Effects of Relative Humidity and Temperature on Gas Transport Properties in MFC and MFC + Lupamin films

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1. Introduction.

Cellulose is one of the most important and abundant biopolymers on earth. It can be found in wood, cotton and other plant-based materials, serving as dominant reinforcing phase in plants' structures. For many years, people have found a large number of applications in which cellulose has proved to be extremely useful, from material support in the recording and transmission of human culture, to energy source, building material and clothing [1]. The use of cellulose is also becoming very common in the elaboration of derivate products such as ethers and esthers, as a material to strengthen polymers and matrixes because it decreases the surface energy of the fibres and increases the compatibility between polymer and matrixes.

In more recent times, the use of nano-cellulose in advanced technological applications has been growing, both due to the excellent properties of this material and to its renewability. According to the IUPAC, a nano material is considered the material that has at least one dimension below 100 nm. Microfibrillated Cellulose (MFC) is formed by aggregates of cellulose micro fibrils with a diameter between 20 and 60 nm and it has a length of several micron meters. During the suspension, under a high - pressure process, the viscosity of MFC increases until it transforms into an aqueous gel whose concentration reaches a level between 2 and 10wt %. Once it dries, the resulting nano-material takes the form of a transparent film with the characteristic of a rigid network [2].

The production of cellulose nano fibres and their applications has gained attention due to their high strength and stiffness combined with low weight, biodegradability and renewability. Other properties such as being a transparent enforcer of polymers, aerogels and paper additives, as well as an emulsion stabilizer, are also well appreciated. These high-value new materials are the subject of continuing research and their commercial use is expanding in terms of new products from the pulp and paper industry, the agricultural sector, the food (food wrappers, enclosures, …) and electronic industries. There is an increasing demand of renewable products made from materials of non-petroleum origin and in this context cellulose is playing a central role as a new raw material able to become a substitute of more dangerous fuels and related materials. The potentiality of nano-cellulosic particles has been demonstrated for special nano-materials, but it is as a bio-based reinforcing nano-filler where it has been receiving more interest over the last decades. Especially important is the increase of the number of publications and reports about cellulose and their applications, mainly in countries of the north of Europe or United States [3].

The present work aims to compare the permeability of different gases (CO_2, N_2 and CH_4) in pure Microfibrillated Cellulose (MFC) membranes, and MFC membranes mixed with Polyvinyl Amine (MFC + Lupamin), in order to have empirical evidence of the conditions and capacity of the membranes. Polyvinyl Amine is an attractive polymer because of the very high content of primary amine groups. It is also a good adhesive for cellulose films due to the introduction of aldehyde groups in the surface of the polymer [4], [5]. In particular, the gas permeability has been characterized at different water concentrations at two different temperatures (35 and 50ºC) under low-pressure conditions (1 bar). In addition, some water sorption experiments have been carried out

in order to better understand the structure of the matrix and to correlate the permeability data with the real water content in the membrane. The differences between membranes of MFC + Lupamin obtained in neutral condition and samples of MFC + Lupamin produced at pH = 11 were also studied. The introduction of OH^- group on the membranes of MFC + Lupamin indeed is expected to improve the CO_2 transport of the membrane because it is an increase of the affinity of the materials to this acidic gas.

2. Experimental

2.1 Materials

Two main materials:

- Microfibrillated Cellulose (MFC), provided by the Centre Technique du Papier in Grenoble. They are provided has a water suspension with 2 % of solid concentration; their measured density is 1,5 g/cm^3, approximately.

- The Polyvinyl Amine (PVAm) is obtained from the commercial polymer Lupamin® 9095 supplied by BASF. Lupamin is a copolymer of vinylformamide / vinylamine, with a degree of hydrolyse > 90 %. The solid in the initial solution is about 20 %, the pH is between 7-9 and the density of the solution at 20ºC is 1,08 g/cm^3, approximately.

2.2 Film preparation and characteristics

Microfibrillated Cellulose (MFC) and Lupamin 9095 have been mixed in a 50:50 proportion on a Pyrex glass of 50 mL of capacity in the following amounts: 15 grams of MFC suspension for 1,5 grams of Lupamin solution. The films of MFC + Lupamin are cast on a polysulphone support in order to improve the conditions of the membrane and avoid some defects and pinholes formation during testing. The polysulphone support has a thickness of 140 microns.

The calculation of how many grams of each component were necessary was done as follows:

1. 15 grams of MFC · 0,02 grams of solid / gram of MFC = 0,3 grams of solid in MFC.
2. 0,03 grams of solid in MFC / 0,2 grams of solid in Lupamin = 1,5 grams of Lupamin have to be added.

The calculations had been done for a 50:50 proportion on the films. After mixing, the solution was stirred at room temperature until it became clear (between one and two hours). To further improve the mixture of the solution, it was then passed twice through a three-role mill apparatus. Finally it was knife cast, on, covering the polysulphone support and placed inside an oven at 40ºC overnight to eliminate the excess of water.

The films of pure MFC were prepared in a solution of water. The MFC was diluted up to 1 % of concentration, mixing it in 50:50 proportions with water. For this purpose, in a

Pyrex glass it was added 12 grams of MFC and 12 grams of water. This solution was also stirred at room temperature during 2 hours approximately and then was putted inside a vacuum apparatus in order to remove the bubbles during 30 minutes approximately. When the bubbles were removed, the sample was cast a Petri glass and introduced into an oven working at 40 º C overnight.

The thickness of the membranes of MFC pure were calculated in the following way:

1. Measurement of the diameter of the petri glass.
2. Calculation of the area of the petri glass.
3. Calculation of the volume of the sample (Area of petri glass · Thickness of the membrane)
4. Calculation of the amount of solution (Volume of the sample · density of MFC). The density of MFC is approximately 1,5 g/cm3.
5. Calculation of the amount of MFC (Amount of solution / Concentration of MFC). The concentration of MFC is 2 wt %.
6. Finally, in order to have a solution of 1 wt % of MFC the same amounts of water and of MFC were mixed in order to reach a fifty per cent concentration.

The final samples had an estimated thickness of around 30 microns.

MFC + Lupamin (50:50) films were also prepared with the addition of KOH increasing the pH up to 11. The procedure is the same as the one used above for other MFC-Lupamin films, but a 1 molar KOH solution (prepared dissolving 0,2 grams of KOH in 39,9 grams of water to obtain 0,1 M concentration) was added drop by drop to the MFC-Lupamin solution to adjust PH. The final amount of KOH solution added was 3,4 grams. The films were casted also on a polysulphone and then dried following the same protocol described above.

2.3 Sorption test measurement.

A sequence of different sorption test was carried out in a range of water activity (0-80 %) in a quartyz spring miscrobalance. The tests have been done at 35 ºC in order to see the differences on the water sorption between MFC pure and MFC + Lupamin, in a different range of activity. The samples were catted in a small piece, weighted and their thickness measured. First of all, the sample was placed inside the column hung attached to the spring. Prior to the experiments the samples has been conditioned under vacuum for approximately 48 h (in order to be sure that there were no water or other species absorbed in the sample) at 35ºC the sample of MFC pure and 55ºC the sample of MFC + Lupamin. After drying, the sample was exposed to defined water vapour activity and the spring elongation over time was measured to obtain solubility value.

