Membrane Separation Technology Applied in a Refrigeration Cycle

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ABSTRACT

This article introduces a tentative to modify an adsorption inverse cycle adopting a membrane separation technology instead of the vaporization separation technology present into a classic absorption refrigerator cycle. The proposed approach consists is in the use of a membrane technology in order to separate the two fluids (refrigerant and absorbent), instead of a separation by distillation. In practice, the cycle is modified by inserting a hydrophobic Membrane Contactor in order to make a liquid-liquid extraction of a solute easily absorbed in water (solvent). In this way, the classical absorption cycle can be modified with the substantial reduction of heat supply at elevated temperature, used to separate the solute from solvent, replacing it with the pump work necessary to pressurize and circulate the fluids involved in the cycle. The latter is enabled because the separation of the two fluids in the Contactor Membrane is obtained thanks to a generation of a concentration gradient. The adopted membrane contactor, commercially available, is realized by means of hollow porous fiber of polypropylene (PP) positioned in a cartridge of polyethylene (PE). So, concentration gradient is realized between the two size of the membrane, i.e. water at high concentration of the solute and the other size in which an organic solvent flows at low concentration of the solute. As secondary fluid, organic solvent, we adopted and tested diesel oil. The result demonstrates the technical feasibility of the proposed cycle through some preliminary results obtained adopting ethylic alcohol and acetaldehyde, both of them absorbed by water.

Key words refrigerant cycle, hydrophobic membrane contactor

NOMENCLATURE	
PP	Polypropylene
PE	Polyethylene
P	Pressure MPa
ΔP_c	Breakthrough Pressure MPa
σ	Surface Tension N/m
COP	Coefficient Of Performances
θ	Contact Angle
r	Pore Radius μm
ΔP	Phase Pressure Differential MPa
C	Weight Concentration %
T	Temperature °C
Subscript	
r	Refrigeration

1. INTRODUCTION

As it is well known, the increase in efficiency of both direct and inverse thermodynamic cycles is one of the keys for the abatement of pollutants and the emission of greenhouse gases into the atmosphere. Therefore, a great research effort is carried out to identify technologies suitable for this purpose also by revising classic thermodynamic cycles modifying them with innovative solutions. In the present paper the tenet of modifying a reverse absorption cycle is presented.

In a traditional absorbing cycle, an absorber dissolves the refrigerant in a suitable liquid, a liquid pump provides to increase the pressure, while a generator, by heat addition, drives off the refrigerant vapor from the high-pressure liquid through a distillation process. In this way the pure refrigerant obtained, is ready to be introduced in the evaporator after a pressure reduction, and the cycle can be repeated. The liquid

pump requires some mechanical work but, for a certain quantity of refrigerant, it results to be much smaller than needed by the compressor in a vapor compression cycle. Although the efficiency of the regenerative cycles is lower than the vapor compression cycles, for a series of applications the latter are more advantageous as, for example, in plants for three generations, in which high temperature heat can be conveniently used for the refrigeration.

In an absorption refrigerator, is used a suitable combination of refrigerant and absorbent. The most common combinations are: ammonia (refrigerant) and water (absorbent); or water (refrigerant) and lithium bromide (absorbent) etc.. In any case the separation of the refrigerant and the absorbent are realized supplying heat at a suited temperature.

The physical principle adopted is the separation, by distillation, of two fluids with different vaporization temperature. Perhaps distillation processes present a relatively high efficiency only in the case of separation of two fluids with very different relative volatility (i.e. different boiling temperature) as show in the Fig. 1, in which, according to Crespo and Böddeker [1], distillation efficiency versus relative volatility is reported.

