

Supported **ionic liquid** membranes for selective separation of volatile organic vapour and pollutants from gas stream

LD14094 (04/2014-04/2017)



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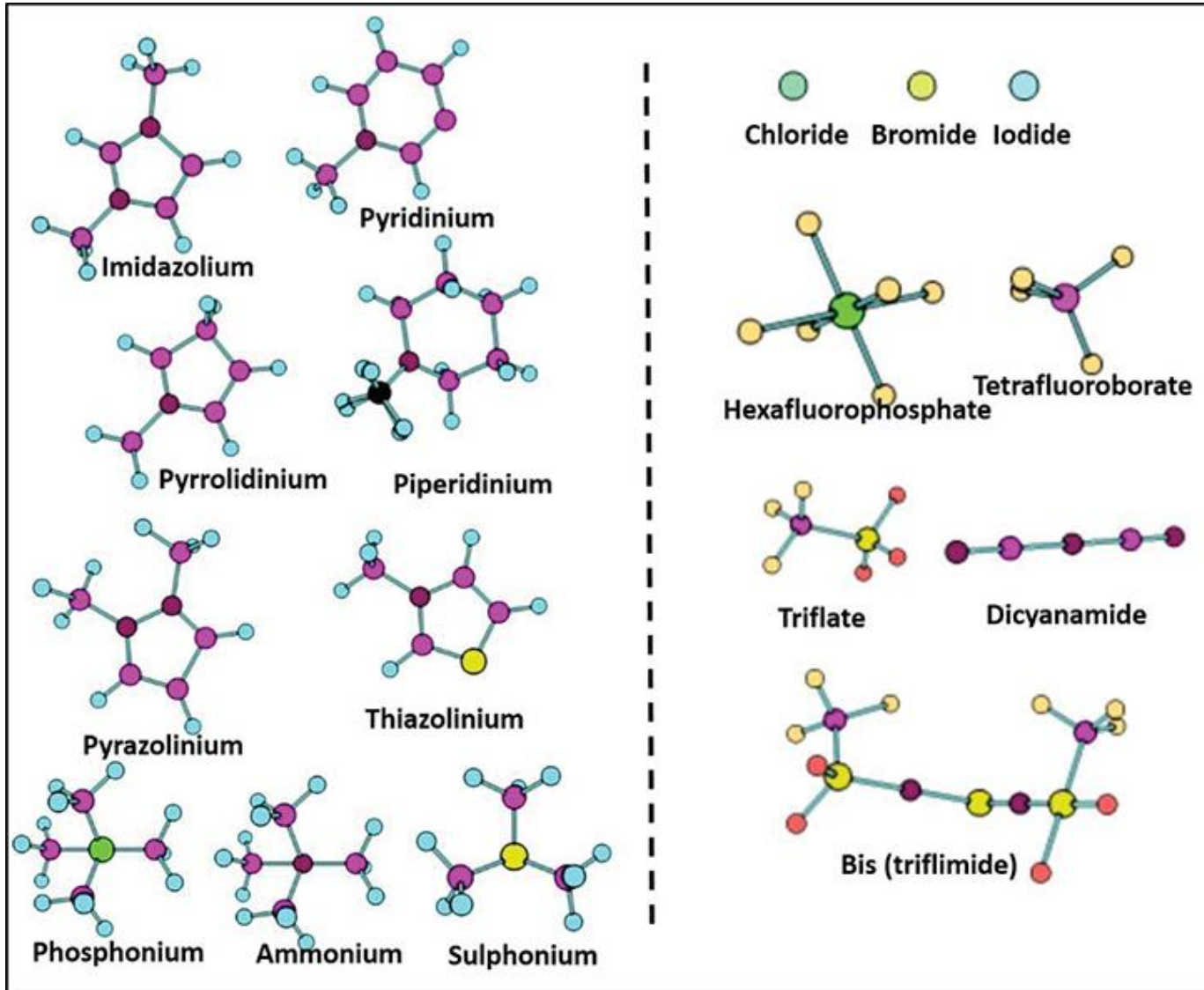
at Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, v.v.i.

**COST INFORMATION DAY in the Czech Republic**

# EXIL (European network for Exchange of knowledge about Ionic Liquids)



# IONIC LIQUIDS

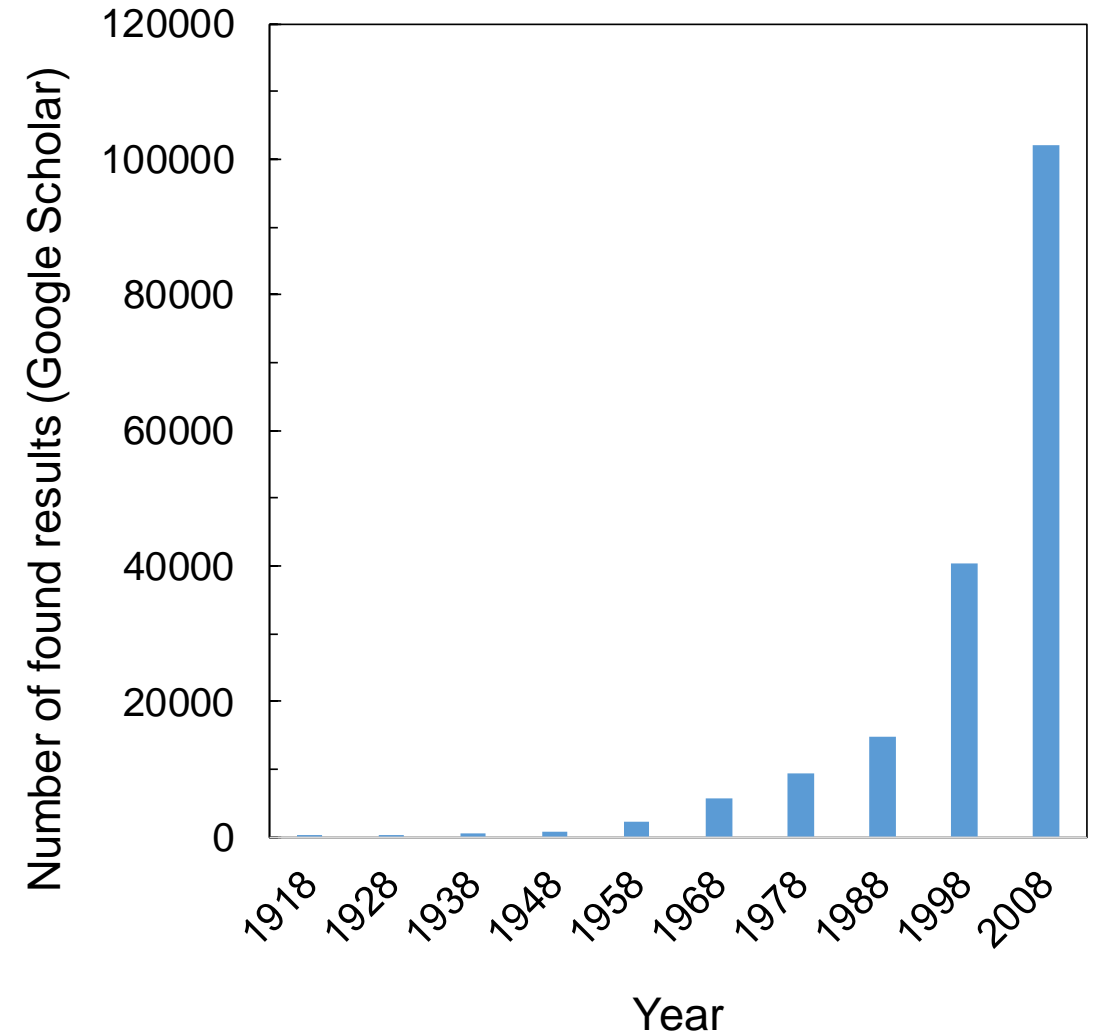


... they are magic  
... they conduct electricity  
... they do not evaporate  
... they are said to be green solvent  
...

