



# Membrane contactors operating in mild conditions for liquid phase partial oxidation of methane

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## ABSTRACT

An integrated catalytic membrane system for liquid phase partial oxidation of light hydrocarbons such as methane in mild operating conditions has been studied and tested. On the basis of tests on methane solubility and chemical stability of some candidate solvents, water was chosen as the reaction medium. The low methane solubility in water was enhanced by working under moderate pressure (0.4 MPa) and then integrating the catalytic system with a gas–liquid membrane contactor. Catalytic tests, using the Fenton reagent ( $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$ ), were carried out in a batch system to study the influence of some operating conditions on system performance. Best results were obtained under the following operating conditions:  $[\text{Fe}^{2+}] = 2.70 \text{ mmol L}^{-1}$ ;  $[\text{H}_2\text{O}_2] = 54 \text{ mmol L}^{-1}$ ;  $T = 25^\circ\text{C}$ ;  $\text{pH} = 2.98$ . GC–MS analyses evidenced production of dimethyl peroxide (DMP), that can be potentially converted to methanol (two moles per mole of DMP). Then results obtained in the batch system were applied carrying out some catalytic tests in the integrated membrane system. It was evidenced the influence of inside membrane diameter and material type on system performance and the positive effect of the membrane contactor to disperse methane in the liquid phase. Among three tested membranes the ceramic tubular membrane (0.2  $\mu\text{m}$  pore size) gave the best performance avoiding problems related to membrane degradation, plugging and fouling. It was pointed out that integration of the catalytic system with a membrane contactor enhanced system performance decreasing  $\text{H}_2\text{O}_2$  consumption, thanks to a lower oxidation of methane to  $\text{CO}_2$ , thus resulting in an increase of system selectivity.

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## 1. Introduction

Methane, the main component of natural gas, represents the most abundant and low energetic cost reserve on earth, with reserves equal to amount of petroleum. As many of these reserves are located in remote areas, particular attention has been devoted to the study of methane conversion to liquid fuels [1–3].

Methanol, the initial product of methane oxidation, is the most desirable because it preserves a lot of the original methane energy. Besides, methanol meets the technical requirement for logistic transport and storage [4].

Conversion of methane to liquid products is mainly manufactured through an energy intensive two step process involving generation of syn-gas intermediate. It is a highly endothermic and thermodynamically balanced process operated at high temperature (800–1400 °C) and high pressure, involving significant costs.

Thus, in last years, considerable efforts have been made in the area of direct and selective methane conversion to methanol

because: i) one step methane oxidation process to methanol has the potential to be more energy efficient; ii) energy intensive step of syn-gas production is bypassed [5,6]; iii) high chemical stability of methane (C–H bond energy = 104 kcal/mol) makes it the least reactive hydrocarbon, thus its chemical utilization remains a great challenge to scientists [7].

Partial oxidation of methane to methanol can be carried out either in gas phase or in liquid phase medium.

In gas phase it is generally carried out by using oxygen as the oxidant under high temperature (200–500 °C) and high pressure (30–200 atm). Selectivity to methanol (30–40%) and methanol yield are low because high temperature promotes thermodynamically favoured over oxidation reactions [8–12].

In liquid phase best results were obtained by working in protic media, where methanol is protected from over oxidation by in situ esterification. Periana et al. [13,14] used 100% sulphuric acid as both reaction medium and the oxidant, and mercury(II) or a more safe bi-pyrimidine platinum complex as the catalyst. Methane was converted to methyl bisulphate ( $\text{CH}_3\text{OSO}_3\text{H}$ ), working at 120–180 °C and 34 bar, with satisfactory methane conversion (50 and 90% for the two catalysts, respectively) and selectivity to methyl bisulphate (85 and 81%, respectively). This product can be subsequently hydrolyzed to methanol, with an hypothetical final methanol yield

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of 43 and 73%. Similar results were obtained by Chen et al. [15] by using, in the same reaction medium, vanadium as the catalyst at 180 °C and 40 bar.

Lin et al. [16] studied the partial oxidation of methane in a different medium (6:1 v/v perfluorobutyric acid and water) by using  $\text{RhCl}_3$  in the presence of  $\text{Cl}^-$  and  $\text{I}^-$  ions, as catalytic system and molecular oxygen as oxidant obtaining methyl perfluorobutyrate as the main product. Later Lin et al. [17], Chepaikin et al. [18,19] and Yamanaka et al. [20] studied different catalysts placed in solution or in concentrated trifluoroacetic acid using molecular oxygen as oxidant, obtaining methyl trifluoroacetate ( $\text{CF}_3\text{COOCH}_3$ ) as main product that can be converted to methanol by another reaction step.

All the above works are characterized by the use of a very aggressive medium (concentrated acid) under harsh operating conditions producing a methanol ester. To obtain methanol another reaction step therefore becomes necessary.

The high operating pressure used is directly related to the intrinsic limitation of this catalytic process: the substrate to be partially oxidized (methane), the catalyst and the oxidant are in different phases, resulting in an heterogeneous catalytic process where the poor methane solubility in the liquid medium represents a key limitation. The use of a gas–liquid membrane contactor could overcome this limitation [21,22]. Generally a gas–liquid membrane contactor is based on the use of a polymeric hydrophobic membrane that does not act as a selective barrier, but simply as a support to provide a large contact area between the gas and the liquid phases [23]. The main advantages of a membrane contactor with respect to other gas–liquid contactors are: i) compact design; ii) easy scale up, thanks to system modularity; iii) high operational stability and flexibility; and iv) low energy consumption. When a membrane contactor acts as a gas–liquid distributor it works by dispersing gas micro-bubbles in the liquid thus achieving a better contact between the two phases.

Employing this approach Williams et al. [3] studied the oxidation of methane to methanol derivative in two different reactor types. The first one was a commercial batch autoclave. The second one was a semi-continuous ceramic porous tube reactor working as a gas–liquid distributor. Although the observed initial reaction rate appeared promising, the yield of methyl trifluoroacetate was less than 2%.

Another approach on the use of a membrane in a catalytic process was the partial oxidation of alkenes proposed by Espro et al. [24]. In particular the authors studied the selective oxidation of light alkanes (methane, ethane, propane) at 80–120 °C and 140 kPa by using the Fenton system ( $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$ ) in a three phase catalytic membrane reactor assembled with a flat membrane. The results evidenced the advantage of the liquid phase reaction system integrated by the membrane allowing simultaneous reaction and product separation in continuous mode.

Being partial oxidation of light hydrocarbons a very interesting process for the petrochemical industry, the integration of catalytic systems with membrane processes could potentially provide many benefits in this field. On this basis in the present preliminary work an experimental study of an integrated catalytic membrane system for the partial oxidation of methane in liquid phase in very mild operating conditions (low temperature, low pressure, reaction medium not aggressive on materials) is described.

In previous works we studied the one-step production of phenol by selective oxidation of benzene [25] by using iron(II) as the catalyst and hydrogen peroxide as the oxidant (Fenton system) in aqueous medium, obtaining encouraging results. The present work applies the same catalytic system in liquid phase but problems are different because methane is a gaseous substrate.

