ALTERNATIVE SOLUTIONS TO OPTIMALISATION OF THE GASSING-UP OPERATION AFTER TANKS INERTING USING PRESSURE SWING ADSORPTION (PSA) AND MEMBRANE TECHNIQUES

ALTERNATYWNE ROZWIĄZANIA DLA OPTYMALIZACJI PROCESU ZAGAZOWANIA ZBIORNIKÓW ŁADUNKOWYCH PO INERTOWANIU W ODNIESIENIU DO PSA (*PRESSURE SWING ADSORPTION*) I TECHNOLOGII MEMBRANOWEJ

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Abstract: The article constitutes the introduction to finding a solution to a problem concerning carrying gassing-up operation in a more efficient way in terms of loosing ethylene cargo. To begin with, the impact of nitrogen presence on ethylene cascade cycle's technical work and cooling capacity has been described. Further, the results of investigation into methods of nitrogen removing from cargo tanks after gassing-up have been presented. Possibility of pressure swing adsorption (PSA) and membrane techniques use has been analyzed with reference to ethylene carriers.

Keywords: gas separation, pressure swing adsorption, membrane technology, nitrogen-ethylene composition.

Streszczenie: Artykuł stanowi wprowadzenie do rozwiązania problemu przeprowadzenia operacji *gassing-up* w sposób bardziej efektywny w odniesieniu do znacznych ilości „traconego" ładunku. W pierwszej kolejności opisano wpływ obecności azotu na pracę obiegu. W dalszej części przeanalizowano dostępne metody usunięcia azotu podczas operacji *gassing-up*. Opisano metody PSA (*Pressure Swing Adsorption*) oraz membrany i przeanalizowano je w odniesieniu do etylenowców.

Słowa kluczowe: separacja gazów, technologia membranowa, mieszanina azot-etylen.

1. INTRODUCTION

Ethylene carriers are semi-refrigerated vessels intended for carriage cargoes like LPG, ammonia, VCM, but primarily for carriage ethylene. The problem of ethylene carriage during the voyage by the sea appears during gassing-up operation after tanks inerting. The process of inerting relies on introducing nitrogen to tanks in order to make a non-flammable atmosphere inside. The gassing-up operation is aimed at pushing the nitrogen out of tanks before cooling the cargo of ethylene [ChemTech, Ship owner's documentation 2015]. Nonetheless, because of similar densities of both gases and the absence of permanent parameters and work conditions the gassing-up process is performed in a very ineffectual way during which huge quantity of ethylene is vented to the atmosphere or returned to shore (mixed with nitrogen). Both operations have been in-depthly described in paper [Wieczorek 2017].

2. THE IMPACT OF NITROGEN PRESENCE ON ETHYLENE CASCADE CYCLE'S TECHNICAL WORK AND COOLING CAPACITY

The reason of problems related to the ethylene condensing pressure in cascade cycle is the presence of nitrogen crowded into tanks during inerting operation [Nanowski 2016]. During gassing-up operation 'heavier' gas is crowded into the tank by a lower purge line to push out a 'lighter' gas [Ship owner's documentation 2015]. Density of a gas depends on its temperature [Mieczyński 2003]. In the end, in case of ethylene and nitrogen, both gases, being at the same temperature have very similar densities to each other. A very minor difference of density between ethylene and nitrogen leads to difficulties to carry the gassing-up operation on properly [Nanowski 2016]. Densities of ethylene and nitrogen in regard to different temperatures are correlated in Table 1.

Table 1. Ethylene and nitrogen density [Nanowski 2016]
Tabela 1. Gęstości etylenu oraz azotu [Nanowski 2016]

Temperature (°C)	ETHYLENE (kg/m³)	NITROGEN (kg/m³)	Temperature (°C)	ETHYLENE (kg/m³)	NITROGEN (kg/m³)
0	1,2456	1,2344	-100	2,0043	1,9546
5	1,2227	1,2121	-95	1,9442	1,8990
10	1,2006	1,1907	-90	1,8877	1,8465
15	1,1793	1,1699	-85	1,8345	1,7969
20	1,1588	1,1499	-80	1,7843	1,7498

Analyzing particular components of the whole system may be drawn a few conclusions. First of all, according to the Raoult's law [Serwiński 1982], the presence of nitrogen does not increase the pressure in tanks. In contrast, analyzing

inter-stage cooler of the cargo compressor, which decreases temperature of a vapor after first stage compression and sub-cools the ethylene condensate up to approximately minus 65°C, ascertained that the presence of nitrogen has substantive influence on retaining equilibrium of liquid ethylene pressure. Another component is cargo receiver, temperature of ethylene in receiver is about minus 35°C, nonetheless condensation pressure amounting 18,5 bar g is much too low to condense vapor mixture. Here is why. If in liquid composition stays 1 fraction of nitrogen in 10.000 fractions of the mixture, in vapor phase will be 1 fraction of nitrogen in 100 fractions of the mixture (Table 2). Along with the growth of nitrogen fraction, bubble pressure also goes up [Ship owner's data 2015].