In particular the following protocol was followed during tests. With the sample under vacuum and isolated inside the column, the liquid reservoir was purged, to be completely sure that there was only water inside the reservoir. Then, a certain amount of water wapor was loaded in a prechamber endowed with a manometer to monitor the pressure and thus the water activity [6]. When the system reaches the desired

equilibrium pressure the water reservoir was closed and the column was open to start the test. The spring elongation due to soprtion was monitored th ough a dedicated CCD camera until the steady state was reached then a new activity step was performed with the sane procedure.

Sorption kinetics was determined by measuring pressure change as a function of time. The following expresion is obtained which gives the instant relative water uptake in each sorption test as a function of time (M).

$$M := Minf\cdot\left[1 - \sum_{n}\frac{8}{(2\cdot n+1)^2\cdot\pi^2}\cdot\exp\left[\frac{-D\cdot(2\cdot n+1)^2\cdot\pi^2\cdot t}{4\cdot L^2}\right]\right] \qquad (1)$$

Where Minf is the final amount of water in the sample, π are the positive, non-zero solutions of the equation tan (π) = -n π. The dimensional length of solution (n) is the ratio between membrane area (A) and the film thickness (L). The diffusion coefficient (D), considered constant during each experimental sorption step, is thus determined from the best fit of the Eq. (1) to the experimental data [7].

2.4 Permeability measurement

The permeability of three different gases (N_2, CO_2 and CH_4) at different temperatures (35 and 50 ° C), and in a range of different relative humidity (between 40% and 95 %, was measured during the experiment campaign. For the test, a humidity permeometer apparatus was used that evaluates the amount of gas permeated through the membrane resulting through the ressure change in a calibrated downstream side volume of the permeometer (V_d). To perform the permeations tests a membrane was putted on a cell (Milipore HP filter holder, diameter 47 mm, filtration area A = 9,6 cm^2). After loading the sample in the cell, a vacuum pretreatment was performed in order that any residual species were absorbed in the film. Then, the sample was exposed to water vapour at the desired partial pressure; the system reached an equilibrium condition; the upstream side of the membrane was fed with a humidified stream of gas, at the same water vapour activity (the ratio between partial pressure and vapour pressure of water) of the preconditioning step, while the downstream side was monitored with a manometer. Under these conditions, only the gas molecules other than water permeate through the membrane, being the water chemical potential equal on both sides of the membrane, and the pressure of the downstream side increases directly with the gas flow [8].

When the steady state is reached, the permeability *P* of the selected gas can be calculated from the increase of downstream pressure (p_d) in the calibrated volume by the Eq. (2):

$$P = \left(\frac{dp_d}{d_t}\right)_{t\to\infty} \cdot \frac{V_d}{R \cdot T \cdot A} \cdot \frac{\delta}{(P_u - P_d)} \qquad (2)$$

Where:

R: Gas constant.

T: Operative temperature

δ: Thickness of the membrane.

P_d: Downstream pressure.

P_u: Upstream pressure

A: Cell area.

V_d : Downstream volume. It was calibrated at 90,5 cm^3 the big volume and 25,7 cm^3 the small volume.

The pressure of the upstream side (p_u) was kept constant at the value of 1 bar. As no leak was detected during the experiments, the term of the leaks was not included in the equation.

The selectivity (α_{ij}) between two gases was calculated by the ratio between the permeability values of the two gases:

$$\alpha_{ij} = \frac{P_i}{P_j} \qquad (3)$$

3. Results and discussion.

3.1 Sorption Test results.

Water vapour sorption tests were performed for both MFC pure and MFC + Lupamin films at 35°C. The results are shown in Figure 1 and 2, which present the sorption isotherm and the values of water diffusivity obtained for the two materials, as well as in Table 1.

As it is shown in the Figure 1, the sample of MFC + Lupamin absorbs more water than MFC pure probably due to the high hydrophilicity of Lupamin which more readily sorbs water with respect to MFC. It should be said however that the sample of MFC pure was dried at lower temperature (35ºC) than the sample of MFC + Lumapin so it is possible that there was still some residual water in the sample of MFC pure at the beginning of the experiments which would results a small underestimation of the data of MFC pure solubility. A similar error however would not change the previous conclusion since especially at high activity the difference between the two materials is very high as MFC + Lupamin films sorbs about 5 time the water that is dissolved in MFC.

The Figure 2 shows instead the diffusion coefficient of water in the membranes. Interestingly, the sample of MFC + Lupamin has also higher values of diffusivity than the MFC pure, revealing a faster sorption kinetics.

These results suggest that the addition of Lupamin opens up the MFC inter febrile network thus allowing the system to swell more freely thus increasing both the water uptake and the diffusion coefficient.

