Solar thermal splitting of methane in a volumetric reactor for combined production of hydrogen and carbon nano-materials

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The Chemical Reaction

$CH_4 \rightarrow C\ (solid) + 2\ H_2$ $\quad \Delta H_{298}=75.6\ Kj$

$\Delta H_{1773}=90.7\ Kj$

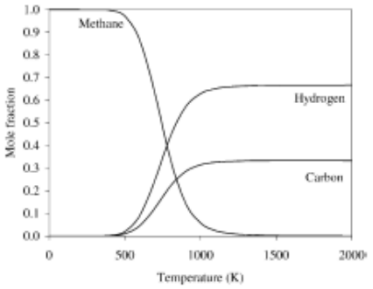
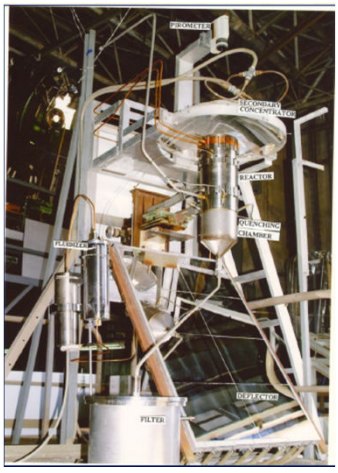


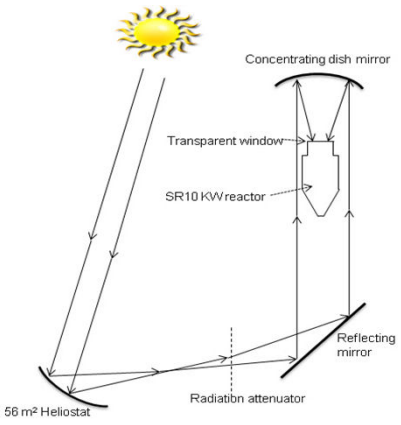
Fig. 3. Equilibrium composition of the system CH_4, as a function of temperature.

Some important introductory remarks

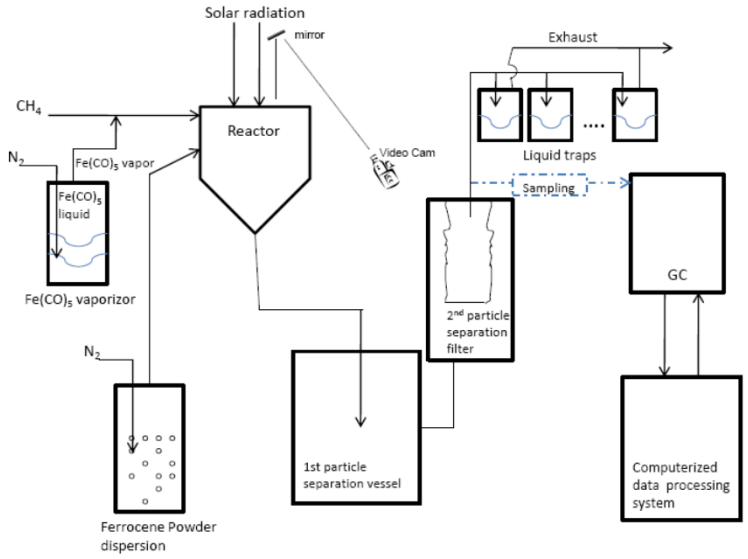
- A major problem in operating a directly heated solar volumetric reactor is keeping the transparent window through which the solar radiation enters, clean window protection and directional streaming flow of a swirling nature.
- Once the quality of the carbon product can be upgraded to carbon nanotubes (CNT), the hydrogen can become an economical by-product.
- Organometallic catalyst decomposes at the gas phase and the metal forms a cluster on which carbon atoms nucleate and grow. Such organometallic compounds can be iron pentacarbonyl, $Fe(CO)_5$, and ferrocene ($Fe(C_5H_5)_2$).
- Other processes, which make use of different catalysts, use radiation spectra similar to or alike the solar spectrum, e.g. we find useful laser wavelengths of 0.532 microns. Those findings suggest that there might be a photo-catalytic effect in the CNT formation.

