

# Performance Analysis of Joule-Thomson Cryocooler Supplied with Gas Mixture

M. Chorowski, A. Piotrowska

Wroclaw University of Technology  
Wybrzeze Wyspianskiego 27, Poland

## ABSTRACT

Joule-Thomson (J-T) cryocoolers working in open and closed cycles and supplied with gas mixture have been studied theoretically and experimentally for a variety of applications. This paper presents the thermodynamic analysis of the processes observed in the J-T coolers filled with gas mixtures. Mixture stability and solid phase origin is discussed. Special attention is paid to the optimization analysis of the mixture composition.

The application of the cooler depends on the temperature level of cooling power. The cooler can be coupled with “warm” gas separation technology like membrane or PSA to produce a chosen mixture component in the liquid phase. The analysis of the system performance results based upon the overall energy consumption are presented and discussed. The paper also gives the results of the cooler tests, as well as introduces the concept of small, independent generators of liquid nitrogen and oxygen.

## INTRODUCTION

Small capacity liquefiers and refrigerators based upon a Joule-Thomson cycle are competitive in domains where high reliability and relatively low investment cost are essential. The application of gas mixtures has significantly improved their relatively low thermodynamic efficiency and enabled the use of standard refrigerator compressors. In spite of the fact that mixture supplied Joule-Thomson refrigerators have been studied for over 40 years and the concept has been applied both in small scale refrigeration and in large capacity natural gas liquefiers, there are still doubts concerning the stability of operation of such refrigerators. The stable performance of the refrigerator which guarantees a nominal cooling power and temperature profile along the heat exchanger is strongly dependent on the mixture composition. A mixture well matched to a required cooling load of the refrigerator should be characterized by the following features:

1. High isothermal throttling effect of the isenthalpic expansion  $\Delta h_T$ , even for a relatively low compression pressure, to allow the use of commercially available compressors.
2. The lowest evaporation temperature should not exceed the value resulting from the refrigerator application field, e.g. to guarantee natural gas (methane) liquefaction it should be near 100 K.
3. The compression temperature should not exceed 393 K (120°C). In the case of closed systems this enables the use of standard refrigeration compressors.

4. The liquid phase should be stable and the solid phase should not originate in the whole temperature range (with the exemptions discussed below).

A proper choice of the mixture components and their concentrations requires the knowledge of Vapor-Liquid (V-L) phase equilibrium and the stability of the liquid phase. The V-L phase equilibrium can be calculated from the condition that the fugacities of the mixture components are equal in all phases:

$$\begin{aligned} f_1^1 &= f_1^2 = \dots = f_1^m \\ f_2^1 &= f_2^2 = \dots = f_2^m \\ f_n^1 &= f_n^2 = \dots = f_n^m, \end{aligned} \quad (1)$$

The stability condition of the phases is given by:

$$\begin{vmatrix} \frac{1}{f_1} \frac{\partial f_1}{\partial X_1} & \frac{1}{f_1} \frac{\partial f_1}{\partial X_2} & \dots & \frac{1}{f_1} \frac{\partial f_1}{\partial X_{(n-1)}} \\ \frac{1}{f_2} \frac{\partial f_2}{\partial X_1} & \frac{1}{f_2} \frac{\partial f_2}{\partial X_2} & \dots & \frac{1}{f_2} \frac{\partial f_2}{\partial X_{(n-1)}} \\ \frac{1}{f_{(n-1)}} \frac{\partial f_{(n-1)}}{\partial X_1} & \frac{1}{f_{(n-1)}} \frac{\partial f_{(n-1)}}{\partial X_2} & \dots & \frac{1}{f_{(n-1)}} \frac{\partial f_{(n-1)}}{\partial X_{(n-1)}} \end{vmatrix} > 0, \quad (2)$$

The fugacity  $f_m$  of each component can be calculated from the Eq. (3):

$$\ln \frac{f_m}{z_m p} = \ln \gamma_m = \frac{1}{RT} \left[ \int_0^p \left( v_m - \frac{RT}{p} \right) dp + \int_0^p \left( \frac{\partial v_m}{\partial z_m} \right) dp - \sum_j z_j \int_0^p \frac{\delta v_m}{\delta z_m} dp \right], \quad (3)$$

where  $Z_i$  denotes molar concentration of the component in the mixture.

To calculate the Eq. 3 equation of state,  $f(Vm, p, T, Z_i) = 0$  must be known. The equation of state should take into the account the intermolecular binary interaction and variable mixing rules coefficients, like a modified cubic Redlich-Kwong equation.

