

## Development and Application of Hybrid Membranes by The sol-gel Process for The Enrichment of Hydrogen and Methane Gases

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### Abstract

The production of renewable energies is an important topic in our present-day society. Many researchers are currently working in processes for the production of biofuels and also the use of them. Among biofuels the production of hydrogen and methane from different wastes play an important role today. Normally biohydrogen and methane biogas are produced in anaerobic biodigesters using different organic wastes. Nevertheless the produced gas in both cases has undesirable gases like carbon dioxide and sulphur compounds among others. Then it is necessary to decrease the concentration of undesirable gases and at the same time to increase the quantity of hydrogen and methane gas.

Taking into account the aforementioned, our research group has made an extensive work for the development of some hybrid membranes to separate the hydrogen and methane from carbon dioxide and in general from undesirable gases. The hybrid membranes were prepared using colloidal silica by the sol-gel process and polyvinyl acetate, PVAc. The membranes were characterized by Thermogravimetric Analysis, Optical Microscopy, Scanning Electron Microscopy and Raman Spectroscopy. Also mechanical tests like tensile strength, penetration and superficial hardness were performed on the hybrid material used for the production of the membranes.

A homemade device was fabricated for testing the diffusion of gases through the membranes. It was demonstrated that the best performance of the membranes was attained using a ratio silica/PVAc of 35/65 %w/w, methanol as solvent and annealed at temperature 40°C. From the results it was fabricated a device of three columns of 6" for using it in a biodigester prototype of 7.0 tons that will be used for the production of hydrogen and methane.

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**Keywords:** Biohydrogen, membranes, sol-gel.



## Introduction

Biogas (colorless and flammable gas) is produced from different organic wastes (domestic, agricultural and agro-industrial) [1, 2, 3], and it is an alternative kind of energy with high ecological impact. The biogas production is usually made using bio-digesters and the produced gas is composed by approximately 20 - 50 % v/v of  $\text{CO}_2$ , 1% - 4% de  $\text{N}_2$ , small amounts of other gases like Hydrogen,  $\text{H}_2$ , Hydrogen Sulfide ( $\text{H}_2\text{S}$ ) and 50 - 80 % v/v of methane as main component of the biogas [2, 3, 4]. Because of this fact, the biogas can be enriched to increase the obtained  $\text{CH}_4$  using hybrid membranes [5]. A membrane can be defined as a selective barrier used to separate two different phases and blocks the free transport for one or more components if a mixture is treated. Also it may be defined as a region between two fluids that hinders or favors the movement through it of some gases [6, 7, 8, 9]. It is necessary to consider that the size and the shape of the gas molecule affect positively or negatively its movement through the membrane [9]. As it is described, the biogas from biodigesters is a mixture of gases and for this reason to increase the % of hydrogen or methane in it [6] (to enrich the biogas) the use of polymeric membranes has a high potential, due to their low cost investment [7, 8].

In the bibliography is mentioned the use of polymeric membranes for the elimination of  $\text{CO}_2$  from a gas mixture of  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{O}_2$  [10 - 16] and hybrid membranes (normally an inorganic material with some kind of resins) membranes for a gas separation process [17 - 43]. Among the means used for gas separation, polymeric membranes have importance due to their advantages such as low cost, high efficiency and low ecological footprint [43, 44]. Also some authors discuss how the transport through polymeric membranes follows the solution-diffusion transport mechanism; that is, dissolution of penetrant molecules in the polymer and their diffusion through the membrane [45]. The selection of a suitable polymeric material is crucial in determining the gas separation performance of the membrane. The chemical structure, crystallinity and morphology of the polymer play an important role in determining the transport properties of the membrane [46].

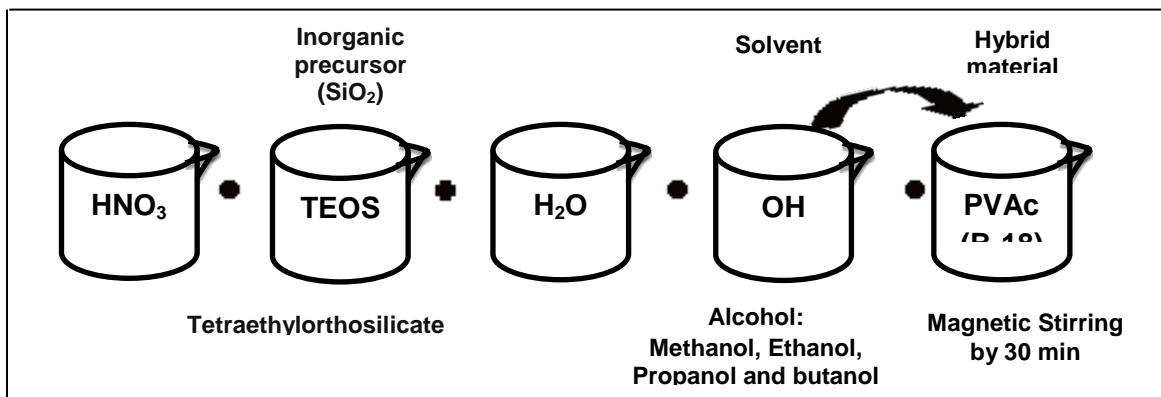
An article by Thomas Graham was published in 1866, where the author established the basic principles for the diffusion-dissolution model, which governs the transport and gas separation through porous polymeric membranes [47]. On the other hand, the market of gas separation membranes has increased significantly since 1970. In this way some articles and reviews describe the advancement in materials, specifically in polymers, for the production of gas separation membranes [13, 48].