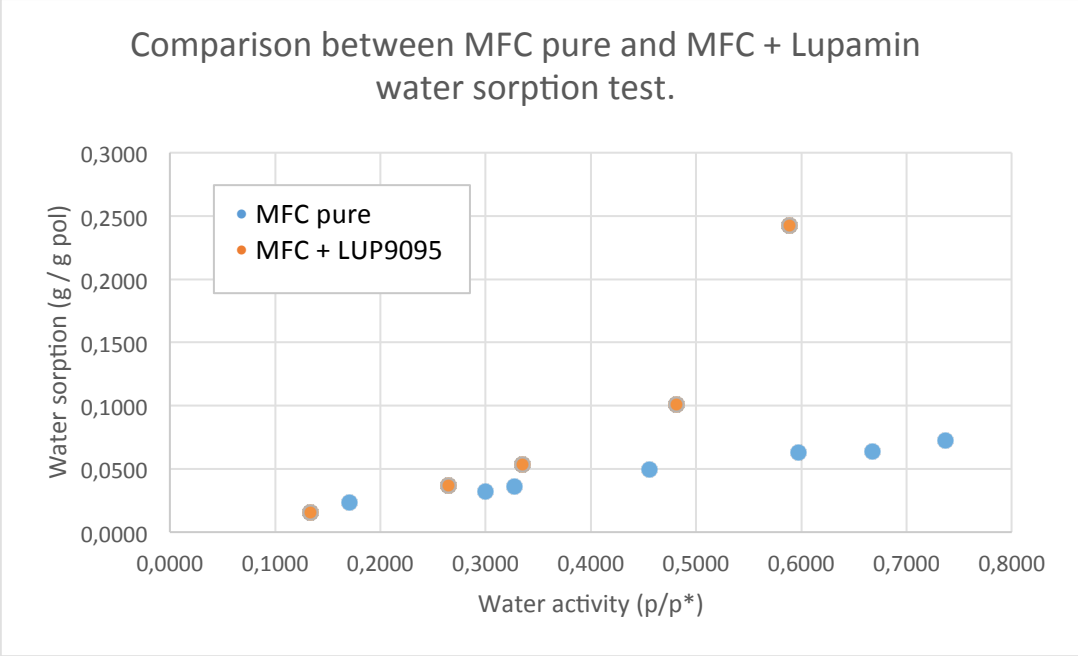

Figure 1. Water sorption test of MFC + Lupamin and MFC pure films

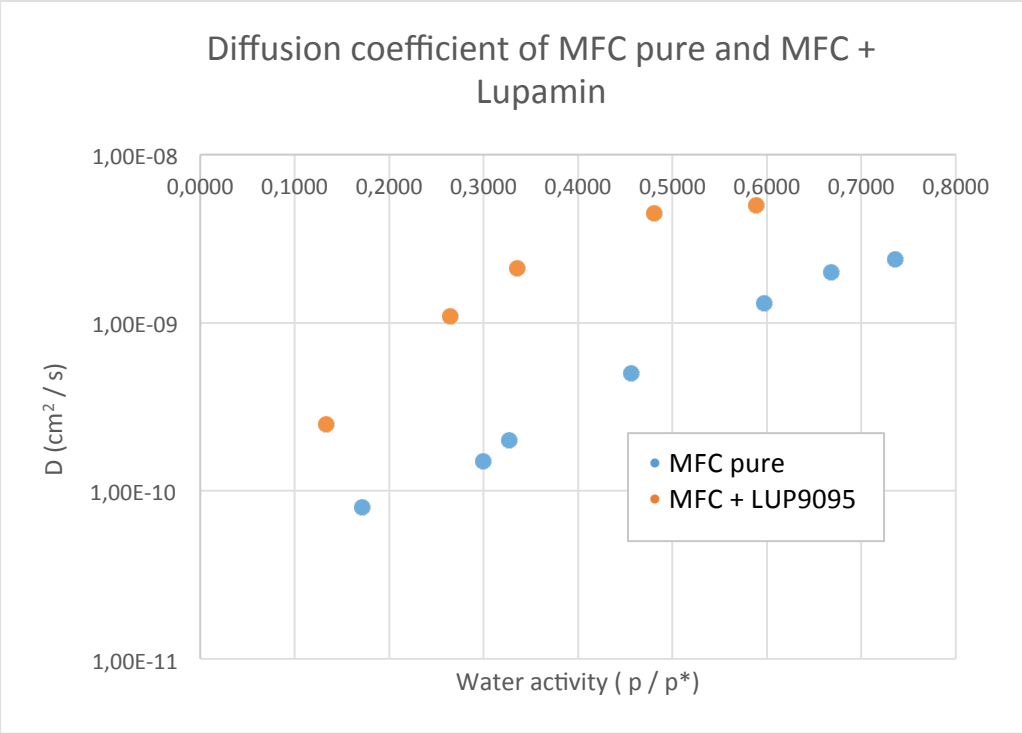

Figure 2. Coefficient diffusion of MFC + Lupamin and MFC pure

MFC+Lup			MFC pure		
Activity	**Final**	**D**	**Activity**	**Final**	**D**
	(g / g pol)	cm^2/s		(g / g pol)	cm^2/s
0,1709	0,0235	8,00E-11	0,1339	0,0153	2,50E-10
0,2996	0,0324	1,50E-10	0,26432	0,03684	1,10E-09
0,3278	0,0364	2,00E-10	0,3348	0,0537	2,10E-09
0,4564	0,0495	5,00E-10	0,4811	0,1004	4,5E-09
0,5974	0,0626	1,30E-09	0,5885	0,2425	5,00E-09
0,6678	0,0641	2,00E-09			
0,73656	0,07241	2,40E-09			

Table 1. Values of sorption water and diffusion coefficients (D) of MFC + Lupamin and MFC pure films

3.2 Permeability results

3.2.1 Comparison of permeability of MFC + Lupamin films at different temperatures

The Figure 3 shows the values of the permeability of CO_2, CH_4 and N_2 for the samples of MFC + Lupamin at 35 ° C in a range of different relative humidity levels. The selection of these gases is justified by the industrial interest of separation of CO_2-CH_4

and CO_2-N_2. Furthermore, all the permeability values obtained for those gases at 35ºC and at all R.H. are reported in the Table 2. The value of permeability is in Barrer unities. (1 Barrer = $3{,}364 \cdot 10^{-16}$ mol s^{-1} m^{-1} Pa^{-1}).

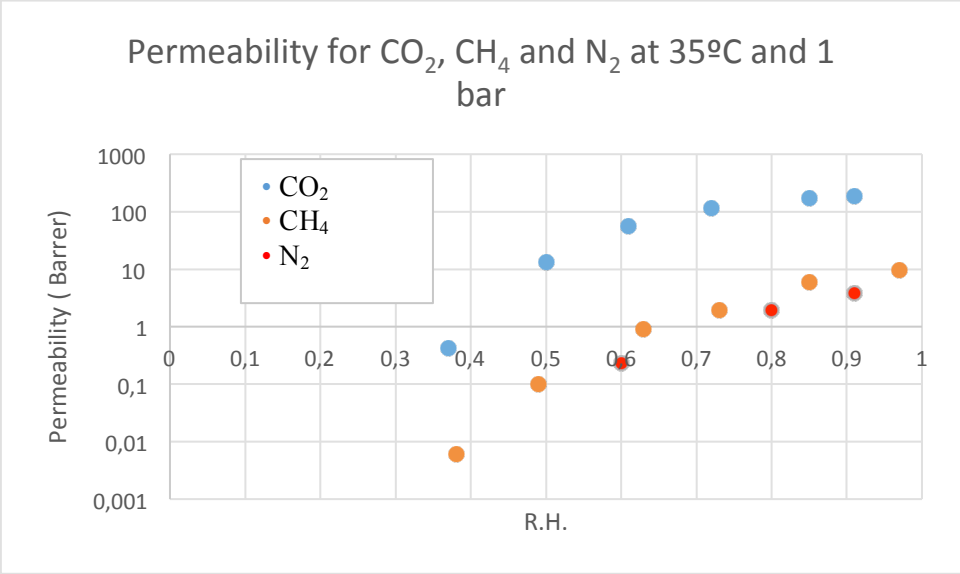

Figure 3. Permeability values at 35ºC and 1 bar for CO_2, CH_4 and N_2 for MFC + Lupamin films

CO_2			CH_4			N_2		
Test	**R.H.**	**Permeability**	**Test**	**R.H.**	**Permeability**	**Test**	**R.H.**	**Permeability**
1	0,37	0,42	1	0,38	0,0060	1	0,60	0,23
2	0,50	13,30	2	0,49	0,10	2	0,80	1,96
3	0,61	55,90	3	0,63	0,90	3	0,91	3,80
4	0,72	117,44	4	0,73	1,97			
5	0,85	168,40	5	0,85	5,96			
6	0,91	187,11	6	0,97	9,40			

Table 2. Permeability to CO_2 and to CH_4 values at 35ºC and 1 bar for MFC + Lupamin films.

