UNIVERSITÀ DEGLI STUDI DI TRIESTE

Dipartimento di Ingegneria e Architettura

THERMOCHEMICAL HYDROGEN PRODUCTION METHODS

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A.A. 2023-2024

OUTLINE

1. Hydrogen production methods: an overview*
2. Steam methane reforming*
3. Additional (reforming) processes*
4. Novel thermochemical technologies*

* Not topic for the exam

BIBLIOGRAPHY

Reference	Chapters
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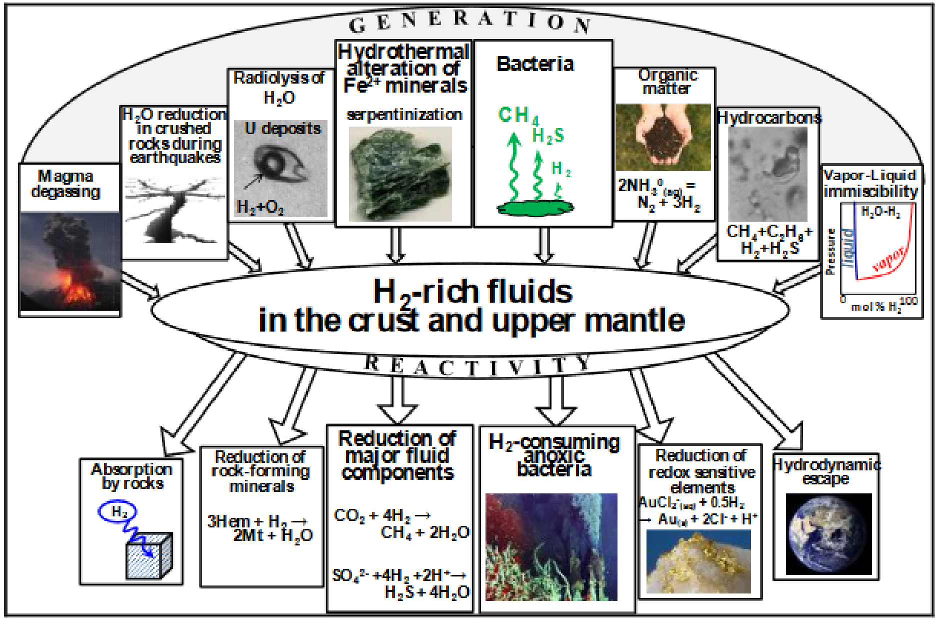
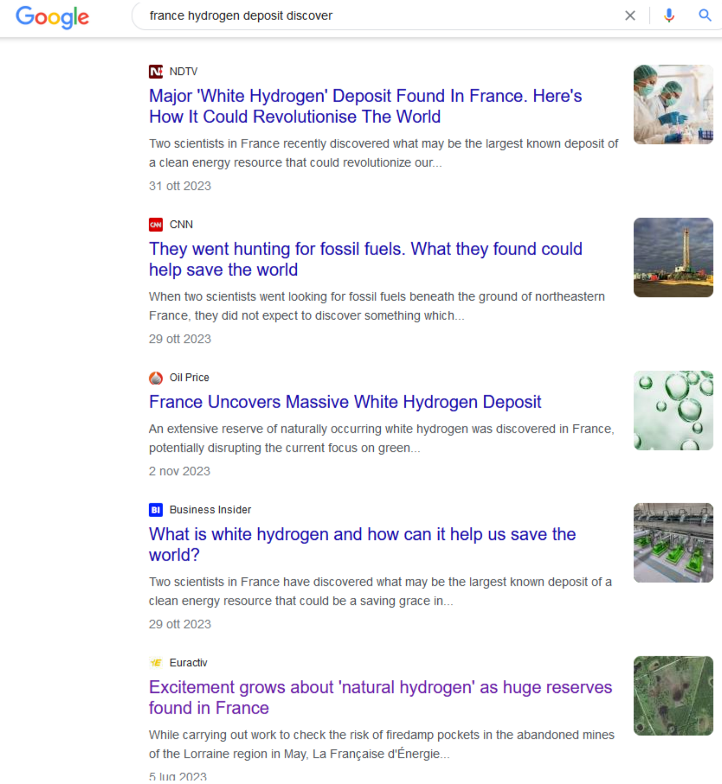
Wunsch A. et al., Membranes 2018, 8, 107 https://doi.org/10.3390/membranes8040107	

1. HYDROGEN PRODUCTION METHODS: AN OVERVIEW

HYDROGEN IN NATURE



Truche L., Bazarkina E.F., ES3 Web of Conferences 98, 03006 (2019)



france hydrogen deposit discover

NDTV

Major 'White Hydrogen' Deposit Found In France. Here's How It Could Revolutionise The World

Two scientists in France recently discovered what may be the largest known deposit of a clean energy resource that could revolutionize our...