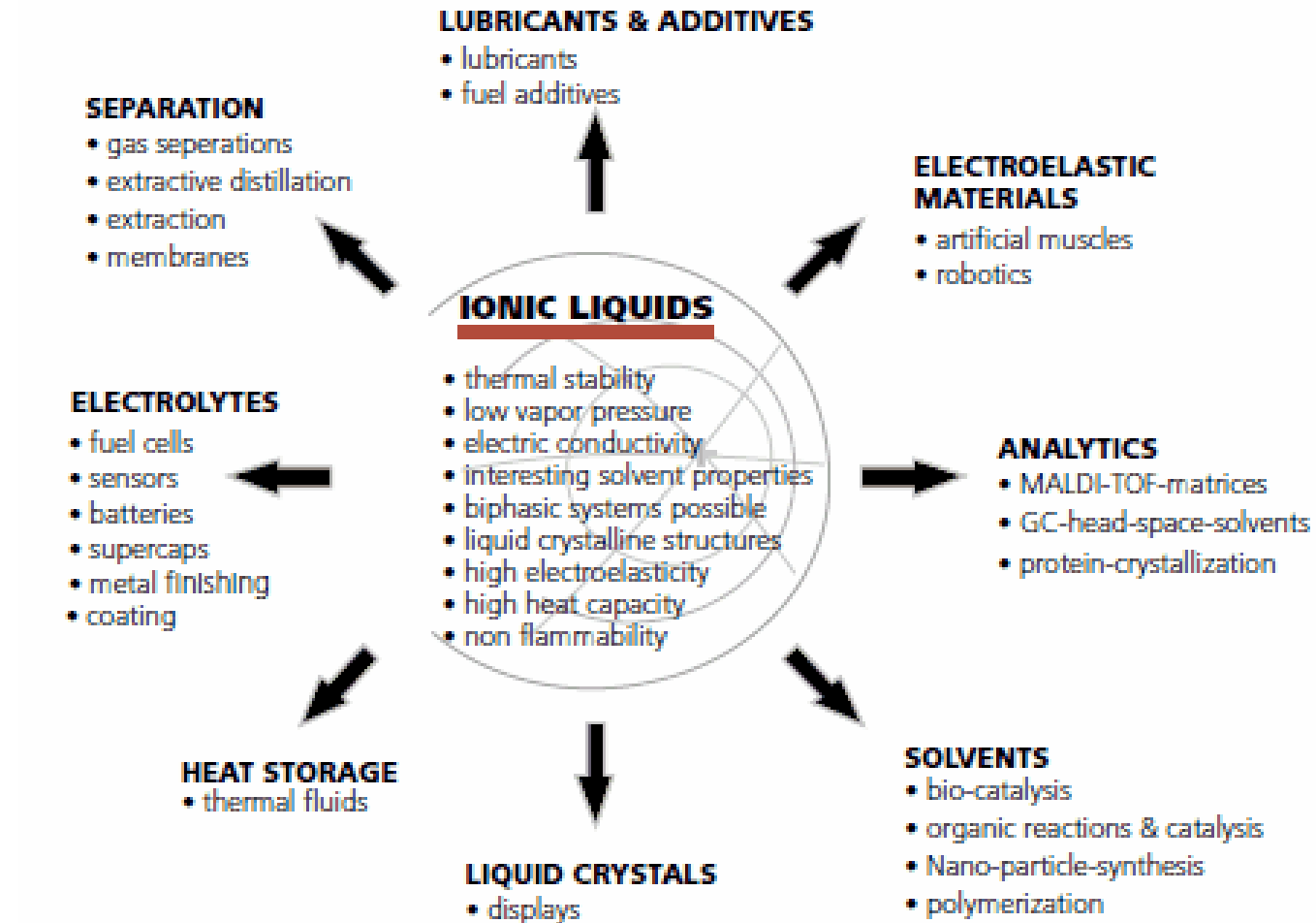
- Unsymmetrical organic cation and organic/inorganic anion
- Salts (neutral) that are liquid at low temperature (below 30°C) ... RTILs
- Works at mild conditions

# IONIC LIQUIDS

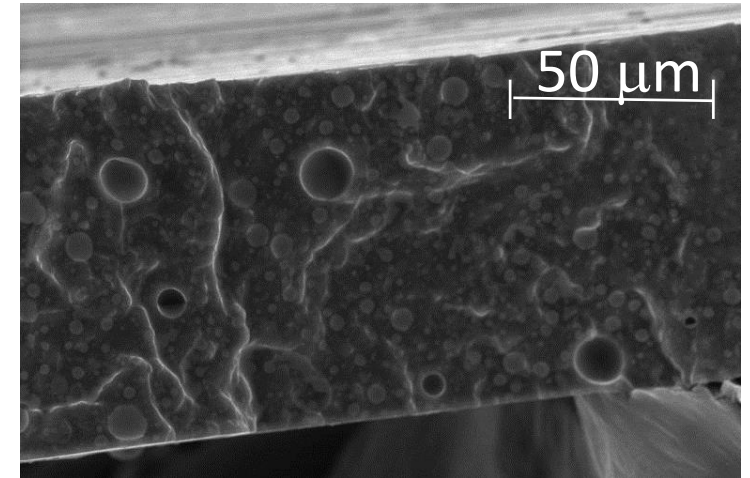
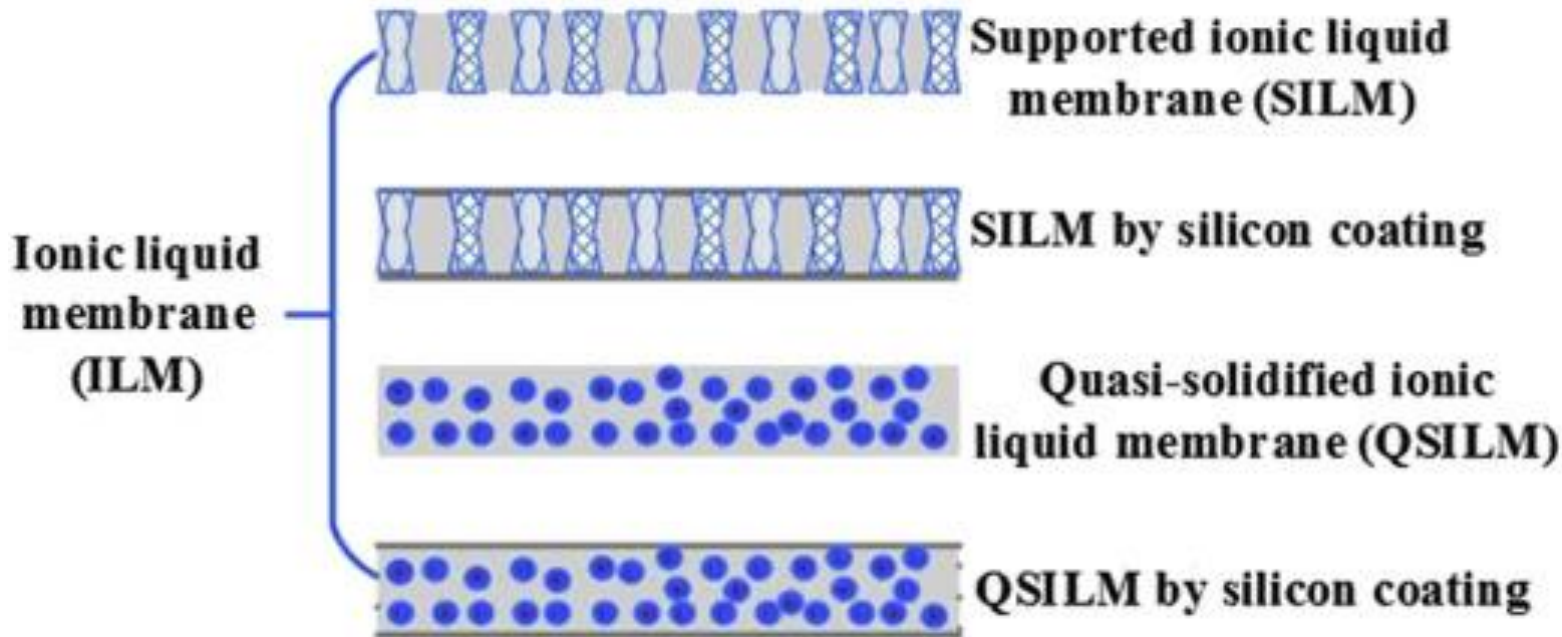
- Rapid growth of interest
- Tailored to address the needs of a specific application
- High thermal stability and chemical inertness
- Relatively low cost
- Easily separated and recycled
- Non-toxic to enzyme or fermentation



