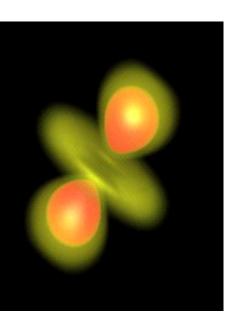
## Hydrogen 2012 Production of hydrogen



#### Introduction

Hydrogen can be produced by a variety of methods. Hydrogen has ideal characteristics as an energy carrier. It can be transported for long distance with less transportation loss than electricity. It can be stored in the forms of compressed gas, liquid, or hydrogenated compounds using hydrogen-absorbing alloys. It can not only be used as a fuel in a wide variety of industrial sectors, but also be transformed into electricity by fuel cells. Also, it is very clean in the sense that water is the only waste material after burning. Therefore, hydrogen is a promising candidate of alternative energy carriers in our future energy system.



Wizualizacja wodoru

Wasności fizyczne wodoru

Stan skupienia gazowy 0,0899kg/m3 Gęstość bezbarwny Barwa Zapach bez zapachu -259,13 st. Celsjusza Temperatura topnienia Temperatura wrzenia -252,88 st. Celsjusza -239,9 st. Celsjusza Temperatura krytyczna Ciśnienie krytyczne 1,3 MPa Geptoparowania 0,44936kJ/ml 0,05868kJ/ml Cieptotopnienia Ciśnienie pary nasyconej 209Pa(23K) 1270m/s (298,15K) Preckość dźwięku

#### Fact box

\_

Group	1	Melting point	-434.49°F,
Period	1	Boiling point	13.99 K -252.879°C, -423.182°F, 20.271 K
Block	S	Density (g cm <sup>-3</sup> )	0.000082
Atomic number	1	Relative atomic mass	1.008
State at 20°C	Gas	Key isotopes	<sup>1</sup> H, <sup>2</sup> H
Electron configuration	1s <sup>1</sup>	CAS number	133-74-0
Sound velocity	1270 ms		

## Key plant types

#### **Olefin Plants**



- Products: — Ethylene — Propylene — Butadiene
- Aromatics
- Polymers

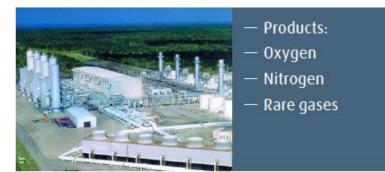
#### Natural Gas Plants



#### Hydrogen and Synthesis Gas Plants



#### Air Separation Plants

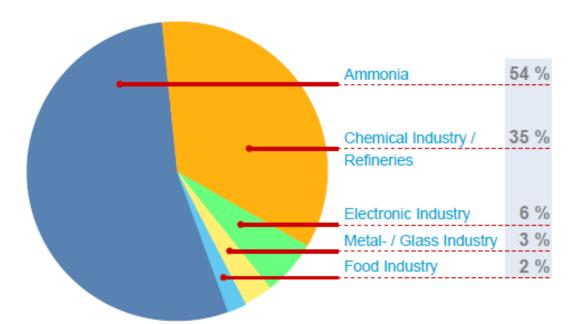


## Industrial Hydrogen Market

#### Installed capacity worldwide:

#### 600 Billion Nm<sup>3</sup>/year

#### Hydrogen Consumers:



#### Trends shaping future Hydrogen demand:

- Increase of World Oil Consumption
- Decline of Overall Crude Oil Quality
- More Stringent
  Environmental Standards
- New Applications (Automotive fuel, Fuel cell)

#### Reactions

#### Non Oxygen Consuming:

• Steam Methane Reforming (SMR)

 $CH4 + H_2O \rightarrow CO + 3 H_2$  endothermal

• Carbon Monoxide Conversion (CO-Shift)

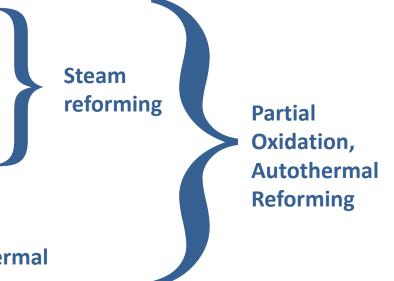
 $CO + H_2O \rightarrow CO_2 + H_2$  exothermal

