*Desalination and Water Treatment*
www.deswater.com

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doi: 10.5004/dwt.2010.1018

14 (2010) 119–126
February

# Integrated membrane/PSA systems for hydrogen recovery from gas mixtures

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Received 30 June 2009; accepted 4 November 2009

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## ABSTRACT

This paper is focused on the recovery of hydrogen from multicomponent gas mixtures by integrated membrane/PSA system. The paper presents the following results: computational estimation of the five-component mixture ($H_2/CO/CO_2/N_2/H_2S$) separation by means of membrane modules; estimation of the integrated membrane/PSA system efficiency; experimental results of gas mixtures separation by integrated membrane/PSA system with commercially available membranes (GENERON hollow fiber membrane module and PVTMS flat sheet membrane module). The influence of a purge to feed ratio, pressure, half cycle time and feed composition on the PSA performance was studied. The $H_2S$, CO and $H_2O$ permeability through the membranes was estimated by means of the correlation analysis.

It was shown that in some cases $H_2$ recovery degree can achieve 90–97% for bio-synthesis gas and petrochemical gas if $H_2$ concentration was equal 70% after pre-concentration at the membrane stage. The experiments were carried out using model gas mixtures ($O_2/N_2$ and $He/CO_2/O_2$ which imitate $H_2/CO_2/CO$ mixture). Obtained results could be considerably improved by application of new membrane materials and new adsorbents.

*Keywords:* Permeability; Hydrogen recovery; Separation of multicomponent gas mixtures; Integrated processes

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## 1. Introduction

Nowadays, the study of hydrogen-containing multicomponent gas mixtures separation is of great importance because the demand of hydrogen is increasing. Hydrogen purification is an essential step for its production by means of catalytic steam reforming of natural gas, naphtha or refinery gases. Moreover, purification and separation technologies allow to recover hydrogen from different petrochemical streams and bio-sources [1–3] (bio-hydrogen obtained by means of bacteria [4–6] and bio-syngas produced as a result of solid organic waste or wood pyrolysis [7]). Hydrogen is used in many important chemical process industries, such as hydro-cracking, methanol production, manufacture of silicon, etc. Due to the environmental concern, clean-burning characteristics of $H_2$ make it attractive as vehicular fuel, especially for urban areas. There are a lot of available gas mixtures seems to be promising sources for hydrogen production (Table 1). According to these data the impurities must be removed in order to attain required purity of hydrogen (more than 99%) for different application [8].

Traditional gas separation and purification techniques include cryogenic, adsorption, absorption and membrane technologies. Each of these processes is based on a different separation principle, and consequently, the process characteristics differ significantly.

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*Presented at the Fourth Membrane Science and Technology Conference of Visegrad Countries (PERMEA 2009), Prague, 7-11 June, 2009.*

Table 1
The composition of $H_2$-containing gas mixtures [1,4–7]

| | Gas composition (% vol) | | | | | |
|---|---|---|---|---|---|---|
| Hydrogen sources | $H_2$ | $CO_2$ | CO | $CH_4$ and $C_2$-$C_4$ | $N_2$ | $H_2S$ |
| Gas from butadiene production | 74–82 | 5–9 | 0–14 | 6–12 | – | – |
| Waste gas from acetylene production | 50–63 | 3–10 | 27–30 | 5–8 | 2–3 | – |
| Coke oven gas | 55–60 | 2–3 | 5–7 | 20–30 | 4 | Trace |
| Char gas | 6–18 | 12–15 | 7–12 | 34 | 7–8 | Trace |
| Bio-syngas | 25–42 | 10–35 | 25–42 | 1 | 2–5 | 1 |
| Bio-hydrogen | 80 | 20 | – | – | – | Trace |

Selection of the appropriate hydrogen separation process depends not only on economics, but also on both performance criteria (hydrogen recovery and feed and product conditions) and operational requirements (flexibility, reliability, feed pretreatment, by-product recovery and easiness of futures expansion). The problem of hydrogen recovery from multicomponent gas mixtures requires the development of safe technology with low power consumption. Membrane and adsorption methods are examples of such processes since they do not require energy for phase transition. The PSA systems maintain an advantage in the high-purity region while membranes become clearly advantageous when the product purity requirements are less severe.

