

# Production and purification of hydrogen-methane mixtures utilized in internal combustion engines

M. C. Annesini<sup>1</sup>, R. Augelletti<sup>1</sup>, M. De Falco<sup>2</sup>, S. Frattari<sup>1</sup>,  
F. Gironi<sup>1</sup> & M. A. Murmura<sup>1</sup>

<sup>1</sup>*Department of Chemical Engineering Materials Environment,  
Sapienza University of Rome, Italy*

<sup>2</sup>*University Campus Biomedico of Rome, Italy*

## Abstract

Blends of hydrogen and methane (hythane) with 20–25% of H<sub>2</sub> can be used in internal combustion engines in order to reduce the CO<sub>2</sub> and unburned hydrocarbon emissions and greenhouse effect. In this paper we show that solar steam reforming of natural gas at 500–550°C is a suitable process to produce such a mixture, but the reformed gas must be purified to reduce the CO<sub>2</sub> concentration to less than 3%. To this aim, a first Pressure Swing Adsorption (PSA) unit, which uses activated carbon as adsorbent material, is proposed to remove carbon dioxide, with H<sub>2</sub> and CH<sub>4</sub> recovery of about 99 and 43%, respectively; to enhance CH<sub>4</sub> recovery, a second PSA unit, using carbon molecular sieve (CMS) as adsorbent, can be introduced. The whole suggested process produces an enriched methane mixture with a hydrogen content of 25%, with an energy consumption of about 270 kJ/kg of hydro-methane, mainly due to the electrical energy required for gas compression and vacuum pumps.

*Keywords: hydrogen methane mixtures, solar steam reforming, pressure swing adsorption.*

## 1 Introduction

Environmental problems due to the extensive use of fossil-derived energy in our societies are leading to devote research and innovation efforts to the study of novel technologies for de-carbonizing the fuels, thus reducing the carbon dioxide (CO<sub>2</sub>)



emissions and mitigating the GreenHouse effect. The most decarbonized fossil fuel is the methane, with a 75% wt. of carbon and 25% wt. of hydrogen which is extensively used in industrial and production processes. The end of the line of the energy decarbonation process is hydrogen itself, an energy vector which does not contain carbon and, consequently, does not produce CO<sub>2</sub> during its combustion process [1, 2]. Although many efforts and resources have been devoted to the development of solutions for hydrogen applications, the technology has not yet reached a proper level of competitiveness since many problems regarding production, storage, distribution and use have not been solved. Enriched methane (EM) constitutes an intermediate step toward decarbonation. EM is a mixture composed by 10–30% vol of hydrogen and methane, which means that the mixture is 26%–29%wt of H and 71%–74% of C. The stoichiometric combustion of 1 kg of EM with 30% vol. H<sub>2</sub> leads to the production of 2.61 kg CO<sub>2</sub>, versus 2.75 kg emitted when burning pure CH<sub>4</sub>. Therefore, using EM instead of methane allows a reduction of distributed CO<sub>2</sub> emissions by 5% approx. Unlike hydrogen, EM does not need specific solutions for distribution, storage and application, since, if the content of hydrogen is lower than 30% vol, the traditional natural gas technologies can be properly applied [3], so that EM can be immediately used by exploiting the already available Natural Gas (NG) infrastructures. One of the main applications of the blends of hydrogen and methane is in the field of sustainable mobility, since EM can be efficiently burned in NG Internal Combustion Engines. As attested in the literature [4], increasing hydrogen content in the NG engine allows the reduction of unburned hydrocarbons and carbon monoxide and the reduction of the overall production of CO<sub>2</sub> as the EM stoichiometric carbon dioxide emission is lower. Furthermore, the use of EM increases the engine efficiency (1–3%), so reducing specific fuel consumption. On the other hand, due to the higher flame temperature, an increase of NO<sub>x</sub> emissions could occur and an efficient catalytic converter may be required. Some papers dealing with the optimization of hydrogen percentage in EM fuel [5] reported that a hydrogen content in the blend of 20–25% vol may be utilized for optimizing the engine conversion efficiency. In this framework, the solar-driven steam reforming of natural gas at low temperature (500–550°C) [6] appears as a very interesting process to produce the amount of hydrogen needed by the EM blend.

