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LIGASE: An Automated Apparatus for Gas Permeability and Separation Measurements*

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Abstract

An automated computer-controlled apparatus for gas permeability measurements through polymeric membranes is described in detail. The apparatus was specifically designed to operate with hydrocarbon streams and acid gases (CO_2, H_2S) and therefore special care was devoted to the control devices. The maximum capacity of the apparatus is 100 L/h at temperatures up to 70°C and pressures in the 0–15 atm range. Permeability measurements of biogas components (CH_4, CO_2, H_2S) and their separation factors through experimental hollow fiber membranes are presented as typical data of the equipment described.

INTRODUCTION

Gas separations with membranes for purification, recycling, or recovery applications have attracted attention because of both the conceptual and process simplicity of the membrane permeation technique. The absence of troublesome phenomena (fouling, scale formation,

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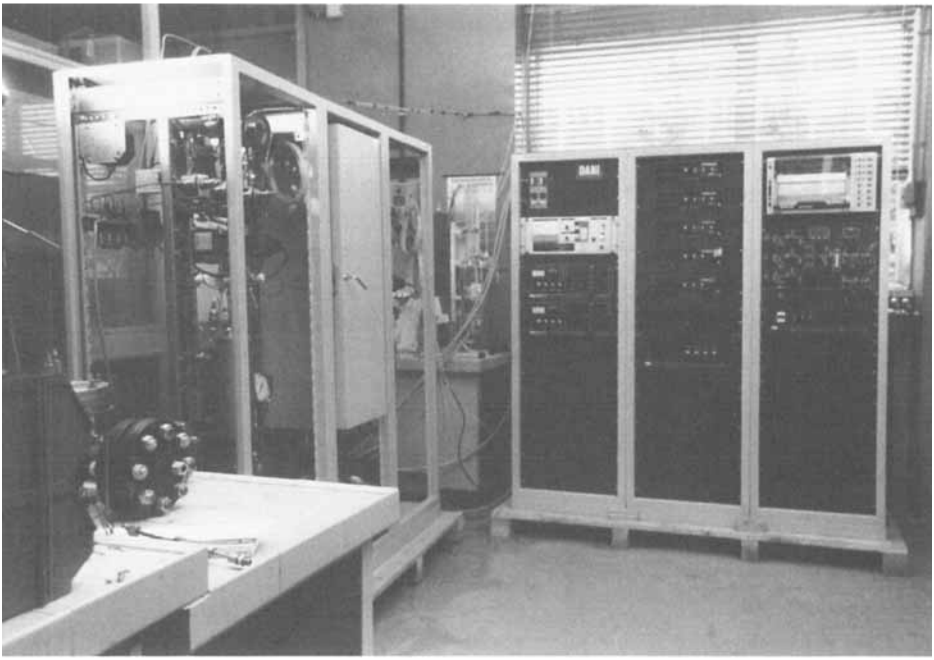


FIG. 1. General view of the LIGASE apparatus.

etc.) met in other membrane applications has contributed to this interest (*1*). However, the availability of membranes suitable for gas separation is not wide enough to support the above expectation. Therefore, work on membrane formulation and characterization is still very intense.

To support this effort in membrane development, various apparatuses have been conceived and realized (*2, 3*) with the aim of obtaining reliable data on gas permeation and separation coefficients, while looking at the same time for automated solutions to save repetitive work and to simulate industrial applications as closely as possible.

In this work an automated computer-aided apparatus for membrane permeability measurements is described. The apparatus operates with the flow-cell technique. It was designed by taking into account the possibility of handling toxic and flammable gases in long duration experiments. In these cases, automation is an important condition for extensive experimental work.

Some data obtained by using the above facility are presented. They represent a preliminary characterization of a composite hollow fiber membrane for the separation of acid gases (e.g., CO_2 and H_2S) from mixtures of interest in the energy field. The reported data concern pure components and mixtures of biogas, i.e., the methane-based mixture produced during the anaerobic degradation of organic wastes.

Cost analysis versus conventional gas purification techniques have shown the potential advantage of membrane-based purification processes, especially for small to medium plant capacities (*4–6*).

