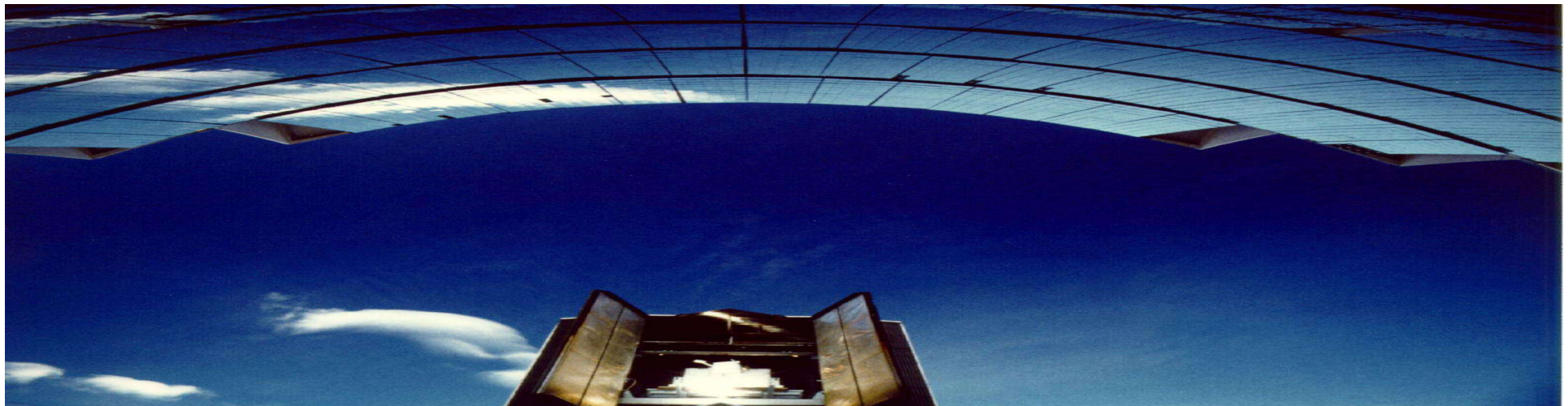
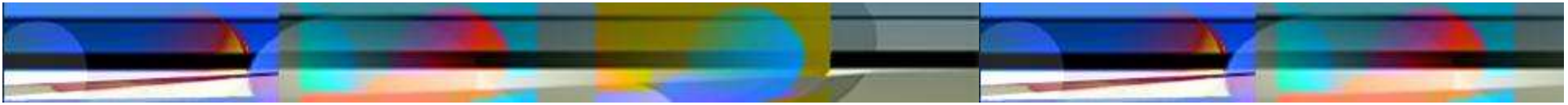


# Coproduction of Hydrogen and Carbon Black from Natural Gas Cracking under Concentrated Solar Radiation

**S. Rodat, S. Abanades, G. Flamant**  
*PROMES Laboratory*

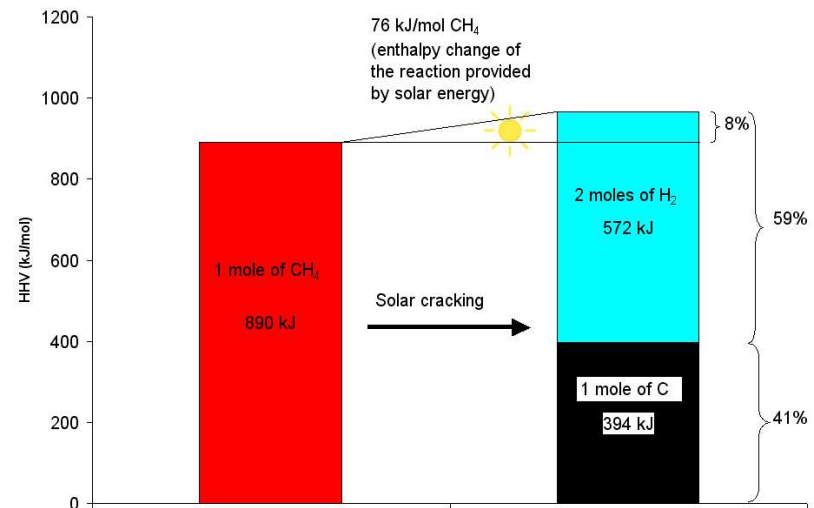




# Solar methane cracking: 10 and 50 kW multi-tubular solar reactors with cavity receiver (indirect heating)



European project  
**SOLHYCARB**



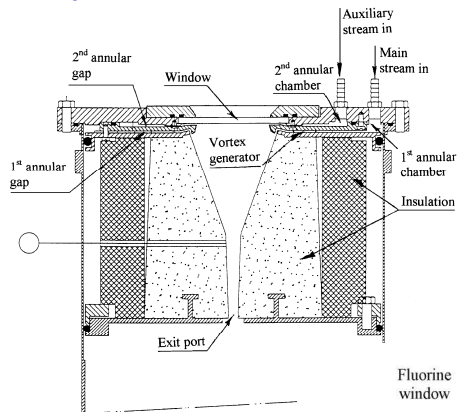
Steam Methane Reforming (SMR) and the furnace process are the commonly used H<sub>2</sub> and carbon black production processes respectively