The distillation technique is not the only technology available in order to separate two substances, but others are commonly available (i.e. inverse osmotic, microfiltration, ultrafiltration, dialysis, pervaporization, etc.). In particular, the mentioned separation techniques are obtained adopting suitable membranes, hydrophobic, hydrophilic, porous, high density and so on.
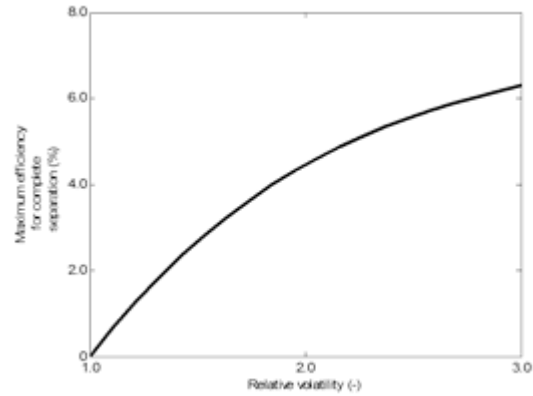

Figure 1. Effect of relative volatility on maximum efficiency for complete separation of a binary mixture by simple distillation

In the present paper we decided to investigate one of those techniques, in particular a pertraction technique. The latter has been adopted in order to separate an organic substance, used as refrigerant, from water, used as absorbent. In order to do that a commercially available membrane has been adopted, in particular we adopted a hydrophobic Membrane Contactor. The main motivation in the adoption of this technique is in the relatively high transmembrane flow rate obtainable with contactor membrane, especially if compared with other techniques like inverse osmotic, hydrophilic etc.

Table 1. Membrane characteristics

Liquid Flow Guidelines	$0.023 - 0.68 \text{ m}^3/\text{h}$
Porosity	~ 25%
OD / ID	300 / 200 μm
Pore Size	0.03 μm
Fiber Number	6752
Fiber Length	220 mm
Membrane Material	Polypropylene PP
Potting Material	Polyethylene PE--
Membrane Surface Area	1.4 m^2
Shellside Volume	0.40 liters
Lumenside Volume	0.15 liters
Maximum Shellside Working Temperature/Pressure	40°C, 0.72 MPa 70°C, 2.0 bar
Maximum Lumenside Liquid Temperature/Pressure	15°-25°C, 0.48 MPa
Total Surface of Pore Transition	0.01458 m^2
Surface/Volume Ratio (membrane surface/membrane volume)	480000 1/m
Surface/Volume Ratio (membrane surface /total volume)	3500 1/m

This kind of membrane, which main characteristics are reported in Tab.1, is realized with hollow hydrophobic porous fiber of polypropylene (PP) positioned in a cartridge of polyethylene (PE) as shown in Fig.2, in which the external/internal dimension respectively of 300 μm and 200/220 μm are indicated. In the same figure also, an enlargement of the fiber is reported highlighting the pore which have typically a dimension of the order of magnitude of 0.03 μm.
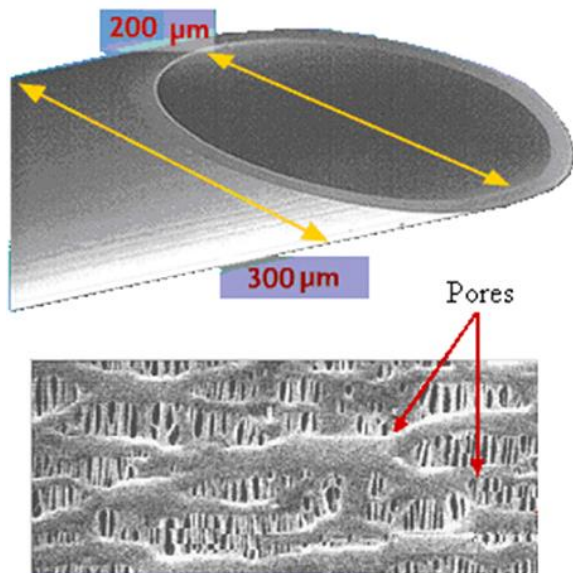

Figure 2. Example of hollow hydrophobic fiber with an enlargement of the pore present in the wall

