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Methane Decarbonization in Indirect Heating Solar Reactors of 20 and 50 kW for a CO₂-Free Production of Hydrogen and Carbon Black

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Solar methane decarbonization is an attractive pathway for a transition toward an hydrogen-based economy. In the frame of the European SOLHYCARB project, it was proposed to investigate this solar process extensively. At CNRS-PROMES, two indirect heating solar reactors (20 and 50 kW) were designed, built, and tested for methane decarbonization. They consist of graphite cavity-type receivers approaching the blackbody behavior. The CH₄ dissociation reaction was carried out in tubular sections inserted in the solar absorber receiving concentrated solar irradiation. The 20 kW solar reactor (SR20) was especially suitable to study the chemical reaction and methane conversion performances depending on the experimental conditions (mainly temperature and residence time). The 50 kW solar reactor (SR50) was operated to produce significant amounts of carbon black for determining its properties and quality in the various possible commercial applications. The main encountered problem concerned is the particle evacuation. Solutions were proposed for large-scale industrial applications. A process analysis was achieved for a 14.6 MW solar chemical plant on the basis of a process flow-sheet. A production of 436 kg/h of hydrogen and 1300 kg/h of carbon black could be obtained for 1737 kg/h of methane consumed, with an hydrogen cost competitive to conventional methane reforming. This paper summarizes the main results and conclusions of the project.

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Keywords: hydrogen, carbon black, solar reactor, pilot scale, methane decomposition, cracking

1 Introduction

Hydrogen is viewed as a potential energy carrier for the future, [1] but it is not available in nature and it must be extracted from available sources (fossil fuels, biomass, or water). Carbon black (CB) has many industrial application fields related to their key properties such as in rubbers reinforcing (mechanical properties), inks (pigment properties), and conductive polymers (electrical properties), etc. [2]. Today, applications in tire and rubber product manufacturing industry represent 90% of world carbon black production [3]. The total world CB production is about 8 Mt/yr and the selling price depends on the product nanostructure. It may vary from 0.6 €/kg for standard CB to 3 €/kg for high-grade conductive CB. In contrast to classical soot that always contains a lot of inorganic contaminants and extractable organic residues, commercial CB contains mainly elemental carbon (97–99%) depending on the manufacturing process [2]. At present, more than 90% of the CB is produced by incomplete combustion processes and the remaining part by thermal decomposition of hydrocarbons, depending upon the presence or absence of oxygen. In the furnace process, CB is produced by combustion of oil (feedstock) in a natural gas flame [4]. The steam-methane reforming and the furnace process (incomplete combustion of hydrocarbons in air) are the conventional production processes of hydrogen and CB, respectively. However, they release large amounts of CO₂ in the atmos-

phere. CO₂ sequestration is limited and new technologies have to be investigated [5]. Consequently, it is necessary to think about sustainable ways of production. Current processes for H₂ and CB production are performed at an industrial scale but are not combined. Moreover, the process heat is supplied by burning a significant portion of the feedstock. Solar methane dissociation thus appears as an attractive step toward an hydrogen-based economy [6]. It takes advantage of the co-production of hydrogen and CB without fossil fuel combustion for energy supply. The use of solar energy for processing heat avoids both gaseous products contamination and pollutants emission (e.g., CO, CO₂, NO_x, SO_x). Actually, this solar route avoids energy consumption and pollution associated with both H₂ and CB production by classical methods. Quantitatively, it was estimated that the solar-thermal process saves 277 MJ of fossil fuel and avoids 13.9 kg-equivalent CO₂ per kg of H₂ produced in comparison to conventional steam-methane reforming and furnace black processing [7]. CB can be sold on the market, thereby leading to a possible competitive process for hydrogen production. Alternatively, CB can also be safely stored keeping a value in terms of CO₂ credits. The targeted applications for the solar produced CB concern polymer composites (rubber and plastics) and primary and secondary batteries. Methane decomposition is a topic of growing interest in research centers. Numerous reactor configurations have been studied at laboratory scale (up to 5 kW): direct [8,9] or indirect [10,11] heating reactors (tubular or vortex type), catalytic [12–14], or noncatalytic [15] reactions. The process is now ready for preindustrial tests. Industrial patents were also applied [16,17]. Regarding the economics of the process, the valorization of both products (i.e., hydrogen and CB) is of primary importance [7]. Therefore, not only the

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62 chemical conversion has to be investigated but also the CB properties.
 63 The reactors developed previously involved usually a flow
 64 of CH₄ laden with fine carbon particles that serve simultaneously
 65 as radiant absorbers and nucleation sites for the heterogeneous
 66 decomposition reaction. Thus, such a route subjected to carbon
 67 particle addition pertains to the thermocatalytic decomposition
 68 of methane since these added carbon particles may act as reaction
 69 catalysts. The following work presents the performances
 70 assessment of two solar reactors developed for methane splitting
 71 at 20 and 50 kW scales without any addition of carbon material in
 72 the reactor. Both hydrogen and CB productions are discussed in
 73 terms of chemical conversion and CB quality.

