

## Direct Oxidation of Cyclohexene with Inert Polymeric Membrane Reactor

Maria G. Buonomenna,<sup>\*,†</sup> Giovanni Golemme,<sup>†,‡</sup> Maria P. De Santo,<sup>§</sup> and Enrico Drioli<sup>†,‡</sup>*Department of Chemical, Engineering and Materials, University of Calabria and Consortium INSTM, ITM-CNR, and CEMIF.CAL, CNR-Licryl Laboratory, Physics Department, University of Calabria, Via Pietro Bucci, 87030 Rende (Cosenza), Italy***Abstract:**

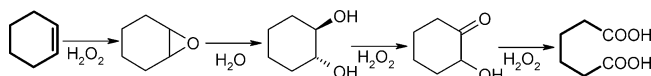
In this work, the use of PVDF flat membranes as contactors for direct solvent-free biphasic oxidation of cyclohexene to adipic acid has been reported. The oxidation has been carried out using 30% H<sub>2</sub>O<sub>2</sub> and ammonium molybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>) in the presence of succinic acid. The effect of different membranes as interfaces between the organic phase, containing cyclohexene, and the aqueous phase, with the oxidant and catalyst, has been studied and related to conversion and selectivity.

**1. Introduction**

Adipic acid (AA) is of great importance commercially in that it is used in the manufacture of nylon 6,6, which is extensively used in many products such as tire reinforcements, adhesives, upholstery, specialty foams, carpet fibers and several items of clothing.<sup>1</sup> Currently, its main method of manufacture is a costly, multistep process involving homogeneous catalysts and aggressive oxidants such as concentrated nitric acid. The scientific challenge addressed by this work is to devise a one-step synthesis operating in an environmentally friendly, solvent-free, biphasic or monophasic system using green co-oxidants such as oxygen (air) or hydrogen peroxide.<sup>2,3</sup>

Dugal et al.<sup>4</sup> have shown that, with microporous FeAlPO-31 as a heterogeneous catalyst, a one-step, solvent-free conversion of cyclohexene to AA may be effected at 100–130 °C and 1.5 MPa of air.

Raja et al.<sup>5</sup> have shown that it is also possible to produce AA starting from a linear hydrocarbon such as *n*-hexane. By using a heterogeneous aluminophosphate catalyst (AlPO-18), typically having a cobalt:phosphorous ratio of 0.08 or greater,

**Scheme 1. Pathway for the synthesis of adipic acid by oxidation of cyclohexene with hydrogen peroxide<sup>6</sup>**

it is possible to achieve simultaneous, end-on oxidation of both terminal methyl ends of *n*-hexane, using air as an oxidant under moderate conditions.

Research on the clean synthesis of adipic acid has been reported by Sato et al.<sup>6</sup> cyclohexene has been efficiently oxidized to adipic acid with aqueous 30% H<sub>2</sub>O<sub>2</sub> in the presence of small amounts of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and [CH<sub>3</sub>(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N]-HSO<sub>4</sub> as a phase-transfer catalyst.

Cyclohexene (CH) is transformed into adipic acid (AA) in a “one-pot” synthesis following the reaction shown in Scheme 1.

In the pathway proposed by Sato et al.<sup>6</sup> the controlling step is the hydrolysis of cyclohexene oxide to 1,2-cyclohexanediol under acidic conditions.

Deng et al.<sup>7</sup> reported a cheaper and environmentally benign peroxytungstate–organic complex which could be used as a highly efficient catalyst for the direct catalytic oxidation of cyclohexenes to adipic acid with hydrogen peroxide without any phase transfer catalyst.

The peroxytungstate was complexed with organic acids, and the resultant catalyst system not only possessed the capability of carrying active oxygen species but also became oleophilic; therefore, a very good catalyst system for the oxidation of cyclohexene could be formed. Similar to peroxytungstate, when the peroxytungstate was complexed with the organic acid, it became oleophilic, and the substrate/catalyst ratio could be raised to about 1000, whereas it is 40 for analogous biphasic systems.<sup>7,8</sup>

In recent years, surfactant-type catalysts (STC) containing polyoxoperoxy metalates have been successfully used on various typical organic synthetic reactions with hydrogen peroxide.<sup>9</sup> In principle, through combining the anion of polyoxometalate with surfactant to form a STC and tuning the hydrophile–lipophile balance of surfactant, the amphiphilic catalyst can be adapted

\* Corresponding author. E-mail: mg.buonomenna@unical.it.

