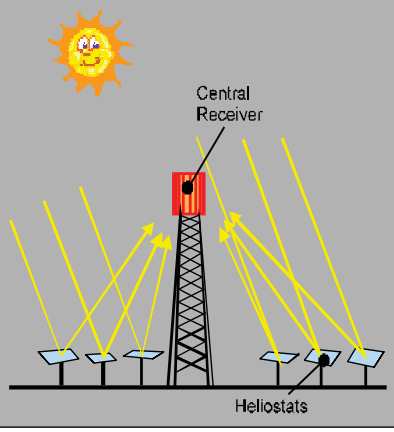
Solar Gasification of petroleum coke



Alfonso Vidal
Energy Department
CIEMAT-PSA

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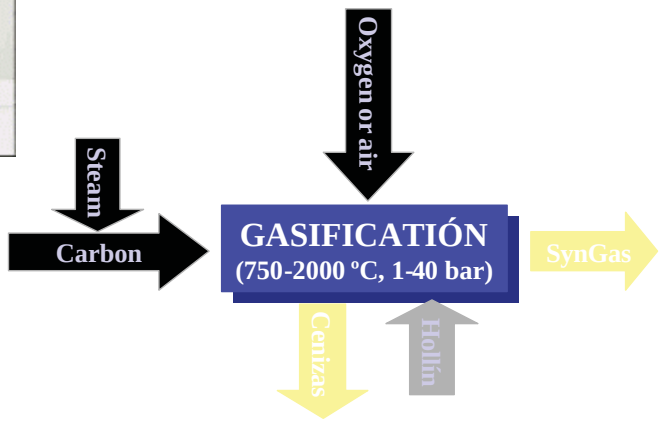
Gasification & Combustion

$$C(s) + H_2O(l) \longrightarrow CO(g) + H_2(g)$$



2

Thermodynamics

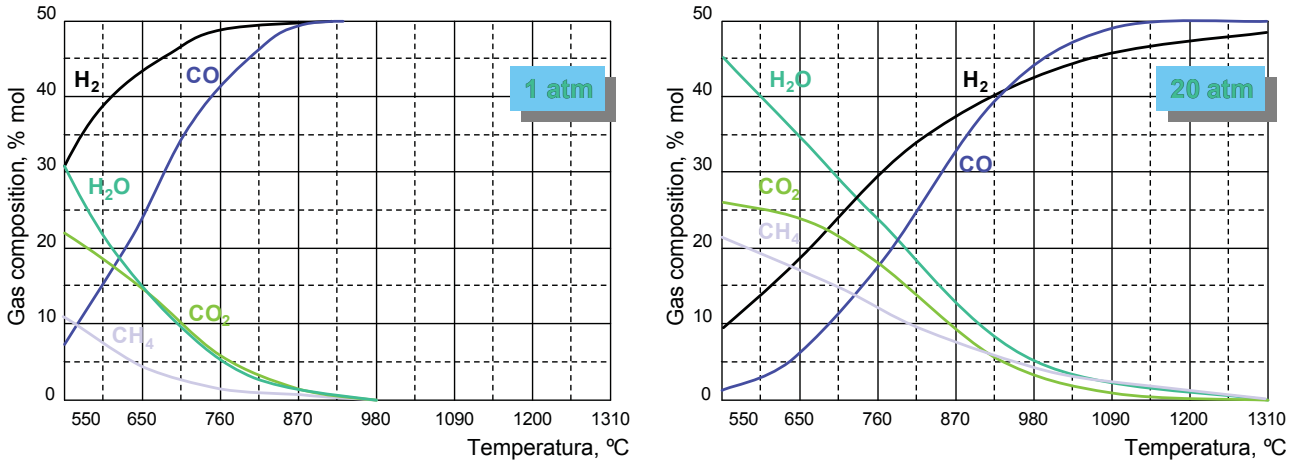
$$C + CO_2 \xrightleftharpoons{\uparrow T} 2\,CO$$

$$C + H_2O \xrightleftharpoons[\uparrow P]{} CO + H_2$$

$$C + 2\,H_2 \xrightleftharpoons{\uparrow T} CH_4$$

$$CO + 3\,H_2 \xrightleftharpoons[\uparrow P]{} CH_4 + H_20$$

$$CO + H_2O \xrightleftharpoons{\uparrow T} H_2 + CO_2$$

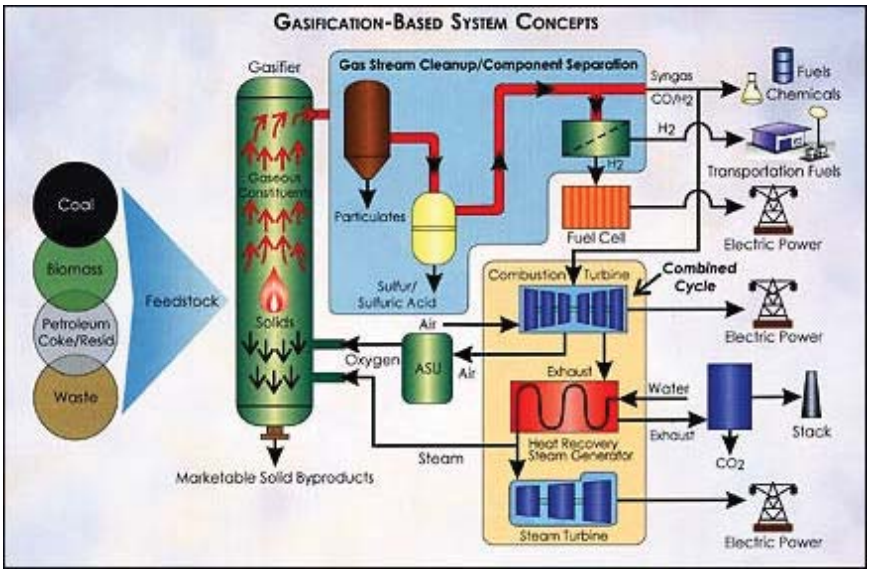


	H_2O	H_2	CO	CO_2	CH_4
↑T	↓	↑	↑	↓	↓
↑P	↑	↓	↓	↑	↑

Gasification

- **Gasification is a commercial technology, widely used around the world and is poised for significant worldwide growth**
  - **World gasification capacity is 45.000 MWth equivalent**
  - **Worldwide gasification capacity is projected to grow 70 percent by 2015, with 80 percent of the growth occurring in Asia. (See World Syngas Capacity Growth).**
- **Gasification also opens the way for carbon-based feedstocks to compete with natural gas and petroleum to produce value added products.**
  - **Chemicals**
  - **Fertilizers**
  - **Fuels (pipeline gas & F-T liquids)**
- **Gasification can be used to produce electricity via Integrated Gasification Combined Cycle (IGCC). IGCC cleanest coal/residue-based alternative for power generation, reducing natural gas dependency for electricity.**
- **It is a versatile process that can use all carbon-based feedstocks, including coal, petroleum residues, biomass, etc Gasification adds value to world coal reserves and other "distressed" fuels/feedstocks.**
- **Implications for: National Energy Security, Fuel Diversity, Geographical Conversion Diversity**

Gasification products



Gasifier Types

Gasifier Type	Moving (fixed bed)	Fluid Bed	Entrained Bed
Process Description	Moving bed, also known as fixed bed, gasifiers, feed coal in the top. The coal moves down through the reactor by gravity. Steam and oxygen are fed in through the bottom of the gasifier. 	The solid particles are fluidized with the gas and then the gases and remaining solid particles are separated. The gasifier typically operates at a low temperature (non-slagging). Attempts are being made to operate at high temperature (slagging). 	Solid and gas flow together in an "entrained" bed. Short residence times and high temperature operation. High carbon conversion is achieved through the use of high-purity oxygen. These gasifiers operate in the slagging mode. 
Pressure	1-100 bar	1-25 bar	1-40 bar
Gas Temperature	300-600ºC	700-1100ºC	1000-1500ºC
Technology Providers	BGL, Lurgi	HTW, KRW, KBR transport reactor, Winkler	ConocoPhillips, Future Energy, GE Energy, ICCT, Shell, Texaco.
Installed Capactiy	18.7 GWth (42%)	0.9 GWth (2%)	25.4 GWth (56%)

