Seminario sobre
ENERGIA SOLAR

20-21 de Febrero 2006
Consejo Social, Universidad Politécnica de Madrid

2ª Jornada, día 21 de febrero, 2006

2ª Sesión: Tecnología y aplicaciones especiales de la energía solar

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"Producción de hidrógeno con energía solar: la oportunidad de un desafío multidisciplinar"

Seminario Solar UPM

20-21 de febrero, 2006

Producción de hidrógeno con energía solar: la oportunidad de un desafío multidisciplinar

José MªMartínez-Val
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Director del Seminario sobre Energía Solar

- **Atractivo de la economía del hidrógeno**
- **Necesidad de producirlo a partir de moléculas naturales, particularmente H_2O**
- **Vector energético, no fuente energética**
- **Su producción con renovables: SOLAR**

European Hydrogen & Fuel Cell Technology Platform

Strategic Research Agenda

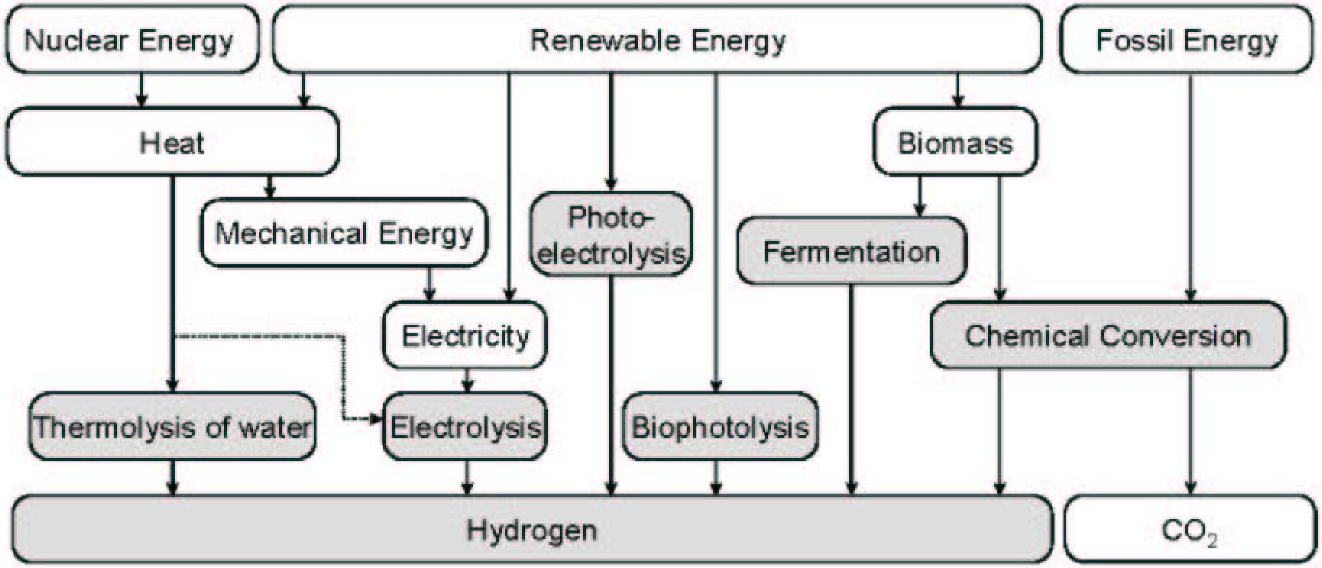

Nuclear Energy
Renewable Energy
Fossil Energy
Heat
Biomass
Mechanical Energy
Photo-electrolysis
Fermentation
Electricity
Chemical Conversion
Thermolysis of water
Electrolysis
Biophotolysis
Hydrogen
CO2

Figure 2.1-1: Hydrogen production pathways. Adapted and expanded from: John A. Turner, Science 285, 687 (1999).

A challenging European hydrogen vision

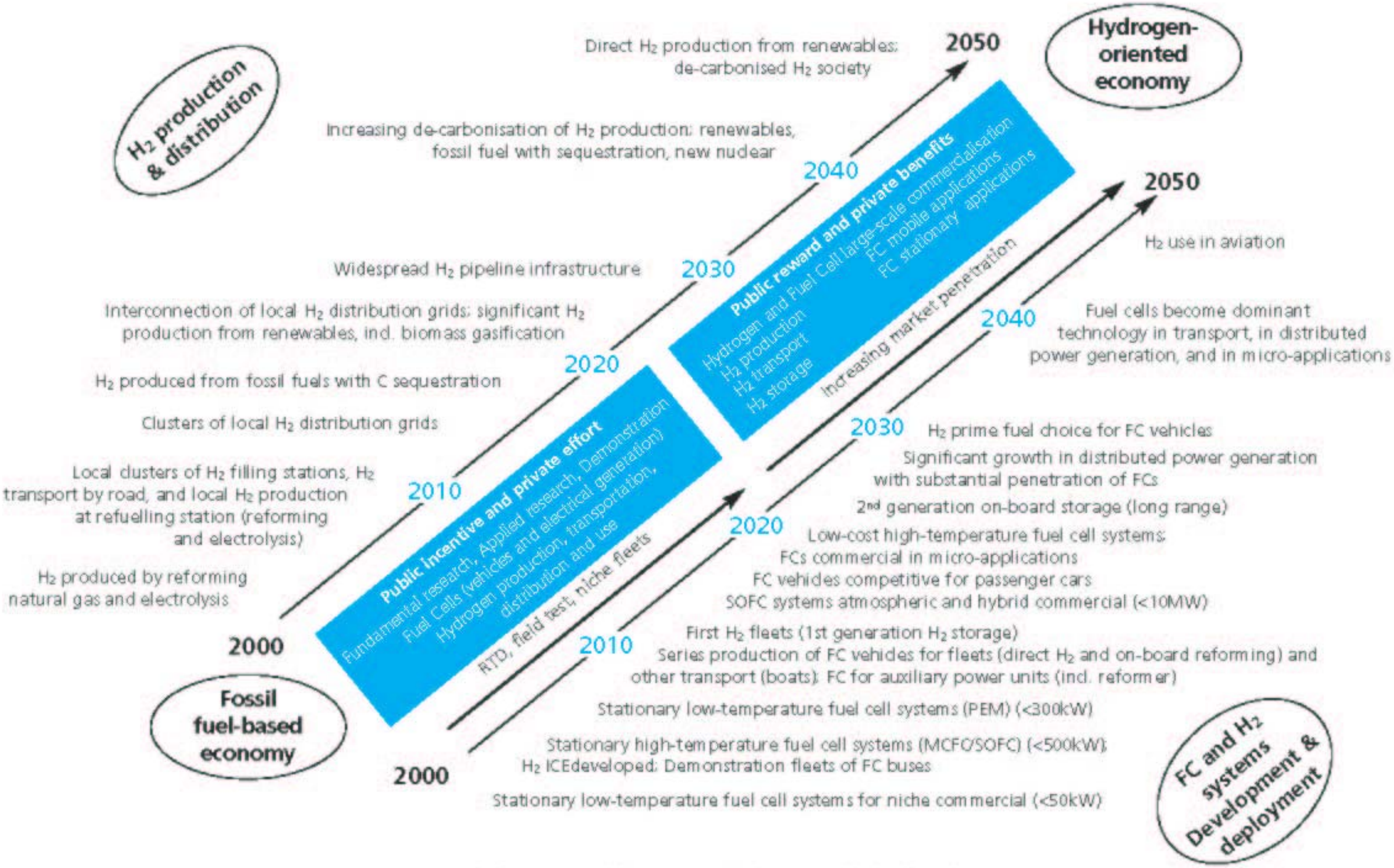
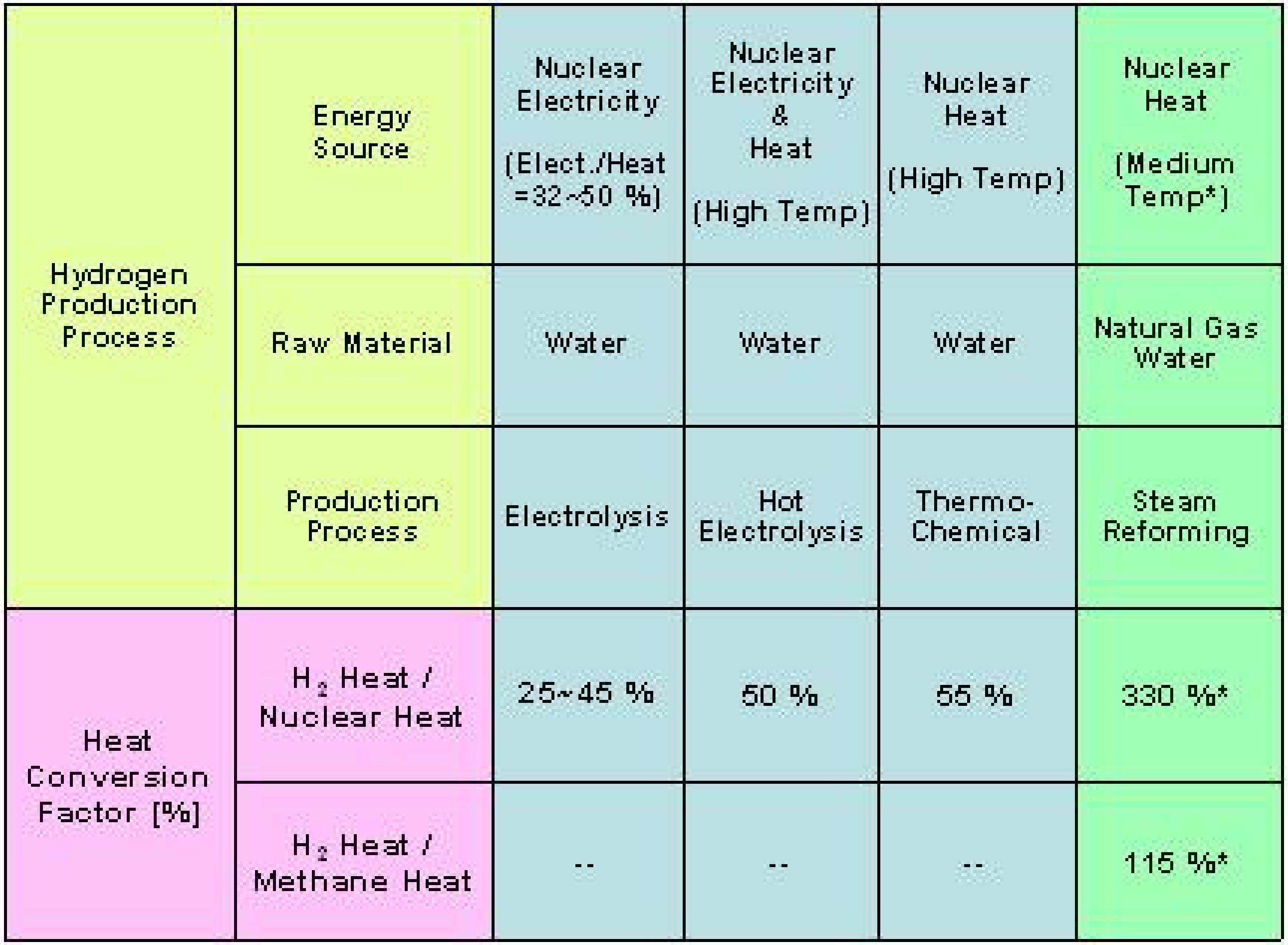