Membrane systems do not allow to obtain high purity $H_2$ (typically from 90 to 95%) due to the noticeable amount of $CO_2$ in gas mixtures (Table 1) and low $H_2/CO_2$ selectivity of membranes. For membrane process application $H_2$ concentration in the feed gas should be more than 15%. Nevertheless membrane processes could be used as an intermediate stage due to the possibility of obtaining high recovery degree of $H_2$ and recovery of the major part of impurities [3,9].

The PSA process requires the relatively high $H_2$ concentration in the feed gas (typically more than 50%) at a moderate pressure in order to provide higher recovery degree [9]. This process shows the best results if $H_2$ concentration in the feed gas is more then 70%.

The hydrogen content in the majority of considered multicomponent gas mixtures is of 25–80% (Table 1). Since, the increasing of $H_2$ concentration in feed gas leads to the improvement of PSA processes efficiency. Gas mixtures with low $H_2$ content can be preconcentrated by membrane process. Therefore, it is reasonable to expect that an optimized integrated membrane/PSA gas separation process will lead to simultaneously improvement of $H_2$ purity and recovery degree as compared to the standalone systems. Moreover, this combination leads to compensation of disadvantages of both methods. Depending on membranes, gases and adsorbents the combination can be realized by different ways [10–25].

Fig. 1 shows a scheme of the integrated membrane-adsorption system where gas mixture is firstly separated by a membrane module and then by adsorption system, this process can be also organized vice versa [10,15] or with more complicated integration [16,19].

Membrane and adsorption technologies combination is developing since the eighties of the 20th century [10,15–27]. Nowadays, a number of plants apply for vapor recovery experimental setups which consist of modules based on polymeric membrane and PSA [26]. However the described systems are not commercialized for hydrogen recovery. In general, such integrated systems are proposed to use for $H_2$/CO and $H_2/CO_2$ separation [15,17,18,20–22], $H_2$/methan separation [19,23], and $H_2$/hydrocarbon separation [15,24,25]. Integrated membrane adsorption system can be used not only for $H_2$ extraction, but also for Ar recovery from $H_2$-containing purge gas in ammonia production process [27]. The hollow fibers based on polysulfone [15,17–23], poly-di(alkyl)siloxane [22,24] are mainly used in membrane module, as well as polystyrene [18], polyacrylonitrile [18], cellulose acetate and some other polymers on graphite support [19,25].

The aim of present work is to estimate the potential of membrane-adsorption systems combining

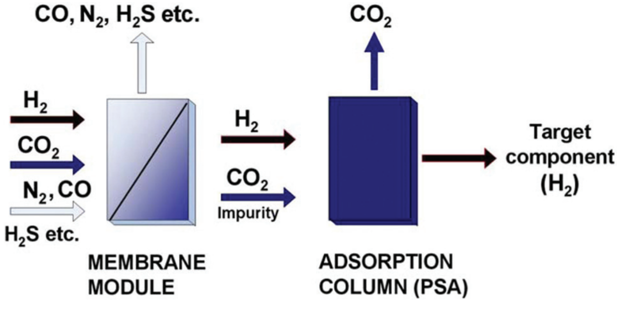

Fig. 1. The scheme of the integrated membrane-adsorption system.

Table 2
The selectivity of some commercially available polymeric membranes [3,29]

| | Polymers | | | | | |
|---|---|---|---|---|---|---|
| Ideal selectivity | Cellulose acetate | Polysulfone | TBPC | Polyimide | PVTMS | Polydimethyl-siloxane |
| $H_2/CO_2$ | 2.4 | 2.5 | 3.5 | 3.8 | 1.3 | 0.2 |
| $H_2/N_2$ | 72 | 56–80 | 90 | 83 | 14–17 | 22 |
| $H_2/CO$ | 60–80 | 40–56 | 123 | 50–125 | 9.1 | 0.7 |
| $H_2/CH_4$ | 60–80 | 80 | 120 | 100–200 | 8.5 | 0.8 |

gas-separation properties of polymer membranes and porous carbon adsorbents for hydrogen extraction from waste multicomponent gas mixtures.