DESCRIPTION OF THE APPARATUS

The apparatus is named LIGASE (line for gas separations) and was assembled by Dany (Monza, Italy). It was conceived as a fully automated computer operated device for measuring pure gas and mixture permeability and separation factors. Because of the planned applications in biogas and other energy fields, special attention was devoted to safe operation and to the continuous control of gas composition in different sections of the apparatus.

The following description focuses on the biogas components CH_4, CO_2, and H_2S. The equipment has a maximum capacity of 100 L/h at a temperature between 25 and 70°C and a pressure between −1 and 15 atm.

A general picture of LIGASE is shown in Fig. 1. The apparatus is divided into three sections: 1) the mixing section with the permeability cell enclosed in the forced air thermostated chamber, 2) the process and security control section, and 3) the analytical and operative section which includes the gas chromatograph (DANI model 3800) and the microcomputer (IBM PC/XT). The whole assembly is operated through the computer whose program selects testing conditions (temperature, flows of gas streams, pressures), sample sequences for gas analysis, sequences of operations for the control of valves, and finally collects all the experimental data. Figure 2 shows the flow diagram of the apparatus. Pure gases and synthetic mixtures are provided by three gas lines which converge into a mixing tank. These three gas streams can be mixed according to a preset program by means of Matheson Dyna Blender modules provided with mass flow control units (Matheson model 8350). The percentages of gas components in the mixture are fixed independently from temperature and pressure. The permeate and unpermeate flows can also be regulated by similar mass flow controls. Electrical transducers provide for the pressure values of the three gas streams. Eight sampling points are for the control of gas purity before mixing of the feed, for permeate and unpermeate composition analysis before and after separation, and for gas composition analysis before the vent (for CH_4 discharge) and the scrubbers for H_2S retention.