As the results show, the gas which higher permeability is CO_2, then CH_4 and finally N_2, having this two gases a similar trend, probably because of their similarities in terms of properties and characteristics. The permeability of the gases increases in the presence of water, due to the hydrophilic characteristics of cellulose and the presence of Lupamin (PVAm), which are highly swollen in presence of water.

The Figure 4 shows that the performance in terms of permeability of MFC + Lupamin films to CO_2 and CH_4, when the operating temperature increases until 50ºC, and

compares it with the permeability performance at 35ºC, which was showed before. The values of permeability at 50ºC are reported in the Table 3.

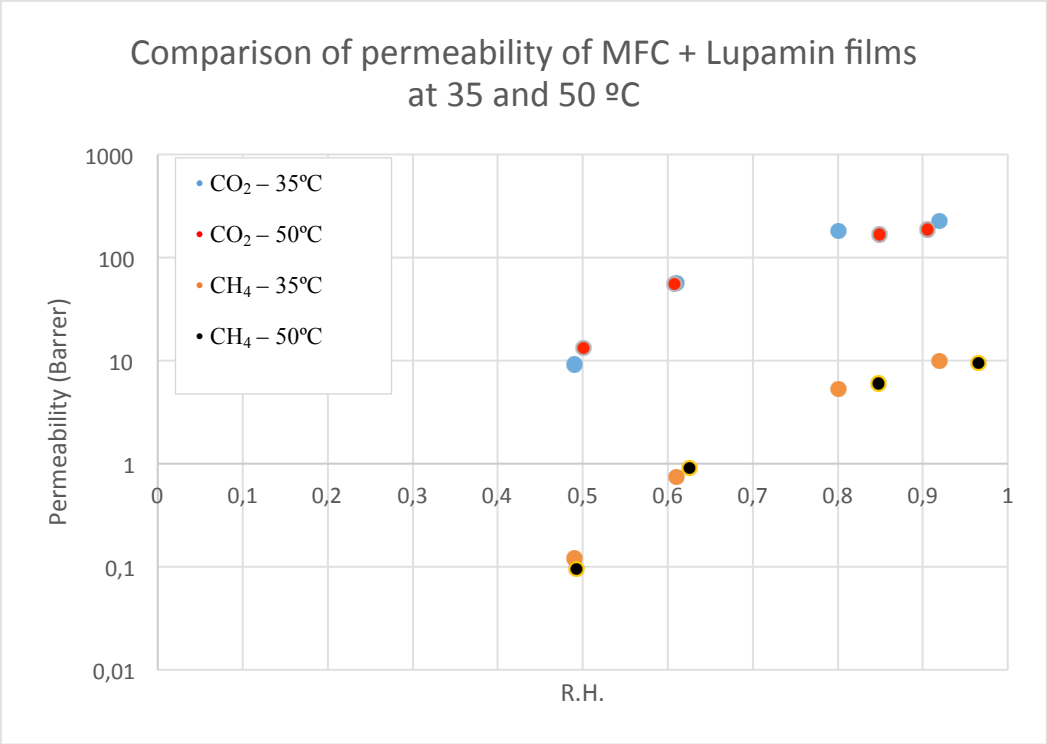

Figure 4. Permeability of MFC + Lupamin films: Comparison at 35º and 50 ºC.

CO_2			CH_4		
Test	**R.H.**	**Permeability**	**Test**	**R.H.**	**Permeability**
1	0,49	9,15	1	0,49	0,12
2	0,61	56,60	2	0,61	0,74
3	0,80	180,13	3	0,80	5,33
4	0,92	224,87	4	0,92	9,80

Table 3. Permeability to CH_4 values for MFC + Lupamin films at 50 ºC.

The values of permeability in Table 2 and the representation of the data points in Figures 3 and 4, indicate that differences in temperature do not seem to affect the permeability performance of the films in a significant amount. Only at a higher relative humidity there is a slightly increase of the permeability but not in a minor amount.

3.2.2 Selectivity results of CO_2 / CH_4 and CO_2 and N_2

With respect to the results on selectivity, the Figure 5 shows that selectivity decreases as the amount of water in the membranes increases. This decrease in the selectivity is probably explained by the larger swelling degree induced by the more hydrophilic character of the membrane..

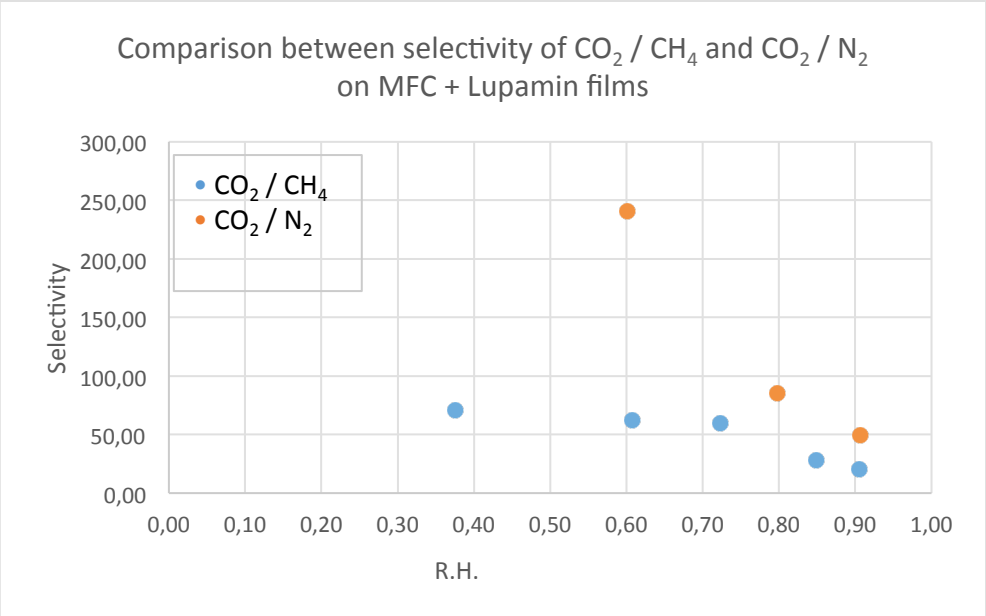

Figure 5. Selectivity values of CO_2/CH_4 and CO_2/N_2 in MFC + Lupamin films

The data points shown in Figure 5 indicate higher values of selectivity for CO_2 / N_2 than for CO_2 / CH_4, due to the lower values of permeability of N_2 on MFC + Lupamin films.