## 2. Correlation estimation of perm-selectivity of polymers and computational calculation of gas separation by commercially available modules

There are particularities of non-porous polymeric membranes gas separation. Among thousands of gas separation polymers only 7–8 polymers are used for gas separation membranes production [3,11,28]. Since the gas separation mechanism of non-porous polymeric membrane is diffusion solubility, permeability coefficient depends on gas solubility in the polymeric matrix and gas diffusion rate in the membrane medium [3]. The ideal polymeric membrane selectivity is generally determined as the ratio of gas permeability coefficients. Ideal selectivity of binary gas mixture can be defined as product of solubility selectivity and diffusion selectivity: $\alpha_{i/j} = P_i/P_j = D_i/D_j \times S_i/S_j$. The reason of extremely high permeability and low $H_2/CO_2$ selectivity of non-porous polymeric membranes is that $D_{H2} >> D_{CO2}$ and $S_{CO2} >> S_{H2}$. From the other hand, these membranes are able to effectively separate $H_2/CO$ and $H_2/N_2$ mixtures (Table 2).

Table data confirms that separation of $H_2$ from multicomponent mixtures containing CO, $CO_2$, $N_2$ by membranes is complex task.

Tetrabromopolycarbonate (TBPC) and polyvinyltrimethylsilane (PVTMS) polymers were selected for the study and calculation because of high selectivity (Table 2) of the first and high productivity of the second (Table 3). Experiments were carried out using two commercially available gas separation membrane modules: hollow fibers membrane module GENERON based on TBPC [11] and flat sheet membrane module based on PVTMS. The experimental and correlative estimated [29] gas permeance of selected membranes is listed in Table 3.

High $H_2$ purity can be achieved by membrane methods only at low recovery degree. On the other hand, as it is mentioned above, membrane methods of gas separation can be used for the pre-concentration of hydrogen with high recovery degrees and its further purification in PSA stage.

Computational estimation of membrane separation characteristics was carried out for the components of waste gas from acetylene production (50% $H_2$, 10% $CO_2$, 10% $CH_4$, 4% $N_2$, 28% CO) and bio-syngas (40% $H_2$, 15% $CO_2$, 1% $CH_4$, 5% $N_2$, 38% CO, 1% $H_2S$) to produce hydrogen with a necessary extent of recovery. Cross flow model was used for the calculation of membrane module separation characteristics. Optimization methods and general approach for membrane module modeling are well known from literature [30–35]. These approaches use some models of membranes unit process parameters, mainly for binary gas mixtures separation. Taking into account well known algorithm based on equilibrium in point, we created the computer program for calculation of multicomponent gas mixture separation. This algorithm correlates gas composition in point X in feed gas with gas composition in point Y in permeate. The values of X and Y as a function of membrane length give two concentration profiles [30].

Table 3
Gas permeance of TBPC and PVTMS based membranes [3,29]

| | Gas permeance, l/(m$^2$ h atm) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Membrane | He | $H_2$ | $CO_2$ | $CH_4$ | $N_2$ | $O_2$ | $C_3H_8$* | CO* | $H_2S$* | $SO_2$* |
| TBPC (0.1 μm) | 180 | 160 | 45 | 1.3 | 1.8 | 13 | 0.1 | 1.6 | 4 | 10.3 |
| PVTMS(0.2 μm) | 1800 | 2000 | 1600 | 220 | 120 | 450 | 40 | 150 | 350 | 1000 |

* Correlation estimations.

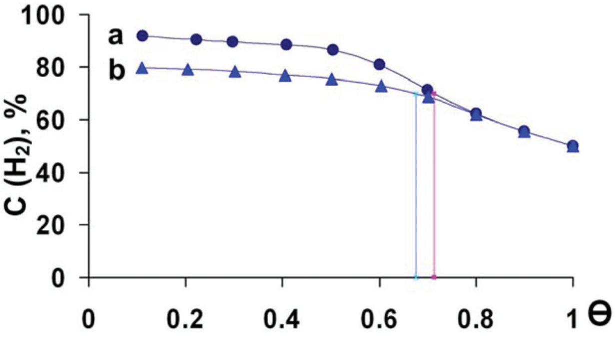

Fig. 2. The dependence of $H_2$ concentration in permeate on stage cut (θ) for waste gas from acetylene production separation. (a TBPC, b PVTMS, calculation parameters: feed 15 $Nm^3/h$, pressure drop 10/1 atm).

