p, h and s – temperature, pressure, specific enthalpy and entropy of the working mixture of the refrigerant; $C_{cryo\_i=1..n}$, $C_{ref\_i=1..n}$ - circulating refrigerant compositions circulating refrigerant compositions *i=1..n* - component of working mixtures in the corresponding refrigeration stage; $\dot{m}_{cryo}$, $\dot{m}_{ref}$ - the mass flow rate of the working mixture in the corresponding refrigeration stage; $\eta_{\det}$, η_{compr_cryo} and η_{compr_ref} - performance factors (efficiency) of the expander, compressors of the cryogenic and refrigeration stages, respectively; variable indices correspond to indices in Figure 1; the expression like $h\left(s_6, p_6, C_{cryo\_i=1..n}\right)$ means the calculation of the specific enthalpy depending on two independent thermodynamic variables (in this case, entropy and pressure) and the composition of the working mixture using the equation of state.

The working mixture flow separation $\dot{m}_{cryo}$ at point 3 (see Figure 1) of the cryogenic stage, which divided on two flows $\dot{m}_{cryo\_1}$ and $\dot{m}_{cryo\_2}$, and later $\dot{m}_{cryo\_2}$ is cooled in the heat exchanger Hex-1, due to the cold of the backflow of the refrigerant, is shown in the equation for flow mixing:

$$\dot{m}_{cryo}h\left(T_5, p_5, C_{cryo\_i=1..n}\right) = \dot{m}_{cryo\_1}h\left(T_{3\_1}, p_{3\_1}, C_{cryo\_i=1..n}\right) + \dot{m}_{cryo\_2}h\left(T_{3\_2}, p_{3\_2}, C_{cryo\_i=1..n}\right), \quad (12)$$

this equation is used to calculate the temperature T5 of the hot flow at the inlet to the recuperative heat exchanger Hex-II of the refrigeration stage.

The calculation of the flow temperatures at the outlet of the Hex-II and RHEx heat exchangers included both the calculation of the total heat balance of the heat exchanger and the calculation of the T-q diagram mandatory.

With using the above equations (1) - (12), preliminary estimation calculations of both stages of the cryogenic system were carried out and the required compositions of the working components were selected to achieve the specified operating temperatures.

The main results of the calculations are shown in Table 1. During the thermodynamic calculation of both cycles with different refrigerant (working substance), the same heat load of 0.5 kW was considered and supplied to the cryogenic stage. The work also assessed the degree of thermodynamic perfection of whole cryogenic cycle in relation to the ideal refrigeration Carnot cycle, which for this system is about 0.84.

As can be seen from Table 1, the highest refrigeration coefficient is possessed by cycles in which cooling is realized using a mixed refrigerator operating according to the Linde-Hampson scheme.

Table 1. The most representative results of system calculations

№	The type of analyzed cryogenic system	Cycle's coefficient of performance	Carnot coefficient	Thermodynamic degree of performance
1	He cryogenic @ T=22.4 K without precooling	0.015	0.084	0.018
2	He cryogenic @ T=22.4 K with N_2 precooling.	0.012	0.084	0.14
3	Ne-He @ 22.4 K, with N_2 precooling	0.011	0.084	0.13
4	H_2 @ 22.4 K with LN_2 precooling	0.02	0.084	0.24
5	^{2}H-Ne-He @ T=22.4 K without precooling.	0.02	0.084	0.23
6	^{2}H-Ne-He @ T=22.4 K with mix ref. precool @ 96.6 K (subcooling flow rate - 0.1)	0.023	0.084	0.28
7	^{2}H-Ne-He @ T=22.4 K with mix ref. precool @ 96.6 K (subcooling flow rate - 0.2)	0.025	0.084	0.3
8	^{2}H-Ne-He @ T=22.4 K with mix ref. precool @ 96.6 K (subcooling flow rate - 0.4)	0.031	0.084	0.37
9	^{2}H-Ne-He @ T=22.4 K with mix ref. precool @ 96.6 K (subcooling flow rate - 0.6)	0.039	0.084	0.47

These calculations did not take into account heat losses from the environment and hydraulic losses in devices that are present in real systems.

Figures 2 and 3 show graphs of the calculated system coefficient of a performance degree. Figure 2 also shows the refrigeration coefficients of other calculated cryogenic systems from Table 1. As can be seen from the graphs, the refrigeration coefficient of the cryogenic system increases when using a refrigeration cascade based on the Linde-Hampson refrigeration cycle.

Based on the results of the calculations from Table 1 and the graphs shown in Figures 2, 3, it is obvious that the cycles in which precooling is used have a higher degree of thermodynamic perfection. This is due to the fact that obtaining and using moderate cold for precooling in cryogenic plants requires an order of magnitude less work. As a result, the refrigerating factor of the same cryogenic cycle with intermediate cooling is higher than the refrigerating factor of a simple cycle without intermediate cooling.

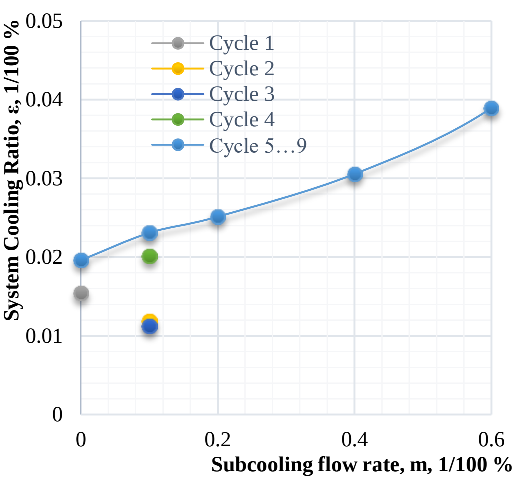


Figure 2. The System Cooling Ratio for different cryogenic cycles. The figures in the legend correspond with figures/numbers of the cryogenic cycles in Table 1.