The typical arrangement of the fibers is reported in Fig. 3. In particular the Contactor Membrane is commonly adopted in order to separate ammonia, or other organic substances, from waste water or in a degasification application of liquids. In available literature a huge amount of well written paper and textbook are available, and some examples are reported in [2-11], describing the membrane technology. In particular in the article of Klaassen et al. [12] a scheme is available, reported in Fig. 4, in which membrane contactor is adopted in order to extract a pollutant from contaminated water. The scheme adopts a pertraction technique (i.e. a liquid-liquid separation of two substances by using gradients of concentration) in order to extract, by means of the membrane contactor technology, the pollutant present in a liquid extractant with an afterwards separate, in a pure form, through an evaporative process. It seems that the described scheme of Fig. 4 works exactly like the absorber-generator scheme of a simple ammonia-water absorption refrigeration system. The only important difference seems to be the necessity to use a third fluid (not volatile at least at the temperature involved in the application) in order to carry out the fluid from the water. In fact, pertraction is a nondispersive membrane based on liquid–liquid extraction process. Nonpolar organic substances, such as aromatics or chlorinated hydrocarbons, can

be recovered from process or wastewater flows by pertraction, according with Gugliuzza and Drioli [13] and Baker [14]. The organic components are removed from the water by extraction into an organic extractant, which is immiscible with water. The extractant is flowing by one side of the membrane while the water phase on the other.
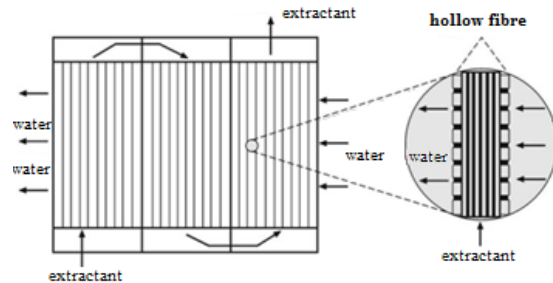

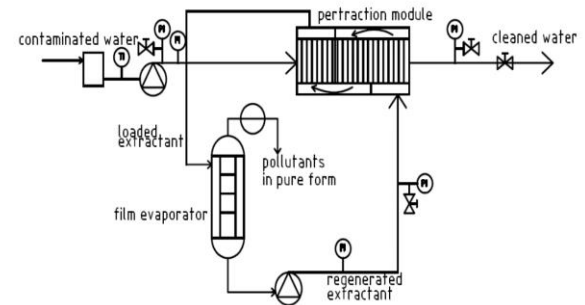**Figure 3.** Scheme of hollow fibers arrangement in a cartridge

Figure 4. Scheme of a pertraction–regeneration process, with component released in pure form

The role of the membrane is to keep the phases separated and to provide a stable interface between the two phases. The membrane itself has no selectivity. The selectivity process must come from the extractant [12]. Interface between wastewater and extractant is immobilized using a hydrophobic microporous hollow fiber membrane through a small transmembrane pressure gradient (0.01 MPa) [13]. In practice the extractant is led in counterflow through the membrane modules and refrigerant is concentrated on the extractant. The latter can be sent

in a heat exchanger, working as evaporator, allowing the evaporation of refrigerant, and can thus continue to circulate in the system, while the refrigerant is released in pure form, realizing, basically a refrigerator cycle.

2. MEMBRANE WORKING PRINCIPLE

Principle of membrane contactor operation is based on the natural phenomenon of capillary force. When one side of a hydrophobic microporous membrane is brought in contact with water or an aqueous liquid, the membrane is not ''wetted'' by the liquid, i.e., the liquid is prevented from entering the pores, due to surface tension effect. The interface between a liquid and a solid substrate can be characterized by the parameter ''contact angle'' θ (Fig. 5). The wettability of a solid surface by a liquid surface decreases as the contact angle increases. A contact angle θ of less than 90° implies that the liquid will tend to wet the substrate (hydrophilic), whereas if contact angle θ is greater than 90° the liquid will not tend to wet the surface (hydrophobic).
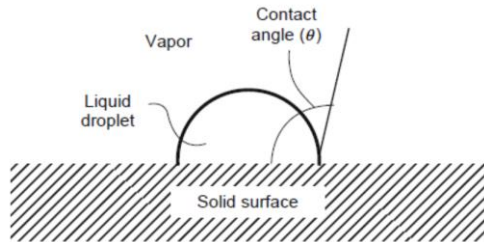