# IONIC LIQUIDS

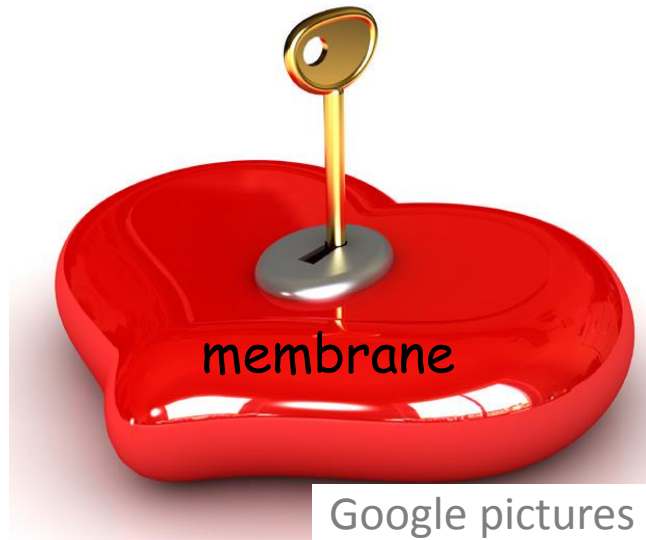


# How to prepare membrane with IL?



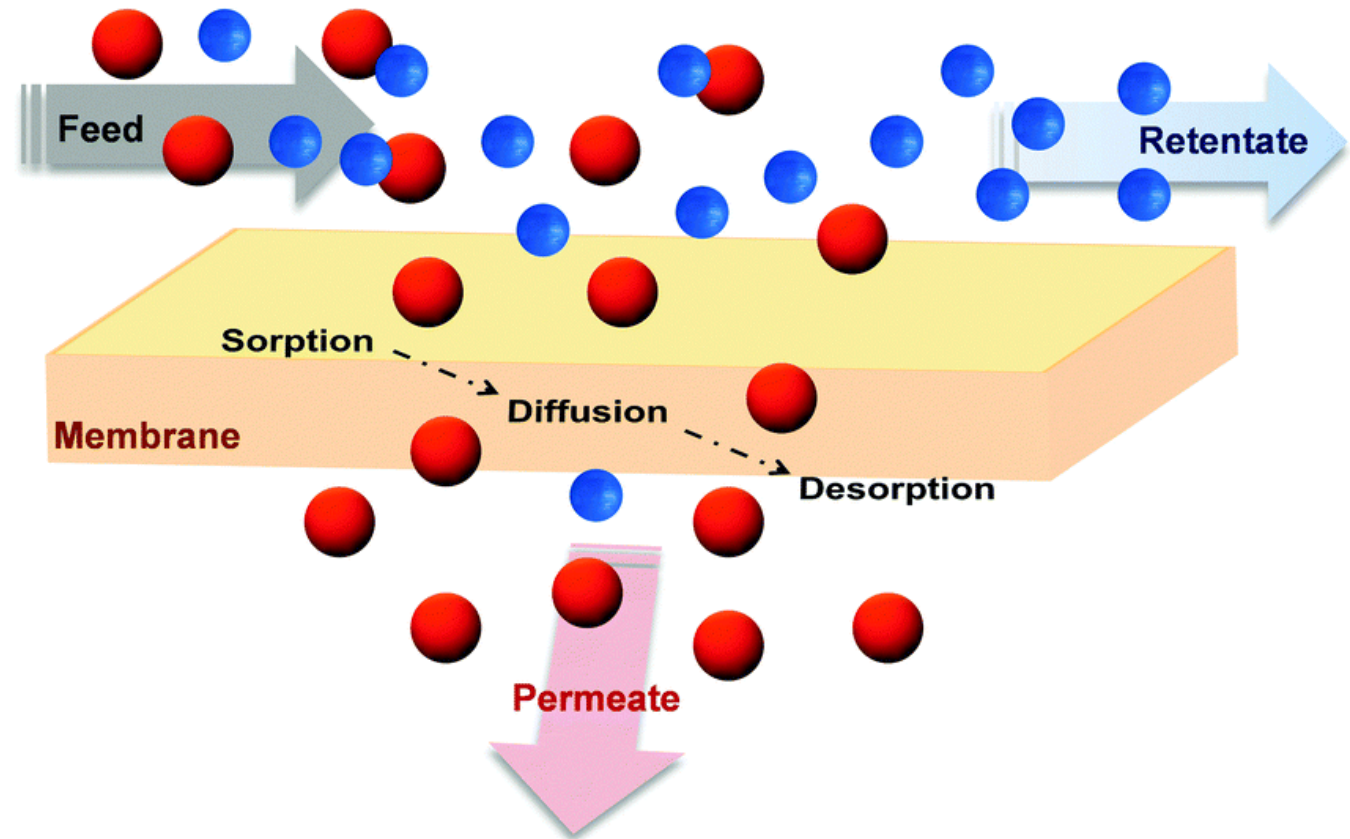


# Membrane separation



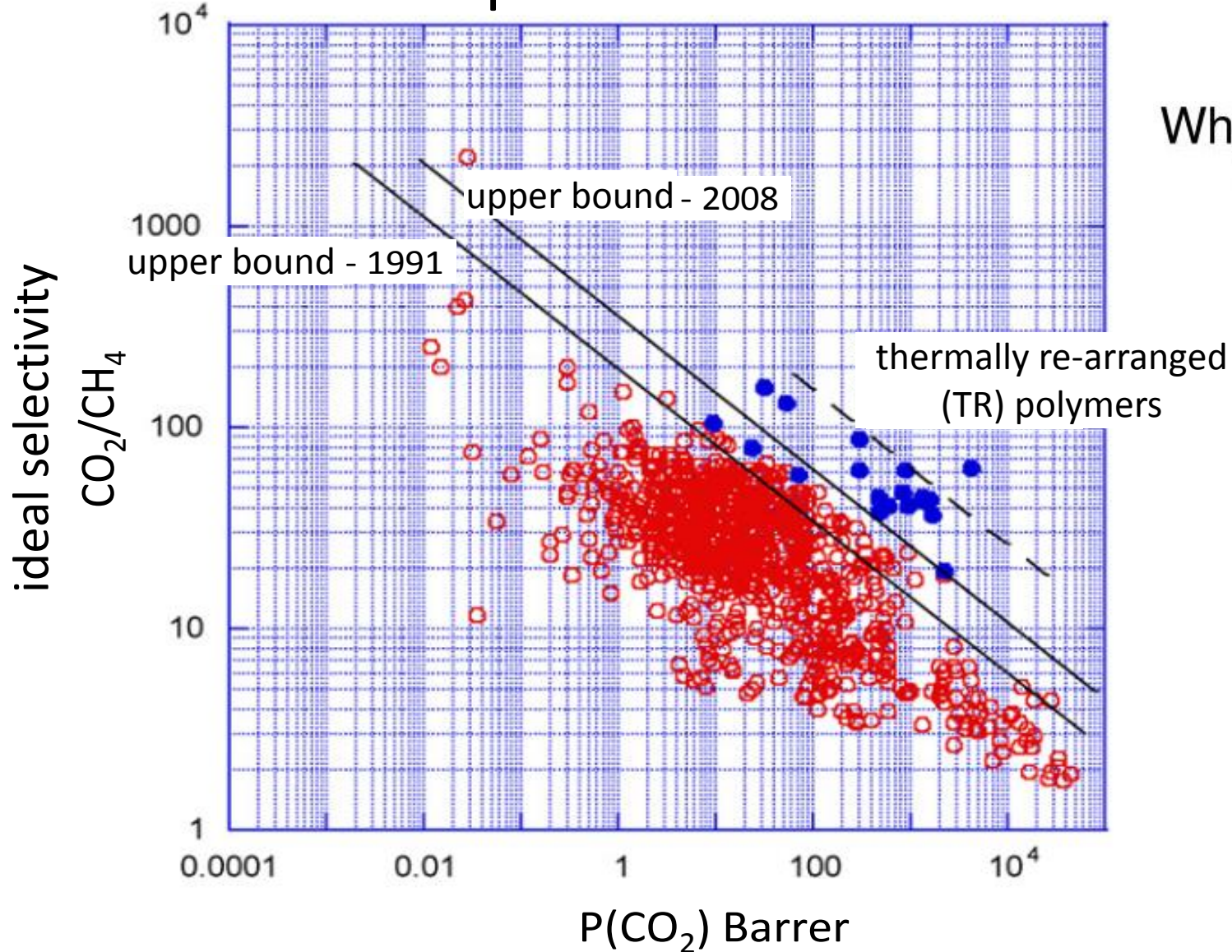
heart of membrane process

→ key parameter for the successful  
of membrane separation



$$S(c)_i \times D(c)_i = P_i$$

# Robeson plot

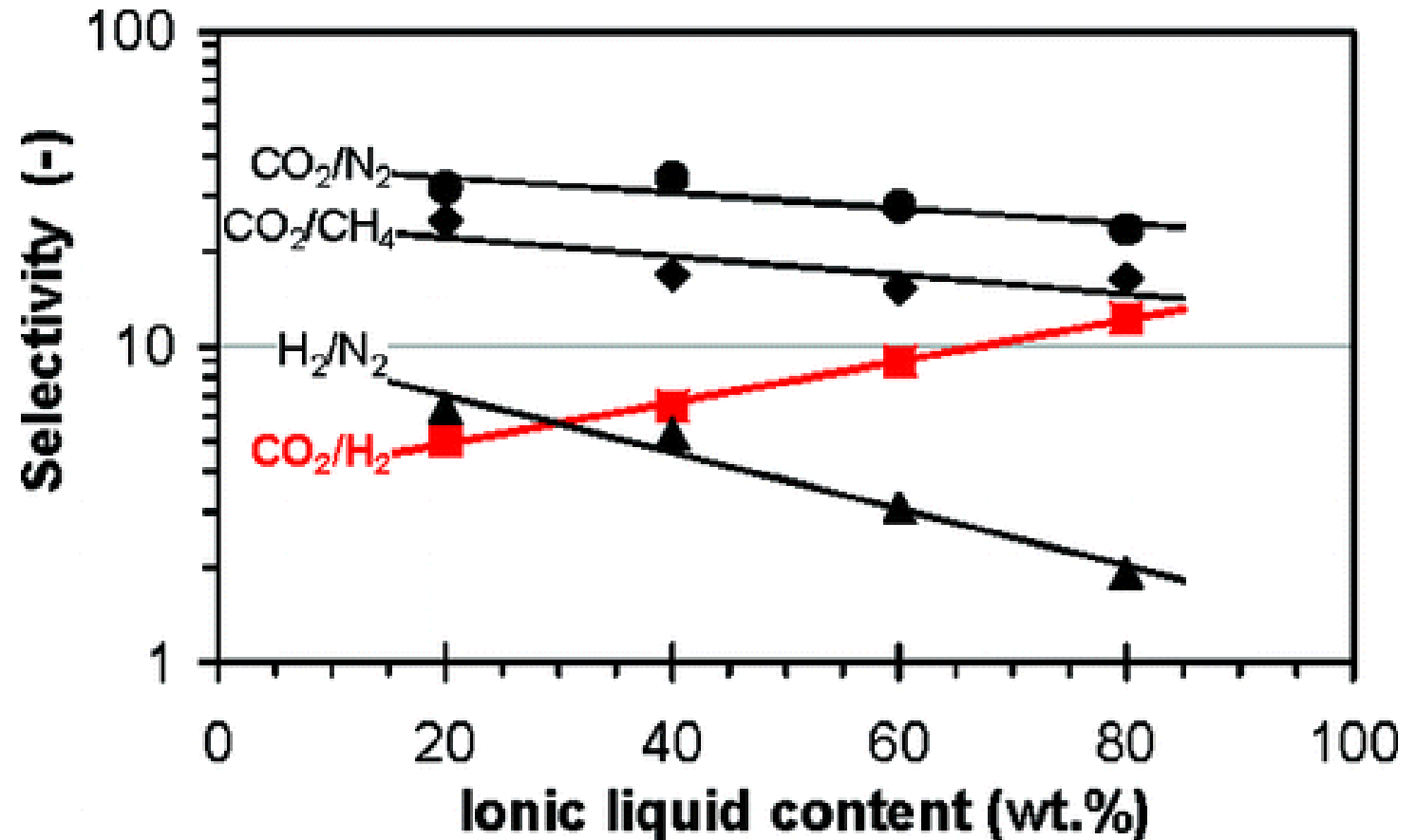


Why must the cell membrane maintain  
**SELECTIVE PERMEABILITY?**

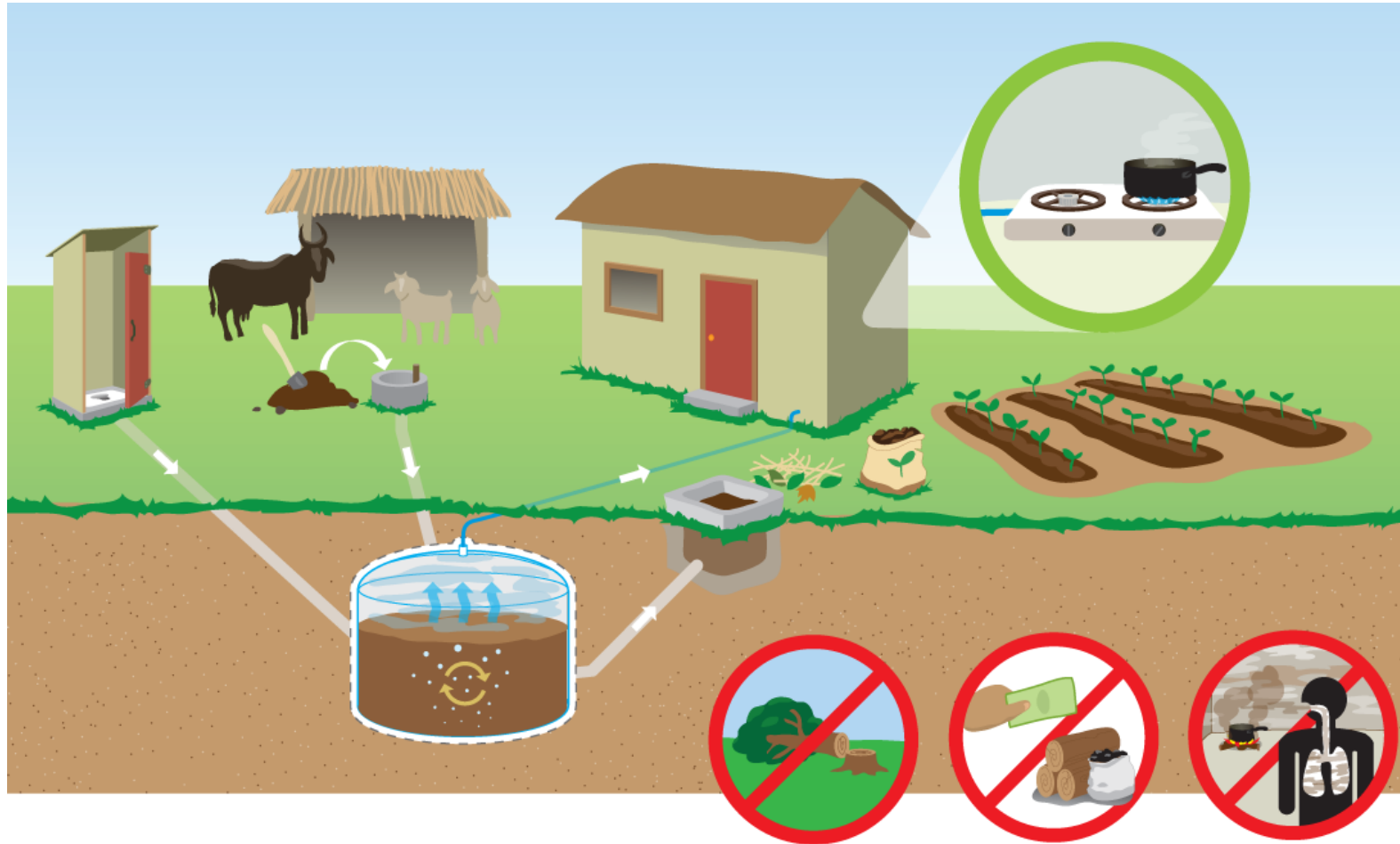




# Improvement of separation properties thanks to IL



# Biogas as a source of ecological energy



- Gaseous mixture contains mostly  $\text{CH}_4$  and  $\text{CO}_2$
- Other components like  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  or siloxanes are present in trace concentrations
- Exact composition of biogas depends on its origin
