Methane Conversion into Higher Hydrocarbons in MR

by Angelo Basile, Luca Paturzo, Antonino Vazzana, Enrico Drioli

In this investigation, a dense Pd/Ag (25% Ag w/w) Membrane Reactor (MR) and a Traditional Reactor (TR) are analysed referring to experimental data over Ru/Al_2O_3 catalyst. The experimental results of MR are compared with the experimental results of TR and with results from other authors. The effect of reaction temperature at different exposure times was considered.

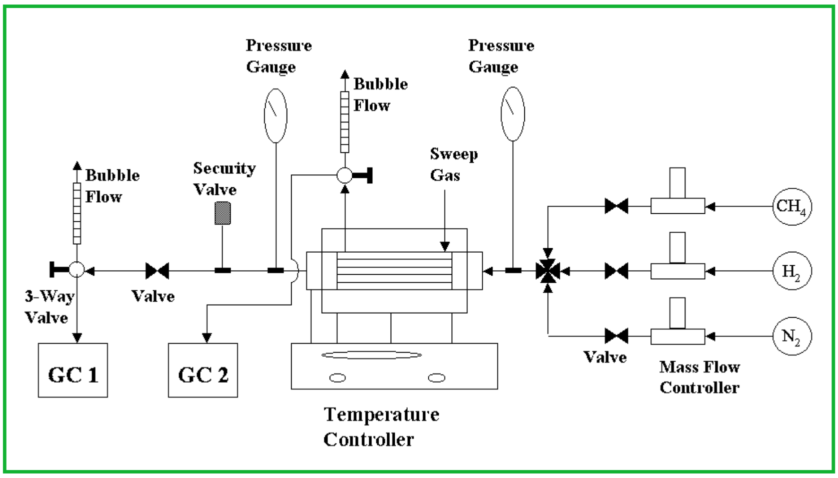

Figure 1 - Scheme of the laboratory plant using MR

Direct methane conversion into higher hydrocarbons is a thermodynamically-constricted problem: in fact, it can only take place at temperature values above 1200 K [1]; at this temperature, for example, considering methane as reactant without catalyst, graphite carbon is more stable than hydrocarbons such as ethylene.

One of the exploited ways to overcome the thermodynamic constriction is the oxidative coupling of methane [2-4], which also results in the production of water: unfortunately, oxygen reacts with methane giving thereby carbon oxides, so the reaction selectivity is decreased; further, this kind of process still requires high temperatures (650÷800 °C).

Another route for producing lighter hydrocarbons from methane uses an indirect way: methane conversion into syngas and subsequent Fischer-Tropsch synthesis; however, this way is not commercially useful [5].

In order to increase catalyst lifetime and reaction selectivity, low temperatures would be needed. In fact, some authors demonstrated that methane conversion into higher hydrocarbons can occur at low temperature if methane is activated. The overall process can be viewed as a 2-step sequence: methane decomposition (at higher temperature) and subsequent hydrogenation (at constant or lower temperature). For what concerns the first step (i.e. methane chemisorption and its decomposition on the catalyst surface) several studies carried out until 1974 were summarised by Frennet [6] and later by Pitchai and Klier [7].

The reaction system can be carried out in two different ways: isothermal or non-isothermal one. In the last case, methane deposition at high temperature is followed by hydrogenation at low temperature. For what concerns the isothermal way, Belgued *et al.* [8] produced lighter hydrocarbons (from C_2 to C_7, saturated form) from methane at a constant temperature of 250 °C and atmospheric pressure: isothermal cycles were carried out by exposing catalyst surface (Pt supported) first to the methane feed stream and then to a pure hydrogen stream; in particular, they produced hydrogen and ethane in the first step and then higher hydrocarbons until C_7 in the second step. Later, the same authors [9] used Ru as catalyst, but no ethane was produced in the first step; however, higher hydrocarbons until C_7 were produced in the second step, in particular during the first 4-5 seconds: ethane was the most produced species. Further, the same scientists [10] demonstrated that hydrogen removal in the first step gives higher yields in higher hydrocarbons. In regard to the non-isothermal way, Koerts *et al.* [11] carried out the first step using diluted methane at 450 °C and then the second step at 100 °C: only 12% of the carbonaceous decomposed species was hydrogenated to ethane and traces of propane.

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Table 1 - Main literature works for methane conversion into hydrogen and higher hydrocarbon using a Ru catalyst

Authors	*Reactor type*	*Catalyst*	*Process way*	*Feed*	
				1st Step	*2nd Step*
Koerst *et al.* (1991)	Traditional Reactor	300 mg 5% Ru/SiO_2	Not Isothermal	CH_4/He T=100-500 °C	H_2 T~100 °C
Belgued *et al.* (1996)	Traditional Reactor	100 mg 5% Ru/Al_2O_3	Isothermal	CH_4 T=80-200 °C	H_2 T=80-200 °C
Garnier *et al.* (1997)	Membrane Reactor	1 g 5% Ru/Al_2O_3	Not Isothermal	CH_4/Ar T=200-500 °C	H_2/Ar T=100-120 °C

Moreover, Koerst *et al.* [12] found that Ru and Co are more selective for the formation of higher hydrocarbons with respect to Rh, Ir, Pt and Ni; the same authors confirm that alumina support gives better results than silica support. Further, Solymosi *et al.* [13] found that Rh and Pd are the most active catalytic metals for methane decomposition and above 423 K this step takes place with hydrogen and ethane production.

Both ways did not produce insatured hydrocarbons and they are in agreement with the experimental evidence that at temperature above 180 °C ethane is decomposed producing hydrogen [14], so short contact time and low temperature are needed in the second step.

The objective of this investigation is to apply a palladium membrane reactor to this reaction system.

A membrane reactor is an engineering device that offers the possibility to overcome the thermodynamic limitations giving the possibility to attain a high methane conversion at lower temperature. In fact, a membrane reactor combines the separation properties of membranes with the typical characteristics of catalytic reactions [15-20].

