

# Experimental stand for CO<sub>2</sub> membrane separation<sup>☆</sup>

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## Abstract

This paper deals with the construction of a CO<sub>2</sub> membrane separation system and the fundamental processes at work. Results from research testing of membranes with low flows are discussed. The aim of the tests was to check the apparatus and how it performs for the needs of research into the characteristics of ceramic and polymer membranes with the use of gas-simulant mixtures of combustion gases - typical for power systems. Selected results of research into ceramic and polymer membranes conducted on the experimental stand are presented.

*Keywords:* membrane separation, CO<sub>2</sub>, experimental investigation

## 1. The introduction

Membranous methods are widely used in the petrochemical industry, as well as in natural gas cleaning processes. The 1980s saw exponential growth in the use of polymer membranes, which contributed greatly to the commercial success of this separation technology. The same era saw advances in the industrial membranous separation of air (O<sub>2</sub>/N<sub>2</sub>). A key factor is cost: Membranous separation methods require much less power than absorption and the cryogenic fractional processes.

As membranes for the separation of CO<sub>2</sub> from combustion gases are undergoing continual improvement, this technology will likely develop applications in the power sector. This technology looks set

to be competitive in future in terms of cost and efficiency compared to other methods of the separation. In connection with other related scientific research in this area at the Institute of Power Engineering and Turbomachinery of the Silesian Technical University, an experimental stand was constructed to research the membranous separation of CO<sub>2</sub>.

## 2. General characterization of the process of membranous CO<sub>2</sub> separation

The membrane is the phase barrier which divides two phases. In mass transportation it can act as the permitting barrier for the selective diffusion of substances. The flow feeding membranous system is divided into the flow of permeate and retentate. Permeate is the part of feed dilution which diffused through the membrane, whereas the part of the stream retained by the membrane is called retentate. The most important parameters affecting the efficacy of the process of separation through a membranous system are the permeability and selectivity of membrane. Permeability regulates the flow of the ingredient in

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the mixture which diffused through the membrane, whereas selectivity is defined as the relation of the permeability of individual ingredients of the mixture through the membrane [1].

Membrane selectivity in terms of the separation of gases depends primarily on the properties of the membrane material. Membranes may be synthetic or natural, and the structure may be porous, non-porous and liquid membranes [1, 2]. The mechanism of separation of the individual ingredients of the mixture varies depending on the kind of membrane. Membranous separation technology makes use of differences between physical properties and the chemical composition of individual ingredients in the gas mixture and the separative membrane, which makes the diffusion of ingredients of the gas through material of the membrane at different speeds. The flow through the separative membrane is determined as the difference in the speed of the diffusion of different ingredients of the gas through the membrane. A driving force in the process is the difference in partial pressures of the given ingredient over both sides of the membrane [1, 2].

Membranes can be polymer, ceramic, glass, carbonic, metallic or zeolite [1]. For the purpose of capturing CO<sub>2</sub> the membranes that have been used for separation are ceramic and polymer including hybrids, or alternatively absorbing gas membranes.

In view of their properties, the most often used are still polymer [3] membranes, with selectivity of usually below 100. Their greatest advantage is the ability to produce them in the form of hollow fibers with a large surface area, which enables material reductions in the size of the membranous kit. Over the last dozen or so years great strides have been made in the development of membranes for CO<sub>2</sub>/N<sub>2</sub> separation. The use of high selective materials, especially polymers, has made it possible to produce membranes with selectivity levels of over 200 and even in the region of 400 [4, 5].