  - sewage digester
  - farm biogas plant
  - landfilland can vary at different seasons

Biogas rises during anaerobic digestion of animal and vegetable waste.

# Biogas upgrading processes

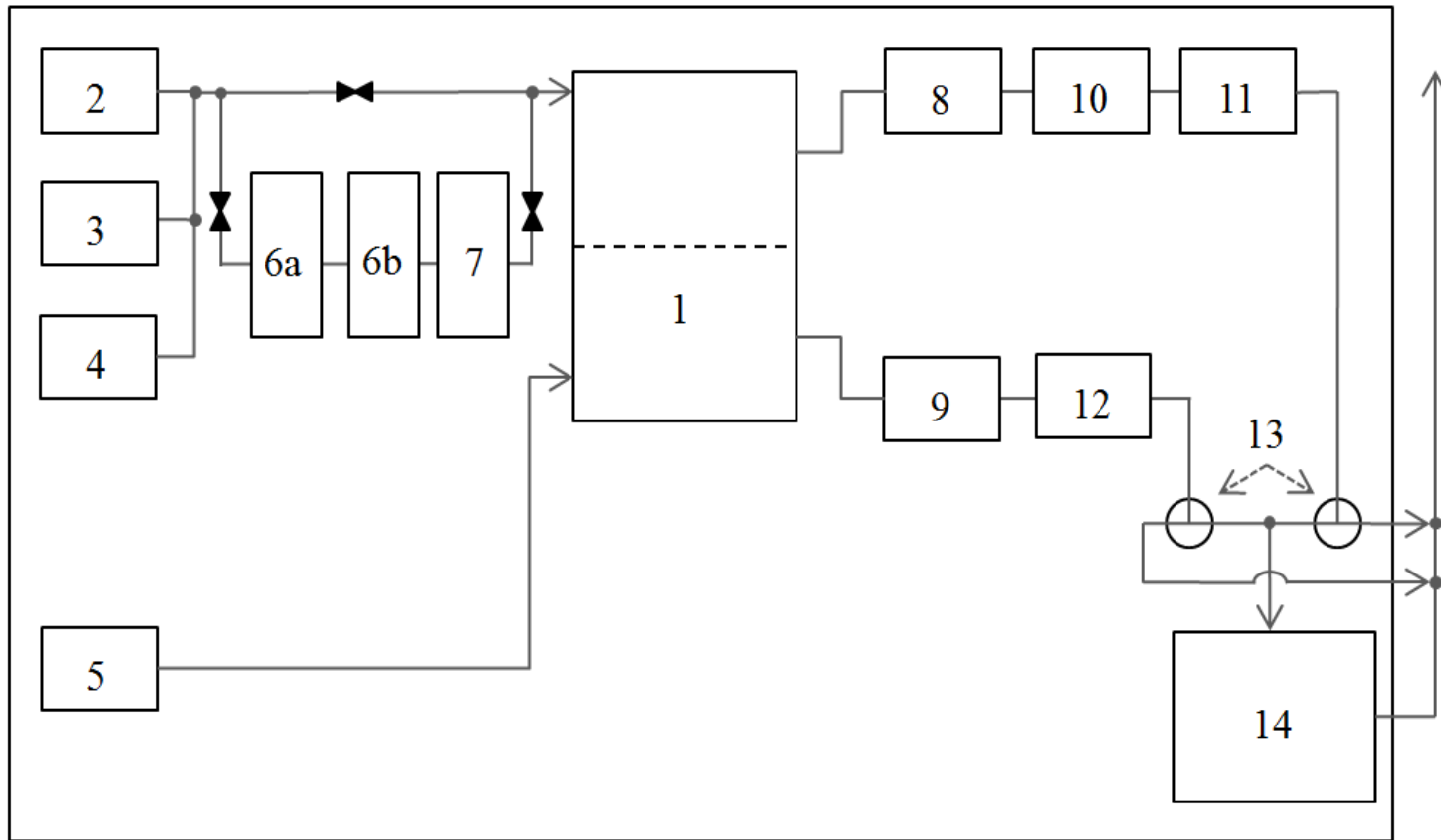
- ❑ Drying – water vapor removal
- ❑ Desulfurization
- ❑ Removal of other trace compounds (ammonia and siloxanes)
- ❑ Carbon dioxide removal
  - ❑ Absorption (water scrubbing, amines)
  - ❑ Adsorption (porous solids – zeolites or active carbon)
  - ❑ Cryogenic separation
  - ❑ Membranes separation

# Membrane separation

- ❑ Energy savings
- ❑ Environmental friendliness
- ❑ Easy handling
- ❑ Continuous process
- ❑ Compact design and small footprint
- ❑ polyimides (PI)
- ❑ facilitated transport membranes
- ❑ mixed matrix membranes (MMMs)
- ❑ carbon molecular sieves (CMS)
- ❑ polyethyleneoxide (PEO)
- ❑ liquid membranes (LMs)