Referring to the transformation of methane into more useful products, the membrane reactor, by selectively removing one of the products (generally hydrogen) from reaction mixture, was already employed in improving the conversion of CH_4 by means of steam reforming [21-23], dry reforming [24-25] and partial oxidation reactions [26-30].

The application of a Pd-based membrane reactor to this reaction system could improve the overall methane conversion at a given temperature; on the other hand, it is possible to obtain the same amount of decomposed methane at lower temperature with respect to a traditional reactor, so the total yield in lighter hydrocarbons increases, as reported by Garnier *et al.* [1].

For the reaction object of this study we refer to Garnier *et al.* They used a Pd/Ag (23% Ag w/w) membrane reactor for hydrogen removal in the first step, using Ru/Al_2O_3 (5% Ru w/w, surface area=250 m^2/g) as catalyst; at 500 °C methane conversion in the membrane reactor was about 100%, instead of the corresponding value for the traditional reactor, which was about 85%. The maximum difference in methane conversion between the two kinds of reactor was 50% at 300 °C: 65% for membrane reactor against 15% for traditional reactor. Moreover, the same methane conversion can be obtained at lower temperature in membrane reactor.

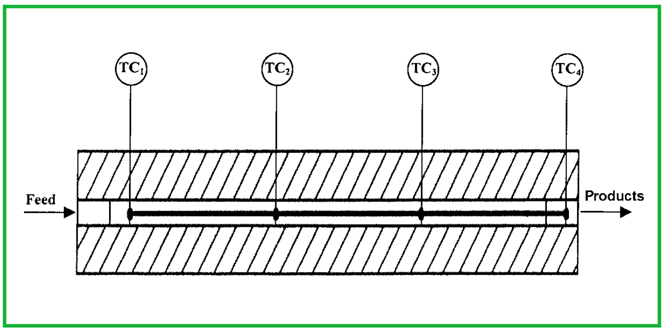

Figure 2 - Scheme of the Traditional Reactor

Table 1 shows the main literature works for methane conversion into hydrogen and higher hydrocarbons using a Ru catalyst. The aim of this work is to produce lighter hydrocarbons using a dense Pd/Ag (25% Ag w/w) membrane reactor (MR). Experimental results are compared with the results obtained using a traditional reactor (TR) and with some literature data. Both of the suggested ways are followed.

Experimental setup

Reaction plant

Figure 1 shows a scheme of the laboratory plant.

The reactor feed is regulated by mass-flow controllers (Bronkhorst Hi-Tec Type E-5752, operating inlet pressure=4 bar rel), while outlet streams flow rates are measured by means of bubble flow-meters; gas compositions were determined by gas chromatograph (Perkin-Elmer Autosystem GC) using a TCD and a metal packed column, type Porapak-Q 50/80 (SS) 8 ft x 1/8 inch, with Ar as carrier gas at a flow rate of 8 ml/min. For what concerns the oven temperature, a ramp was adopted: 45 °C for 3 minutes, then an increase of 20 °C/min until 205 °C; this last value was held until the end of the analysis: the total analysis time was 12 minutes. Moreover, in order to determine gas composition of both permeate and retentate streams simultaneously, another gas chromatograph was used (Carlo Erba 4200), adopting a TCD and a metal

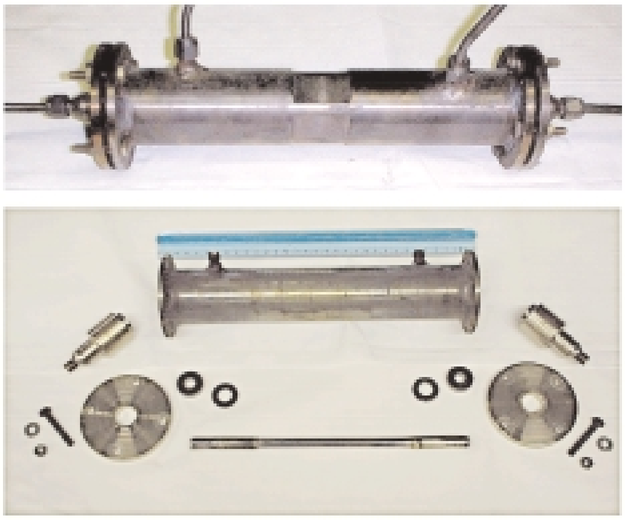

Figure 3 - Membrane Reactor module and related equipment

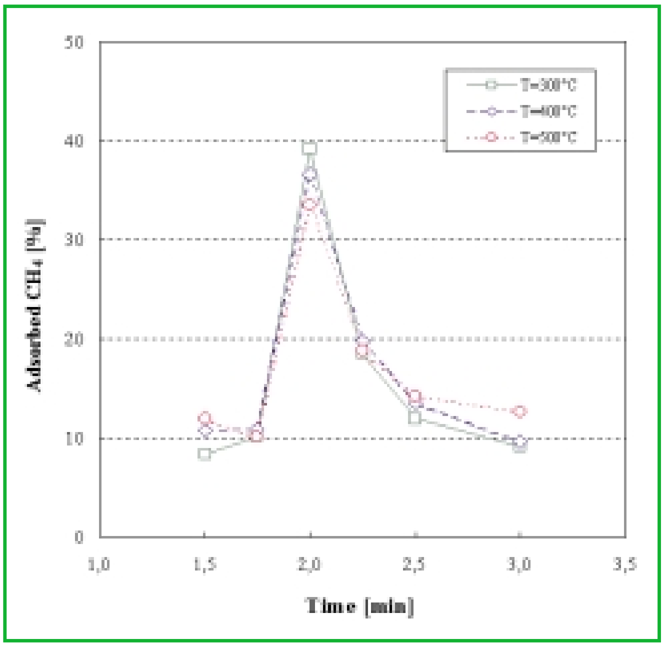

Figure 4 - Amount of adsorbed CH_4 versus time for TR, 1st step, Ru catalyst

packed column, type Carboxen 1000, T_{oven}=45 °C, carrier flow rate (Ar)=25 ml/min: in particular, this gas chromatograph was used to determine permeate composition when membrane reactor was investigated.