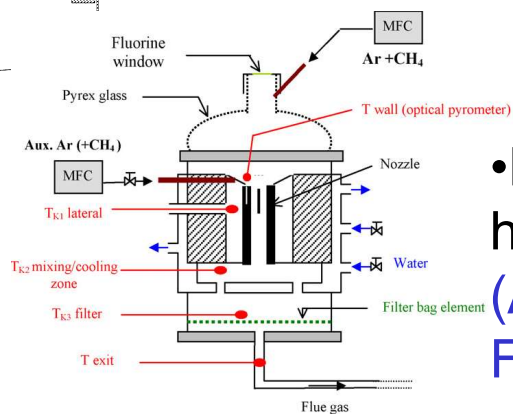
# State of the art: solar methane cracking

- Tubular fluid-wall solar reactor (indirect heating) (Dahl et al., 2001) NREL-USA

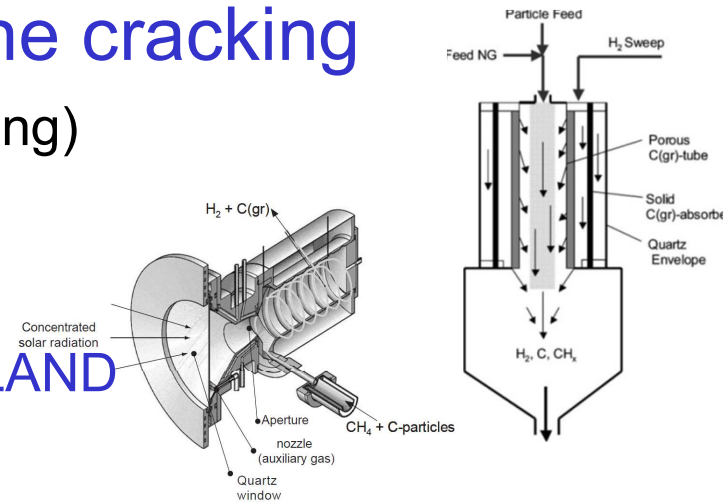
- Vortex flow reactor (direct heating) (Hirsch and Steinfeld, 2004) ETH-SWITZERLAND

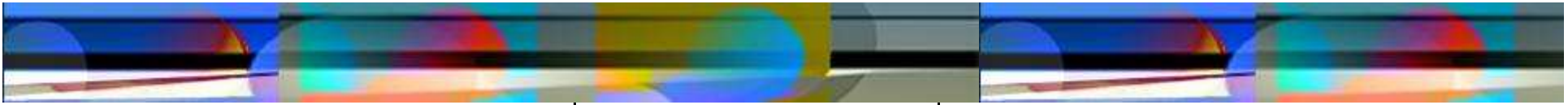


- Tornado flow reactor (direct heating) (Kogan and Kogan, 2003) WIS-ISRAEL



- Nozzle-type solar reactor in graphite (direct heating) (Abanades and Flamant, 2005) CNRS-FRANCE