#### **Oxygen Consuming**

Hydrocarbon Conversion

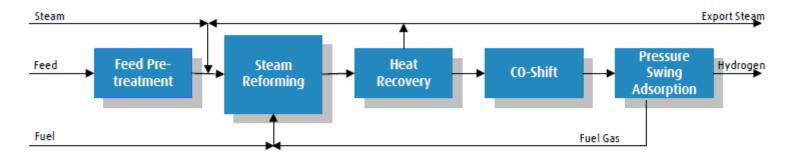
CnHm + n/2  $O_2 \rightarrow$  nCO + m/2  $H_2$  exothermal

#### Requested Products is H<sub>2</sub> H<sub>2</sub> Separation + Purification required

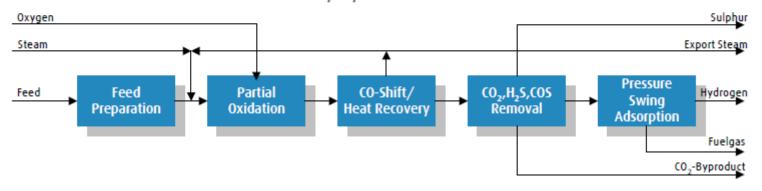


## Typical Basic Block Diagrams for H<sub>2</sub> Production

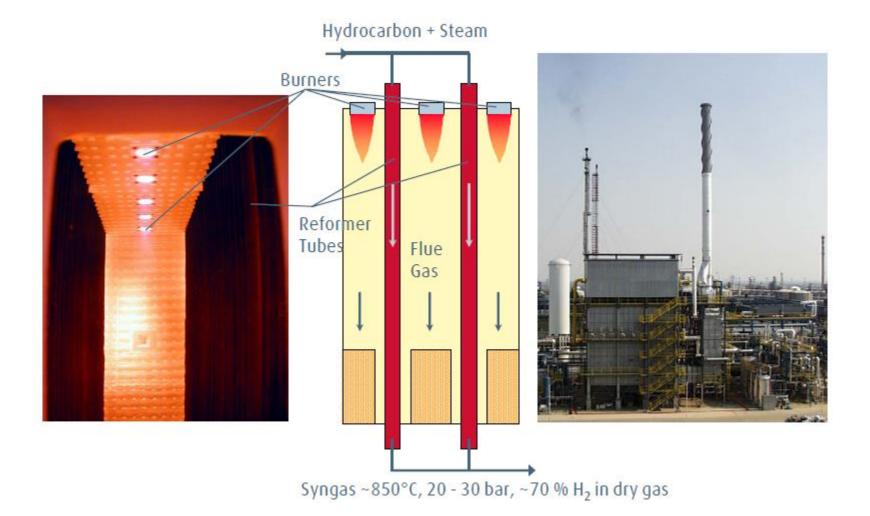
#### Light Hydrocarbons



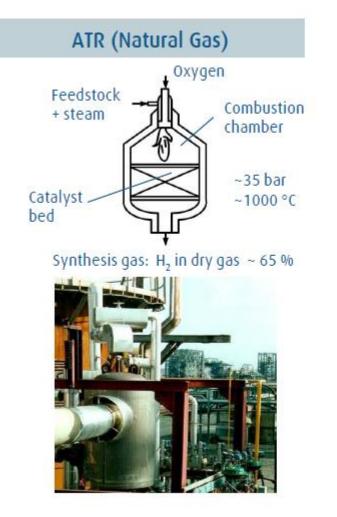
Heavy Hydrocarbons

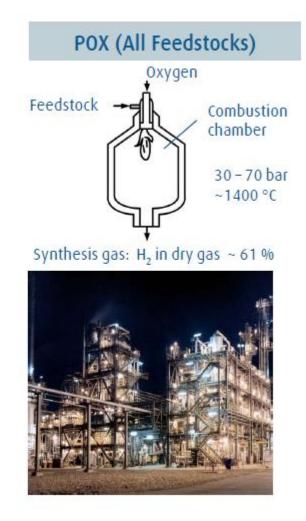


## **Steam Reformer**



## Autothermal Reforming Reactors/Partial Oxidation





#### **CO-Shift Reactor**

• Shifts undesired C0 to  $H_2$ C0 +  $H_2$ O  $\rightarrow$  CO<sub>2</sub> +  $H_2$ 