<sup>†</sup> Department of Chemical, Engineering and Materials, University of Calabria and Consortium INSTM.<sup>‡</sup> ITM-CNR.<sup>§</sup> CEMIF.CAL, CNR-Licryl Laboratory, Physics Department, University of Calabria.(1) Davis, D. D.; Kemp, D. R. *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley-VCH Verlag: New York, 1991.(2) D'Alessandro, N.; Liberatore, L.; Tonucci, L.; Morvillo, A.; Bressan, M. *New J. Chem.* **2001**, *25*, 1319–1324.(3) Centi, G.; Perathoner, S. *Catal. Today* **2003**, *77*, 287–297.(4) Dugal, M.; Sankar, G.; Raja, R.; Thomas, J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2310.(5) Raja, R.; Sankar, G.; Thomas, J. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2313–2313.(6) Sato, K.; Aoki, M.; Noyori, R. *Science* **1998**, *281*, 1646–1647.(7) Deng, Y.; Ma, Z.; Wang, K.; Chen, J. *Green Chem.* **1999**, *1*, 275–276.(8) Jiang, H.; Gong, H.; Yang, Z.; Zhang, X.; Sun, Z. *React. Kinet. Catal. Lett.* **2002**, *75*, 315–321.

to different organic reactions. Zhu et al.<sup>9</sup> prepared and used surfactant-type peroxotungstates and peroxomolybdates in the synthesis of adipic acid.

In our previous work,<sup>10</sup> we reported the oxidation of benzyl alcohol to benzaldehyde in a membrane system by using polyoxoperoxo metalates with one compartment containing the organic phase with the substrate and the product, and the other one, the aqueous phase with the catalyst and hydrogen peroxide.

In the present work, for the first time, the one-step oxidation of cyclohexene to adipic acid has been proposed without organic solvents or a phase transfer catalyst. Compared to sodium tungstate catalyst, used by Deng et al.<sup>7</sup> in the absence of phase transfer catalysis, the catalyst of the present work, (ammonium molybdate) is 30% cheaper. A polymeric microporous membrane compartmentalizes the organic phase containing cyclohexene, and the aqueous phase, with the oxidant, the catalyst and succinic acid. Succinic acid has been added<sup>7</sup> to favor the contact at the membrane–aqueous interface between the catalytic active species, formed in the aqueous compartment, and the cyclohexene substrate, transported across the membrane. The membrane has two roles: (1) to stabilise the contact between the two immiscible phases and (2) to separate the cyclohexene from the adipic acid. In addition, the advantages common to membrane contactors remain: as membrane contactors operate without phase dispersion, independent adjustment of the feed is possible. The membrane provides a fixed interfacial area that is independent of fluid mechanics, complete loading is achieved even at low-flow conditions, and membrane contactors are modular in design. When an application requires several contactors in series or in parallel, this modular design allows a given process to be tested on a reduced scale.<sup>11</sup> On these bases, the full-scale process can be easily simulated. However, the cost of hydrogen peroxide today is higher than allowable for the commercialization of the proposed reaction, even taking into account the environmental advantages. Therefore, the introduction of this process, and in general all processes based on hydrogen peroxide, require the development of new routes for the synthesis of hydrogen peroxide.<sup>3</sup>

## 2. Experimental Section

**2.1. Chemicals.** Cyclohexene (MW = 82.14 g/mol, purity 99.99%) from Sigma-Aldrich was used both as reagent and as solvent. Ammonium molybdate tetrahydrate (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (MW = 1235.86 g/mol, purity 99.98%) from Sigma-Aldrich was the catalyst. Hydrogen peroxide H<sub>2</sub>O<sub>2</sub> (30 wt % solution in water) from Sigma-Aldrich was the oxidant.

For the preparation of polymeric membranes, PVDF Solef 6010 ( $M_n = 64,000$ ,  $d = 1.78$  g/cm<sup>3</sup>) was supplied by Solvay Inc.; *N,N*-dimethylacetamide (DMA, reagent grade) and acetone were purchased from Fluka; water, used for the coagulation bath, was double distilled.

**2.2. Apparatus.** Experimental tests were carried out in a reactor made with a two-compartment cell to separate the



**Figure 1.** (Top) Biphasic equipment for the membrane allocation. (Bottom) System mounted for the reaction.

organic and the aqueous phases. The system was in a flat sheet configuration with a membrane surface area of  $4.91 \times 10^{-4}$  m<sup>2</sup>. The phases were thermostatted by a water bath at 90 °C. Two condensers (one for each compartment) were assembled to guarantee the absence of cyclohexene and water evaporation during the course of the reaction. Figure 1 shows the glass cell (top) and the system used for the oxidation reactions (bottom).

**2.3. Membranes.** Three different membranes have been used. In Table 1 some characteristics of the tested membranes are reported.

M1 is a commercial membrane supplied by Alfa Laval (former DSS) (Sweden). M2 and M3 have been prepared by means of phase inversion technique.<sup>12</sup>

The polymer (10 wt %) was dissolved at 60 °C in DMA (24 wt %) and acetone (64 wt %). The solution was magnetically stirred for one day to guarantee complete dissolution of the polymer.