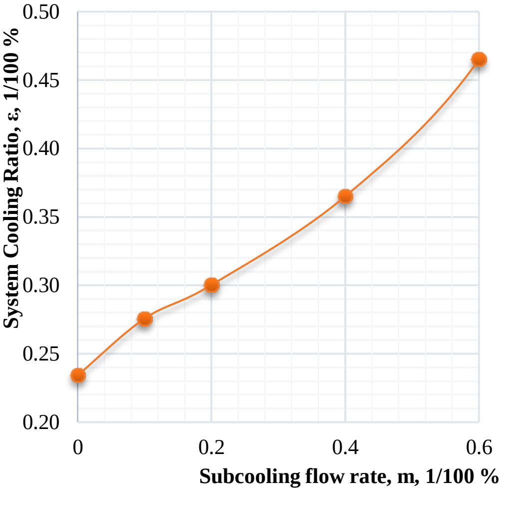


Figure 3. The degree of thermodynamic perfection of the calculated cryogenic system. A graph showing the dependence of the degree of thermodynamic perfection for a cycle with two cryogenic and refrigeration stages.

4. INNOVATIVE PART OF THE WORK

In previous studies of working systems at a temperature level of 20...50K a neon, helium and hydrogen mixtures were used for cryostatting (Quack et al., 2015; Kloeppel et al., 2017; Kloeppel et al., 2015; Zhoutuo et al., 2018). In these papers, the work of cryogenic systems on a mixture of neon with helium and hydrogen-based on balance equations was investigated. However, the classical approach to the description of such systems based on balance and exergy equations has one very significant drawback. This approach idealizes the system and neglects the complex interaction of some elements of the system with others. However, when e. g. there is a phase transition, the equations of state do not completely describe the real system conditions. The outlet temperatures of the flows from heat exchangers determine each other. This has to be taken into account especially in systems operating on mixtures of substances, where the relationships between pressures and temperatures of phase transitions are distorted. So, the mathematical model cannot provide accurate results. Hence, to describe such systems, a multi-parameter method describing the elements with the help of nonlinear equations can be solved numerically. Also, in previous research studies, the deuterium was not considered as a refrigerant in working low-temperature mixtures. It was the use of deuterium that showed a significant increase in the refrigeration capacity of the cryogenic cycle (see Table 1).

Thus, an innovative solution in present paper is using the ^{2}H as a component for the low temperature refrigerant mixtures. The use of ^{2}H increases the thermodynamic efficiency of the refrigeration cycle, and its cost is slightly higher than neon, thus it does not affect the capital costs of the installation.

The second innovative solution/part in the work is the algorithm for the calculation and design assistance of the refrigeration system in which the working fluid, temperature hydraulic characteristics, and other parameters of the machine are calculated and defined. This algorithm has proven itself well in previous developments, and shows a very encouraging calculation result for this system for an operating temperature level of 30...50 K. The result of such calculations planned to use for the development of the refrigeration and low-temperature system for the isotope recovery systems (also for cooling, liquefaction of gas flows, and thermal stabilization system as well).

5. CONCLUSION

The result of the current work is a thermodynamic calculation of a cryogenic system operating at a temperature range of about 20...90 K and using a mixture: ^{2}H-Ne-He as the main working fluid. The proposed system uses an intermediate precooling implemented by the Linde-Hampson cycle using hydrocarbon mixtures as a refrigerant.

The main factor limiting the widespread use of ^{2}H and the as well neon in cryogenic technology is its high cost in comparison with helium. In connection with the growth in the consumption of neon in industries that are not related to cryogenics, the cost of production decreases, since the high cost of neon is associated with small volumes of its production. However, at the present time, the price of ^{2}H and neon is not so high as to neglect its use as a refrigerant. On the world market, the price of neon varies depending on the manufacturer within 0.05...0.06 € per liter of neon with a purity of 99.999 vol.%. A slightly higher value is for the ^{2}H. Price for ^{2}H on the world market which is on the level of about 0.08 ... 0.12 € per liter of ^{2}H.

The preliminary calculations show that the estimated volume of refrigerant needed for a refrigeration unit with a cooling capacity of 500 W for operation at a temperature level of 30 K is only about 2...3.5 kg, which corresponds to the cost within 1000...1500 Euros. Therefore, the use of neon and ^{2}H as a refrigerant will be beneficial and will not significantly affect the cost of the installation.

The reason why these refrigeration cycles are still not used and do not find application is associated with the fact that when calculating and designing the units based on such refrigeration cycles, it is necessary to solve several optimization problems associated with the choice of the percentage ratios of the refrigerant components for both cooling cascades (pre-cooling cycle and low-temperature cycle). Also, tasks related to thermodynamic optimization of the cycle and the selection of components that often have to work at increased loads in the phase transition zones, etc. However, this calculation algorithm has already been used in the design of low-temperature units operating at a temperature level of up to 80 K, and has shown a high reproducibility of the computational and physical model.

In the future, it is planned to create a functional model of this system to confirm the calculation algorithm.

The presented technical solution provides a number of advantages over existing systems operating at a temperature level from 20 K to 90 K, and is distinguished by relatively high energy efficiency, environmental friendliness, fire safety, compactness and economic competitiveness in the modern market.

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