Unfortunately, the process produces also one mole of carbon dioxide per mole of reacted methane: this means that the mixture obtained from steam reforming has a CO<sub>2</sub> percentage too high to be used as fuel in an internal combustion engine, so that the carbon dioxide has to be removed to obtain a CO<sub>2</sub> content lower than 3%. Obviously, a separation process able to operate with high recoveries of hydrogen and methane and low energy consumption is desirable. In this work the separation will be carried out by means of a double stage pressure swing adsorption process (PSA), the first one for the CO<sub>2</sub> removal and the second one for the recovery of CH<sub>4</sub>. To demonstrate the technological feasibility and assess its performance, simulations have been carried out by feeding the PSA with a stream obtained from solar steam reforming of natural gas at 500–550°C and results are assessed and discussed.



## 2 The reforming process

The methane steam reforming (MSR) process is the most used massive hydrogen production route and is based on following reactions



which together yield



The reactions are very fast on nickel based catalysts and conditions near to the equilibrium are easily reached. Since the global process is highly endothermic, operating temperature in the range 850–950°C have to be used to obtain high conversions. On the other hand, if the aim of the process is to produce EM blend, a low methane conversion is acceptable and the process can operate at a lower temperature, thus allowing the coupling of MSR with solar powered technologies, such as the molten salt based concentrating solar plant. In this way the reforming process becomes environmentally friendly and requires only renewable energy.

For a quantitative evaluation of the performances of the process, the equilibrium conditions for reactions (1) and (2) can be easily obtained from thermodynamic data. Fig. 1 reports the hydrogen-to-methane ratio as a function of temperature and pressure for a natural gas feed (97% CH<sub>4</sub> and CO<sub>2</sub> 3%) with a steam to carbon ratio equal to 3; fig. 2 reports the carbon dioxide concentration obtained in the reformed gas after water separation. The figures show that the required H<sub>2</sub>/CH<sub>4</sub> ratio can be theoretically obtained even when operating at very low temperatures (near 400°C); in order to enhance the reaction kinetics, a higher temperature is suggested. In this work we consider a temperature in the range 500–550°C: this temperature can be easily obtained with a concentrating solar plant; furthermore efficient catalyst are suitable for the production a mixture with hydrogen content up to 30% even operating at high pressure in order to reduce the reactor size. On the other hand, the reforming reaction produces about one mole of carbon dioxide per mole of reacted methane: therefore, as shown in fig. 2, a CO<sub>2</sub> content greater than 13% is obtained in the reformed gas. Indeed this content is too high for an automotive fuel and a separation process is required to reduce the CO<sub>2</sub> content up to 3%. In this paper, we consider the purification of a reformed gas obtained from a molten-salt heated reactor operating in the range 500–517°C, with a steam to carbon ratio 3; according to the kinetic model previously published [7] the gas composition on the water free basis is CH<sub>4</sub> = 48%, CO<sub>2</sub> = 12% and H<sub>2</sub> = 40% by volume, while the flow rate is adjusted to produce, after all the separation steps required, about 350 kg/h of enriched methane.



