

Vapour and acid components separation from gases by membranes principles and engineering approach to membranes development

G G Kagramanov^{1,2}, I P Storojuk² and E N Farnosova^{1,2}

¹ Chemical Engineering Faculty, D. Mendeleyev of Chemical Technology of Russia, 125047 Moscow, Russia

² “Membranica” Ltd, 125047 Moscow, Russia

Abstract. The modern commercially available polymer membranes and membrane modules for purification of gases, containing acid components, simultaneously with dehumidification of treated gas streams, were developed and commercialized in the very end of XXth century. The membranes basic properties – selectivity (separation factor) and permeation flow rates – are relatively far from satisfying the growing and modern-scale industrial need in purification technologies and corresponding equipments. The attempt to formulate the basic principles, scientific and engineering approaches to the development of prospective membranes for the purification of gases, especially such as natural and oil gases, from acid components, simultaneously with drying them, was being made. For this purpose the influence of various factors – polymer nature, membrane type, structure, geometrical and mass-transfer characteristics, etc. – were studied and analyzed in order to formulate the basic principles and demands for development of membranes, capable to withstand successfully the sever conditions of exploitation.

1. Introduction

World-wide production of natural and oil gases is constantly growing, achieving approximately 3 500 billion m³/year. Russia, as one of world’s leaders in this field, produces 640 billion m³/year of natural gas and 65 billion m³/year of oil gas.

All these gases, before delivering to the market, must undergo the indispensable treating procedure, namely, the purification from “acid” gas components – CO₂, H₂S, COS, CS₂, etc., as well as dehumidification [1,2]. These two processes are absolutely indispensable, as well, in production of liquefied hydrocarbons – methane up to butane etc. [3].

Purification by absorption of acid gases, well-known and spread all over the world, is being constantly replaced by membrane separations due to their evident advantages, such as lower capital and exploitation cost [4, 5]. Moreover, membrane separations allow, simultaneously with extraction of acid components from natural and oil gases, to minimize the vapor content in gas processed.

So, the advantages of membrane technology in this field are very promising and prospective. [6].

2. Membranes

The existing commercially available polymer membranes were developed mainly at the very beginning of XXI century and their properties are far from being optimal and should be ameliorated in



order to correspond to nowadays demand. Their main characteristics – permeability and selectivity – are presented in Tables 1 (a) and 1 (b) [7, 8].

Table 1 (a). Commercially available membranes and their permeability

Gases	Permeability coefficient $[(\text{mol}\cdot\text{m})/(\text{m}^2\cdot\text{s}\cdot\text{Pa})]\cdot 10^{15}$			
	Cellulose acetate “Gasep”	Cellulose acetate “Du Pont”	Polysulphone (bisphenol) “Ube”	Polyimide “Ube”
CO ₂	5.5	13.9	2.32	4.36
H ₂ S	9.1	–	1.04	–
CH ₄	0.18	0.58	0.084	0.134
N ₂	0.17	0.73	0.061	0.201
C ₂ H ₆	0.09	–	0.074	0.027
C ₃ H ₈	–	–	–	0.005

Table 1 (b). Separation factor (selectivity)

Material (polymer)	Separation factor				
	CO ₂ /CH ₄	H ₂ S/CH ₄	C ₂ H ₆ /CH ₄	C ₃ H ₈ /CH ₄	N ₂ /CH ₄
Cellulose acetate “Gasep”	30.6	50.6	0.50	–	0.94
Cellulose acetate “Du Pont”	24.0	–	–	–	1.30
Polysulphone (bisphenol) “Ube”	27.6	12.4	0.88	–	0.73
Polyimide “Ube”	32.5	–	0.20	0.04	1.50

The analysis of these (Tables 1 (a) and (b)) data shows, that all materials, chosen for extraction of acid components from methane, are glassy polymers in their nature utilizing diffusion (size) selectivity mode of separation. The main disadvantage, to our mind, is that for these polymers, the permeability values for higher hydrocarbons diminish considerably in the “methane” – “ethane” – “butane” row. So, permeate is to be enriched by carbon dioxide and hydrogen sulphide; the retentate – by hydrocarbon components. Taking into account the boiling point (condensability) values, rising from methane to butane it could lead to the partial condensation of hydrocarbons on the high pressure side of membranes which is extremely undesirable for mass-transfer process, influencing (lowing) the values of permeability coefficients drastically.