Experimental System

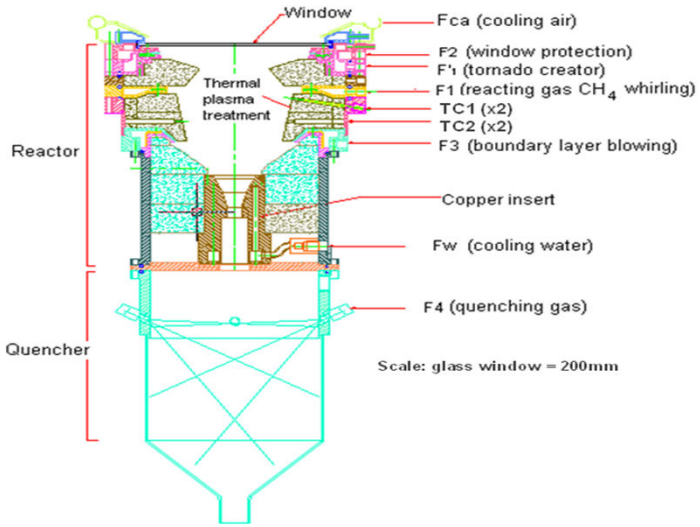




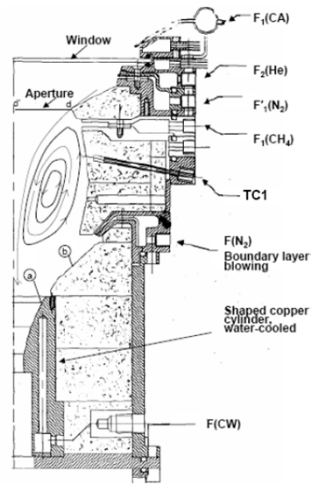
Scheme of Reaction System

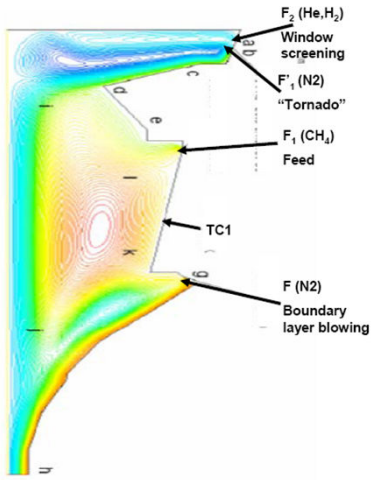


Axial cross section of the WIS 10 kW prototype solar reactor



CFD - Computational Fluid Dynamics





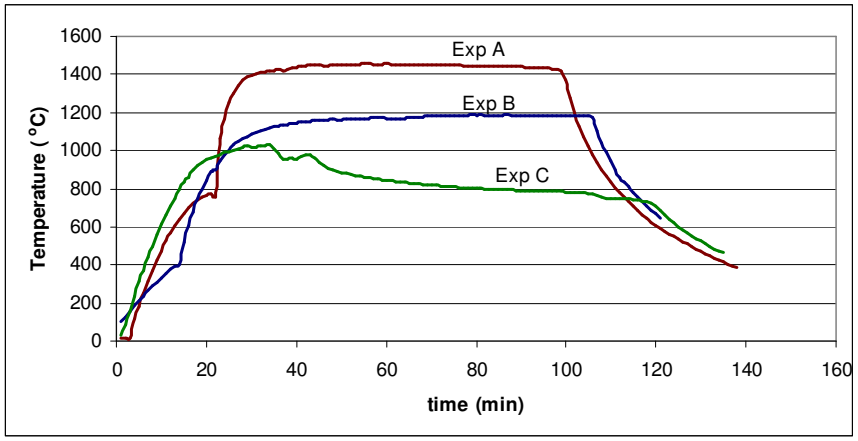
Experimental Results

Table 1 – Experimental parameters.

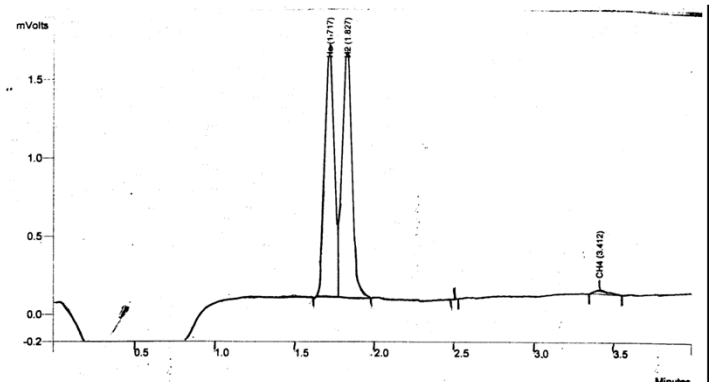
Experiment (type)	A	B	C
Catalyst	None	$Fe(CO)_5$	$Fe(C_5H_5)_2$
Mass flow of catalyst (g/min)	None	0.97	0.7
Molar Fe/C ratio (in CH_4 feed)	None	2.4%	1.8%
Solar insolation striking the heliostat (W/m^2)	950	600–650	500–540
Inlet flow composition and rate (standard liters per minute-SLM)			
F1 – reacting gas	CH_4 9.7	CH_4 5.0	CH_4 5.0
F2 – window protection	He 3.9	He 3.4	H_2 3.0
F'1 – tornado generator	N_2 30.0	N_2 30.0	N_2 30.0
F3 – boundary layer flowing	N_2 20.4	N_2 20.4	N_2 20.4
F4 – exit gas quenching	N_2 71.4	N_2 71.4	N_2 71.4
Average operating temperature (°C)	1450	1200	800