H_2 production & distribution
Hydrogen-oriented economy
Fossil fuel-based economy
FC and H_2 systems Development & deployment
2000
2010
2020
2030
2040
2050
H_2 produced by reforming natural gas and electrolysis
Local clusters of H_2 filling stations, H_2 transport by road, and local H_2 production at refuelling station (reforming and electrolysis)
Clusters of local H_2 distribution grids
H_2 produced from fossil fuels with C sequestration
Interconnection of local H_2 distribution grids; significant H_2 production from renewables, incl. biomass gasification
Widespread H_2 pipeline infrastructure
Increasing de-carbonisation of H_2 production: renewables, fossil fuel with sequestration, new nuclear
Direct H_2 production from renewables: de-carbonised H_2 society
Public incentive and private effort
Fundamental research, Applied research, Demonstration
Fuel Cells (vehicles and electrical generation)
Hydrogen production, transportation, distribution and use
Public reward and private benefits
Hydrogen and Fuel Cell large-scale commercialisation
FC mobile applications
FC stationary applications
H_2 production
H_2 transport
H_2 storage
RTD, field test, niche fleets
Increasing market penetration
2000
2010
2020
2030
2040
2050
Stationary low-temperature fuel cell systems for niche commercial (<50kW)
Stationary high-temperature fuel cell systems (MCFC/SOFC) (<500kW); H_2 ICEdeveloped: Demonstration fleets of FC buses
Stationary low-temperature fuel cell systems (PEM) (<300kW)
First H_2 fleets (1st generation H_2 storage)
Series production of FC vehicles for fleets (direct H_2 and on-board reforming) and other transport (boats); FC for auxiliary power units (incl. reformer)
SOFC systems atmospheric and hybrid commercial (<10MW)
FC vehicles competitive for passenger cars
FCs commercial in micro-applications
Low-cost high-temperature fuel cell systems;
2nd generation on-board storage (long range)
Significant growth in distributed power generation with substantial penetration of FCs
H_2 prime fuel choice for FC vehicles
Fuel cells become dominant technology in transport, in distributed power generation, and in micro-applications
H_2 use in aviation

Figure 4: Skeleton proposal for European hydrogen and fuel cell roadmap

Table 3. Hydrogen production methods



Hydrogen Production Process	Energy Source	Nuclear Electricity (Elect./Heat =32~50 %)	Nuclear Electricity & Heat (High Temp)	Nuclear Heat (High Temp)	Nuclear Heat (Medium Temp*)
	Raw Material	Water	Water	Water	Natural Gas Water
	Production Process	Electrolysis	Hot Electrolysis	Thermo-Chemical	Steam Reforming
Heat Conversion Factor [%]	H_2 Heat / Nuclear Heat	25~45 %	50 %	55 %	330 %*
	H_2 Heat / Methane Heat	--	--	--	115 %*