In this our current research, we prepared, by the sol-gel process, a hybrid membrane made of polyvinyl acetate and silica for gas separation. This is both a very simple material and easy to prepare and additionally so different from that presented for other researchers. We do not discuss the mechanism for gas separation because this was not the objective of this work. This will be discussed later in other paper. The point is that when we use the material for the preparation of membranes, we have obtained excellent results and it is possible to enrich the hydrogen and methane gases to acceptable levels for being used in motor vehicles or the generation of electricity using motogenerators [5].

## Methodology for preparing the membranes

Hybrid  $\text{SiO}_2$ -PVAc (PVAc known commercially as B-18) solutions were prepared by the sol-gel process [49] in concentrations of 50, 65 and 75 % w/w of PVAc resin and using four different solvents (methanol, ethanol, propanol and butanol in different ratios for controlling the porosity. Figure 1 is an schematic representation of the used methodology for preparing the solutions.





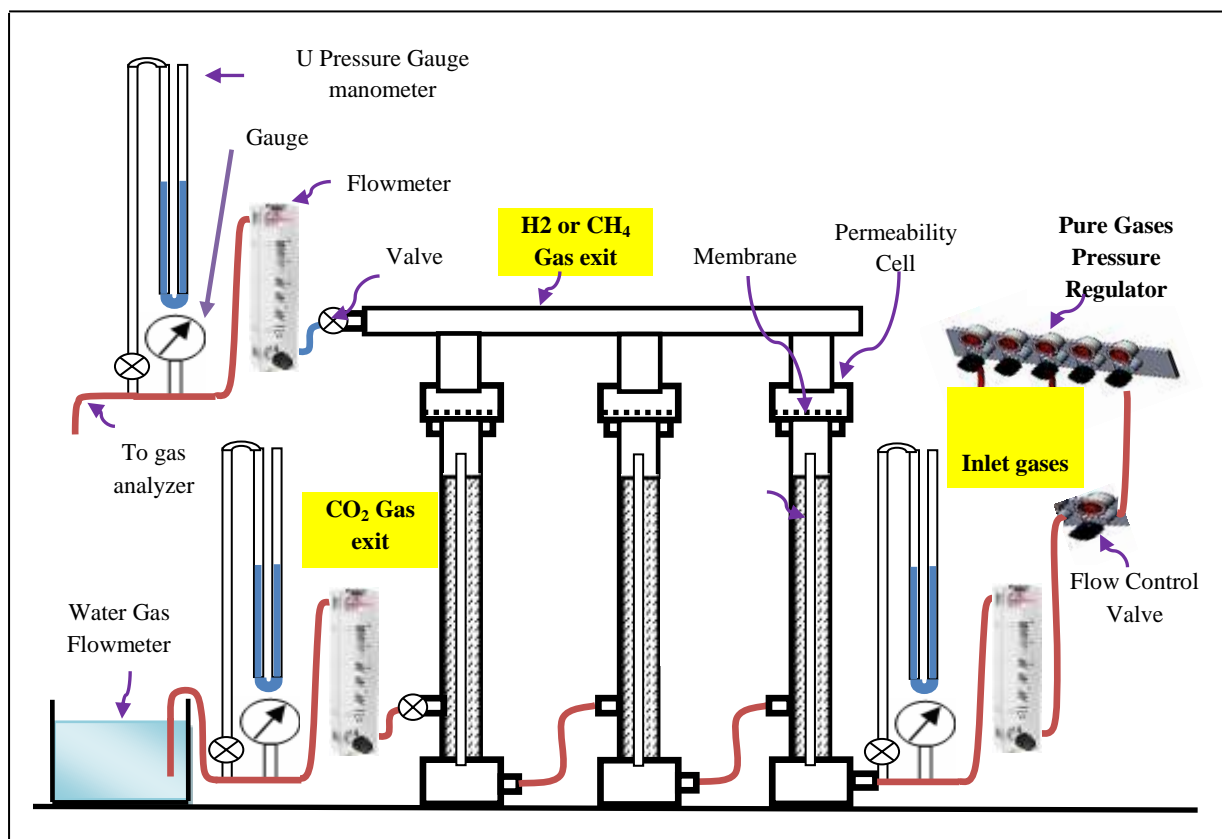
**Figure1. Methodology for preparing the hybrid  $\text{SiO}_2$ -PVAc solutions by the sol-gel process**

Once the hybrid solutions were ready the membranes were made by dip coating, introducing a small piece of stainless steel mesh as a support (275 and 325 mesh) of 1 in x 3 in, and withdrawing it at a constant rate of 3.33 mm/sec. The membranes prepared as described above were heat treated at 25, 40 and 100°C for 15 hours. For a second coating the aforementioned steps were repeated, but in this case the time for the heat treatment was only 20 min.

The obtained membranes were characterized by Termogravimetric Analysis (TGA), Optical Microscopy (OM), Scanning Electronic Microscopy (SEM) and Raman Spectroscopy (RS). Also mechanical tests like tensile strength, penetration and superficial hardness were performed on the hybrid material used for the production of the membranes. In addition,  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{CO}_2$  pure gases were diffused through the membranes to test their efficiency for the enrichment of methane. Below only the best results using methanol are presented. Sometimes ethanol is mentioned only for comparison.