74 **2 Experimental Set-up of Solar Reactors SR20 and**
 75 **SR50**

76 **2.1 Reactor Designs.** Two solar reactors were designed,
 77 built, and tested. Both of them are based on the concept of indirect
 78 heating reactors, i.e., the solar irradiated zone is separated from
 79 the reacting flow, and thus particles deposition on the optical win-
 80 dow cannot occur. They are approaching the blackbody behavior,
 81 thanks to a graphite cavity absorber with a small aperture. These
 82 cavities are insulated and inserted in a metallic box equipped with
 83 a water-cooled front face. The reactors are lined with several insu-
 84 lating layers surrounding the graphite cavity (total thickness of 15
 85 cm) to reduce thermal losses. The insulating materials are carbon
 86 felt as a first layer in contact with the graphite cavity ($\lambda = 0.46$
 87 $W\ m^{-1}\ K^{-1}$), an intermediate refractory ceramic fibers resistant
 88 up to 1600 °C (62% Al₂O₃, 30% SiO₂, $\rho = 200\ kg/m^3$, $\lambda = 0.25\ W$
 89 $m^{-1}\ K^{-1}$ at 1200 °C, $\lambda = 0.35\ W\ m^{-1}\ K^{-1}$ at 1400 °C, $\lambda = 0.48$
 90 $W\ m^{-1}\ K^{-1}$ at 1600 °C) and an outer layer of a very efficient
 91 microporous insulator operating up to 1000 °C (20% ZrO₂, 77.5%
 92 SiO₂, 2.5% CaO, $\rho = 300\ kg/m^3$, $\lambda = 0.044\ W\ m^{-1}\ K^{-1}$ at 800
 93 °C). A transparent hemispherical quartz window prevents the cavi-
 94 ty oxidation. SR20 is presented in Fig. 1. The cavity is of cubic
 95 shape (20 cm-side). It is crossed by four independent vertical
 96 graphite tubes and has an aperture diameter of 9 cm. The tubes are
 97 equally separated and placed at about 2.5 cm from the backside of
 98 the cavity. Each reaction zone is composed of two concentric
 99 graphite tubes. The gas enters the inner tube and flows out by the
 100 annular space between the outer and inner tubes. This design per-
 101 mits to increase the gas residence time and to preheat the reac-
 102 tants. The inner tube diameters are 12 mm o.d. and 4 mm i.d. The
 103 outer tube diameters are 24 mm o.d. and 18 mm i.d. More details
 104 can be found elsewhere [18,19].

105 The 50 kW solar reactor is displayed in Fig. 2. It is twice the
 106 size of SR20. The reactor body is made of an aluminum shell (800
 107 mm × 780 mm × 505 mm) and a water-cooled front face with a
 108 13 cm-diameter aperture to let concentrated solar radiation enter-
 109 ing within the reactor cavity. The graphite cavity side is about 40
 110 cm and it is crossed by seven horizontal graphite tubes (800 mm
 111 length, 26 mm o.d., 18 mm i.d.). Additional information can be
 112 read in Ref. [20].