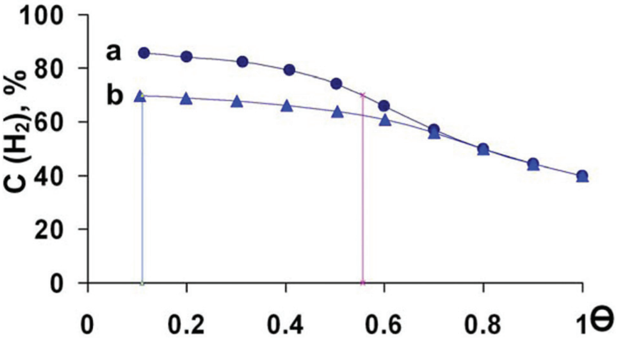

Fig. 3. The dependence of $H_2$ concentration in permeate on stage cut (θ) for bio-syngas separation. (a TBPC, b PVTMS, calculation parameters: feed 15 $Nm^3/h$, pressure drop 10/1 atm).

If driving force is evaluated as activity $a_i$ of I component, then mass quantity $dq_i$ passed through elementary area of membrane dS could be calculated according to mass transfer equation:

$$-dq_i = dSK_i\left(a_i^{I} - a_i^{II}\right) \quad (1)$$

where superscripts I and II relate to the feed gas and permeate. The interference of components is supposed to be insignificant and in order to express the flux through membrane the only mass transfer coefficient $K_i$ is used. In case of multi-component system the Eq. (1) should be presented for each component to result in a system of differential equations that could be solved by means of approximations. However these equations are not enough for estimation of equilibrium correlation in a point in case of complicated membrane processes where different phenomena such as concentration polarization, longitudinal mixing and pressure drop along membrane occur and influence the mass transfer. Using equations describing these side processes it is possible to integrate Eq. (1) and circumscribe the equilibrium in a point. We calculated the same data for other gas mixtures, but they are not represented here in order to save space.

Herein we present results of calculation for some compositions of waste gas from acetylene production (Fig. 2) and bio-syngas (Fig. 3). Table 4 depicts the calculated data for the case when hydrogen concentration in permeate increases up to 70%. In some cases widely used polymeric membranes and modules can solve the problem of hydrogen pre-concentration in mixtures containing 40–50% of hydrogen (Figs. 2, 3 and Table 4). However the target calculations in each specific case are still required. Stage cut (θ, a ratio of permeate flux to feed flux) which corresponds to $H_2$ concentration 70% in permeate is pointed out.

According to obtained results, TBPC membranes can be used for the separation of both mentioned gas mixtures. Hydrogen concentration achieves more than 70% at the recovery degree of 90–97% whereas PVTMS membranes are not suitable for this process because of their too low level of recovery degree (10–70%). Maximum pre-concentration corresponds to the low recovery degree (Table 5).

Major part of such impurities as CO and $N_2$ can be removed on membrane stage and $CO_2$ and $H_2$ could be separated after by PSA unit as it is shown in the scheme (Fig. 1). It is supposed that such combination would allow decreasing of adsorbent amount, cost of adsorbent regeneration and thus prolong PSA-unit service life.

## 3. Experiment and discussion

The PSA process for hydrogen purification is based on the ability of adsorbent to adsorb more impurities at high gas-phase partial pressure than at low partial pressure. Admixtures adsorb under high pressure and desorb during pressure decrease. The impurity partial pressure is lowered by ''swinging'' the adsorber pressure from feed pressure to the tail gas pressure and by using a high-purity hydrogen purge. The process operates on a cyclic basis. It is well known that hydrogen is a practically non-adsorbing gas and the adsorbents ability to adsorb admixtures almost completely provides purification of $H_2$ up to 99.9%. Therefore, the PSA process performs a separation in a chromatographic fashion as describe in [36].

In general, the weakest adsorbed impurities are the first to appear as contaminants in the hydrogen product. These particular gases can be removed at membrane stage. Nowadays one of the best adsorbents is carbon. That is why the object of our research is carbon