Figure 5. Representation of contact angle θ

If a dry microporous hydrophobic hollow fiber membrane with gas or vapor-filled pores was surrounded by water there would not be any penetration by water into the pores until the water pressure exceeds a certain critical breakthrough pressure ΔPc. This pressure is calculable by means of the Laplace's equation:

$$\Delta Pc = \frac{2\sigma \cos\theta}{r} \tag{1}$$

Where:
σ surface tension
θ contact angle
r pore radius

For a hydrophobic porous material with contact angle greater than 90°, the ΔPc is >0 and depends on the liquid surface tension and the membrane pore size. As an example, considering water–air–polypropylene

system, one can calculate that for a dry membrane with a pore size of 0.03 mm the critical entry pressure of water is of the order of magnitude of several MPa (≅ 2 MPa).

Since the liquid phase does not enter the pores, a stable gas–liquid phase interface can be created and maintained (as illustrated in Figure 6) as long as the liquid phase pressure is higher than the gas phase pressure and the phase pressure differential ΔP is between 0 and ΔPc. The pores remain gas filled at this condition. The liquid and the gas phases could be flowing at different flow rates on either side of the membrane wall, but the phase interface remains stable all along the membrane. Thus, by proper control of pressures, the two immiscible phases come in constant contact without a need to disperse one into the other. This allows mass transfer or mass exchange between phases, such as gas absorption or gas stripping (desorption) only with the formation of gradients of concentration (Fig. 7).

The same principle of operation as described above is applicable also to liquid–liquid extraction where an aqueous liquid and an organic liquid contact each other inside the contactor for extraction of a solute selectively from one phase to another. Further variation of membrane contacting technology is called gas membrane or gas–gap membrane where two different liquid phases flow on either side of the membrane, but the membrane pores remain gas filled. In this situation two separate gas–liquid contact interfaces are supported on each side of a single membrane.
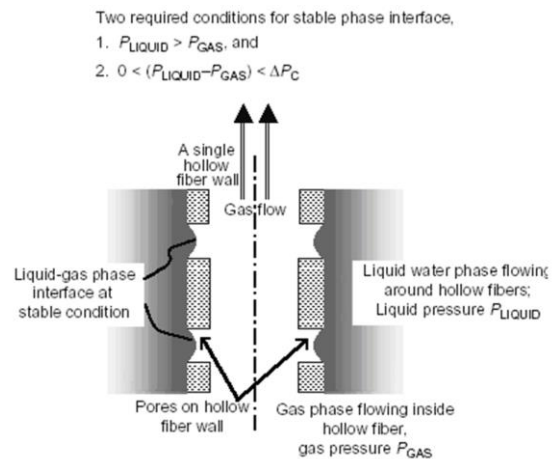

Figure 6. Liquid–gas interface in a membrane contactor
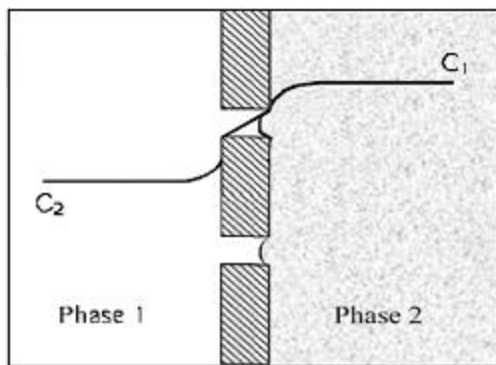
Figure 7. A detail of the pore in the hydrophobic membrane in which the water surface tension act as liquid barrier and concentration gradient (from C1 to C2) is realized