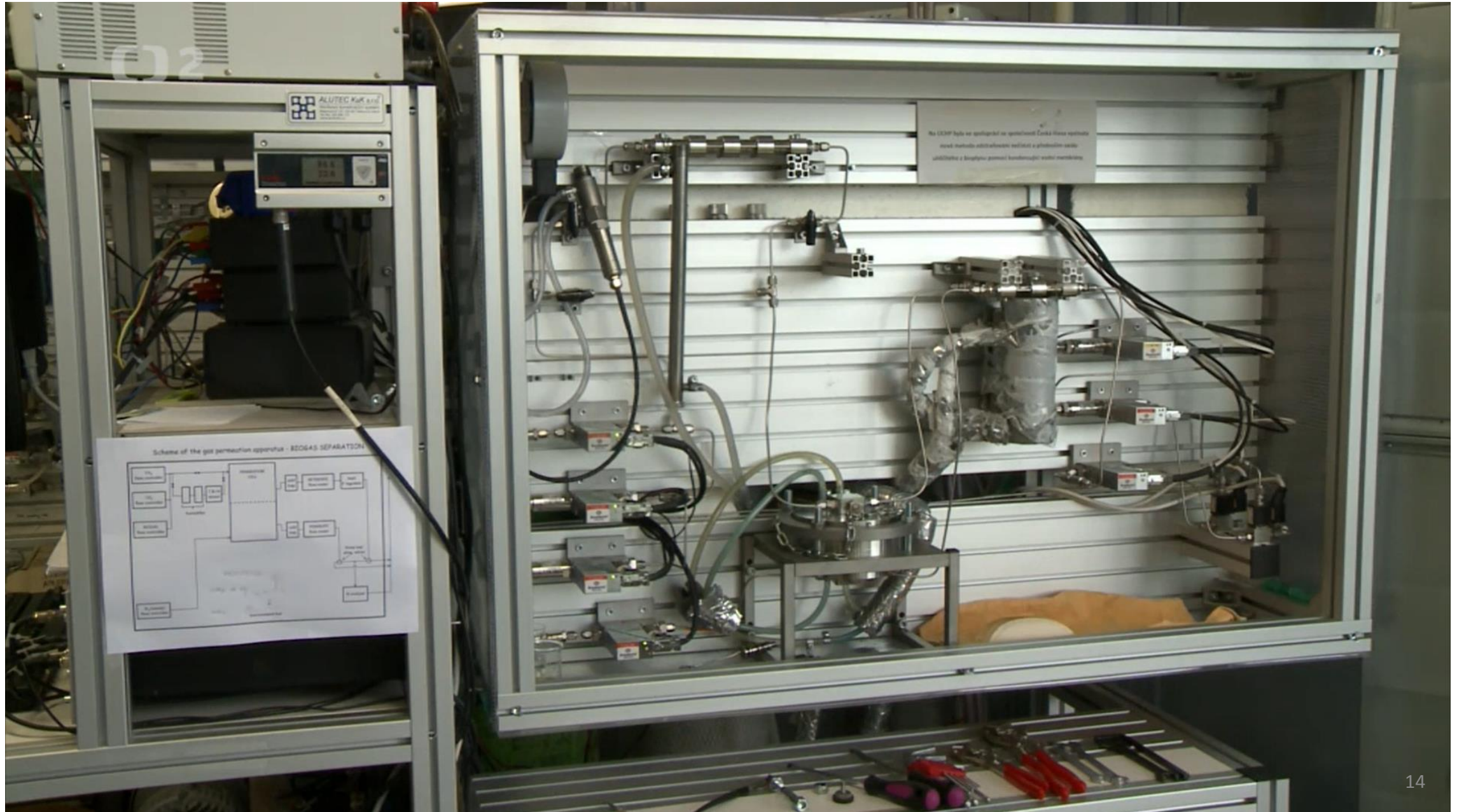


# Gas permeation apparatus

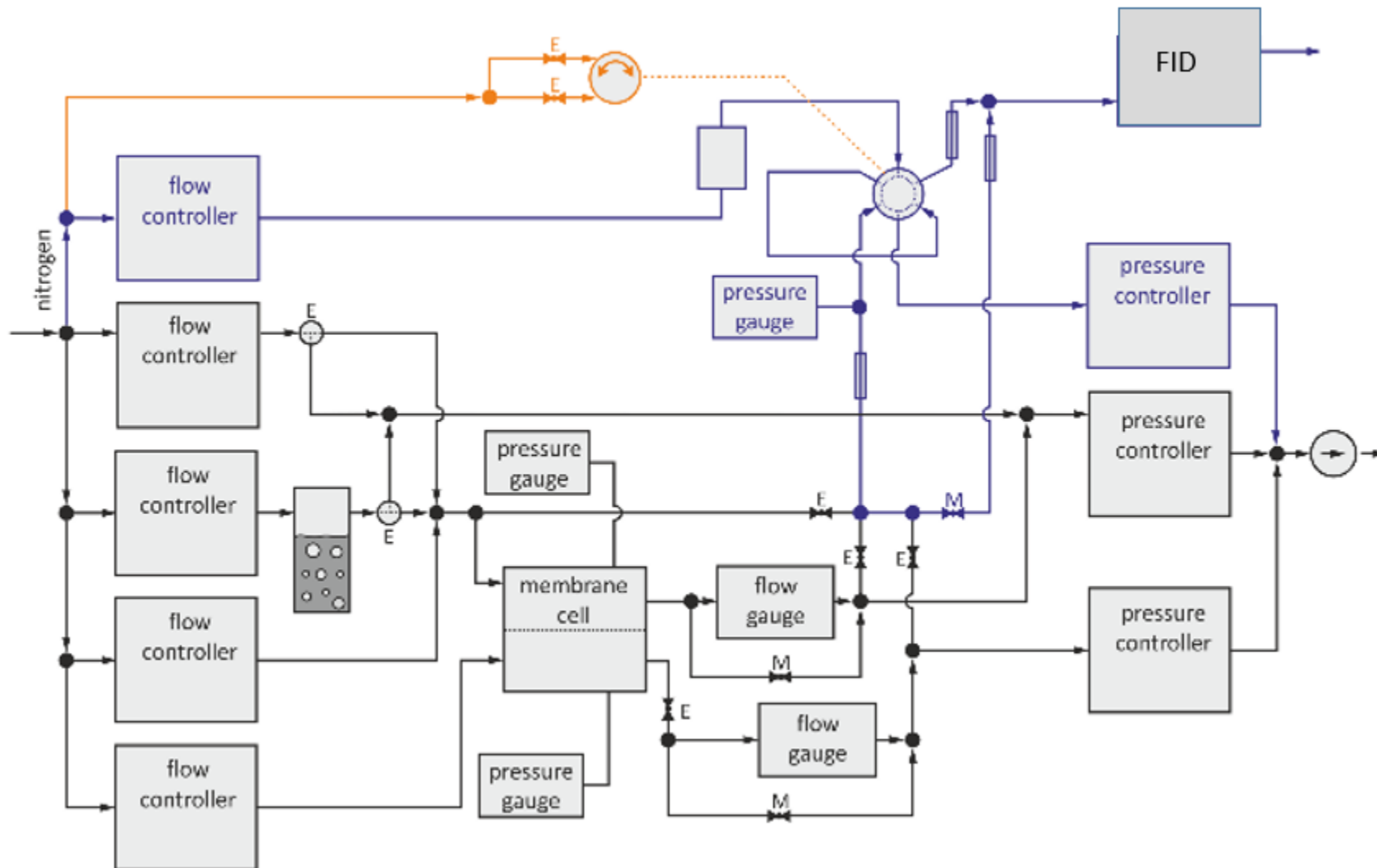


- 1: permeation cell,
- 2: raw biogas flow controller,
- 3: CH<sub>4</sub> flow controller,
- 4: CO<sub>2</sub> flow controller,
- 5: N<sub>2</sub> flow controller,
- 6: humidifier (6a at  $T_{lab}$  and 6b is heated),
- 7: temperature and humidity sensor,
- 8,9: cold traps,
- 10: back pressure regulator,
- 11: retentate flow meter,
- 12: permeate flow meter,
- 13: three-way electromagnetic valves,
- 14: IR analyzer.