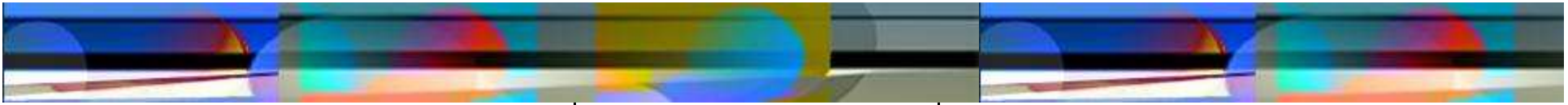


Experimental set-up

Results

CB Characterisation





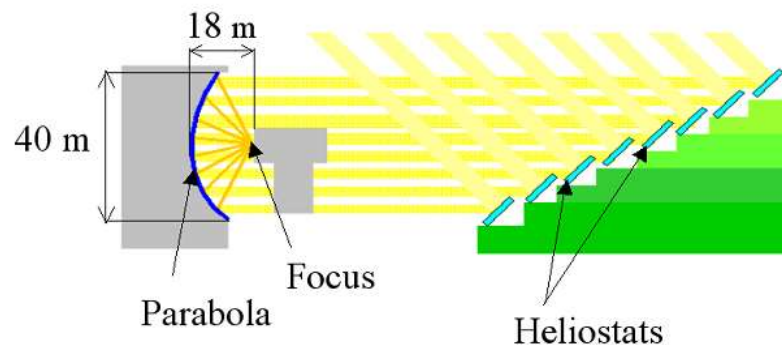
Experimental set-up

Results

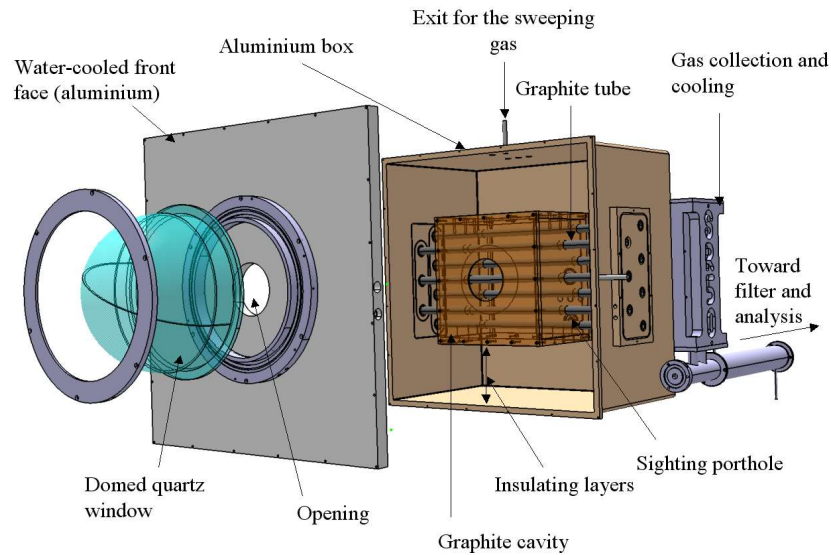
CB Characterisation



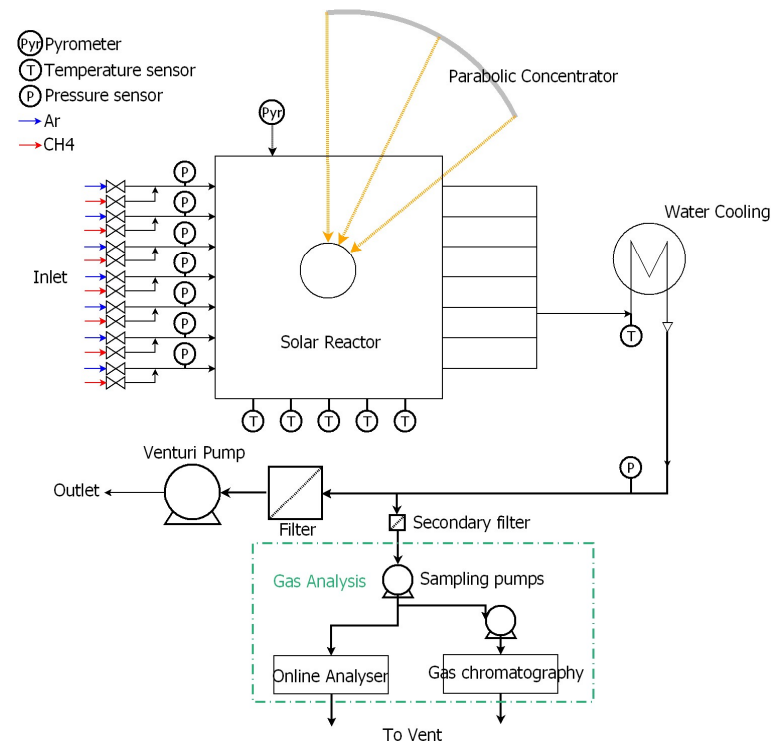
- Investigation of the **indirect heating** concept: solar irradiated zone separated from the reacting flow
- **Main advantages:**
  - No carbon particle deposition issue on the window
  - Carbon particle seeding (radiant absorber) not required in theory
- **Concentrating system:** 1 MW solar facility of Odeillo CNRS laboratory  
 $C_{\max} = 9000$  suns (1 sun = 1 kW/m<sup>2</sup>), Gaussian solar flux density distribution



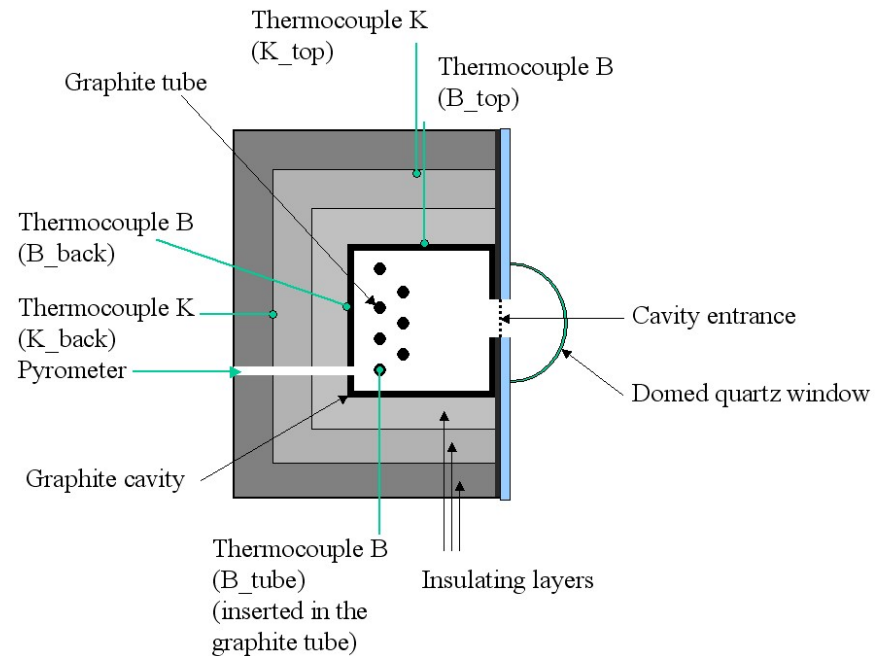
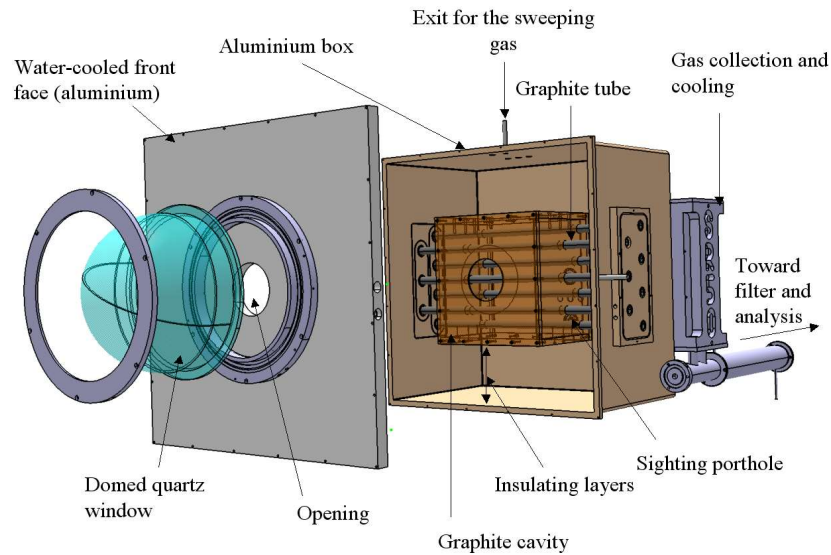
# 50 kW CNRS solar reactor