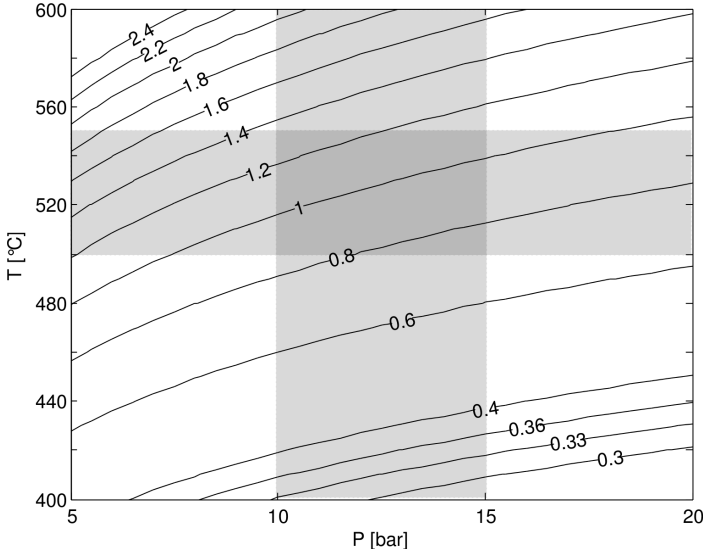


Figure 1: Hydrogen-to-methane ratio in the reformed gas as function of temperature and pressure. Feed: natural gas mixture (97% CH<sub>4</sub>, 3% H<sub>2</sub>) steam-to-carbon ratio 3.

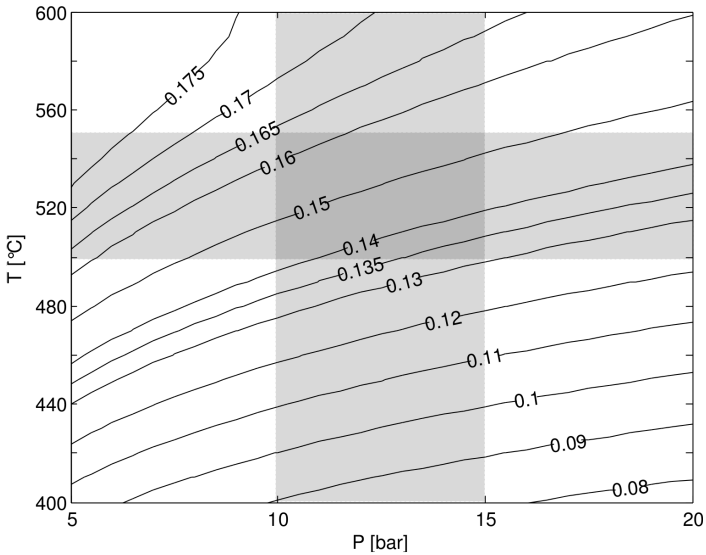


Figure 2: Carbon dioxide content in the reformed gas as function of temperature and pressure. Feed: natural gas mixture (97% CH<sub>4</sub>, 3% H<sub>2</sub>) steam-to-carbon ratio 3.

### 3 Pressure swing adsorption for reformed gas purification

A very selective process to remove carbon dioxide is chemical absorption with amine solutions; this process is continuous, therefore plant design and operation are quite simple. The drawback of this process lies in the energy consumption due to the high temperature of the regeneration of amine solution; furthermore, these solvents are toxic, corrosive, and hazardous substances. Therefore this process does not seem to be suitable for small installations. Pressure Swing Adsorption (PSA) has attracted increasing interest because of its low energy requirements and investment costs. In a PSA unit, an adsorbent material is subjected to pressure changes to selectively adsorb and desorb the undesired gas components; the process operates near ambient temperature, without any need of thermal regeneration. In its basic configuration pressure swing adsorption has four steps (adsorption, blow-down, purge and pressurization) of equal or different time duration, implemented in two or more columns in order to make the gas treatment continuous. Many combinations of the cyclic adsorption, desorption, and complementary steps and their operating conditions in conjunction with a variety of adsorbents can be utilized to obtain the desired separation goals. A realistic simulation model is useful to evaluate the process performances in terms of purity, recovery and energy requirement, and then for screening between different adsorbent materials and process cycle or scheduling. In this work a dynamic literature non-isothermal model is used [8]. This model is based on the linear driving force approximation for the adsorption/desorption kinetics with a single lumped transport parameter for each component,  $k_{LDF}$ ; thermal equilibrium between gas and solid phase and no heat exchange with the external environment are assumed; further details on the mathematical model are reported in the original paper [9].