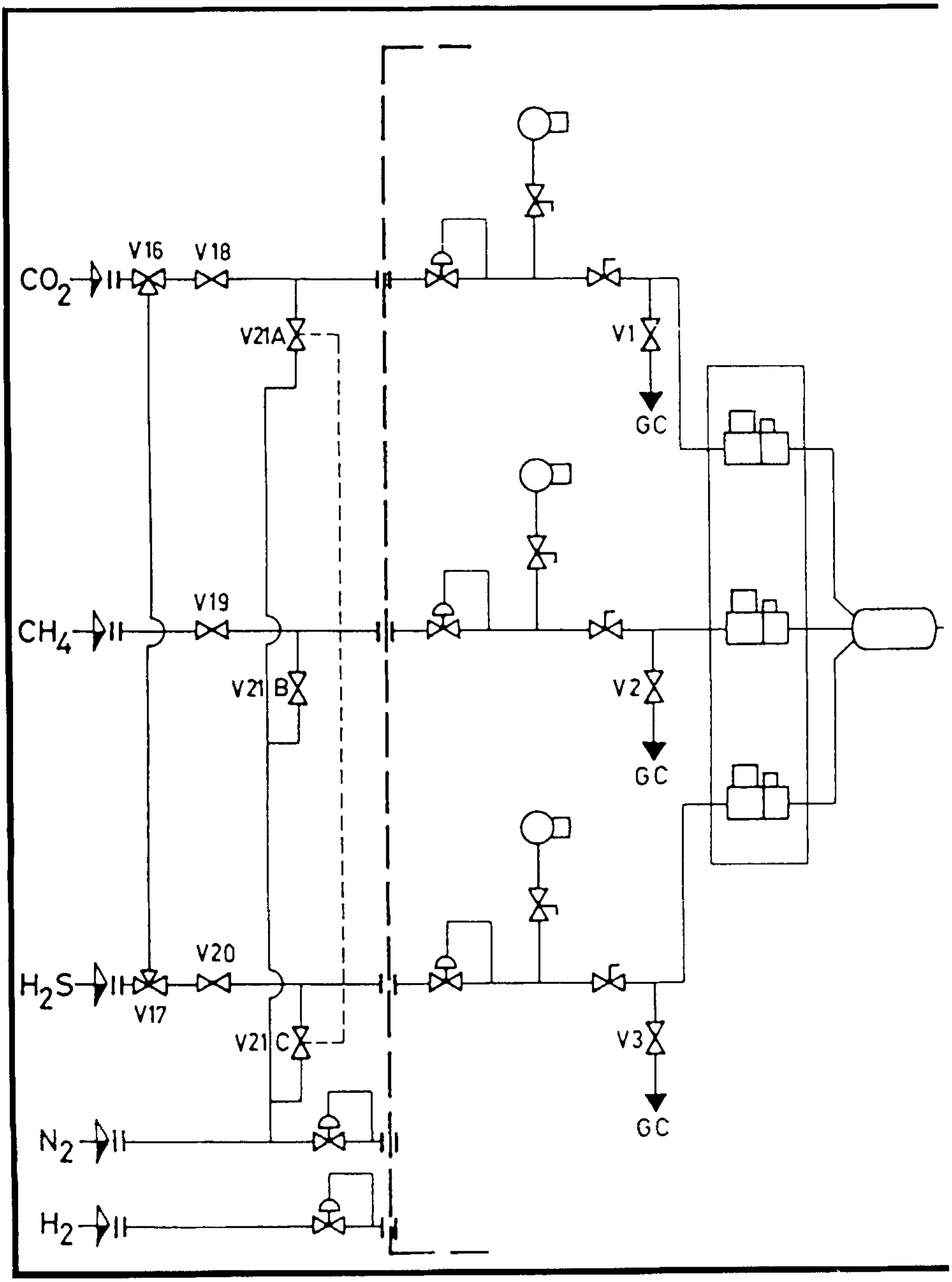
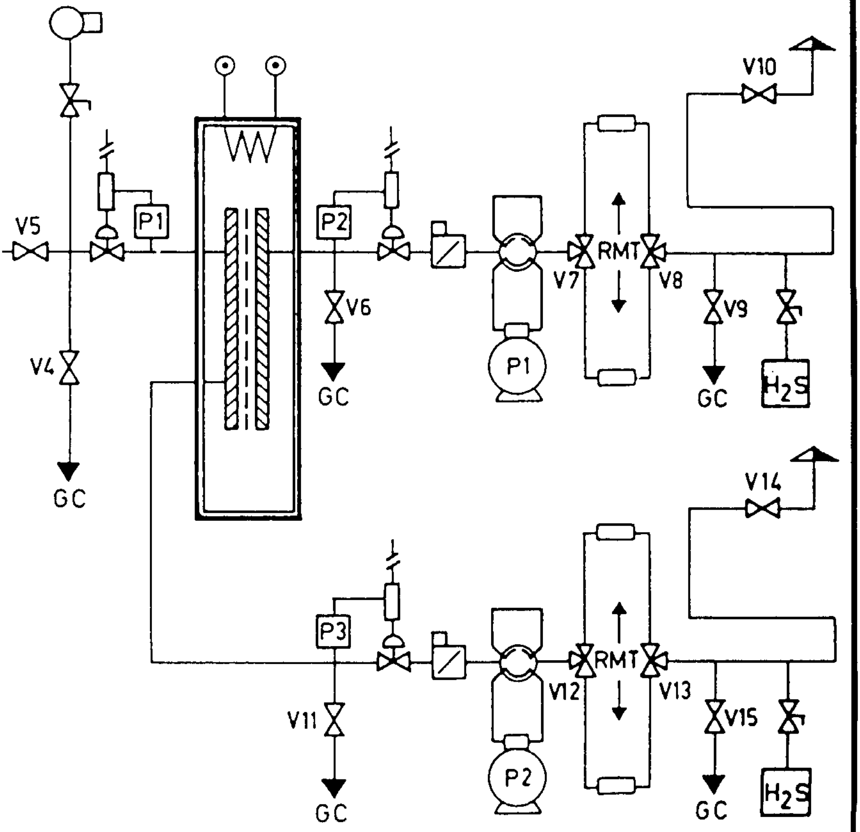


FIG. 2. Flow system diagram indicating valves (V), pressure transducers (P), sampling



points (GC), and gas lines of LIGASE.

