

# SOLAR HYDROGEN AND C-NANOFILAMENTS BY THERMAL DECOMPOSITION OF CH<sub>4</sub> USING A 5 kW VORTEX-FLOW REACTOR

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The solar thermal decomposition of CH<sub>4</sub> for co-producing hydrogen and carbon is experimentally investigated. The solar chemical reactor features a vortex flow of CH<sub>4</sub> confined to a cavity-receiver and laden with carbon particles that serve simultaneously as radiant absorbers and nucleation sites. A 5 kW reactor prototype, tested at PSI's solar furnace and ETH's high-flux solar simulator with power flux intensities exceeding 3500 kW/m<sup>2</sup>, yielded 67% chemical conversion of CH<sub>4</sub> to H<sub>2</sub> and C(gr) at 1600 K and 1 bar. Carbon formed was of nano-filamentary nature. The proposed solar hybrid chemical process conserves natural gas, reduces CO<sub>2</sub> emissions, and provides a transition path to solar hydrogen.

## 1 INTRODUCTION

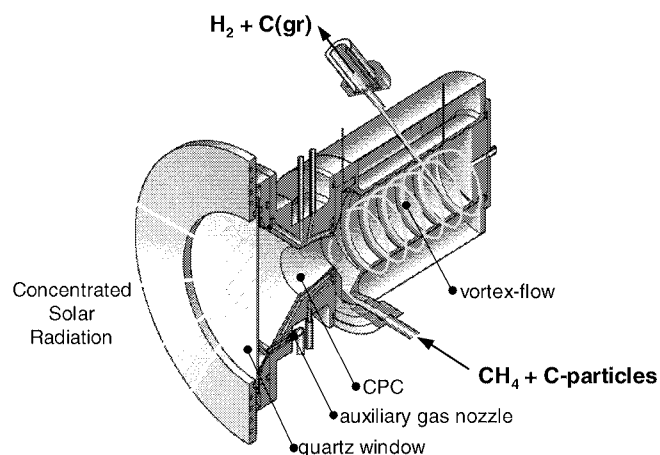
The solar thermal decomposition of natural gas (NG) establishes an energy efficient route for a clean decarbonization process. The overall reaction can be represented by:



Reaction (1) proceeds endothermically in the 800-1500 K range. The use of concentrated solar radiation as the energy source for high-temperature process heat offers several important advantages. Firstly, no pollutants are being discharged during the decomposition process and, if the carbon produced is finally sequestered, no CO<sub>2</sub> emission results from the complete process chain to electricity generation. Secondly, since there is no combustion taking place inside the reaction chamber, the H<sub>2</sub> produced (assuming near complete conversion) is not contaminated by oxides of carbon and, therefore, suitable to fuel PEM fuel cells without inhibiting Pt-based catalysts. Finally, the solar-driven process upgrades the calorific value of the feedstock by adding solar energy in an amount equal to the enthalpy change of the reaction [1]. Reaction (1) has been previously effected using solar process heat with CH<sub>4</sub> and C<sub>4</sub>H<sub>10</sub> for the catalytic production of filamentous carbon [2]. Recently, an aerosol tubular quartz reactor containing fine carbon black particles suspended in a CH<sub>4</sub> feed gas stream was tested in a solar furnace and yielded up to 90 % dissociation [3]. This note describes the solar chemical reactor technology and presents results of a solar experimental campaign with a 5 kW prototype reactor [4].

## 2 REACTOR TECHNOLOGY

The reactor configuration is depicted in Figure 1 and features a vortex flow of CH<sub>4</sub> confined to a cavity-receiver and laden with carbon particles that serve simultaneously as radiant absorbers and nucleation sites for the heterogeneous decomposition reaction. Such a reactor concept has been applied successfully for other gas/solid thermochemical processes [5]. A 5 kW prototype reactor was fabricated and tested at PSI's solar furnace [6] and at ETH's high-flux solar simulator [7]. Carbon particles fed were from Fluka 03866 (specific area 180 m<sup>2</sup>/g, mean particle size 15 μm, carbon content 79.5 %, ash content 5 %, water content 6 %).



**Fig. 1:** Schematic configuration of the solar chemical reactor for the thermal decomposition of CH<sub>4</sub>, featuring a vortex flow of CH<sub>4</sub> confined to a cavity-receiver and laden with C-particles that serve as radiant absorbers and nucleation sites.

## 3 SOLAR EXPERIMENTAL RESULTS

Operational conditions and summary of results obtained under approximate steady-state conditions are shown in Table 1. Assuming a first order decay rate law catalyzed over elemental carbon, the temperature dependence of the reaction rate can be well described by the Arrhenius law with an activation energy in the range 147-162 kJ/mole and a frequency factor in the range  $2.75 \cdot 10^5$ - $1.94 \cdot 10^6$  s<sup>-1</sup>, for either a plug flow or a mixed flow reactor model, respectively. The thermal efficiency is defined as:

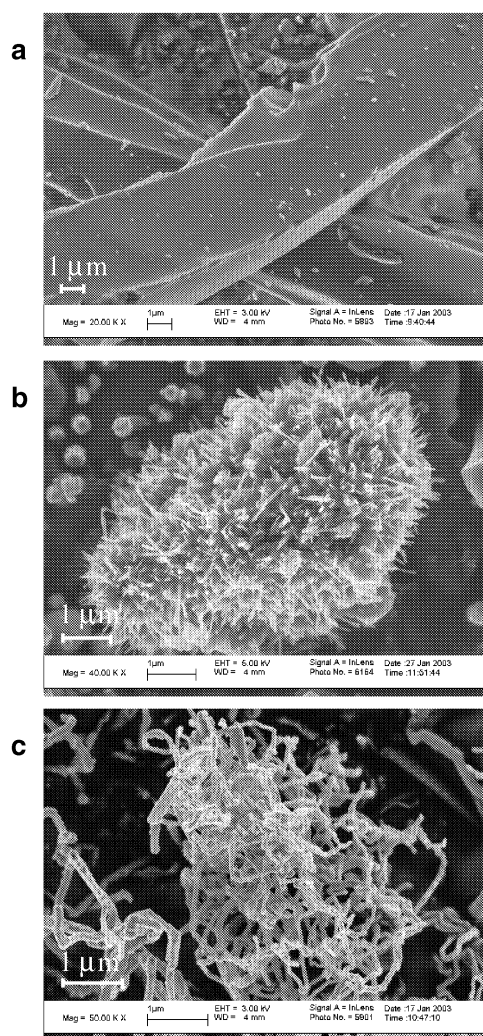
$$\eta_{thermal} = \frac{x_{reaction} \cdot \dot{m}_{CH_4} \cdot \Delta H}{Q_{solar}} \Big|_{\text{Reactants}@298K \rightarrow \text{Products}@T_{reactor}} \quad (2)$$

where  $\Delta H$  is the enthalpy change of the reaction,  $T_{reactor}$  is the nominal reactor temperature (measured by pyrometry),  $Q_{solar}$  is the solar power input (measured by a CCD camera),  $\dot{m}_{CH_4}$  is the mass flow rate of CH<sub>4</sub> (measured by electronic flow controllers), and  $x_{reaction}$  is the degree of chemical conversion (measured by GC). Values of  $\eta_{thermal}$  experimentally obtained were in the 7-16 % range. Heat losses were principally due to absorption/reflection at the window (~7% of  $Q_{solar}$ ), re-radiation through the aperture (~18% of  $Q_{solar}$ ), and conduction through the reactor walls (~15% of  $Q_{solar}$ ).

Run #	1	2	3	4	5	6	7	8	9	10	11
CH <sub>4</sub> flow rate (l <sub>n</sub> /min)	1.4	2.7	3.2	3.2	2.0	3.0	3.0	15.0	16.0	16.0	16.0
Ar flow rate at aperture (l <sub>n</sub> /min)	10.0	14.4	15.2	15.2	14.9	15.2	16.0	4.0	4.0	4.0	4.0
Carbon mass flow rate (g/min)	4.0	2.0	1.8	1.9	1.2	1.7	2.0	1.6	2.2	1.6	1.9
Solar power input (kW)	5.7	5.7	5.4	5.4	5.4	5.4	5.1	5.0	6.0	6.6	5.4
Mean flux intensity (kW/m <sup>2</sup> )	2840	-	-	-	-	-	2725	2342	3000	3536	2559
Duration (min)	53	21	23	26	20	24	15	20	18	13	12
T <sub>Reactor</sub> (K)	1601	1044	1052	1059	1011	1021	1372	1294	1172	1192	1227
Mean residence time (s)	10.0	9.3	9.1	9.1	9.8	9.0	7.3	7.3	6.9	6.9	6.9
CH <sub>4</sub> conversion (%)	67.0	31.4	33.6	34.1	31.7	30.4	44.1	6.8	16.4	9.3	13.7
H <sub>2</sub> production rate (l <sub>n</sub> /min)	1.96	1.70	2.15	2.18	1.27	1.82	2.65	2.03	5.24	2.98	4.37
Thermal efficiency (%)	13.3	7.9	9.2	9.3	7.0	8.4	9.8	16.2	14.0	11.9	16.2

<sup>a</sup> l<sub>n</sub> means liters at normal conditions; mass flow rates are calculated at 273 K and 1 bar.

**Table 1:** Operational conditions and summary of results obtained in the solar experimental campaigns at PSI's solar furnace and ETH's high-flux solar simulator.



**Fig. 2:** SEM of particles (a) fed with CH<sub>4</sub>; (b) sediment inside the reactor; (c) products collected downstream.

Figure 2 shows SEMs taken from C-particles samples before and after the reaction. Figure 2(a) shows the SEM of particles fed with CH<sub>4</sub> for run #1, characterized by their poly-dispersity, irregular shape, and

smooth flat surfaces. Figure 2(b) shows the SEM of a sample of particles taken from sediments inside the reactor after run #1, revealing the beginning of the carbon growth process and the formation of whiskers. Figure 2(c) shows the SEM of particles collected in the filter downstream. Filaments of about 50 nm diameter and several microns length have grown during the cracking of CH<sub>4</sub>, were carried by the vortex flow, and finally collected downstream. These filaments are randomly interlaced and, as revealed by TEM, non-hollow. The filament growing mechanism appears to be by surface growth: a carbon particle or cluster of about 50 nm diameter serves as the nucleation site for the next carbon particle or cluster layer of same size.

#### 4 ACKNOWLEDGEMENTS

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