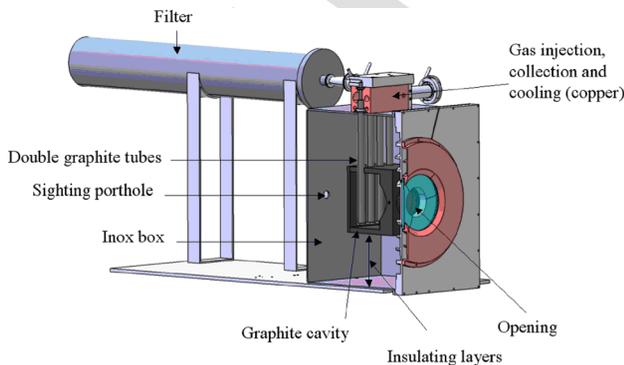


Fig. 1 Scheme of the 20 kW solar reactor

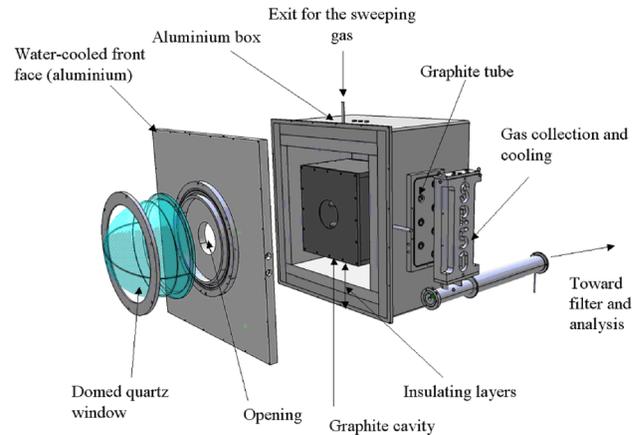


Fig. 2 Scheme of the 50 kW solar reactor

113 **2.2 Experimental Methods.** For both reactors, the first ex-
 114 perimental step was the heating of the reactor with an argon flow
 115 in the tubes. Once the desired temperature has reached, the mix-
 116 ture of argon and methane was injected with a controlled compo-
 117 sition. Two mass-flow meters were dedicated to each tube to
 118 control accurately the Ar and CH₄ flow-rates. The temperature
 119 was measured by a solar blind optical pyrometer (wavelength:
 120 5.14 μm) pointing toward the outer wall of a graphite tube inside
 121 the cavity through a lateral fluorine (CaF₂) window. Pt-Rh ther-
 122 mocouples were also used. Temperatures at various locations
 123 (especially in the insulation zone against the cavity wall) were
 124 monitored and recorded continuously. At the exit of each tube, the
 125 exhaust gas-solid flows were collected, cooled, and mixed to-
 126 gether. The solid and gaseous products were cooled down and
 127 flowed through a filter bag to separate carbon particles. The pres-
 128 sure was monitored by pressure sensors placed at each tube en-
 129 trance and was regulated thanks to the use of a Venturi vacuum
 130 pump (absolute operating pressure of about 40 kPa). The filtered
 131 gas was then analyzed online to determine the gas composition
 132 during the progress of the reaction. A continuous analyzer per-
 133 mitted to monitor the concentration of H₂ and CH₄. The methods
 134 used for H₂ and CH₄ analysis were thermal conductivity and non-
 135 dispersive infrared detections, respectively. A gas chromatograph
 136 also measured online the outlet concentrations of CH₄, C₂H₆,
 137 C₂H₄, C₂H₂, and H₂. The chromatograph (Varian CP 4900) was
 138 equipped with two columns: MolSieve 5A PLOT calibrated for
 139 H₂ and CH₄ and PoraPLOT U calibrated for light hydrocarbons
 140 (C₂H₆). The chromatography analysis was based on thermal con-
 141 ductivity detection and the carrier gas was argon, also used as
 142 buffer gas during methane cracking experiments, so that it was
 143 not detected during analysis.

144 The gas composition was measured as a function of different
 145 parameters (temperature, inlet gas flow-rates, and CH₄ mole frac-
 146 tion in the feed). Once the mole fractions of gas species were
 147 determined, the total outlet gas flow-rate F was obtained from the
 148 Ar flow-rate (F_{Ar}) and from the outlet mole fractions (y_i) of every
 149 i-species except Ar:

$$F = F_{Ar} / (1 - \sum_i y_i) \quad (1)$$

150 The CH₄ conversion rate (X_{CH_4}) was then calculated as

$$X_{CH_4} = \frac{F_{0,CH_4} - F y_{CH_4}}{F_{0,CH_4}} \quad (2)$$

151 where F_{0,CH_4} denotes the inlet molar flow-rate of methane.

152 The experiments were carried out at the 1 MW solar furnace of
 153 CNRS-PROMES (Odeillo, France). The furnace is composed of a

154 field of 63 heliostats for full power (45 m^2 per heliostat) and of a
 155 parabolic concentrator with horizontal axis (1830 m^2 , 40 m height,
 156 54 m width) delivering up to 9000 suns ($1 \text{ sun} = 1 \text{ kW/m}^2$) at the
 157 focal plane. The solar reactor was settled at the focal point of the
 158 concentrator (18 m in front of the parabolic reflector) where high
 159 flux densities are available. During experiments, only a fraction of
 160 the parabola was used by limiting the number of heliostats track-
 161 ing the sun and by using a shutter and a diaphragm. The mean solar
 162 flux density at the reactor aperture was in the range $200\text{--}300$
 163 W/cm^2 (concentration factor: $2000\text{--}3000$).

164 3 Experimental Results

165 **3.1 Chemical Performances at 20 kW Scale.** At 20 kW
 166 scale, chemical performances were widely investigated. During
 167 one experiment, several operating conditions (flow-rates and tem-
 168 perature) were investigated. On the one hand, this leads to a large
 169 number of experimental data concerning chemical conversion. On
 170 the other hand, it was not possible to correlate the CB properties
 171 with the experimental conditions. Indeed, the filter was only
 172 cleaned after operating at various experimental conditions and so
 173 the CB was a mixture of products as a result of various operating
 174 parameters. These results were especially used to study the chemi-
 175 cal performances and kinetics of the reaction [21]. The influence
 176 of the temperature and the residence time was showed to be of pri-
 177 mary importance. In Fig. 3, the methane conversion is plotted ver-
 178 sus the residence time for increasing temperatures between 1740
 179 K and 2073 K . It appears that the methane conversion is enhanced
 180 when increasing temperature for a given residence time and also
 181 when increasing residence time for a given temperature. The
 182 C_2H_2 mole fraction is also reported. No clear trend appears with
 183 the temperature but it can be noted that the lowest C_2H_2 concen-
 184 trations are achieved for the highest residence times. This last pa-
 185 rameter has significant importance for decreasing the amount of
 186 the main by-product of the reaction (C_2H_2) that has a high carbon
 187 content. Temperature and residence time are critical parameters
 188 for the chemical reaction. At 50 kW scale, the influence of these
 189 two parameters on the properties of CB particles will be
 190 discussed.