- 7 single graphite tubes (26-18 mm)
- Graphite cavity (360x400x300 mm)
- Aperture diameter 13 cm



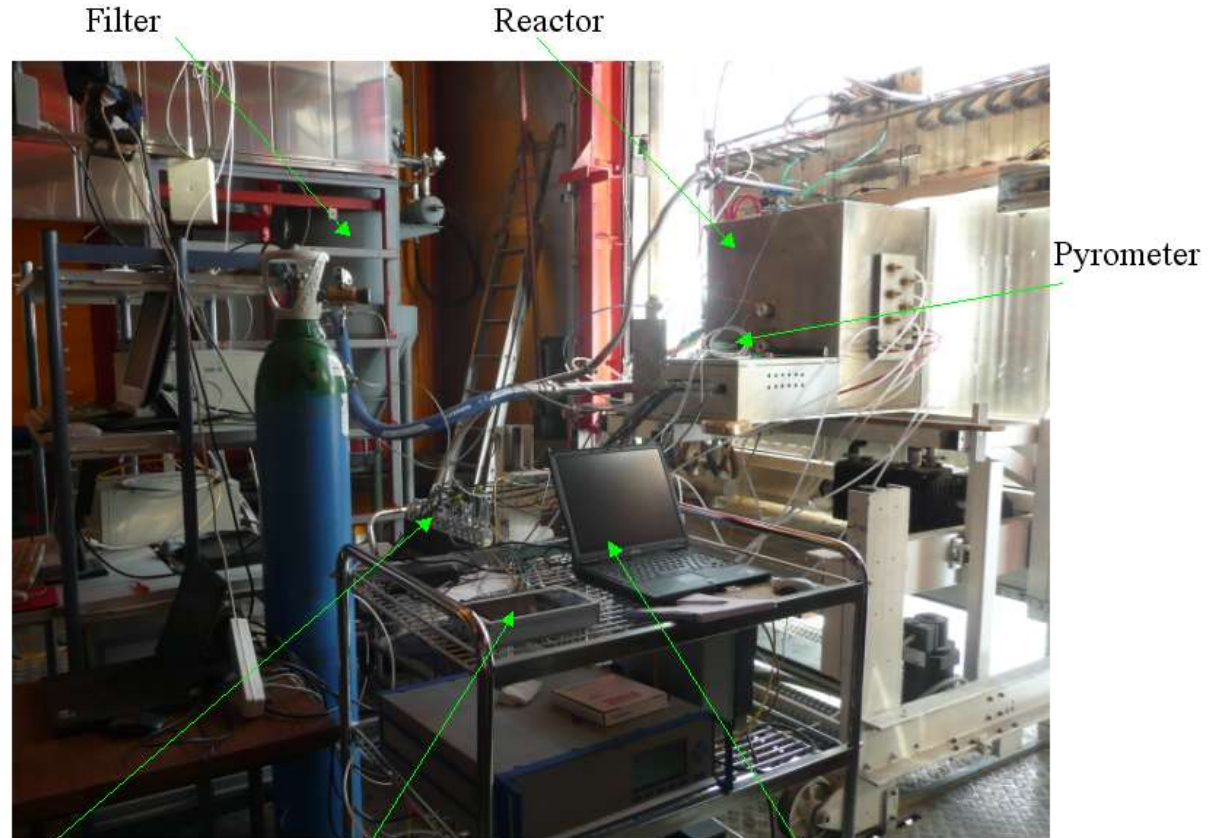
# 50 kW CNRS solar reactor



- 7 single graphite tubes (26-18 mm)
- Graphite cavity (360x400x300 mm)
- Aperture diameter 13 cm



