Membrane permeance test

Membrane permeance test unit (Figure S1) includes the mass flow controllers FG-201 CV (Netherland, Bronkhorst), which are used to supply individual gases. These controllers may be applied separately or in gas mixing mode to prepare the desired mixture into the mixing tank in real-time. Another two controllers F-201 CV and F201 CM (Netherland, Bronkhorst) supply purge gas (helium) and internal standard (argon) into the pipelines of the test unit (in the case when the permeance of these gases is not the object of research). In order to purge the distribution pipeline system from previously used gases and prepare the unit before the experiment, the helium is used. A two-position pneumatically-actuated valve is used to connect the membrane module's feed side with mixing tank or helium supply pipeline. The retentate side of a membrane module is equipped with P702 CM pressure regulator (Netherland, Bronkhorst) to keep the pressure level constant along the membrane.

The permeated gas enters the vacuum chamber which is part of pump station, which is Hi-Cube ECO 300 (Germany, Pfeiffer). These pumps ensure the discharge of gases from the membrane module. The pressure value in the permeate side is defined by a pressure transmitter MPT200 (Germany, Pfeiffer). A solenoid-operated diaphragm valve DVC 025 PX (Germany, Pfeiffer) installed in between the membrane module and pump station is used to shut down the vacuum equipment in case of pressure surges resulting from damage to the membrane samples. Further, permeated gas goes to the QMG 250 M2 quadrupole mass spectrometer (Germany, Pfeiffer), which is connected to another pump station Hi-Cube 80 (Germany, Pfeiffer). The pressure level in mass-spectrometer chamber is monitored via second pressure transmitter (Kryuchkov et al., 2024).

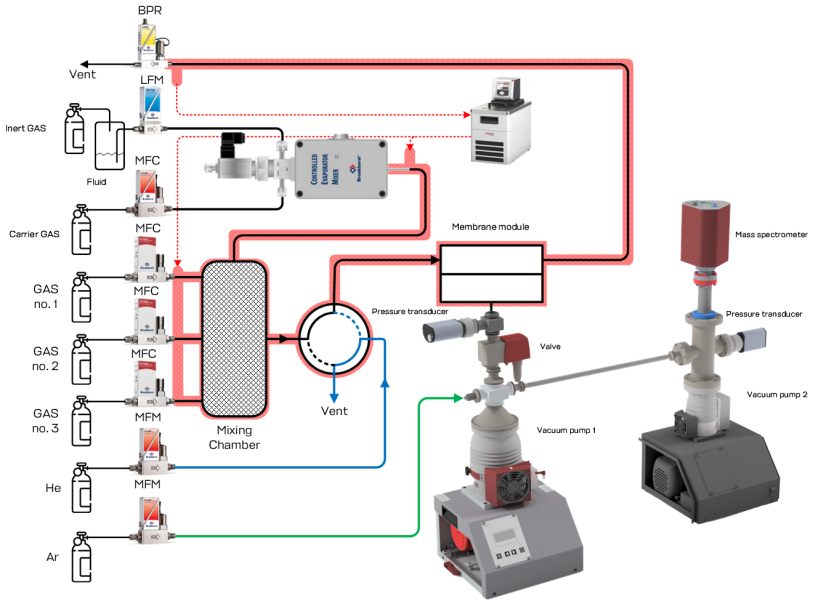

Figure S1 Schematic diagram of mass spectrometer coupled experimental unit for membrane mass transfer properties study

Before the experiments, the membrane module is swept out using helium (at a volume flow rate of 50 - 150 cm^3 min^{-1}) and the mixing tank is fed with pure gases separately or multiple gases to prepare the gas mixture (total volume flow rate - up to 750 cm^3 min^{-1}). Argon is also supplied to the vacuum side of the gas distribution system (volume flow rate 4 cm^3 min^{-1}), unless an argon permeance study is required. Helium purging is necessary to remove air or gases remaining in the system after previous experiments. The permeation process is monitored by a mass spectrometer that refreshes the raw data every 1 ms.. At the end of the purge procedure, the switching valve connects the mixing tank and feed side of the membrane module with an 8 ms delay. The FlowPlot software is used to record the membrane module pressure level and all mass flows. The PV MassSpec and PV TurboViewer are used to record the pressure level under the membrane and obtain mass-spectra. In this way, all raw data is collected in real-time and it allows to calculate the permeance value in every single point according following equations:

Permeance Q is determined in accordance with:

$$Q = {}^{J_i}/_{\Delta pA} \quad (1)$$

In equation (1) J_i – component i volumetric flow rate, cm^3 min^{-1}; Δp is component i partial pressure difference across the membrane, cmHg; and the membrane area is A, cm^2.