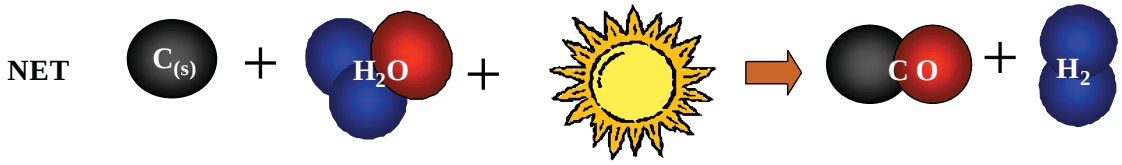
Solar Gasification

Motivation
Why Solar Gasification:

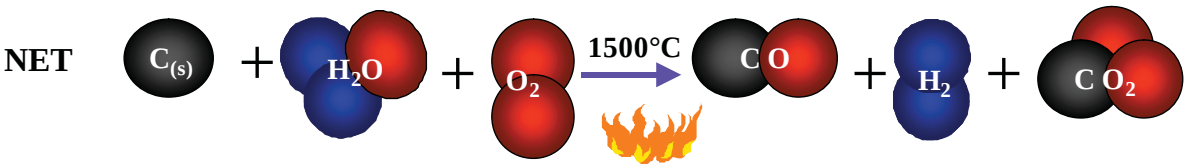
$$C_xH_y + xH_2O = \left(\frac{y}{2} + x\right) \cdot H_2 + xCO$$

- *Gasification is a well established process in chemical industry*
- *Highly endothermic reaction (i.e. net process is endothermic by about 40-50% of the feedstock's LHV).*
- *Process heat can be provided completely by solar energy using solar-thermal concentrating systems.* **Implications for:**
  - ***Saving of (fossil) fuels**. High level policy objective regarding security of energy supply (DS).*
  - ***Reduction of CO2-Emissions**. High level policy objective regarding reduction of GHG emissions (DS)*