Table 2. *Incondensables in ethylene-nitrogen compositions [Nanowski 2016]*

Tabela 2. Zawartość nieskroplonych części w mieszaninie etylen-azot [Nanowski 2016]

Conditions	Mixture (liquid) composition (Mass)		Results	Vapor fractions (Bubble) (Mass)	
Temperature (°C)	ETHYLENE	NITROGEN	Bubble pressure (bar g)	ETHYLENE	NITROGEN
-95	0,9991	0,0009	0,82	0,91	0,09
-95	0,9993	0,0007	0,78	0,93	0,07
-95	0,9995	0,0005	0,75	0,95	0,05
-95	0,9997	0,0003	0,71	0,97	0,03
-95	0,9998	0,0002	0,69	0,98	0,02
-95	0,9999	0,0001	0,67	0,99	0,01
-95	1,0000	0,0000	0,65	1,00	0,00

Due to the fact that discharge of the second stage of the compressor is limited to 19 bar g, there is no possible way to evaluate the amount of nitrogen mixed with ethylene during its trip to cascade cycle. As presented in Table 3, for tank temperature of minus 40°C, more than 2 fractions of nitrogen in 100 fractions of the mixture results in the pressure impossible to work at by the compressor [Ship owner's data 2015].

Table 3. *Incondensables in mixture vapor composition [Ship owner's data 2015]*

Tabela 3. Części nieskroplone mieszaniny w postaci pary [*Ship owner's data* 2015]

Conditions	Mixture vapor composition (Mass)		Results
Temperature (°C)	ETHYLENE	NITROGEN	Bubble pressure (bar g)
-40	0,97	0,03	21,44
-40	0,98	0,02	18,81
-40	0,99	0,01	16,17
-40	1,00	0,00	13,52

Furthermore, growth of the condensation pressure simultaneously makes decline of refrigeration capacity [Bohdal, Charun and Czapp 2003] what is contrary to the carrier's purpose and mechanism of action.

## 3. METHODS OF NITROGEN REMOVING FROM CARGO TANKS DURING GASSING-UP OPERATION

To a gas recovery from gas mixtures, compound among N_2, CO, NH_3, CO_2, CH_4, C_2H_4 and higher hydrocarbons, membrane techniques, pressure swing adsorption (PSA) plant and cryogenics methods are used [Białecka and Nowak 2006]. There is also other possibility – thermodynamics, but about this method there is the least information so far. In this paper, cryogenics methods will not be under discussion.

3.1. Pressure Swing Adsorption (PSA) plant

Processes carried with the use of adsorption phenomenon play a significant role among new techniques of gas separation and those already existing in industry. Particular case represents pressure swing adsorption [Bałys and Buczek 2007], mostly because of its simplicity and low operating costs [The Linde Group].

The PSA technology is based on physical binding of gas molecules to the adsorbent material. Force that acts between gas molecules and the adsorbent material depends on a few factors like a gas component, type of adsorbent material, operating temperature and partial pressure of the gas component [Białecka and Nowak 2006; The Linde Group]. The result of separation is based on differences within binding forces to the material of absorbent.

Figure 1 shows a qualitative ranking of the adsorption forces. Components such as hydrogen with a low polarity, are very volatile and practically impossible to be adsorbed. However, components like nitrogen and ethylene have higher polarity which makes them adsorbable [The Linde Group]. The process of adsorption is carried in very short cycles, 3–6 minutes, afterwards, the stream of gas is directed to the adsorber containing regenerated adsorbent, and used adsorbent is put under regeneration by lowering the pressure to the atmospheric pressure in adsorber, at that time, contamination impounded in adsorbent desorbs [Białecka and Nowak 2006]. Conventional PSA schematic is shown in Figure 2.
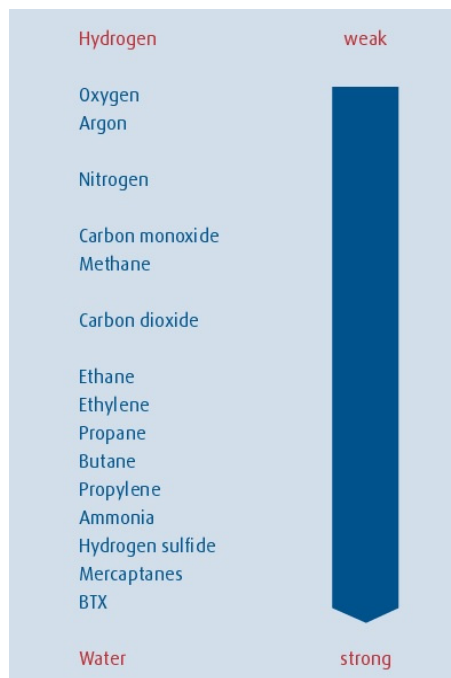
Fig. 1. A qualitative ranking of the adsorption forces [The Linde Group]