## EXEMPTIONS FROM DESIRED MIXTURES FEATURES

There may be some exemptions from rule 4, like when the split of the liquid phase may increase the cooling capacity at the lowest temperature level, or a periodical formation of solid phase at the throttling valve may be used to engineer a self-regulating mechanism<sup>1</sup>. This specific feature has been observed during the operation of the miniature Joule-Thomson liquefier depicted in Fig. 1 which comprises a 5 layer Linde-Hampson recuperative heat exchanger. The micro-liquefier has been operated in an open system and has been fed from a gas bottle filled with a dedicated mixture.

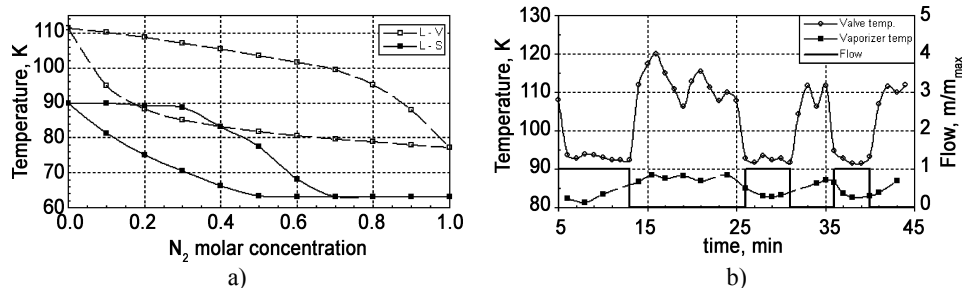
### Solid State Formation as a Flow Controller

Figure 2a presents the L-V and L-S phase equilibriums of the  $N_2$ - $CH_4$  binary mixture at 1 bar. It is evident that for the temperature of about 90 K and the  $N_2$  concentration between 0.2 – 0.4, a solid phase can occur. Such conditions may be encountered in a throttling zone, when a relatively high amount of liquid phase is accumulated in the evaporator, finally touching the throttling valve and cooling it down below the mixture freezing temperature. When the liquid level decreases and the valve gets warmed up, the flow starts again. The temperature in the vaporizer remains in the range 82 – 88 K (see Fig. 2b).

The described process of self-blocking of the flow can be used to enlarge the working time of micro-refrigerators supplied with gas from cylinders.



**Figure 1.** J-T microliquefier, length of the 5 layer heat exchanger - 78 mm, diameter - 11 mm.



**Figure 2.** Solid phase occurrence and the flow self-regulation in the Joule-Thomson micro-refrigerator supplied with  $N_2$ - $CH_4$  gas mixture; a) L-V and L-S phase equilibrium, b) dynamic characteristic<sup>1</sup>.

### Instability of the Liquid Phase

The mixture  $N_2$ - $CF_3Cl$  is characterized by a positive value of the determinant in Eqs. (2), only for the  $N_2$  concentration above 85%. Below 85% the liquid phase splits into two – see Fig. 3.

The instability of liquid phase leads to a minimum temperature in a vaporizer being very close to the temperature of the lower boiling component, what guarantees that some cooling power is available at very low temperature level and it can be matched to the requirements, e.g., the first step of a hydrogen microliquefier – compare Fig. 4.

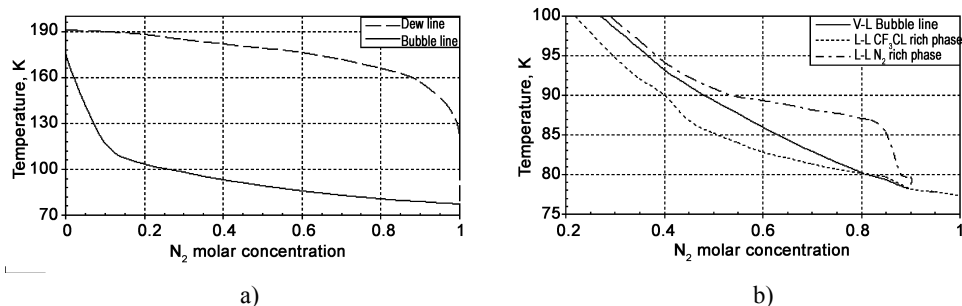
### HYBRID J-T SYSTEMS FOR GAS SEPARATION AND LIQUEFACTION

Joule-Thomson refrigerators fed with gas mixtures and working in closed cycles are especially suitable for providing the cooling power required to liquefy small amounts of gases like nitrogen or oxygen. The gases can be delivered in cylinders or separated from air. Coupling of J-T refrigerators with warm gas separation technologies like adsorption or polymeric membrane is especially promising. Figure 5 presents schematically exemplary hybrid systems for both liquid nitrogen and liquid oxygen production in small quantities.