Solubility and stability tests were carried out to choose the best reaction medium.

Optimization of operative conditions (catalyst and oxidant amounts, temperature and pH) was performed by doing some tests on partial oxidation of methane in a batch system.

Finally, the batch system was integrated with a membrane contactor assembled with three different membranes. The performance of the so obtained catalytic membrane reactors was tested and compared with the batch one.

## 2. Experimental

### 2.1. Materials

Methane (purity = 99.995% v/v), carbon dioxide (purity 99.998% v/v) and helium (purity 99.999% v/v) were purchased from Pirossigeno.

Methanol (MW = 32.042 g mol<sup>-1</sup>; purity = 99.9%) was purchased from Carlo Erba Reagenti.

The solvents, tested in the solubility and stability tests, were: ultrapure water (Milli-Q grade); acetic acid (MW = 60.05 g mol<sup>-1</sup>; purity = 99.9%) from Romil SA selected assured solvent; dimethyl sulfoxide (DMSO, MW = 78.13 g mol<sup>-1</sup>; purity = 99.9%) and ethanol (MW = 46.07 g mol<sup>-1</sup>; purity = 99.8%) from Sigma Aldrich; acetonitrile (MW = 41.05 g mol<sup>-1</sup>; purity = 99.5%); diethyl ether (MW = 74.124 g mol<sup>-1</sup>; purity 99.0%) and hexane (MW = 86.18 g mol<sup>-1</sup>; purity 96%) from Carlo Erba Reagenti; cyclohexane (MW = 84.16 g mol<sup>-1</sup>; purity = 99.5%) from Riedel de Haën. Polarity of these solvents, reported in terms of relative dielectric constant, is in the order: hexane (2.0) < diethyl ether (4.3) < acetic acid (6.2) < ethanol (24) < acetonitrile (37) < DMSO (47) < water (80).

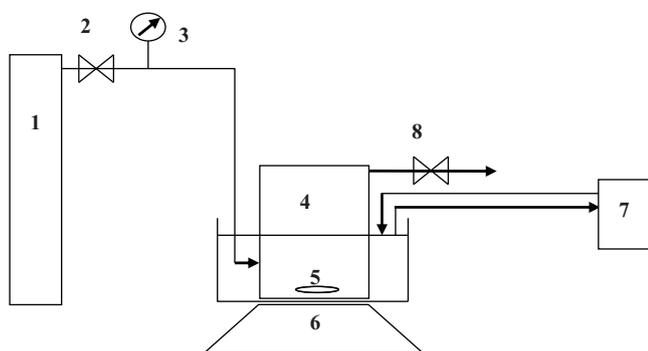
Iron(II) sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; MW = 278.05 g mol<sup>-1</sup>; purity 99.0%) from Carlo Erba Reagenti was used as the catalyst and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ; 50% w/v in water; density = 1.11 g cm<sup>-3</sup>) from Sigma Aldrich was the oxidant.

### 2.2. Tests on solubility and chemical stability of solvents

The characteristics of a liquid solvent, where the partial oxidation of methane takes place, should be: i) adequately dissolve the methane substrate from the gas phase; ii) inert in the reaction environment. On the basis of these requirements, the feasibility to use a particular solvent as reaction medium was checked by methane solubility tests and by chemical stability tests of the solvent. They were carried out at atmospheric pressure in an open glass jacket batch ( $V = 500$  mL), connected to a thermostat (Haake C40P, by Thermo Haake) to work in isothermal conditions ( $T = 25$  °C). A magnetic stirrer ensured homogeneity of the gas dispersion/solution in the solvent.

Solubility tests were performed employing 250 mL of each solvent in the batch at 25 °C. Methane was injected by means of a tubular porous membrane in polypropylene (5 mm inner diameter, 0.2 μm pore size) at 0.1 MPa (1 bar) pressure. At established time interval (30 min) 0.2 μL of solution were withdrawn and methane concentration was measured. Each solubility test was stopped when methane concentration in the liquid phase reached a constant value.

Solvents showing higher methane solubility were submitted to stability tests for evaluating their chemical stability in the oxidant reaction environment. Every test was repeated three times obtaining a complete reproducibility of the results. 250 mL of solvent were fed in the batch and after waiting 10 min for temperature stabilization, the catalyst Fe(II) (3.12 mmol L<sup>-1</sup>) and the oxidant  $\text{H}_2\text{O}_2$  (6 mmol L<sup>-1</sup>) were added. Three samples were withdrawn with a time interval of 60 min; they were analyzed by GC–MS to evaluate the formation of oxidation by-products. 6 mmol L<sup>-1</sup> of the oxi-



**Fig. 1.** Scheme of the experimental set-up used to study the partial oxidation of methane in batch: (1) methane cylinder, (2) regulation valve, (3) manometer, (4) reactor, (5) magnetic bar, (6) magnetic stirrer, (7) thermostat, (8) sampling valve.

dant were added to the reacting medium after each sampling. The amount of the catalyst and the oxidant (this last added a little at a time in sequence) were fixed on the basis of our previous work [25].

### 2.3. Batch system for partial oxidation of methane in liquid phase

In Fig. 1 the experimental set-up, where the partial oxidation of methane was carried out, is reported. It was made by a stainless steel reactor ( $V = 90$  mL), closed on the top by a transparent polycarbonate disc high pressure resistant. The reactor was immersed in a thermostated bath to operate at constant temperature ( $T = 25$  °C). A magnetic stirrer coupled to a magnetic bar ensured the homogeneity of the liquid phase.

The catalytic tests were carried out by introducing in the reactor: 60 mL of solvent, the catalyst, acetic acid and finally the oxidant. The remaining 30 mL were occupied by the gaseous phase which was methane injected at 0.4 MPa (4 bar) from a pressure cylinder. At the beginning of each test the reactor was purged for 0.5 min flushing methane. After 30 min and then each 60 min, samples of solution were withdrawn through the sampling valve (8) in Fig. 1 and submitted to the analysis. Then the system was purged again for 0.5 min and the run continued working in methane saturation conditions. Each catalytic test had a time course of 390 min.

### 2.4. Integrated membrane system for partial oxidation of methane in liquid phase

Typical limitations of batch systems for catalytic gas–liquid reactions are: i) gaseous reactant depletion, because of its not continuous feeding, which have deleterious effect on catalytic process performance; ii) poor solubilisation of the gaseous reactant in the liquid reaction medium.

In this work, to enhance methane feeding and dissolution in the liquid phase, a membrane contactor was integrated in the catalytic system for achieving: i) increase methane concentration in the liquid phase (e.g., by reaching oversaturation conditions); ii) enhance methane dispersion in the liquid phase (e.g., by micro-bubbles dispersion), thus increasing the contact area between the liquid phase containing the oxidizing agents and the gaseous phase containing the methane substrate; iii) continuous transfer of gas to liquid permeating it through the membrane. Both the i) and ii) conditions would result in higher availability of the organic substrate to oxidize that could increase the catalytic performance of this heterogeneous system.