Ambient control for possible CH_4, H_2S, and CO_2 leakages is assured by two air monitors (Sieger FS 1A for methane and TS 1A for H_2S) which operate with two sensors which control the ambient and the thermostated chamber air and by an IR monitor for CO_2. Each monitor can interrupt the gas flow when the air content for one of the quoted gases exceeds a preset maximum value. Finally, a thermocouple system fixes and measures the cell chamber and the membrane cell temperatures. All valves (which are duplicated for manual and automatic operation), pipes, and connections are stainless steel. A multirecorder stores the pressure, flow, and temperature values while the computer printer provides a complete table of operating conditions, analytical data (including peak integrations, permeabilities, and separation factors.

Procedure for Permeability Measurements

Pure gases, stored in gas cylinders outside the laboratory building, flow into the mixing tank through the Dyna Blender section where the final composition of the mixture is established. Before mixing, the purity of the components is checked. Besides the three main gas lines for mixture formation, a fourth line is provided for pipe cleaning with N_2 before and after each experiment. Especially when using CH_4, care must be taken to avoid the formation of air/methane mixtures in the pipes.

The gas mixture formed in the 10-L tank is sent to the membrane permeator after analysis of the mixture composition. The feed mixture pressure and flow are fixed. The gas separated in the permeator is divided into two streams (permeate and unpermeate), and for each of them the pressure and flow is measured. After analysis, the gases are sent to the vent through the H_2S scrubbers. A final analysis of the gases to be eliminated is made before the vent. The chromatographic peaks are directly integrated, and these data, together with the process conditions and the membrane characteristics, are used to evaluate permeabilities and separation factors.

The apparatus described can work with any membrane and membrane cell geometry above and below atmospheric pressure. Two vacuum pumps are present to operate the apparatus around 1 atm below ambient pressure.

Modules as long as half a meter can be located in the thermostated chamber.

EXPERIMENTAL

LIGASE is now being used to characterize experimental hollow fiber composite membranes manufactured by S.N.I.A. Fibre (Cesano Maderno, Italy). These hollow fibers are under study for the specific problem of biogas up-grading and, more generally, for the separation of the acidic components in hydrocarbon mixtures.

Hollow fibers are assembled in a cylindrical perspex module. The module, 15 cm of useful length and 1 cm of internal diameter, can accommodate a maximum of 50–60 fibers, corresponding to approximately 200 cm of membrane area.

Some characteristics of the fibers used are collected in Table 1. Figure 3 shows electron micrographs of the fibers. As can be seen, the PS support has a cellular structure and no fingerlike voids show up.

The presence of passing pores in the specimen was investigated with an ENKA Porotester (ENKA, West Germany) which allows for the measurement of the maximum pore size (correlated with the lower pressure at which the fiber saturated with a wetting liquid, alcohol, becomes permeable to a given gas) and the pore distribution (calculated from the dependence of the gas flow from the differential pressure acting across the fiber wall). Typical plots obtained with a bundle of 15 fibers 30 cm in length for a total surface of 111 cm^2 are shown in Fig. 4. The insert in the figure represents the recorded differential pressures applied inside the fiber lumen (P_1) and measured outside the wetting liquid (P_2) as a function of time. From the plots reported the pore distribution can be calculated. The extrapolated value on the x-axis represents the bubble point corresponding to the maximum dimension of the passing pores.

The measurements reported show that for fiber C (composite type) practically no pores are present apart from very large ones, possibly due to coating inhomogeneities. Similar measurements made on the support used for the coated fiber. showed passing pores in the 0.4 to 0.5 mm range.

The permeabilities of the fibers were measured according to the procedure outlined. Recorded plots for N_2 and CO_2, which show the flux dependence on the transmembrane pressure differential, are reported in Fig. 5 with the permeabilities P measured as $cm^3/s \cdot cm^2(cmHg)$. From the slopes of these curves and the geometrical dimensions of the fibers (Table 1), the permeabilities of Table 2 were obtained at different temperatures in the 25 to 55°C range. The results of two different experimental sets are reported in Table 2.