### 3. The experimental stand

#### 3.1. The concept and development of the measuring-stand

In its primary version, the stand for the membranous separation of CO<sub>2</sub> consisted of a “helicopter”

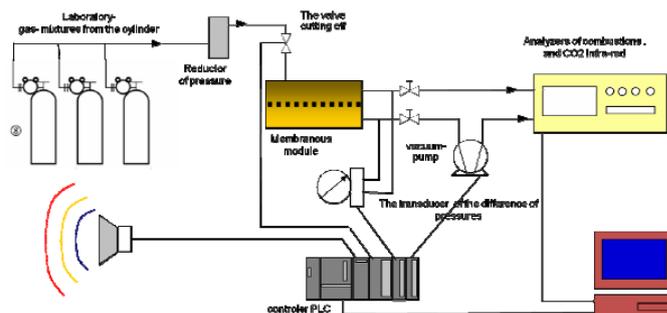


Figure 1: Chart of the experimental stand to research CO<sub>2</sub> separation using ceramic membranes

type membranous module for testing tubular ceramic membranes (see Fig.1), a dual channel gas analyzer of CO<sub>2</sub> (in the range 0–100% CO<sub>2</sub> and 0–20% CO<sub>2</sub>) with a built-in gas-path system serving to prepare the gas sample for measurement, plus a vacuum pump on the permeate side.

The stand is designed to control the pressure difference between the permeate and retentate. The system was connected to a computerized archiving data system and measuring equipment. For testing purposes, the use of a membranous equipped module containing a ceramic membrane with an experimental coating was a very difficult process. Defining its properties became possible as measurement data became available.

Initial tests were made to calibrate the stand and adapt it for the purpose of research into the properties of ceramic membranes. To this end, a simulant mixture of typical combustion gases from energy systems was used, with a composition N<sub>2</sub> 80%, CO<sub>2</sub> 20%. Testing showed that the rotameters used do not permit research in the full flow range; also in light of the behavior of the membrane during its feeding with pressure from the cylinder there was no need at this stage of research to use a vacuum-pump or to control the pressure difference. The small surface of membrane used (about 23 cm<sup>2</sup>), and the small resistances of the flow caused minimal pressure drops between feed and retentate. Regulating valves on the permeate and retentate outlets sufficed to establish constant work parameters. Only the CO<sub>2</sub> concentrations on the retentate and permeate outlets were measured. The system was re-equipped with a suitable kit of rotameters (for feed, permeate and retentate), thereby enabling full range measurement (to the ex-

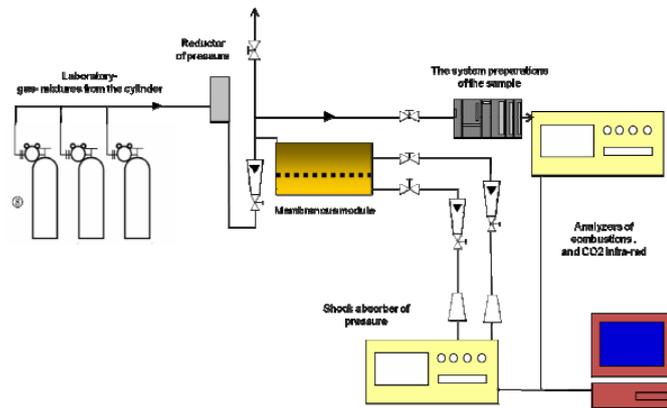


Figure 2: Chart of the experimental stand to research CO<sub>2</sub> separation using ceramic and polymer membranes

tent allowed by the equipment) of the concentrations.

Fig.2 shows a development in the concept of the stand in its upgraded version, adapted fully to research into CO<sub>2</sub> separation with polymer and ceramic membranes. Earlier tests and research had demonstrated the need to re-equip the unit to gain a useful, additional measuring path for the analysis of the following ingredients: CO<sub>2</sub>, O<sub>2</sub>, CO. In short, an additional analyzer of combustion gases.