191 **3.2 Carbon Black Production at 50 kW Scale and Material**
 192 **Properties Assessment.** Each experimental run carried out with
 193 SR50 prototype corresponds to one single experimental condition.
 194 Consequently, the CB recovered at the end in the filter corre-
 195 sponds to specific temperature and flow-rates. The online monitor-

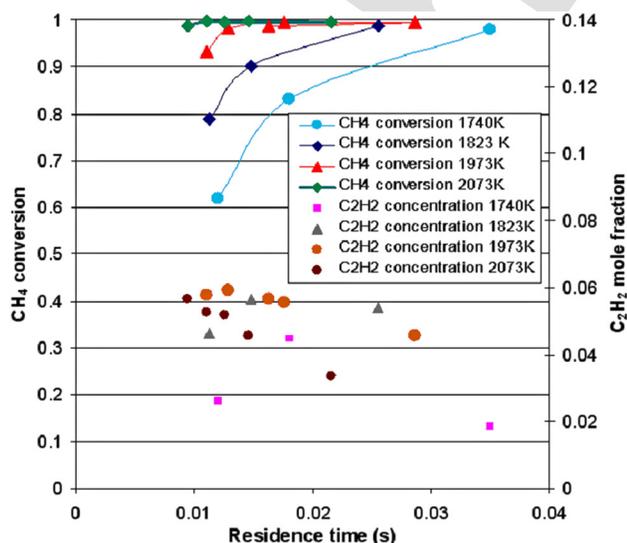


Fig. 3 CH_4 conversion and C_2H_2 off-gas mole fraction for vari-
 ous temperatures and residence times

ing for one experiment at 1928 K is reported in Fig. 4 for 10.5
 NL/min of CH_4 and 31.5 NL/min of Ar in the feed gas: the tem-
 perature indicated by the pyrometer pointing on a tube wall is
 plotted along with the temperature of a thermocouple inserted in
 the same tube; direct normal irradiance (DNI) and CH_4 , C_2H_2 ,
 and H_2 outlet mole fractions are also reported. The methane injec-
 tion period is indicated with a double arrow. It can be pointed out
 that this experiment was carried out with a constant DNI (960 W/
 m^2). After a heating period of less than 1 h , the targeted tempera-
 ture is reached and methane is injected. Straight away, the hydro-
 gen mole fraction increases. Less than 1% of CH_4 remains in the
 off-gas. Along the time, a slight increase of the H_2 mole fraction
 is observed. At the same time, the C_2H_2 concentration decreases.
 This is explained by a progressive carbon deposition in the tubes
 that leads to a higher pressure and so to a higher residence time of
 the gases. In addition, a catalytic reaction on the accumulated par-
 ticles may occur. After 45 min , the H_2 mole fraction declines
 sharply because several tubes were clogged and their methane
 feed was stopped. The temperature given by the pyrometer is con-
 stant at about 1928 K . The one given by the thermocouple is 150
 K less because the thermocouple is positioned 24 cm far from the
 tube entrance, so the gas is not perfectly heated and the endother-
 mic reaction has also a cooling effect. After about 1 h of experi-
 ment, the shutter of the furnace is closed and the reactor is no
 longer irradiated. Consequently, the temperature decreases due to
 passive cooling. At the end of the experiments, the carbon black is
 collected and analyzed. A material balance on carbon shows that
 the amount of carbon recovered in the filter is 23% of the amount
 of carbon injected as methane in the feed. The fraction of carbon
 found either in the deposits in the reactor tubes or dispersed in the
 various components of the reactor (exit path toward the filter,
 unremoved deposits, and nonrecovered carbon in the filter) repre-
 sents about 42% of the carbon injected. The remaining part of car-
 bon is found as C_2H_2 in the outlet gas (35%). Concerning the
 material balance on hydrogen, 82% of the hydrogen contained in
 the fed CH_4 is found as H_2 in the outlet gas, 9% is in the form
 of C_2H_2 , and 9% is in the form of other hydrocarbons.

Figure 5 plots the specific surface area (BET) of the samples
 measured by TIMCAL company (Belgium), one of the project
 partners. The specific surface area is one of the most important
 properties of a carbon black in terms of end use applications [2].
 The maximum specific surface area obtained is $100 \text{ m}^2/\text{g}$ for the
 test at the highest temperature and it can be observed that it
 decreases when decreasing the temperature for a given gas flow-
 rate. The higher the gas flow-rate, the lower is the specific surface
 area. From the BET measurements, it is possible to evaluate the
 mean diameter of CB particle with the following formula [2]:

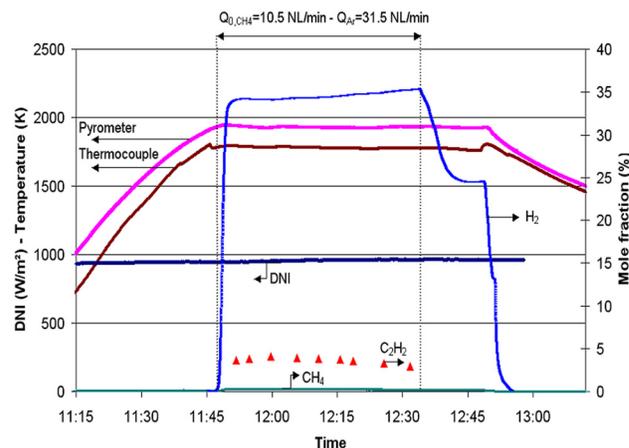


Fig. 4 Online monitoring of temperatures, DNI, H_2 , C_2H_2 , and
 CH_4 off-gas mole fractions

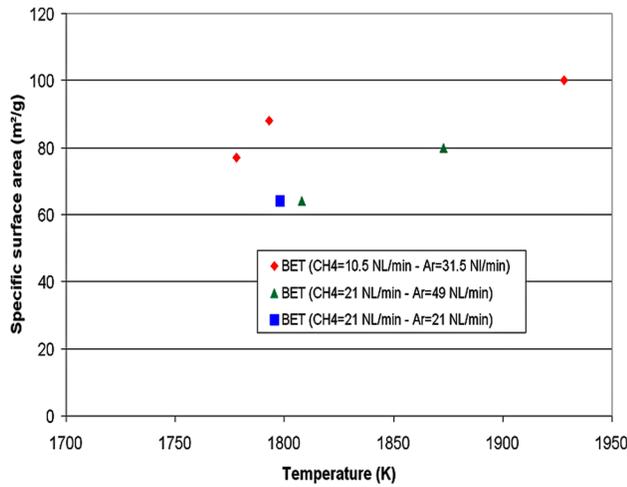


Fig. 5 Specific surface area of the carbon black particles for various experimental conditions (courtesy of TIMCAL, Belgium)

$$d_p = 6000/\rho \cdot S \quad (3)$$

S is the specific surface area (m²/g), ρ is the density (= 2 g/cm³), and d_p is the mean particle diameter (nm). This formula leads to $d_p = 30$ nm for 100 m²/g and $d_p = 50$ nm for 60 m²/g. The mean particle diameter is ranging between these two limits. These diameters seem too high for ink-type application that requires very small particles (9–16 nm). Nevertheless, specific surface area between 60 and 100 m²/g is found for conductive carbon black or rubber grades [22]. Microscopy analysis was also carried out via transmission electron microscopy (TEM). A shot of the sample obtained at the highest temperature (1928 K) is given in Fig. 6. The particle size distribution is between 20 and 70 nm. Nanosized particles are confirmed.

3.3 Solar Process Design and Analysis. The solar reactor experiments proved that it is possible to produce carbon black from methane decomposition with a controllable specific surface area and with possible commercial applications. As observed in Fig. 4, the reactor cannot be operated during a full sunny day without clogging. The particle deposition issue has to be addressed. Several solutions can be proposed. In order to adapt the presented solar reactor at the top of a solar tower, it was proposed to increase the gas velocity. Indeed, in the conventional furnace process for CB production, velocities up to 0.8 M are reached [2]. It was also proposed by other authors to carry out the reaction in molten metals [23], in a hot carrier gas [24], or in a

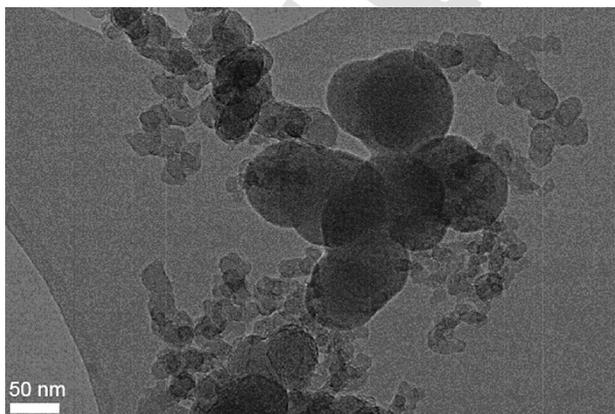


Fig. 6 TEM image of a carbon black sample obtained at 1928 K (courtesy of APTL, Greece)

fluid-wall aerosol flow reactor [10]. The thermal process [2] that consists of heating a bed (refractory-lined furnace that is fitted with a grid structure of fire bricks) in a first step and then dissociating an hydrocarbon on it in a second step could also be adapted to a solar field. However, this process is not largely used now due to its sole ability to produce large particles that have only niche applications.