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CNN

They went hunting for fossil fuels. What they found could help save the world

When two scientists went looking for fossil fuels beneath the ground of northeastern France, they did not expect to discover something which...

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Oil Price

France Uncovers Massive White Hydrogen Deposit

An extensive reserve of naturally occurring white hydrogen was discovered in France, potentially disrupting the current focus on green...

2 nov 2023

Business Insider

What is white hydrogen and how can it help us save the world?

Two scientists in France have discovered what may be the largest known deposit of a clean energy resource that could be a saving grace in...

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Euractiv

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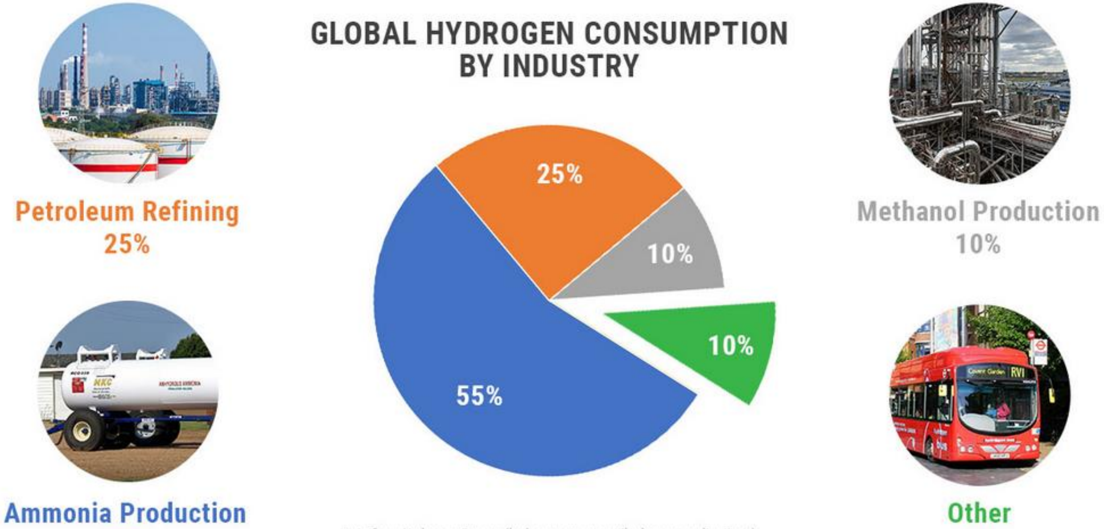
5 lug 2023

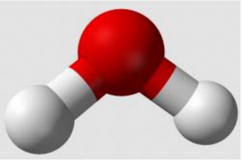
HYDROGEN DEMAND

Like electricity, hydrogen is an energy carrier and must be converted from other sources of energy. Thus, a feedstock to be processed is required in order to produce hydrogen in large amounts, as pure hydrogen is used in several industrial sectors.

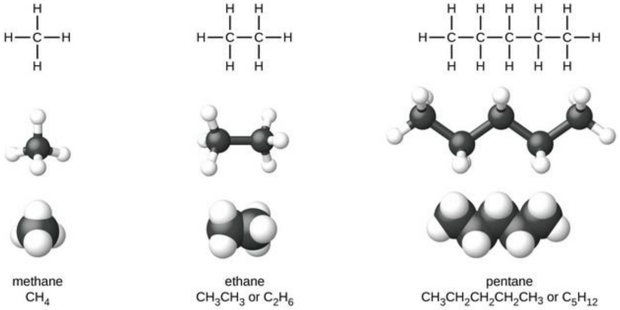


Data from Hydrogen Europe (hydrogeneurope.eu/hydrogen-applications)
Illustration © WHA International, Inc. (wha-international.com)

