Project no.: 019770

Project acronym: SOLHYCARB

Project title: Hydrogen from solar thermal energy: high temperature solar chemical reactor for co-production of hydrogen and carbon black from natural gas cracking.

Instrument: STREP

Thematic Priority: 6.1, Sustainable Energy Systems

Final Publishable Executive Summary

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Organisation : Gilles Flamant

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Publishable executive summary

Project objectives and challenges

The SOLHYCARB project addresses the development of a nonconventional route for potentially cost-effective hydrogen production and carbon nanomaterial synthesis by concentrated solar energy. The novel process thermally decomposes natural gas (NG) in a high temperature solar chemical reactor. Two products are obtained: a H_2-rich gas and a high-value nano-material, Carbon Black (CB). Therefore H_2 and marketable CB are produced by renewable energy. The project aims at designing, constructing, and testing innovative solar reactors at different scales (5 to 10 kW_{th} and 50 kW_{th}) for operating conditions at 1500-2300 K and 1 bar. This experimental work is highly combined with advanced reactor modelling, study of separation unit operations, industrial uses of the produced gas, and determination of CB properties for applications to batteries and polymers. The design of decentralized and centralized commercial solar chemical plants (and hybrid plants) -50/100 kW_{th} and 10/30 MW_{th} respectively- closes the project.

The main scientific and technical challenges are: design and operation of high temperature solar chemical reactors (10 kW_{th} and 50 kW_{th}) containing nano-size particulates, production of two valuable products (hydrogen and carbon black) in the same reactor, proposition of a methodology for solar reactor scaling-up based on modelling and experimental validation. The reactor will operate in the 1500K-2300K temperature range that causes severe material issues. The production of both hydrogen-rich gas and carbon black with desirable end-use properties is also a big challenge because the operating conditions satisfying both specifications are probably narrow.

Co-ordinator and Contractors

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APTL-CERTH/CPERI, Greece
DLR, Germany

Companies/Industries:

TIMCAL BE, Belgium
SOLUCAR R&D, Spain

CREED, France
N-GHY, France

Expected end results

The targeted results are: methane conversion over 80%, H_2 yield in the off-gas over 75%, and CB properties equivalent to industrial products. Quantitatively, 3 sm^3/h H_2 and 1 kg/h CB are expected at the 50 kW_{th} scale. Potential impacts on CO_2 emission reduction and energy saving are respectively: 14 kg CO_2 avoided and 277 MJ per kg H_2 produced, with respect to conventional NG steam reforming and CB processing by standard processes. The expected cost of H_2 for large scale solar plants depends on the price of CB; 14 €/GJ for the lowest CB grade sold at 0.66 €/kg and decreasing to 10 €/GJ for CB at 0.8 €/kg.

Moreover the project will contribute to the development of high temperature solar receivers/reactors technology; in particular concerning the design and scaling-up methodologies, the materials issues and the evaluation of performances.

Current achievements

The project includes five main activities.

1- Solar reactor design and modeling

Three solar reactors (SR) have been designed and manufactured: a 10 kW direct heating tornado solar reactor (SR10W) and two indirect heating tubular reactors 10 kW (SR10C) and 50 kW (SR50, pilot scale).

Concerning reactor modelling works have addressed 5 main points: (1) methane decomposition reaction kinetics (experimental and simulation works); (2) comparison of a kinetic model (simulation tool) with experimental results obtained with SR10C; (3) development of a model for carbon particle formation and growth; (4) complete model development including radiation heat transfer, heat and fluid flow and chemical reaction in solar reactor prototypes and (5) comparison of the complete model with experimental results obtained at 10 kW scale. Finally, the validated complete model was used as a scaling-up tool for designing the industrial process.

2- Solar reactors testing and qualification

This part was the key target of the project.

Solar reactor SR10W
SR10W tornado solar reactor operates successfully. The obtained methane conversion was ranging from 88% to 100% with a 9.7 sl/mn CH_4 flowrate without particle seeding. The flowrate of tornado and auxiliary flows (He and N2) was varied.

Solar reactor SR10C
Reaction temperature varied between 1670K and 2070K, the CH_4 flow-rate in the feed varied between 0.8 and 12 sl/min with a CH_4 mole fraction between 10 and 100%. The gas space time ranged from 10 ms to more than 100 ms. The influence of temperature was clearly

demonstrated: the higher the temperature, the higher the conversion for a given space time. For a 11 ms space time, CH_4 conversion is 62%, 79%, 93%, and 100% at 1740 K, 1823 K, 1973 K, and 2073K, respectively. The methane conversion is total for temperatures higher than 1823 K and space times higher than 25 ms. Concerning C_2H_2 mole fraction in the off-gas, it was more affected by space time than by temperature. A space time of 70 ms was needed in order to reach an off-gas C_2H_2 mole fraction lower than 0.5% and consequently, 95% H_2-yield and 90% C-yield were reached.