The solution was cast onto a glass substrate by means of a hand-casting knife (BRAIVE Instruments) with a knife gap set at 250 μm and exposed to air for 3 min (M2) and 6 min (M3). Then, the cast films were immersed in a coagulation bath of water.

After complete coagulation, the membranes (M2 and M3) were transferred into a pure water bath, which was refreshed frequently, for at least 24 h to remove the traces of solvent. For SEM, AFM, contact angle, and thickness measurements, the membrane samples were dried at 60 °C under vacuum.

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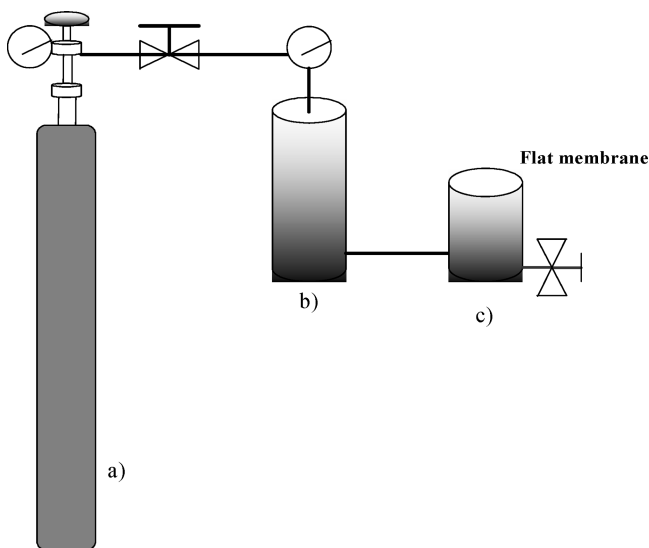
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**Table 1.** Characteristics of the PVDF membranes used as membrane contactors

membrane code	type	material	thickness $\delta$ ( $\mu\text{m}$ )	bulk porosity $\varepsilon$ (%)	surface porosity $S_p$ (%)	pore size ( $\mu\text{m}$ )
M1	composite	fluoropolymer (top layer) PP (bottom layer)	30 <sup>a</sup> (238) <sup>b</sup>	—	52	0.2
M2	symmetric	PVDF	27	47	70	0.4
M3	symmetric	PVDF	22	46	95	1.2

<sup>a</sup> Thickness of the selective layer. <sup>b</sup> Total thickness.

**Scheme 2.** Schematic experimental set-up used for membrane  $\text{LEP}_w$  measurements

The membrane thickness was determined by a digital micrometer (Carl Mahr D 7300 Esslingen a.N.) and by SEM observation of the freeze-fractured cross sections.

The bulk porosity,  $\varepsilon$ , of the membranes was calculated according to eq 1:

$$\varepsilon = 100(1 - \text{density}_{\text{membrane}}/\text{density}_{\text{PVDF}})\% \quad (1)$$

in which the density of the membrane was determined gravimetrically by weighing a sample of known area and thickness.

Pore size and surface porosity have been estimated from SEM images by using ImageJ 1.37 V software.

The resistance to liquid entry pressure of water ( $\text{LEP}_w$ ) was measured in static mode according to Scheme 2.

The pressure was read on a calibrated gauge after pressurization of the water container. The pressure difference at which the liquid penetrates into the pore of the membrane is indicated as  $\text{LEP}_w$ .

The morphology of the dried membranes (at 60 °C overnight) was examined using scanning electron microscopy (SEM), Cambridge, Stereoscan 360, at 20 kV. For cross-section analysis the membrane samples were freeze fractured in liquid nitrogen. All samples were sputter-coated with gold before analysis.

Contact angles of water droplets on the membrane surfaces were measured by sessile drop method using CAM 200 contact angle meter (KSV Instruments Ltd., Helsinki, Finland).

The roughness of the investigated membrane surfaces was evaluated by using atomic force microscopy (AFM), Nanoscope

III (Digital Instruments, VEECO Metrology Group) on a scan area of 0.5  $\mu\text{m} \times 0.5 \mu\text{m}$ . Tapping Mode (TM) AFM was operated with a scanning tip attached to the end of a cantilever oscillating across the sample surface. The cantilever was oscillated at or near its resonance frequency with amplitude ranging typically from 20 to 100 nm. Silicon probes, with resonance frequencies of 200–400 kHz and nominal tip radius of curvature 10 nm and cantilever length 125  $\mu\text{m}$ , were used. Surface roughness was estimated with respect to the root mean squared difference,  $R_q$ , between the actual surface height and that of the line dividing the surface of the investigated profile into two equal areas. Specimens were analysed without any particular treatment.