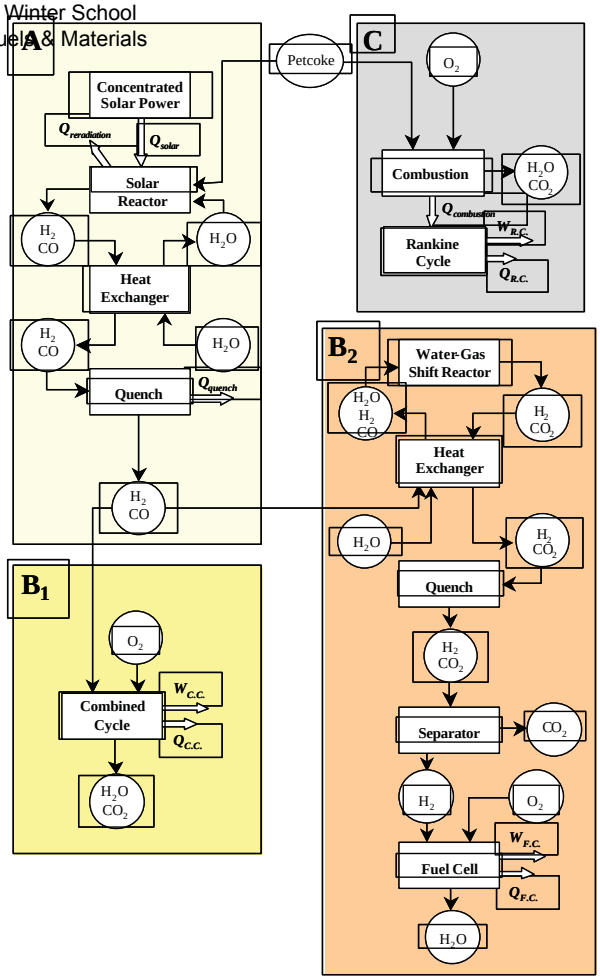
Thermal vs Solar Gasification



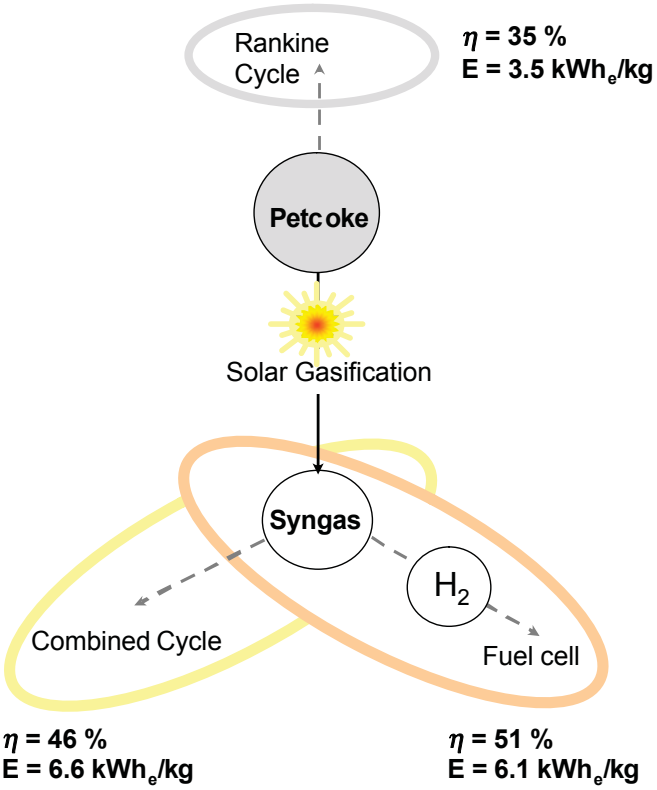
CO_2- Free

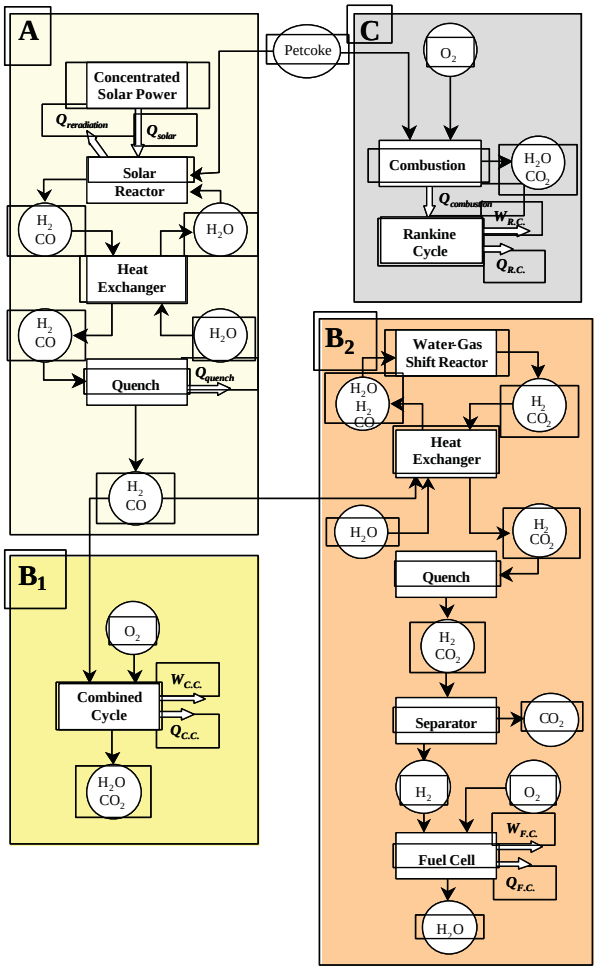


CO_2 Generation

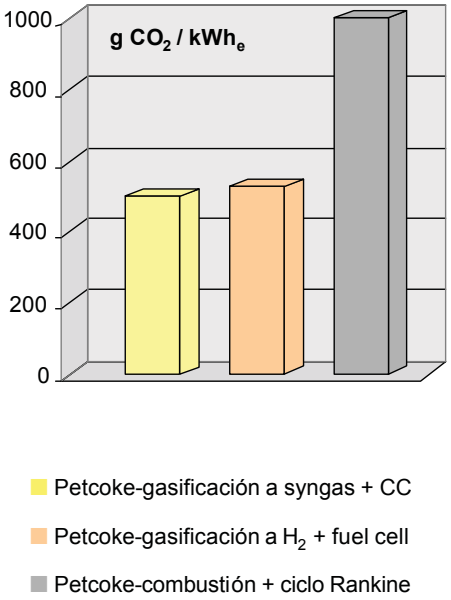


$$\eta = \frac{Work\ \ Output}{Q_{solar} + LHV_{coke}}$$



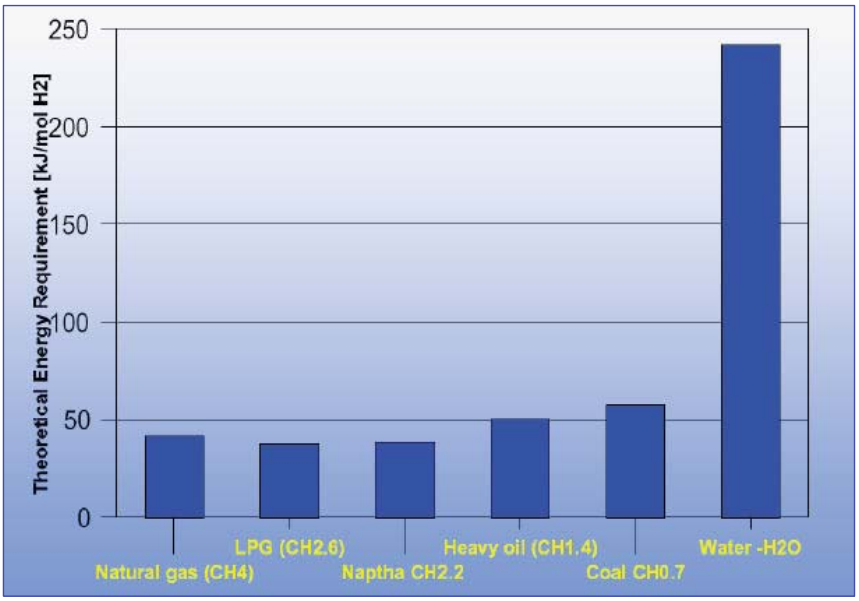


Emisiones específicas CO_2

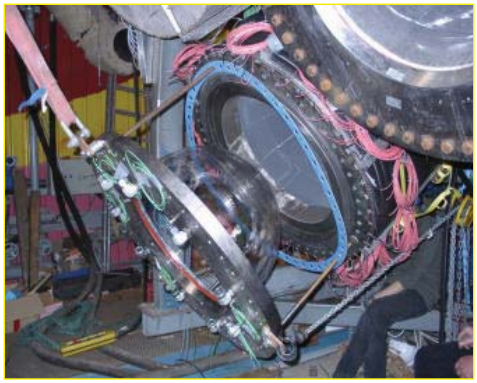


Water splitting thermodynamics

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2$$

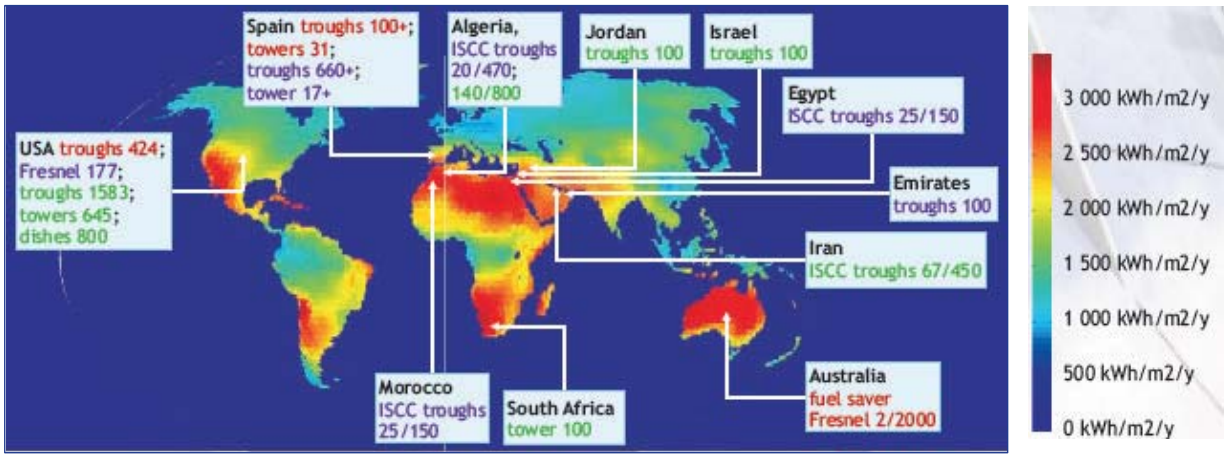


Status of Concentrating Solar Plants



- Mature low-cost large-area heliostats below 150€/m^2.
- Volumetric receivers and directly illuminated receivers demonstrated > 1000°C and > 2 MW/m^2
- Advanced controls developed
- Still 2.5x more expensive than fossil
- 60% cost reduction by 2015.
- First solar plants in Spain and EEUU

Status of the Concentrating Solar Plants

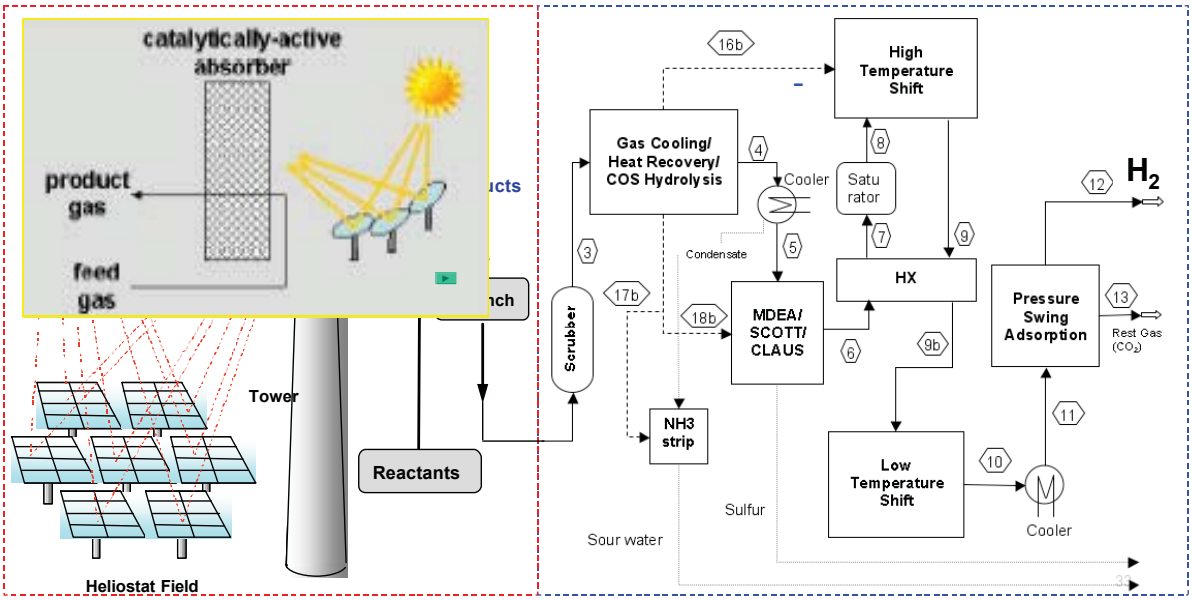


Legend: existing capacities; capacities under construction; announced capacities; xx: capacity in MWe. +: indicates large storage capacities (the capacity of the power plant is larger than the electrical capacity indicated); xx/yy: for Integrated Solar Combined Cycle or fuel saver systems, xx indicates the solar capacity, yy indicates the overall capacity.

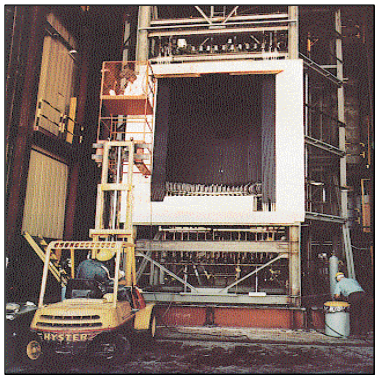
- CSP technology showed especially strong growth in Spain and the United States since 2006. Installed capacities near 1 gigawatt (GW) and projects under development or construction exceed 15 GW worldwide.