The integrated membrane system, was built by connecting the batch system with a membrane contactor for accomplishing methane feeding (Fig. 2). The liquid phase, where the reaction occurs, is recirculated in the loop (6), thanks to a peristaltic pump (7), and it flows in the membrane contactor (inside the lumen of

cylindrical membranes) while methane is fed in the shell at the desired pressure (0.1–0.4 MPa) controlled by the regulation valve (2). The liquid and gaseous phases in the membrane contactor are contacted at the membrane interface thus the liquid phase is enriched with micro-bubbles of gaseous substrate to be oxidized (see zoom in Fig. 2).

At the beginning of each test the membrane contactor was purged opening the drainage valve (12) for 0.5 min. Samples of solution were withdrawn through the sampling valve (11), with the same time interval of the batch tests, and submitted to the analysis. Each catalytic test had a duration of 390 min and at each end the system was progressively depressurized by means of the drainage valve (12).

### 2.5. Membrane contactors

Three different membranes were tested for assembling the membrane contactor: i) polypropylene fibers; ii) polypropylene capillary membranes; iii) a tubular ceramic membrane.

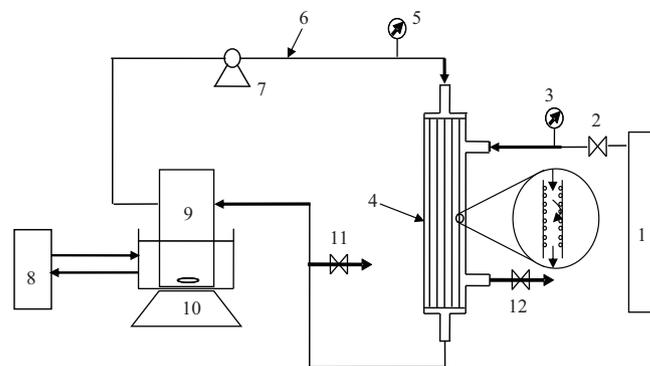
The membrane contactors assembled with polypropylene membranes were made in laboratory. Membranes were fixed in a tubular polycarbonate module (length = 20 cm, outside diameter = 1.5 cm, inside diameter = 1.2 cm) using a two component epoxy glue (Sty Cast 1266 from Emerson & Cuming). Two types of membranes were used: i) 18 polypropylene fibers (Celgard X20; Hoechst Celanese, Charlotte, NC, USA, outside diameter = 0.46 mm, inside diameter = 0.40 mm, average pore size = 0.03  $\mu\text{m}$ , porosity = 40%) with total lumen useful surface = 45.24  $\text{cm}^2$ ; ii) 4 polypropylene capillary membranes (Membrana, Accurel Capillary Fibers, outside diameter = 2.5 mm, inside diameter = 1.7 mm, average pore size = 0.2  $\mu\text{m}$ , porosity = 83%) with total lumen useful surface = 42.73  $\text{cm}^2$ .

The last membrane contactor was a commercial type (Membralox® T 1-70 from Pall Corporation) assembled with one zirconium porous tubular membrane (Pall Corporation, length 25 cm, outside diameter = 1.0 cm, inside diameter = 0.7 cm, average pore size = 0.2  $\mu\text{m}$ ) with total lumen useful surface = 54.98  $\text{cm}^2$ .

### 2.6. Analytical methods

Analyses of the samples were performed with a GC (Agilent 6890N) equipped with a thermal conductivity detector (TCD) and a capillary column Supelco Q Plot (30 m  $\times$  320  $\mu\text{m}$ ). Helium was used as carrier gas.

The identification of reaction products was carried out by using a GC–MS (Shimadzu QP 2010S), equipped with a capillary column Equity 5 (10 m  $\times$  0.1 mm) from Supelco and using helium as carrier gas.



**Fig. 2.** Scheme of the integrated membrane system: (1) methane cylinder, (2) regulation valve, (3) and (5) manometers, (4) membrane contactor, (6) recirculation loop, (7) peristaltic pump, (8) thermostat, (9) reactor, (10) magnetic stirrer, (11) sampling valve, and (12) drainage valve.

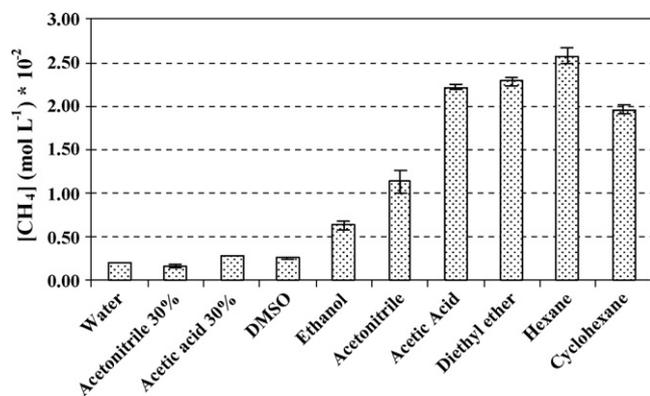


Fig. 3. Methane solubility in water and in the tested organic solvents ( $V=250$  mL,  $P_{\text{CH}_4} = 0.1$  MPa,  $T=25$  °C except for diethyl ether (10 °C)).

Samples withdrawn during the catalytic tests could contain methanol and other oxidation products in traces, resulting in very difficult analysis. To avoid this possible analytical complication the Solid Phase Micro Extraction (SPME) technique was used [26]. SPME involves the use of a fiber coated with an extracting phase which extracts different analytes (including both volatile and non-volatile) from different kinds of media, which can be in liquid or gas phase. In particular, in the present work a Carboxen/PDMS coated fiber (thickness = 75  $\mu\text{m}$ ) from Supelco was used. This one was the best polymeric coating for pre-concentrating diluted samples of methanol in water. Some experiments were repeated several times finding an agreement of the peaks area within 5–10%.

Hydrogen peroxide concentration in the aqueous reacting medium was determined by using the classic iodometric method. It is based on the reaction of hydrogen peroxide with an excess of potassium iodide in presence of an ammonium molybdate catalyst to produce triiodide ions, which are subsequently titrated with a standard thiosulfate solution.

A pH meter (WTW Inolab Terminal Level 3) with a glass pH-electrode SenTix 81 (WTW) was used for pH measurements.

### 3. Results and discussion

#### 3.1. Tests on methane solubility and chemical stability of solvent

It is known that a high substrate concentration in solution gives, generally, higher reaction rate thus methane solubility tests in different solvents were carried out and the results are reported in Fig. 3. They show that methane solubility in the liquid phase decreases by increasing the polarity of the solvent. The decreasing solubility order is: *n*-hexane > diethyl ether > acetic acid > cyclohexane > acetonitrile > ethanol > water.