Membranes without the mesh were prepared to determine the mechanical properties of tension, according to the standard NMX-E-082-SCFI-2002 [50]. Those membranes were prepared by casting [13, 51], in a mould of 12.5 cm x 2.5 cm x 2 mm (length, width, thickness). In that way dried membranes of 0.5 mm of thickness was obtained. Tension tests were run in a Texturometer Texture Analyzer, model TA-TX2. For knowing the response of them when they are under an extreme load like that of the pressure of the gas during the diffusing process. This parameter can be related to the pressure during the diffusion process [52]. The deformation under load allows us to evaluate and quantify the most outstanding properties of the membranes like the elastic and plastic behavior. Those properties are so important because let us know the elastic limit where the original dimensions of the material are re-established and the point where the membranes break.





**Figure 2. Schematic diagram of the device for testing the selectivity of membranes**

For carrying out the diffusion tests, a device was designed and constructed, according to the schematic diagram, shown in Figure 2. The purpose of these tests was to determine the conditions for the best selectivity in the separation of methane, from nitrogen,  $N_2$  and carbon dioxide,  $CO_2$ .

The device for measuring the diffusion of gases through the membranes is in reality bench test equipment which is made up of a system for feeding the gases and three gas separation columns. The permeability cell is the main part of the equipment, which contains the prepared hybrid membranes whose properties are going to be determined. The gas fed through the system diffuses slowly through the membranes and it is transferred to a manifold set in the upper part of the system. The gas molecules that do not diffuse through the membrane are diffused through a sand bed (-200 +325 Mesh Tyler) for delaying the flow of the remaining gases. Both streams of gases can be analyzed using an Orsat gas analyzer or any other equipment when a mixture of gases is fed.

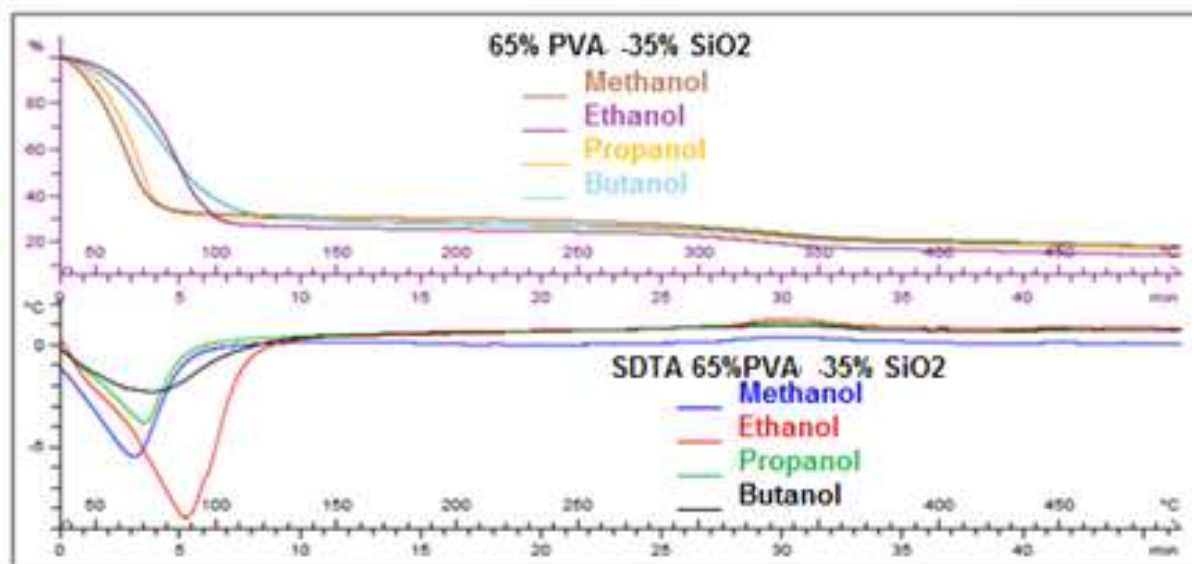
Each test was carried out at constant gauge pressure, increasing it from 2.5 to 30 psig at increments of 2.5 psig. The tests were run taking note of the gas flow and pressure at the input and at the exit of the system, besides the average temperature at the time of the day. This procedure was followed for each one of the prepared membranes, using different silica/polymer ratio and annealed at different temperatures.