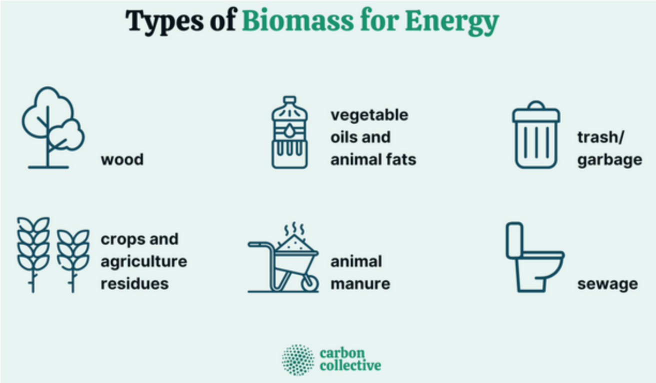
HYDROGEN SOURCES



https://en.wikipedia.org/wiki/Water

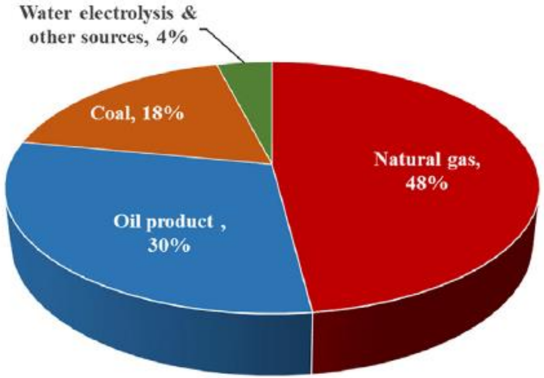


https://pressbooks-dev.oer.hawaii.edu/chemistry/chapter/hydrocarbons/

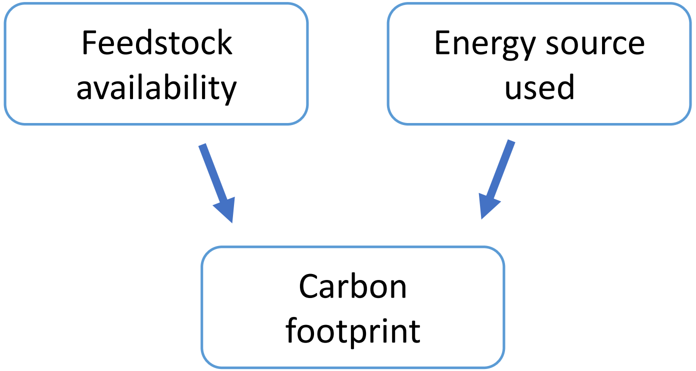


HYDROGEN PRODUCTION RATES

While hydrogen as an energy carrier has low environmental impact at the point of use, there may be significant impacts from the production and distribution of hydrogen. To date, the most widely used hydrogen production technology is steam reforming of a natural gas (such as methane) and contributes for about half of the overall hydrogen produced, followed by oil reforming and coal gasification. Electrolysis is an emerging technology, overall due to its limited impact in terms of carbon emission, while biomass processing still need to face some technological and economic challenges.



Ji, M. et al., Int. Journal Hydrogen Energy, 46 (2021) 38612-38635



Feedstock availability

Energy source used

Carbon footprint

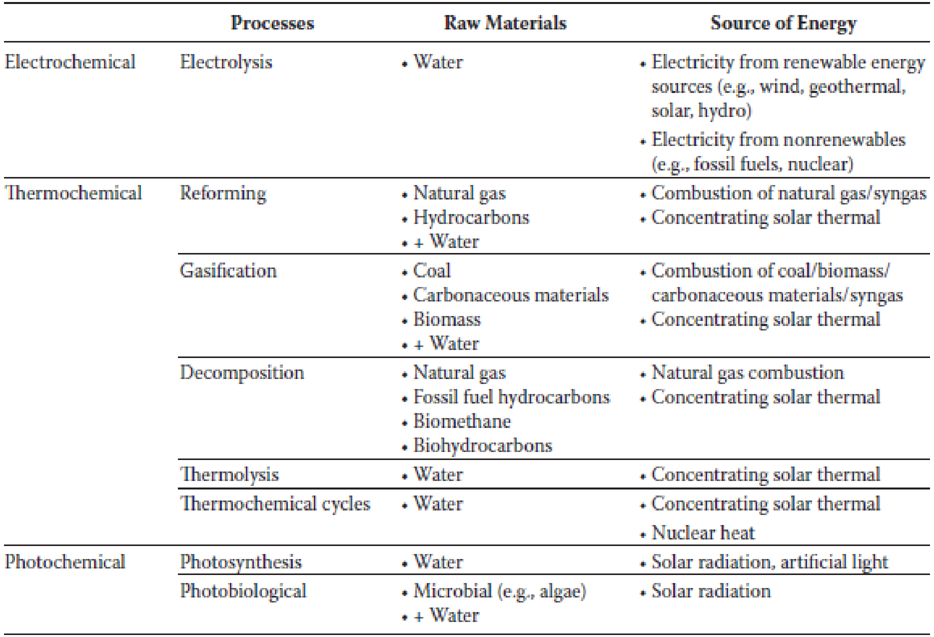
HYDROGEN PRODUCTION PROCESSES: A FIRST CLASSIFICATION