Diethyl ether was excluded because of its relatively high volatility. Acetic acid was also excluded because it is aggressive on materials used for experimental set-up building. Acetonitrile, that showed a discrete ability to dissolve methane, was excluded because in the chemical conditions needed for methane activation it oxidizes giving by-products (formaldehyde, formic acid and carbon dioxide) that can interfere with methane oxidation products [27].

Ethanol was excluded because it is similar to methanol, giving the same problems of further oxidation like methanol.

A widely used and inert solvent is water but methane solubility in water is too low. The attempt to increase the lipophilic character of water by adding acetic acid or acetonitrile (30% v/v) did not give satisfactory results. Higher acetic acid concentration was not considered to avoid high acidic environment for the materials exposed in the process.

Summarizing, the results of the solubility tests showed that hexane and cyclohexane were the best solvents in terms of methane solubility. These solvents were tested in oxidant conditions to verify their chemical stability. The results evidenced that both hexane and cyclohexane were not inert; indeed, hexanal and cyclohexanone were the main oxidation by-products for the two considered solvents, respectively.

On the basis of the results of stability tests, water was chosen as the reaction medium, also considering that it is a green solvent.

The methane solubility in water was enhanced by providing a slight operating pressure of about 0.4 MPa in the batch reactor and subsequently by integrating the catalytic system with a membrane contactor. This pressure is not significant in terms of energy consumption however it improved the methane solubility by about twice ( $(4.58 \pm 0.4) \times 10^{-3}$  mol L<sup>-1</sup>) in comparison to solubility under normal atmospheric conditions ( $(2.03 \pm 0.05) \times 10^{-3}$  mol L<sup>-1</sup>).

#### 3.2. Liquid phase partial oxidation of methane in the batch system

Some catalytic tests for partial oxidation of methane in liquid phase were carried out in batch choosing water as reaction medium based on previous study. In these tests the influence of the following operating parameters on performances of the catalytic system was carried out: i) amount of iron(II) catalyst, ii) amount of hydrogen peroxide oxidant, iii) temperature, and iv) pH.

##### 3.2.1. Partial oxidation of methane in liquid phase in the batch system: catalyst optimization

It is worthwhile noting that during the catalytic tests, only two peaks were detected by GC analysis: the first one, with a retention time (RT) of 7.2 min (equal to methanol RT) and the second one with a RT of 7.4 min.

In Fig. 4 the results obtained using different catalyst amount are reported in terms of areas of the two GC peaks versus time. The best results were obtained with a catalyst amount of 2.70 mmol L<sup>-1</sup>.

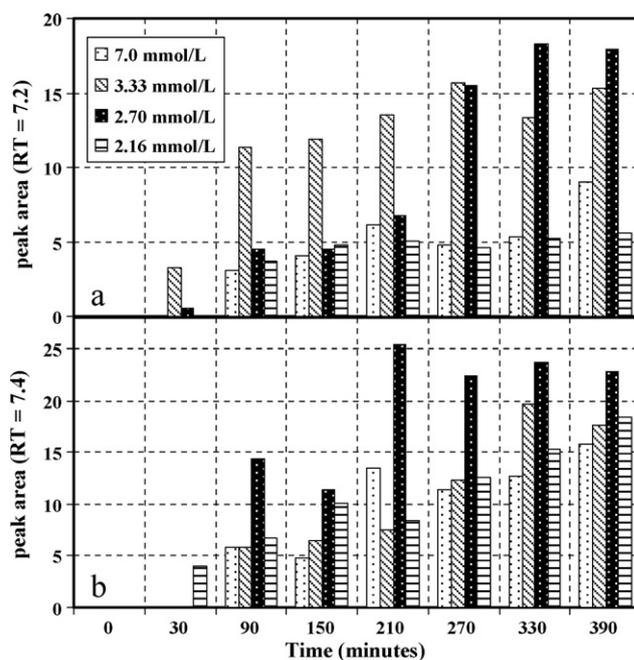
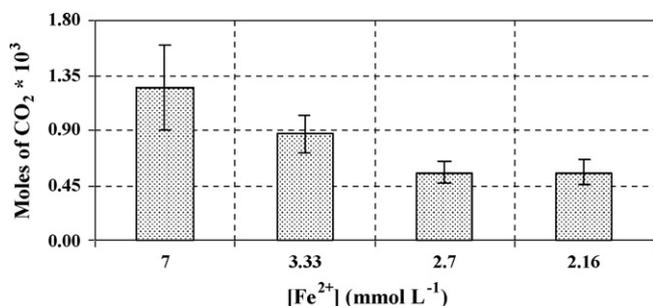


Fig. 4. Area versus time for the peaks with retention times of 7.2 (a) and 7.4 min (b) in the catalytic tests at different iron(II) amounts ( $[\text{H}_2\text{O}_2] = 54$  mmol L<sup>-1</sup>;  $[\text{CH}_3\text{COOH}] = 30.7$  mmol L<sup>-1</sup>;  $T = 25$  °C;  $P_{\text{CH}_4} = 0.4$  MPa; aqueous phase volume = 60 mL).



**Fig. 5.** Moles of CO<sub>2</sub> produced in the catalytic tests at different iron(II) amounts ([H<sub>2</sub>O<sub>2</sub>] = 54 mmol L<sup>-1</sup>; [CH<sub>3</sub>COOH] = 30.7 mmol L<sup>-1</sup>; T = 25 °C; P<sub>CH<sub>4</sub></sub> = 0.4 MPa; aqueous phase volume = 60 mL).

The data on CO<sub>2</sub> production, reported in Fig. 5, show that amount of methane totally oxidized decrease by decreasing catalyst amount. The lowest CO<sub>2</sub> amount was obtained at 2.70 and 2.16 mmol L<sup>-1</sup> of Fe(II) present in the reacting medium. Thus, excessive catalyst amount, increasing the oxidant capacity of the catalytic system, resulted in an increase of total oxidation of methane.

By combining the results on peaks area and CO<sub>2</sub> production, it was found that best results were obtained by using a catalyst amount of 2.70 mmol L<sup>-1</sup>, corresponding to a more selective catalytic system; indeed, the areas of the two peaks increased while decreased the amount of organic substrate completely oxidized to CO<sub>2</sub>.

Thus, all the successive catalytic tests are carried out by using this catalyst amount.

### 3.2.2. Partial oxidation of methane in liquid phase in the batch system: oxidant optimization

Table 1 shows the effect of the amount of H<sub>2</sub>O<sub>2</sub> on system performance.

CO<sub>2</sub> production increases with the oxidant amount showing that system reactivity increases. This means that amount of methane fully oxidized to CO<sub>2</sub> increased and, subsequently, the areas of the two peaks at 7.2 and 7.4 min (see Table 1) decreased. At 27 mmol L<sup>-1</sup> of oxidant, the oxidizing capacity of reaction medium is low showing a lower CO<sub>2</sub> production, but the ratios of peaks area and CO<sub>2</sub> production show best results by using an oxidant amount of 54 mmol L<sup>-1</sup>.