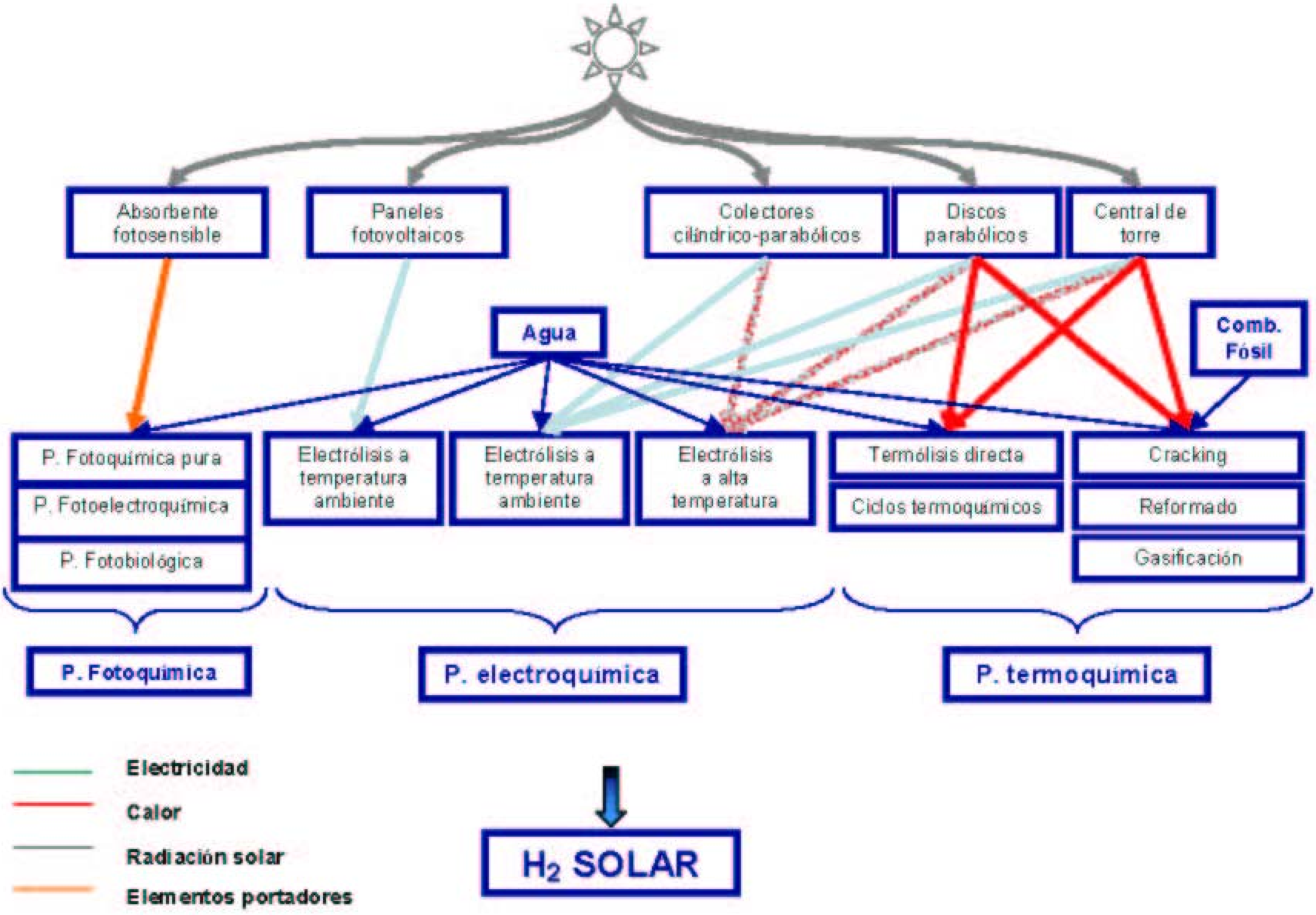
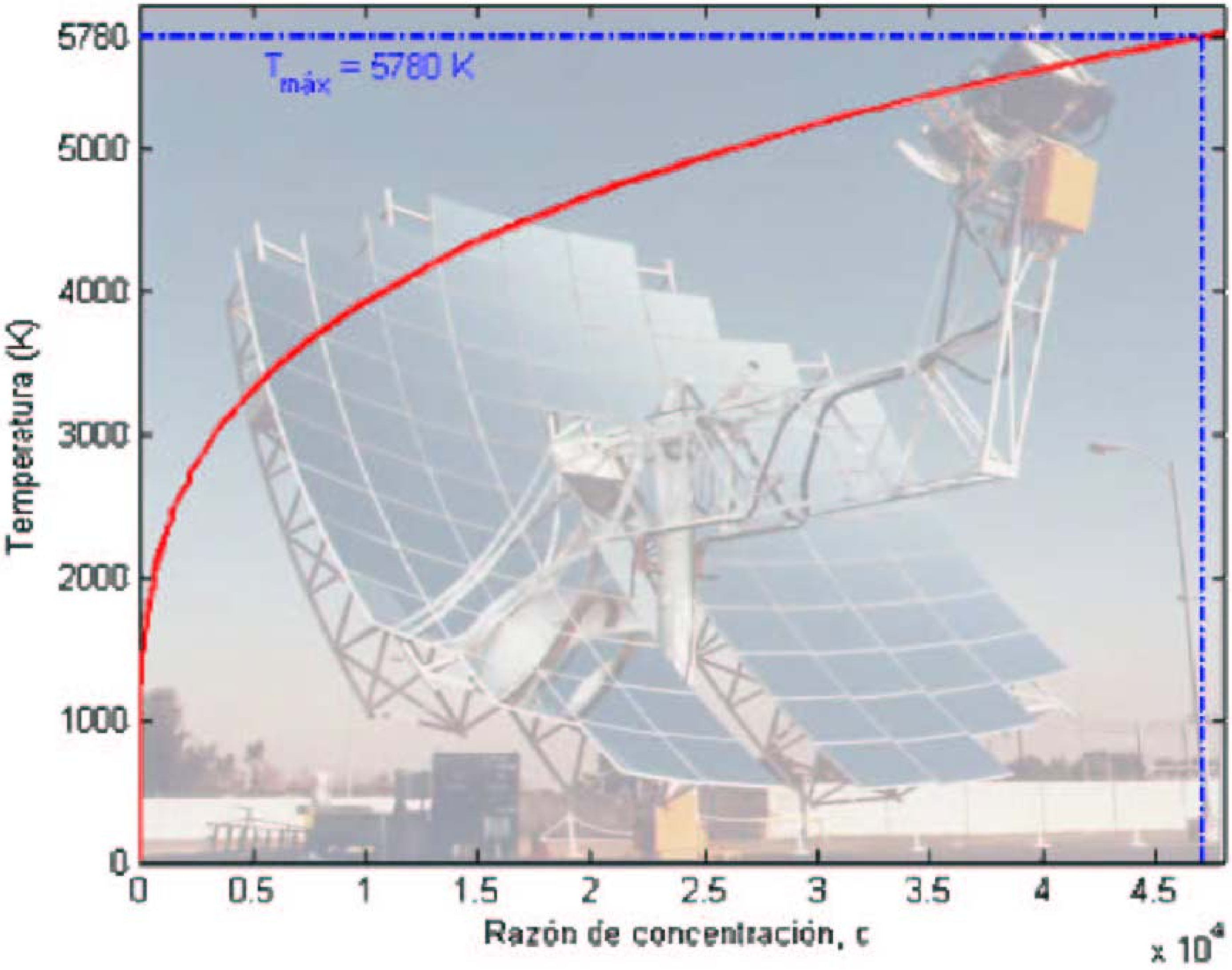
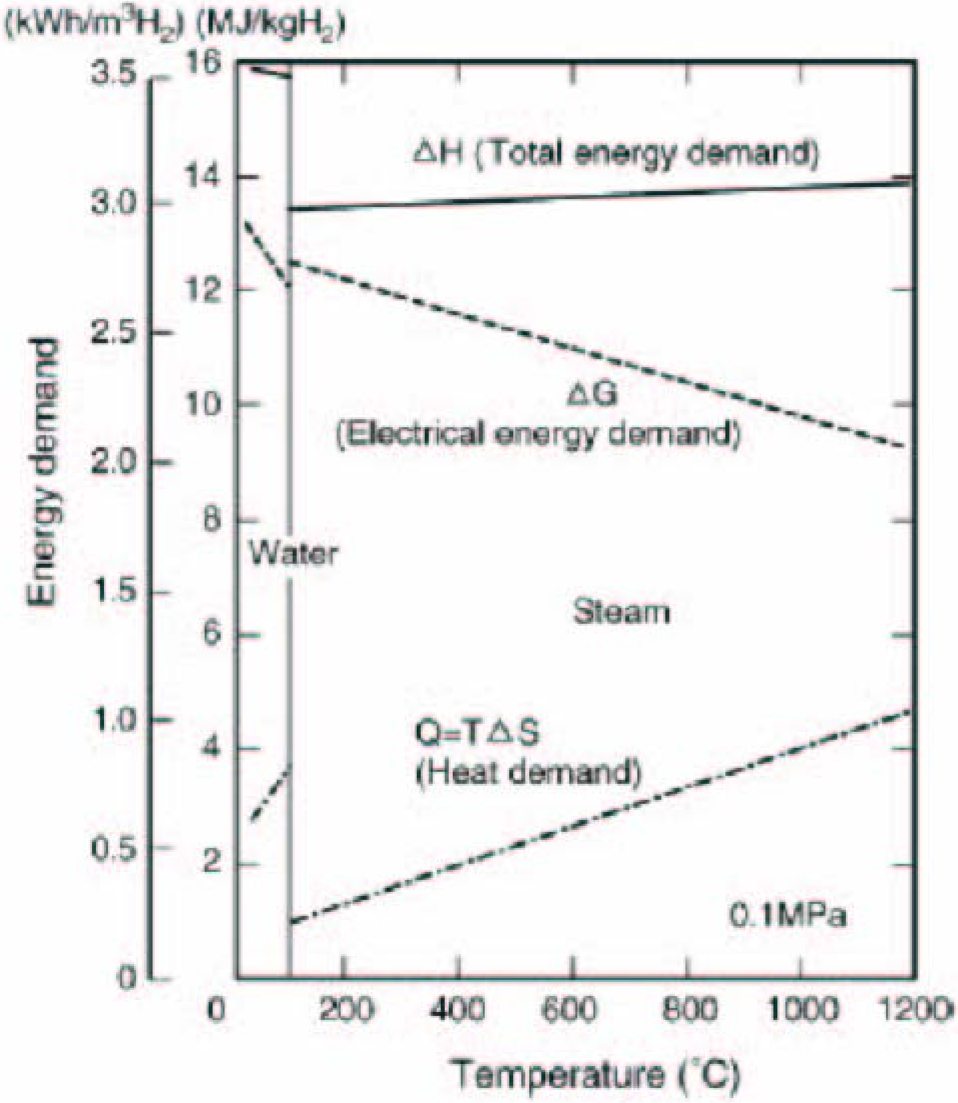
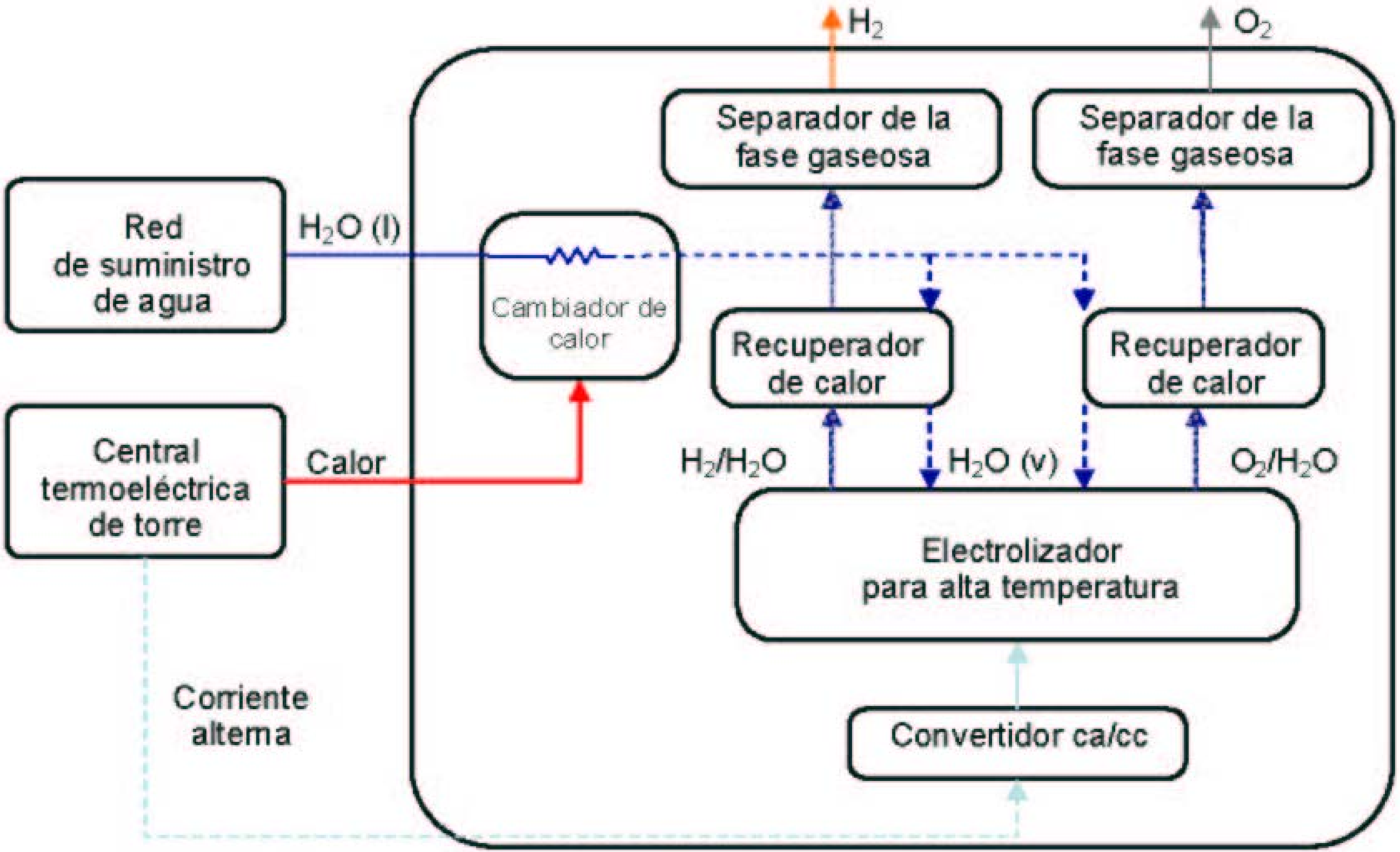

Absorbente fotosensible
Paneles fotovoltaicos
Colectores cilíndrico-parabólicos
Discos parabólicos
Central de torre
Agua
Comb. Fósil
P. Fotoquímica pura
P. Fotoelectroquímica
P. Fotobiológica
Electrólisis a temperatura ambiente
Electrólisis a temperatura ambiente
Electrólisis a alta temperatura
Termólisis directa
Ciclos termoquímicos
Cracking
Reformado
Gasificación
P. Fotoquímica
P. electroquímica
P. termoquímica
Electricidad
Calor
Radiación solar
Elementos portadores
H_2 SOLAR

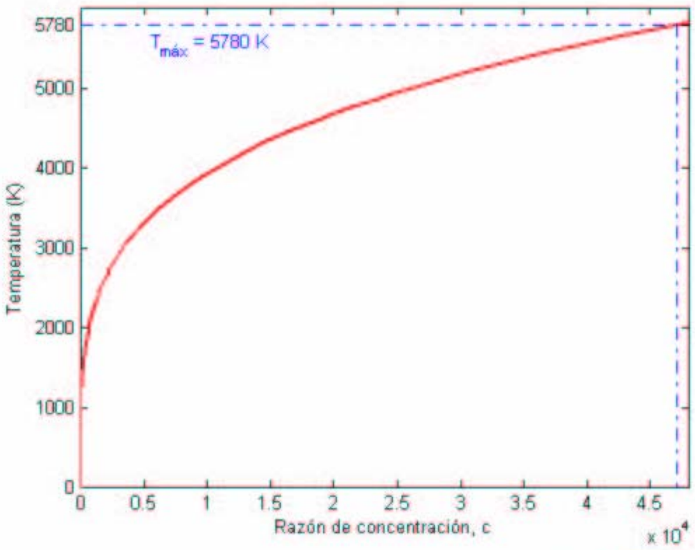
Fig. 1. Métodos de producción de hidrógeno solar


5780
5000
4000
3000
2000
1000
0
$T_{máx}$ = 5780 K
Temperatura (K)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Razón de concentración, c
x 10^4