The heating system was a thermolyne heating tape (Sigma-Aldrich) connected to an automatic PID controller (EC 4-133, Nuova-Thermics). Both traditional and membrane reactors contained a multiple (4 points) thermocouple for temperature measurements.

Traditional and Membrane Reactors

Traditional reactor consists of a stainless steel tube, length=25 cm, *i.d.*=0.67 cm, wall thickness=1.25 cm. A scheme of this kind of reactor is reported in Figure 2.

Membrane Reactor (Figure 3) consists of a stainless steel module containing a dense Pd/Ag (25% Ag w/w) membrane produced by a rolling technique: membrane thickness=$50\cdot10^{-6}$ m, *i.d.*=1.0 cm, length=15 cm, with an internal movable ceramic support containing the catalyst. Operating constrictions for the membrane reactor system: temperature up to 400 °C and transmembrane pressure difference up to 2 ata.

Operating conditions

For both TR and MR the same experimental conditions were used. In the first step of the reaction, the analysis was developed mainly considering both MR and TR with a feed stream ratio CH_4/N_2=1/5, methane feed stream=10^{-3} mol/min, operating in a co-current flow configuration, N_2 sweep=$1.15\cdot10^{-2}$ mol/min (the last two conditions are valid only for MR). Temperature was in the range between 200 °C and 500 °C (400 °C for MR). Pressure values were close to the atmospheric condition. Exposure time was ranged between 1.5 min and 3 min. Pure hydrogen ($2.43\cdot10^{-3}$ mol/min) was fed in the second step for both reactors.

After each run, the catalyst was treated with pure hydrogen flow ($1.5\cdot10^{-3}$ mol/min) at 400 °C for 2 hours. Gas were used with purity percentage >99.995%.

Catalyst

Two kinds of catalyst (both furnished by Engelhard) were used:

- Ru/Al_2O_3 (0.5% Ru w/w) in cylindrical pellets: l=d=3 mm (surface area=90 m^2/g); both traditional and membrane reactor were packed with 1.03 g of this catalyst plus 6.0 g of glass spheres (2 mm diameter). Activation procedure was carried out by reducing this catalyst by means of a diluted hydrogen stream (20 ml/min, H_2/N_2=12/8), at 450 °C for 5h;
- Ni-5256 E 3/64" containing Ni highly dispersed on silica support; traditional reactor was packed with 6.0 g of this catalyst. Activation procedure was carried out by means of a nitrogen stream (290 ml/min) at 480 °C for 6 h.

Ways for carrying out the two steps reaction

Experimental tests were carried out at first in the traditional reactor. For what concerns the reaction system carried out using the Ru/Al_2O_3 catalyst, several feed conditions were adopted in order to find the right condition for gas chromatograph measurements: in fact, Perkin Elmer gas chromatograph sampling loop produced a considerable pressure drop because of its small internal diameter (this loop consists of a capillary stainless steel tube, volume=100 µl).

Feed ratio adopted by Garnier *et al.* [1] was used in the first step of the reaction process:

$$Q_{CH_4,in} = 2.26\ ml/min \Rightarrow x_{CH_4} = 2.52\%$$

$$Q_{N_2,in} = 87.56\ ml/min \Rightarrow x_{N_2} = 97.48\%$$

At time t=0 methane valve was open (nitrogen flow was always constant) and at time t=3 min it was closed and a run for GC analysis started.

Then, for the second step (hydrogenation), traditional reactor was cooled down to 100 °C (natural convection in about 24 hours).

No lighter hydrocarbons were detected, probably because of the high pressure drop given by the sampling loop: so, this phenomena could obstruct the tube way to the loop.

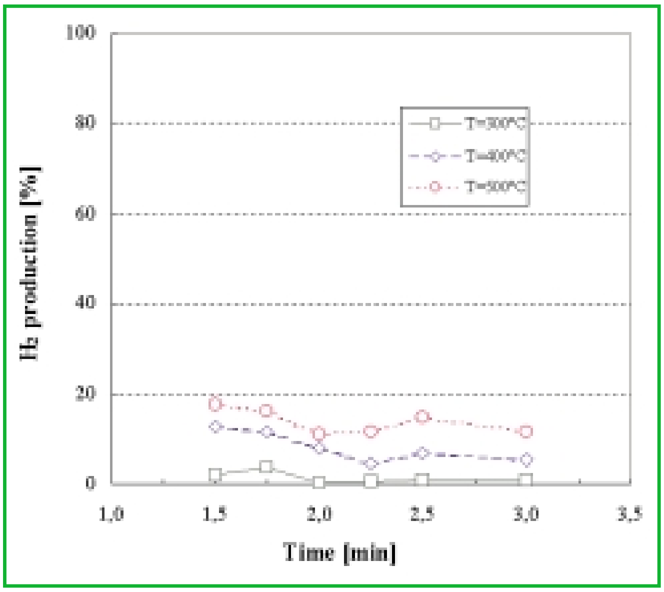

Figure 5 - Hydrogen production versus time for TR, 1st step, Ru catalyst

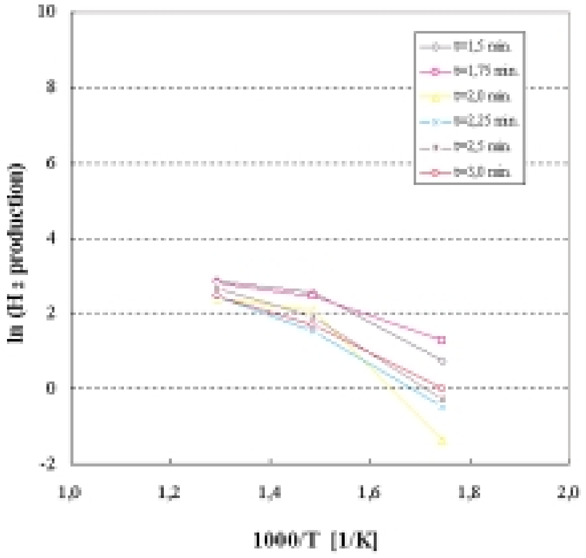

Figure 6 - Arrhenius plot for the produced hydrogen in the TR, for several time values, Ru catalyst