TABLE 1
The Main Characteristics of Composite Hollow Fibers C

HF type:	
Compact layer	External
Coating	Aliphatic copolymer
Support polymer	Polysulfone
Dimensions (μm):	
External diameter	735 + 9
Internal diameter	389 + 12
Coating thickness	3.5 + 1.5
Porosity:	
$d_a/(d - d_a)$, empty/compact weight ratio	0.60 + 0.03
Maximum pore diameter (μm)	0.78
Pore number of maximum pore diameter (N/cm^2)	0.018
Mechanical properties:	
Specific load (kg/mm^2)	1.14 + 0.06
Extensibility (%)	42 + 10
Young's modulus (kg/mm^2)	31 + 1
Burst pressure (kg/cm^2)	36

The ideal separation coefficient for CO_2/N_2 mixtures is about 17 at 25°C.

The temperature effect on permeability for an ideal permanent gas is described by an Arrhenius-type law with a linear log P vs $1/T$ plot at constant pressure difference (*1*). This effect could be of interest in the biogas application because of the possibility of using such a gas mixture at a temperature different from standard conditions (*4*). The permeation curves for N_2 and CO_2 and the permeability coefficients at different temperatures have been obtained at a transmembrane pressure of 0.5 bars with a feed flow of 30 cm^3/min. From the data of Fig. 5 and Table 2 it is seen that while permeabilities increase exponentially as expected, the ideal separation factor slowly decreases. From the Arrhenius plots of Fig. 6, the activation energies for N_2 and CO_2 permeation through membrane C were obtained. They are higher for N_2 than for CO_2. The energies obtained, however, are smaller than those reported for the same gases and polyethylene membranes (*7*).

Moreover, the absolute values of the activation energies seem too low. This could be due to the presence of passing holes or defects in the hollow fiber wall corresponding to the few pores observed in the porosity measurement curves (Fig. 4).