Electrochemical

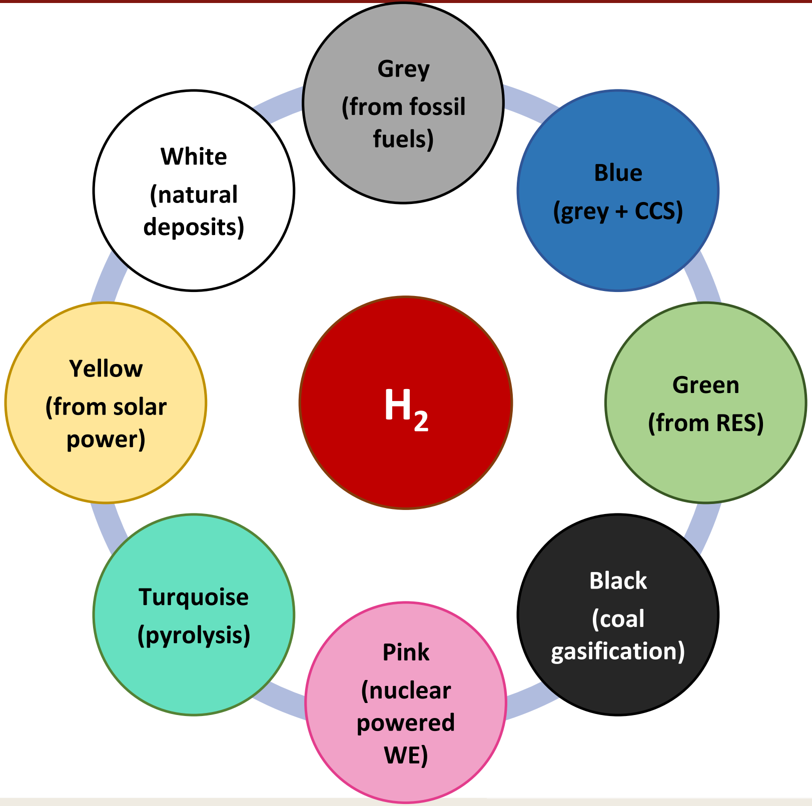
Thermochemical

Photochemical

HYDROGEN PRODUCTION PROCESSES: A FIRST CLASSIFICATION



	Processes	Raw Materials	Source of Energy
Electrochemical	Electrolysis	• Water	• Electricity from renewable energy sources (e.g., wind, geothermal, solar, hydro) • Electricity from nonrenewables (e.g., fossil fuels, nuclear)
Thermochemical	Reforming	• Natural gas • Hydrocarbons • + Water	• Combustion of natural gas/syngas • Concentrating solar thermal
	Gasification	• Coal • Carbonaceous materials • Biomass • + Water	• Combustion of coal/biomass/carbonaceous materials/syngas • Concentrating solar thermal
	Decomposition	• Natural gas • Fossil fuel hydrocarbons • Biomethane • Biohydrocarbons	• Natural gas combustion • Concentrating solar thermal
	Thermolysis	• Water	• Concentrating solar thermal
	Thermochemical cycles	• Water	• Concentrating solar thermal • Nuclear heat
Photochemical	Photosynthesis	• Water	• Solar radiation, artificial light
	Photobiological	• Microbial (e.g., algae) • + Water	• Solar radiation



H_2

Grey (from fossil fuels)

Blue (grey + CCS)

Green (from RES)

Black (coal gasification)

Pink (nuclear powered WE)

Turquoise (pyrolysis)

Yellow (from solar power)

White (natural deposits)