We consider the design of a PSA process to treat a three component mixture (the reformed gas above reported) to reduce its carbon dioxide content to less than 3% and to obtain a high recoveries for both hydrogen and methane. As a first step, we design a four-column PSA unit, using activated carbon as adsorbent materials. Adsorption equilibrium is described by multicomponent Langmuir adsorption isotherm:

$$\frac{q_i}{q_{max,i}} = \frac{b_i p_i}{1 + \sum_j b_j p_j} \quad (4)$$

where  $q_i$  and  $p_i$  are the adsorbed amount and the partial pressure of each component and  $q_{max,i}$  and  $b_i$  are temperature dependent parameters

$$q_{max,i} = k_{1i} + k_{2i}T \quad b_i = k_{3i} \exp(-k_{4i}/T) \quad (5)$$

Adsorption isotherm parameters and kinetic parameters for CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> adsorption onto activated carbon are reported in table 1.

The PSA working cycle, reported in fig. 3, includes a) a feed (adsorption) step where the gas is fed to the column at high pressure (13 bar); a low-CO<sub>2</sub> content gas is obtained from the column; b) an equalization step, where the high pressure



Table 1: Equilibrium and kinetic parameter of activated carbon [10] and carbon molecular sieve [11] ( $k_1$  mol/kg,  $k_2$  mol/kgK,  $k_3$  bar<sup>-1</sup> k<sub>4</sub> K,  $\Delta H_{ads}$  kcal/mol,  $k_{LDF}$  s<sup>-1</sup>).

	Activated carbon			CMS	
	CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>
$k_1$	28.80	23.86	16.94	2.88	1.76
$k_2$	-0.07	-0.056	-0.021	0	0
$k_3$	$1 \cdot 10^{-2}$	$3.5 \cdot 10^{-3}$	$6.2 \cdot 10^{-5}$	$2.4 \cdot 10^{-2}$	$6.3 \cdot 10^{-4}$
$k_4$	1030	1159	1229	1312	2046
$\Delta H_{ads}$	1.25	1.02	0.54	2.61	4.10
$k_{LDF}$	0.036	0.195	0.700	0.013	$7.5 \cdot 10^{-5}$

Bed 1	FE			EQ	RIC	BD	PU			EQ	PR		
Bed 2	EQ	PR			FE			EQ	RIC	BD	PU		
Bed 3	PU			EQ	PR			FE			EQ	RIC	BD
Bed 4	EQ	RIC	BD	PU			EQ	PR			FE		

Figure 3: Scheduling of four-column PSA cycle for CO<sub>2</sub> removal. FE: feed, EQ: equalization, RIC: recycle, BD: blow-down, PU: purge, PR: pressurization.

gas present in the interstitial spaces of the column at the end of the feed phase is used to partially pressurize another column; c) a recycling step, where the gas still present in the column is compressed and used to further pressurize a different column; d) a blow-down step when the column is depressurized until vacuum conditions (0.1 bar) are reached, in order to remove the adsorbed carbon dioxide; e) a purge step, where the column is fed with the reformed gas at low pressure, in order to complete the adsorbent bed regeneration f) an equalization step where the column is partially pressurized with the high pressure gas withdrawn from an other column; g) a pressurization step where the column is pressurized, firstly with a recycled stream, and subsequently with the reformed gas. The pressure profile in the cycle is reported in fig. 4; in the same figure, we also report the flow rates of different components at the top and bottom of the adsorption column.