**2.4. Oxidation Reaction.** In a typical experiment, the membrane was located between the cell compartments with the top surface interfacing with the aqueous-phase side.

Cyclohexene was pumped at a rate of 2.9 mL/h (28.6 mmol/h) to the organic cell compartment; in the other cell compartment 116 mmol of hydrogen peroxide (pumped at a rate of 5 mL/h),  $1.7 \times 10^{-1}$  mmol of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , and  $6.52 \times 10^{-1}$  mmol of succinic acid were loaded.

All reactions were performed at 90 °C for 6 h.

The reactions were stopped, and the aqueous compartment was cooled at 0 °C overnight. A white crystalline solid, separated out, and filtered after washing and drying had purity >99% (GC analysis) and mp 151–152 °C.

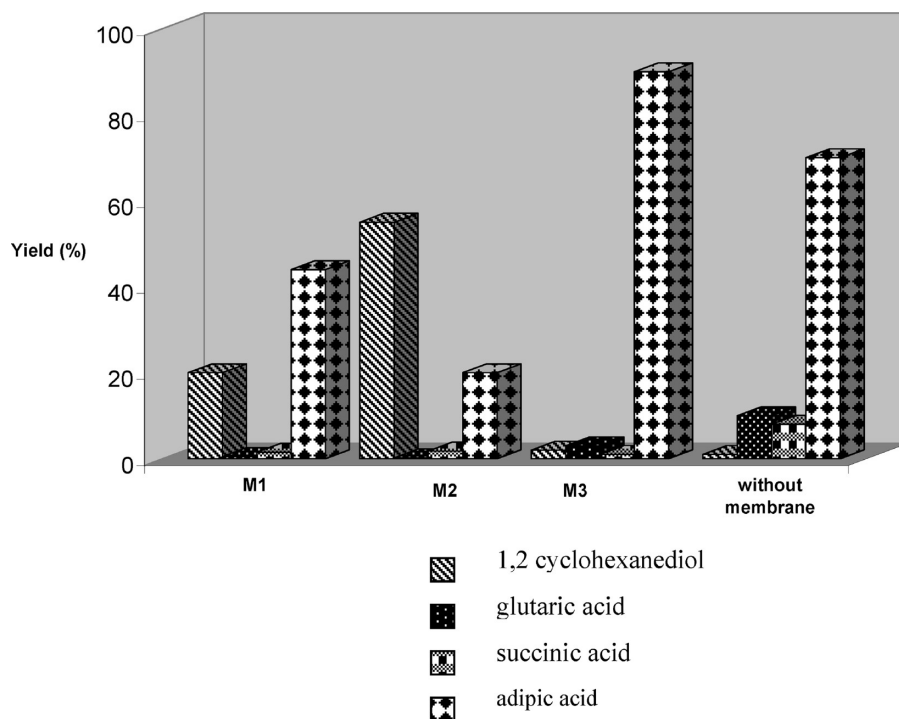
The aqueous mixture was directly analyzed using a 6890 network GC system of Agilent on a HP-5 (30 m  $\times$  0.320 mm  $\times$  0.25  $\mu\text{m}$ ) column.

### 3. Results and Discussion

**3.1. Reaction Performance and Membrane Hydrophobicity.** In Figure 2, the reaction yields (%) after 6 h for the membrane system using M1–M3 membranes and for the blank reaction in the system without a membrane, as comparison, have been reported.

The experimental results showed that the membrane type affected the distribution of oxidation products of cyclohexene. In particular, it is evident that the best yield and selectivity (90% of adipic acid) have been observed for the use of membrane M3. Without a membrane, the main product is adipic acid with a yield of 70%, lower than that obtained with M3. This result depends on the fast decomposition of hydrogen peroxide in the presence of metal catalyst. In the case of compartmentalization by the membrane, it is possible to tune the quantity of the oxidant and to reduce this problem, thus obtaining a higher yield in adipic acid.

With M1 and M2, lower yields of adipic acid have been obtained: 44% and 20%, respectively, and the by-product 1,2-



**Figure 2.** Performances of the membranes M1–M3 used as contactors and of the system without a membrane in the oxidation of cyclohexene

**Table 2.** Contact angle values ( $\theta$ ) to water and roughness ( $R_q$ ) of M1–M3 for the two membrane layers (top and bottom)

membrane	$\theta$ (deg)		$R_q$ (nm)	
	top layer	bottom layer	top layer	bottom layer
M1	$90 \pm 2$	$140 \pm 3$	$9.8 \pm 4$	$24.4 \pm 3$
M2	$92 \pm 2$	$93 \pm 2$	$17.8 \pm 3$	$5.5 \pm 4$
M3	$111 \pm 3$	$128 \pm 3$	$57.2 \pm 2$	$2.6 \pm 3$

cyclohexanediol has been produced with yields of 20% and 55%, respectively.