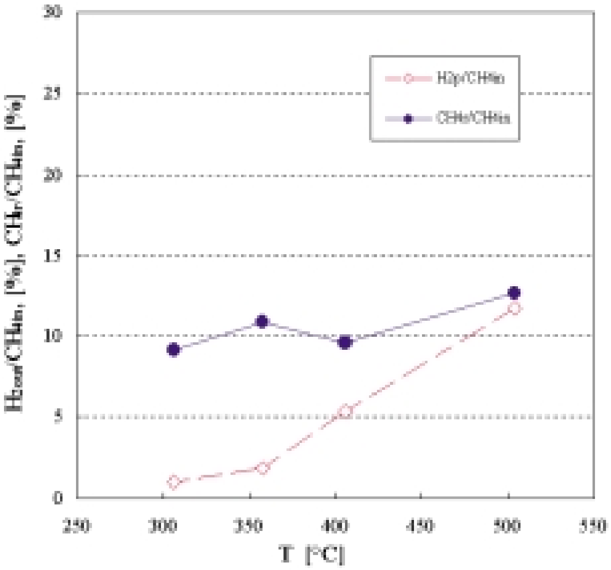

Figure 7 - Adsorbed methane and hydrogen produced versus temperature for TR, time=3 min, P=1 bar, 1st step, Ru catalyst

The best fluidodynamic found condition for the first step was the following:

$$Q_{CH_4,in} = 20.16\ ml/min \Rightarrow x_{CH_4} = 15.55\%$$

$$Q_{N_2,in} = 109.45\ ml/min \Rightarrow x_{N_2} = 84.45\%$$

The overall feed flow stream permitted to overcome the sampling loop pressure drop; in this way, methane mass flow controller was set near its maximum valve index, so it was not possible to feed pure methane at high flow rate to overcome the sampling loop pressure drop with this stream only.

Several ways for conducing the second step were adopted. They can be summarised as following:

1) Traditional reactor was cooled down to 100 °C by natural convection, and then at time t=0 this stream was fed:

$$Q_{H_2} = 64.3\ ml/min \Rightarrow x_{H_2} = 71.5\%$$

$$Q_{N_2,in} = 25.7\ ml/min \Rightarrow x_{N_2} = 28.5\%$$

At time t=3 min, a run to gas chromatograph started and, simultaneously, hydrogenation was carried out increasing temperature (heating rate about 17 °C/min) until 500 °C and successive runs were performed with the gas chromatograph.

2) This procedure was the same as the procedure 1, but a different reactor cooling was adopted: a quenching by means of water stream (cooling rate about 200 °C/min).
3) After rapid cooling (quenching) down to 80 °C, pure hydrogen was fed to the reactor with a flow rate ranged between 34 and 116 ml/min; gas chromatograph run started after 2 min. Then, temperature was increased until 500 °C (desorption) using nitrogen stream only: hydrogen was fed again when temperature reached values of 170 °C and 450 °C, corresponding to the desorption of higher hydrocarbons.
4) After rapid cooling down to room temperature, pure hydrogen was fed to the reactor as procedure 3 and the outlet stream was collected in a gas cylinder (volume=100 cm^3) until pressure value increased to 0.5 bar rel: then, a GC run started in order to analyse the cylinder content. Afterwards, desorption procedure was carried out like procedure 3.
5) After rapid cooling down to room temperature, pure hydrogen was fed to the reactor and then temperature was increased until 450 °C: during this process, all products were collected in a closed loop (including GC sampling loop) immersed in a liquid nitrogen bath; then, this bath was removed and a GC run started after products reached room temperature value and gas composition was homogeneous in the loop.
6) This last procedure is isothermal [9,10,14]: after the first step, hydrogen (54.6 ml/min) was fed into the reactor keeping constant the temperature value.

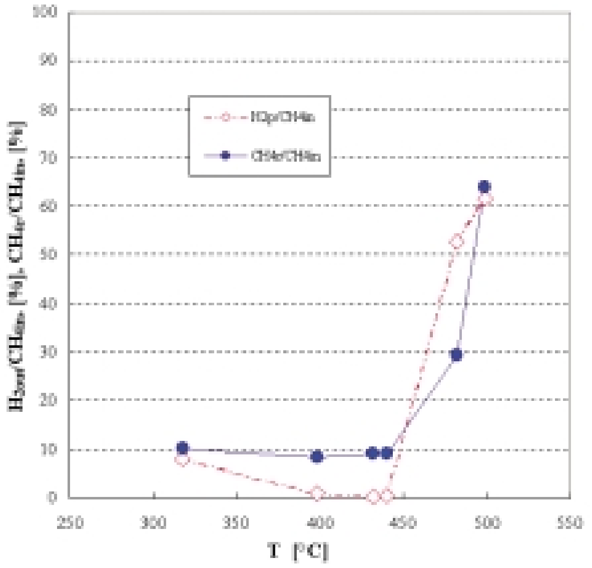

Figure 8 - Adsorbed methane and hydrogen production versus temperature for TR, time=3 min, P=1 bar, Ni-based catalyst