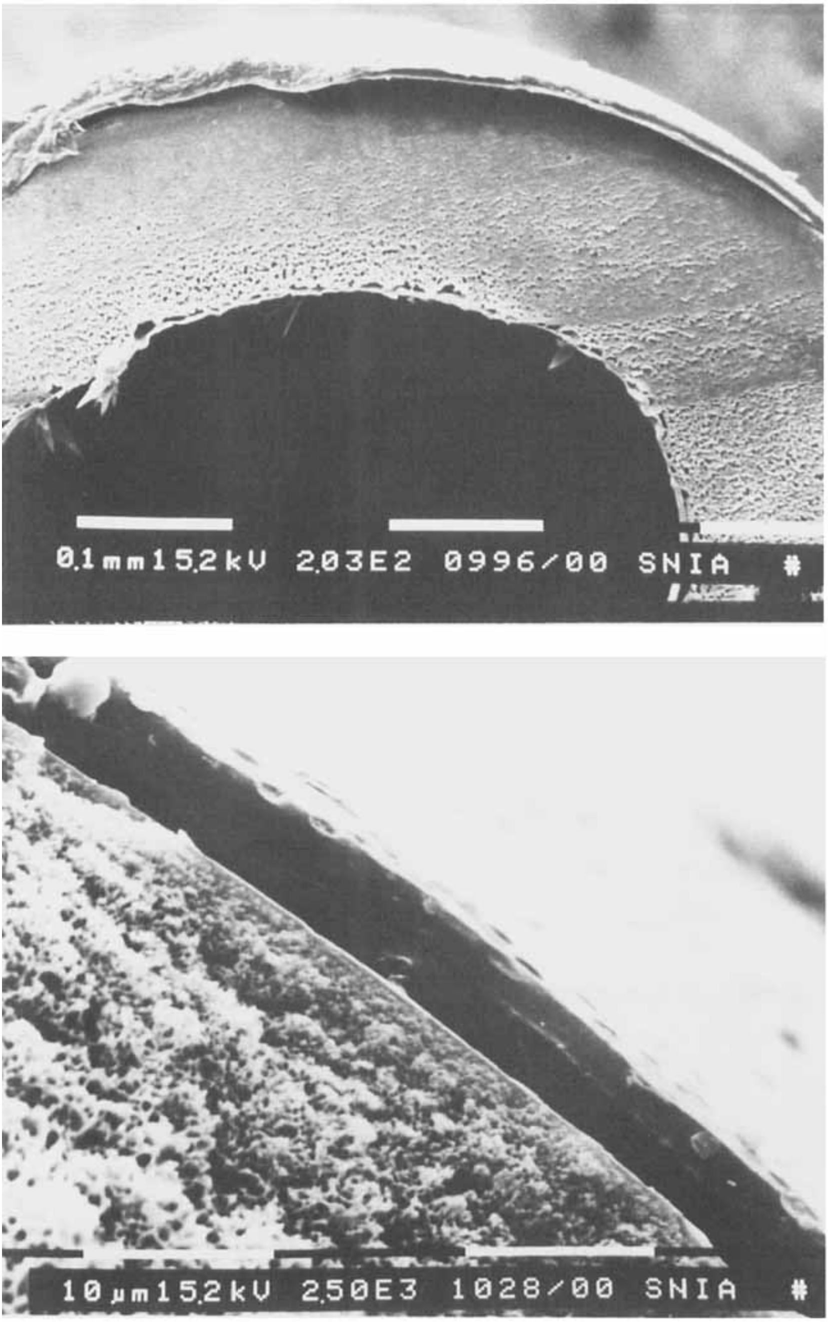


FIG. 3. Electron micrographs of the experimental hollow fibers.

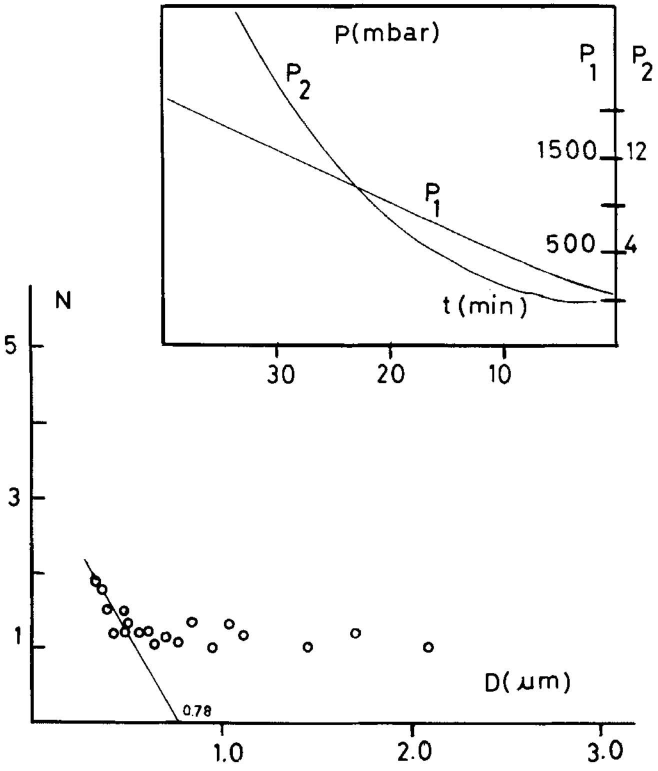


FIG. 4. Pore distribution in hollow fibers. Number of pores N (for 111 cm^2 membrane surface area) vs pore diameter D (μm). Insert: The pressure-time curve of the ENKA porotester.

Gas Mixture Separations

Similar results were obtained in separation experiments performed with a synthetic biogas. Feed fluxes of 30 cm^3/min were used at a 1-atm transmembrane pressure difference (2 atm in the pressurized stream). The mixture composition was: N_2 0.5%, CH_4 60%, CO_2 39%, H_2S 0.5%. The experiment was repeated at three different temperatures between 25 and 55°C, and the results in volume % in the permeate are reported in Table 3. The CO_2/CH_4 separation effect of membrane C decreases with temperature, showing that the activation energy for methane is higher than for carbon dioxide. At the moment we do not have permeability data for pure CH_4. A very rough evaluation of the CO_2/CH_4 separation factor can be performed from the above results. By assuming a perfect mixing model