- The BLUE scenario of the IEA publication, *Energy Technology Perspectives 2008*, foresees that CSP will provide 5% of world electricity by 2050. Preliminary results of the forthcoming IEA CSP Roadmap suggest a contribution of 12% to global electricity supply by 2050.

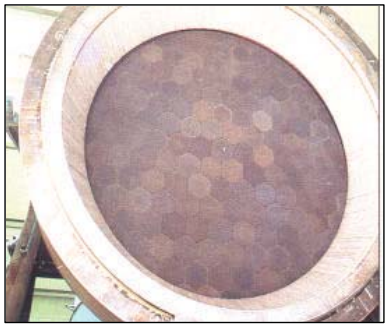
High Temperature Solar Thermochemical Plants



Solar Receiver Types



Cavity

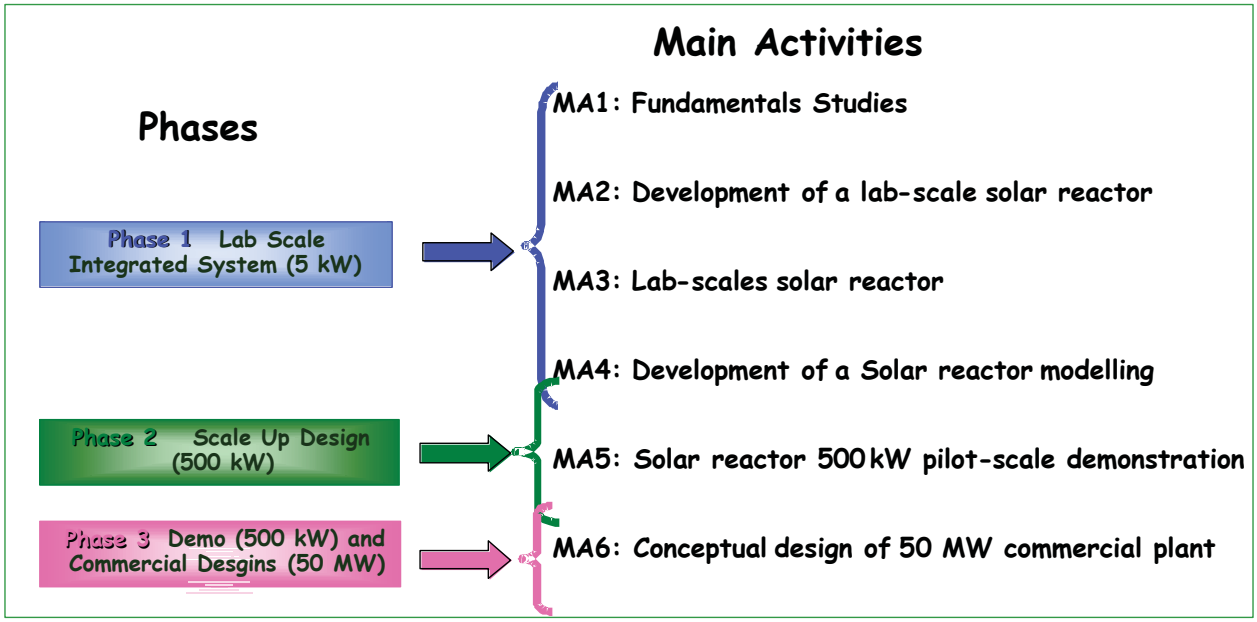


Volumetric

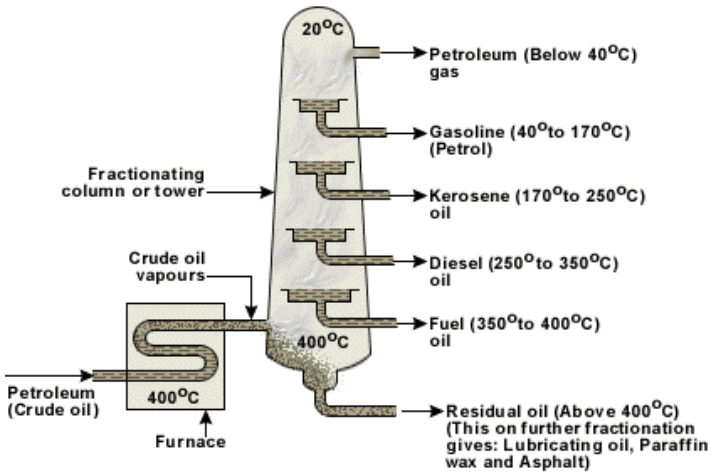
SYNPET Project

Project SYNPET
Partners: PDVSA (Venezuela), ETH/PSI (CH) and CIEMAT (Spain)

Solar thermochemical application for production of syngas from heavy crude oil



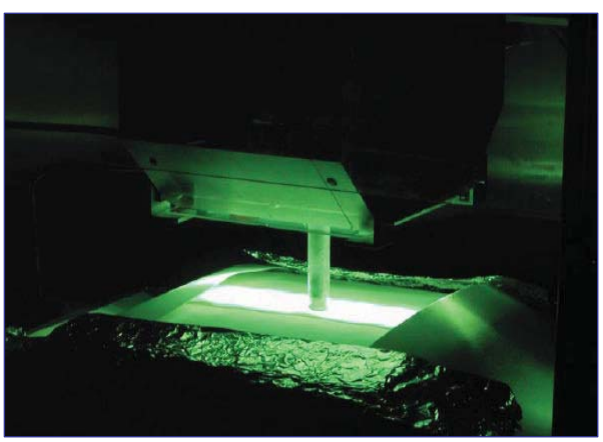
Feedstock: Petroleum coke

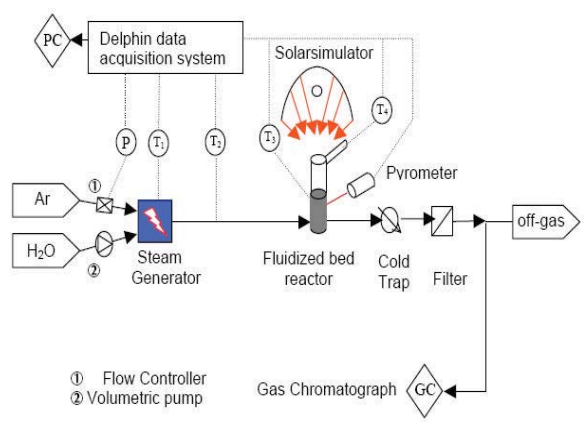


Fractional distillation of petroleum.

Element	Amount	Units
Carbón	88,12	%
Hydrogen	4,14	%
Oxygen	1,47	%
Nitrogen	2,28	%
Sulfur	4,16	%
LHV	35.876	kJ/kg
H/C	0,56	mol/mol
O/C	0,012	mol/mol