Rys. 1. Możliwość adsorpcji dla różnych związków chemicznych [The Linde Group]

In adsorption processes a basic problem is to select a proper adsorbent, that is, the one that would show suitably high selectivity in relation to components of separated mixture [Bałys and Buczek 2007]. In case of mixture ethylene and nitrogen balance selectivity would be higher for ethylene. Differences in kinematic diameters of molecules: ethylene 0,39 nm [Dudzińska 2016], nitrogen 0,364 nm show, that it should be possible to separate the mixture as a result of kinetic selectivity [Bałys and Buczek 2007].

As it was said previously, gas carriers dispose of PSA plants, what means that those plants could also be used to ethylene recovery during gassing-up operation. However, the problem constitutes adaptation the PSA plan to a separation of ethylene and nitrogen mixture. Force that acts between components of oxygen (used to produce nitrogen for inerting) is entirely different than acting force and adsorbent for ethylene and nitrogen mixture. What is more, in PSA plant for oxygen adsorber is filled with carbon molecular sieve [*Ship owner's data* 2015] and cannot be used for ethylene. It is extremely difficult or even impossible to achieve and overwhelmingly too expensive to adopt one plant for two different processes – nitrogen and unpolluted ethylene 'production'.
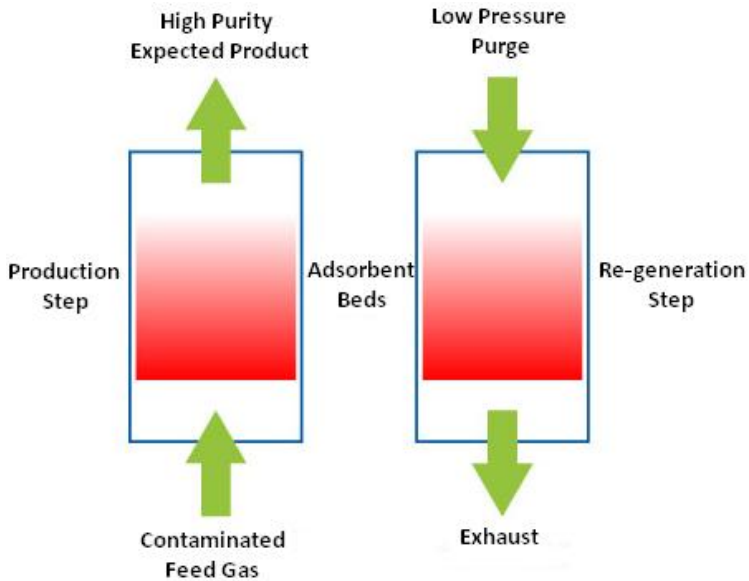
Fig. 2. *Conventional PSA schematic [Xebec Inc.]*

Rys. 2. Schemat PSA [Xebec Inc.]

3.2. Membrane technology

Membrane gas separation is one of the most basic techniques of clear gases used for many industrial processes realization [ChemTech]. In general, membrane methods use a difference of permeability of gas mixture composition via membrane. On the grounds of different molecule or atomic weights components diffuse with differet speeds. Gas mixture is passed along membrane surface, which pores are small enough that only lighter molecules could pass through (Fig. 3).
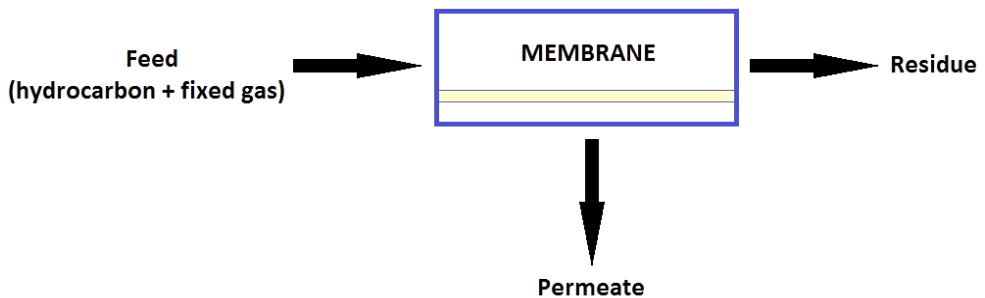