Whole installation in operation at the focal zone



Filter

Reactor

Pyrometer

Mass-flow controllers

Data acquisition for the thermocouples and the online gas analyser

Control of the pyrometer and the gas chromatography



Experimental set-up

Results

CB Characterisation



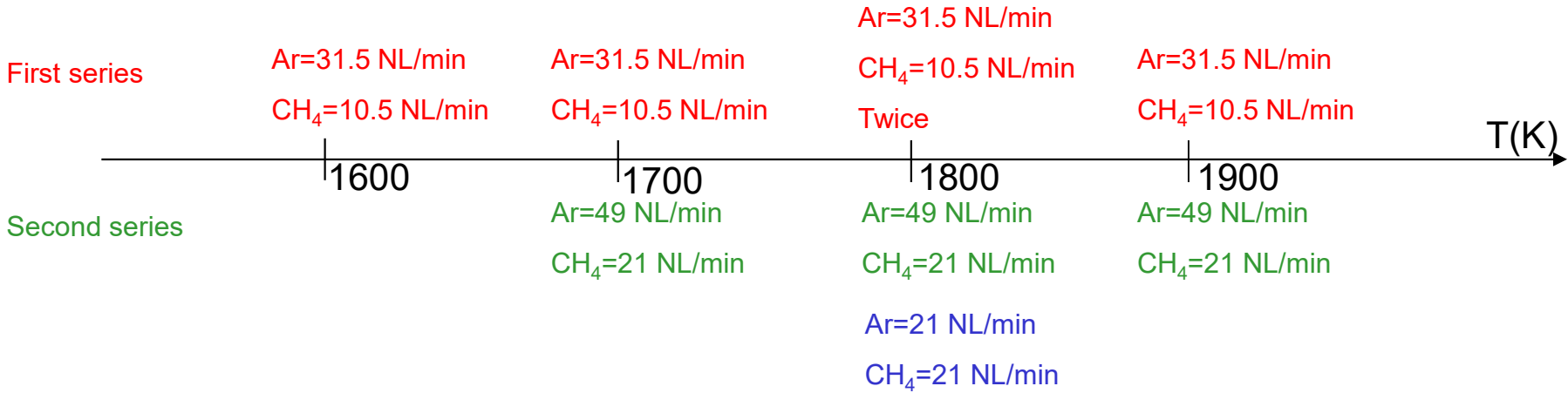


Experimental set-up

Results

CB Characterisation

9 experimental conditions, 2 series:



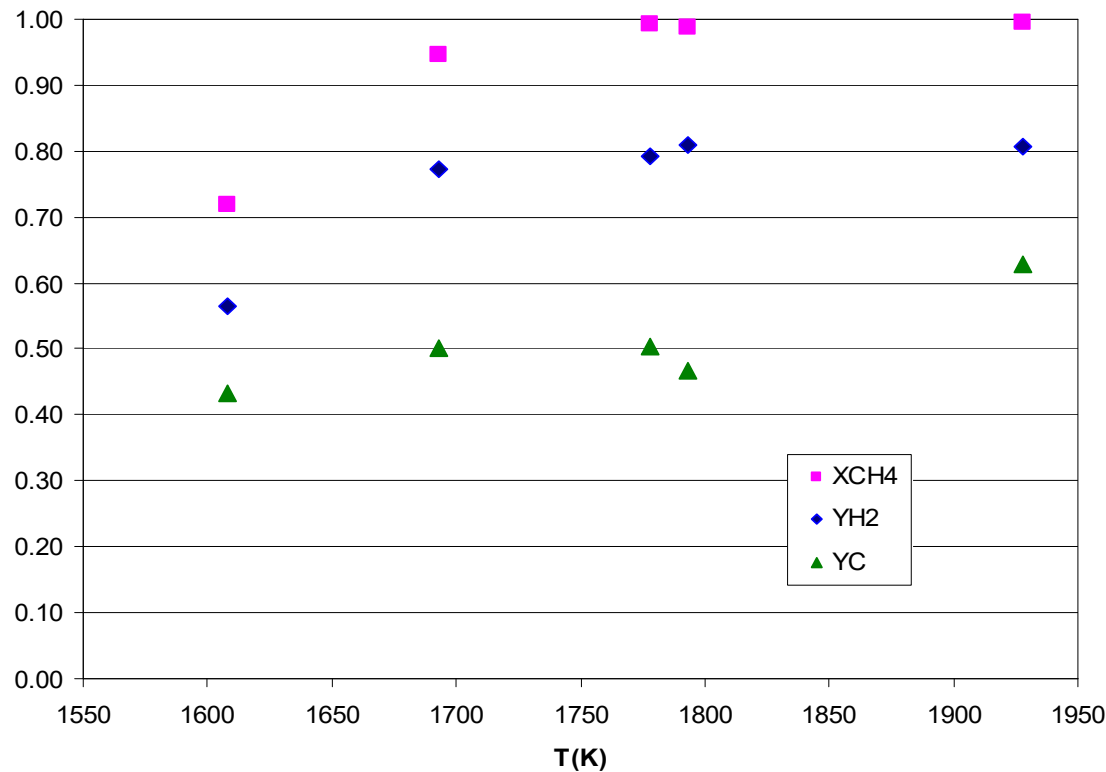
Methane conversion: 
$$X_{CH_4} = \frac{F_{0,CH_4} - F \cdot y_{CH_4}}{F_{0,CH_4}}$$