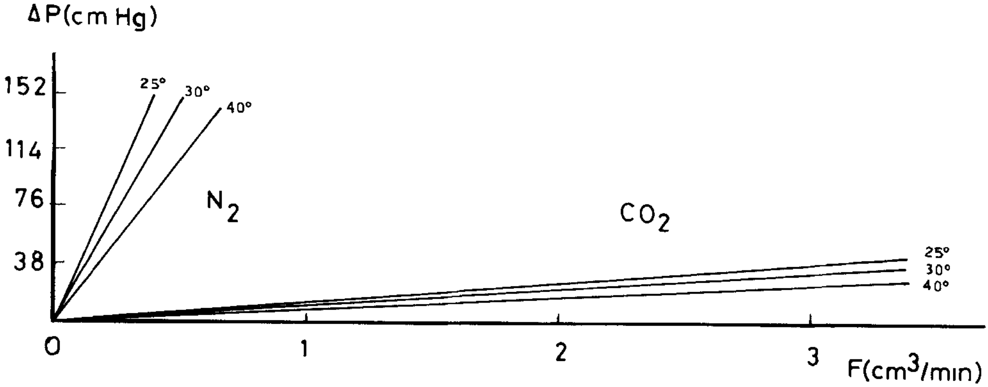


FIG. 5. Permeability as a function of temperature for N_2 and CO_2 across experimental composite hollow fiber C.

TABLE 2

Permeabilities P ($cm^3\ cm\ s^{-1}\ cm^{-2}\ cmHg^{-1}$), Ideal Separation Factor α, and Activation Energies E_a (kcal/mol) for Permeation Through the Composite C Hollow Fiber

Specimen		$P_{N_2} \times 10^{10}$	$P_{CO_2} \times 10^{10}$	α_{N_2/CO_2}
C (PS coating)	(T, °C)			
i)	25	0.010	0.17	17.0
	30	0.011	0.18	16.4
	35	—	—	
	40	0.016	0.24	15.0
	45	—	0.26	
	50	—	0.26	
	55	—	0.29	
ii)	25		0.16	
	30		0.17	
	35		0.20	
	40		0.23	
	45		0.24	
	50		0.27	
	55		—	
		$E_a = 2.32$	$E_a = 1.83$	

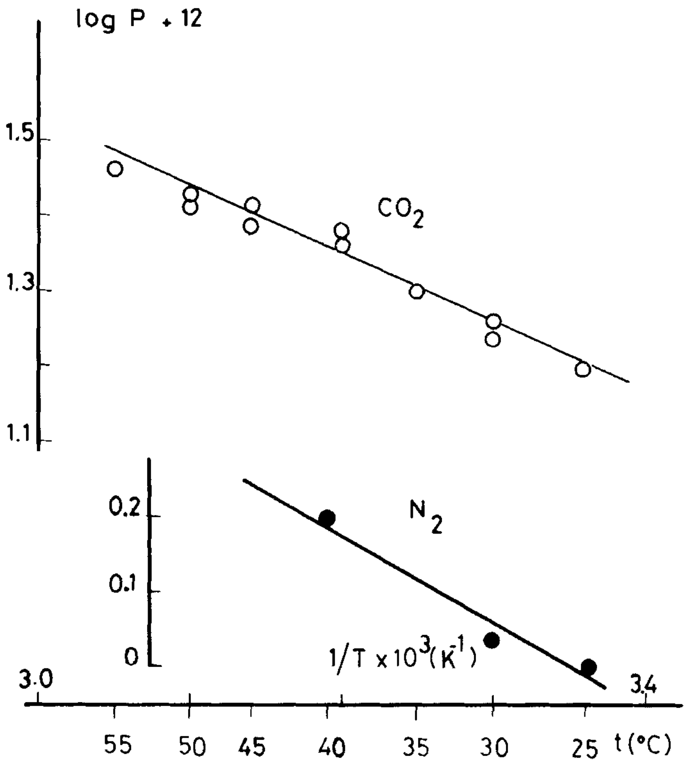


FIG. 6. Arrhenius plots for the temperature dependence of N_2 and CO_2 permeation through composite hollow fiber C.