exothermal

- Simple catalytic reactor
- CO conversion depends on Temperature High Temperature Shift: ~ 75 % Low Temperature Shift: ~ 90%
- H<sub>2</sub> in dry gas ~ 75 %



#### Wash Unit for POX Synthesis Gas

- e.g. for Syngas from Coal Gasification
- Methanol as washing solvent
- Rectisol<sup>®</sup> process separates CO<sub>2</sub>, H<sub>2</sub>S, COS
- H<sub>2</sub> Purity ~ 98 %



### H<sub>2</sub> Purification: Pressure Swing Adsorption

 Pressure Swing Adsorption for high Purity H<sub>2</sub>

based on selective adsorption using different kinds of adsorption materials (e.g. molecular sieves)

- H<sub>2</sub> Purity up to 99.9999 %
- H<sub>2</sub> Recovery up to 90 %



#### Introduction to the IS process

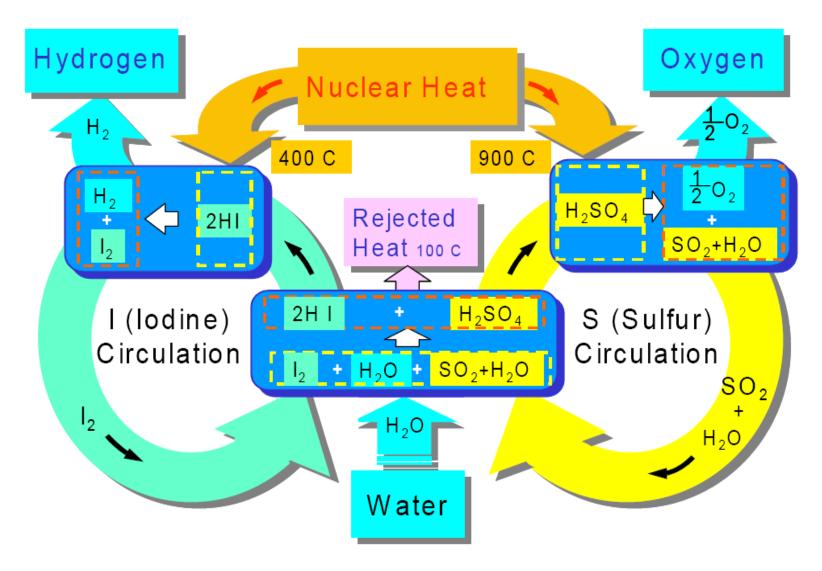
Thermochemical hydrogen production process produces hydrogen from water by absorbing high temperature nuclear heat supplied by High Temperature Gas-cooled Reactors. Production by IS (Iodine-Sulfur) hydrogen and oxygen could be produced with stable rate and with molar ratio of 2 to 1, the stoichiometric ratio of water splitting. Thermochemical water-splitting cycle is a method for the large-scale production of hydrogen.