Research also revealed that the overpressures that occurred made it impossible to correctly measure the CO<sub>2</sub> concentration in the hitherto existing measuring paths of the analyzer, which were not adapted to work at hyperbaric pressures. The measuring system of the stand was re-equipped with a gas reducer, reducing the pressure of the gas mixture by about 8 bar to the ambient pressure. The reducer is an integral part of the preparing system and is used for preparing the sample for the combustion gas analyzer. The existing dual channel CO<sub>2</sub> analyzer was additionally re-equipped with an external shock-absorber for the pressure, which involves running an inflow gas sample to the analyzer at hyperbaric pressures. The system in this form permits research into membranous ceramic working modules at raised pressures of about 4 bar, as well as of polymer modules working at higher pressures of about 6.5 bar.

### 3.2. Construction of the stand and the fundamentals of how it works

Fig.3 shows a schematic diagram of the experimental stand for researching membranous separation

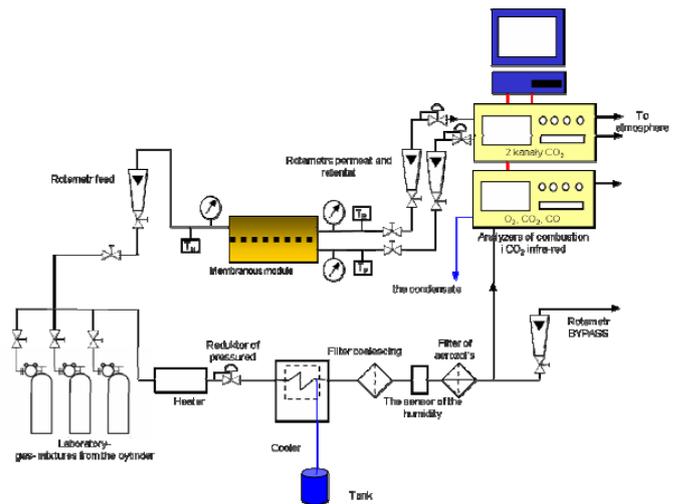


Figure 3: Schematic diagram of the experimental stand to research CO<sub>2</sub> separation

of CO<sub>2</sub>. Feeding the membranous modules are a mixture of three components (CO<sub>2</sub> 15%, CO 15%, N<sub>2</sub> 70%) and two components of composition: (CO<sub>2</sub> 50%, N<sub>2</sub> 50%), (N<sub>2</sub> 80%, CO<sub>2</sub> 20%), situated in 50 liter cylinders under a pressure of 200 bar.

The measuring-system is equipped with two gas analyzers: Atest Gaz (hand-made for the customer) dual channel gas analyzer for CO<sub>2</sub> and the Servomex 4900 gas analyzer for O<sub>2</sub>, CO<sub>2</sub> and CO. To assure pure samples of mixture gas feed for the analyzer, the stand was equipped with a system for the induction and preparation of samples. The Atest Gaz dual channel analyzer of CO<sub>2</sub> has a built-in gas path system to prepare the gas sample for measurement. It consists of:

- a set of electromagnetic valves
- a dehydrator along with a small condensate pump
- charcoal filters (to remove coarse-grained particulate pollution, hydrogen sulfide, ammonia and other aggressive agents)
- exact filters (for other coarse-grained pollution)
- gas sample distributor (dryer and air fan keep the humidity of the sample at close to atmospheric – 30–60% RH)

- small gas pumps and shock-absorber of the small pump (if there is insufficient pressure or vacuum pressure, it provides specific gas flow up to the mark 0.5 l/min)
- flow indicator and a no-flow sensor
- additional external shock-absorber for pressure

This analyzer is adapted to continuous monitoring in two independent measuring-channels of the concentration gases at about atmospheric pressure, but can also work at light vacuum pressure and overpressure (from 20 mbar to 150 mbar of overpressure). Table 1 gives selected technical parameters of the analyzer. The main units of the analyzer are infra-red sensors for the detection of CO<sub>2</sub>. It uses the phenomenon of absorption of infrared radiation as it passes through the gas. The greater the concentration of CO<sub>2</sub>, the less radiation will make it through the sampling tube from the IR source to the sensors. Table 2 sets out the measuring accuracies of analyzers. The measuring methods of analyzers are in accordance with reference Polish statutory methods set forth in the Regulation of Environment Ministry (Journal of Laws No. 283, item 2842, 23 December 2004).