The selectivity results of MFC + Lupamin for CO_2 / CH_4 at 50 ºC have been also studied in order to have a more complete understanding of the effects of changes in temperature on performance. According to Figure 6, selectivity remains relatively constant in a range of values of low humidity levels. After some point, as the amount of water in the membrane increases, selectivity decreases, probably for the same reason than what we observed it happened at 35ºC. The selectivity for MFC at 35ºC and 50 ºC does not seem to change significantly with the temperature, which is a somehow surprising result given the permeability of CO_2 on polymers.

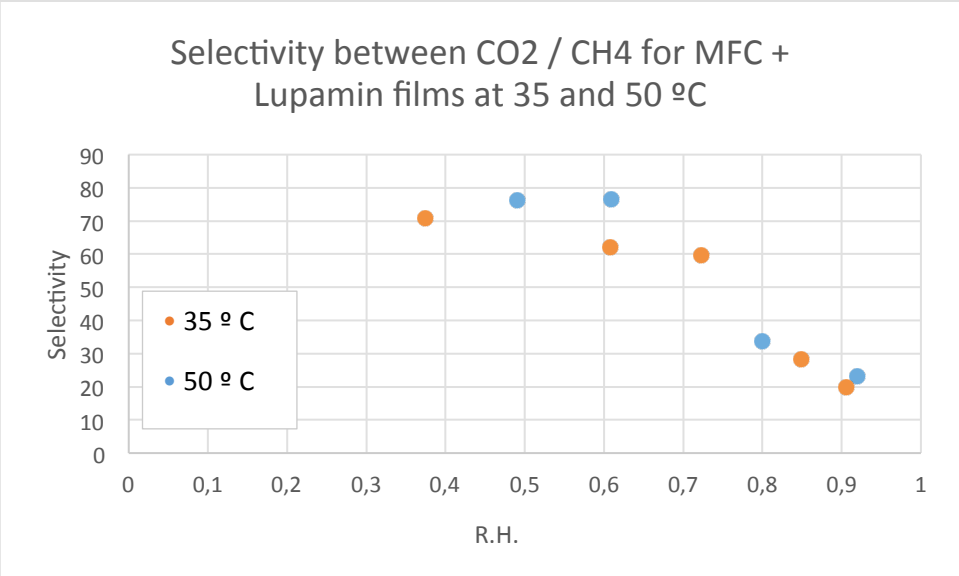

Figure 6. Selectivity between CO_2 / CH_4 in MFC + Lupamin films at 35ºC and 50ºC

The conclusion drawn from the results of the experiments is that the permeability of MFC + Lupamin films to CO_2 and CH_4 gases increases with the amount of water, that is with the relative humidity of the membrane. This means that the conditions and productivity of the membrane increase with higher relative humidity. However, this increase in permeability is at a cost of the decrease in the selectivity between the gases.

3.2.3 Permeability and Selectivity in MFC pure films.

We now show the performance of permeability to the selected gases of pure MFC films, in a similar manner as we just did for the MFC+Lupamin films, in order to to find out the mass transport properties of the blend. The results are presented in Figure 7 and Table 4.

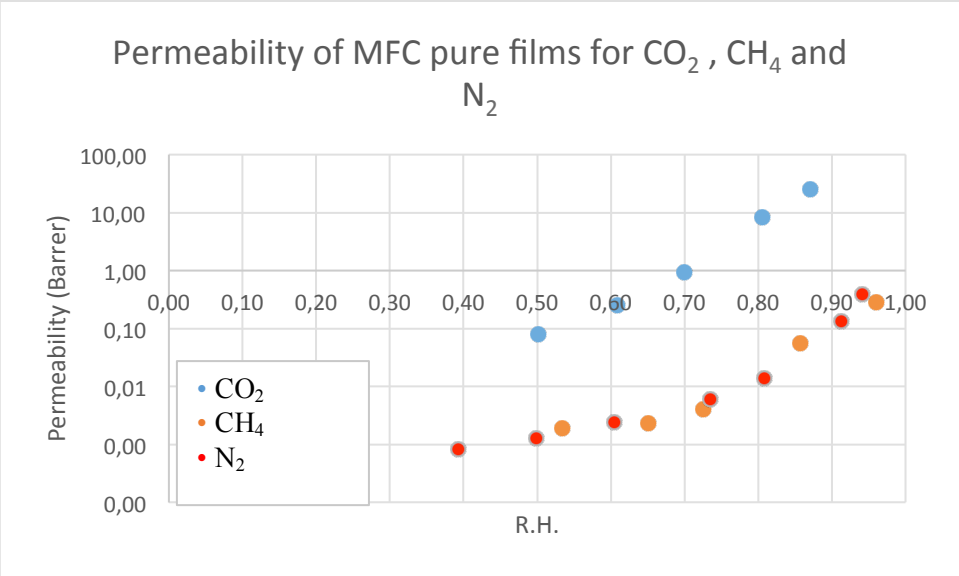

Figure 7. Permeability to CO_2, CH_4 and N_2 in MFC pure films at 35 ºC and 1 bar

CO_2			CH_4			N_2		
Test	**R.H.**	**Permeability**	**Test**	**R.H.**	**Permeability**	**Test**	**R.H.**	**Permeability**
1	0,50	0,08	1	0,53	0,0019	1	0,39	0,0008
2	0,61	0,24	2	0,65	0,0023	2	0,50	0,0013
3	0,70	0,93	3	0,73	0,0040	3	0,60	0,0024
4	0,81	8,32	4	0,86	0,0573	4	0,74	0,0060
5	0,87	25,52	5	0,96	0,2820	5	0,81	0,0137
						6	0,91	0,1325
						7	0,94	0,3911

Table 4. The permeability values of the three gases to MFC pure at 35 º C and 1 bar

The results are similar to those found for the MFC + Lupamin. The CO_2 permeates faster than CH_4 and N_2 while the permeability of all gases is positively influenced by the presence of water. The values of CH_4 and N_2 are very similar to those obtained in the MFC + Lupamin films, probably because of the similar characteristics of both gases. Permeability values, however, are definitely lower than those observed in the blend in agreement with the fact that pure MFC films are usually considered gas barrier materials.

The selectivity values of MFC pure films for CO_2 / CH_4 and CO_2 / N_2 have completely different values than those observed in MFC + Lupamin films, as the Figure 8 shows. While on MFC + Lupamin the selectivity decrease with an increase of the amount of water, for MFC pure what we observe is an increase of selectivity values as the amount of water on the membrane also increases. The values of selectivity of MFC pure are higher than those of MFC + Lupamin, which is an unexpected result.