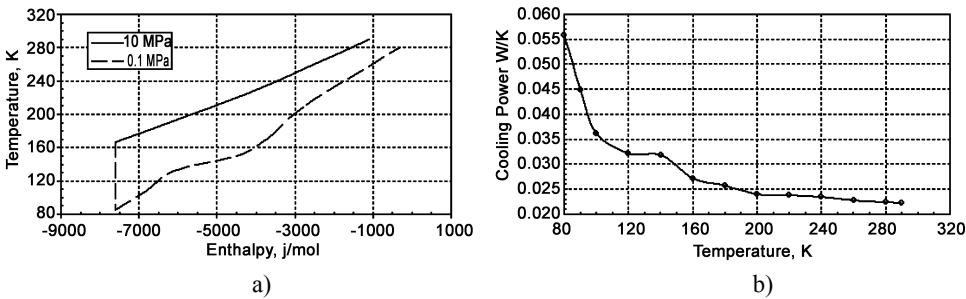
### Separation and Liquefaction of Nitrogen

Figure 6 depicts a conceptual scheme of a small capacity system for liquid nitrogen production. The system couples a Joule-Thomson refrigerator with a polymeric membrane air separator. The coupling element is a recuperative heat exchanger ( $N_2$ -MIX).

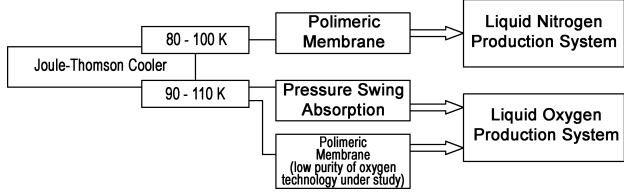
Compressed, dried and purified atmospheric air (process 1\*-2\*-3\*, see Fig. 7a) enters the polymeric membrane tube. A dominant fraction of nitrogen is stopped by membrane fibers creating a high-pressure product stream (process 3\*-4\*). Oxygen, carbon dioxide, water vapor and the residual amount of nitrogen pass through the membrane. The gases are relieved as a waste stream to environment. The separated and compressed nitrogen is cooled down (process 4\*-5\*) and liquefied (process 5\*-6\*) inside the heat exchanger ( $N_2$ -MIX). A required cooling power for the process 4\*-5\*-6\* is produced by a



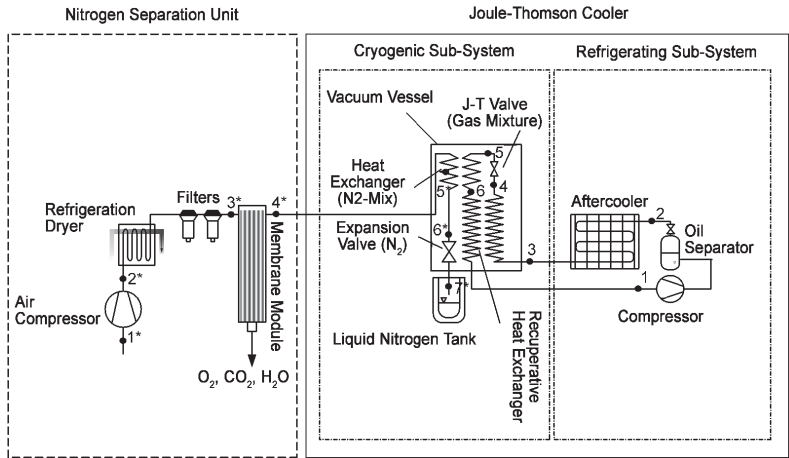
**Figure 3.** L-V equilibrium of a  $N_2$  -  $CF_3Cl$  mixture a) one liquid phase, b) with split liquid phase<sup>1</sup>.