3. Experimental apparatus

In order to test the possibility to use the previously described separation technology, we realized a small facility to test the membrane performances, especially in terms of separation capability between water and organic fluids. Beginning this work, the use of the traditional fluids commonly used in the adsorbing refrigeration machines appeared a natural choice. In particular the use of water and ammonia has been kept in consideration. Unfortunately, the commercially available membrane that we adopted, is commonly used in order to separate ammonia from waste water and, particularly for the shell, the maximum working. pressure has been limited to 0.72 MPa (as reported in Tab. 1). At this pressure the saturation temperature of the ammonia is less than 20 °C, as reported in Fig. 8, too low in order to have a good control of the experiment. So, we decided to try different fluids (organic). In particular we started using ethylic alcohol (ethanol). Also, this fluid presents some disadvantages, in an opposed way than ammonia. In fact, ethanol presents an unfavorable saturation curve, reported in Fig. 8, due to the relatively low saturation pressure also at room temperature. Despite this limitation, however, we have performed some experiments using ethanol in order to practice the use of membranes.
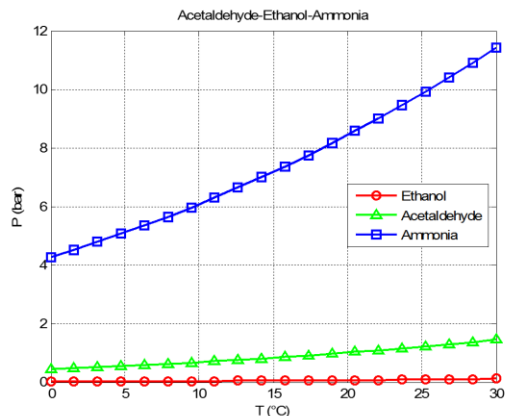

Figure 8. Ethanol, acetaldehyde and ammonia saturation curves

The results of this preliminary tests consist essentially in the fact that we have learned how to handle the contactor membrane, and if we exceed with the amount of ethanol diluted in water, the membrane can be "wetted" and the aqueous solution can pass through the pore. In practices the entry pressure drops down at a few kPa. In the case of a mixture of ethanol in water the wettability limits, in terms of concentration, are around 35% of ethanol in distilled water (in weight). In the experiments we extracted alcohol, not pure because ethanol and water form an azeotropic solution, adopting a pervaporization technique, i.e. the extraction of ethanol vapor by means of air as a stripping gas and a successive vapor condensation with the help of thermostatic bat of tap water and ice (0 °C). Experiments with ethanol demonstrated the feasibility of its extraction from water.

At the end of this step, another organic fluid has been selected: acetaldehyde (C_2H_4O). This fluid presents a very good solubility in water, and a favorable saturation curve, as reported in Fig. 8 and Fig. 9. In fact, at the environmental pressure (1 bar) its boiling temperature is as high as 22 °C, so it is quite easy to handle it in the liquid phase. Last, but not least, the acetaldehyde, chemical grade, is not very expensive.

In order to realize a pertraction technique the problem was the selection of a proper solvent able to entrap the vapor as soon as it emerges from the pore of the membrane. In this selection our mechanical engineering background has suggested the use of common diesel oil (average composition $C_{12}H_{23}$).
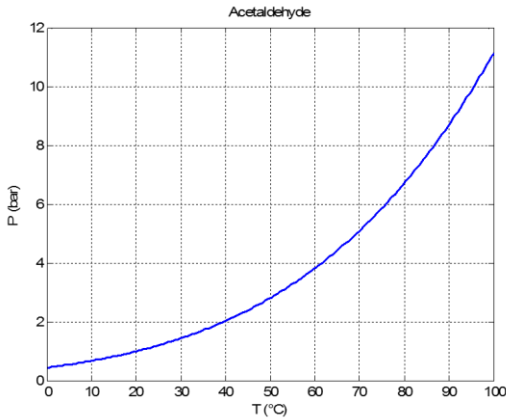
Figure 9. Saturation curve for acetaldehyde