# Gas permeation apparatus



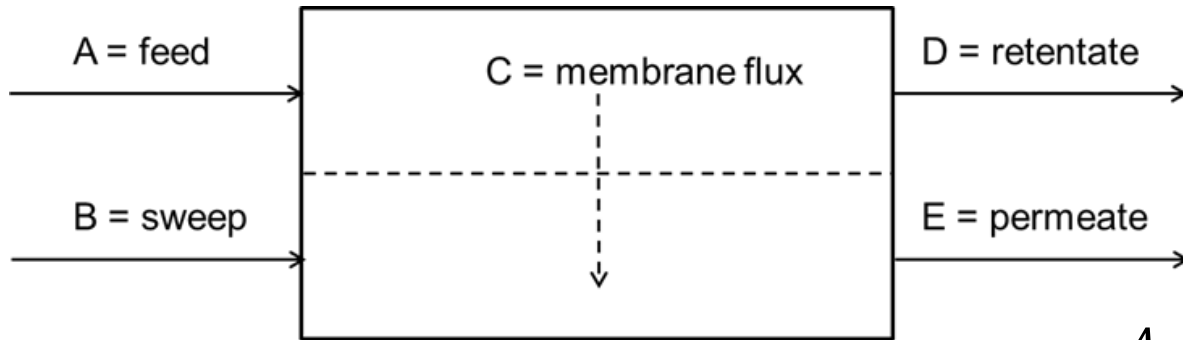
# Organic vapour separation



**Modification:**  
➤ Cold trap for permeate stream

**Innovation:**  
➤ Inline-FID analyses of all streams

# Study of vapour permeation



$$A_{N_2} - C_{N_2} - D_{N_2} = 0, \quad \text{Eq. (1)}$$

$$A_{VOC} - C_{VOC} - D_{VOC} = 0, \quad \text{Eq. (2)}$$

$$B_{N_2} + C_{N_2} - E_{N_2} = 0, \quad \text{Eq. (3)}$$

$$B_{VOC} + C_{VOC} - E_{VOC} = 0, \quad \text{Eq. (4)}$$

$$(1 - x_{E,VOC}) \cdot E_{VOC} - x_{E,VOC} \cdot E_{N_2} = 0, \quad \text{Eq. (5)}$$