## Results and discussion

### 1. Analysis Termogravimetric



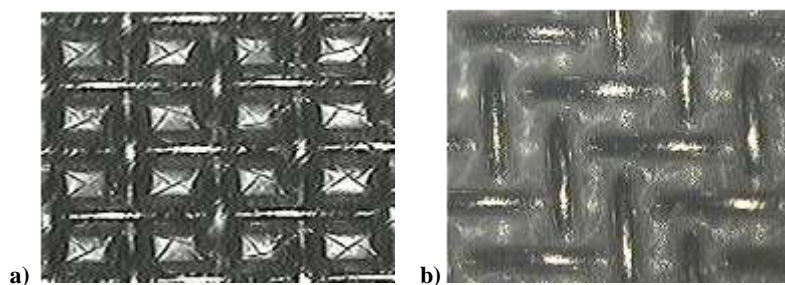
In Figure 3 it is shown the obtained thermogravimetric analysis, TGA, for the hybrid precursor suspension of 35/65 % w/w of  $\text{SiO}_2$ /PVAc solutions obtained with different solvents, methanol, ethanol, propanol and butanol. From the thermogram it is possible to observe that the material loses the larger part of the solvent about 100 °C, which it is the limit temperature for annealing the produced membranes. It was determined in some tests, that it is better to anneal the membranes at temperatures no more than 50 °C. Higher temperatures to that decrease the adherence of the material to the mesh used as support, giving raise also to the appearing of microcracks and consequently the selectivity of the membrane is low. From the thermogram it is observed also that the used material for the preparation of the membranes is stable about 300 °C, beyond that temperature the material suffers degradation. For those reasons it was decided to anneal the membranes at temperatures no longer than 100 °C and times of 15 hours for assuring the decreasing of the solvent inside the membrane at acceptable levels and at the same time to obtain the proper porosity.



**Figure 3. Hybrid materials TGA analysis prepared with two different solvents**

## 2. Characterization by Optical Microscopy

The inspection of the 35/65 w/w  $\text{SiO}_2$ /PVAc membranes under the optical microscopy, using methanol as solvent and annealed at 100 °C is presented in Figure 3. Optical microscopy results in Figure 4 shows that membranes are of homogeneous porosity and have small microcracks. When a second coating was deposited over the first one, that microcracks almost disappeared, as it is observed in Figure 3b. When ethanol, propanol and butanol were used as solvents, the obtained membranes were of bad quality, showing abundant microcracks, visible to the eye, and for this reason they were rejected and not tested for the gas separation process.



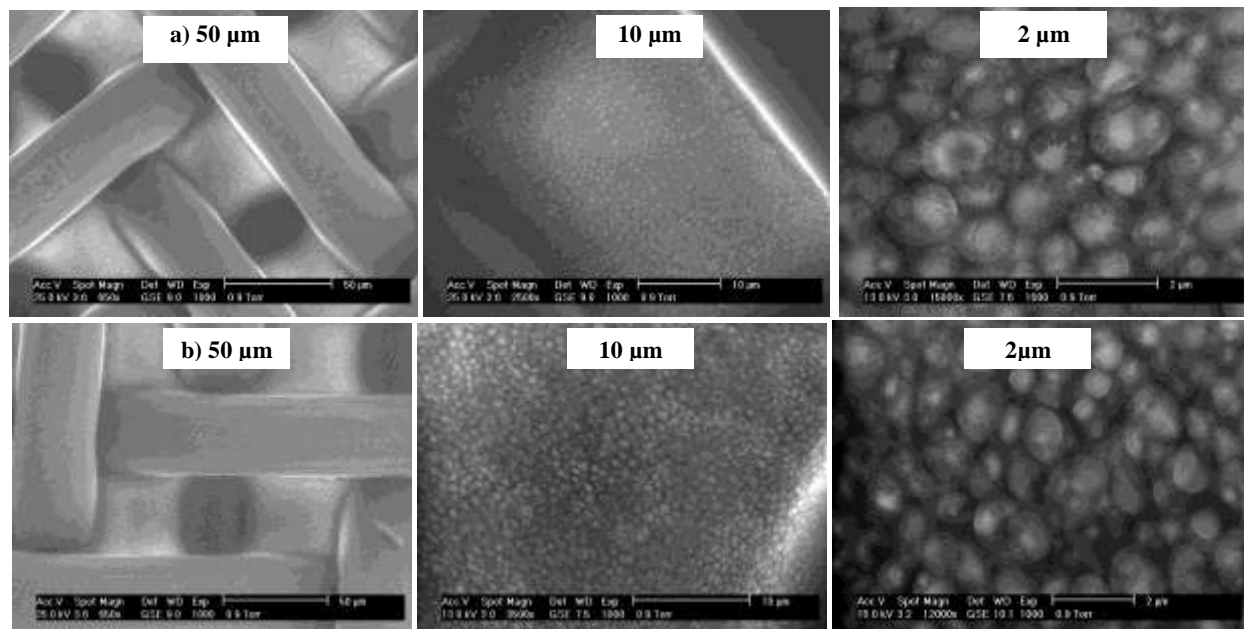
**Figure 4. Optical microphotographs of membranes prepared using methanol as solvent, annealed at 100 °C, with a ratio of 35/65 w/w  $\text{SiO}_2$ /PVAc at 10X. a) coated with one layer and b) with two layers respectively**