The solar process for methane dissociation was designed using PROSIMPLUS3 software. The process flow diagram is shown in Fig. 7. The feed gas is composed of methane diluted with hydrogen (carrier gas) and mixed with the recycled gases (methane, acetylene, and hydrogen). The pressure of the inlet gas is fixed at 0.12 MPa to avoid any air entrance inside the process. Unconverted acetylene and methane are recycled to the solar reactor in order to produce hydrogen and carbon black only. The process is self-sufficient with respect to dilution gas because the hydrogen flow used as diluting gas is withdrawn from the produced stream. The H₂ mole fraction in the feed gas is fixed at 50%. Before entering the solar reactor, the gas mixture is first preheated at 900 °C in a heat exchanger by the gas stream exiting the solar reactor. This temperature of preheating is below the temperature of the reaction, and it is fixed accounting for the available industrial heat exchanger technologies. The solar reactor is composed of three operation units in the flow-sheet: a heat exchanger for reactants heating up to the reaction temperature (1600 °C) by solar-thermal energy, and two reactors in series to carry out the chemical reactions, 2CH₄ → C₂H₂ + 3H₂ ($\Delta H^\circ_1 = 188$ kJ/mol) and C₂H₂ → 2C + H₂ ($\Delta H^\circ_2 = -227$ kJ/mol), respectively. A two-step mechanism is thus considered and the chemical yield of these two reactions is set at 0.9. At the solar reactor outlet, the products flow through the heat exchanger for reactants preheating before being cooled at 25 °C to allow their admittance in the filter unit. A downstream high efficiency particulate absorbing (HEPA) filter eliminates the carbon black residues. The efficiency of the filters is fixed at 99.9%. Then, the gas mixture is compressed (two-stage compression, intermediate cooling at 25 C, isentropic yield of 0.7) to reach the necessary pressure required in the pressure swing adsorption (PSA) unit (1 MPa) selected for the purification of hydrogen (yield of hydrogen recovery: 0.8). The products at the top of column are recycled to the process inlet at 0.12 MPa along with a part of pure hydrogen obtained at 0.95 MPa. In order to warrant a 50% mole fraction of hydrogen in the solar reactor, the opening of the three-way valve is controlled by the SPEC module (concentration regulation by adjustment of the valve opening). A SCRIPT is implemented to fix the solar power input in the solar reactor by adjusting the inlet methane flow-rate. A solar power of 10 MW entering the reactor is taken as a reference and a thermochemical reactor efficiency of 57% is assumed (fraction of solar power transferred to the reactants). This thermochemical efficiency is estimated assuming a blackbody receiver at 1600 °C, a concentration ratio of 3000, and accounting for 10% of conductive losses and 10% of convection losses in the reactor. The available power for the chemical reaction is thus 5.7 MW and the corresponding methane consumption is 1737 kg/h for a production of 436 kg/h of hydrogen and 1299 kg/h of carbon black. Assuming an optical efficiency of 68% for the solar concentrating system (80% for the heliostat field, 90% at the receiver aperture due to concentration defects, and 95% at the window due to reflection losses), the total power of the installation would be 14.6 MW. This power will be the basis for the economic assessment.

A sensitivity analysis was performed regarding the preheating temperature and the dilution ratio. The higher the preheating temperature, the larger the production of hydrogen and carbon black (Fig. 8). If no preheating was included, the production would be 295 kg/h of hydrogen and 877 kg/h of carbon black, which corresponds to a production decrease of more than 30% compared to the reference case (preheating at 900 °C). The influence of the preheating temperature on the production rates increases as the temperature increases (because the calorific value increases with temperature).