# Closed-cycle H<sub>2</sub> production by thermochemical water-splitting IS process

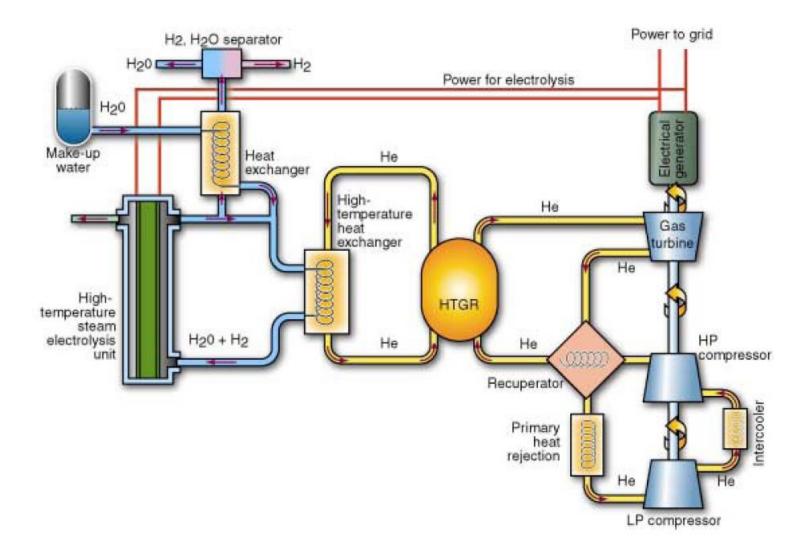
This cycle is named IS process after the elements used in the process, iodine and sulfur. It has attractive features such that all the chemicals are used in the fluid phase and the endothermic sulfuric acid decomposition reaction proceeds stoichiometrically with large entropy change.

 $2H_2O+SO_4+I_2 \rightarrow H_2SO_4+2HI$   $H_2SO_4 \rightarrow H_2O+SO_2+(1/2)O_2$   $2HI \rightarrow H_2+I_2$   $H_2O \rightarrow H_2+(1/2)O_2$ 

## **Thermochemical Water Splitting**



#### High Temperature Electrolysis using a Nuclear Reactor Heat Source



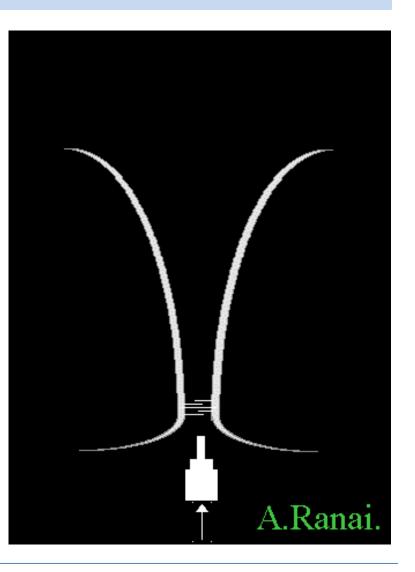
# The characteristics of the S-I process can be described as follows:

All fluid (liquids, gases) process, therefore well suited for continuous operation; High utilization of heat predicted (about 50%), but very high temperatures required (at least 850 deg C); Completely closed system without byproducts or effluents; Corrosive reagents used as intermediaries; therefore, advanced materials needed for construction of process apparatus; Suitable for application with solar, nuclear, and hybrid sources of heat; More developed than competitive thermochemical processes.

# H<sub>2</sub>S is therefore an abundant source for potentially the cheapest Hydrogen

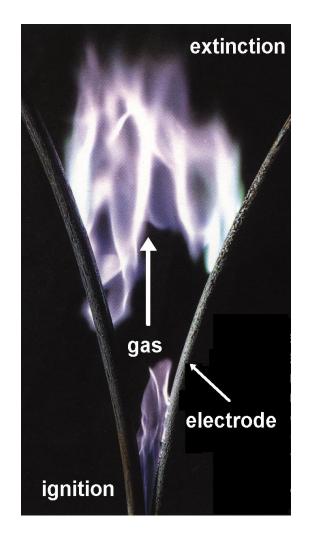
## We can obtain hydrogen using method called GlidArc.

How does it work??



## GlidArc

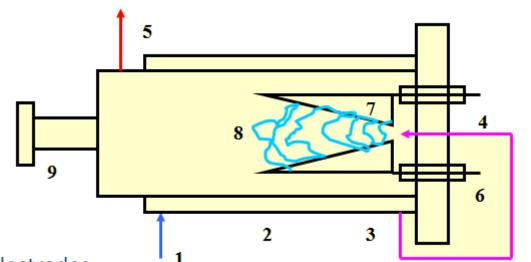
cold electric discharge, 5 - 25 kV, < 5 A, DC or AC, power from 0.05 to 50 kW 0.03 - 12 bar enhances and stabilises exothermic processes via active catalytic species bring active energy to endothermic processes not cooled electrodes any gas, vapour, droplets or dust accepted any initial feed temperature accepted multiple-discharge/electrode system can be installed for a large scale