Membrane selectivity is calculated according to equation:

$$\alpha_{AB} = {}^{Q_A}/_{Q_B}. \quad (2)$$

The membrane selectivity is determined by simple division of membrane permeance values of two gases of interest.

The software of the mass spectrometer allows transformation of the signal of each component into the value of its partial pressure. Thus, the permeate volumetric flow rate may be estimated by the formula:

$$\frac{J_i}{J_{Ar}} = \frac{p_i}{p_{Ar}} \quad (3)$$

where J_{Ar} is the volumetric flow rate of argon, cm^3 min^{-1}; pi is the partial pressure of component i in the permeate, cmHg; and pAr is the partial pressure of argon in the permeate, cmHg. The error does not exceed ±2.2 % of the measured value.

Schematic diagram of a membrane-absorption gas separation module

The configuration of membrane-assisted gas absorption cell for natural gas sweetening is shown in Fig. S2 and the photos of the cell are given in Fig. S3. In that cell two different types of membranes are used for realization of the separation process: ultrafiltration hollow fiber membrane provided by the Laboratory of Membrane Processes of the Institute of Physical and Organic

Chemistry of the National Academy of Sciences of Belarus, and asymmetric hollow fiber gas separation membrane made of polysulfone provided by Airrane Co., Ltd. The outer diameter of the gas separation fiber is about 450 μm. The inner diameter of the ultrafiltration fiber is about 1 mm with a wall thickness of about 0.28 mm. The total effective area of the gas separation membrane is ~ 27.5 cm^2, and the ultrafiltration ~ 147 cm^2. Plexiglas made of polymethylmethacrylate was used as a casing for the membrane module, allowing visual control of the process.

An important design solution for the applied MAGA unit is the use of two types of hollow fibers simultaneously. In the ends of the cylindrical casing of the module, using an epoxy resin, fixation and sealing of polymeric ultrafiltration fibers, which is used to ensure contact of two phases (separated gas mixture and liquid absorbent), is implemented. In this unit configuration, the gas separating polysulfone fibers are placed inside the ultrafiltration membrane. The gas separating hollow fibers are used to remove desorbed gases from the absorbent. Gas separating hollow fibers are not fixed and sealed in the end parts of the module casing, as in the case of the ultrafiltration one. They are fixed at the ends of specially made fittings (tees) located at the ends of the cylindrical module casing. That membranes arrangement ensures that there is a gap between the two fibers. At the same time, that approach to fibers fixation allows to prevent leakage of liquid component. The cylindrical containers located on the tees serve for filling with liquid absorbent. These containers themselves are arranged to allow the liquid to flow into the gap between the two types of fibers described above. Through one of the fibers the feed stream is brought into contact with the liquid absorbent, and through the other the absorbed component is removed. Two connections are fixed on the outer surface of the device, one for the input of the feed stream and one for the output of the retentate. The characteristics of the membrane-assisted gas absorption cell in details are given in Table S1.

The separation process is realized as in the following procedure. Through one of the nipples attached to the outer surface of the shell of the MAGA module, a flow of feed gas mixture is introduced, which fills the inner volume of the shell and comes into contact with the liquid absorbent through the ultrafiltration fiber. Then the gases which have been dissolved in the absorbent are moved toward the surface of gas separation membrane under the pressure gradient and passes through the polysulfone hollow fiber to form a flow enriched with highly soluble gases. Gases that are low soluble in the absorbent are removed from the module through a fitting mounted on the opposite side of the housing as the retentate stream. The permeate side of the described module is a flow-through volume. In the laboratory tests it is swept by a helium flow, meanwhile at the gas processing plant heated air may be used to enhance the desorption.

Table S1 – The characteristics of membrane-assisted gas separation cell.