An experimental apparatus has been realized as reported in the scheme of Fig. 10. In practices two pumps have been interposed between two vessels and the membrane contactor modulus. The scheme is completed by means of valves, thermocouples, pressure gauges, etc..
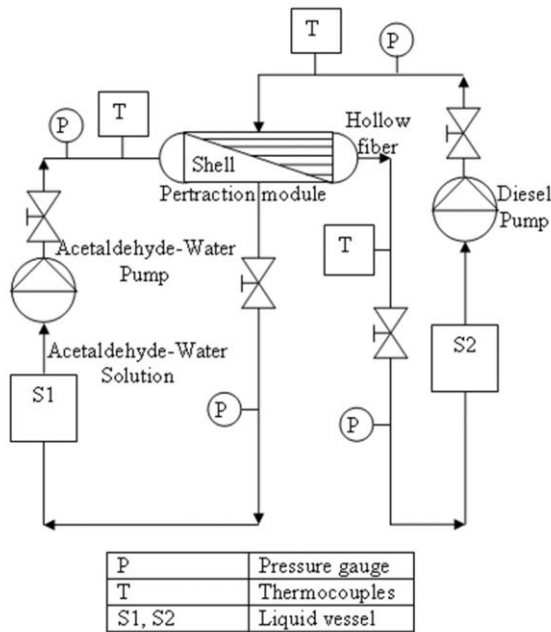

P	Pressure gauge
T	Thermocouples
S1, S2	Liquid vessel

Figure 10. Scheme of the circuit used for the membrane performances

The first pump provides to the pressurization and recirculation of the aqueous solution of acetaldehyde at 30% in weight, while the second one provides to the pressurization and recirculation of the diesel oil. The realized differences of pressure between the two size of the membrane was as high as 0.2 MPa. With an absolute pressure of 0.4 MPa for the aqueous solution and 0.2 MPa for the diesel oil. According to the saturation curve, reported in Fig. 9, the

acetaldehyde was in liquid phase in both size of the membrane, even if present in pure form, due to the working temperature not exceeding 30 °C.

The observations of the performed experiments are focused on the measurements of the amount of acetaldehyde transferred from the aqueous solution to the diesel oil. Particularly, both pumps have been switched-on at the same time and after a defined time (ten minutes, usually) the pumps have been switched-off. A certain amount of diesel oil has been extracted from the circuit and its density measured by means of a graduated beaker and a digital balance. Of course, in any experimental conditions, the measurements carried out have been repeated at least ten times, averaging the results.

4. RESULTS AND DISCUSSION

The main obtained results consist in the measurements of the acetaldehyde amount extracted from the aqueous solution. As mentioned, the mass transfer between the two fluids was obtained due to the concentration gradient realized between the two sides of the membrane, i.e. the two sides of the pore. The Experiments have been focused on the measures of the mass transfer obtained starting with different concentration of acetaldehyde in aqueous solution. Of course, at the beginning of any experiment, the diesel oil was free of acetaldehyde. So, the amount of acetaldehyde extract and dispersed in the diesel oil, as a function of the initial concentration, is reported in Fig. 11.
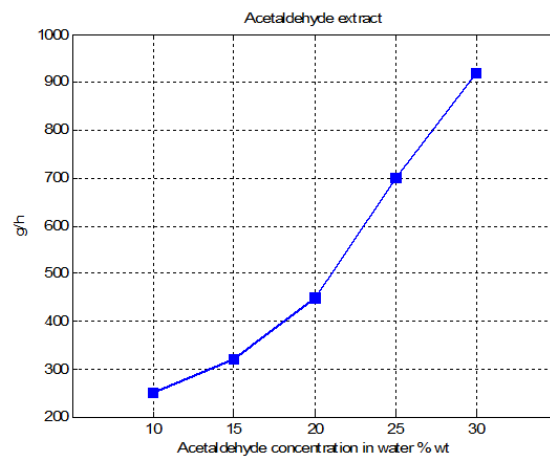

Figure 11. Mass flow rate of acetaldehyde extract as a function of the initial concentration in the aqueous solution