Table 4
Calculation of separation of waste gas from acetylene production (stage cut θ = 0.71 for TBPC and θ = 0.68 for PVTMS) for pre-concentration of $H_2$ up to 70% (pressure drop 10/1 atm, feed 15 $Nm^3$/h)

| Gas | TBPC, area =133 $m^2$ | | PVTMS, area = 1.7 $m^2$ | |
|---|---|---|---|---|
| | Concentration in permeate (%) | Concentration in retentate (%) | Concentration in permeate (%) | Concentration in retentate (%) |
| $H_2$ | 70 | 0.3 | 70 | 8.3 |
| $CO_2$ | 14 | 0.7 | 14 | 2.6 |
| $CH_4$ | 2.8 | 21 | 4.2 | 16 |
| $N_2$ | 1.8 | 9.4 | 1.3 | 9.1 |
| CO | 11 | 69 | 11 | 64 |

based materials. The choice of the optimal adsorbents for gas separation is a complex task and strictly depends on physicochemical properties and adsorption ability of the gas mixture components. For our study we have chosen the molecular carbon sieves and two model gas mixtures. One of them is a binary gas mixture consisting of $N_2$ and $O_2$. In this case retentate after membrane stage is supplied directly to PSA unit. Experimental data are in a good accordance with calculation. Another one is a ternary gas mixture consisting of He, $O_2$ and $CO_2$ which imitates $H_2/CO/CO_2$ model mixture. For the second model gas mixture permeate is a product gas and it should be compressed before supply to PSA stage. According to the data from Table 3 helium permeability is almost the same as hydrogen one and it was used in our experimental research instead of $H_2$.

Fig. 4 shows the scheme of typical 2- bed PSA unit which was used in the study of PSA parameters [37,38].

### 3.1. Results of binary gas mixtures separation

The separation of (79% $N_2$, 21% $O_2$) gas mixture by using a PSA employing molecular carbon sieves as the adsorbents coupled membranes module with selectivity $\alpha_{O2/N2} = 7.2$ (TBPC) and $\alpha_{O2/N2} = 3.8$ (PVTMS) was studied. For this case retentate is a product gas ($N_2$) for membrane stage.

It is seen from Fig. 5 that $O_2$ concentration in retentate decreases via pressure increase in feed gas at constant stage cut and it possible to obtain high purity product gas at high feed pressures and high stage cut. The recovery degree of target component is low in this case.

The effect of the following operating parameters on the PSA performance was studied: purge to feed ration, half cycle time of one adsorber's operating, pressure and feed composition. Obtained result are shown in Figs. 6–7.

Fig. 6 shows influence of adsorption pressure on $O_2$ concentration in a product gas (ratio (purge flux)/(feed flux) = 0.32), it is seen that purity of product gas ($N_2$) increase with pressure increase in feed gas.

The minimum of curves in Figs. 6, 7 corresponds to optimal half cycle time (time of one absorbers' operating) at the given operation parameters (such as feed pressure or purge to feed flux ratios). It is seen that optimal half cycle time concentration of $O_2$ in product gas almost independent on purge to feed flux ratio. But

Table 5
Calculation of separation of waste gas from acetylene production by membrane based on TBPC and bio-syngas gas by membrane based on PVTMS: at maximum pre-concentration of $H_2$ (one stage, pressure drop 10/0.2 atm, feed 15 $Nm^3$/h)

| Gas | TBPC, stage cut θ = 0.08 | | PVTMS, stage cut θ = 0.07 | |
|---|---|---|---|---|
| | Concentration in permeate (%) | Concentration in retentate (%) | Concentration in permeate (%) | Concentration in retentate (%) |
| $H_2$ | 93 | 44 | 88 | 35.3 |
| $CO_2$ | 6.1 | 10.1 | 10.7 | 14.9 |
| $CH_4$ | 0.2 | 9.2 | 0.02 | 1.1 |
| $N_2$ | 0.1 | 4.6 | 0.2 | 5.5 |
| $H_2S$ | – | – | 0.07 | 1.1 |
| CO | 0.7 | 32.2 | 1.1 | 42.1 |