The analysis of data presented in tables 1 (a) and 1 (b) shows, as well, that these characteristics are rather far from modern needs and can not satisfy the growing interest of engineering and industrial society in membrane gas separation technology.

So, the authors of presented study tried, first of all, to formulate the basic principles and demands for development of gas separation membranes – polymer nature, membrane type and structure, geometrical and mass-transfer characteristics.

The main principles for the development of polymer membranes for natural and oil gas purification and dehydration are as follows:

- membranes are to be highly permeative for acid components and water vapor;
- polymer materials are to be highly selective towards acid components and vapor;
- membranes are to be anisotropic in structure, having extremely thin nonporous selective layer (40-100 nm), based on porous support;
- both selective layer and support should be made of the same material, i.e. to be asymmetric;
- membranes should be made in hollow fibers form;

- geometrical parameters of hollow fibers should provide the maximal packing density in membrane module – up to 20 000 m²/m³, as well as to be able to withstand the process pressure drop up to 70 – 100 bar;

Taking into account these numbers (up to 20 000 m²/m³ and $\Delta P=70 - 100$ bar) the hollow fibers geometrical parameters should be: outer diameter of 250-500 μm and inner diameter of 100-250 μm ;

- polymer material (and it's properties) should be resistant to physico-chemical interaction with gas mixture's components, i.e. resistant to so called “plastification” effect.

So, in our work we dared to analyze all physical phenomena during membrane separations, deciding to combine the main advantages of two types of polymers – glassy and rubbery – in a form of block-copolymers [9, 10].

Block-copolymers, having microheterogeneous structure and containing completely mixed amorphous and crystalline phases should provide the significant growth of permeability and selectivity values due to the combination of diffusion and solubility mechanism's advantages.

For this purpose, the block copolymers, made of polysulphone-polybutadiene, varying the molecular weights of precursors and their composition in membrane material, were synthesized and their gas permeabilities were measured and selectivities calculated (Tables 2 (a) and (b)).

Table 2 (a). Permeability coefficients for synthesized block-copolymers

Gases	Permeability coefficient [(mol·m)/(m ² ·s·Pa)] 10 ¹⁵		
	Block copolymer I	Block copolymer II	Block copolymer III
CO ₂	21.9	18.7	18.6
H ₂ S	33.6	67.2	156.6
CH ₄	0.22	0.21	0.21
C ₂ H ₆	1.07	1.81	6.85
C ₃ H ₈	26.4	40.1	74.3
N ₂	0.51	0.51	0.51

Table 2 (b). Separation factor

Block-copolymers	CO ₂ /CH ₄	H ₂ S/CH ₄	C ₂ H ₆ /CH ₄	C ₃ H ₈ /CH ₄	N ₂ /CH ₄
I	99.5	152.7	4.9	120.0	2.3
II	89.0	320.0	8.6	191.0	2.3
III	88.6	745.7	32.6	353.8	2.3

3. Conclusion

The comparison of data, obtained for “glassy” and block-copolymers (Tables 1 (a), (b) and 2 (a), (b)) shows that synthesized block-copolymers exhibit substantially and simultaneously greater values of both permeability and selectivity for acid gases extraction.

Very interesting is the controversial character of selectivity data in pairs methane – ethane (butane, nitrogen) compared with “glassy” polymer membranes. This fact, to our mind, can change considerably the engineering approach to membrane technology application in natural and oil gas treating (purification) processes – to withdraw at first separation step all “impurities” (CO₂, H₂S, C₂-C₃), obtaining in retentate high-quality methane and, at the second stage, to separate acid gases and ethane-methane mixture using “glassy” polymers.

The greater values of permeabilities, exhibiting by block-copolymers, will diminish considerable the capital cost, especially, for the first separation step.

At present, the development of hollow fiber block-copolymer membranes for these purposes is being carried out.

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