Hydrogen yield: 
$$Y_{H_2} = \frac{F \cdot y_{H_2}}{2 \cdot F_{0,CH_4}}$$

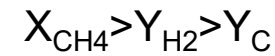
Carbon yield: 
$$Y_C = \frac{F_{0,CH_4} - \sum x \cdot F \cdot y_{C_xH_y}}{F_{0,CH_4}}$$



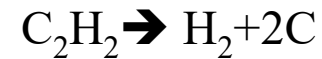
First series: CH<sub>4</sub> (10.5NL/min), Ar (31.5NL/min)



If T increases, all the chemical performance criteria increase

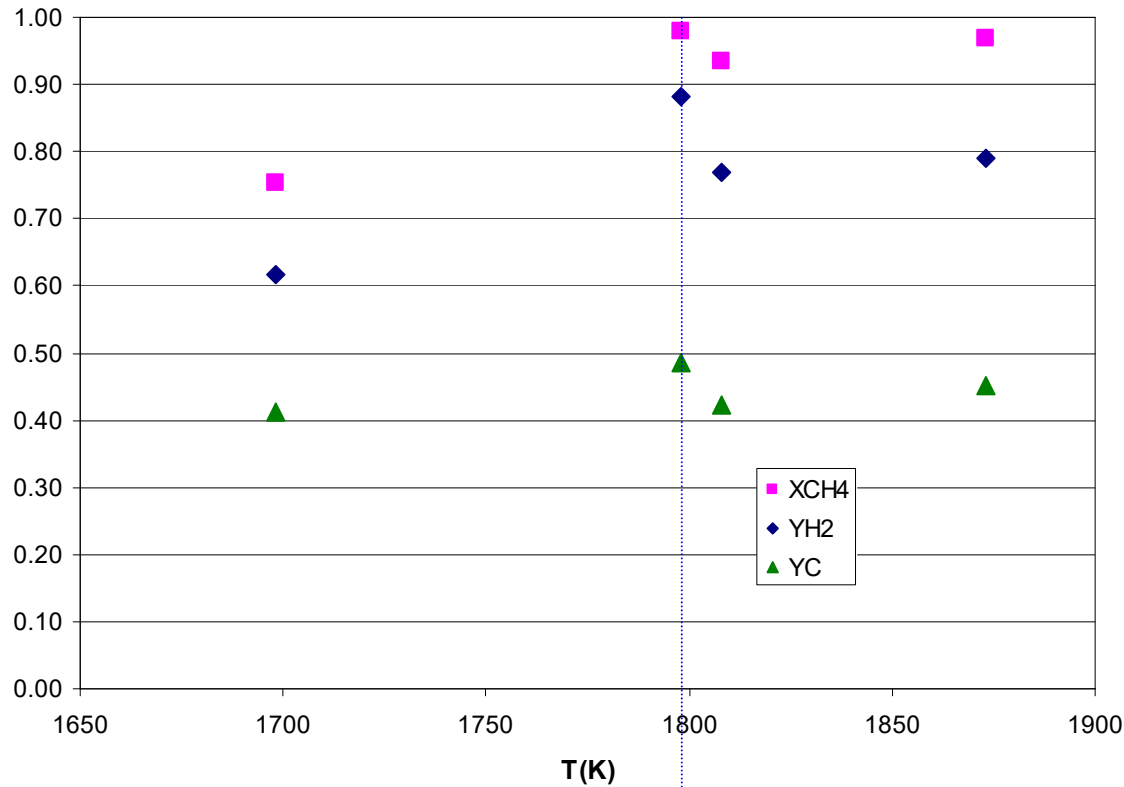


Two-step reaction mechanism:



Similar runs lead to close results

Second series: CH<sub>4</sub> (21NL/min), Ar (49NL/min)



Ar=21 NL/min

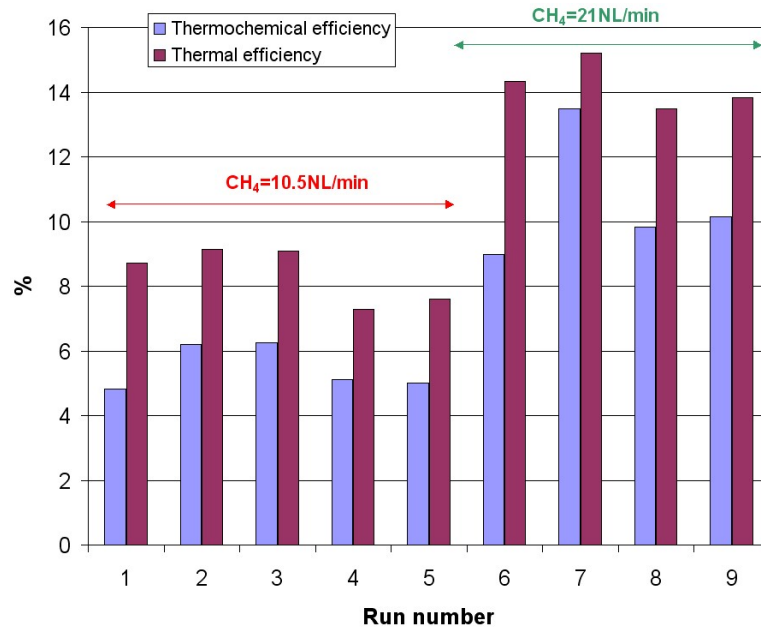
CH<sub>4</sub>=21 NL/min

If T increases, all the chemical performance criteria increase

Lower dilution leads to better chemical performances as a result of residence time increase