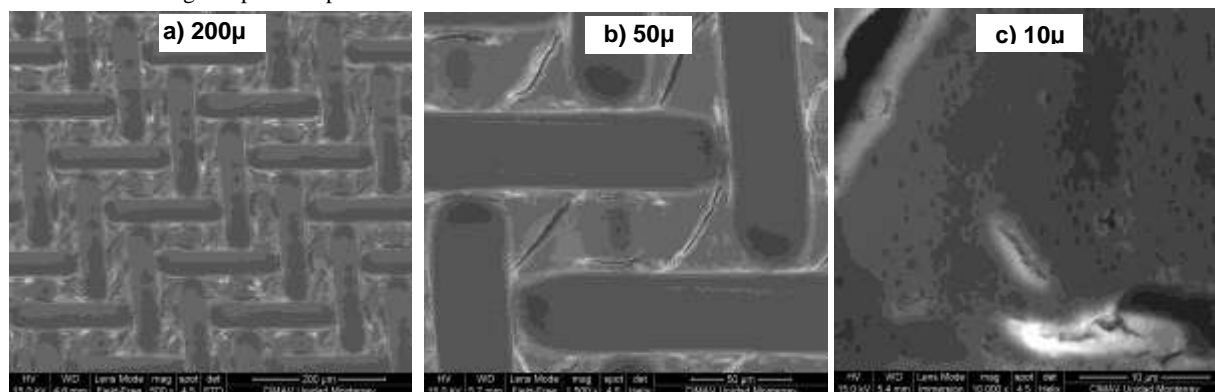
### 3. Characterization by Scanning Electron Microscopy (SEM)

These results were corroborated by means of SEM microphotographs. In Figure 5 it is shown a micrograph of a membrane annealed at 25 °C. In Figures 5a and 5b it is noticeable the good adherence of the hybrid material to the 325 mesh. Notice that fractures due to the annealing are not observed. In Figure 5c it is appreciated both that the polymeric resin is covering the silica particles and micro cavities where gases that will be separated from a stream will be diffused.



**Figure 5. SEM micrographs of membranes with 65 % w/w PVAc annealed at a). 25 °C and b). 40 °C.**

In Figure 6a, b and c shows a good coating when 325 mesh is used. The uniformity of the membrane is attributed to the methanol, which has the smallest size, volatilizes both easily and gradually, properties that help to obtain a proper porosity, with a minimum microcracks for the gas separation process.



**Figure 6. SEM microphotographs of membranes prepared with 35/65 w/w SiO<sub>2</sub>/PVAc, annealed at 100 °C and using methanol as solvent in the silica preparation.**



#### 4. Testing of gas diffusion

For determining the ability of the prepared membranes toward the gas separation, some tests were accomplished diffusing pure gases through the membrane and measuring the flow of the exit gases, at an inlet gas pressure of 110 cm in water column. From Figure 7, the diffusion of gases follows the next order:  $H_2$  diffuses first, starting with a flow of 8 mL/sec, increasing in an approximately exponential way in the next 5 min and after this the flow keeps constant at 10.5 mL/sec. Later  $CH_4$  and  $N_2$  gases were diffused through the membrane with a flow between 4 and 5 mL/sec for methane and between 2 and 3 mL/sec for nitrogen. Finally carbon dioxide diffuses through the membrane, starting with a flow of 2 mL/sec and after 10 min the flow decays to zero.

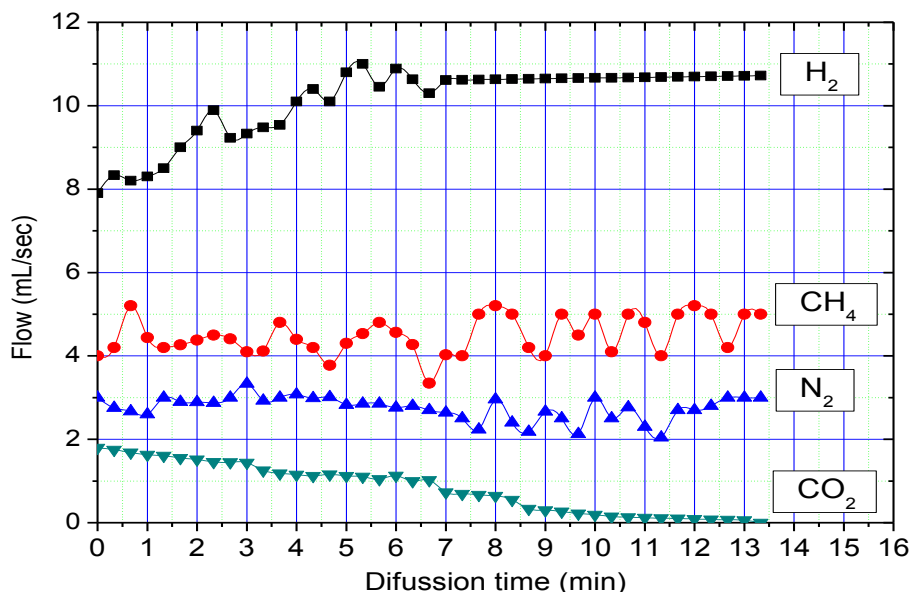


Figure 7. Gas diffusion test through a membrane 35/65 w/w  $SiO_2$ /PVAc, annealed at 40 °C.