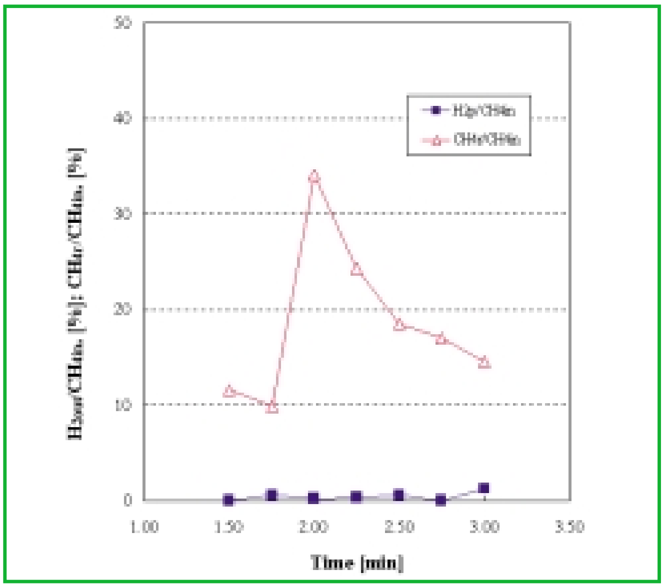

Figure 9 - Adsorbed methane and hydrogen production versus time for MR, T=300 °C, P=1 bar, Ru catalyst

For what concerns membrane reactor, procedure 6 was adopted in order to avoid thermal stress for the Pd/Ag membrane.

Moreover, for what concerns the reaction system carried out using the Ni catalyst, the first step was carried out using the best fluidodynamic condition that was possible to find; the second step was carried out as described in the previous procedure 5. This catalyst was only used for traditional reactor.

Definitions and Results Reproducibility

These definitions were used:

$$\text{adsorbed } CH_4\,\% = \frac{CH_{4\,in} - CH_{4\,out}}{CH_{4\,in}} \cdot 100 \quad \text{[dimensionless]}$$

$$H_2 \text{ produced } \% = \frac{H_{2\,out}}{CH_{4\,in}} \cdot 100 \quad \text{[dimensionless]}$$

$$C_2 \text{ yield } = \frac{\chi_{C_2} \cdot V_{loop}}{22{,}4}$$

(χ_{C_2} is the molar fraction of C_2 in the gas chromatograph sampling loop of volume V_{loop}). After each process, the catalytic bed was treated using hydrogen flow (34 ml/min) for 2 h at 400 °C in order to have total desorption of each species from the catalyst surface. This way led to a good results reproducibility.

Membrane Preparation and Characterisation

Pd/Ag membrane was produced by a lamination technique in Enea laboratories (Frascati, Italy); the starting material was a Pd/Ag (25% Ag w/w) commercial foil (127 mm thickness) purchased from Metalli Preziosi (Milano, Italy); details have been presented by Tosti *et al.* [31]. The apparent activation energy from hydrogen permeation experimental tests is E_a=10.3 kJ/mol, while the pre-exponential factor is $Pe_0=7.63 \cdot 10^{-8}$ mol·m/(s·m^2·Pa$^{0.5}$).

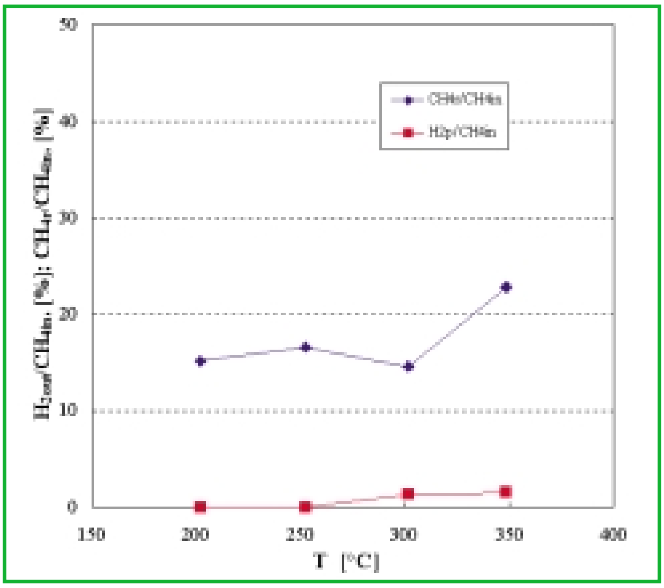

Figure 10 - Adsorbed methane and hydrogen production versus temperature for MR, time=3 min, P=1 bar

Results and Discussion

Traditional Reactor

Figure 4 shows the amount of adsorbed CH_4 versus time at three different temperatures for TR. It can be observed that the total amount of CH_4 is quite constant with temperature; for time >2.5 min the three curves seem to be different, probably because at high temperatures hydrogen desorption is faster and so fresh methane could be adsorbed. However, since the surface area of the catalyst (90 m^2/g) is lower with respect to the catalyst used from other authors [1, 12], catalytic surface can be rapidly covered at all the investigated temperatures. To be noted that each curve shows a maximum for time=2 min.

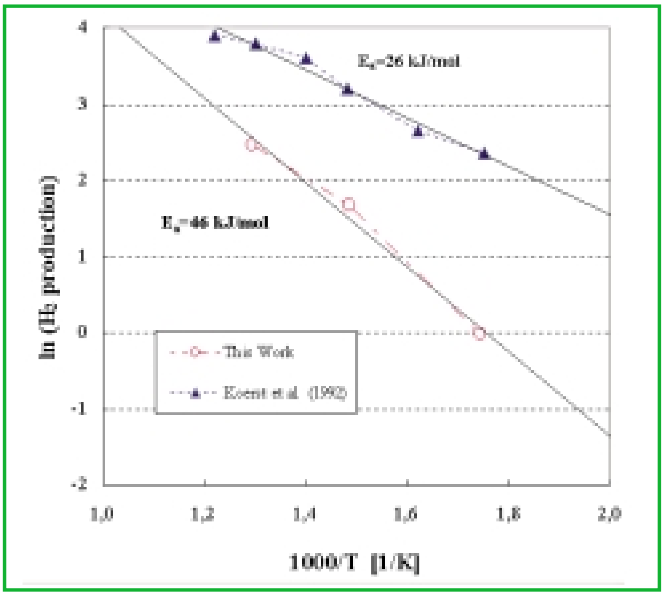

Figure 11 - Comparison between this work (1.03 g 0.5% Ru/Al_2O_3, surface area=90 m^2/g, time=3 min, feed stream consists of diluted methane [Q_{tot}=130 ml/min, 15.55% CH_4 in N_2]) and Koerst et al. *(300 mg 5% Ru/SiO_2, surface area=300 m^2/g, time=3min, feed stream consists of diluted methane [Q_{tot} = 45 ml/min, 0.5% CH_4 in He])*