Characteristic	Value	
Cell diameter	30 mm	
Overall cell length	240 mm	
	Membrane	
	Ultrafiltration	Gas separation
Material	Polysulfone	Polysulfone
Overall length	195 mm	130 mm
Active length	130 mm	95 mm
Outer diameter	445 µm	1 560 µm
Inner diameter	290 µm	1 000 µm
Number of fibers	20	20

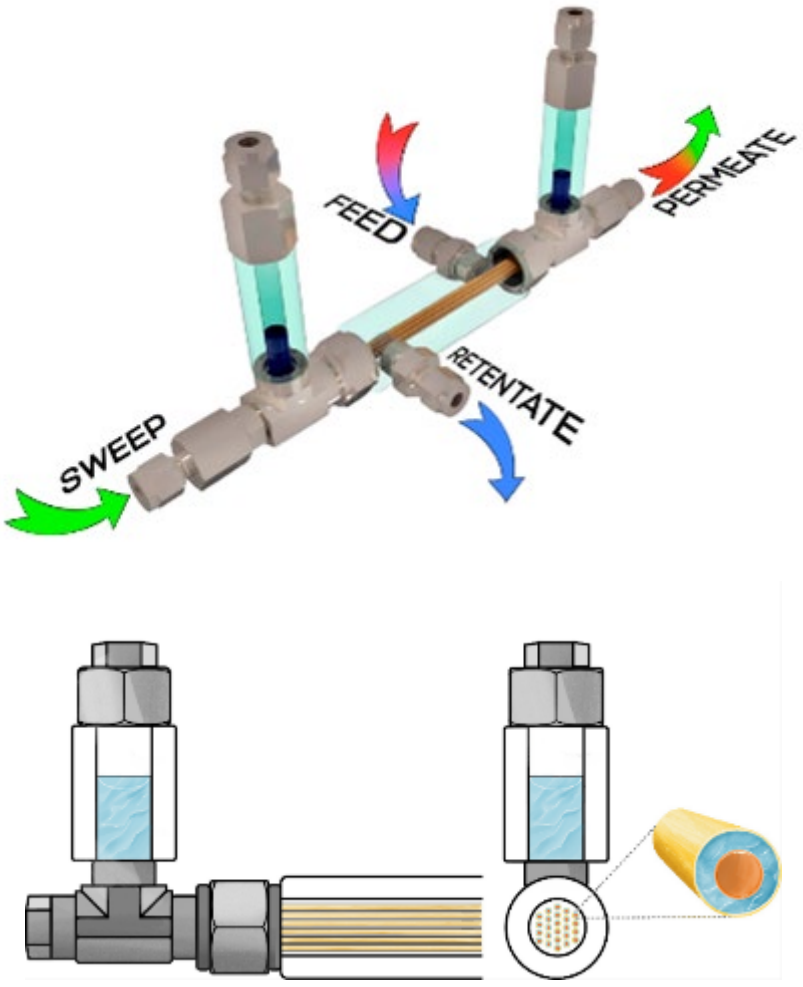

Figure S2 – 3D image of the membrane-assisted gas absorption unit and its schematic diagram