The system of collection and distribution of the sample enables the induction of the reference gas or any combustion gases and the preparation of them for analysis in the Servomex model 4900 analyzer, Fig.3. The analyzer basically used for the measurement of the concentration of gas in the sample before the membrane CO<sub>2</sub> separator. At the first stage the system consists of a heated line of about 5m in length. It permits the gas to be warmed up to the temperature range 40–200°C. Then on the path of the sample (tube) a pressure regulator is installed which makes it possible to reduce the gas pressure from the range 6–8 bar (the pressure given at the inlet to the membrane) to the required pressure (<0.07 bar) to ensure safe delivery of the sample to the analyzer. Placed after the regulator is the MAK 10 condenser, which lowers the temperature of the sample to 3°C. It performs primarily the task of separating and expelling the condensate from the sample gas. The next elements in the system are: the coalescing filter, the humidity sensor and the aerosol filter. The sample

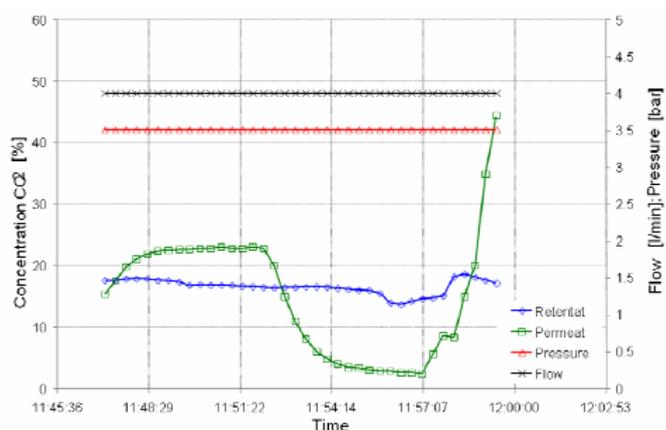


Figure 4: Test of the stand and the ceramic tubular membrane – zeolite with a layer of type MFI, feed composition: 50% CO<sub>2</sub>/50% N<sub>2</sub>

prepared in this way passes to the analyzer, and a rotameter vents the excess gas through the bypass valve. The sample line is made from PTFE tube with an external diameter of approximately 6mm. For the measurement of inflows and outflows of gases to and from the membranous module flow meters were used (rotameters – Type DK800, in the ranges 6–60 l/h, 25–250 l/h, 50–500 l/h, 240–2400 l/h, calibrated for air at pressure 1 bar and temperature 20°C).

#### 4. Chosen tests and preliminary investigations on the measuring- stand

Initial tests were run on the stand to check installation and whether it was adapted in the first instance to the needs of research into the properties of tubular ceramic membranes, and subsequently to research into polymer membranes with the use of simulative mixtures of combustion gases typical for power systems.

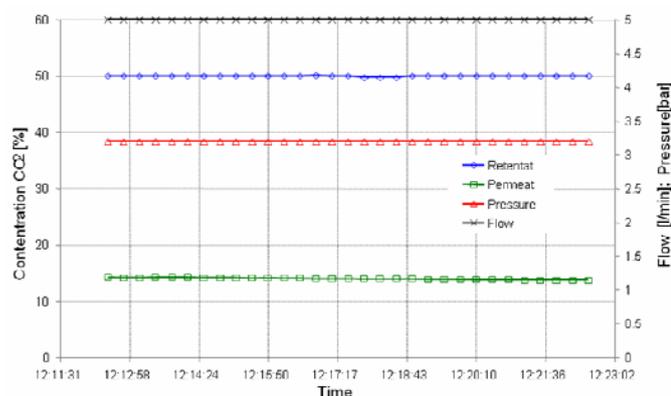
Fig.4 shows the test results demonstrating the behavior of the membranous module from the angle of leakages occurring during the work. Checked in particular were the responses of the measuring apparatus to the speed of changes in registration (during) in the running-track of the measurement of the concentration of gases. The module was started and the pressure raised to 4 bar, then after the process was stabilized, gas leakage to the environment was simulated. It caused a temporary decrease in the CO<sub>2</sub> concentration in the retentate to about 5% and then growth