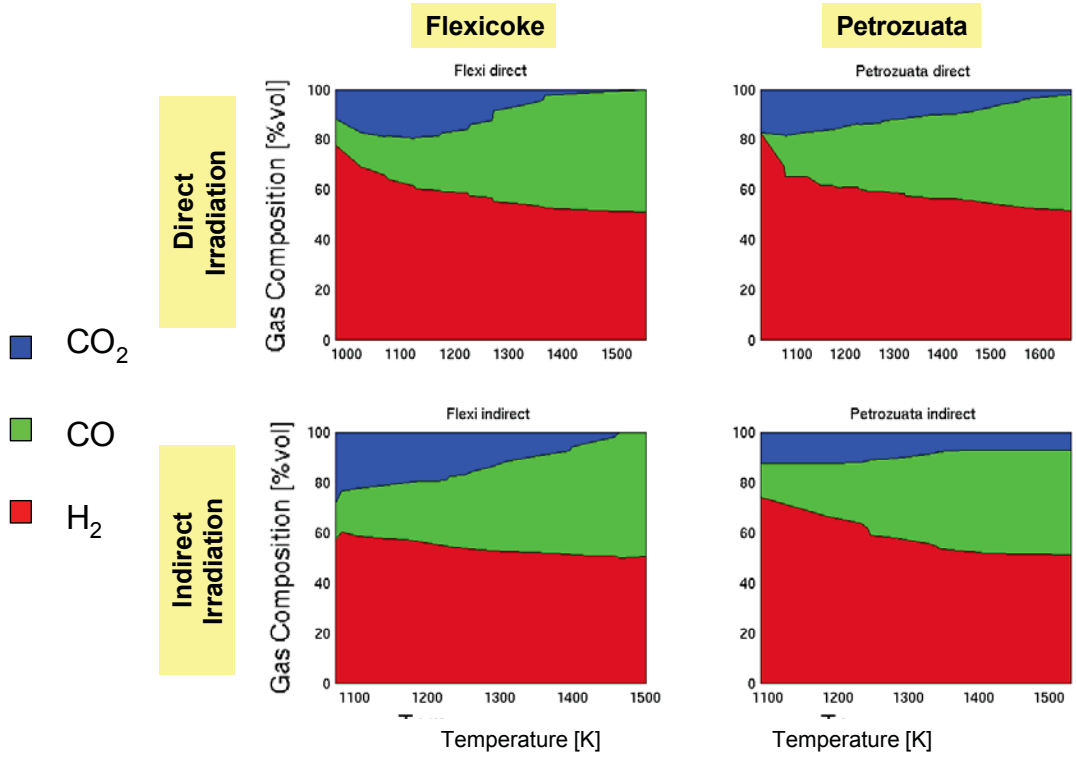
Phase I: Experimental Set-Up



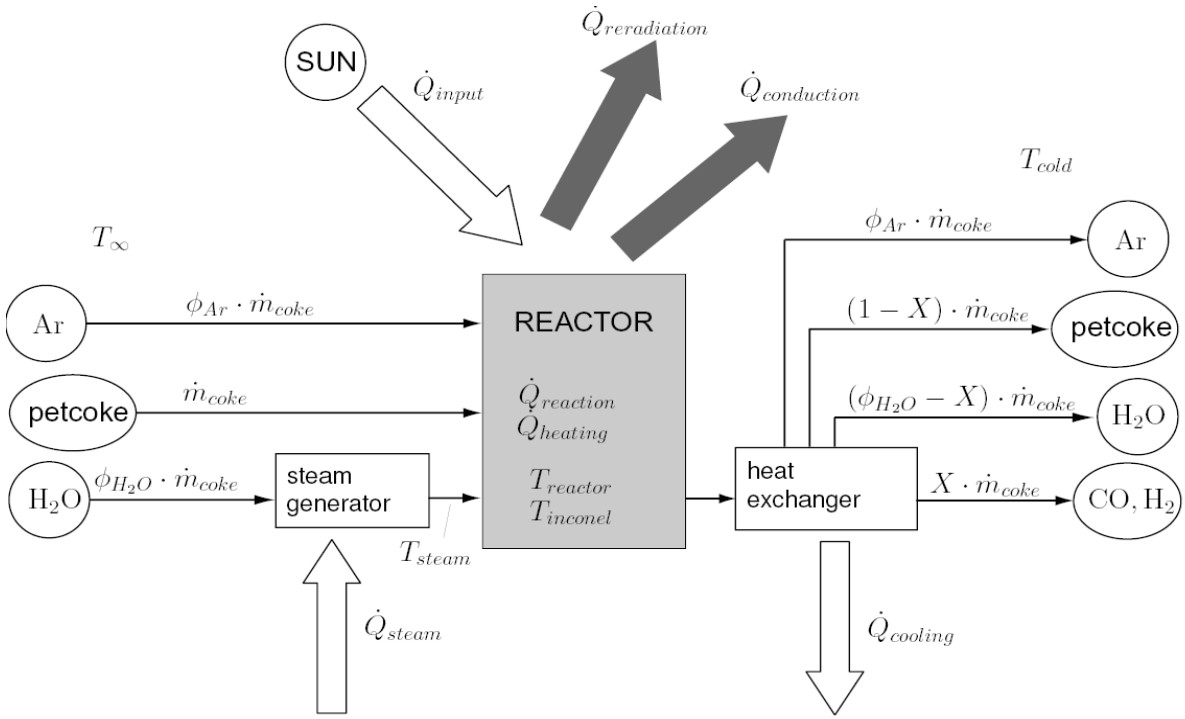


	PD coke		Flexicoke	
	E_A [kJ/mol]	k_0 [k_i]	E_A [kJ/mol]	k_0 [k_i]
k_1 [mol/(g s Pa)]	78.9	$1.05 \cdot 10^{-6}$	158	$4.74 \cdot 10^{-3}$
k_2 [mol/(g s Pa)]	91.5	$1.94 \cdot 10^{-6}$	66.5	$1.02 \cdot 10^{-6}$
k_3 [1/Pa]	-125	$2.92 \cdot 10^{-9}$	-200	$1.09 \cdot 10^{-12}$