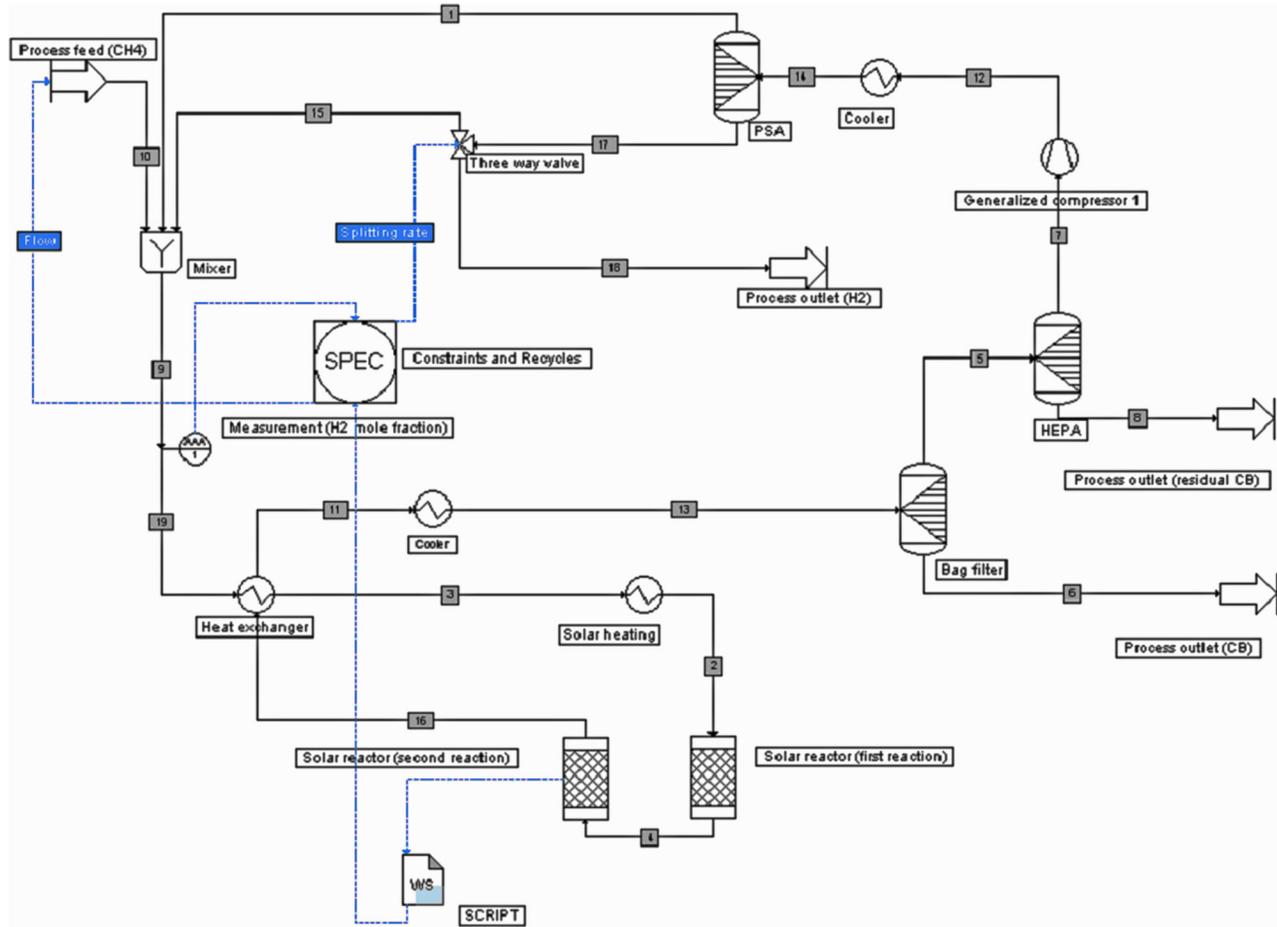


Fig. 7 Process flow-sheet for solar-thermal dissociation of methane

337 Increasing the dilution of methane with hydrogen reduces the
 338 process efficiency (Fig. 9). A mole fraction of H₂ below 0.3 is not
 339 considered because hydrogen is systematically recycled with the
 340 by-products at the top of the PSA column. It is not possible to get
 341 rid of this hydrogen dilution with the proposed separation method
 342 and because of the by-products recycling imposed in the flow-
 343 sheet. Indeed, although a very pure hydrogen stream is produced
 344 (99–99.99% H₂), the PSA process does not allow the complete re-

covery of the hydrogen contained in a gas stream (yield of H₂ re- 345
 346
 347

348 An economic analysis was conducted on the basis of a model 347
 349 proposed by DOE (2004) [25]. The main assumptions concerning 348
 349 the characteristics of the chemical plant regarding the size and 349
 350 cost of the solar concentrating system are listed in Table 1. The 350
 351 hydrogen production cost from solar methane dissociation is 1.42 \$/ 351
 352 kg in the reference case (total power of the heliostat field: 14.6 MW). 352

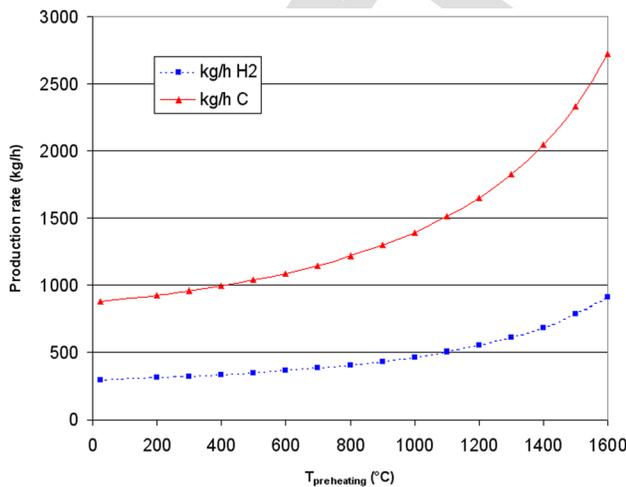


Fig. 8 Influence of the preheating temperature on the production of hydrogen and carbon black

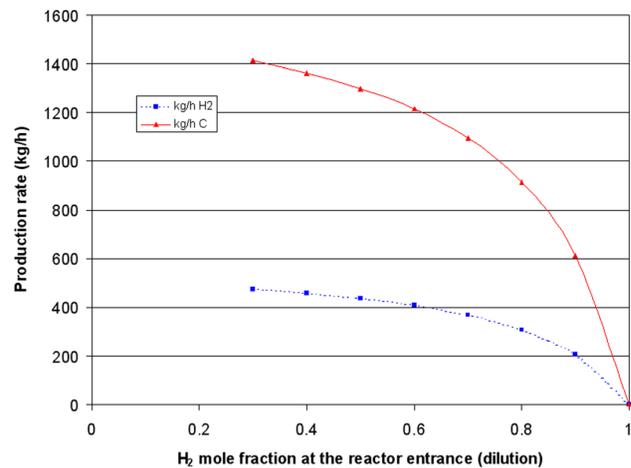


Fig. 9 Influence of the H₂ dilution on the production of hydrogen and carbon black