Table 1: Elementary technical parameters of the dual channel CO<sub>2</sub> analyzer

	Measured gas	
	Channel 1	Channel 2
Gas	CO <sub>2</sub>	CO <sub>2</sub>
Nominal measuring range	0–20% vol CO <sub>2</sub>	0–100% vol CO <sub>2</sub>
Accuracy of the measurement	±2% FS	±2% FS
Pressure variability	<0.02%FS/mbar	<0.02%FS/mbar
Stability of measurement	±2% FS/ year	±2% FS/ year
Temperature range of gas measured	+5 to 40°C	+5 to 40°C

Table 2: Measuring accuracies of CO<sub>2</sub> analyzers

	Dual channel CO <sub>2</sub> analyzer AtestGaz		Combustion gases analyzer Servomex model 4900		
	0–20% vol CO <sub>2</sub>	0–100% vol CO <sub>2</sub>	0–100% vol CO <sub>2</sub>	0–3,000 ppm CO	0–100% vol O <sub>2</sub>
Nominal measuring range	0–20% vol CO <sub>2</sub>	0–100% vol CO <sub>2</sub>	0–100% vol CO <sub>2</sub>	0–3,000 ppm CO	0–100% vol O <sub>2</sub>
Accuracy of measurement	±2% FS	±2% FS	±1% FS	2 ppm	±0.5% FS

Figure 5: Test of the stand and the ceramic tubular membrane – zeolite with a layer of type MFI, feed composition: 50%CO<sub>2</sub>/50%N<sub>2</sub>

to a CO<sub>2</sub> concentration of 48%, which resulted from the fact that the feed stream was directed to the retentate outlet. The fall in concentration in the retentate may be interpreted as being due to the valves opening and sucking air through the sucking system of the analyzer and moved the unestablished condition for required position to the normal work of the gas analyzer. During this test the flow and pressure of the gas-mixture feed were not changed.

Fig. 5 shows the state of stabilized work of the membranous module with an experimental ceramic



Figure 6: The view of the membranous module with the ceramic-membrane with the measuring instrumentation

tubular membrane with a single module. The system was supplied with the mixture at a pressure of 3.2 bar and flow of 5 liter/minute.

#### 4.1. The chosen test of the ceramic membrane with the use of model gases

The research aim was to investigate the potential application of the experimental tubular ceramic membrane to the separation of CO<sub>2</sub> and to determine its characteristics. The membrane was installed in the single module shown on Fig.6. The membrane was successfully tested on the separation of liquid and steams, in other words pervaporations.

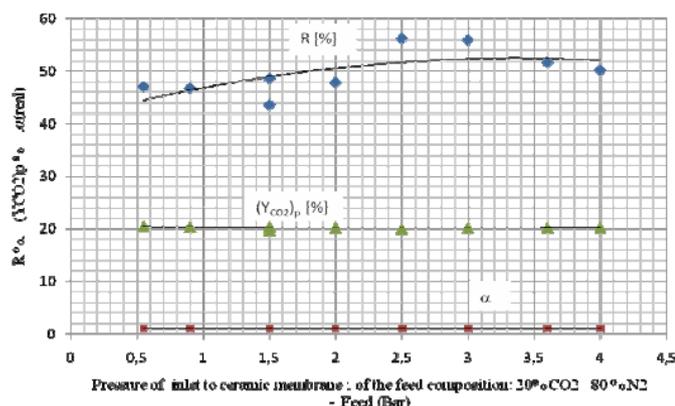


Figure 7: Test of the ceramic tubular membrane – zeolite with a coating layer of type MFI, feed composition: 20% CO<sub>2</sub>/80% N<sub>2</sub>