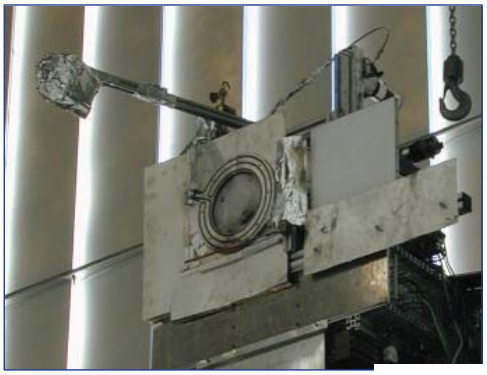
Phase I: Experimental Results

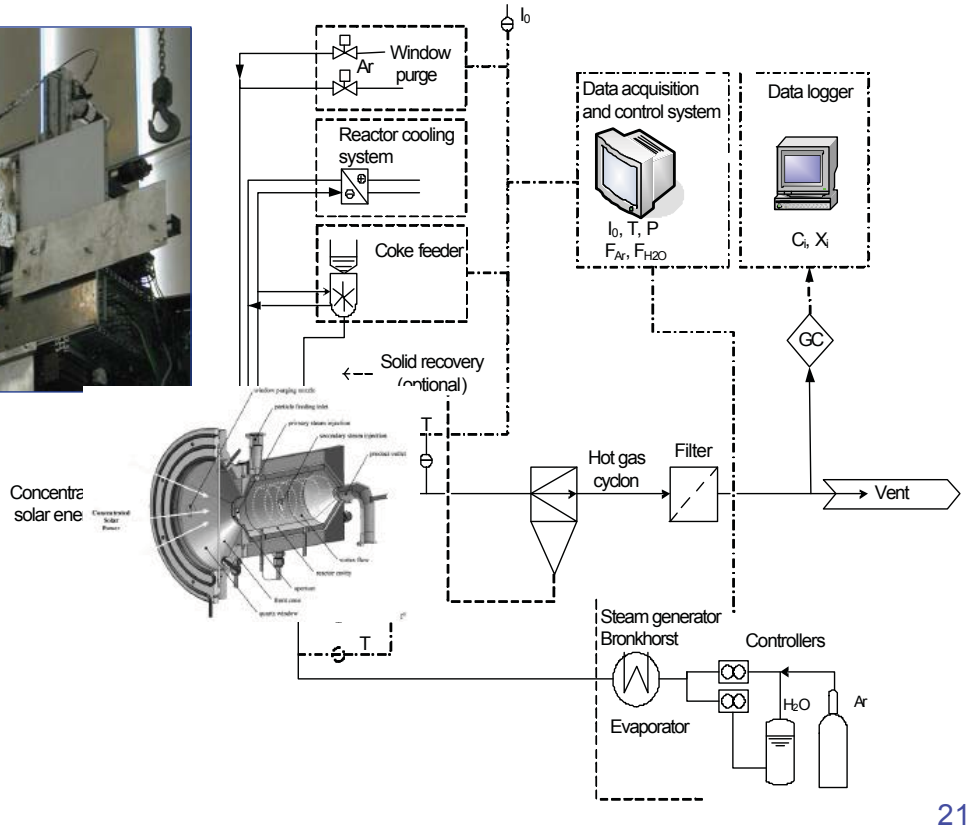


Phase I: Reactor and System Modeling

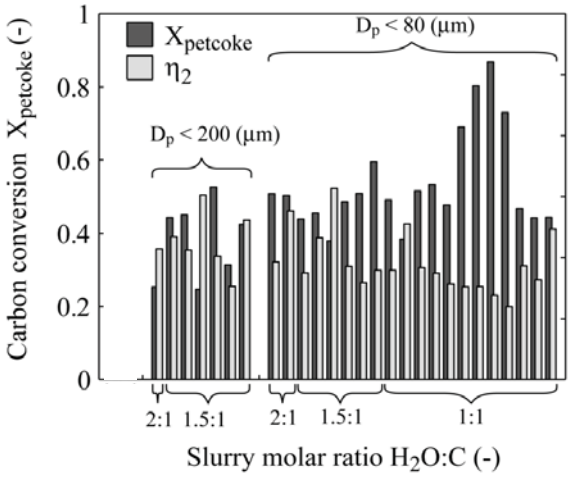


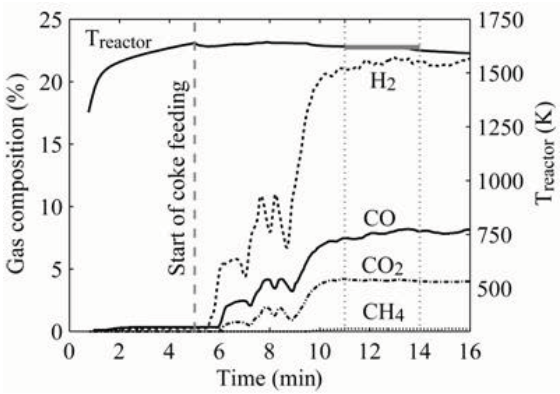
Phase I: Experimental Set-up at PSI solar furnace





Phase I: Experimental Set-Up

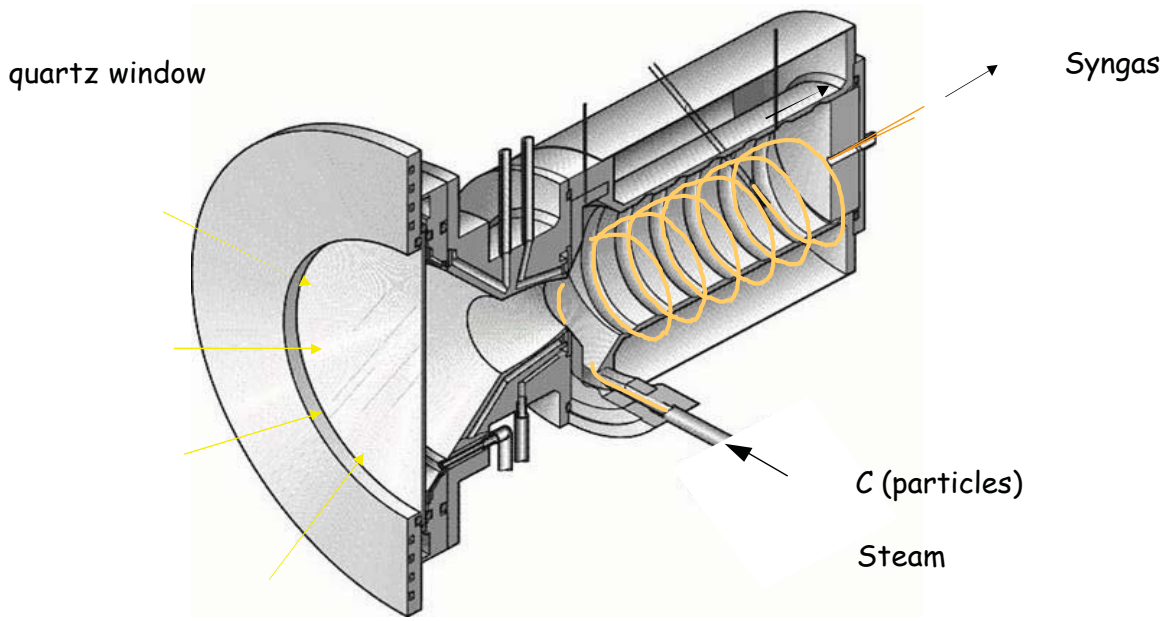




Phase II: Construction and Evaluation 500 kW reactor

Direct absorbing particle receiver-reactors

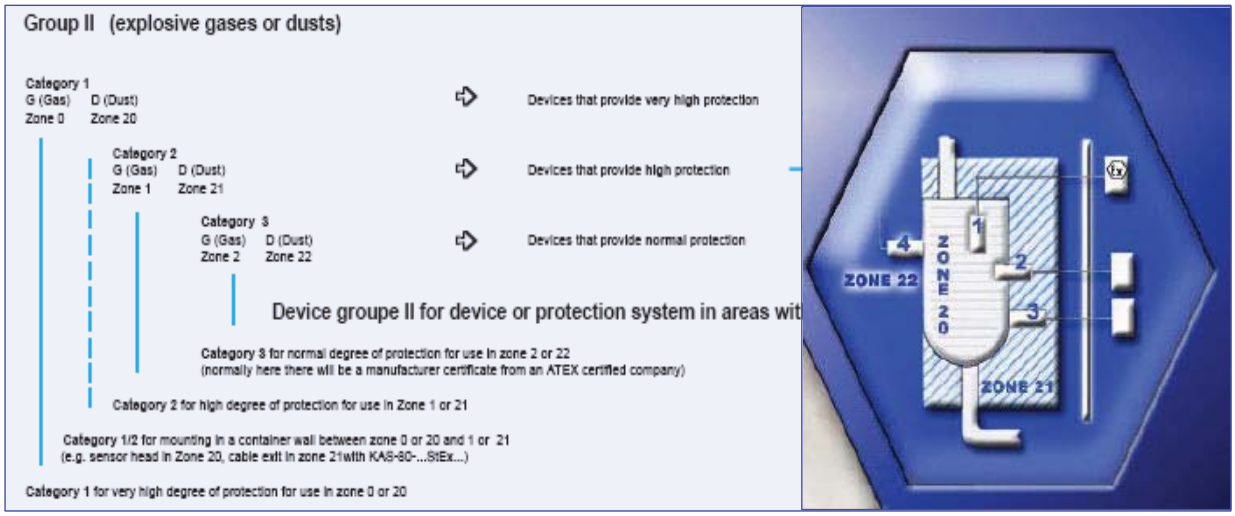
Entrained flow reactors



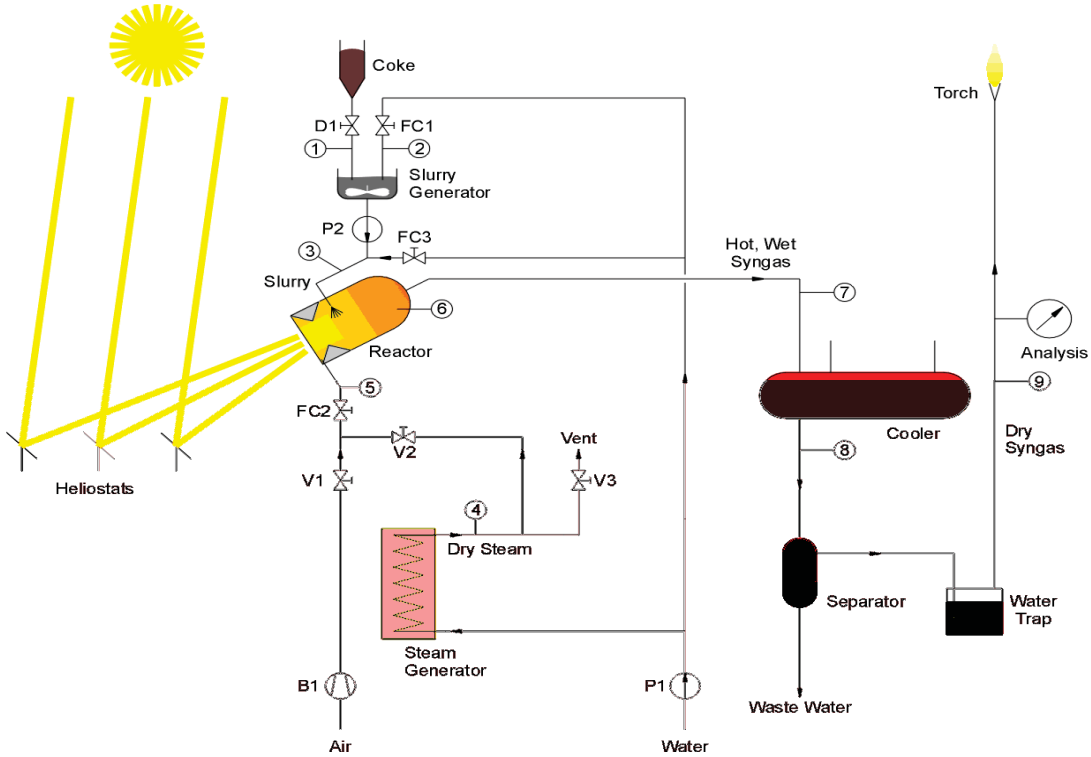
SSPS-CRS (Small Solar Power System-Central-Receiver System)