TABLE 3

Biogas Separation Tests: Permeate Composition as a Function of Temperature for Hollow Fiber Type C (composite). Feed: Synthetic Biogas (30 cm^3/min; P = 1 atm)

		Permeate, T (°C)		
Composition (vol%)		26	40	55
N_2	0.5	0.3	0.4	0.4
CH_4	60.0	39.5	43.3	46.7
CO_2	39.0	59.5	55.3	52.1
H_2S	0.5	0.7	1.0	0.8

for a binary mixture (*1*), the mole fraction of the more permeable component (CO_2 in this case) in the feed, N^f, permeate, N^p, and unpermeate, N^{up}, streams can be written

$$N^p = \frac{\alpha - \left(\frac{P_h - P_l}{\beta}\right)}{\alpha - 1} \tag{1}$$

$$N^{up} = \frac{(\beta + P_l)N^p}{P_h} \tag{2}$$

$$N^f = \phi N^p - (1 - \phi)N^{up} \tag{3}$$

where P_h and P_l are the pressure on the high and low pressurized side of the membrane, respectively, ϕ^l is the stage cut (in our case $\phi = 0.1$), and $\beta = F^{up}/(A/\delta)P_{CO_2}$ with F^{up} the flow rate of the unpermeate stream. From this set of equations and the data of Tables 2 and 3, it is possible to calculate the ideal separation factor α and the P_{CH_4} permeability at different temperatures. This estimation leads to the following values for methane permeability: 1.96 (26°C), 4.45 (40°C), and 7.06 (55°C) $\times 10^{-12}$ $cm^3 cm \cdot s^{-1} cm^{-2} (cmHg)^{-1}$. These results agree with the observed decrease in separation efficiency shown in Fig. 7. The temperature dependence of the permeation of CH_4 through membranes of type C corresponds to an activation energy of 3.6 kcal/mol. The observed sequence of activation energy for hollow fiber C is $CH_4 > N_2 > CO_2$, similar to that reported for polyethylene membranes (*7*).

CONCLUSION

The main characteristics of an automated, computer-controlled apparatus for studying membrane separation processes for gas mixtures have been presented, and the experimental preliminary data of a composite hollow fiber membrane discussed. Composite membranes formed by a polysulfone support and an aliphatic copolymer coating show a medium level separation efficiency for CO_2/CH_4-based gas mixtures (biogas) at ambient temperature. Due to the higher activation energy for CH_4 than for CO_2, the separation decreases with increasing temperature. The activation energies for CH_4, N_2, and CO_2 for the composite membrane follow the same order observed in polyethylene membranes.

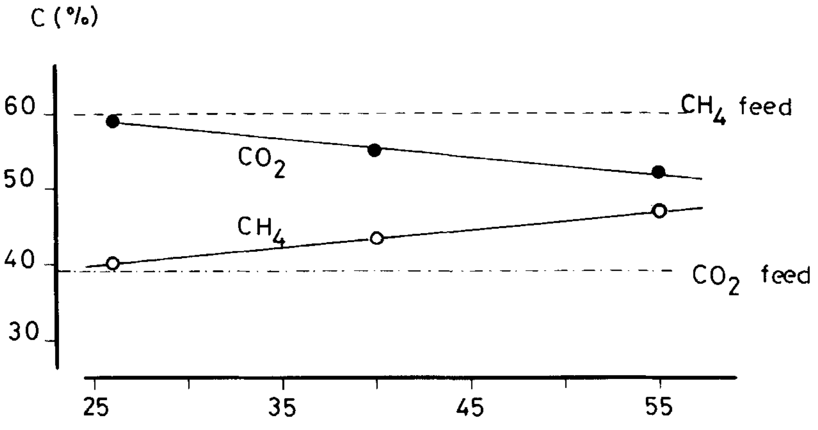


FIG. 7. Decrease in separation efficiency of composite hollow fiber C for a synthetic biogas at different temperatures (data from Table 3).

Acknowledgments

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