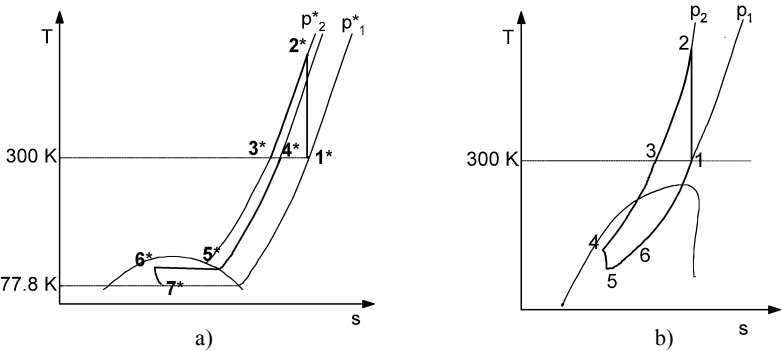
**Figure 4.** Cycle of Joule-Thomson liquefier supplied with 92%N<sub>2</sub> - 8%CF<sub>3</sub>Cl mixture – a), first step cooling power density of 0.3 W @ 20.3 K hydrogen microliquefier – b)¹.



**Figure 5.** Classification of hybrid systems for liquid nitrogen or liquid oxygen production



**Figure 6.** Hybrid system for liquid nitrogen production



**Figure 7.** Processes in T-s diagram, a) nitrogen separation unit, b) Joule-Thomson cooler

closed-cycle Joule-Thomson refrigerator supplied with gas mixture. The J-T cycle is presented on T-s diagram in Fig. 7b. A high-pressure liquid nitrogen is throttled to atmospheric pressure (process 6\*-7\*) and is partly flashed. The remaining liquid can be removed from the system to an external dewar vessel. Vapors can be used to precool the separated nitrogen entering the heat exchanger.

### Mechanism of the Particle Transport through the Membrane

Membrane separation technology is broadly recognized and vastly used. Dense, nonporous polymeric membranes are applied for air separation process,. Commercially available units produce nitrogen with a purity of 95-99.9% and a compression pressure not exceeding 20 bar.

The stream of two or more components is separated by a semipermeable barrier (fibers) through which molecules of one component move easier than the molecules of other components. In chemical engineering nomenclature three process streams are recognized: **feed stream** (stream to be separated), **retentate** (part of the feed stream stopped by the membrane material) and **permeate** (the molecules that have passed through the membrane fibers). Figure 8 shows schematically basic streams of membrane separation process.

The solution-diffusion model (based on Fick's and Henry's Laws) of Lonsdale, Merten, and Riley<sup>2</sup> is commonly applied to analyze the mechanism of molecules transport through the membrane. A mathematical description of the tested membrane is based on the following assumptions:

- Mass transport is analyzed only in nonporous layer. The thickness of the active layer of polysulfone fibers is of 2mm.
- Feed stream (air) is treated as a two component ideal mixture of nitrogen and oxygen.
- The influence of the concentration polarization phenomenon and of the Joule-Thomson effect are negligible.
- There is no pressure loss in support layer and the molecules are not accumulated inside the membrane material.
- Retentate (nitrogen) pressure is equal to the pressure of the feed mixture (air).

To model the membrane nitrogen separation process, the Eqs. (4) have been applied:

$$\begin{cases} x_{O_2}^R = \frac{(1-x_{O_2}^R)(x_{O_2}^F - \theta x_{O_2}^P)}{\theta(1-x_{O_2}^P) + x_{O_2}^F - 1} \\ \alpha_{O_2/N_2} = \frac{x_{O_2}^P/x_{O_2}^R}{(1-x_{O_2}^P)/(1-x_{O_2}^R)} \\ \alpha_{O_2/N_2} = \alpha_{O_2/N_2}^* \left[ \frac{x_{O_2}^R(\alpha_{O_2/N_2}-1) - r \cdot \alpha_{O_2/N_2}}{x_{O_2}^R(\alpha_{O_2/N_2}-1) - r} \right] \end{cases} \quad (4)$$

where  $x_{O_2}^F$ ,  $x_{O_2}^R$ ,  $x_{O_2}^P$  are mole fractions of oxygen in the feed stream, retentate, and permeate, respectively;  $\theta$  is the distribution coefficient;  $\alpha_{O_2/N_2}$  is a separation factor;  $\alpha_{O_2/N_2}^*$  is the ideal separation factor, and  $r$  is the ratio of permeate and feed stream pressures.