The energy requirement, mainly due to the vacuum conditions reached in the blowdown and purge steps, is about 1700 kJ/kg of produced hydrogen. The process allows to obtain a gas with less than 3% of CO<sub>2</sub> and an almost complete hydrogen recovery; unfortunately, the off-gas has still a high methane content and, as a consequence, the methane recovery is low (see table 3). If a high methane recovery is desired, a second PSA unit can be added to separate the methane-carbon dioxide mixture. In this work we studied this second option. In this PSA unit,

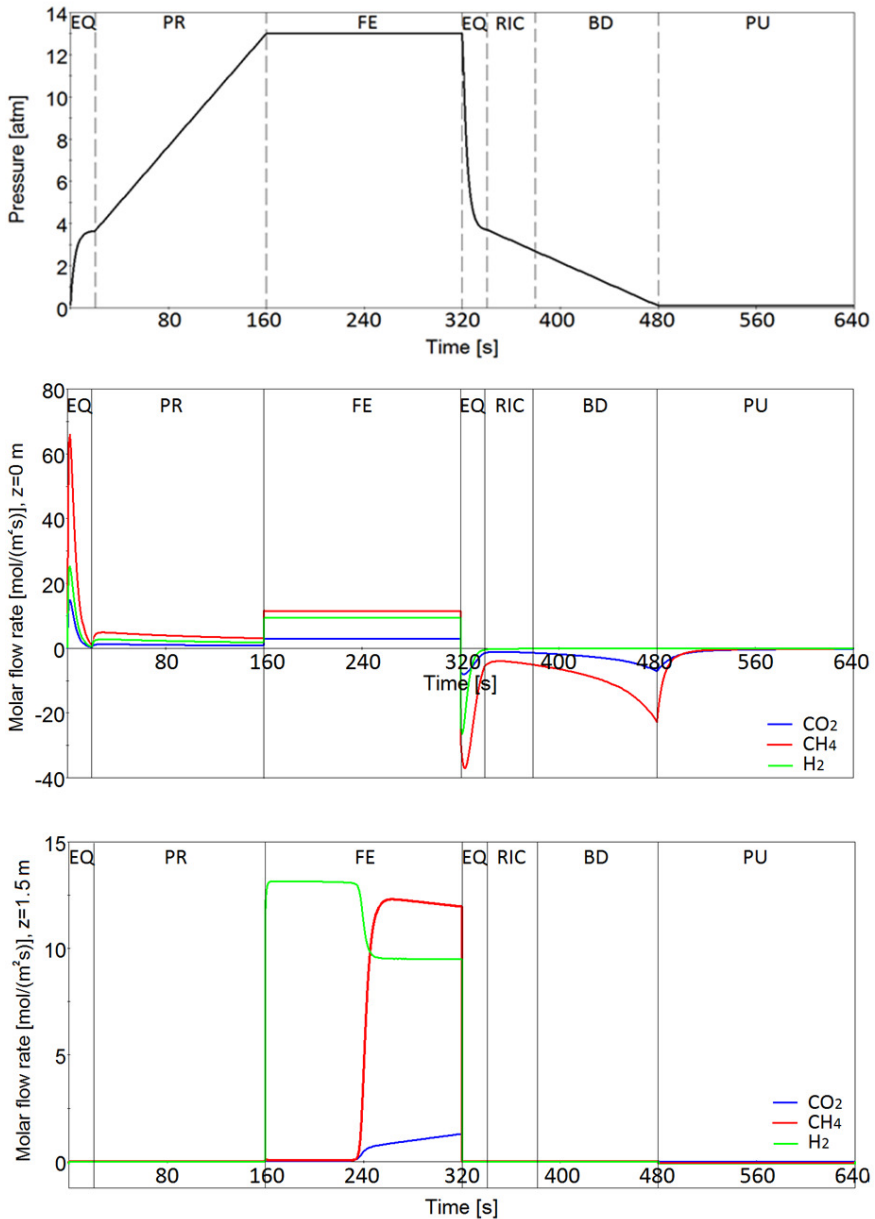


Figure 4: Pressure profile and flow rates in different steps of the PSA cycle for CO<sub>2</sub> removal (column size in table 2).

Table 2: Column characteristics and pressure operating conditions of PSA columns.