### 3.2.3. Partial oxidation of methane in liquid phase in the batch system: temperature optimization

In Table 2 the results obtained at different temperature are reported. They show a poor catalytic activity by operating at 15 °C, as it is evidenced by the low areas of the two peaks with respect to the ones obtained at higher temperature.

In the tests performed at 40 °C, the catalytic system showed a higher initial rate with respect to 25 °C till 150 min. After this initial trend, the areas of the two peaks stabilized at values lower than that ones obtained at 25 °C. A possible explanation of this

**Table 1**

Effect of oxidant amount on catalytic system performance ([Fe<sup>2+</sup>] = 2.70 mmol L<sup>-1</sup>; [CH<sub>3</sub>COOH] = 30.7 mmol L<sup>-1</sup>; T = 25 °C; P<sub>CH<sub>4</sub></sub> = 0.4 MPa; aqueous phase volume = 60 mL).<sup>a</sup>

Oxidant amount (mmol L <sup>-1</sup> )	Peak area (7.2 min)	Peak area (7.4 min)	CO <sub>2</sub> production (mol)
27	5.11	14.21	4.73 × 10 <sup>-4</sup>
54	18.27	23.68	5.59 × 10 <sup>-4</sup>
108	5.90	9.10	9.13 × 10 <sup>-4</sup>

<sup>a</sup> All values referred to 330 min.

**Table 2**

Effect of temperature on catalytic system performance ([Fe<sup>2+</sup>] = 2.70 mmol L<sup>-1</sup>; [H<sub>2</sub>O<sub>2</sub>] = 54 mmol L<sup>-1</sup>; [CH<sub>3</sub>COOH] = 30.7 mmol L<sup>-1</sup>; P<sub>CH<sub>4</sub></sub> = 0.4 MPa; aqueous phase volume = 60 mL).<sup>a</sup>

Temperature (°C)	Peak area (7.2 min)	Peak area (7.4 min)	CO <sub>2</sub> production (mol)
15	2.80	5.46	4.66 × 10 <sup>-4</sup>
25	18.27	23.68	5.59 × 10 <sup>-4</sup>
40	11.79	16.30	8.55 × 10 <sup>-4</sup>

<sup>a</sup> All values referred to 330 min.

**Table 3**

Effect of pH on catalytic system performance ([Fe<sup>2+</sup>] = 2.70 mmol L<sup>-1</sup>; [H<sub>2</sub>O<sub>2</sub>] = 54 mmol L<sup>-1</sup>; T = 25 °C; P<sub>CH<sub>4</sub></sub> = 0.4 MPa; aqueous phase volume = 60 mL).<sup>a</sup>

pH	[CH <sub>3</sub> COOH] (mol L <sup>-1</sup> )	Peak area (7.2 min)	Peak area (7.4 min)	CO <sub>2</sub> production (mol)
2.49	122.67	3.38	0.83	3.72 × 10 <sup>-4</sup>
2.98	30.7	18.27	23.68	5.59 × 10 <sup>-4</sup>
3.17	7.67	4.95	14.05	3.55 × 10 <sup>-4</sup>

<sup>a</sup> All values referred to 330 min.

trend can be attributed to the increase of oxidant capacity of the system with increasing the temperature giving higher tendency to complete oxidation of methane to CO<sub>2</sub>.

The influence of temperature on system performance was also confirmed by the moles of CO<sub>2</sub> produced (see Table 2) showing that methane oxidation to CO<sub>2</sub> increased with the temperature. Considering both areas of the two peaks and CO<sub>2</sub> production, best results were obtained working at 25 °C.

### 3.2.4. Partial oxidation of methane in liquid phase in the batch system: pH optimization

Change of the operating pH was studied by adding different amount of acetic acid in the aqueous medium. In particular, considering that previous catalytic tests were carried out at pH = 2.98 ([CH<sub>3</sub>COOH] = 30.7 mmol L<sup>-1</sup>), two other pHs were considered: 2.49 and 3.17, by adding acetic acid amounts equal to 0.25 and 4 times the previous one, respectively.

The results, summarized in Table 3, evidence the influence of the operating pH on system performance. Analysing the data as in the previous paragraph, best results were obtained at the operating pH 2.98.

### 3.2.5. General consideration on results obtained in the batch system

From previous experiments in batch the following optimal conditions are obtained:

- [Fe<sup>2+</sup>] catalyst concentration: 2.70 mmol L<sup>-1</sup>;
- [H<sub>2</sub>O<sub>2</sub>] oxidant concentration: 54.0 mmol L<sup>-1</sup>;
- Temperature: 25 °C;
- [CH<sub>3</sub>COOH] acid concentration: 30.7 mmol L<sup>-1</sup> (pH = 2.98).

These operating conditions were used in the oxidation tests in the integrated membrane system.

As previously reported, during the catalytic tests only two peaks were detected by GC analysis. To identify the compounds that correspond to these two peaks, some GC–MS analyses were carried out. Obtained results permitted to identify only dimethyl peroxide (DMP, H<sub>3</sub>C–O–O–CH<sub>3</sub>) as product of partial oxidation of methane. In particular, in Fig. 6 the mass spectrum corresponding to the GC peaks is reported. The fragments with weights 62 (DMP molecular weight) and 31 (H<sub>3</sub>C–O– fragment) typical of DMP fragmentation are clear.

Calibration of the quantitative analytical method for DMP was not carried out because of safety problems (the pure compound is a

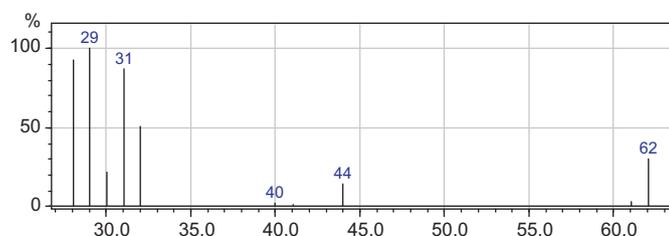


Fig. 6. Mass spectrum of the significant peak detected during the GC–MS analyses.

powerful explosive extremely sensitive to heat or shock, so it is not commercially available) and because of the explorative character of the work. For this reason the quantitative results in this work are analyzed in terms of area of the two GC detected peaks (RT 7.2 and 7.4 min) and of produced moles of carbon dioxide.

The following reaction mechanism can be hypothesized for DMP production:



In reaction (1) the catalyst Fe(II) is oxidized by hydrogen peroxide to Fe(III) producing the hydroxyl radical  $\text{OH}^\bullet$ . This high reactive species attacks methane molecules (reaction (2)) producing the methyl radical  $\text{CH}_3^\bullet$  that reacts with the oxygen contained in the reaction environment [28] giving the methyl peroxide radical in reaction (3). Finally, the methyl peroxide radical could react with another methyl peroxide radical (4) giving DMP and  $\text{O}_2$ . On the basis of the hypothesized mechanism, one DMP molecule is produced by the combination of two methane molecules.