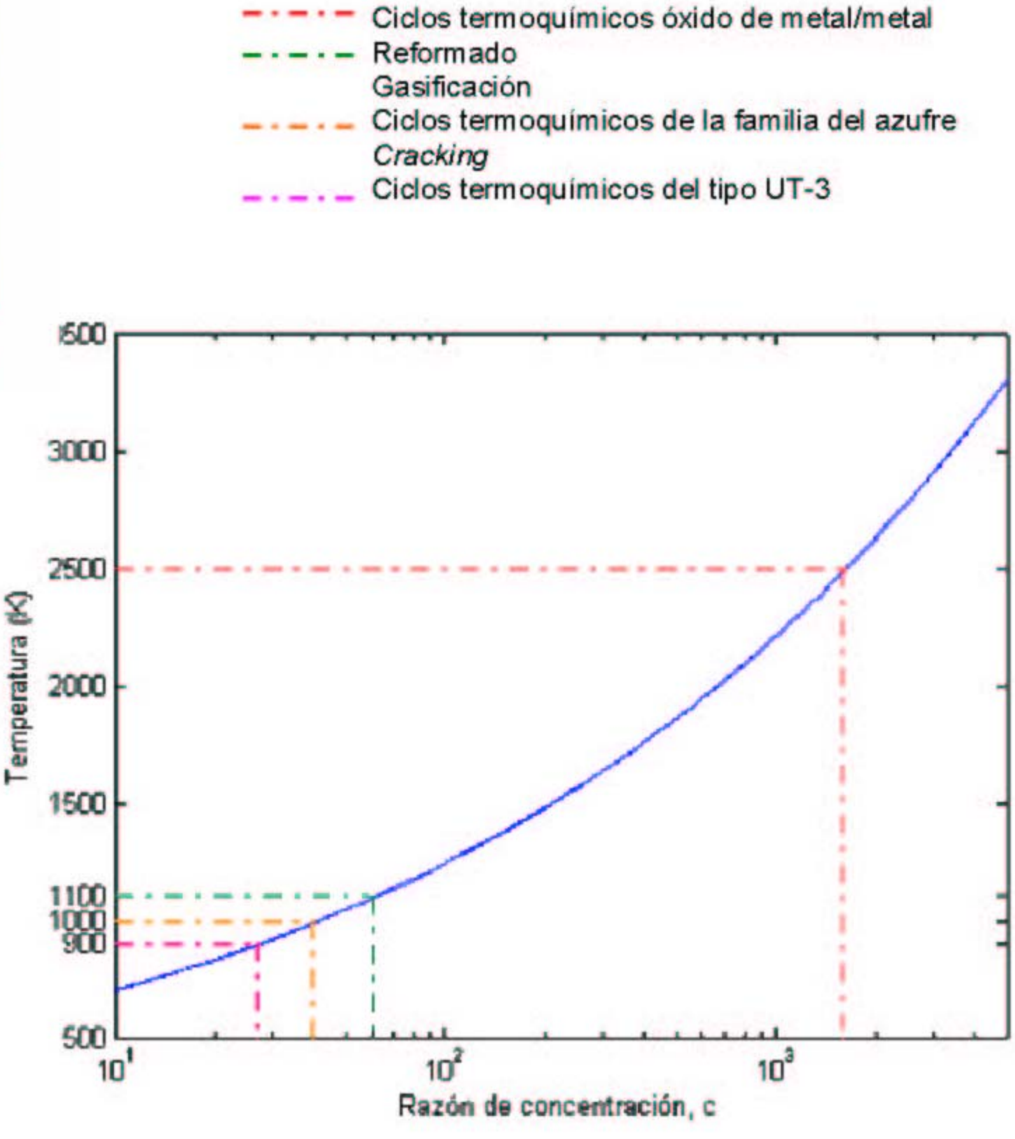

(kWh/m^{3}H$_2$)
(MJ/kgH$_2$)
Energy demand
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
16
14
12
10
8
6
4
2
0
200
400
600
800
1000
1200
Temperature (°C)
ΔH (Total energy demand)
ΔG
(Electrical energy demand)
Water
Steam
Q=TΔS
(Heat demand)
0.1MPa

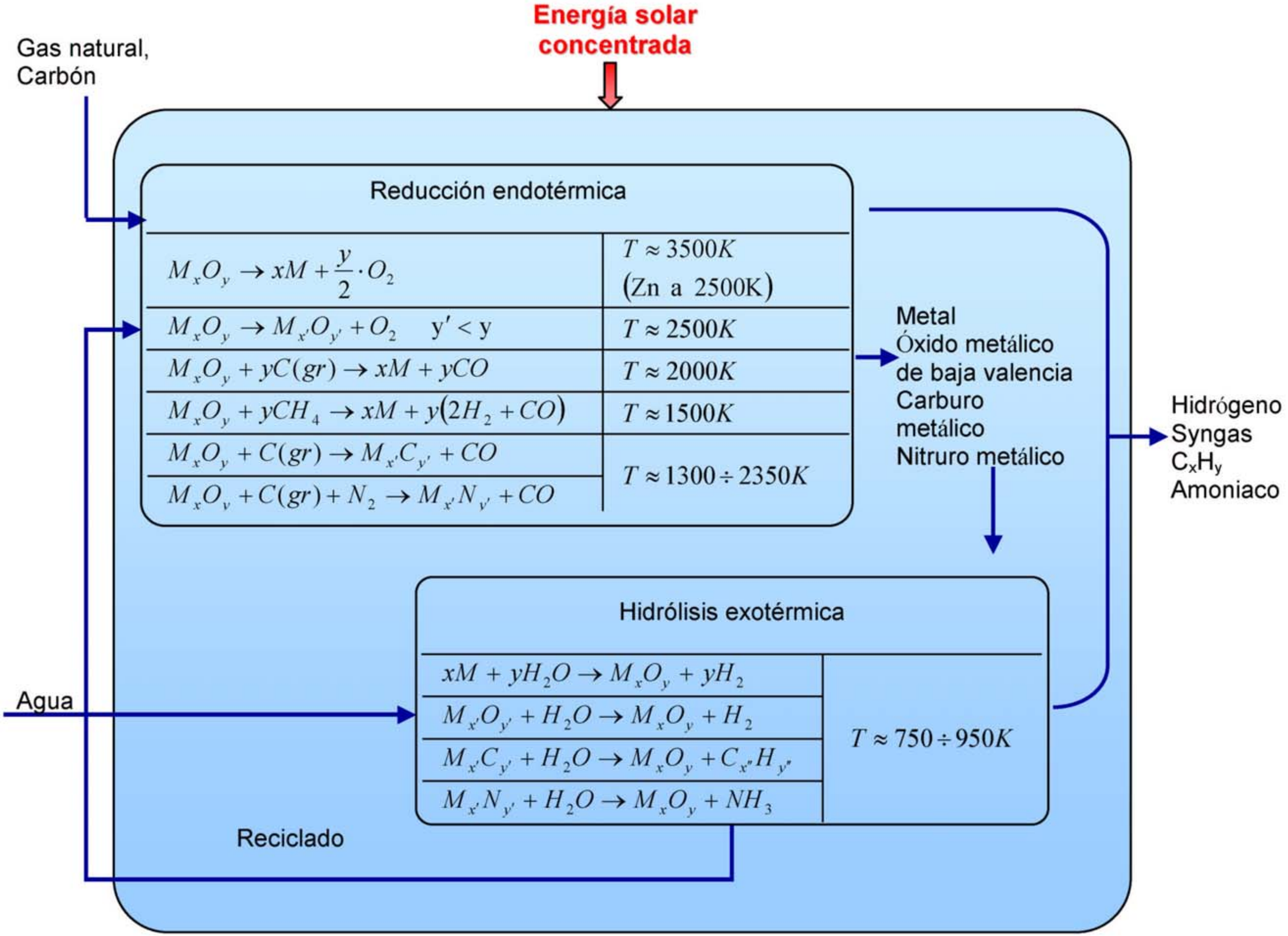

H₂
O₂
Separador de la fase gaseosa
Separador de la fase gaseosa
Red de suministro de agua
H₂O (l)
Cambiador de calor
Recuperador de calor
Recuperador de calor
Central termoeléctrica de torre
Calor
H₂/H₂O
H₂O (v)
O₂/H₂O
Electrolizador para alta temperatura
Corriente alterna
Convertidor ca/cc

Clase I			**T≤1000K**
Proceso		**Reacción endotérmica**	**T(K)**
Ciclos termoquímicos de temperaturas “moderadas”	Ciclos de la familia del azufre	Descomposición del ácido sulfúrico $H_2SO_4(g) \rightarrow SO_2(g) + H_2O(g) + \frac{1}{2}O_2(g)$	T≈1000
	Ciclos del tipo UT-3	Hidrólisis del bromuro de calcio y del bromuro de hierro $CaBr_2(s) + H_2O(g) \rightarrow CaO(s) + 2HBr(g)$ $3FeBr_2(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 6HBr(g) + H_2(g)$	T≈900
Clase II			**1000K≤T≤2500K**
Proceso		**Reacción endotérmica**	**T(K)**
Ciclos termoquímicos de temperaturas elevadas	Reducción óxidos metálicos	Disociación del óxido metálico $M_xO_y \rightarrow xM + \frac{y}{2} \cdot O_2$	T≈2500
Descarbonización de combustibles fósiles	*Cracking*	Descomposición térmica de hidrocarburos $C_xH_y \rightarrow xC(gr) + \frac{y}{2} \cdot H_2$	T≈1000
	Reformado	Descarbonización de hidrocarburos ligeros $C_xH_y + xH_2O \rightarrow \left(\frac{y}{2} + x\right) \cdot H_2 + xCO$	T≈1100
	Gasificación	Descarbonización de hidrocarburos pesados $C_xH_y + xH_2O \rightarrow \left(\frac{y}{2} + x\right) \cdot H_2 + xCO$	T≈1100
Clase III			**T>2500K**
Proceso		**Reacción endotérmica**	**T(K)**
Termólisis directa del agua		Disociación del agua $H_2O \rightarrow H_2 + \frac{1}{2}O_2$	T>2500



Concentración en
escala logarítmica





Energía solar concentrada

Gas natural, Carbón

Reducción endotérmica

$M_xO_y \rightarrow xM + \frac{y}{2}\cdot O_2$	$T \approx 3500K$ (Zn a 2500K)
$M_xO_y \rightarrow M_{x'}O_{y'} + O_2 \quad y' < y$	$T \approx 2500K$
$M_xO_y + yC(gr) \rightarrow xM + yCO$	$T \approx 2000K$
$M_xO_y + yCH_4 \rightarrow xM + y(2H_2 + CO)$	$T \approx 1500K$
$M_xO_y + C(gr) \rightarrow M_{x'}C_{y'} + CO$	$T \approx 1300 \div 2350K$
$M_xO_y + C(gr) + N_2 \rightarrow M_{x'}N_{y'} + CO$	