Table 1 Assumptions for the economic analysis in the reference case

Starting year	2030
Internal rate of return (IRR)	10%
Depreciation type	MACR
Plant life	40 yr
Inflation rate	1.90%
Effective tax rate	33% (French legislation)
Hydrogen production	436 kg/h
Annual operating hours	2000 h
Financing	100% equity financing
Construction period	2 years
Total investment	12.5 M\$
Heliostats cost	200 \$/m ²
Heliostats surface	17,200 m ²
(14.6 MW at a DNI of 850 W/m ²)	
Land cost	1 \$/m ²
Total surface	86,000 m ²
Employees	5
Labor cost	25 \$/h
Operation and maintenance costs	562,000 \$
Natural gas consumption	1737 kg/h
Natural gas price	0.24 \$/Nm ³
kg C/kg H ₂	2.98
Carbon black selling price	0.9 \$/kg
Subventions (CO ₂ credits)	Not considered

353 The cost of hydrogen produced by methane reforming is 1.03 \$/kg
 354 without CO₂ sequestration and 1.22 \$/kg with CO₂ sequestration
 355 [5]. The reference cost is 1 \$/kg [26] even though H₂ costs up to
 356 2.6 \$/kg were reported [27]. The cost of hydrogen from solar
 357 methane reforming is estimated to be roughly 2 \$/kg [27]. Figure
 358 10 shows the hydrogen production cost as a function of the carbon
 359 selling price (natural gas price of 0.24 \$/m³ (6\$/GJ HHV) for refer-
 360 ence year 2005). The reference case is plotted for a 10% internal
 361 rate of return (IRR) and 12.5 M\$ of investment. As expected, the
 362 production cost decreases when the added value of carbon
 363 increases and the process becomes competitive with solar reform-
 364 ing at a carbon black selling price of 0.7 \$/kg, which is a typical
 365 price of standard carbon black [28]. Besides, it is competitive with
 366 conventional reforming at a carbon black price above 1.05 \$/kg.
 367 The results of the economic analysis of Dahl et al. [7] are also
 368 reported for comparison (total investment of 12.7 M\$, IRR
 369 15%, 500 kg/h H₂, 3300 h/yr), which shows moderately lower
 370 H₂ production costs because of a higher H₂ production due to a
 371 capacity factor of 0.38 against 0.23 in the present study (ratio
 372 between the number of operation hours and the total number of
 373 hours per year).

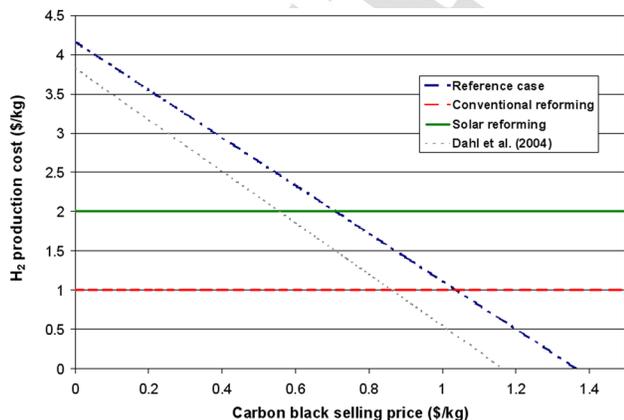


Fig. 10 H₂ production cost as a function of the carbon black selling price

4 Conclusion

Two solar chemical reactors for CH₄ dissociation were tested at the 1 MW solar furnace of CNRS-PROMES (France). SR20 was developed to study the chemical performances as functions of operating conditions. Increasing the temperature led to the methane conversion increase but increasing residence time appeared as a more efficient solution for reducing the C₂H₂ mole fraction (the main by-product) at the exit. SR50 gave information on carbon black properties. The specific surface area of the carbon particles was between 60 and 100 m²/g, which corresponds to commercial grades. It was observed that increasing the temperature permits to increase the specific surface area and so, this provides a certain ability to the designed reactor to produce various carbon grades. Moreover, even though the gas composition at the exit will be changed, the temperature variation in a certain range will not change the hydrogen purity after the purification step (provided that it is well sized). C₂H₂ should be recirculated to reach complete conversion. Consequently, it can be concluded that varying the temperature will mainly affect the carbon black properties since hydrogen will always be produced but with more or less thermal efficiency due to the varying by-product concentrations. The main issue dealing with the methane splitting process is the particle transportation. Several options were discussed and increased gas velocities could be a solution. A process design was proposed for a 14.6 MW solar chemical plant (10 MW available at the receiver/reactor aperture) and an H₂ production cost of 1.42 \$/kg was estimated for a carbon black selling price of 0.9 \$/kg, which can be competitive to the conventional steam-methane reforming.

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