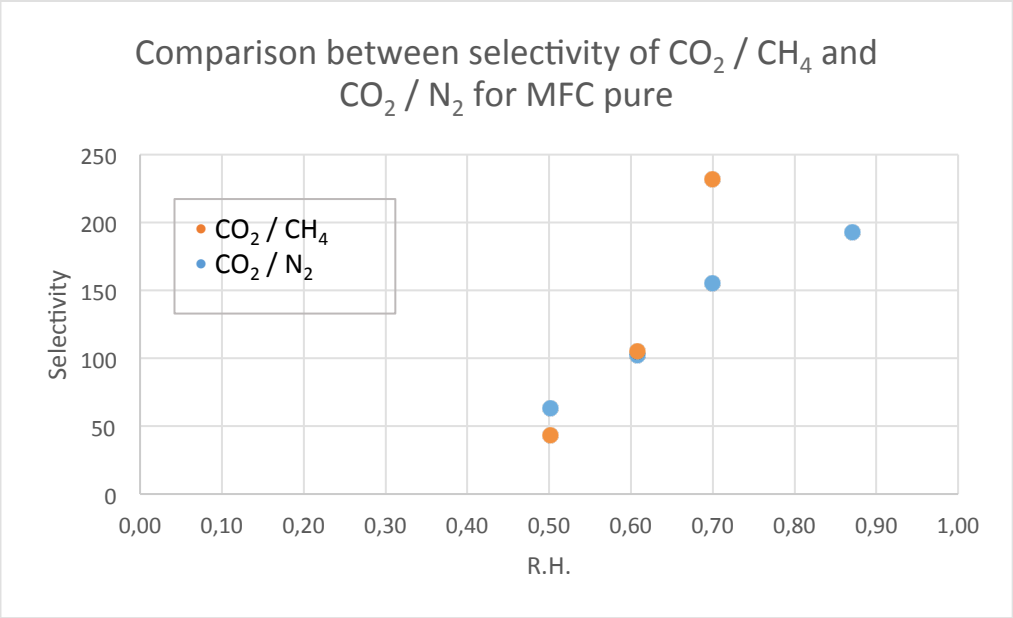

Figure 8. Comparison of selectivity values for MFC pure films in two pairs of gases

The Figure 9 shows all the selectivity values found in the different experiments for MFC + Lupamin films and for MFC pure films. It is remarkably important the different performance of MFC pure compared with the performance of MFC + Lupamin, because, theoretically, the superior performance of MFC pure firms is difficult to justify. The black point represented in Figure 9 is the selectivity on pure water of CO_2 / N_2. This point is represented to have an idea on how the trends of selectivity go [9].

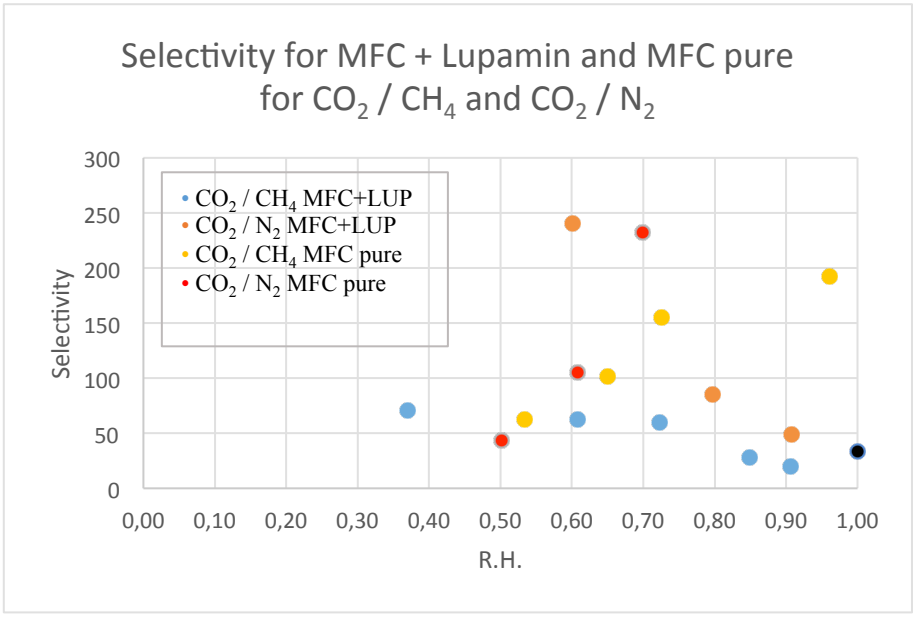

Figure 9. Selectivity values of MFC pure and MFC + Lupamin films for CO_2 / CH_4 and CO_2 / N_2

3.2.4 Comparison of permeability of MFC + Lupamin and MFC pure films

The comparison of permeability of MFC pure and MFC + Lupamin values, at 35°C, appear represented in Figures 10, 11 and 12 for the three CO_2, CH_4 and N_2 respectively.