Metal
Óxido metálico de baja valencia
Carburo metálico
Nitruro metálico

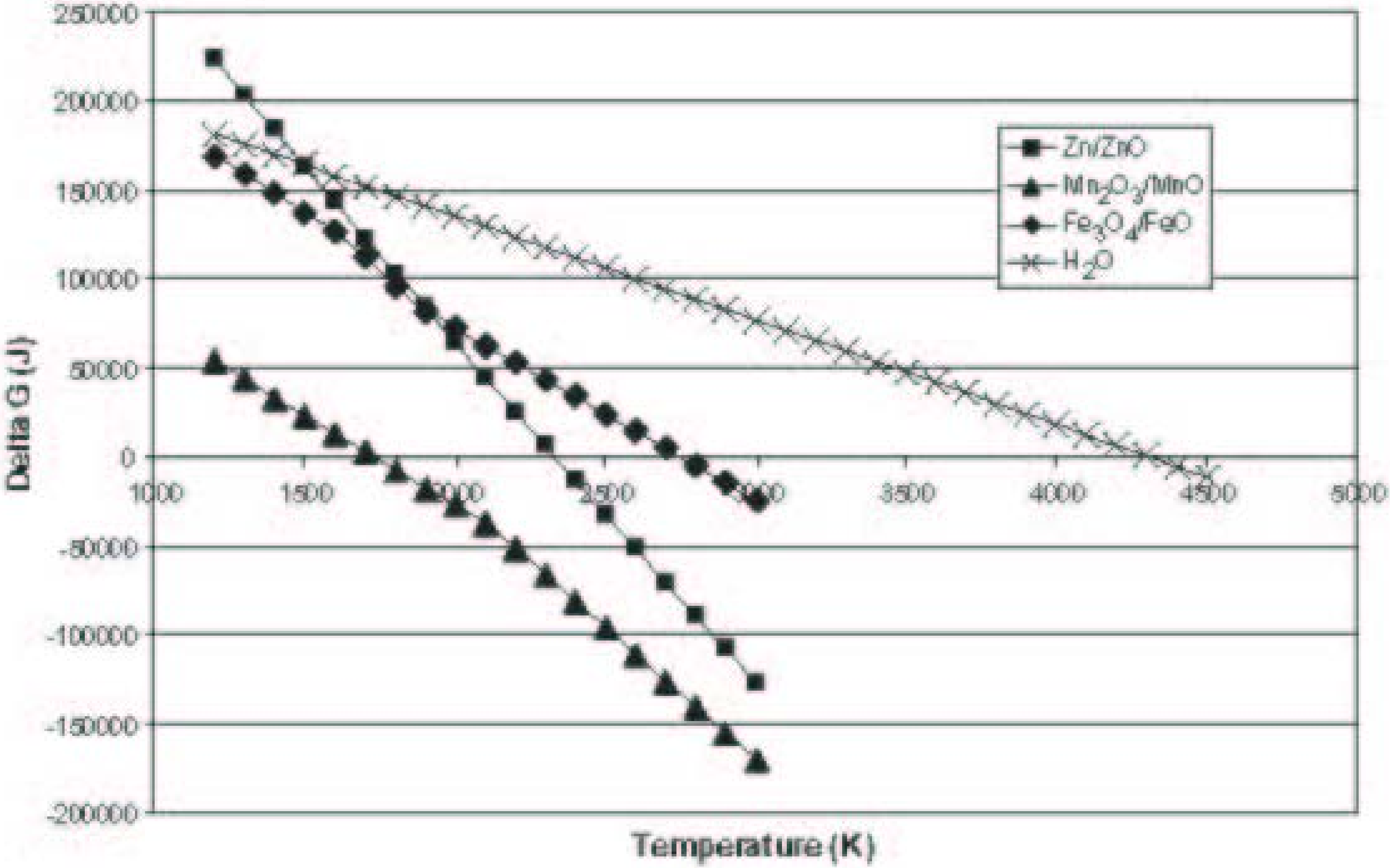
Hidrógeno
Syngas
C_xH_y
Amoniaco

Agua

Hidrólisis exotérmica

$xM + yH_2O \rightarrow M_xO_y + yH_2$	$T \approx 750 \div 950K$
$M_{x'}O_{y'} + H_2O \rightarrow M_xO_y + H_2$	
$M_{x'}C_{y'} + H_2O \rightarrow M_xO_y + C_{x''}H_{y''}$	
$M_{x'}N_{y'} + H_2O \rightarrow M_xO_y + NH_3$	

Reciclado



250000
200000
150000
100000
50000
0
-50000
-100000
-150000
-200000
Delta G (J)
1000
1500
2000
2500
3000
3500
4000
4500
5000
Temperature (K)
Zn/ZnO
Mn_2O_3/MnO
Fe_3O_4/FeO
H_2O

Reacción endotérmica

$$ZnO(s) \rightarrow Zn(g) + 0{,}5O_2(g)$$

Reacción exotérmica

$$Zn(l) + H_2O(v) \rightarrow ZnO(s) + 0{,}5H_2(g)$$

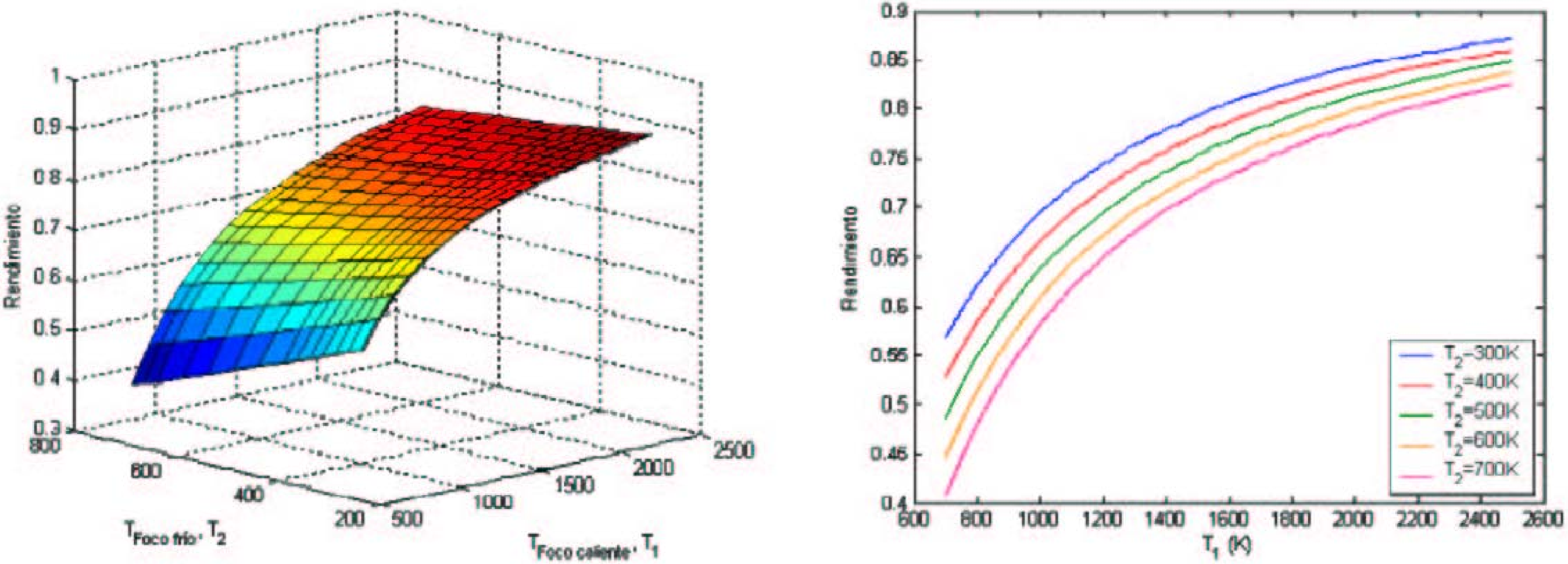


Fig.9. Variación del rendimiento termodinámico en el ciclo *ZnO/Zn*, en función de las temperaturas del foco caliente y del foco frío

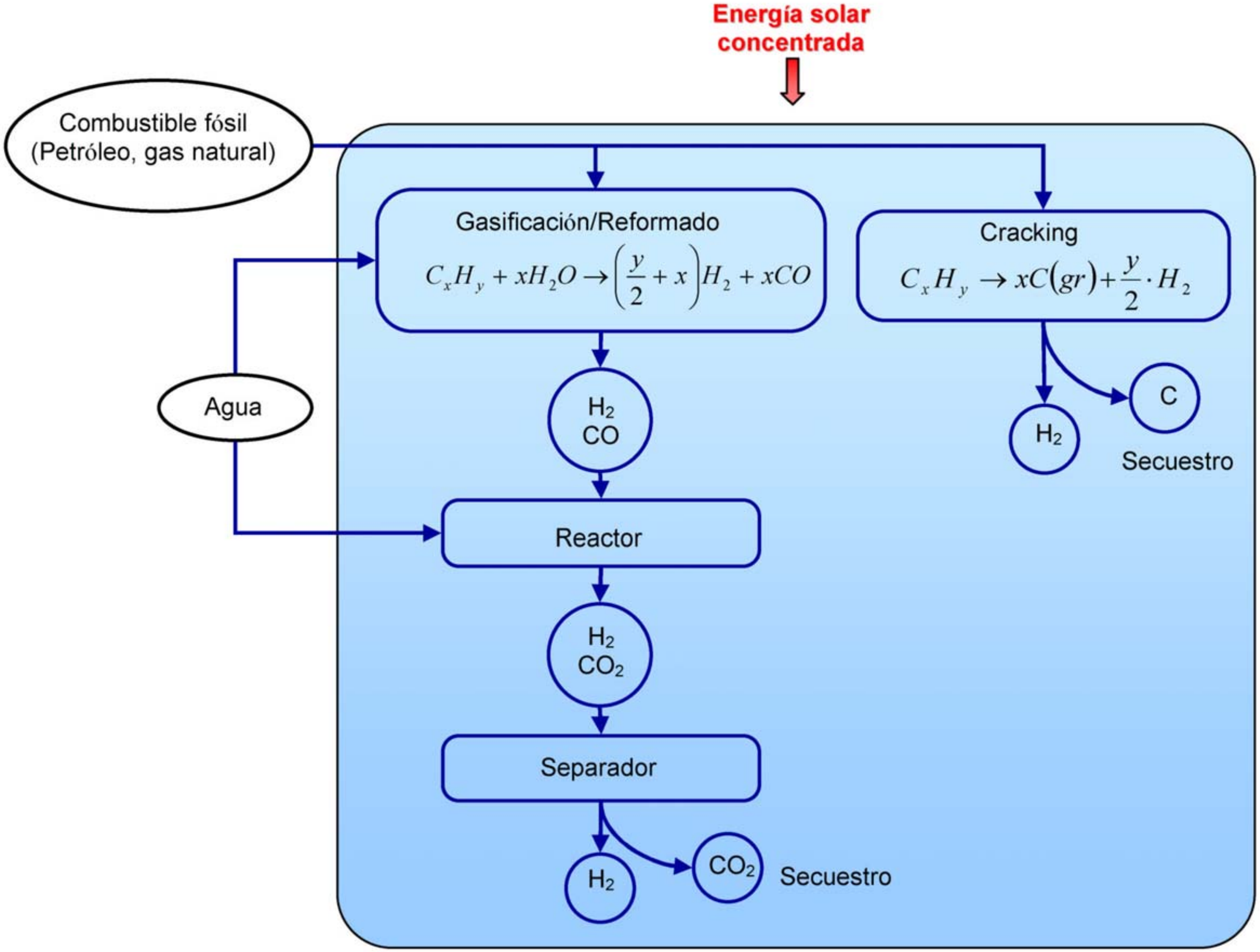

Energía solar concentrada
Combustible fósil (Petróleo, gas natural)
Agua
Gasificación/Reformado
$C_xH_y + xH_2O \rightarrow \left(\frac{y}{2} + x\right)H_2 + xCO$
Cracking
$C_xH_y \rightarrow xC(gr) + \frac{y}{2} \cdot H_2$
H_2
CO
Reactor
H_2
CO_2
Separador
H_2
CO_2
Secuestro
H_2
C
Secuestro