#### 5. Characterized by Raman Spectroscopy

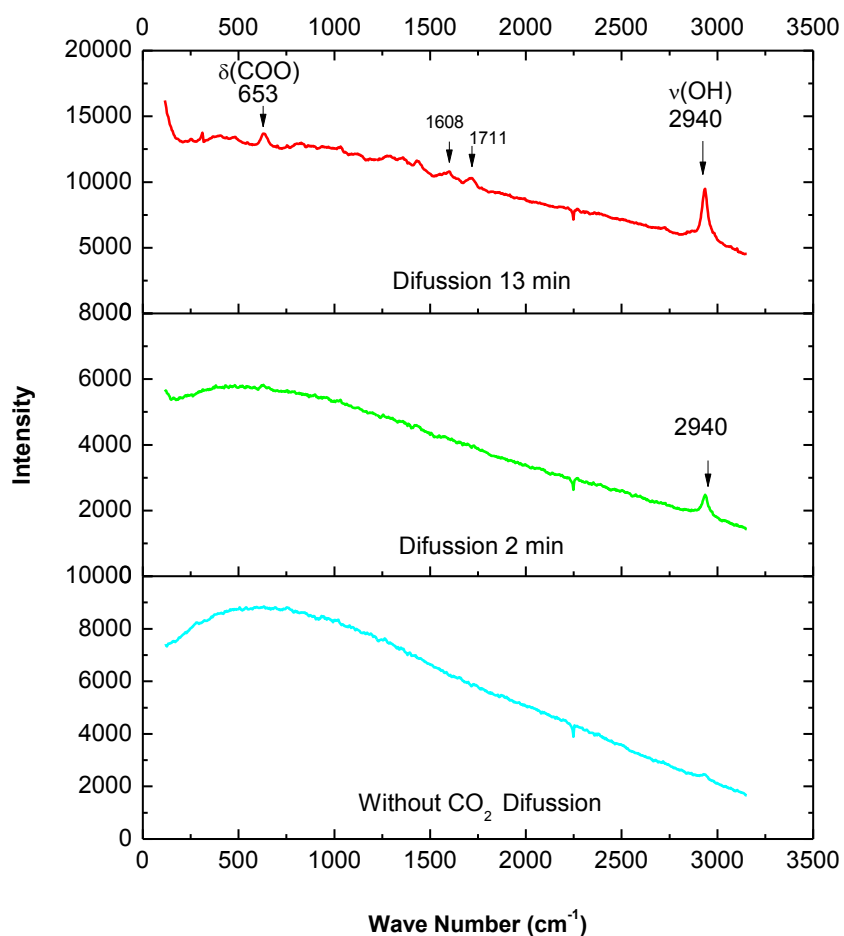
For establishing why this behavior of the membrane toward the gases, after being prepared the membrane was characterized by Raman Spectroscopy at zero time, after 2 min and then after 13 min of diffusion of  $CO_2$  gas. The results of this characterization are presented in Figure 8. At 2 min, it is clearly demonstrated that during the diffusion of  $CO_2$  some kind of bond between the carbon of the polymer and that of the  $CO_2$  is formed. In this way, the entrapped  $CO_2$  hinders the diffusion of the remaining gases, promoting the selective separation of them.



According to our Raman observations, in the literature has been reported the presence of a very strong band around  $2976\text{ cm}^{-1}$  for the stretching of OH groups and also a band between 641 and  $684\text{ cm}^{-1}$  assigned to  $\delta(\text{COO})$  groups [49]. Mitterdorfer et. al [53] mention that some di and polycarboxilic acids show the existence of some small Raman bands in the region between  $1607$  and  $1782\text{ cm}^{-1}$ , corresponding to the assimetric stretching of the C=O group; as a consequence of the connection of the OH group to the carboxylic group or directly to a carbon atom. This can be observed for both the alfa form ( $1630\text{ cm}^{-1}$ ) and the beta form ( $1608\text{ cm}^{-1}$ ). This suggests that the  $\text{CO}_2$  was entrapped on the surface and also inside the pores of the membrane or probably it can exist the formation of carbonic acid in those sites. In that way the entrapped  $\text{CO}_2$  occupies the existent active sites and consequently hinders the formation of new bonds on the surface of the membrane or inside the pores. The result is an effect of repulsion against the new molecules which try to pass through the membrane. This can explain the selectivity of the membrane to  $\text{CH}_4$  gas as it was observed in our experiments.

## 6. Tensile mechanical strength tests

In Table 1 the strength-deformation curves are obtained for the membranes without the mesh and for 50, 65 and 75 % w/w of PVAc. According to the results, the elastic limit for the membranes with 50 % w/w of PVAc is located at 7 MPa, with an elastic deformation of 5 mm and a breakdown limit at 8.5 MPa, with a limit deformation of 9.5 mm. For the membranes with 65 % w/w of PVAc, the limit deformation is presented at 1 MPa with a deformation of 40 mm and elastic limit at 1.25 MPa with a deformation of 150 mm. Finally, the membranes with 75 % w/w of PVAc present an elastic limit at 1.5 MPa with a deformation of 5 mm and a breakdown limit deformation at 2 MPa and a deformation of 95 mm.