Fig. 3. *Schematic of membrane separation process*

Rys. 3. Schemat procesu membranowej separacji gazów

Most ethylene recovery by membrane technology in gas separation use dense, nonporous polymer membranes. Permeability of polymers depends on working conditions, pressure, temperature and composition of separated mixture. The influence on permeability has also solubility and diffusion. Selectivity of mixture separation in membrane is defined only by diffusion factor:

$$\alpha_{ij} = \sqrt{\frac{M_i}{M_j}} \tag{1}$$

M_i and M_j constitute molecular masses of components i and j correspondingly. Nevertheless, to achieve high degree of separation, several membrane modules must be used. The rate of gas transfer through the membrane is inversely proportional to a membrane thickness. To increase the rate of the process, the efficient thickness of the membrane must be decreased [Zhanat and Sharipzhan 2012].

Transport via polymer material occurs by diffusion. In presence of a driving force, gas molecules dissolve in polymer according to Henry's law [Serwiński 1982] and diffuse through material according to Fick's first law:

$$J = -D\frac{dc}{dx} \tag{2}$$

here:

J – flow through membrane,

D – diffusion coefficient,

$\dfrac{dc}{dx}$ – concentration gradient.

The whole process takes place in the presence of a driving force that occurs by the difference in chemical potential among two sides, feed and permeate. The difference is accomplished by maintaining the feed side of the polymer membrane at a higher pressure that permeate side. Solubility sets down the number of gas molecules, diffusivity sets down the mobility of gas molecules [Kujawski 2009]. Nonetheless, polymer membranes posses high coefficient of diffusion. They are definitely not suitable for separating full, condensable gases or vapor of organic substances from permanent gases. Very often it is necessary to remove small amount of easily volatile organic components or higher hydrocarbons from mixtures with fixed gas (like nitrogen). To decrease necessary area of membranes and expenditures for compressing membranes are required, mainly permeable for grosser molecules of organic vapors and impermeable for molecules of fixed gases. Produced from glasslike polymers membranes are more permeable for smaller molecules of fixed gases and much less permeable for grosser molecules of organic vapors. Rubber-like polymers are more proper for higher hydrocarbons than for fixed gases [Zhanat and Sharipzhan 2012].

It must be emphasized that parameters of membrane efficiency depend on feed composition, wherefore total characteristics requires defining values of these parameters in such feed composition, in which membrane is going to be used [Kujawski 2009]. Membrane module calculation model to separate gases presents paper [Zhanat and Sharipzhan 2012]. This necessity of defining parameters may constitute difficulty with choosing membrane solution on ethylene carriers than that inerting is carried at ambiet temperature (0–35°C), pressure depends on intensivity of opening valves on purge lines, this in turn makes impossible to evaluate force acting on membrane [Wieczorek 2017]. Therefore, exact quantities of gases, theirs temperatures and pressures are impossible to determine mounting adequate membrane on a ship.

However, at present, testing new membrane materials is one of the most intensively developing solution of gas separation. Nanocomposite membranes comparing to any hybrid membranes seemed to overcome the selectivity-permeability compromise of polymeric membranes. Its heterogeneous structure is generally composed of organic polymer and also inorganic nanoparticle insertions. What pushes researchers to nanocomposite membranes is achieving improved performance, it means high selectivity, good mechanical strength, chemical stability of inorganic nanoparticles, lower costs and ease of processability of polymers. Nowadays several researchers work on development of this innovation solution [Idris and et al. 2016].

4. CONCLUSION

On the grounds of in-depth reporting of work parameters of ethylene cascade system during transport by the sea and research of gas separation methods that would be proper for ethylene and nitrogen, is therefore deduced that the use of neither pressure swing adsorption (PSA) nor membrane techniques would divide a mixture of these two gases during gassing-up operation after inerting. PSA that exists on ships cannot be used in problematic process due to the fact that elements of the system (primarily adsorbent) are intended to production of nitrogen from the air. PSA adaptation to ethylene and nitrogen is practically impossible. The only solution would be the PSA installation destined for these two gases separation. As it was previously emphasized, membrane techniques are also inappropriate for this purpose. For the time being, qualifying beginning parameters of gassing-up process like one particular temperature in tanks, pressure and speed of ethylene passing, exact quantities of both gases, exact time of the operation, are impossible to manage. For adjusting membrane properties to the process being discussed it would be necessary to determine all of these parameters. Moreover, new membrane techniques are in test phase and membrane technology still develops.

To sum up, it is essential to find other solution for solving this particular problem. It is therefore necessary to make an attempt to separate the ethylene and nitrogen in a very traditional way – thermodynamics.

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