Fig. 8. Producción termoquímica de hidrógeno, a partir de combustibles fósiles y agua

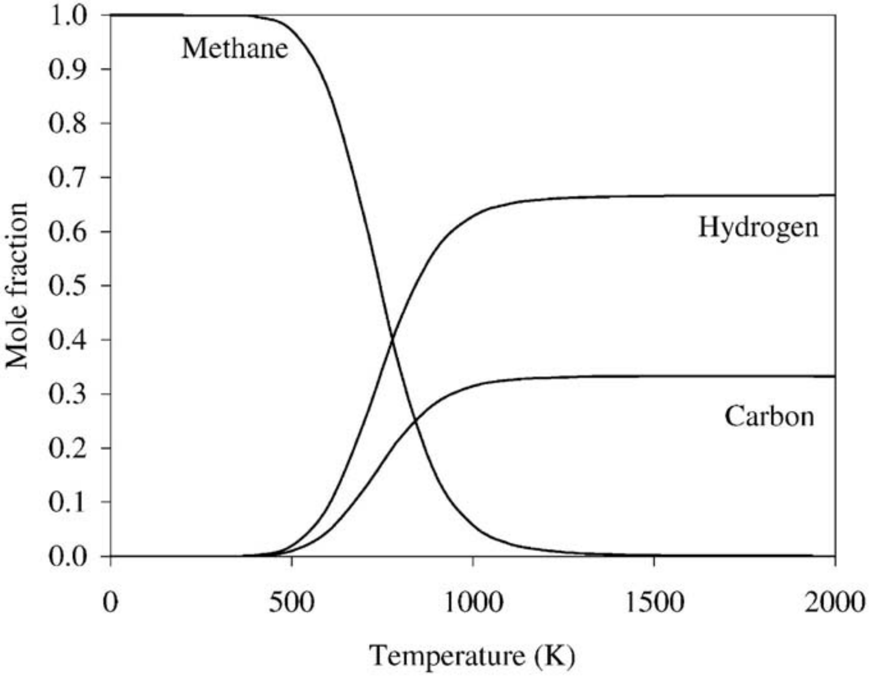
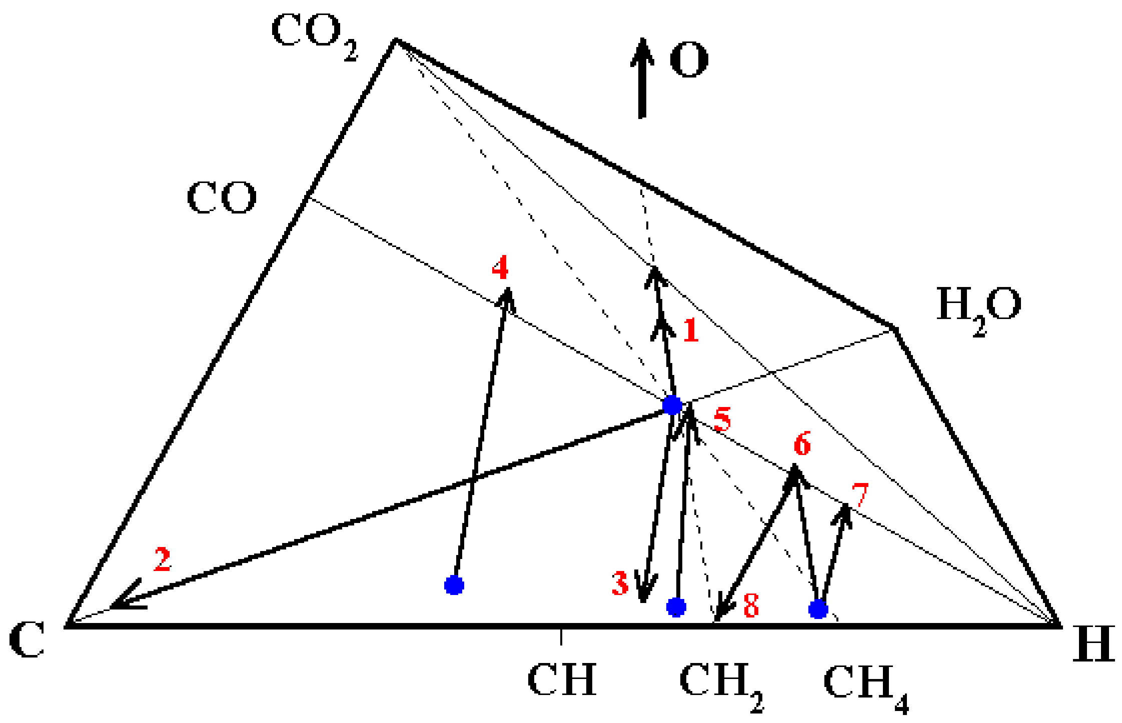


Fig. 3. Equilibrium composition of the system CH_4, as a function of temperature.

Some conceptual thinking on hydrocarbons


CO_2
O
CO
4
1
H_2O
5
6
7
2
3
8
C
H
CH
CH_2
CH_4

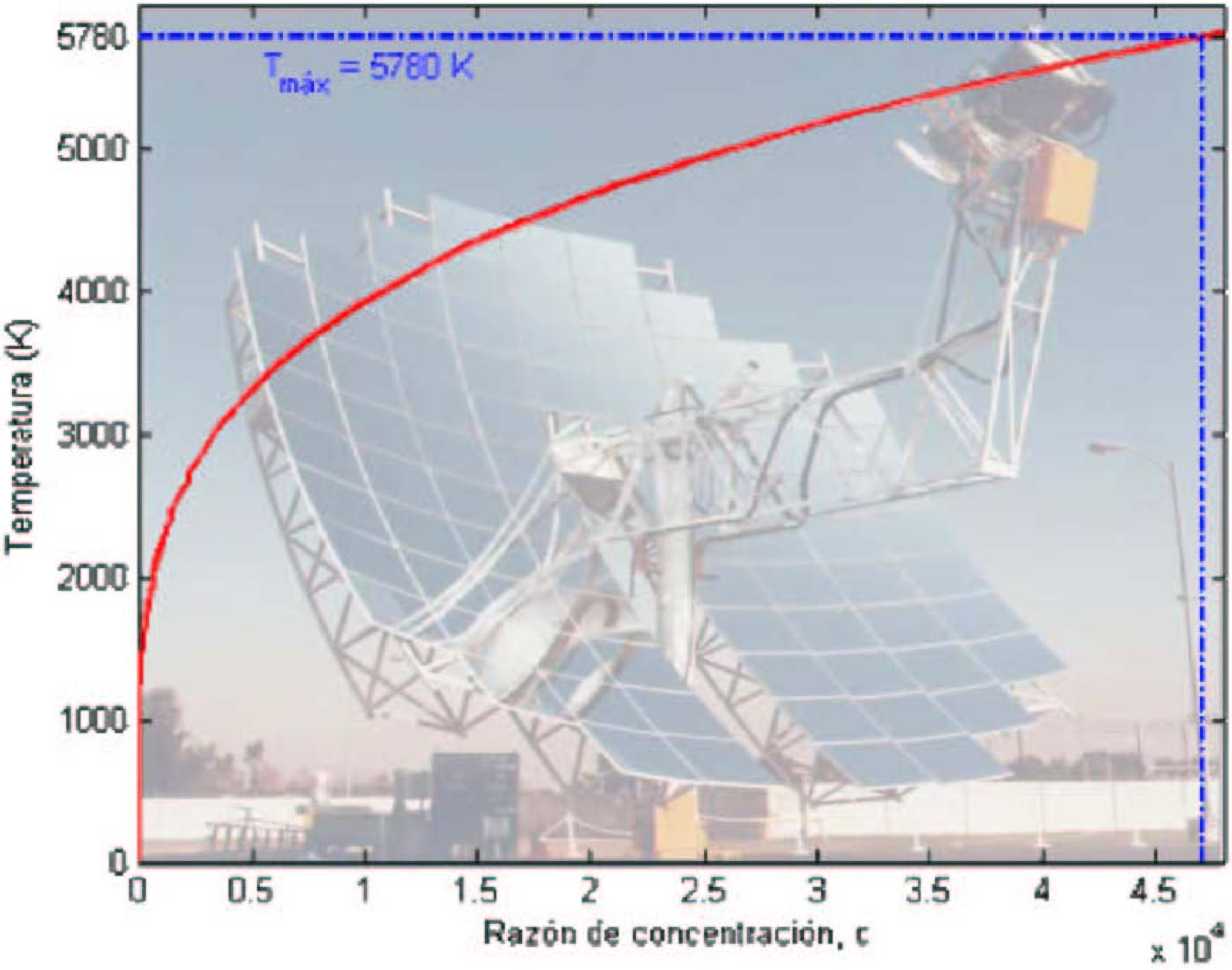
1. Biomass Gasification
2. Biomass Coaling
3. Hydrothermal Upgrading
4. Coal Gasification
5. Oil Gasification
6. Natural Gas Partial Oxidation
7. Natural Gas Steam Reforming
8. Fischer and Tropsch Synthesis

Solar heat for thermo-chemical processes

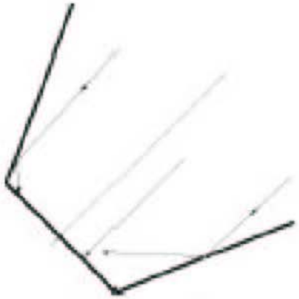
- **The SI method**
- **The UT3 process**
- **The hybrid W scheme**
- **The Ispra hybrid scheme**
- **The ZnO/Zn cycle**