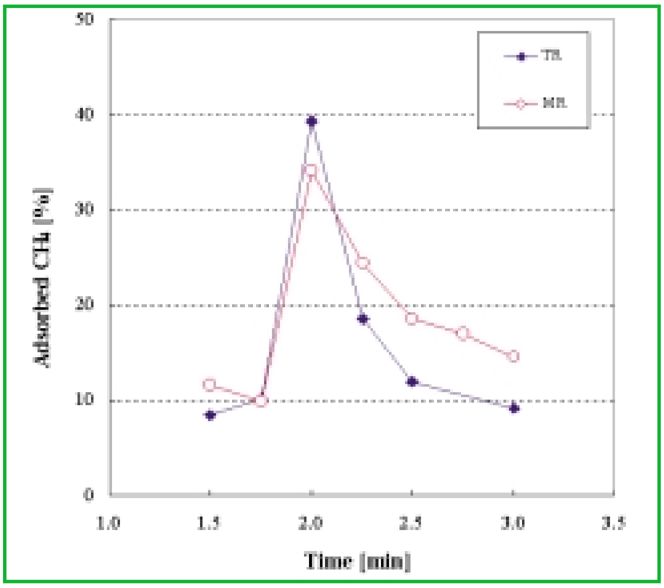

Figure 12 - Amount of adsorbed CH_4 versus time for TR and MR, T=300 °C, P=1 bar, Ru catalyst

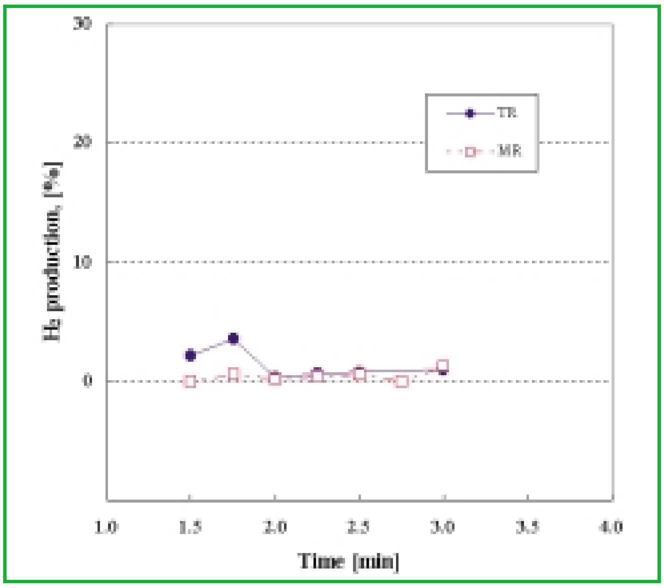

Figure 13 - Hydrogen production versus time: comparison between TR and MR, T=300 °C, P=1 bar, Ru catalyst

A specification is necessary for this data arrangement: each point is referred to a GC run started after the time reported in the horizontal axis, but each run was performed after a whole cycle of the process (i.e. first step+second step+catalyst reduction). To be noted that the behaviour of the total amount of adsorbed CH_4 would be increasing with increasing time, until the total covering degree of catalytic surface is reached.

With increasing temperature, the hydrogen production increases, as shown in Figure 5: it seems to depend on the different character of the deposited carbonaceous species on the catalyst surface.

This behaviour is in agreement with Koerst *et al.* [12]. Let's consider another kind of interpretation: if the total amount of adsorbed methane is quite constant with increasing temperature, probably at high temperature the amount of the decomposed methane is higher than the one at low temperature. In other words, it seems that the amount of decomposed methane (among the total adsorbed methane) increases with increasing temperature. The final answer to this problem can be found by carrying out specific analysis on the deposited species.

Figure 6 shows an Arrhenius plot for the hydrogen production, for several time values: this type of data arrangement is useful to confirm that the first step is an activated process. In fact, this is an activated process showing activation energy ranged between 25 and 60 kJ/mol [32-35].

Figure 7 shows the behaviour of adsorbed methane and hydrogen produced versus temperature for TR, time=3 min. Both curves are increasing with increasing temperature, but hydrogen production increases more rapidly than adsorbed methane.

These experimental results are related to the first step of the process (i.e. methane decomposition). No higher hydrocarbons were detected following the several procedures previously reported for the second step (i.e. hydrogenation). This is probably due to the low Ru percentage (0.5%) on the catalyst surface, compared with the value reported from other authors.

For what concerns the Ni-based catalyst, experimental results for the first step reaction are reported in Figure 8, in which both adsorbed methane and hydrogen production versus temperature are reported for TR, time=3 min, P=1 bar: for temperature up to 450 °C experimental values are lower than the ones related to the Ru catalyst and they are almost constant; for temperature above 450 °C, experimental values rapidly rise.

To be noted that Ni-based catalyst amount is almost 6 times the Ru-based one. No higher hydrocarbons were detected in the second step following the several procedures previously reported. This last result is in agreement with Kuijpers *et al.* [34], confirming that the only product of this kind of hydrogenation carried out between 30 °C and 450 °C is methane.