DMP production in mild operating conditions could be interesting considering the results reported in literature on liquid phase partial oxidation of methane where, to activate the methane molecule, a very aggressive medium (concentrated acid) was used [3,13–20] obtaining sulphonate methane and methane ester ( $\text{CH}_3\text{OSO}_3\text{H}$ ,  $\text{CF}_3\text{COOCH}_3$ ) as main products.

Results of the present work show that the C–H bond of the methane molecule was broken by working in a really mild condition ( $T = 25^\circ\text{C}$ ,  $P = 0.4\text{ MPa}$ ) and by using water as reaction media, with the advantages that such choice involves on many aspects before mentioned. DMP can be converted to methanol through thermal decomposition [29,30], photocatalysis [31,32] or hydrogenation [33]. By using hydrogenation two moles of methanol can be potentially obtained from a mole of DMP, with potential advantages in terms of methane storage and then methanol productivity.

### 3.3. Partial oxidation of methane in liquid phase in the integrated membrane system

The batch reactor was modified to connect it with a membrane contactor containing different cylindrical membranes (polypropylene membrane fibers; polypropylene capillary membranes;

Table 4

Amount of methane solubility/dispersion in the aqueous phase of the membrane contactor assembled with polypropylene fibers operated at three different recirculation flow rates ( $P_{\text{CH}_4} = 0.1\text{ MPa}$ ;  $T = 25^\circ\text{C}$ ).

Flow rate ( $\text{mL min}^{-1}$ )	Re	$[\text{CH}_4]$ ( $\text{mol L}^{-1}$ )
110	326	$(4.08 \pm 0.27) \times 10^{-3}$
190	563	$(3.90 \pm 0.38) \times 10^{-3}$
273	808	$(4.26 \pm 0.15) \times 10^{-3}$

Table 5

Amount of methane solubility/dispersion in the aqueous phase of the membrane contactor assembled with polypropylene fibers operated at three different pressures (flow rate =  $110\text{ mL min}^{-1}$ ;  $T = 25^\circ\text{C}$ ).

$P_{\text{CH}_4}$ (MPa)	$[\text{CH}_4]$ ( $\text{mol L}^{-1}$ )
0.1	$(4.08 \pm 0.27) \times 10^{-3}$
0.25	$(4.47 \pm 0.08) \times 10^{-3}$
0.4	$(7.66 \pm 1.37) \times 10^{-3}$

ceramic tubular membrane). The integrated membrane system was preliminarily characterized by evaluating methane solubilisation. These tests were carried out by recirculating ultrapure water in the integrated membrane system (see scheme of Fig. 2).

After that the catalytic behaviour of the catalytic systems was tested.

#### 3.3.1. Membrane contactor assembled with polypropylene membrane fibers

3.3.1.1. Solubility tests. The influence of some operating parameters on methane solubility by transferring it from gas to the aqueous phase across the membrane was studied.

The first considered parameter was the recirculation flow-rate of the liquid phase, that influences the fluid-dynamics in the membrane contactor. In particular, with increasing recirculation flow rate inside the membrane increases the tangential shear on gas bubbles formed at membrane/aqueous phase interface (see zoom in Fig. 2). As a consequence formation of low size gas micro-bubbles could be promoted, thus increasing methane solubility/dispersion.

The solubility/dispersion tests at different recirculating flow rate were carried out employing a methane pressure of 0.1 MPa and temperature of  $25^\circ\text{C}$ , by changing the rpm of the peristaltic pump (1.5, 2 and 2.5 rpm) corresponding to three different flow rates ( $110$ ,  $190$  and  $273\text{ mL min}^{-1}$ ). The calculated Reynolds number (Re) were 326, 563 and 808, respectively, corresponding to a laminar regime in all the flow rate range, thus only the tangential shear increased.

Obtained results, summarized in Table 4, show no practical differences in methane concentration in the aqueous phase in the considered flow rate range. Thus successive tests were carried out at  $110\text{ mL min}^{-1}$ , corresponding to the lower value of rpm of the peristaltic pump, avoiding pipe failure by mechanical stress in pump head.

Obtained methane concentration in the aqueous phase ( $(4.08 \pm 0.3) \times 10^{-3}\text{ mol L}^{-1}$ ) was about equal to that one obtained by operating in batch mode at a pressure of 0.4 MPa ( $(4.58 \pm 0.4) \times 10^{-3}\text{ mol L}^{-1}$ ). This result confirms that use of a membrane contactor improves methane amount in the aqueous phase: indeed, by operating with lower pressure, compared to the batch, the same methane concentration was obtained. Besides, at same pressure (0.1 MPa) methane concentration was twice by using the membrane contactor compared to the value obtained in batch. Thus, it can be affirmed that use of a membrane contactor promotes the dissolution/dispersion of gaseous phase as micro-bubbles permitting the achievement of improved reaction conditions.

The other operating parameter studied was methane pressure feeding. It was expected, according to the Henry law that methane concentration in the aqueous phase increases with its pressure.

Obtained results, summarized in Table 5, show an improved methane concentration by operating at 0.4 MPa. This value is quite two times that one obtained in the batch system confirming the advantage to use a membrane contactor.

3.3.1.2. Catalytic tests. Considering the inside diameter (0.40 mm) of the fibers, an inline filter was necessary in the system, upstream

**Table 6**

Comparison of catalytic tests in the integrated membrane system, assembled with polypropylene fibers, and in the batch system (flow rate = 110 mL min<sup>-1</sup>; [H<sub>2</sub>O<sub>2</sub>] = 54 mmol L<sup>-1</sup>; T = 25 °C; [CH<sub>3</sub>COOH] = 30.7 mmol L<sup>-1</sup>).<sup>a</sup>

P <sub>CH<sub>4</sub></sub> (MPa)	Inline filter	[Fe <sup>2+</sup> ] (mmol L <sup>-1</sup> )	Peak area (7.2 min)	CO <sub>2</sub> production (mol g <sub>cat</sub> <sup>-1</sup> )
0.1	Yes	2.70	2.55	1.54 × 10 <sup>-2</sup>
0.4	Yes	2.70	7.68	3.06 × 10 <sup>-2</sup>
0.4	No	1.35	4.75	2.23 × 10 <sup>-2</sup>
Batch system (0.4 MPa)		2.70	18.27	6.18 × 10 <sup>-2</sup>

<sup>a</sup> All values referred to 330 min.

the membrane contactor, to avoid fiber blockage by the presence in solution of aggregated catalyst particles. Indeed, the Fe(II) catalyst, which was completely soluble at the operating pH (2.98), was oxidized to Fe(III) (see reaction (1)) during the reaction and precipitated and aggregated as hydroxide considering that solubility product of Fe(III) hydroxide is  $K_{sp} = 6.31 \times 10^{-38}$ . Formation of aggregates was observed when hydrogen peroxide was added to the aqueous solution containing the catalyst and the acid: instantaneously the turbidity of solution increased.