SynPet Project: ATEX Directive

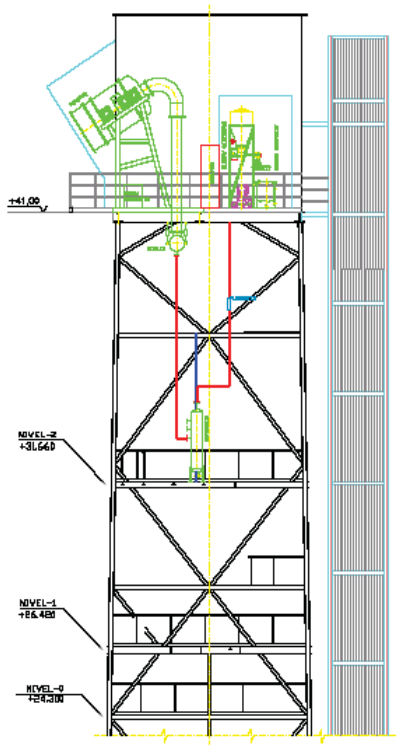
The term **ATEX** comes from **at**moshphere **ex**plosible. From 1- July-2003 only units that meet the ATEX directive 94/9/EG for use in “areas with the risk of explosion“ are permitted.

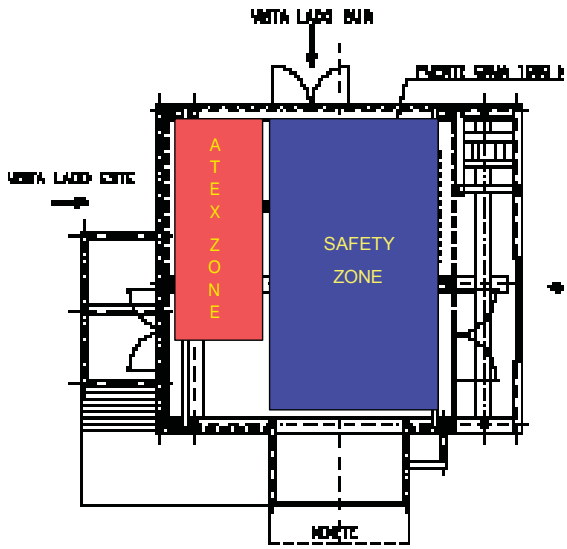


SYNPET: Phase II

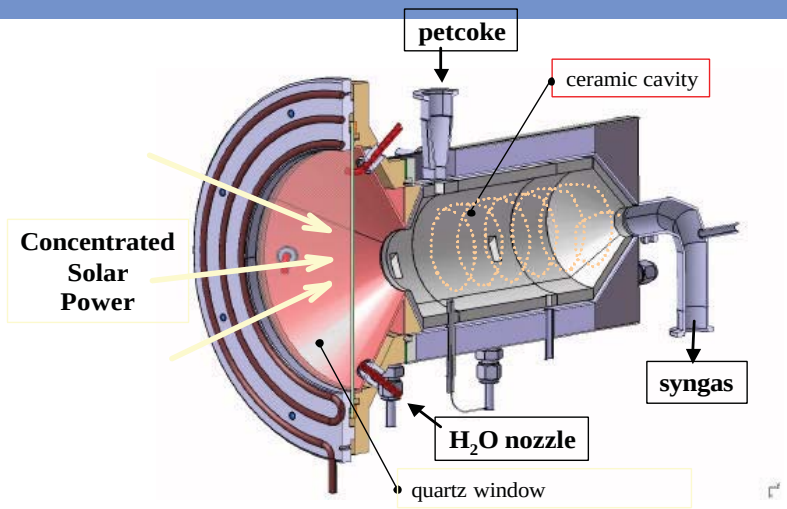


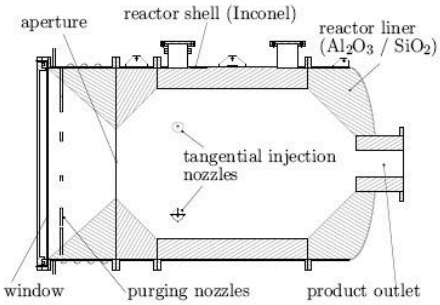
SynPet Project: Classification of Hazardous Areas (Zoning)



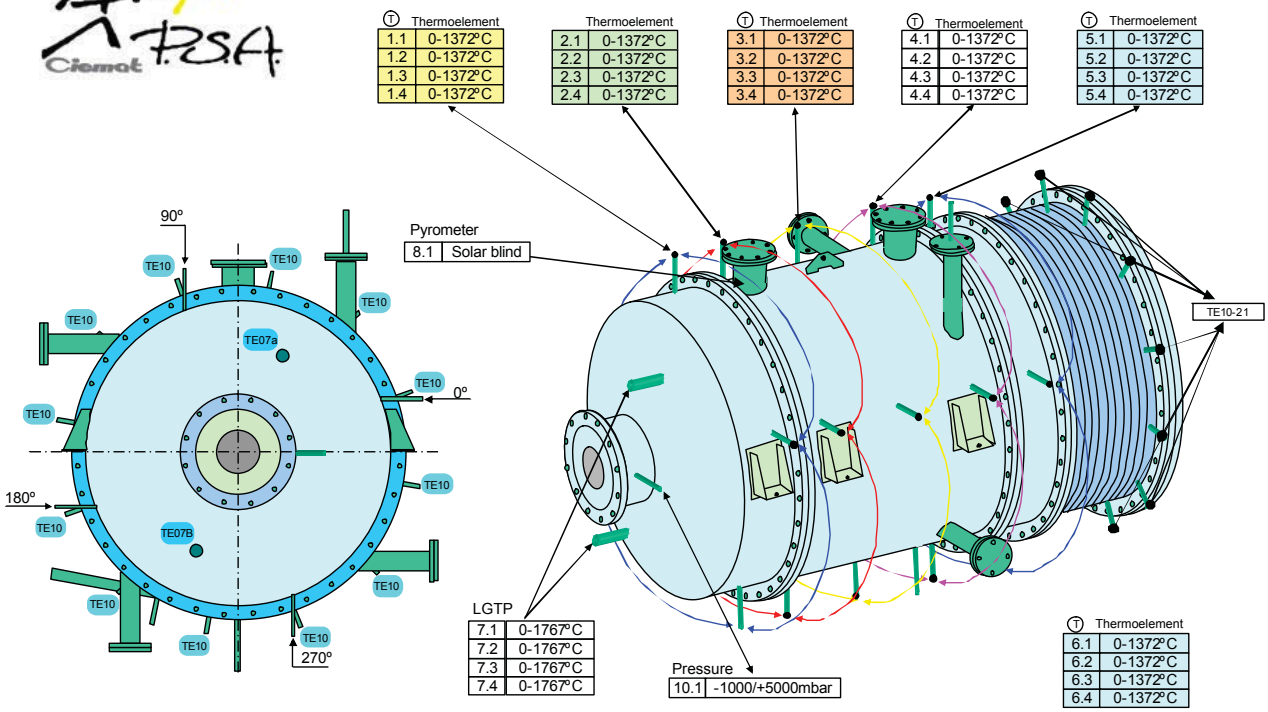


SYNPET : 500 kW Reactor





SYNPET : 500 kW Reactor



Reactor Temperatures

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SYNPET : R&D Needs

Heat Recovery Systems

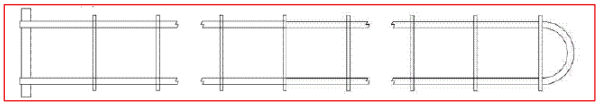
Heat recovery systems reveal essential for the economics of the process.