## **GlidArc reformer**

Schematic view of 1.4-L GlidArc I reformer for H<sub>2</sub>S or sour gas processing

- 1- cold gas entry,
- 2 preheat chamber,
- 3 preheated gas exit,
- 4 injector of the preheated
- gas into the plasma chamber,
- 5 exit of the product,
- 6 high-voltage connectors to the electrodes,
- 7 electrodes (six),
- 8 gliding discharges,
- 9 observation window



## SulfArc advantages

- Products do not contain ballast of added reactants
- No catalyst
- Process does not depend on the chemical composition of effluents
- One can process small quantities of H<sub>2</sub>S or sour gas produced by small industrial units
- Energy expense is quite low
- No thermal inertia, good resistance to corrosion...

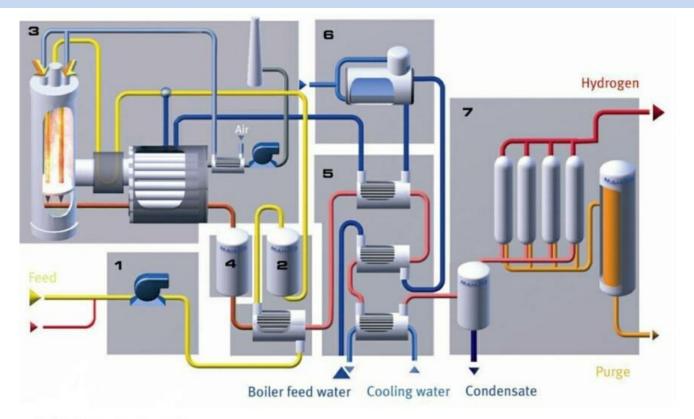
#### Mahler technologies I

The HYDROFORM-C system is based on steam reforming of natural gas, LPG or naphtha.

These processes offer customers a maximum of quality and security, as well as the capability of efficiently meeting hydrogen requirements from 100 to 10.000 Nm<sup>3</sup>/h at purities of up to 99.999+ per cent by volume.



#### Mahler technologies I



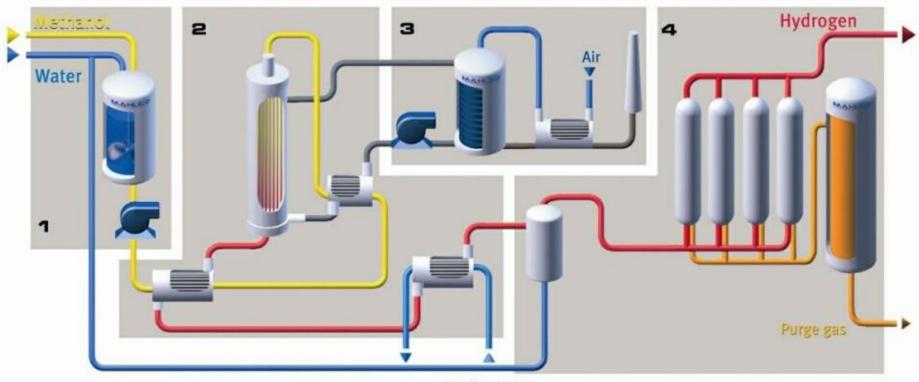
- 1: Feed compression unit
- 2: Feed pretreatment
- 3: Reforming and steam generation
- 4: High temperature conversion
- 5: Heat exchanger unit
- 6: Pretreatment of boiler feed water
- 7: Purification unit HYDROSWING® system

#### Mahler technologies II

The HYDROFORM-M system is based on the reforming process of methanol to cover hydrogen requirements from 100 to 4.000 Nm<sup>3</sup>/h at purities of up to 99.999+ per cent by volume.