**Figure 8. Raman analysis of the preceding membrane at 2 and 13 min of  $\text{CO}_2$  gas diffusion**

**Table 1. Elastic strength and deformation of membranes**

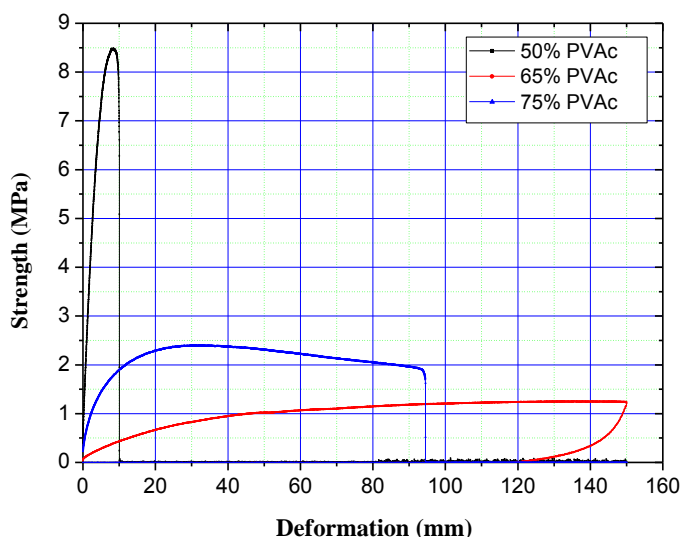
Membrane	Elastic strength (MPa)	Elastic deformation (mm)	Ultimate strength (MPa)	Fracture deformation (mm)	Young's modulus (MPa)
50% PVAc	7.0	5	8.50	9.5	1400
65% PVAc	1.0	40	1.25	150.0	25
75% PVAc	1.5	5	2.00	95.0	300





According to Figure 9, a membrane with an optimum both elastic deformation and strength must be prepared with 65 % w/w PVAc. This could be probably due to a better interaction of the surface groups of the resin with the silanol groups of the nanometric particles of silica. There will be a balance among the surface groups of the resin and those of the silica for having a material with excellent properties that can be used for the preparation of the membranes. When the percentage of the resin is higher than certain value, the interaction among the bonds of the resin itself will prevail. On the other side, when silanol groups of the silica prevail the bonds among them will determine the properties of the whole material. This establishes the difference among the membranes prepared with different ratios of resin and silica. A membrane prepared with a high content of resin will be very elastic but with a low porosity and this makes so difficult the flow of gas molecules through it. Therefore it is possible to have a membrane with a good interaction between the fillers and the polyme; which was confirmed by menans of the charactertization that was carried out using SEM [22].

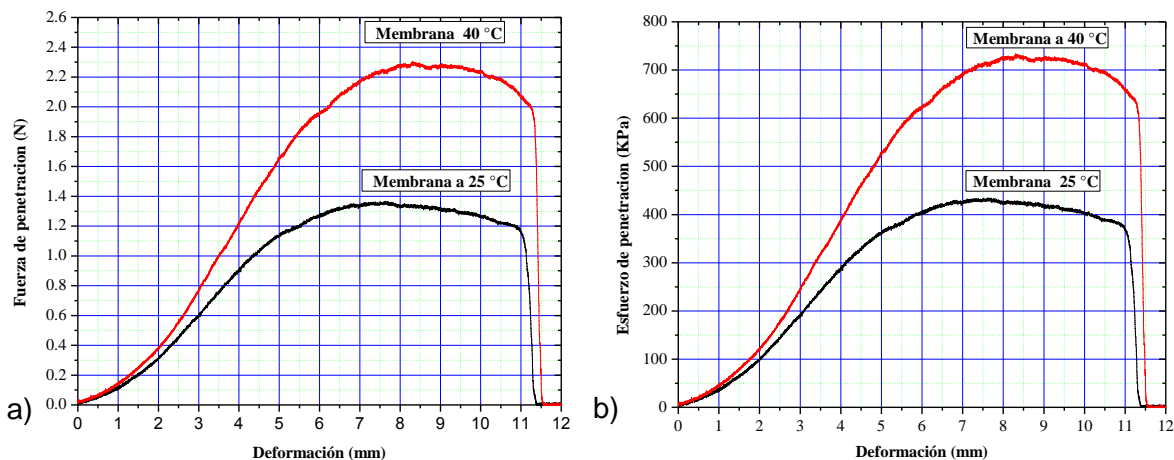
On the contrary, membranes prepared with a high content of silica will be a little elastic and will be affected in a larger degree by the gas pressure, and in this way they will be susceptible of suffering fractures and therefore to decrease their efficiency for the gas permeation. It is preferred a membrane with intermediate content of silica and resin and of course, with intermediate properties of the resin and those of the silica. The membranes obtained with 65 % w/w of resin fulfill the aforementioned requirement, as it is shown in Figure 9.



**Figure 9. Deformation versus strength of membranes with 50, 65 y 75 % w/w of PVAc**

### 7. Resistance to penetration tests

In Figure 10 it is shown the resistance to penetration test of the membrane prepared with 65 % w/w of PVAc resin at temperatures of 25 and 40 °C.



**Figura 10. Deformation vs penetration of membrane without support prepared with 65 % w/w of PVAc a) deformation vs penetration strength and at 25 °C and b) deformation vs penetration strength at 40 °C**



From Figure 10 it was prepared Table 2, which indicates the penetration and the hardness of the film prepared with 65 % w/w of PVAc resin and annealed at 25 and 40 °C, where it is appreciated that the membrane annealed at 40 °C is more resistant to penetration.