It is noteworthy that the intermediate 1,2-cyclohexanediol is accumulated in higher concentration in the case of symmetric membrane M2 (characterized by similar water contact angles ( $90^\circ$ ) for both layers) and in lower concentration in the case of membrane M1. No accumulation of this intermediate has been observed using membrane M3 or in the system without a membrane.

The main difference among the three membranes concerns their different characteristics of hydrophobicity (Table 2).

M3 is characterized by high hydrophobicity (WCA  $> 110^\circ$ ) for both membrane layers: this characteristic induces a mono-directional transport of lipophilic cyclohexene across the overall membrane. In this way quantitative oxidation reaction at the membrane–aqueous phase interface occurs on the basis of the reaction shown in Scheme 1.

In the case of membrane M1, the high hydrophobicity (WCA of  $140^\circ$ ) of the membrane layer in contact with the organic phase assured transport of cyclohexene across the membrane, but the moderate hydrophobicity of the top layer ( $90^\circ$ ) favors partial transport of the aqueous phase, i.e. wetting of the membrane with consequent incomplete oxidation of cyclohexene and formation of the 1,2-diol intermediate (20%). For membrane M2, characterized by similar wettability properties for both membrane layers (WCA  $\approx 90^\circ$ ), the wetting of the membrane with the aqueous phase is enhanced, and the

production of 1,2-diol (55%) is increased compared to that of adipic acid (20%). For the system without a membrane, the vigorous mixing and the presence of the acidic lipophilic ligand (i.e., succinic acid) assured the contact between the organic and the aqueous phases, leading to the production of adipic acid without accumulation of 1,2-cyclohexanediol.

**3.2. Membrane Characterisation.** The different hydrophobic properties of the membranes were consequent upon their morphologies.

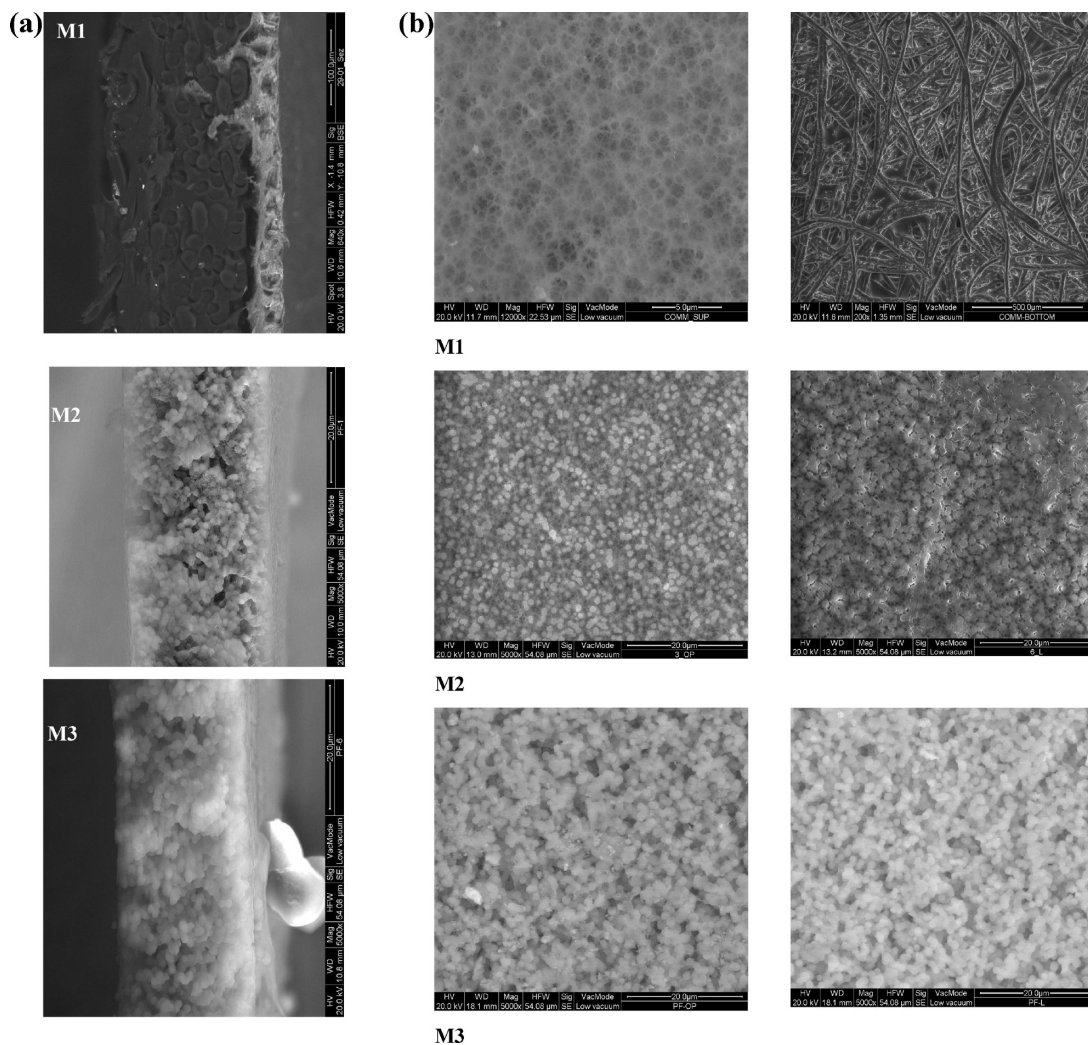
In Figure 3a–b, the SEM pictures of the membrane cross sections and surfaces are reported.