The ceramic membrane consists of a carrier – the composite ceramic support made on the basis titanium oxide Ti<sub>2</sub>O and coating separating layer. One task of the membranous “film” layer is to control the exchange of matter between two neighboring gas (liquid) phases. The membrane plays the role of a barrier, able to separate different particles through cribration or controlling the speed of progress through its micro parts. Transportation through the membrane results from the related driving force, first of all the gradient of pressure, the concentration and temperatures and the electric potential. The ability of the membrane to effectively separate mixtures is described most often by the parameters: purity (YCO<sub>2</sub>)<sub>p</sub> of permeate, recovery rate  $R$  and selectivity  $\alpha$ .

During all measurements temperature was kept constant in the range 21.5–23.1°C. During the first part the test membrane was fed with a standard mixture of composition: 20% CO<sub>2</sub> / 80% N<sub>2</sub> at variable pressure and quasi-constant values of flow; then at constant pressure feed the stream flow was changed and the concentrations of retentate and permeate recorded. During the test the trans-membranous pressure difference between feed and permeate was kept at a constant 0.5 bar. During the research the gas temperature was kept constant at 21°C. Controlling the trans-membranous pressure and the stream of flow was done by retentate and permeate valves.

The characteristics shown on Fig.7 show findings of the membrane at variable feed pressure. The pres-

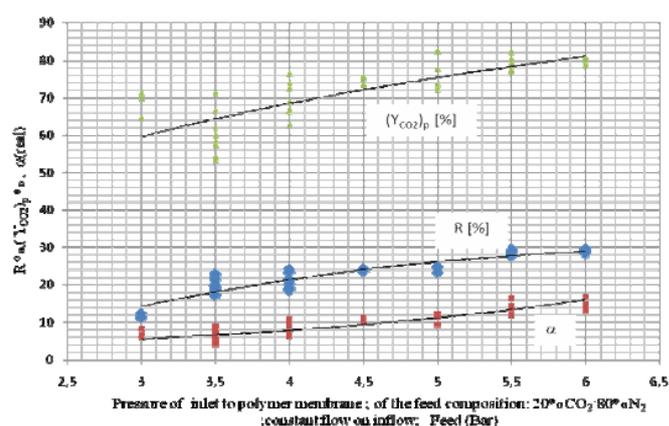


Figure 8: Test of polymer capillary membrane – UMS-A2 UBE Industries, feed composition: 20% CO<sub>2</sub>/80% N<sub>2</sub>

sure was progressively changed by approximately 0.5 bar in the range from 3 bar to 4 bar to keep constant values of the flow at the given measuring point. The obtained research results showed that this membrane did not show abilities in respect of CO<sub>2</sub> separation, giving evidence thereby of the low real factor of selectivity  $\alpha$ , which across the whole range of the variable feed pressure does not exceed 0.96. Furthermore, the CO<sub>2</sub> concentration of did not change in the retentate and permeate, which gives evidence recovery rate  $R$  of up to 50%, at purity (YCO<sub>2</sub>)<sub>p</sub> of 20% in the whole pressure range. During tests varying values of trans-membranous pressure between feed and permeate were generated, from level 0.5 bar to 2 bar, but the change of pressure did not show any other changes in other parameters of the work of the membrane.