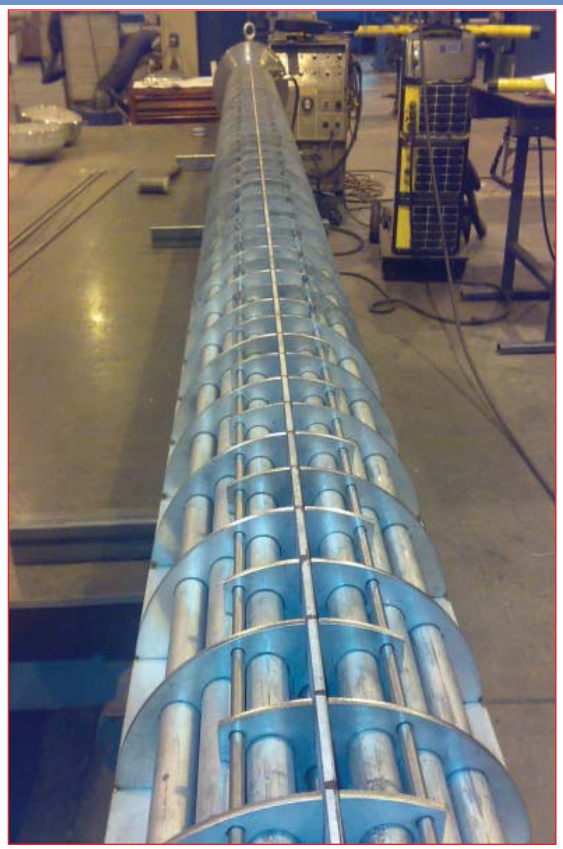
Reactor Window

Windowed pressurized solar reactors need substantial development.

SYNPET : □bo□er

□Lenght: 5130 mm
- Weight: 960 kg
- Water temperatura Inlet/Outlet: 25 / 40º C
- Gas temperatura Inlet / Outlet : 1400ºC / 100 ºC
- Pressure: 2 bar





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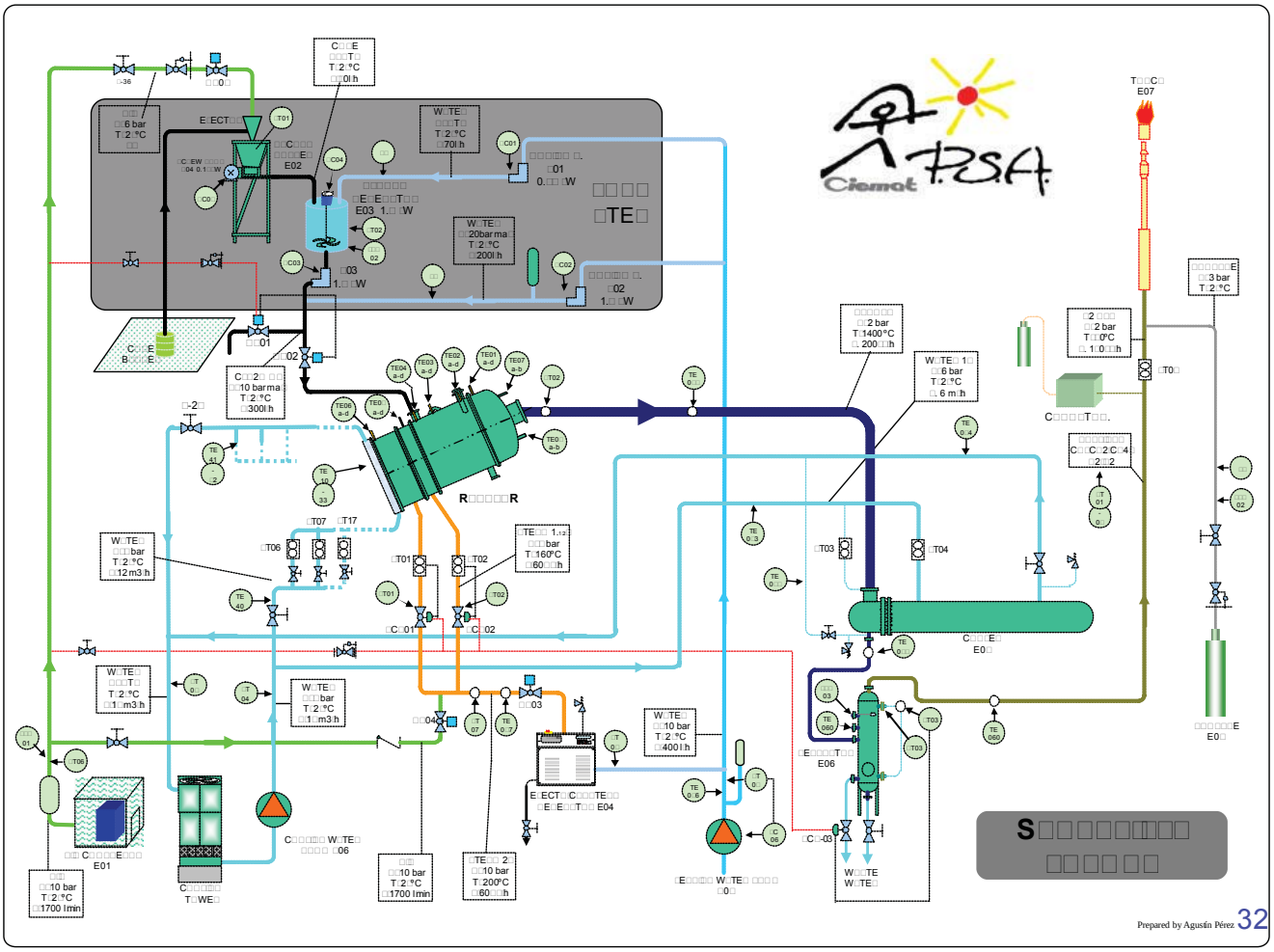

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32

33

SynPet Project: Installation & Assembling

34

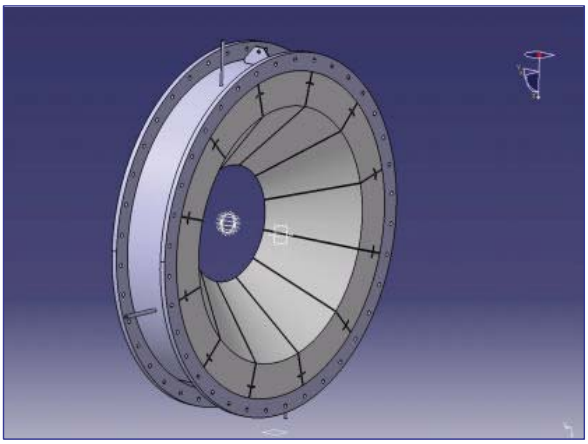
Test Campaign

The test program includes the following tasks:

- Establishing operation procedures, especially for faster start up and shut down (including transition air to steam and steam to steam/coke, and vice versa).
- Steady state tests for evaluation of performance (variation of solar flux conditions, mass flow and feed gas composition).
- Transient tests (controlled defocus of heliostats). Thermal inertia, response to operating conditions, etc
- Thermal evaluation of the heat recovery system and quartz window.
- Development of control tools for normal operation in SCADA.
- Chemical campaign. Chemical yields and receiver efficiencies, gas composition, maximum hydrogen conversion, etc

3

Test Campaign: Problems



Solar Gasification

- Hybrid solar/fossil endothermic processes offer a viable route for reducing CO2 emissions and create a transition path towards solar hydrogen
- In view of the importance of coal as a primary source of energy for the foreseeable future and the fact that it is a greenhouse-intensive fuel, it is likely that efforts to incorporate renewable energy, such as solar, into the new coal gasification-based technologies will increase in the future.
- The world is facing rapid growth in energy demand, persistently high energy prices, and a challenge to reduce carbon dioxide emissions from power generation and manufacturing. No single technology or resource can solve the problem, but gasification can be part of the solution along with oter technologies and energy efficiency programs.
- Solar Gasification offers the opportunity to solve one of the most important problems of solar technology, that is, to provide an effective means of storage. Furthermore, the thermochemical plant could be run producing hydrogen all day and ccoupled with a IGCC to produce power, with the main advantage that could be in operation all day