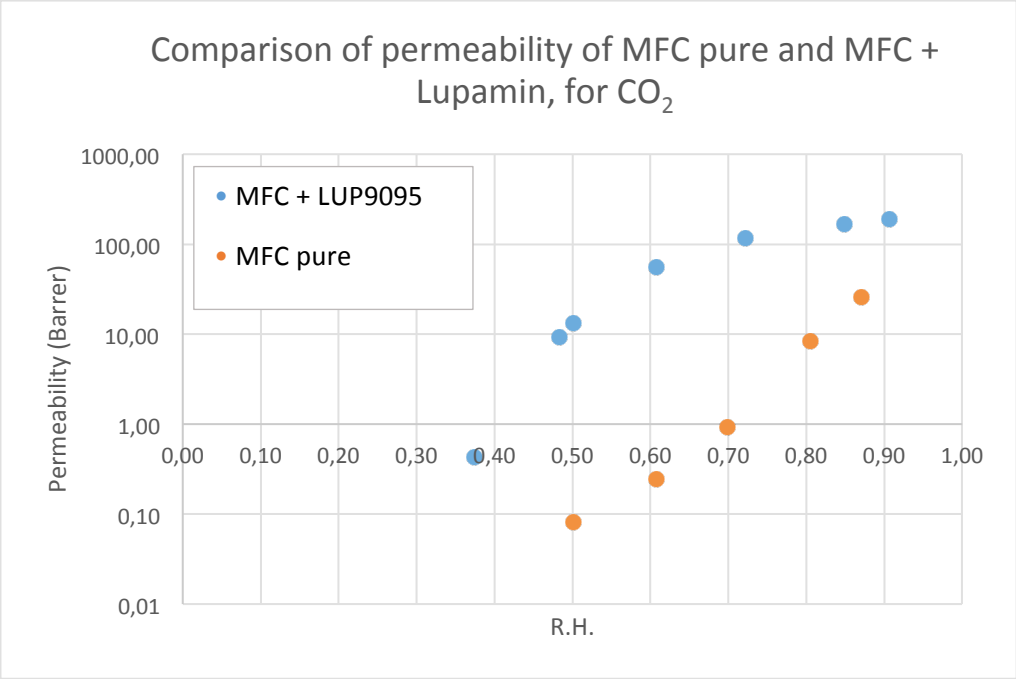

Figure 10. Permeability values of MFC + Lupamin and MFC pure to CO_2

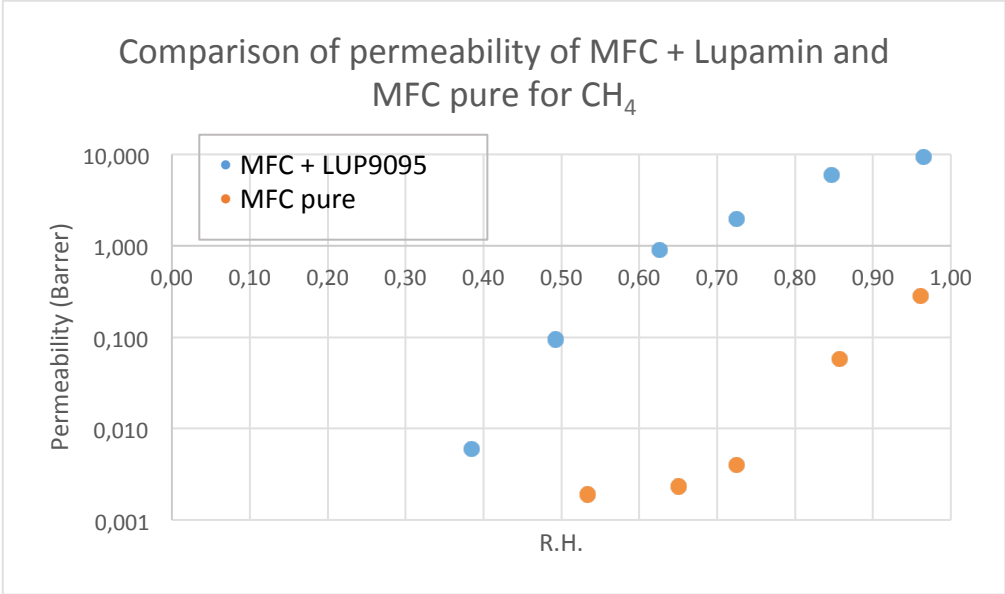

Figure 11. Permeability of MFC + Lupamin and MFC pure for CH_4

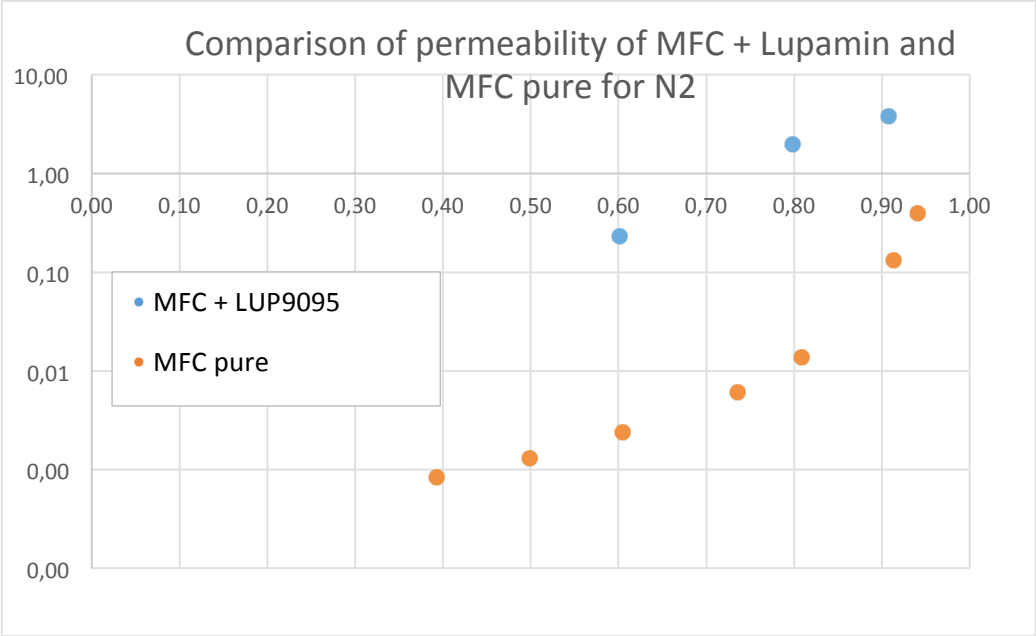

Figure 12. Permeability values of MFC + Lupamin and MFC pure for N_2

When MFC is blended with polyvinyl amine, the data show that with an increase of water, the addition of amine groups increases the hydrophilic character of the membrane and favours water uptake thus definitely increasing the permeability. However the facilitated transport mechanism (based on the amine – CO_2 interaction that should favour the permeation of the latter compound) seems not to be very active in the present experimental conditions, as selectivity of MFC remains slightly higher with respect to that of the blends, especially at high water activity.

3.2.5 Results of the addition of OH^- group to a film of MFC + Lupamin.

In order to prove the existence of a facilitated transport mechanisms, MFC + Lupamin films produced at high pH (11) were also tested for permeation with CO_2 and CH_4; the values of permeability for both gases are reported in the Table 5 while Figure 13 shows the different trends for all experiments with MFC + Lupamin at different pH, and with MFC pure, for CO_2. As it is expected, the addition of OH^- group increase the activation transport between the amine group and CO_2, which leads to an increase of the permeability value in the membrane. The improvement is significantly higher at lower relative humidity, increasing the value almost three times respect the MFC + Lupamin with a lower value of pH. However, with CH_4 the addition of OH^- does not affect so much the value of permeability, and the efficiency of the membrane in the intermediate activity region does not change significantly as is showed in the Figure 14.

Unfortunately, also in this case when water activity is increased the selectivity drops dramatically, returning to the values obtained for the MFC + Lupamin films prepared without KOH, as is shown in the Figure 15.