For the commercial M1, the selective layer coated on the polypropylene sublayer is clearly visible. M2 and M3 are characterized by a similar symmetric nodular structure typical when volatile solvent has been used for the casting solution.<sup>12</sup> Single nodules are well visible across an overall membrane cross section of M2. For M3, aggregates of nodules can be observed.

The difference between M2 and M3 is evident on the basis of SEM (Figure 3b) and AFM (Figure 4) analyses of both membrane layers.

The top and bottom layers of membrane M2 are characterised by a nodular structure, and this is confirmed by AFM analysis (Figure 4).

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**Figure 3.** (a) SEM analyses of cross sections of the membranes reported in Table 2: right, top layer and left, bottom layer.(b) SEM analyses of the surfaces of the membranes reported in Table 1: left, top layer and right, bottom layer.

For membrane M3, agglomerates of nodules are visible on both membrane layers (Figure 3b) and well recognizable in AFM images (Figure 4).

The presence of granule agglomerates on the surface of M3 is due to longer exposure to air during membrane formation for both top and membrane layers.

It is interesting to observe that the top layer of commercial membrane M1 is less rough (9.8 nm) than the bottom layer (24.4 nm) (see Table 2). For M2 and M3, an opposite trend is observed: the top layer is more rough than the sublayer. In particular, this difference is noticeable for M3 with  $R_q$  values of 57.2 nm and 2.60 nm for the top and bottom layers, respectively. The different roughness between the top layers of M2 and M3 is due to the presence of nodule aggregates as observed in SEM and AFM analysis. The structure–property relationships gain a relevant importance if the role of membrane interphase is considered.<sup>13,14</sup>

**3.3. Structure–Property Relationships.** The hydrophobic character of the membrane is one of the most important requirement for processing the film in contactor applications.

The reason is the necessity of preventing the membrane from wetting. The  $LEP_w$  values measured for the membranes M1–M3 showed a gradual decrease as the pore size increased (Figure 5). However, the  $LEP_w$  values for M1–M3 membranes are better than those considered acceptable for processing hydrophobic membranes in contactor devices, i.e. 0.2–0.25 bar.<sup>13</sup>

The different water repellence of PVDF membranes prepared in this work is specifically concerned with the surface topography. The membrane M3 exhibits a surface entirely covered by regular pores uniformly dispersed. This generates the surface roughness responsible for the capture of hydrophobic air inside the pores.

A linear relationship between the density of surface pores and the membrane surface roughness has been found (Figure 6).

The formation of one interface between the probe polar liquid (i.e., water used for contact angle measurements) and the layer of hydrophobic air trapped in the pores consequently provides enhanced water repellence (Figure 6, bottom).

In Figure 7, the flux of the substrate (i.e., cyclohexene) as a function of transmembrane pressure across M1–M3 membranes has been reported.