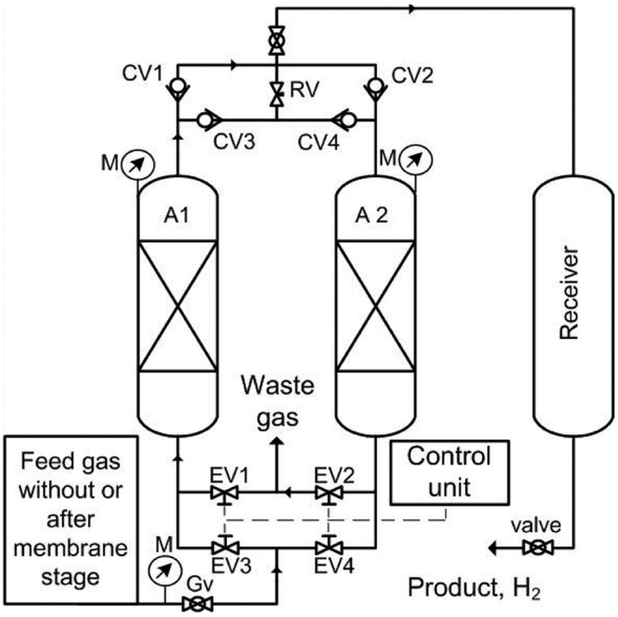

Fig. 4. Scheme of typical two-bed PSA system (A1, A2 adsorbers; Receiver; RV reducing valve; GV globe valve; CV1–CV4 check valve; M manometer; EV1–EV4 electromagnetic valves).

for the other ranges it depends on flux ratio (Fig. 7). In all cases, as the purity decreases the process recovery increases.

Table 6 shows that $O_2$ concentration decrease in feed gas correlates with $O_2$ concentration decrease in product gas. These data were obtained for the same operating parameters (pressure, feed flux, and purge to feed ratio).

### 3.2. *Results of ternary gas mixtures separation*

In the second part of our study the separation parameters of (42.5% He, 32% $CO_2$, 25.5% $O_2$) gas mixture were examined using a standalone PSA coupled with membrane module. Selectivity of membrane was been calculated from the Table 3: α (He/$CO_2$) = 4 and α (He/$O_2$) = 13.8. For this case permeate is product gas (He).

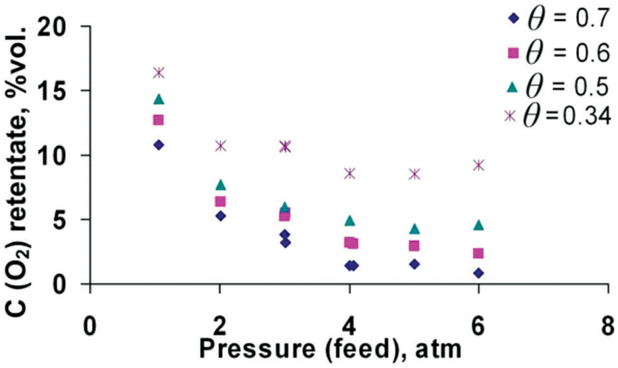

Fig. 5. The dependence of $O_2$ concentration in retentate on feed pressure at constant stage cut (θ) ($T = 20°C$).

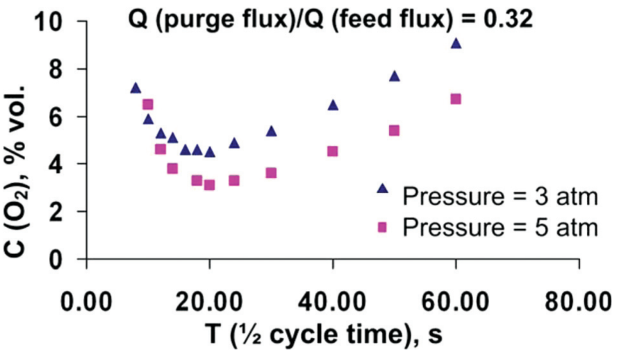

Fig. 6. The dependence of $O_2$ concentration in product gas on half cycle time at different feed pressure and Temperature = 20°C.

It is supposed that difference between experimental and calculated data is related to the difference in feed fluxes (Fig. 8). We failed to provide the required feed flux in experimental study. The real one was of 4,000 L/h. But the best calculated data correspond to flux of 9,000 L/h. At stage cut θ = 0.28 experimental results correspond to C (He) = 60%, *Q* (feed) = 4,000 L/h and α (recovery degree, He) = 35% whereas calculations give C (He) = 67%, *Q* (feed) = 9,000 L/h, α (recovery degree, He) = 45%.

It is seen in the Table 7 how efficiency of PSA process depends on feed gas composition. The product purity and recovery degree increase along with target component concentration in feed gas. The rage of optimal half-cycle time also increases. Obtained results show that integrated membrane–adsorption unit for gas separation allows increasing of gas separation efficiency, such as purity of a product gas and recovery degree.