		Activated carbon	CMS
column length	m	1.5	1.8
column diameter	m	0.44	0.5
column density	kg m <sup>-3</sup>	482	695
column porosity	—	0.43	0.41
pressure feed	bar	13	4
pressure purge	bar	0.1	0.1

Table 3: Performances of the activated carbon - PSA unit for CO<sub>2</sub> removal.

	Composition			Recovery	
	Feed	Product	Off-gas	Product	Off-gas
CH <sub>4</sub>	48%	33.7%	71.9%	43.1%	—
CO <sub>2</sub>	12%	2.8%	26.6%	—	85.4%
H <sub>2</sub>	40%	63.5	1.5%	98.6%	—

activated carbon is not an adequate adsorbent due to the low selectivity between methane and carbon dioxide. Higher selectivity, mainly related to differences in the adsorption kinetics, is obtained with carbon molecular sieves (CMS). Here we refer to a CMS with the properties reported in table 1; since the hydrogen concentration is very low, simulation is carried out considering a two-component (CH<sub>4</sub> and CO<sub>2</sub>) mixture. With this adsorbent, a classical five step cycle, including pressurization, feed, equalization, blow-down and purge steps is able to produce the desired performances. In details, the pressure profile and the flow rates of different components at the top and bottom of the adsorption column, are reported in fig. 5. The gas produced from this unit contains more 95.1% vol of CH<sub>4</sub>. 2.7% of CO<sub>2</sub> and 2.2% of H<sub>2</sub>; the off gas flow rate is quite low with a CH<sub>4</sub> content of about 25%; the methane recovery is greater than 88%. The methane content in off-gas allows this stream to be burned without external fuel. The energy requirement is about 1200 kJ/kg of recovered methane.

The overall process scheme is reported in fig. 6, together with the mass balances and the operating conditions. It is worth noting that a blending of the produced gas with natural gas is considered in order to obtain the optimal hydroged-to-methane ratio in the enriched methane stream.