Three series of tests were carried out in this system: i) catalytic tests at 0.1 MPa; ii) catalytic tests at 0.4 MPa; iii) catalytic tests at 0.4 MPa without the inline filter, by decreasing the catalyst amount (1.35 mmol L<sup>-1</sup>) in order to avoid fiber blockage.

Obtained results are summarized in Table 6 where CO<sub>2</sub> production is normalized with respect to catalyst amount (g<sub>cat</sub>) because of different volumes of liquid contained in the batch and in the integrated membrane systems. The areas of the peaks at 7.4 min are not reported in the table because they were negligible.

The overall results were better at 0.4 MPa with inline filter and operating with the membrane contactor because of the higher ratio peak area/CO<sub>2</sub> production. Elimination of inline filter did not increase system performance because the needs to operate with lower catalyst amount.

Comparing the results obtained in the integrated membrane system and in the batch system (see Table 6) a lower catalytic performance is observed by using the membrane contactor owing to massive deposition of catalyst on the surface of inline filter thus decreasing the catalyst amount dispersed in the liquid phase. Despite the lower CO<sub>2</sub> production (3.06 × 10<sup>-2</sup> mol g<sub>cat</sub><sup>-1</sup> versus 6.18 × 10<sup>-2</sup> mol g<sub>cat</sub><sup>-1</sup>), obtained in the integrated membrane system, the lowest peak area at 7.2 min indicates the batch system as the best in this case.

### 3.3.2. Membrane contactor assembled with polypropylene capillary membranes

On the basis of previous results it was decided to use membranes with higher inside diameter, thus avoiding blockage in membrane contactor.

Polypropylene capillary membranes with inside diameter 1.7 mm were used to build the membrane contactor.

Solubility/dispersion of methane and the catalytic tests were carried out at recirculation flow rate of 110 ml min<sup>-1</sup>, corresponding in this case to a Reynolds number of 345 (laminar regime).

**3.3.2.1. Solubility tests.** The solubility/dispersion tests in this membrane contactor were carried out at three methane pressures (0.1, 0.25 and 0.4 MPa). Results showed that methane concentration in the liquid phase did not change with the feed pressure (concentration values were between 4.24 × 10<sup>-3</sup> and 4.33 × 10<sup>-3</sup> mol L<sup>-1</sup>). These values were very similar to that ones obtained in the batch system.

**3.3.2.2. Catalytic tests.** Considering the results obtained with the previous catalytic membrane contactor the feeding pressure of methane was 0.4 MPa.

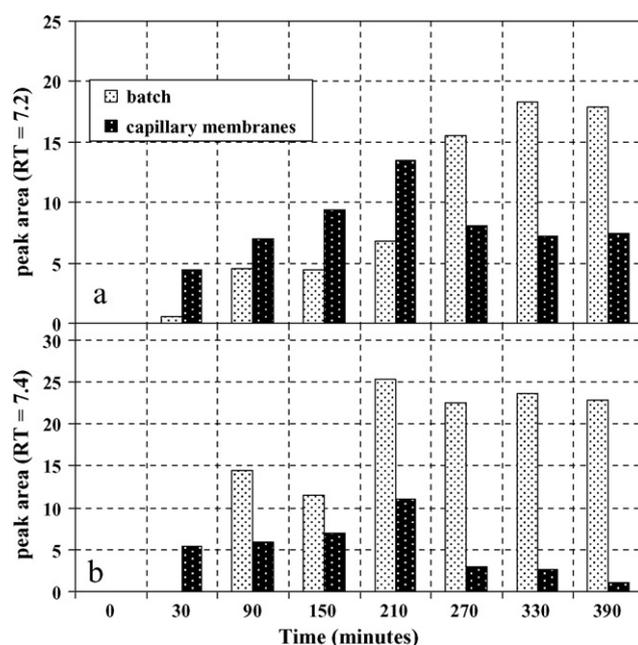
Obtained results, summarized in Fig. 7 (a and b), show a higher catalytic activity with respect to the previous catalytic contactor (see Table 6) but the performance is lower than the batch system.

By analyzing some samples at GC–MS, formation of propylene oxide in addition to DMP was observed; this could be caused by degradation of the polypropylene capillary membranes by the oxidizing agents in the reactive medium. This behaviour was not observed in the case of the polypropylene fibers, probably because of the lowest catalyst amount dispersed in the liquid phase and its deposition on inline filter.

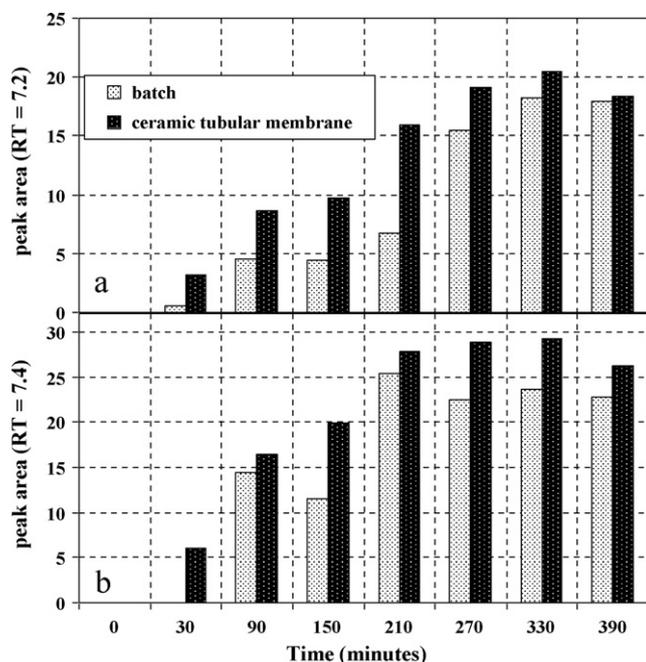
The observed (parasite) oxidative process of the polypropylene membrane could explain the lowest catalytic performance with respect to the batch system and the trend (increasing till 210 min, and then decreasing) of the areas of the two peaks at 7.2 and 7.4 min obtained using the membrane contactor. It can be hypothesized that a certain amount of hydroxyl radicals produced by reaction (1) attacked the polymeric matrix instead of methane reducing the aggressive power of the reaction medium. Thus, further oxidation of the partially oxidized products (e.g., DMP) to CO<sub>2</sub> occurred instead of methane activation, because it is thermodynamically favoured, and the two peaks area decreased.

### 3.3.3. Membrane contactor assembled with a ceramic tubular membrane

To avoid membrane degradation, observed employing the polypropylene capillary membranes, a commercial membrane con-



**Fig. 7.** Comparison of the areas versus time for the peaks with retention time of 7.2 (a) and 7.4 (b) min in the catalytic tests in the batch system and in the integrated catalytic membrane system assembled with polypropylene capillary membranes ([Fe<sup>2+</sup>] = 2.70 mmol L<sup>-1</sup>; [H<sub>2</sub>O<sub>2</sub>] = 54 mmol L<sup>-1</sup>; [CH<sub>3</sub>COOH] = 30.7 mmol L<sup>-1</sup>; T = 25 °C; P<sub>CH<sub>4</sub></sub> = 0.4 MPa).