The SI method

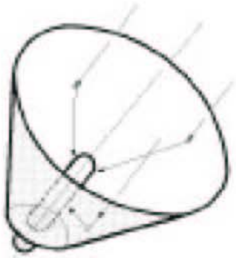
$(9I_2)_l + (SO_2)_g + (16H_2O)_l \Rightarrow (2HI + 10H_2O+8I_2)_l + (H_2SO_4+4H_2O)_l$	$120\ ^0$ C
$L_2 = (2HI + 10H_2O+8I_2)_l \Rightarrow (2HI)_g + (10H_2O + 8I_2)_l$	$230\ ^0$
$(2HI)_g \Rightarrow H_2 + (I_2)_l$	$330\ ^0$
$L_l = (H_2SO_4+4H_2O)_l \Rightarrow (H_2SO_4)_l + (4H_2O)_l$	$300\ ^0$
$(H_2SO_4)_l \Rightarrow (H_2SO_4)_g$	$360\ ^0$
$(H_2SO_4)_g \Rightarrow (SO_3)_g + (H_2O)_g$	$400\ ^0$
$(SO_3)_g \Rightarrow (SO_2)_g + \frac{1}{2} O_2$	$870\ ^0$


5780
5000
4000
3000
2000
1000
0
$T_{máx} = 5780$ K
Temperatura (K)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Razón de concentración, c
x 10^4

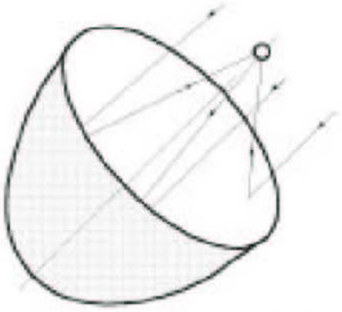
Colectores



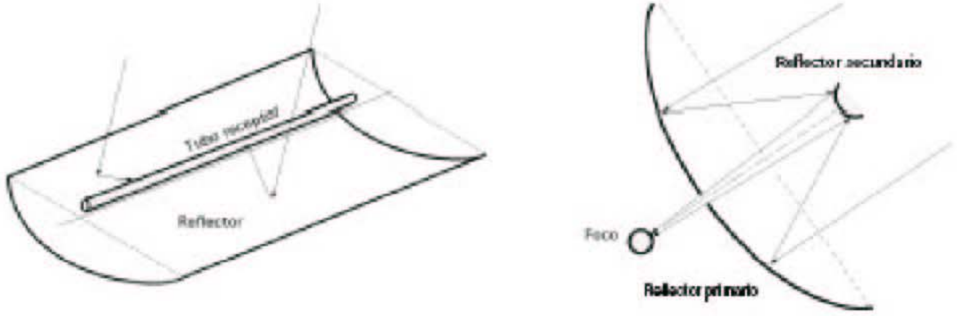
a) Receptor plano
Concentrador plano



b) Receptor cilíndrico
Concentrador troncocónico



c) Concentrador paraboloide
de revolución

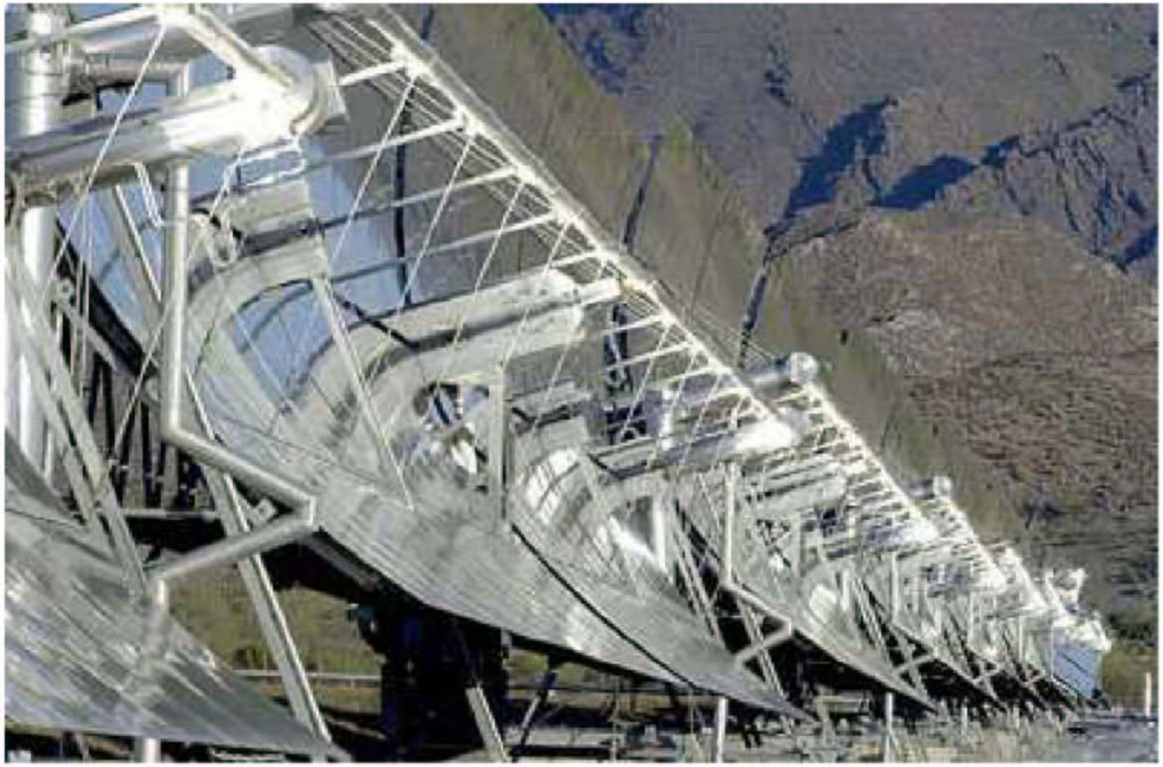

Tubo receptor
Reflector
Reflector secundario
Foco
Reflector primario

a) Concentrador c.p. general

b) Concentrador c.p. con reflector secundario

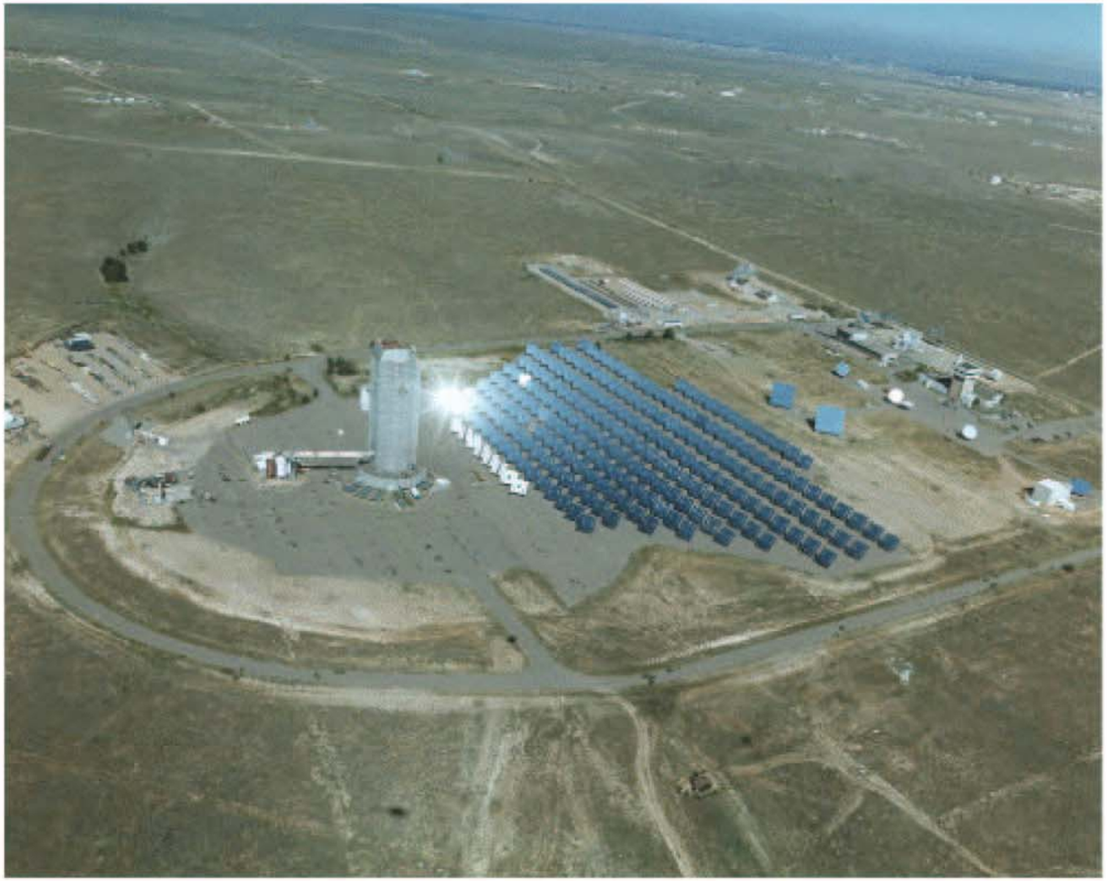
Fig IV.2.- Concentradores cilíndrico-parabólicos