Solar reactor SR50

Solar thermal dissociation of methane was investigated with SR50 pilot solar reactor for mean incident solar irradiation at the aperture in the range 2-2.7 MW/m^2; nine experiments have been done. Two series were carried out: the first one with 10.5 sl/mn CH_4 and 31.5 sl/mn Ar for temperatures between 1608K and 1928K and the second one with 21 sl/mn CH_4 and 49 sl/mn Ar for temperatures ranging from 1698K to 1808K. About 100 g of carbon black sample was recovered after each run and was available for analysis and characterization.

For the investigated experimental conditions, CH_4 conversions between 72% and 100% and H_2 yields in the range 57%-88% were reached. Anyway, the carbon yield never exceeded 63% due to the production of significant amounts of C_2H_2. Thermochemical and thermal efficiencies up to 13.5% and 15.2% were achieved respectively. Representative quantities of carbon black were recovered for further characterisation with respect to industrial product.

3- *Product separation and process safety*.

Product separation issues are related to particle filtering and off-gas purification to obtain hydrogen. Bag filter was design and tested successfully during experimental campaign. PSA was chosen among the different purification process to get pure hydrogen. Concerning safety, two main issues have been examined: hydrogen safety (production process) and hazardous molecule (PAH) formation during the decomposition. It was shown experimentally and by simulation that a residence time of about 100 ms is needed in order to avoid PAH formation (and adsorption on the carbon nanoparticles). Moreover nanoparticles handling was made using gloves and respiratory protection during the project.

4- *Product Characteristics and properties of produced carbon black*.

The filter materials, carbon black, have values of BET surface area in the range of 64 to 100 m^2/g that correspond very well to that of commercial conducting carbon blacks. These values may be associated to diameters of the elementary particle from 30 to 45 nm. The highest temperatures reached in the final trials lead to the highest crystalline level of the carbon particles. This fact is confirmed by the mechanical compression energy necessary to compact the carbon black to a given density. Compared to an industrial conductive carbon black, the carbon blacks obtained by the solar route are still bellow in terms of electrical conductivity, charge carrier concentration and mobility but they are approaching seriously the performances of industrial CB. As a conclusion we can affirm that an enormous progress has been obtained by the up-scaling of the solar reactor, by the improvement of the conditions of the reaction.

Obtained carbon materials are strongly approaching the level of performances of the industrial one for applicationsin the fields of polymer composites (rubber, plastics) and primary and secondary batteries.

5- Industrial solar plant design and prospect.

First evaluation showed that the small scale process will never be beneficial; consequently the efforts have been focused on a 10 MW_{th} plant. The solar reactor design was based on the validated simulation model.

Design of the Plant

Heliostat field: In consideration of all losses, the total heliostat surface is about 20,000 m². Because high concentration is needed (about 3 MW/m^2) CPC are used at the entry of the solar receiver this choice induces a special design of the field/receiver assembly. As a result we attempt to build three fields of heliostats so that the acceptance angle of the CPC's is no more than 30°. The field obtained in this concept, for a tower with 80 m height, has the rear row at about 205 m distance.

Receiver: Three absorber cavities on a tower receiver are planned. The efficiency of the receiver is assumed to be 90%. The aperture of each absorber cavity is composed of a cluster of 7 CPC with the following dimensions: entrance area, 0.636 m² and exit area, 0.159 m² and length, 1.17 m.

Flow sheeting: A flow sheet of the complete solar process has been prepared. It includes the solar reactor operating at 1600°C and 1 atm., a heat exchanger that recovers the heat of the off-gas to preheat the reactants, a filter (particle separation), a compressor and a PSA separator (H_2 separation). The off-gas is supposed to contain 90% H_2. The heat recovery saves nearly 2 MW thermal. Finally, the products of the solar process are either hydrogen and carbon or electricity and carbon. At the design point, the solar reactor is fed by 2,912 kg/h methane and it produces 623 kg/h Hydrogen and 1,786 kg/h Carbon.

Life cycle assessment: energy payback time (EPT) is 1 year.

Economics: The profitability of the solar process depends mainly on the solar reactor performances, on the quality of the produced carbon black and on the hypothesis of the cost estimation. The solar process gets beneficial for CB and H_2 selling price of 0.73 €/kg CB and 0.2 €/sm^3 H_2 in the best case (optimistic hypothesis) and respectively 1.2 €/kg CB and 0.2 €/sm^3 H_2 in a more realistic case.

Intentions for uses and impact

The future industrial uses of the results should be envisioned providing the demonstration of the two following components: (1) a 400 kW_{th} solar reactor that is the mean power delivered by one CPC of the 10 MWth solar reactor; (2) a high temperature heat exchanger aiming at heat recovery at the solar reactor outlet.

Project logo and website

Web-site:

http://www.promes.cnrs.fr/ACTIONS/Europeenes/eng-solhycarb.htm