Membrane Reactor

The same experimental tests performed in the traditional reactor packed with Ru catalyst were used for the membrane reactor, but temperature did not exceed 400 °C, as previously cited.

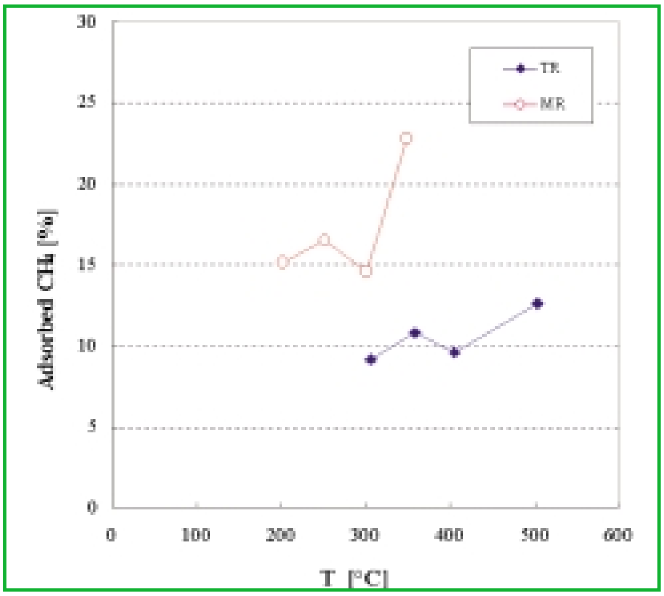

Figure 14 - Comparison between TR and MR in terms of adsorbed methane versus temperature, time=3 min, P=1 bar, Ru catalyst

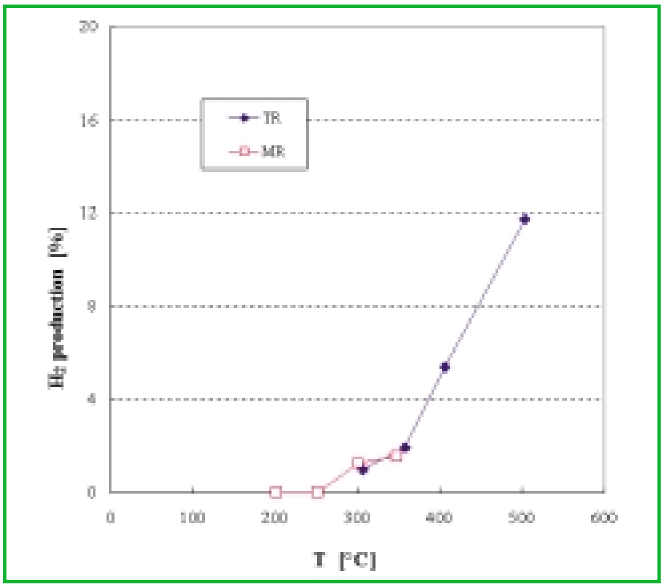

Figure 15 - Comparison between TR and MR in terms of hydrogen production versus temperature, time=3 min, P=1 bar, Ru catalyst

Figure 9 shows the behaviour of adsorbed methane and hydrogen production versus time for MR, T=300 °C and P=1 bar: this behaviour is similar to the one reported for TR, with a maximum value for time=2 min.

Figure 10 shows the behaviour of adsorbed methane and hydrogen production versus temperature for MR, time=3 min and P=1 bar: it can be observed that for temperature up to 250 °C hydrogen production is almost zero, even if adsorbed methane is 15%. The second step (hydrogenation) led to the formation of only ethane; this experimental result will be compared with results obtained by Belgued *et al.* [14].

Comparison between TR and MR and with Literature Results

By referring to time=3 min, experimental results for TR were compared with results obtained by Koerst *et al.* [12] in Figure 11. In this work, activation energy value is 46 kJ/mol, while in Koerst *et al.* [12] this value is 26 kJ/mol: so in both cases activation energy is in the range between 25 and 60 kJ/mol, as previously cited.

Figure 12 shows a comparison between TR and MR in terms of adsorbed CH_4 in the first reaction step at 300 °C versus time. It can be observed that the total amount of CH_4 deposited is higher in MR than in TR. For example, at 3 min CH_4 adsorbed is about 15% for MR and about 9% for TR. At 2 min there is a maximum CH_4 deposition (40% for TR and 34% for MR).

Figure 13 shows a direct comparison between TR and MR for what concerns hydrogen production: for time>2 min, the two curves seem to be identical. The contribute of permeate stream to the hydrogen production was evaluated by indirect way, using the Arrhenius expression with an average hydrogen molar fraction value in the lumen equal to the arithmetic average value between the inlet side (that is zero) and the outlet side (measured by Perkin Elmer GC).

Figures 14 and 15 show a comparison between TR and MR in terms of adsorbed methane and hydrogen production versus temperature. In particular, Figure 14 shows the behaviour of CH_4 adsorbed versus temperature for both TR and MR after 3 min. The values for MR are always higher than the ones for TR. For example, at 350 °C the adsorbed CH_4 is about 23% for MR and 11% for TR. Figure 15 shows that for temperature in the range 300÷400 °C the two curves are almost coincident: this is probably due to the indirect way used to determine the hydrogen produced in the MR.