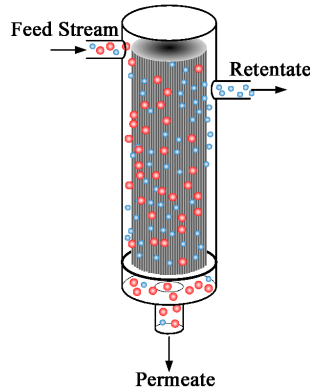


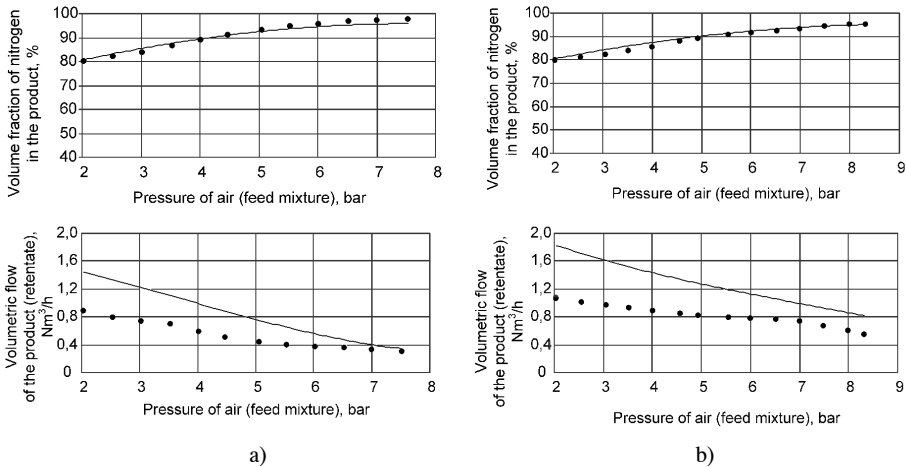
Figure 8. Membrane module

Equations (4) contain four unknowns:  $x^R_{O_2}$ ,  $x^P_{O_2}$ ,  $q$ ,  $a_{O_2/N_2}$ . The value of  $\theta$  lies between 0 and 1. The results of calculations and measurements are presented in Figure 9.

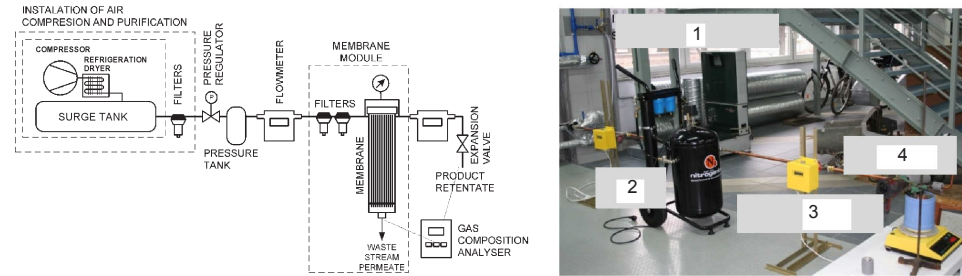
The membrane air separation cycle has been tested to identify the influence of the feed stream pressure on the separated nitrogen purity. Due to the cooling power of 100 W produced by the Joule-Thomson cooler, the maximum flow of air cannot exceed 1.2 Nm<sup>3</sup>/h. On the other hand, the air inlet pressure should not be lower than 7 bar to achieve a minimal level of nitrogen purity of 95% (molar concentration). For pressures higher than 7 bar the purity of nitrogen product still improves. The test stand is shown in Fig. 10.

**Joule-Thomson Cooler**

It has been shown that the separated nitrogen pressure should not decrease below 7 bar. To cool down and liquefy the nitrogen gas initially pressurized to 7 – 20 bar, the cooling power has to be produced within the temperature range from 80 K to 100 K. Nitrogen can be considered as a working fluid of a dedicated J-T cooler, but then very high working pressures (like 200 bar) and very expensive compressors would be required. To decrease the pressure of working medium and increase the isothermal throttling effect  $Dh_T$ , pure N<sub>2</sub> should be replaced with mixture of nitrogen and hydrocarbons. The replacement of N<sub>2</sub> with an exemplary binary mixture of 50% N<sub>2</sub> – 50% C<sub>3</sub>H<sub>8</sub> increases the isothermal throttling effect  $Dh_T$  by about 300%. Applying gas mixture both decreases temperature difference between high- and low-pressure side of recuperative heat exchanger (lowering the exergy losses), and enables the use of commercially available hermetic refrigeration compressors, lowering significantly the investment cost.