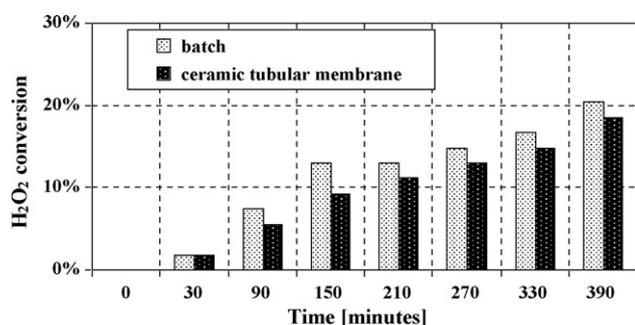
**Fig. 8.** Comparison of the areas versus time for the peaks with retention time of 7.2 (a) and 7.4 min (b) in the catalytic tests in the batch system and in the integrated catalytic membrane system assembled with the ceramic tubular membrane ( $[\text{Fe}^{2+}] = 2.70 \text{ mmol L}^{-1}$ ;  $[\text{H}_2\text{O}_2] = 54 \text{ mmol L}^{-1}$ ;  $[\text{CH}_3\text{COOH}] = 30.7 \text{ mmol L}^{-1}$ ;  $T = 25^\circ\text{C}$ ;  $P_{\text{CH}_4} = 0.4 \text{ MPa}$ ).

tactor (Membralox<sup>®</sup>) assembled with a ceramic membrane, inside diameter 0.7 cm, was tested.

Solubility and catalytic tests were carried out at  $110 \text{ ml min}^{-1}$  recirculation flow rate, corresponding to a Reynolds number of 335 (laminar regime).

**3.3.3.1. Solubility tests.** Results of solubility tests at three methane pressures (0.1, 0.25 and 0.4 MPa) showed that methane concentration did not increase with the pressure also in this case (methane concentrations between  $4.21 \times 10^{-3}$  and  $4.25 \times 10^{-3} \text{ mol L}^{-1}$ ). Despite methane concentration in the aqueous phase is very similar to that one obtained in the batch system at 0.4 MPa, continuous feeding and dispersion, thus high gas/liquid interfacial area, should give higher reaction rate.

**3.3.3.2. Catalytic tests.** The catalytic performance, employing the contactor assembled with a ceramic tubular membrane, was the best of the present work. As evidenced in Fig. 8 (a and b) the areas of the two peaks are higher than that ones obtained in the batch for



**Fig. 9.** Comparison of the  $\text{H}_2\text{O}_2$  conversion in the tests in the batch system and in the system integrated with the membrane contactor assembled with the ceramic tubular membrane ( $[\text{Fe}^{2+}] = 2.70 \text{ mmol L}^{-1}$ ;  $[\text{H}_2\text{O}_2] = 54 \text{ mmol L}^{-1}$ ;  $[\text{CH}_3\text{COOH}] = 30.7 \text{ mmol L}^{-1}$ ;  $T = 25^\circ\text{C}$ ;  $P_{\text{CH}_4} = 0.4 \text{ MPa}$ ).

**Table 7**

Comparison of catalytic tests in the integrated membrane system, assembled with the ceramic tubular membrane, and in the batch system (flow rate =  $110 \text{ mL min}^{-1}$ ;  $[\text{Fe}^{2+}] = 2.70 \text{ mmol L}^{-1}$ ;  $[\text{H}_2\text{O}_2] = 54 \text{ mmol L}^{-1}$ ;  $[\text{CH}_3\text{COOH}] = 30.7 \text{ mmol L}^{-1}$ ;  $T = 25^\circ\text{C}$ ;  $P = 4 \text{ MPa}$ ).<sup>a</sup>

	Batch system	Ceramic tubular membrane
Peak area (7.2 min)	18.27	20.45
Peak area (7.4 min)	23.68	29.22
$\text{CO}_2$ production ( $\text{mol g}_{\text{cat}}^{-1}$ )	$6.18 \times 10^{-2}$	$1.03 \times 10^{-2}$
$\text{H}_2\text{O}_2$ conversion	16.67%	14.81%
Apparent selectivity (7.2 min)	2030	2556
Apparent selectivity (7.4 min)	2631	3653

<sup>a</sup> All values referred to 330 min.

all the time course of the test. GC–MS analyses confirmed formation of DMP as the main partial oxidation product of methane.

The membrane system and the batch were also compared in terms of oxidant conversion which was the limiting reagent while methane was in saturation condition. The results, reported in Fig. 9, evidence higher oxidant efficiency obtained using the ceramic membrane. Indeed a lower percentage of hydrogen peroxide was consumed, despite higher areas of the two peaks.

A further comparison between the two systems was also done introducing an apparent selectivity defined as area of each peak divided by the moles of hydrogen peroxide consumed. The overall results, summarized in Table 7, evidenced higher apparent selectivity employing the ceramic membrane contactor because it enhanced system performance by decreasing the amount of organic substrate ( $\text{CH}_4$ ) oxidized to  $\text{CO}_2$ . This higher selectivity must be probably ascribed to the presence of the ceramic membrane contactor which expresses functions as: i) favors methane dispersion in the oxidant aqueous phase; ii) increases the gas/liquid interfacial area; iii) does not interact with the oxidizing reaction environment; iv) catalyst particles can be freely recirculated; v) increase the probability of methane attack owing to its relatively high amount in the liquid compared to the products of its partial oxidation.

#### 4. Conclusions

A study and testing of an integrated catalytic membrane system for the liquid phase partial oxidation of light hydrocarbons such as methane in mild operating conditions (low temperature, low pressure, reaction medium not aggressive on materials) has been carried out.

Catalytic tests, performed in a batch system, using the Fenton reagent ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ), permitted to study the influence of some operating conditions (catalyst amount, oxidant amount, temperature and pH) on system performance. Best results were obtained by using the following operating conditions:  $[\text{Fe}^{2+}] = 2.70 \text{ mmol L}^{-1}$ ;  $[\text{H}_2\text{O}_2] = 54.0 \text{ mmol L}^{-1}$ ; temperature =  $25^\circ\text{C}$ ; pH = 2.98 ( $[\text{acetic acid}] = 30.7 \text{ mmol L}^{-1}$ ).

GC–MS analyses evidenced only dimethyl peroxide ( $\text{H}_3\text{C}-\text{O}-\text{O}-\text{CH}_3$ ) as product of the partial oxidation of methane.

Different membranes were tested to assemble the integrated membrane contactor observing that membrane size and material type influence system performance. Best results were obtained employing a ceramic tubular membrane working as gas–liquid phase contactor. Such a system avoided the problems related to membrane fouling and degradation, and permitted to obtain the best catalytic activity observed in the present work maximizing the apparent selectivity and minimizing the oxidation of methane to  $\text{CO}_2$ . However, use of different membrane materials or morphology for assembling the membrane contactor and the use of specific catalysts could improve the catalytic performance of the system.

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