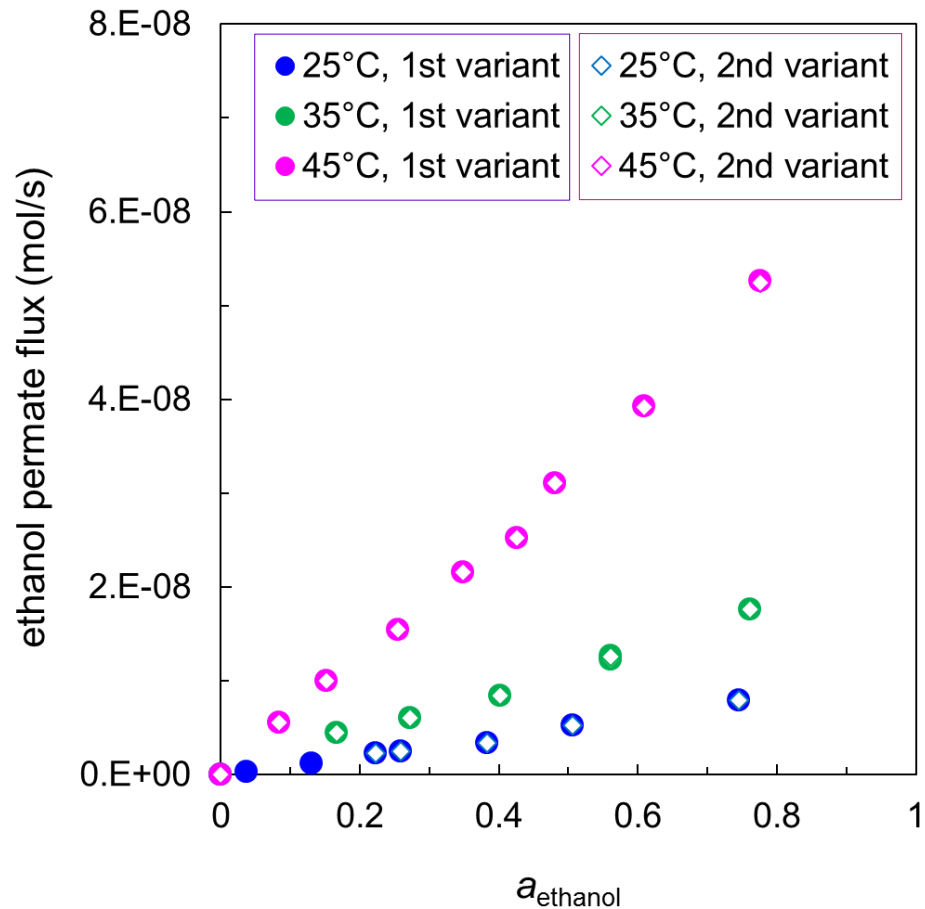
$$C_{N_2} = 0, \quad \text{Eq. (6)}$$

$$C_{N_2} + C_{VOC} = V/(R \cdot T) \cdot (dP/d\tau), \quad \text{Eq. (7)}$$

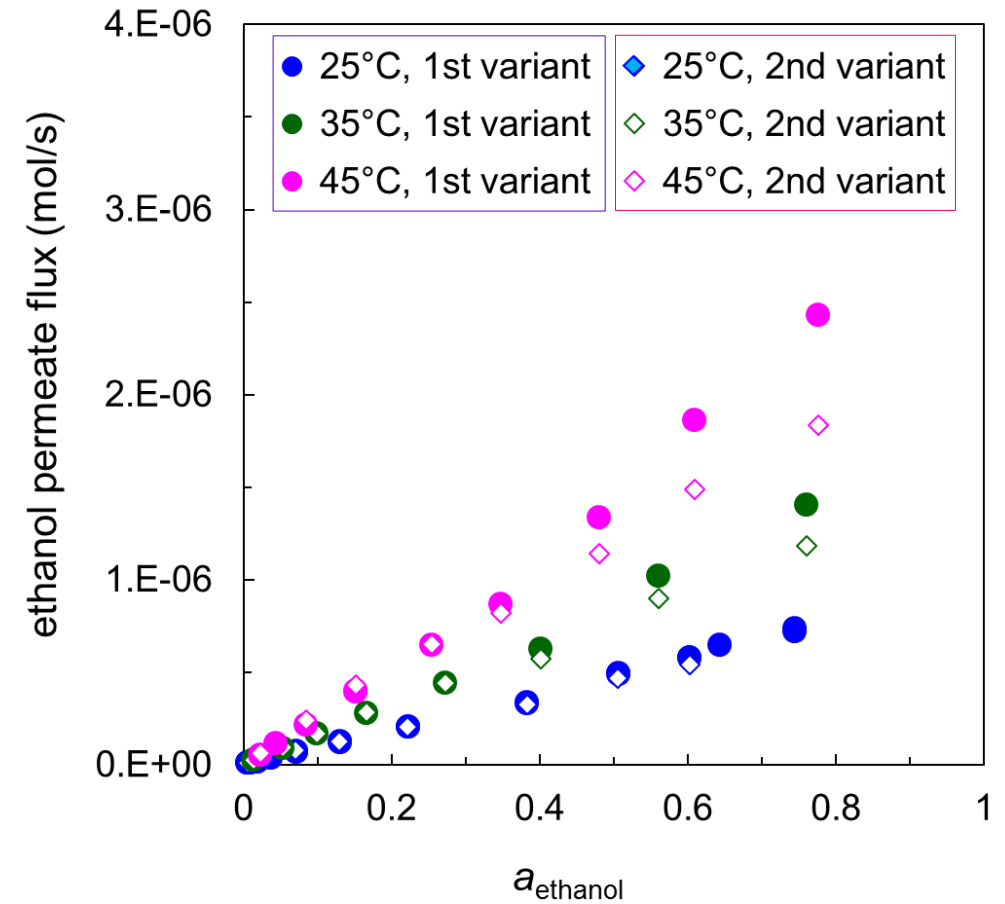


# Study of vapour permeation

## Ethanol vapour permeation in LDPE membrane

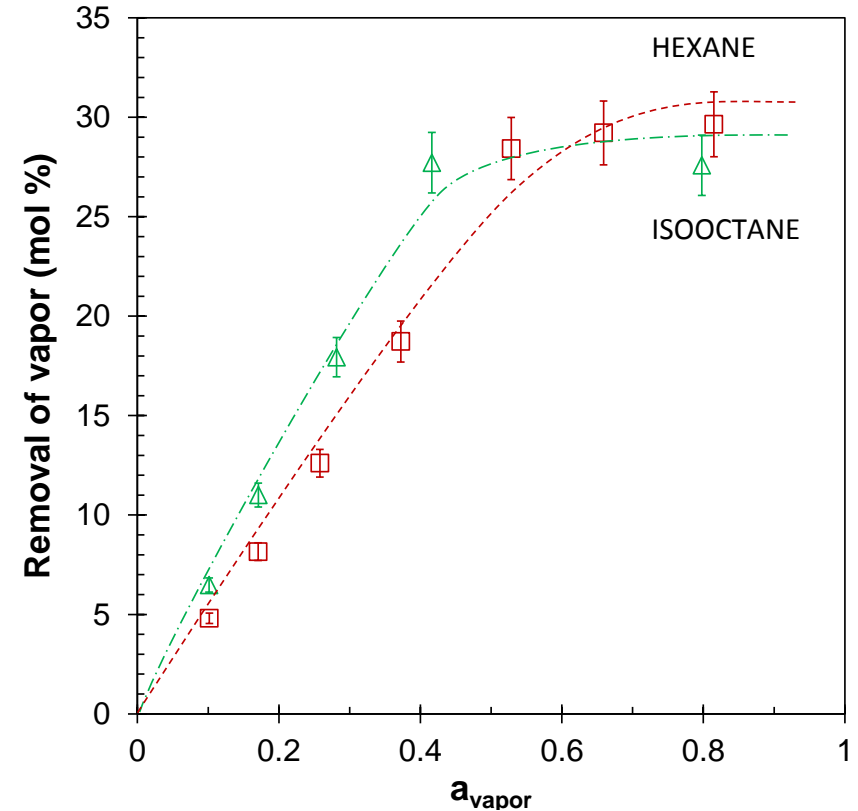
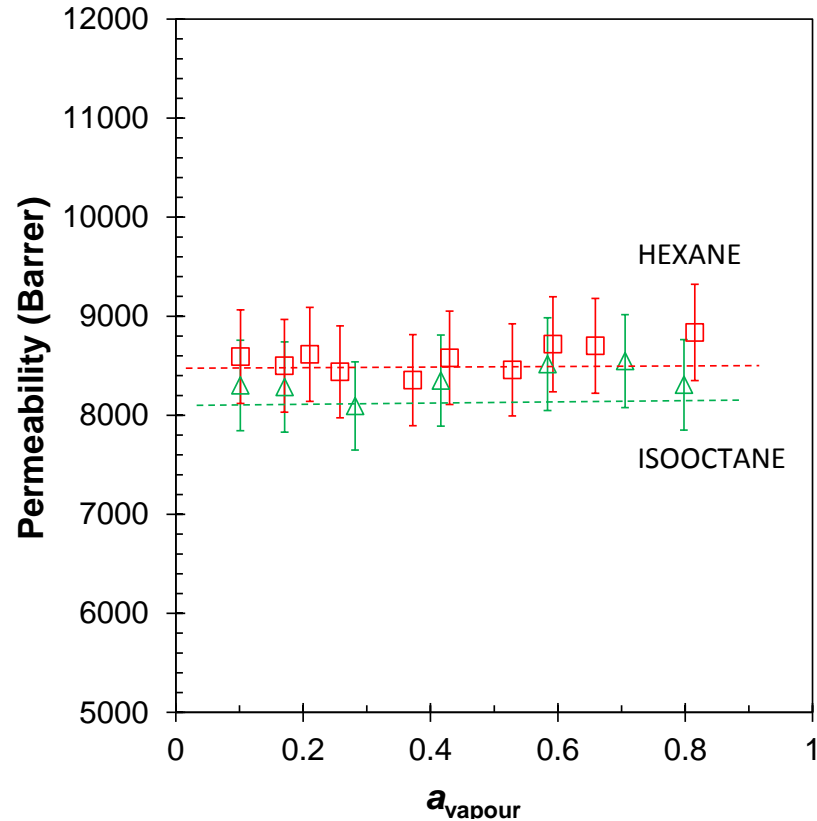


## Ethanol vapour permeation in IL membrane



# Study of vapour permeation

## Hexane and isooctane permeation in IL membrane



□ IL membrane: hexane removal up to 30mol. % × poly(vinylidene fluoride-co-hexafluoropropylene) membrane is impermeable

# Summary of representative published results within the project

## Study of sorption properties

- Randova A. et al.: A New Prediction Method for Organic Liquids Sorption into Polymers. J. Membrane Sci. 475, 545-551 (2015).
- Randova A. et al.: Sorption of Organic Liquids in Poly(ethylene chlorotrifluoroethylene) Halar<sup>®</sup>901: Experimental and Theoretical Analysis. Polym. Test 58, 199-207 (2017).

# Study of vapour transport properties

- Moravkova L. et al.: Vapour Permeation and Sorption in Fluoropolymer Gel Membrane Based on Ionic Liquid 1-Ethyl-3-Methylimidazolium bis(trifluoromethylsulfonyl)Imide. Chem. Pap. 68(12), 1739-1746 (2014).