**Figure 9.** The results of the mathematical analysis (line) and the measurements (points) a) for feed (air) stream of 1Nm<sup>3</sup>/h, b) for feed (air) stream of 1.2 Nm<sup>3</sup>/h



**Figure 10.** Test stand of membrane air separation system, 1: installation for air compression and purification, 2: membrane module, pressure tank, 3: flowmeter, 4 expansion valve

### Parameter Optimization of Nitrogen Separation and Liquefaction System

A total work required to separate and liquefy nitrogen in a hybrid system as (depicted in Fig. 6) can be calculated from Eq. (5):

$$W_S = W_M + W_C, \quad (5)$$

where  $W_M$  – work of the nitrogen separation cycle,  $W_C$  – work of the refrigeration cycle.

Minimal work necessary to separate nitrogen from air in a membrane separation process is described by Eq. (6)<sup>3</sup>,

$$W_M = \dot{n}_F RT \ln \left( \frac{x_{N_2}^F p_F}{x_{N_2}^P p_P} \right), \quad (6)$$

where  $\dot{n}_F$  is mole stream of air,  $R$  is gas constant,  $T$  is temperature,  $x_{N_2}^F$  is mole fraction of nitrogen in air,  $p_F$  is air pressure,  $x_{N_2}^P$  is mole fraction of nitrogen in the permeate,  $p_P$  is the pressure of the permeate.

Assuming that the permeate pressure is equal to 1 bar, and the pressure drop inside the membrane module is negligible<sup>4</sup>, the work of the separation process depends on the feed stream pressure only. The first model of the cooler can be a Carnot refrigerator. Work of the Carnot cycle can be described by Eq. (7)

$$W_C = \frac{\dot{Q}}{\varepsilon} = \dot{Q} \frac{T_H - T_C}{T_C}, \quad (7)$$

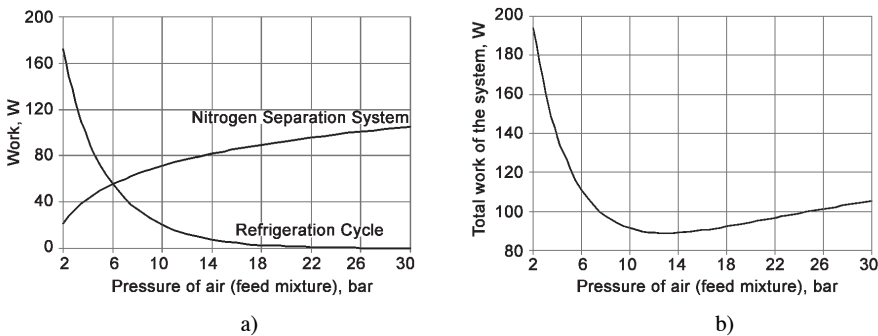
where  $\dot{Q}$  is the cooling power,  $T_H$  is the temperature of the environment and  $T_C$  is the temperature of the cooling effect.

According to the Eq. (7), the energy consumption of the cooler decreases with the increase of the temperature level providing the cooling power. Therefore the increase of nitrogen pressure allows to increase the cooler temperature. This results in a decrease of the refrigerator driving power demand. Based on Eqs. (6) and (7), an optimization analysis has been performed, on the assumption that the refrigerator provides 90 W of cooling power. The results are presented in Fig. 11.

The following conclusions have been formulated based on the results of the simplified optimization analysis:

- inlet feed stream (air) pressure is the main parameter that influences the overall work of the system,
- minimum work of the system should be expected for air inlet pressure of about 12.5 bar, further increase of the pressure does not change the work significantly.

The analysis has been performed using a thermodynamic model of a Carnot refrigerator. A similar results are expected when the Carnot refrigerator is replaced with a real cooler, because in each case a COP depends on the low temperature level. According to the performed thermodynamic analysis, nitrogen separation and liquefaction hybrid system should be operated with the feed stream (compressed air) pressure 12 – 20 bar, the upper limit resulting from the compressor availability.



**Figure 11.** Results of the optimization analysis a) work of separate processes, b) pressure optimization

Mixture Composition Choice

To provide cooling power at the temperature range enabling nitrogen liquefaction, a gas mixture based on nitrogen and hydrocarbons (methane, ethane, propane) has to be used. The comparison of Joule-Thomson closed cycle supplied with pure gas and mixture is presented in Fig. 12 and in Table 1.

The R13 refrigerant ( $\text{CF}_3\text{Cl}$ ) could have been considered as a mixture component due to its very good thermodynamic properties. However, the Montreal Protocol regulations have withdrawn R13 from any applications in refrigeration or cryogenic devices<sup>5</sup>.