Colectores cilindro-parabólicos



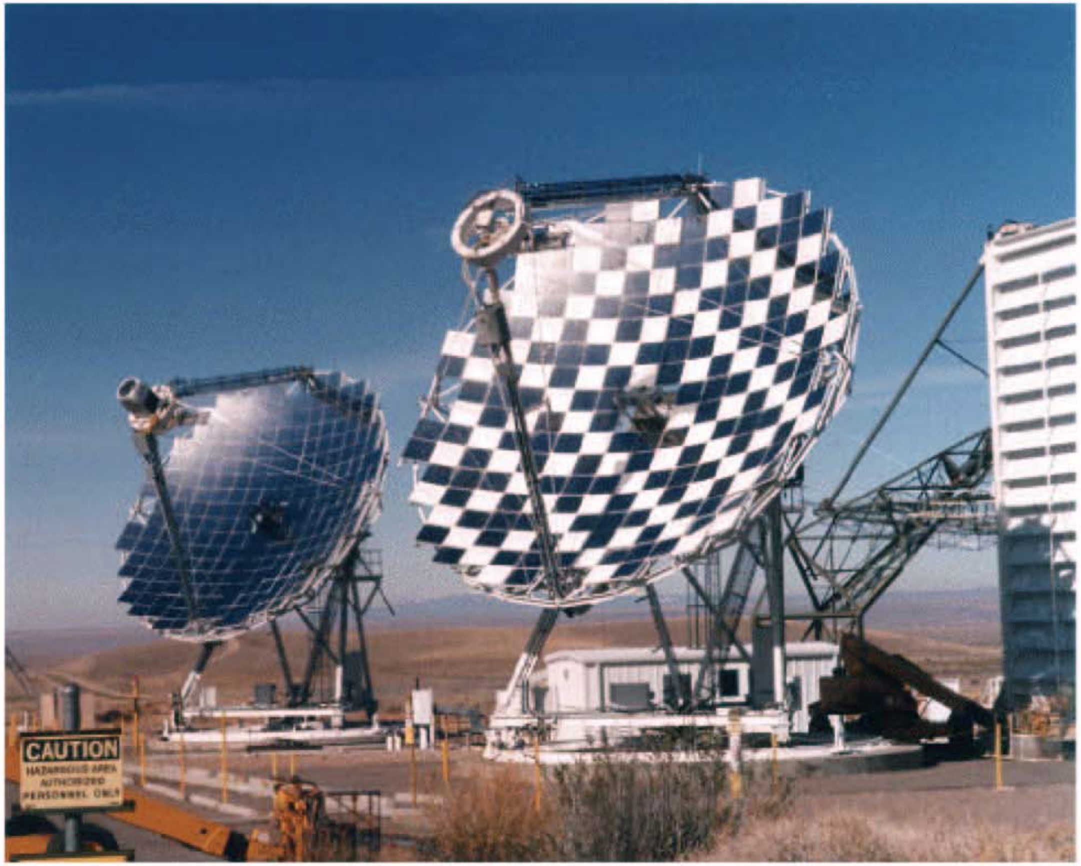
Fuente: Plataforma Solar de Almería – lazo DISS

Sistemas de torre central

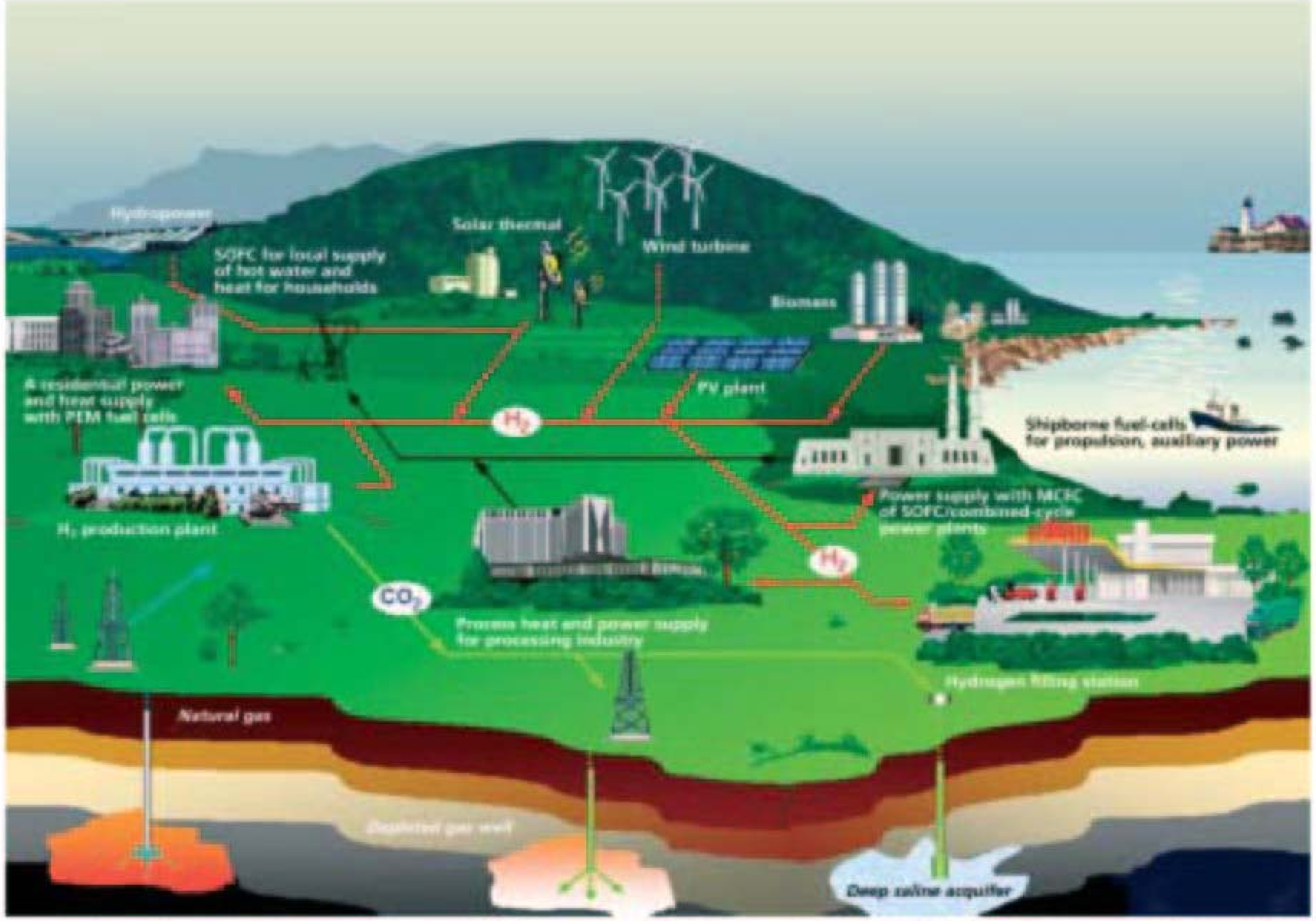


Fuente: NSTTF – Sandia National Laboratory

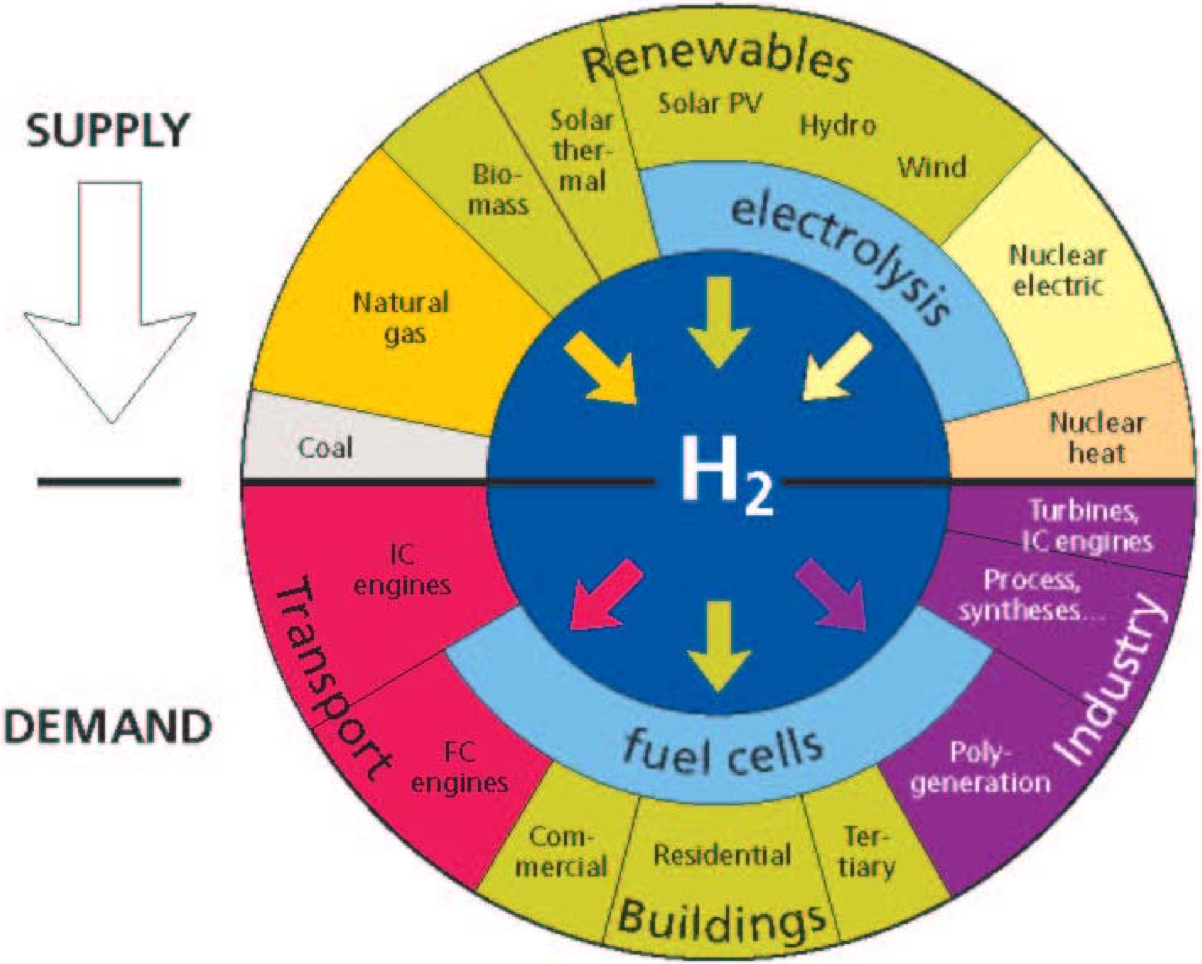
Discos parabólicos


CAUTION
HAZARDOUS AREA
AUTHORIZED
PERSONNEL ONLY

Fuente: NSTTF – Sandia National Laboratory


Hydropower
Solar thermal
Wind turbine
SOFC for local supply of hot water and heat for households
Biomass
PV plant
A residential power and heat supply with PEM fuel cells
H_2
Shipborne fuel-cells for propulsion, auxiliary power
Power supply with MCFC of SOFC/combined-cycle power plants
H_2 production plant
H_2
CO_2
Process heat and power supply for processing industry
Hydrogen filling station
Natural gas
Depleted gas well
Deep saline acquifer

This is how an integrated energy system of the future might look – combining large and small fuel cells for domestic and decentralised heat and electrical power generation. Local hydrogen networks could also be used to fuel conventional or fuel cell vehicles.



SUPPLY

DEMAND

Renewables

Solar PV

Hydro

Wind

Solar thermal

Biomass

Natural gas

Coal

Nuclear electric

Nuclear heat

electrolysis

H_2

fuel cells

Transport

IC engines

FC engines

Buildings

Commercial

Residential

Tertiary

Industry

Turbines, IC engines

Process, syntheses…

Polygeneration

10
Ideas-Fuerza para un Compromiso

Fundación
para
Estudios
sobre la
Energía