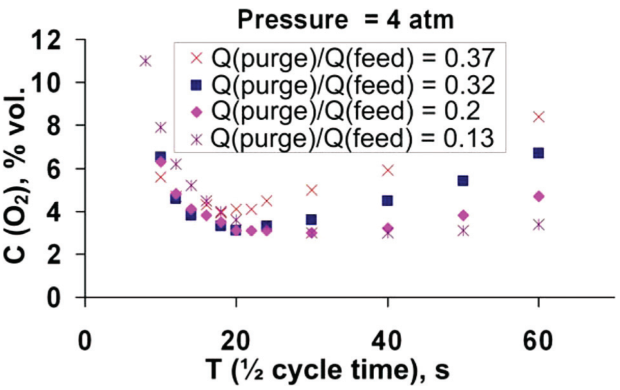

Fig. 7. The dependence of $O_2$ concentration in product gas ($N_2$) on half-cycle time at different purge to feed flux ratios (feed pressure = 4 atm) and $T = 20°C$.

Table 6
Dependence of gas separation efficiency on process organization (PSA process parameters: feed pressure = 3 atm, purge to feed flux ratio = 0.32)

| | Feed gas concentration for PSA stage | | Product gas concentration | |
|---|---|---|---|---|
| Scheme of process organization | $C(O_2)$, % | $C(N_2)$, % | $C(O_2)$, % | $C(N_2)$, % |
| Without pre-concentration | 21 | 79 | 4.3 | 95.7 |
| Pre-concentration using flat sheet membrane module (PVTMS) | 15 | 85 | 3.2 | 96.8 |
| Pre-concentration using hollow fibers membrane module (Generon) | 10 | 90 | 1.5 | 98.5 |

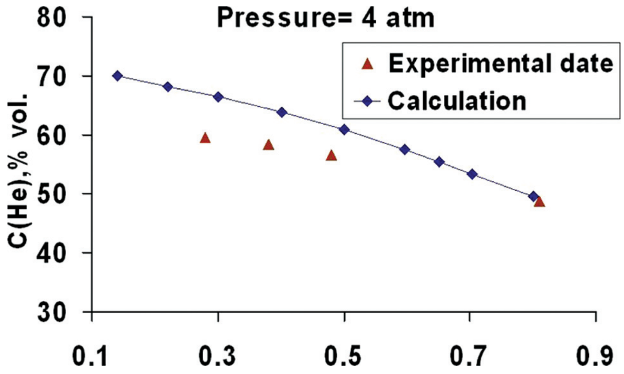

Fig. 8. The dependence of He concentration in permeate (product gas) on stage cut (θ) (membrane area 13 $m^2$, feed pressure 4 atm, $T = 21°C$).

Table 7
Dependence of ternary gas mixture separation efficiency on process organization (PSA process parameters: feed pressure = 4 atm, purge to feed flux ratio = 0.2, half cycle time 20 s)

| | Gas mixture composition (% vol) | | |
|---|---|---|---|
| Scheme of process organization | $O_2$ | $CO_2$ | He |
| Feed | 25.5 | 32 | 42.5 |
| Pre-concentration using GENERON module | 9.8 | 21.3 | 68.9 |
| Product gas after PSA stage without GENERON module | 11 | 0.07 | 89 |
| | 2 | 0.02 | 98 |

## 4. Conclusion

It is reasonable to expect that an optimized gas separation process integrating membrane and PSA can improve product purity and/or recovery level in the comparison with standalone systems. Large number of gaseous mixtures with different requirement to the final product properties still does not allow to develop general rules for creation of membrane–adsorption systems. Thus every case needs personal experimental and theoretical research.

It is shown that hydrogen recovery degree may achieve up to 90–97% for bio-synthesis gas and petrochemical gas in the case of hydrogen pre-concentration level up to 70% at the membrane stage. As a result, the hydrogen of 99.9% purity can be obtained at the PSA stage. The obtained data correspond to well known membranes and adsorbents and can be considerably improved by using of new membrane materials and adsorbents.

## Acknowledgments

The authors would like to acknowledge the partial financial support from FP6 IP no. 019825-(SES6) ‘‘HYVOLUTION’’, Grant RFBR No. 08-03-9249, Goscontract No. 02.526.11.6010, Nikolai PLATÉ Russian-French Laboratory of membranes and molecular separation processes. The authors thank R. V. Greenberg for his help in experimental work and M.U. Periderij for providing the adsorbent.

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