#### 4.2. The chosen test of polymer membrane with the use of model gases

To determine the characteristics of the polymer membrane the initial test consisted of feeding the membranous module at variable pressure. The pressure was increased progressively from 3 to 6 bar at intervals of 0.5 bar. During this time the values of flows of feed, retentate and permeate were measured, Fig 8. The flow was kept below 220 l/h at all times. Control of the constant flow was regulated with the valve on the outlet retentate and the rotameter was observed in order to keep the reading at 200 l/h. Increase of the pressure in the following measuring points he clear and dynamic increase of the CO<sub>2</sub> con-

centration in the permeate (from 53–82% vol CO<sub>2</sub> was observed, while the concentration of retentate kept steady between 17% and 19% vol CO<sub>2</sub>) and with the display of the analyzer for feed at 21% vol CO<sub>2</sub> (this display was corrected and it was found that the analyzer overstate concentrations by about 1.2% vol CO<sub>2</sub>, which was subsequently taken into consideration when analyzing the results). The values of permeate flow varied in the range 8–15 l/h. It was found that changes in the density of gas-mixture on the permeate and retentate resulting from changes in the concentration of the mixture and not the important vacuum pressure occurring in the measuring-path – average 120 mmHg – fluctuated in the range from about 0.17 to 0.90 l/h. Although the readings of flow displays are laden with errors in the interval 1.5–3 l/h depending on the range of the flow of the rotameter used at the time of research, the obtained results lie within the parameters of measuring error and hence have sufficient credibility, particularly if subjected to further analysis. The increase in the pressure feed is accompanied by an increase in recovery rate  $R$ , which reaches the value  $R = 29.6\%$  at the pressure 6 bar, which is the characteristic pressure of membranous module work. Real factor selectivity  $\alpha$  rises in proportion to the increase in recovery rate  $R$ , reaching the value  $\alpha = 16.5$ . Purity  $(YCO_2)_p$  also rises and at its zenith reaches the value  $(YCO_2)_p = 82.3\%$ .

## 5. Conclusions

Due to continuous advances in technology, new kinds of materials become available for the construction of membranes resulting in increased reliability and operating convenience and an ability to reduce the membrane surface while retaining the same selectivity properties.

The same holds true for the technology of membranous separation of gases and in particular CO<sub>2</sub> from combustion gases. This opens up new vistas of use. The track record in this sphere already boasts operational devices with similar parameters, working on the basis of absorption processes.

The tubular experimental ceramic membranes tested on the presented experimental stand do not prove abilities in respect of CO<sub>2</sub> separation. They will find an application only for processes of per-

vaporation for the needs for the petro-chemical, foodstuffs and pharmaceutical sectors as well as in biotechnology and environmental protection. The polymer membrane measurement results obtained from the experimental stand make it possible to determine some features of investigated module:

- The highest values of recovery rate  $R$  for different standard mixtures occur for stream flows in the range 50–200 l/h.
- The best purity of permeate  $(YCO_2)_p$  occurs for pressure feed 6 bar at variable flows and is situated in the range  $(YCO_2)_p = 51–98.8\%$ .
- The highest value the purity of the permeate  $(YCO_2)_p = 98.8\%$  occurs at the flow of feed 1625 l/h for the mixture enriched with the composition: 50% CO<sub>2</sub>/50% N<sub>2</sub>.
- Increasing the stream flow feed to over 200 l/h causes a nosedive in recovery rate  $R$  reaching in the extreme case the value 5% (for flow of 1625 l/h).

The stand presented in the article is an effect of 3 years of connected research into membranous separation of CO<sub>2</sub> relating to CO<sub>2</sub> capture. At present the laboratory:

- researches parameters for the separation of CO<sub>2</sub> membranes and analyzes their properties and utility with regard to CO<sub>2</sub> capture and sequestration technologies (with the use of mixtures of standard gases)
- tests innovative membrane materials solutions for CO<sub>2</sub> capture and sequestration technologies
- tests innovative solutions for constructional membranous modules for CO<sub>2</sub> capture and sequestration technologies.

Scientific research continues in this field and likewise works are ongoing to upgrade and develop the experimental stand at the main unit: The laboratory of membranous techniques and methods using membranous technology for the purpose of CO<sub>2</sub> separation.

### *Acknowledgements*

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