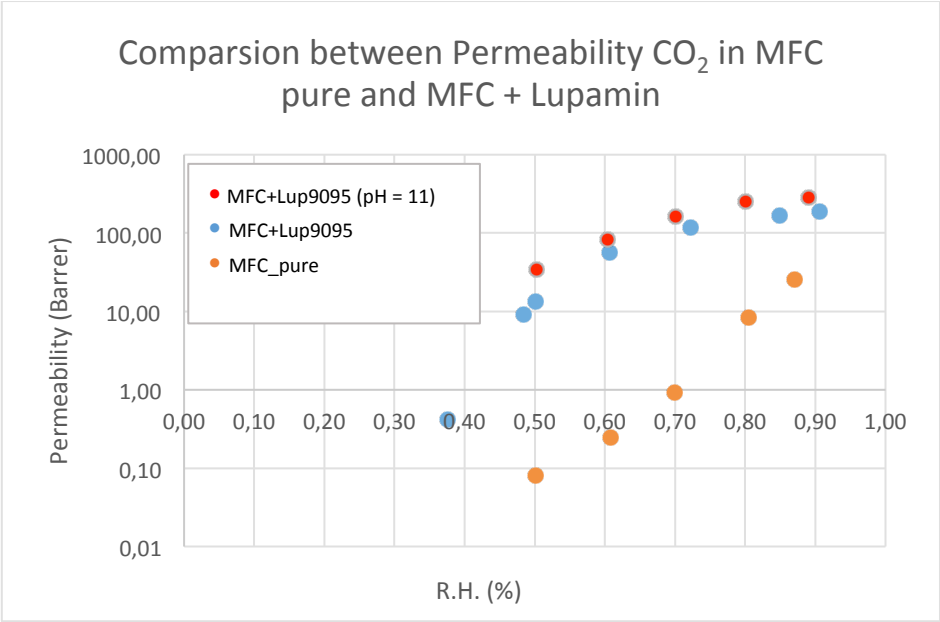

Figure 13. Comparison of permeability of MFC + Lupamin and MFC pure for CO_2

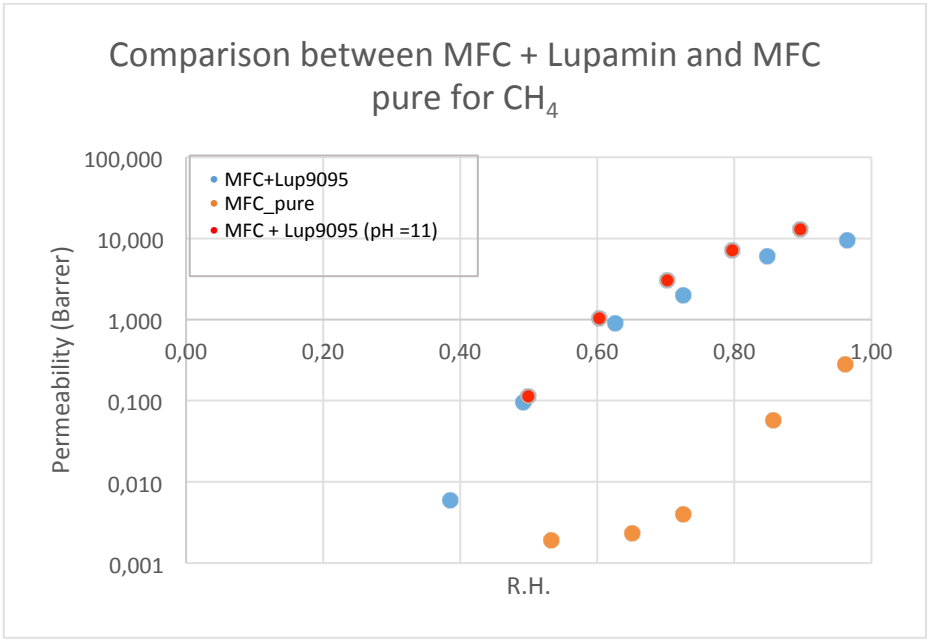

Figure 14. Comparison of permeability of MFC + Lupamin and MFC pure for CH_4

CO_2			CH_4		
Test	**R.H.**	**Permeability**	**Test**	**R.H.**	**Permeability**
1	0,50	33,88	1	0,50	0,11
2	0,60	83,03	2	0,60	1,05
3	0,70	160,48	3	0,70	3,07
4	0,80	255,06	4	0,80	7,07
5	0,89	283,30	5	0,90	12,89

Table 5. Values of permeability of CO_2 and CH_4 for MFC + Lupamin at pH = 11 at 35ºC and 1 bar.

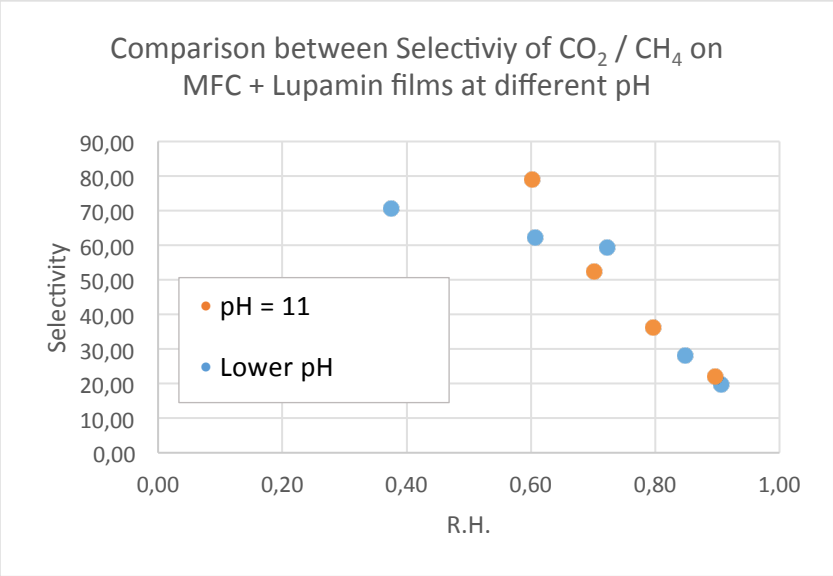

Figure 15. Selectivity of CO_2 / CH_4 on MFC + Lupamin films at different pH

4. Conclusions.

The permeation process for different gases (CO_2, CH_4 and N_2) in MFC and MFC + Lupamin films (50:50) has been investigated in the presence of water as a third component. The results obtained show that gas permeability increases with the amount of water (relative humidity) of the membrane. The reason is that the hydrophilic character of nanocellulose, especially when is blended with Lupamin (Polyvinyl amine), increases the hydrophilic character of the membranes. The MFC + Lupamin films absorb more water, as is shown in the sorption results, resulting in a higher degree of swelling and in a higher permeability, compared with that of the MFC pure films.

The temperature of the process does not seem to affect significantly the performance of the permeation process, because the experimental tests show similar permeability levels of CO_2 and CH_4 gases at 35 and 50ºC with only minor improvements at the higher temperature inspected. Interestingly however also selectivity is not affected

significantly by temperature, which is something unusual as CO_2 permeability in polymers usually increases less than that of the other gases.

As for the selectivity results, the data from the experiments show a decrease of the selectivity levels as the concentration of water in the membrane increases. However, for MFC pure films, the selectivity increases as the concentration of water in the membrane also increases, which is very unusual and interesting. Therefore, an increase of the permeability of gases and of the conditions and capacity of the films leads to a decrease of the levels of selectivity between the gases studied for MFC + Lupamin films. The range of 50 – 60 % of relative humidity appears to be the best conditions of selectivity between CO_2 / CH_4, using the Robeson plot as reference. It will be important to keep in mind this result in cases where it is more preferable having a high value of selectivity, and in cases where it is preferable having higher values of permeability.

Finally, the addition of OH^- group on the MFC + Lupamin films produces an increase in the permeability conditions of the membrane due to an improvement in the activation transport in the membrane. This results in increasing values of permeability of CO_2. In case of CH_4, there are only slightly differences in the higher values of the relative humidity range. The best performance levels in permeability occur in the same range of relative humidity values than in the selectivity tests: 50 – 60 % of R.H. It is in this range when the membranes operate in better conditions and with the highest capacity.

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