- Vopicka O. et al.: Ethanol Sorption and Permeation in Fluoropolymer Gel Membrane Containing 1-Ethyl-3-Methylimidazolium bis(Trifluoromethylsulphonyl)Imide Ionic Liquid. Chem.Eng.Process. 94(SI), 72-77 (2015).
- Petrusova Z. et al.: Comparison of Hexane Vapour Permeation in Two Different Polymeric Membranes via an Innovative In-Line FID Detection Method. Chem. Biochem. Eng. Q. 31(2), 145-160 (2017).



# Study of gas permeation – review papers

- Karaszova M. et al.: Progress in Separation of Gases by Permeation and Liquids by Pervaporation Using Ionic Liquids: A Review. *Sep. Purif. Technol.* 132, 93–101 (2014).
- Karaszova M. et al.: Gas Permeation Processes in Biogas Upgrading: A Short Review. *Chem. Pap.* 69(10), 1277–1283 (2015).
- Izak P. et al.: Catalytic Ionic-Liquid Membranes: The Convergence of Ionic-Liquid Catalysis and Ionic-Liquid Membrane Separation Technologies. *ChemPlusChem* 83(1), 7-18 (2018).

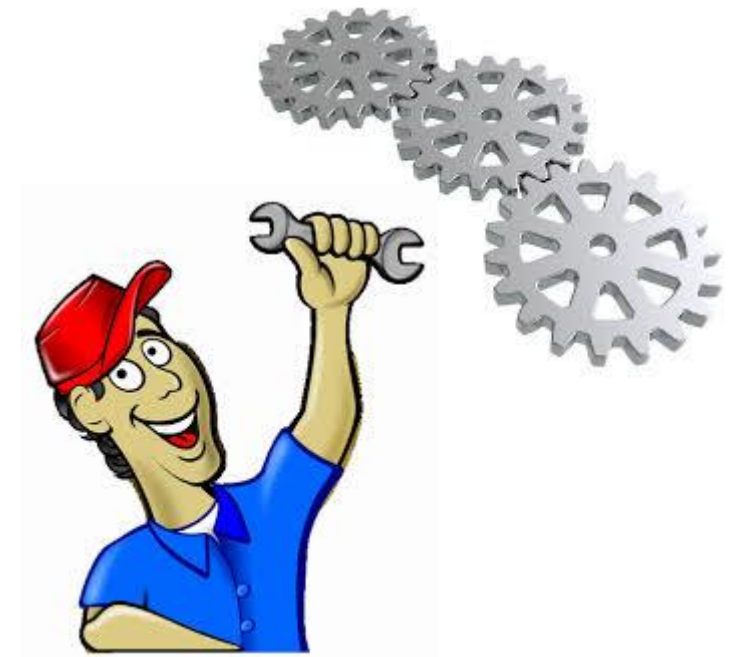
# WHAT DID THE EUROPEAN CONTACTS BRING TO US?

Students training, post-doctoral internship  
and fruitful contacts with new trends at the specialised institutes



# WHAT CAN WE OFFER TO THE WORLD?

Handy workshop and ingenious apparatuses





... FOR YOUR KIND ATTENTION

FINANTIAL SUPPORT FROM CZECH MINISTRY OF EDUCATION, YOUTH AND SPORTS  
(COST PROJECT LD 14094) IS GREATLY APPRECIATED.