As it is possible to observe the maximum flow rate of extracted acetaldehyde do not exceed 1 kg/h, perhaps diluted in diesel oil. After the extraction, depressurizing the mixture, pure acetaldehyde was

vaporized and extract from the oil, with a cooling effect on the remaining mixture. Realizing, in practice, the scheme reported by Klaassen et al. [12]. Unfortunately, the acetaldehyde vaporization was performed off-line, so a refrigeration cycle was not realized, but the possibility to extract a solute (acetaldehyde) from a solvent (water) dispersed as liquid phase in an organic solvent seems to us demonstrated.
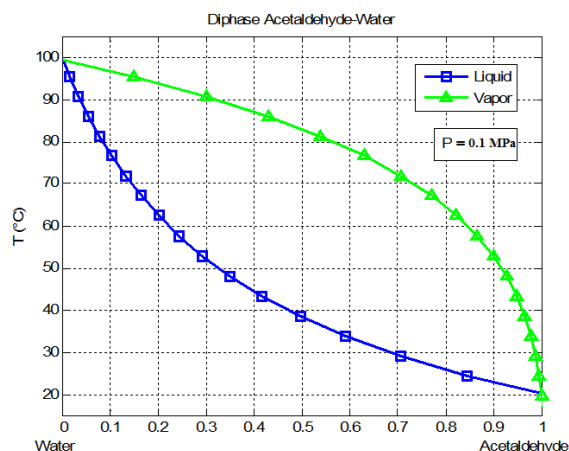

Figure 12. Diphase Acetaldehyde-Water at 0.1 MPa

Observing Fig. 10, in which the diphase acetaldehyde-water is reported, it is possible to see that in the case of a concentration of acetaldehyde at 30% in weight - maximum initial concentration used in the experiments - the boiling temperature (at a pressure of 1 bar) is about 52 °C and the concentration of the fluid vaporized is about 95% of acetaldehyde and 5% of water.

In the experiments, due to the energy introduced by the pumps, we do not exceed 30 °C, extracting acetaldehyde, with the contactor membrane, at a pressure as high as 0.2 MPa. That means that the adoption of a separation in membrane contactor may increase the "distillation efficiency" at least under the conditions adopted in the experiments. Of course, we do not have realized a real "refrigeration cycle" but seems quite interesting to continue the investigations trying, may be, to adopt ammonia instead of acetaldehyde. The limitation to do that is to find a membrane contactor able to work at pressure as high as 1 MPa.

From a thermodynamic point of view, the possible efficiency of a refrigeration cycle which is realized using the pertraction technique, is not easy to estimate. In fact, we adopted commercially available pumps (500 Watts each) and performed the vaporization of the acetaldehyde "off-line". Considering that the heat adsorbed by a unity of mass of acetaldehyde [16] is equal to 25.71 kj/mol, and

considering that the heat of solution in water, at 6 °C, is equal to 7.87 kj/mol (the minimum energy necessary for separate the acetaldehyde from water), we can suppose a maximum theoretical efficiency equal to:

$$COP_R = \frac{25.71}{7.87} = 3.27 \qquad (2)$$

a value higher than the theoretical efficiency of an adsorbing cycle and lower than a vapor compression cycle evolving between 6 °C and 30 °C.

5. CONCLUSIONS

Into the present paper We try to demonstrate it is possible to separate an organic fluid (acetaldehyde) from water, without relevant heat addition, in order to try to realize a refrigeration absorption cycle, adopting a pertraction technique. The pertraction technique has been realized by means of a porous membrane contactor, commercially available. This technology was based on the separation of Acetaldehyde, diluted in water, and diesel oil, acting as extractant. The amount of Acetaldehyde extract has been measured and an estimation of the performance of a hypothetical refrigeration cycle estimated. In the range of temperatures adopted into the experiments, no external heat has been supplied at the system. Also, the experiments performed show that the amount of organic fluid separated from an aqueous solution is a function of the initial concentration of acetaldehyde. More work is necessary in order to demonstrate the possibility to use the pertraction techniques in a real refrigeration cycle.

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