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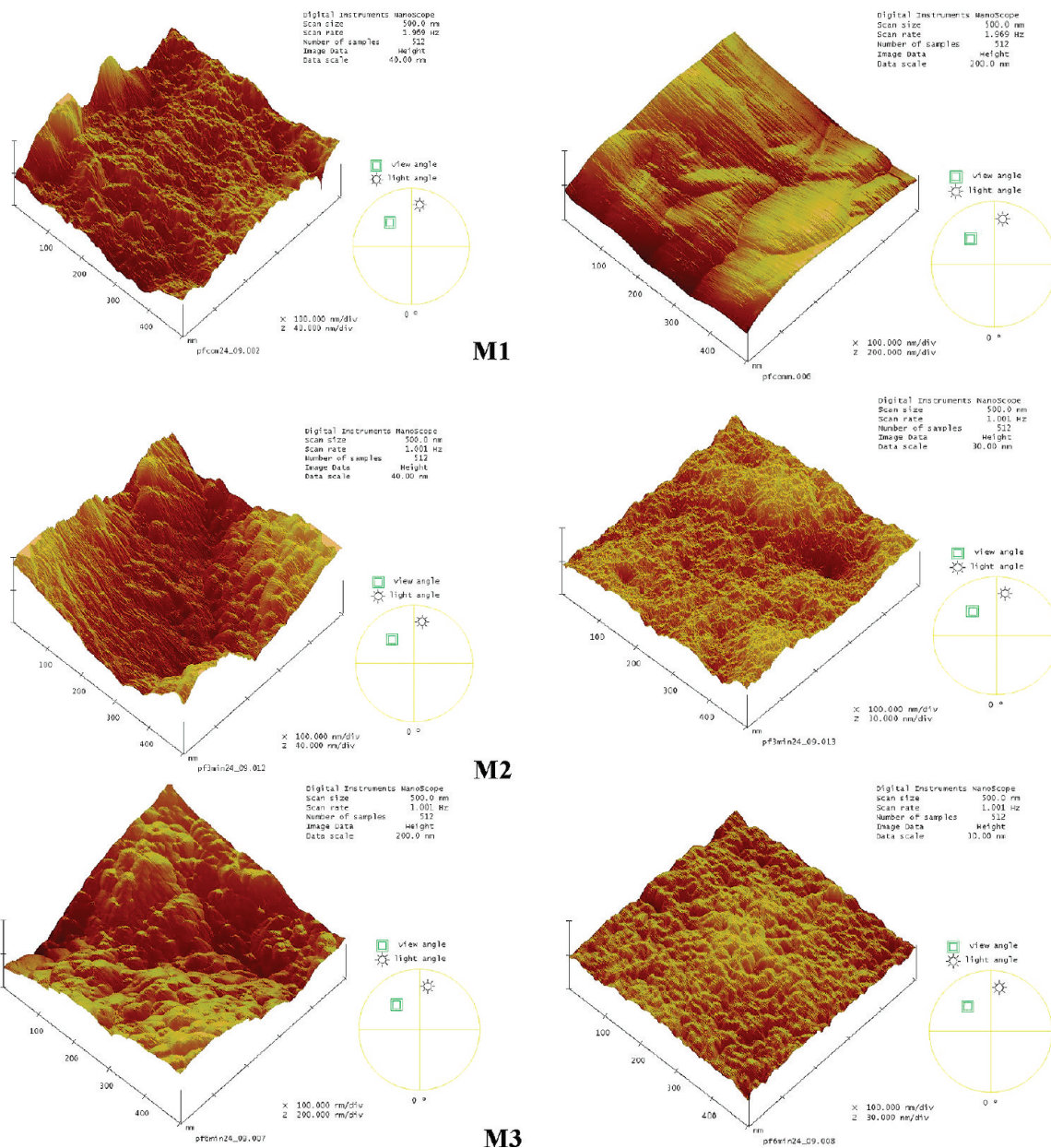


Figure 4. AFM analyses of M1–M3; for each membrane: left, top layer; right, bottom layer.

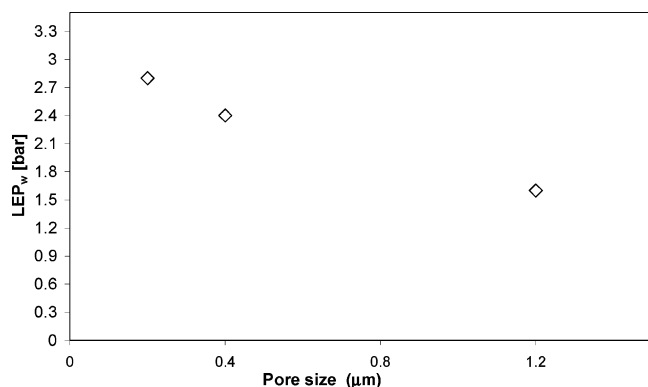
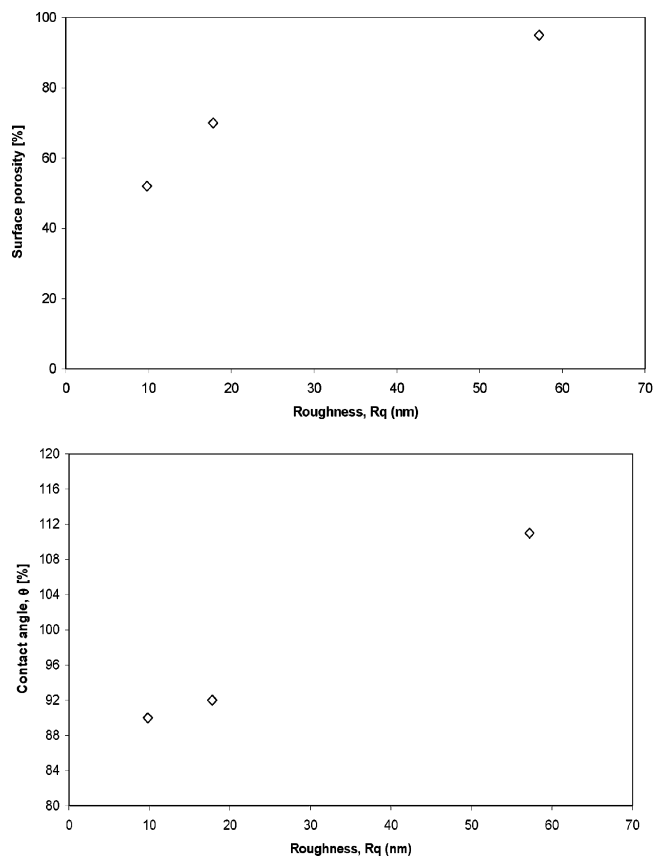