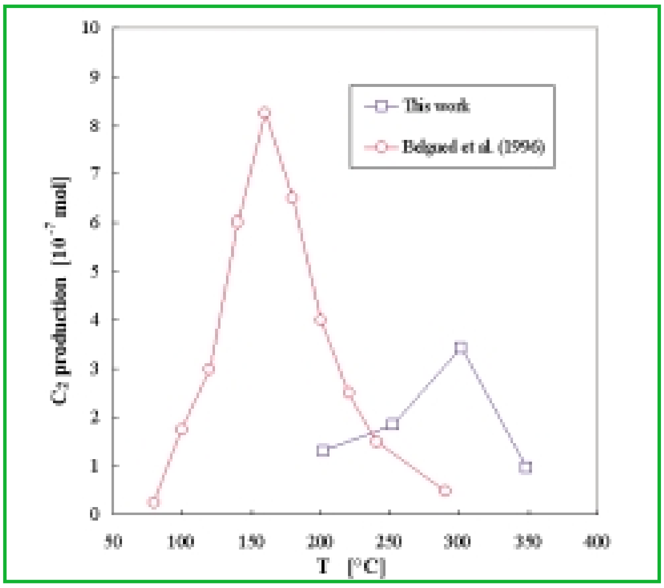

Figure 16 - Comparison between this work and Belgued et al. [14] in terms C_2 production versus temperature

Figure 16 offers a comparison between MR used in this work and a TR used by Belgued *et al.* [14]. However, results were obtained at different experimental conditions. For MR (used in this work), experimental conditions are: 1.03 g of catalyst (0.5% wt Ru/Al_2O_3), diluted methane (15.55%) fed in nitrogen (total feed stream=130 ml/min), pure hydrogen used in the second step (54.6 ml/min), exposure time=3 min, atmospheric pressure; for the TR (used by Belgued *et al.*), experimental conditions were the following: 100 mg of catalyst (5% wt Ru/SiO_2), pure methane fed in the first step (375 ml/min), pure hydrogen used in the second step (50 ml/min), exposure time=5 min, atmospheric pressure. Due to such different ex-

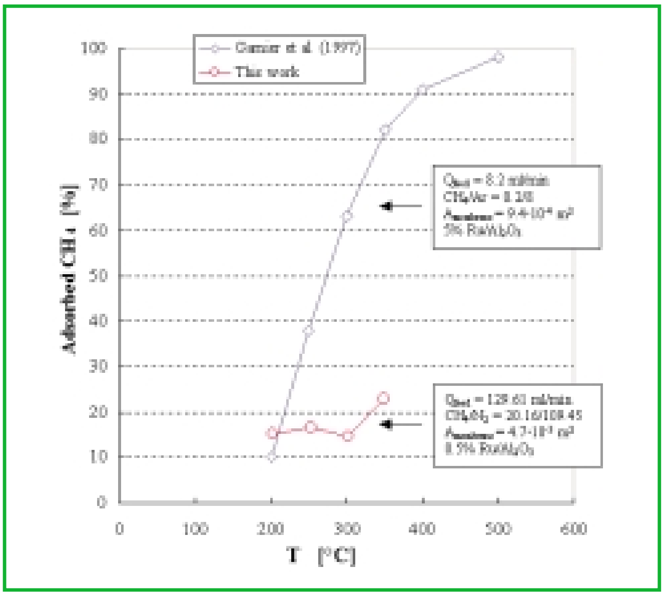

Figure 17 - Comparison between this work and Garnier et al. *[1] in terms of adsorbed methane versus temperature*

perimental conditions, it is quite difficult to get a direct comparison between the behaviours of the two kinds of reactor. However, both curves show a maximum but at different time values: about $8.5 \cdot 10^{-7}$ mol C_2 produced at 160 °C in Belgued *et al.* [14], instead of about $3 \cdot 10^{-7}$ mol C_2 produced at 300 °C in this work. The same authors reported the production of other higher hydrocarbons until C_6 of about 1 order of amount with respect to C_2 production, while in this work the only species produced was C_2: only one chromatogram reported the presence of C_3 (presumably) but this experimental result was not reproducible in other tentatives carried out at 300 °C with an exposure time of 3 min in the first step.

Using the TR in this work, it was not possible to detect lighter hydrocarbons in the outlet stream by using all the procedures described previously for the second step. Instead, by using the MR, C_2 was detected: this indicates that the presence of the membrane in the reaction system could change the catalytic behaviour of the reaction, and the hydrogen removal through the membrane increases the amount of adsorbed methane: so it is possible to produce in the MR a higher amount of lighter hydrocarbons from the same amount of methane fed in the TR.

A comparison between this work and Garnier *et al.* [1] in terms of adsorbed methane versus temperature for the membrane reactor is reported in Figure 17. Operating conditions of Garnier *et al.* are the following: 1 g 5% Ru/Al_2O_3 catalyst, surface area 250 m^2/g, time=3 min, feed=diluted methane (Q_{tot}=8.2 ml/min, CH_4/Ar=0.2/8), sweep gas flow rate=180 ml/min (Ar). To be noted that these conditions are different from the ones used in this work, so it is difficult to make a direct comparison between the two membrane reactor performances. To be noted that at 350 °C the adsorbed methane was 25% in this work versus 82% for Garnier *et al.* [1].

Conclusions

The experiments carried out in this study show that, using a Pd/Ag membrane reactor, it is possible to obtain adsorbed methane values greater than the ones obtained in a traditional reactor for the first step. An indirect consequence should be an increase of the yield in higher hydrocarbons. The maximum C_2 production was $3 \cdot 10^{-7}$ mol at 300 °C, the same order of magnitude of Garnier *et al.* [1], which reported $8.5 \cdot 10^{-7}$ mol C_2 produced at 160 °C. However, poor experimental results in terms of C_2 yields obtained in the second step are probably due to the low selectivity of the catalyst used: if compared with literature, this catalyst has Ru percentage 10 times lower. To confirm this aspect, Koerst *et al.* [12] produced higher hydrocarbons using a 10% Co supported catalyst, while using the same catalyst with a lower Co percentage (0.5% Co) they did not produce higher hydrocarbons. However, a higher amount of adsorbed methane was obtained in the MR with respect to the TR, and the first kind of reactor gave a detectable amount of C_2.

In a future work, an investigation would be carried out by using a catalyst with a higher Ru percentage, since many authors are in accord to the fact that this transition metal has the best properties for producing higher hydrocarbons from methane in a two step process.

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