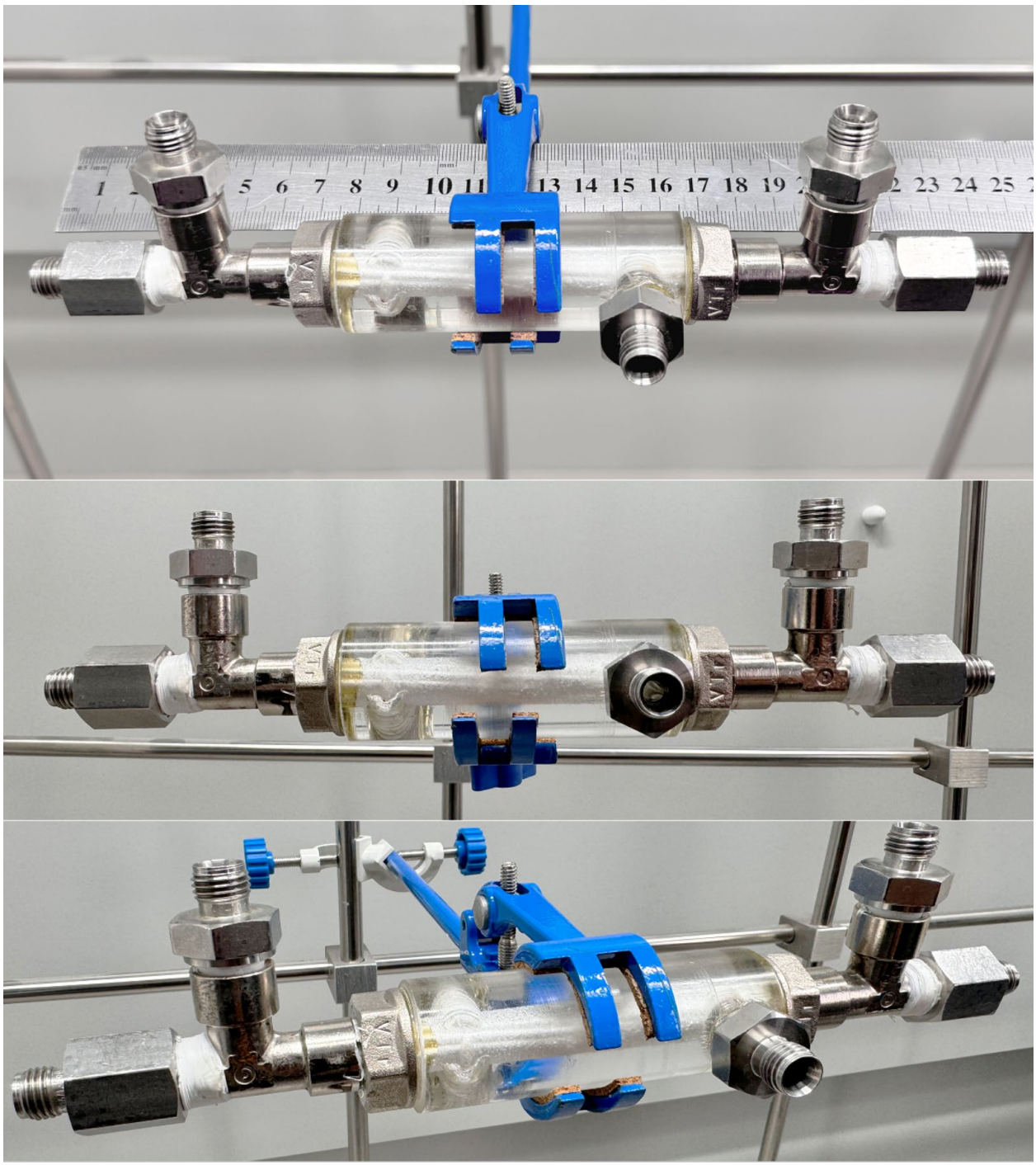

Figure S3 – Photos of membrane-assisted gas absorption cell.

Table S2 - Permeance (Q, GPU) of PSF membranes for single gases

Sample	Q[a], GPU							
	N_2	CH_4	Xe	C_2H_6	C_3H_8	C_4H_{10}	CO_2	H_2S
PSF	13.2	30	6.2	22.9	18.9	17.4	220.4	244.3
PEI+PI	1.6	2.8	0.9	2.0	2.0	2.0	30.7	13.6

@ pressure drop 101 kPa, 25 °C.

[a]1 GPU = 1×10^{-6} cm^3 cm^{-2} s^{-1} cm Hg^{-1}

Table S3 - Selectivity of PSF for single gases

Sample	α (CO_2/x)						
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	H_2S	N_2	Xe
PSF	7.3	9.6	11.7	12.7	0.9	16.7	35.5
PEI+PI	11.0	15.4	15.4	15.4	19.2	34.1	2.3
	α (H_2S/x)						
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO_2	N_2	Xe
PSF	8.1	10.7	12.9	14.0	1.1	18.5	39.4
PEI+PI	4.9	6.8	6.8	6.8	8.5	15.1	0.4

Table S4 - Permeance (Q, GPU) of PSF for gas mixture components

Sample	Q[a], GPU							
	N_2	CH_4	Xe	C_2H_6	C_3H_8	C_4H_{10}	CO_2	H_2S
PSF	18.4	37.2	9.1	27.4	22.8	19.4	296.5	314.7
PEI+PI	4.4	4.8	3.0	3.7	3.5	2.3	33.7	24.5

@ pressure drop across the membrane 101 kPa, 25 °C.

[a]1 GPU = 1×10^{-6} cm^3 cm^{-2} s^{-1} cm Hg^{-1}

Table S5 - Selectivity of PSF membranes for gas mixture components.

Sample	α (CO_2/x)						
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	H_2S	N_2	Xe
PSF	8.0	10.8	13.0	15.3	0.9	16.1	32.6
PEI+PI	7.0	9.1	9.6	14.7	1.4	7.7	11.2
	α (H_2S/x)						
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO_2	N_2	Xe
PSF	8.5	11.5	13.8	16.2	1.1	17.1	34.6
PEI+PI	5.1	6.6	7.0	10.7	0.7	5.6	8.2