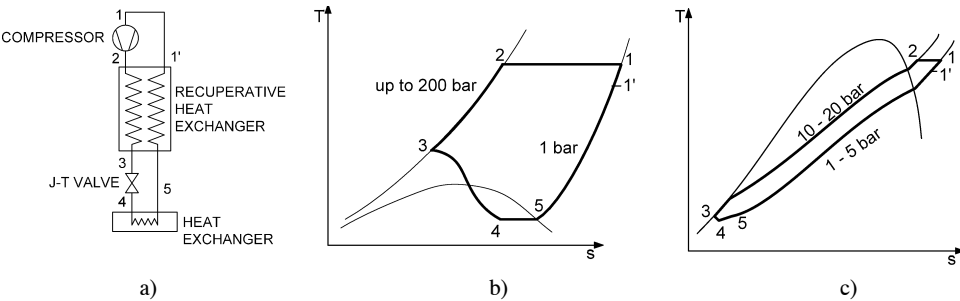
Figure 13 shows the scheme and the photo of the refrigeration device. The cooler comprises regular domestic and commercial refrigerator components (compressor, oil separator, condensing unit used as the after-cooler) with cryogenic technology (heat exchanger in vacuum insulation and needle valve used as the expansion device).

The mixture of 40% of nitrogen, 30% of ethane, and 30% of propane has been chosen based on the analysis of thermodynamic parameters of pure components and mixtures. The isothermal throttling effect  $\Delta h_T$  for 10 bar compression is 10.6 kJ/kg ( $\Delta h_T$  of pure nitrogen is only 1.98 kJ/kg for the same pressure change). Measurement results of the cooler dynamic characteristic and the temperature of the mixture leaving the compressor are presented in Fig. 14.

Minimal temperature after the throttling valve of 114 K was archived after 360 minutes of the cooler operation. The compression temperature did not exceed 110°C during the whole test, validating the possibility of the use of standard refrigeration compressors.

Separation and Liquefaction of Oxygen

The proposed refrigerator which provides 100 W of cooling power at the temperature range 90-110 K can be also used to cool down and liquefy the compressed oxygen. The combination of the Joule-Thomson



**Figure 12.** Thermodynamic processes of Joule-Thomson cycle, a) Joule-Thomson cycle b) pure nitrogen cycle on T-s diagram, c) gas mixture cycle on T-s diagram

**Table 1.** The comparison of Joule-Thomson cycle fed with pure gas and mixture

J-T cooler fed with:	Pure nitrogen	Gas mixture
Pressure of the working fluid	100 – 200 bar	10 – 20 bar
Boiling point of the working fluid	Constant 78 K	Variable 80 – 120 K
Phase transition inside the recuperative heat exchanger	NO	YES
Temperature difference on the cold end of the recuperative heat exchanger	70 – 90 K	5 – 15 K