**Table 2. Penetration and hardness for the membrane with 65 % w/w de PVAc.**

Variable		Annealed at 25 °C	Annealed at 40 °C
Strength to the elastic limit	(kPa)	362.235	460.275
Deformation to the elastic limit	(mm)	5	4.5
Strength to the creep limit	(kPa)	400.433	621.021
Deformation to the creep limit	(mm)	5.8	6
Breaking strength limit	(kPa)	426.215	733.703
Deformation to the penetration limit	(mm)	8.615	8.305
Hardness to penetration	(N)	1.339	2.305

### 8. Hardness test of the membrane

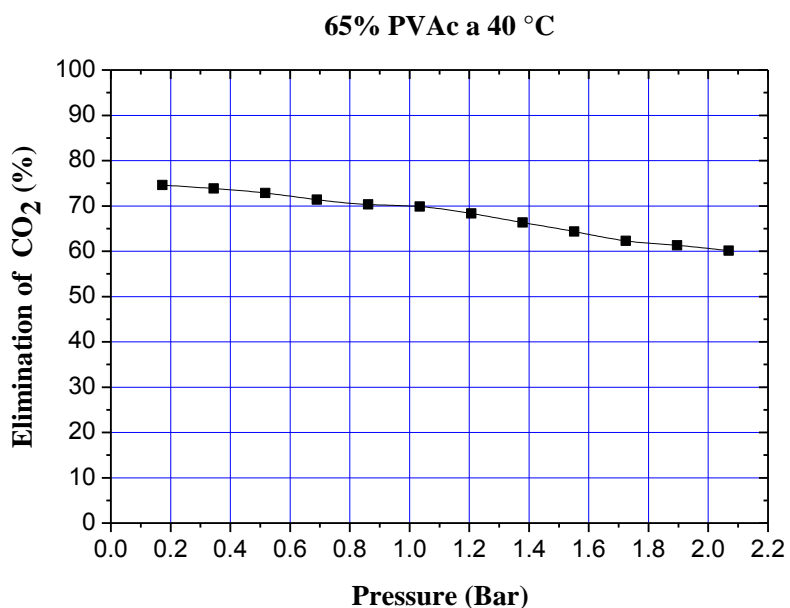
The results of hardness test pencil of membranes are presented in Table 3. The data show that the membrane annealed at 40 °C is composed of a material hard and resistant to the scratch.

**Table 3. Hardness test pencil of membranes**

Membranes	Dureza a lápiz	
	Temperature 25 °C	Temperature 40 °C
50 % w/w PVAc	8 H	9 H
65 % w/w PVAc	6 H	7 H
75 % w/w PVAc	3 H	4 H

### 9. Gas separation tests

Additional tests were carried out using the membrane for the separation of methane from a synthetic mixture of methane and carbon dioxide and analyzing the exit gases with an Orsat Analyzer. The tests were run in the same way like that of Figure 7, saturating first the membrane with pure CO<sub>2</sub> gas and then continuing to diffuse a synthetic gas composed of 80.1 % of CH<sub>4</sub> and 19.9 % of CO<sub>2</sub> under different inlet gauge gas pressures. The results of the elimination of CO<sub>2</sub> are presented in Figure 11. It can be seen from the figure, that 75 % v/v of CO<sub>2</sub> was eliminated at 0.17 Bar (2.5 psi) and 60 % v/v at 2.07 Bar (30 psi).



**Figure 11. Tests for the separation of CO<sub>2</sub> from CH<sub>4</sub> using a membranes prepared with a ratio of 35/65 w/w SiO<sub>2</sub>/PVAc and methanol as solvent**

From the results it is concluded that it is



possible to use these membranes for enriching the hydrogen and methane produced in a biodigester. These results are being implemented in a biodigester prototype of 340 liters of materials Figure 12, putting the membranes in a specially designed device to separate the  $\text{CO}_2$  from  $\text{H}_2$  and  $\text{CH}_4$ .



**Figure 12. Continuous digester 340 liters**

There were carried out tests for the separation of methane from a synthetic mixture of methane and carbon dioxide and analyzing the exit gases with an Orsat Analyzer. The tests were carried out using a membrane prepared with 65 % w/w of PVAc resin annealed at 25 and 40 °C. The initial composition of the gas was 20,0 % v/v of  $\text{CO}_2$ . The results are shown in Table 4. From the table it is concluded that the best results are for a pressure of 20 psig and for the membrane annealed at 40 °C, decreasing the percentage of  $\text{CO}_2$  in the exit gas to 6.7 % v/v, which is equivalent to 65 % V/V of the total volume. These results agree with that obtained from the experimental characterization of the membranes

**Table 4. Percentage of  $\text{CO}_2$  in the exit gas stream using the separation device above described.**

Annealing Temperature	% $\text{CO}_2$ in the exit gas stream	
	20 psig	30 psig
25 °C	11.3 %	11.5 %
40 °C	6.7 %	7.9 %

## Conclusions

Hybrid membranes were prepared for the separation of gases produced in the anaerobius biodigestion process. The membranes were manufactured in a simple way from hybrid suspensions of silica-PVAc prepared by the sol-gel process. It was possible to generate proper porosity for gas separation using both the proper resin composition of the hybrid as well as the proper annealing conditions of the material.



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Membranes produced using propanol and butanol were of bad quality, with abundant microcracks generated during the drying time, and for that reason were not tested for the gas separation process.

From the mechanical test results it was concluded that membranes with 65 % w/w of resin and annealed at 40°C present both the best porosity and of course selectivity with regard to H<sub>2</sub> and CH<sub>4</sub>

The results were illustrated in a separation of the gases of a mixture of a hypothetical and synthetic gas, showing that it is possible to use these membranes for methane enrichment of a biogas.

### Acknowledgments

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