Figure 5. Resistance to liquid entry pressure of water (LEP<sub>w</sub>) for M1 (0.2 μm), M2 (0.4 μm), and M3 (1.2 μm).

The flux observed for M1 is very different from that measured for M2 and M3. This difference reflects that of the

pore sizes among the three membranes (see Table 1), i.e. M3 > M2 > M1.

It is important to note that this trend does not explain completely the different reaction order observed, i.e. M3 > M1 > M2. For the transport experiments of pure cyclohexene, the membranes have been located with the selective layer (i.e., top layer) from the feed side: M3, with pore size of 1.2 μm and WCA of 111°, is more permeable to lipophilic substrate than M2 (0.4 μm) and M1 (0.2 μm). For these two membranes, both characterized by a WCA of ~90° (see Table 2), the different pore size affected the transport. However, during the course of the reaction, the bottom side of each membrane (more hydrophobic than the top side, see Table 2) was in contact with the lipophilic cyclohexene, whilst the selective layer (top layer) was in contact with the aqueous phase: the hydrophobic character of M1 bottom side (WCA = 140°, Table 2) prevents water wetting which occurs in the case of M2 (WCA = 93° for the

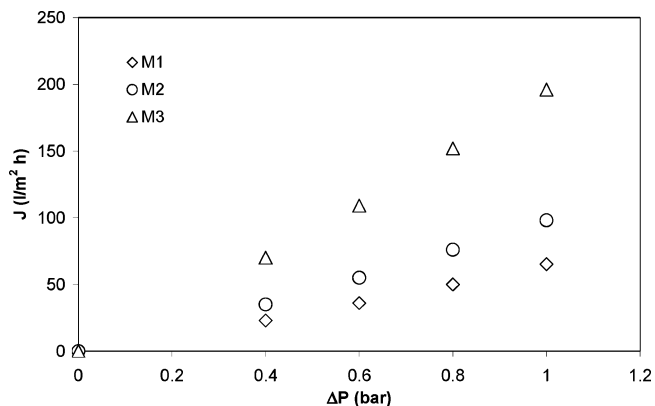


**Figure 6.** Evaluation of the wetting degree for membrane top layers. (Top) Relationship between the surface roughness and surface porosity. (Bottom) Relationship between the surface roughness and contact angle,  $\theta$ .

bottom side, Table 2), and it is the basis for the observed reactivity order, i.e. M1 > M2.

#### 4. Conclusions

To conclude, in this work, three advantages compared to other previous studies can be listed:



**Figure 7.** Cyclohexene fluxes across M1–M3 membranes.

(i) the use of a cheap catalyst ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ ) instead of  $\text{Na}_2\text{WO}_4$ , using succinic acid as ligand and 30%  $\text{H}_2\text{O}_2$ ;

(ii) the possibility to realize the compartmentalization of the two reaction phases by means of polymeric membranes. These resulted in contacting the cyclohexene with the catalytic active species in the aqueous phase promoting the oxidation reaction;

(iii) the dose of the oxidant  $\text{H}_2\text{O}_2$  during the course of the reaction. This reaction mode reduces, in terms of reaction economics benefits, the problem of fast decomposition of hydrogen peroxide in the presence of the metal catalyst, and therefore, it increases the process efficiency.

Cyclohexene can be oxidised selectively to adipic acid (90%) by using a symmetric hydrophobic membrane (M3) characterized by a high water contact angle ( $\alpha > 110^\circ$ ) for both layers.

The system proposed in this work with a membrane across the two reaction phases works not only to produce adipic acid, but also to essentially separate the product from the organic phase.

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