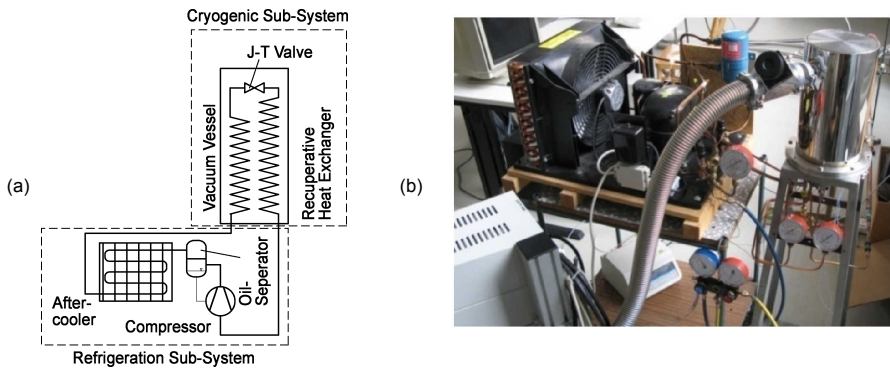


Figure 13. Joule-Thomson cooler: (a) schematic, and (b) photograph

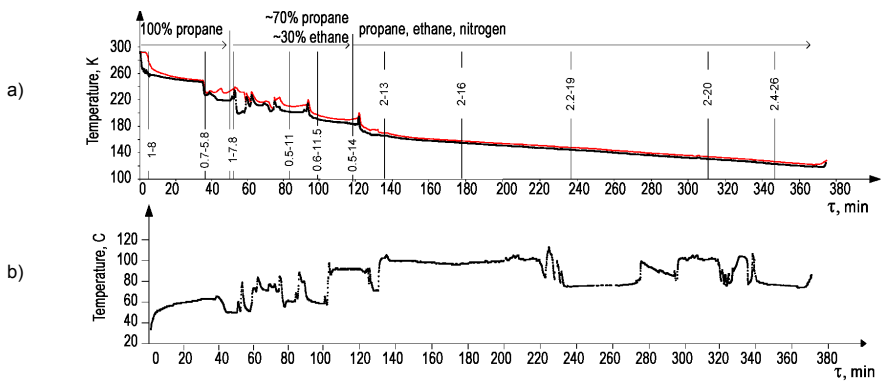


Figure 14. Dynamic characteristic of Joule-Thomson cooler supplied with nitrogen, ethane and propane gas mixture, a) temperature before and after the throttling valve, b) temperature of the mixture leaving the compressor.

cooler with a pressure swing absorption (PSA) oxygen generator allows to design a compact system producing small amounts of liquid oxygen. The conceptual scheme of the hybrid system is shown in Figure 15.

In the PSA unit, absorbers 1 and 2 work in turns. Gas flows through absorbers in absorption and regeneration phases are schematically shown by dotted and continuous lines. Compressed, purified, and dried atmospheric air flows through absorbers 1 or 2 where it is separated into two streams: compressed product (oxygen stream) and waste (nitrogen, carbon dioxide and oxygen stream) which is returned under atmospheric pressure to the environment. Oxygen stream (purity of 95%) flows to the heat exchanger where it is cooled down and liquefied under high pressure. Liquid oxygen, partly flashed due to the throttling process to the atmospheric pressure, can be collected in a dewar vessel.

Test stand of the hybrid oxygen production system is under commissioning at the Wrocław University of Technology. The Joule-Thomson cooler has been updated with a variable rotation compressor and has been preliminary tested with a nitrogen-ethane-methane mixture. The heat exchanger coupling to the PSA unit with the Joule-Thomson cooler is in test phase. Test stand of the PSA and the Joule-Thomson cooler is shown in Fig. 16.

ACKNOWLEDGMENTS

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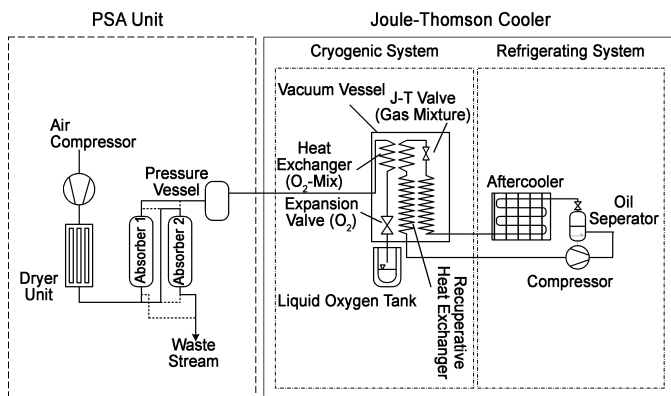


Figure 15. Scheme of oxygen production system

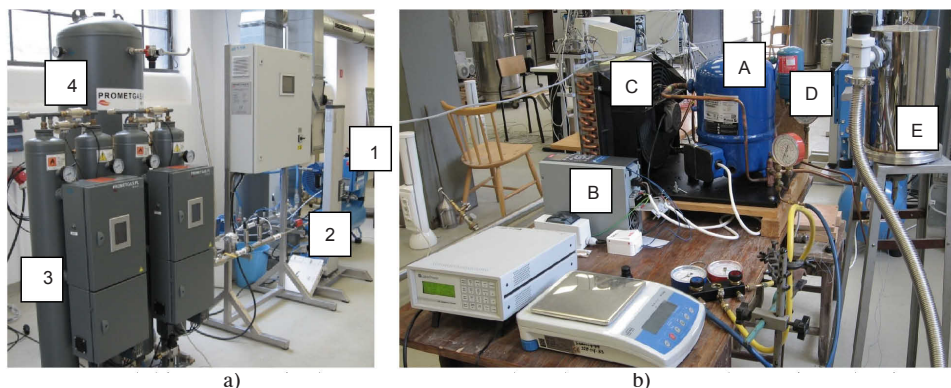


Figure 16. Hybrid oxygen production system a) PSA unit 1: air compressor, 2: dryer unit, 3: absorbers, 4: pressure vessel, b) Joule-Thomson cooler A: hermetic compressor, B: frequency converter, C: after-cooler, D: oil separator, E: cryogenic heat exchanger

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