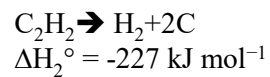
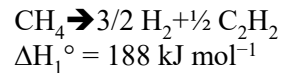


## Thermal and thermochemical efficiencies



- Better efficiencies for the second series due to a higher methane flow rate
- Best thermal efficiency is 15%

Two-step reaction mechanism:



$$\eta_{ch,new} = \frac{F_{0,CH_4} \cdot X \cdot \int_{T_0}^{T_{reactor}} Cp_{CH_4} \cdot dT + F_{0,CH_4} \cdot X \cdot \Delta H_1(T_{reactor}) + 1/2 \cdot F_{0,CH_4} \cdot X \cdot Y \cdot \Delta H_2(T_{reactor})}{P_{solar}}$$

$$\eta_{th,new} = \frac{F_{0,CH_4} \cdot \int_{T_0}^{T_{reactor}} Cp_{CH_4} \cdot dT + F_{0,CH_4} \cdot X \cdot \Delta H_1(T_{reactor}) + 1/2 \cdot F_{0,CH_4} \cdot X \cdot Y \cdot \Delta H_2(T_{reactor}) + F_{Ar} \cdot \int_{T_0}^{T_{reactor}} Cp_{Ar} \cdot dT}{P_{solar}}$$



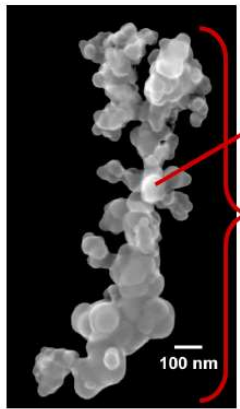
Experimental set-up

Results

CB Characterisation



## Microscopy analysis



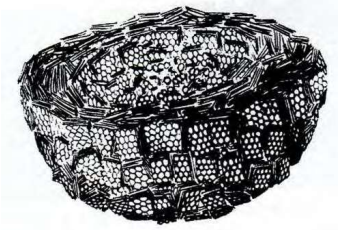
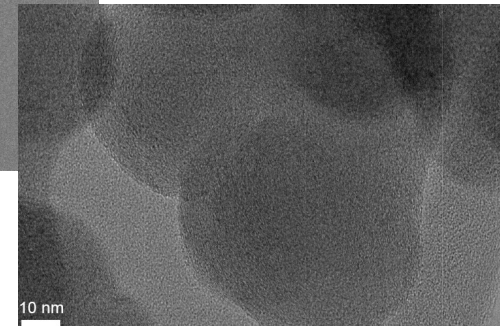
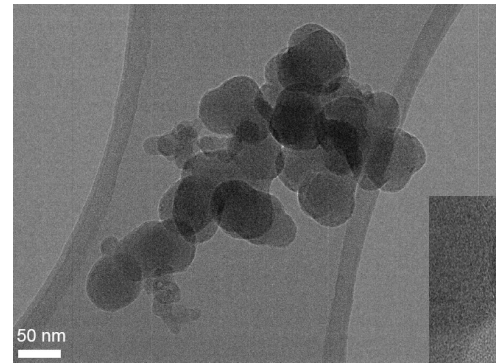
Aggregation of

- Spherical **primary particles**
- Nano-sized

to

- Porous **secondary particles**
- Structured

Agglomeration to **ternary particles**

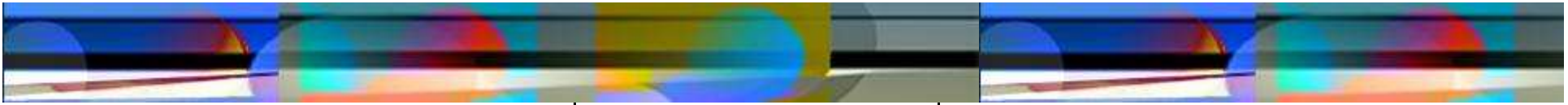


Heidenreich et al.