## Mahler technologies II



**Cooling Water** 

1: Pretreatment of feed mixture

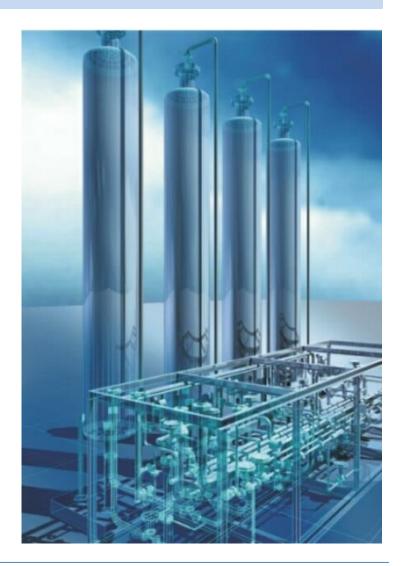
2: Methanol reforming and heat exchanger unit

3: Thermo-oil System

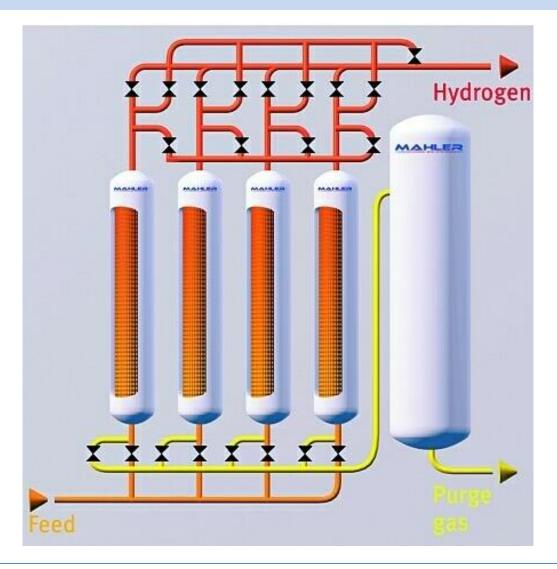
4: Purification unit - HYDROSWING® system

#### Mahler technologies III

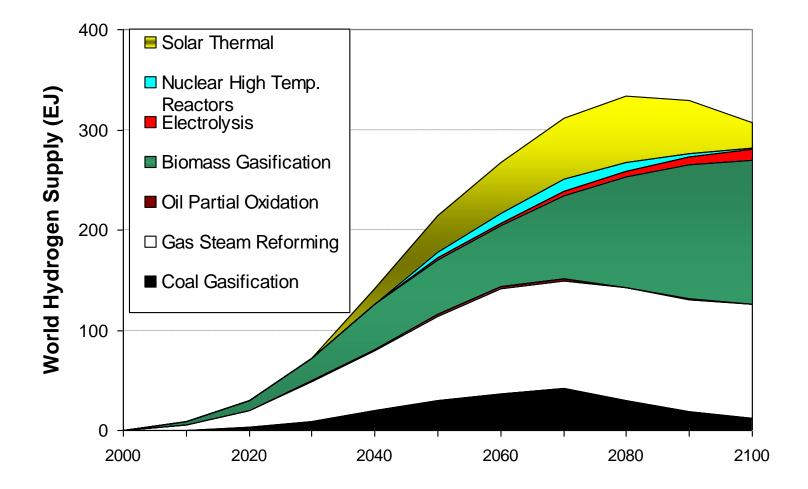
The HYDROSWING® system is based on the pressure swing adsorption process of hydrogen-rich gases to cover hydrogen requirements from 100 to 10.000 Nm<sup>3</sup>/h at purities of up to 99.999+ per cent by volume.



### Mahler technologies III



## Predicted delivery of H<sub>2</sub> in the future



## References

http://en.wikipedia.org/wiki/Sulfur-iodine\_cycle http://pagesperso-orange.fr/albin.czernichowski/ECP/index.htm http://www.iphe.net/meeting\_docs.html http://www.vortexcw.nl/vortex/glidarc.html http://www.hydrogen.energy.gov/production.html http://www.mahler-ags.com/hydrogen/index.htm K. Wawrzinek/ HDV / Nov. 21, 2007 /Industrial H2 Production & Technology.ppt

## Thank you for your attention