Average Temperatures in Reacting Zone

A – none ; B – Iron pentacarbonyl ; C - Ferrocene

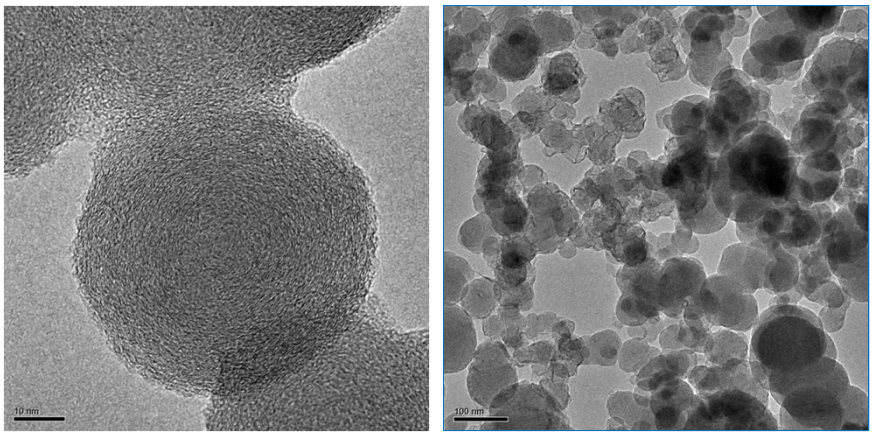


Example of a Report of VARIAN 3900 GC with STAR data acquisition system

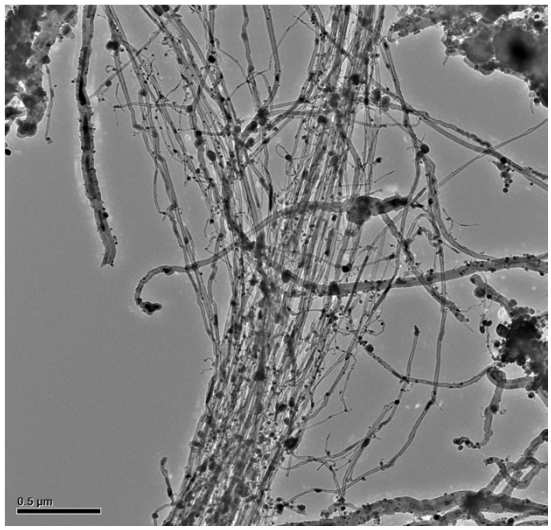


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1	He	47.7018	1.717	-0.024	6441	0.00	BV	3.8		0
2	H2	51.0580	1.827	-0.006	6895	0.00	VB	4.1		0
3	CH4	1.2402	3.412	-0.010	167	0.00	BB	4.6		0
	Totals	100.0000		-0.040	13503					

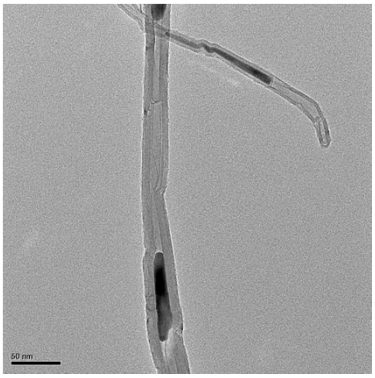
TEM images of carbon particles produced in Experiment A (High temperature, no catalyst)

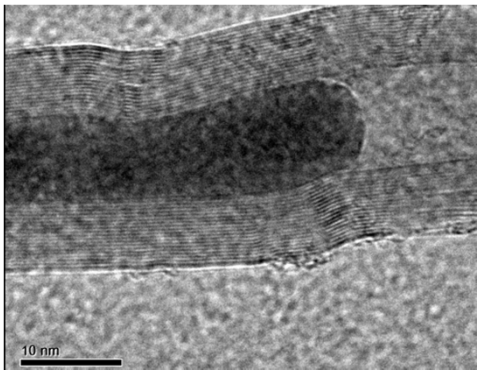


TEM image of carbon nanotubes produced in Exp C (Low temperature, with ferrocene)



TEM images of multi-wall carbon nano-tube (MWCNT) produced with catalysts; metal clusters (dark spots)





Conclusions

This work presents a process demonstrated with a 10 KW solar reactor system for splitting of methane to hydrogen and carbon nano-particles, with the following advantages:

- **A volumetric 3D mode of operation allowing high production throughput.**
- **High scalability to fulfill mass production demands.**
- **Direct irradiation of the reaction space through a transparent window cooled and protected from carbon deposition.**
- **Maintaining average temperature of about 1450°C in the reaction core ensures a complete conversion of the methane.**
- **Continuous and stable mode of operation due to maintenance of proper fluid dynamics regime ("tornado" effect).**
- **Possible recycling of the product hydrogen to replace inert carrier gas (used for the swirling effect and the quenching) which simplify and cancel needs of gas separation**
- **A high value controllable carbon product, spherical onion-like nano-particles (carbon-black) in non catalytic reaction, or MWCNT in the catalytic case were obtained with byproduct hydrogen as the clean energy carrier.**

Abraham Kogan 1921-2009