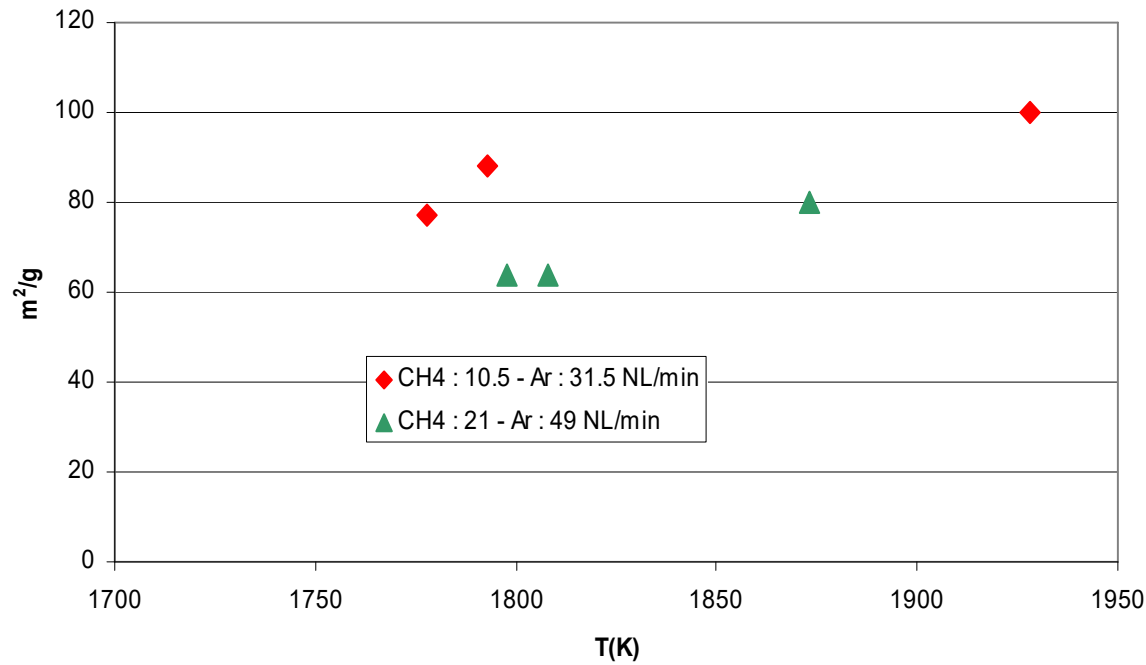
Primary particles size (10-70 nm)

Source: APTL



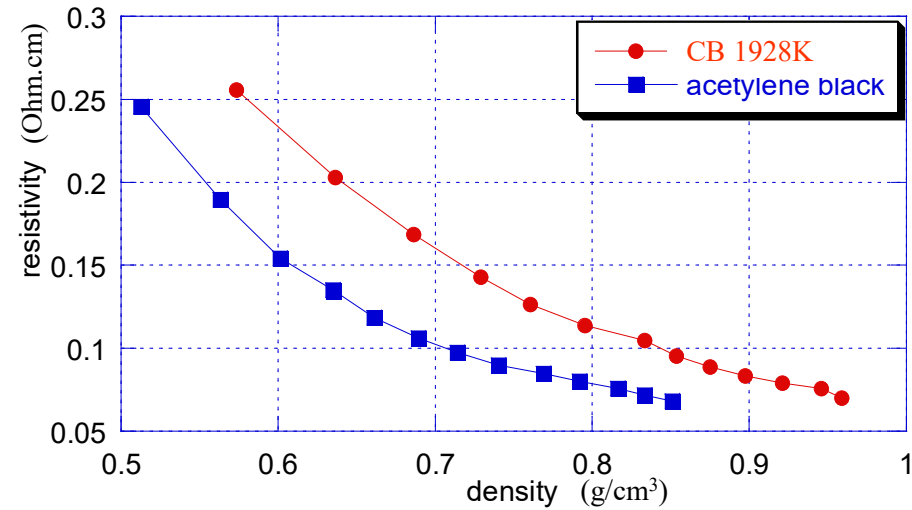
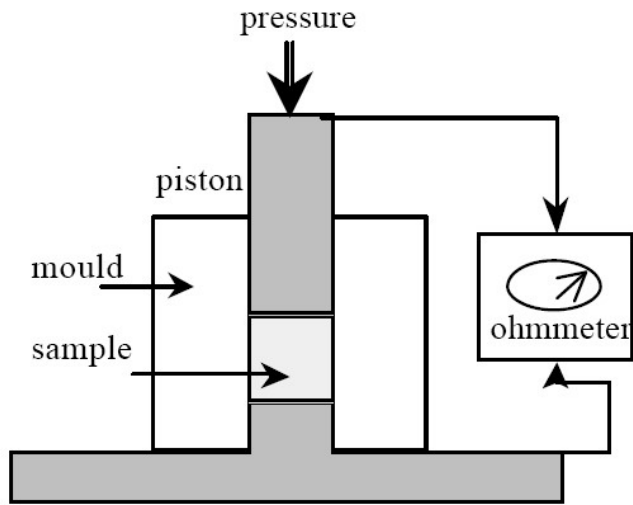


## BET and influence of the temperature



Increasing the temperature increases the specific surface area

Structure evaluation



Source: TIMCAL

Solar carbon black is less conductive than the commercial one, but similar trends are observed



## Conclusion

50 kW solar reactor operated successfully at the 1 MWSF

### Experimental results:

2 main parameters: temperature and residence time

For 1.26 Nm<sup>3</sup>/h CH<sub>4</sub> injected (50% molar, the rest being argon, 60 ms residence time) at 1800K, this reactor produced 2.24 Nm<sup>3</sup>/h H<sub>2</sub> (88% H<sub>2</sub> yield), 330 g/h CB (49% C yield) and 0.30 Nm<sup>3</sup>/h C<sub>2</sub>H<sub>2</sub> with a thermal efficiency of 15%

**CB properties:** close to commercial conductive CB, required properties very dependant on the application

**Up-scale (10 MW):** H<sub>2</sub> production price of 1 \$/kg (reference for steam reforming) is reached for a carbon black selling price of 1.05 \$/kg (possible for specialty carbon blacks)

**Thank you for your  
attention**



**Time for questions !**