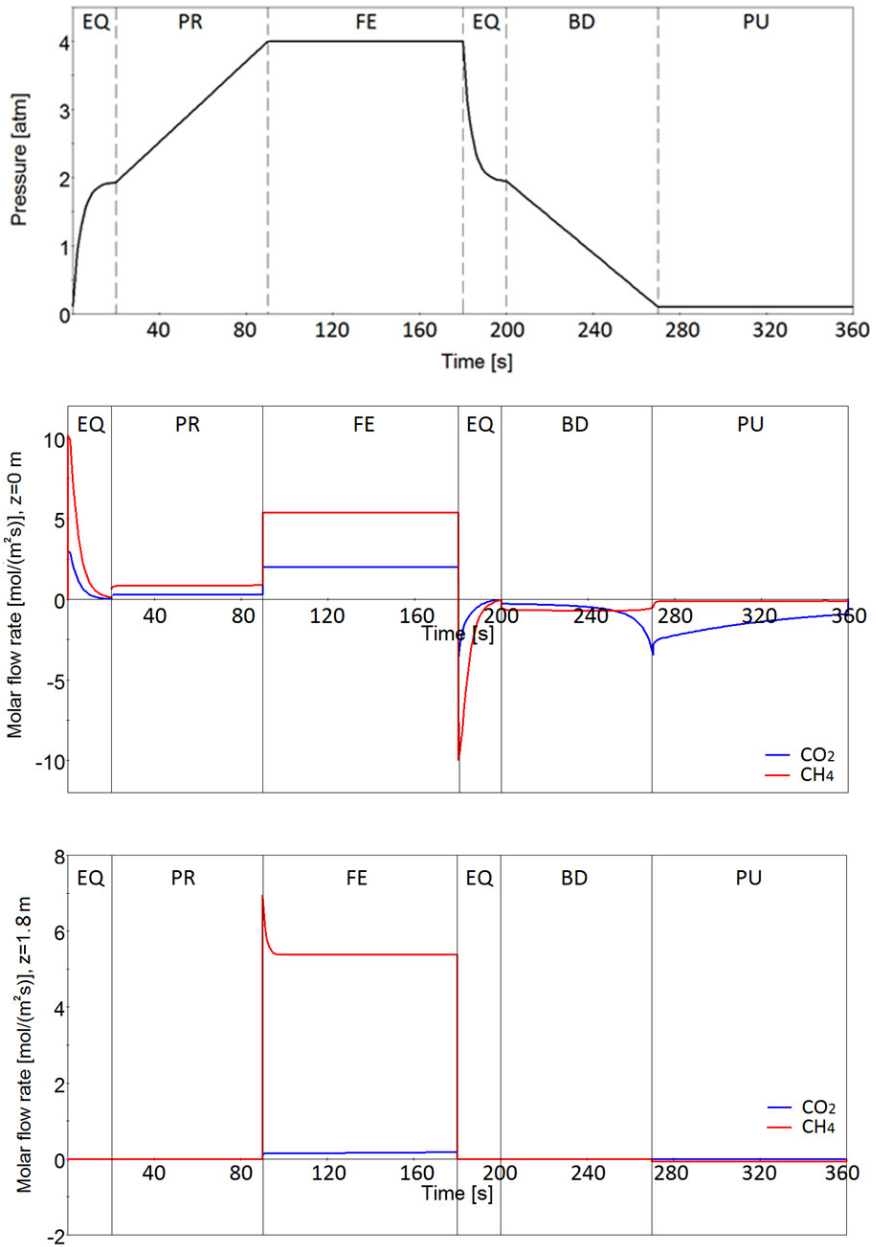
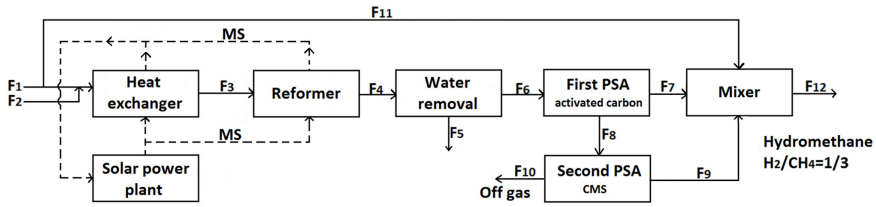


Figure 5: Pressure profile and flow rates in different steps of the PSA cycle for CH<sub>4</sub> recovery (column size in table 2).



	Flow rate		Composition, %				T °C	P atm
	kg/h	Nm <sup>3</sup> /h	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O		
F <sub>1</sub>	157.8	210	97	3	—	—	25	15
F <sub>2</sub>	490.7	611	—	—	—	100	25	15
F <sub>3</sub>	648.5	821.1	24.8	0.8	—	74.4	500	15
F <sub>4</sub>	648.5	891.6	18.9	4.6	15.6	60.9	514	14.5
F <sub>5</sub>	435.8	542.7	—	—	—	100	50	13
F <sub>6</sub>	212.7	348.9	48	12	40	—	25	13
F <sub>7</sub>	75.8	215.7	33.7	2.8	63.5	—	25	13
F <sub>8</sub>	136.8	133.2	71.9	26.6	1.5	—	25	1
F <sub>9</sub>	65.5	89.2	95.1	2.7	2.2	—	25	13
F <sub>10</sub>	72.7	42.1	25	75	—	—	25	1
F <sub>11</sub>	200.8	267.3	97	3	—	—	25	15
F <sub>12</sub>	342.2	570.3	73.1	2.9	24	—	25	13

Figure 6: Process of production and purification of EM mixture.

## 4 Conclusion

Solar driven steam reforming of natural gas with two PSA unit to remove carbon dioxide seems a very interesting process to produce enriched methane mixture with 25% vol H<sub>2</sub> which can be efficiently used in NG internal combustion engine. The process can operate with an almost complete hydrogen recovery and a methane recovery greater than 97%. Using grid natural gas, the energy consumption is about 275 kJ per kg of produced hydromethane.

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