HYDROGEN PRODUCTION PROCESSES: QUALITY AND STANDARDS

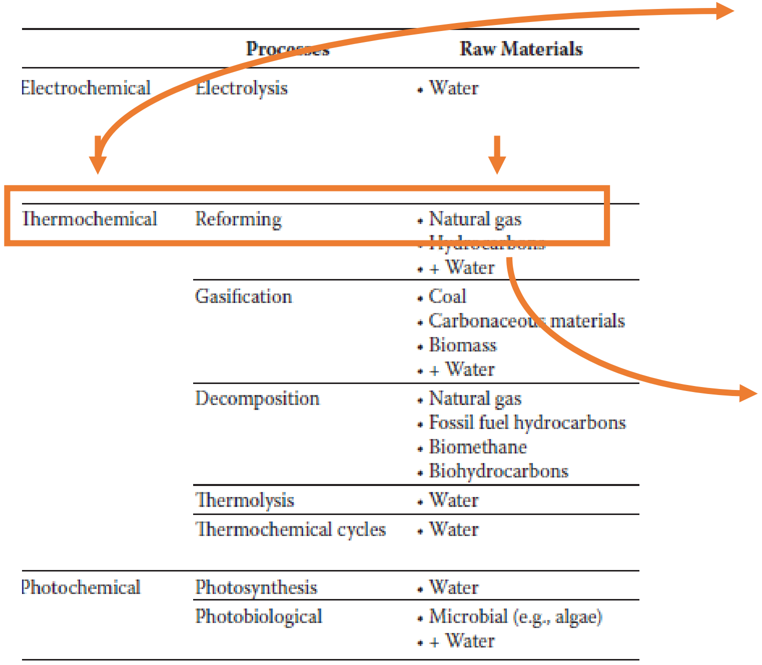
Hydrogen quality required for electric vehicles is standardized within the ISO 14687-2:2012

Impurities need to be reduced as much as possible because they cause reversible, temporal catalyst deactivation (blockage of active sites) and irreversible damage to catalysts and membranes (chemical degradation)

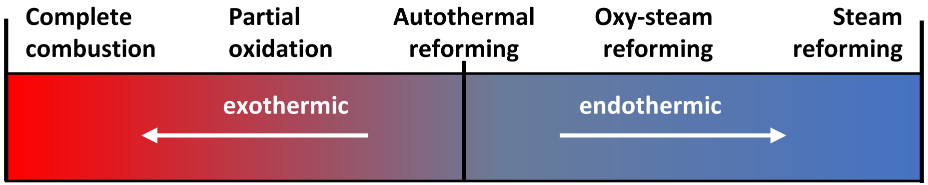
Parameter	Limits
Minimum mole fraction	99.97%
Helium (He)	< 300 ppm
Total nitrogen and argon (N_2+ Ar_2)	< 100 ppm
Water (H_2O)	< 5 ppm
Carbon dioxide (CO_2)	< 2 ppm
Carbon monoxide (CO)	< 0.2 ppm
Total hydrocarbons (CH_4 basis)	< 2 ppm
Total sulphur (H_2S basis)	< 0.004 ppm
Ammonia (NH_3)	< 0.1 ppm

2. STEAM METHANE REFORMING

STEAM REFORMING FROM NATURAL GAS



	Processes	Raw Materials
Electrochemical	Electrolysis	• Water
Thermochemical	Reforming	• Natural gas • Hydrocarbons • + Water
	Gasification	• Coal • Carbonaceous materials • Biomass • + Water
	Decomposition	• Natural gas • Fossil fuel hydrocarbons • Biomethane • Biohydrocarbons
	Thermolysis	• Water
	Thermochemical cycles	• Water
Photochemical	Photosynthesis	• Water
	Photobiological	• Microbial (e.g., algae) • + Water



Adapted from : Mosinska, M. et al., *Catalysts* 2020, *10*, 896.

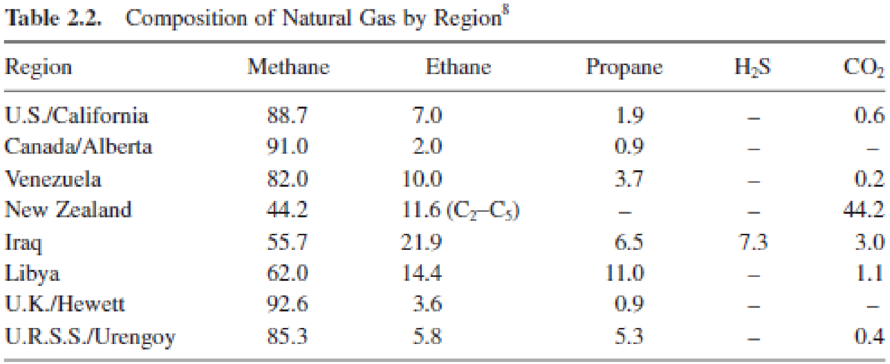


Table 2.2. Composition of Natural Gas by Region[8]

Region	Methane	Ethane	Propane	H_2S	CO_2
U.S./California	88.7	7.0	1.9	–	0.6
Canada/Alberta	91.0	2.0	0.9	–	–
Venezuela	82.0	10.0	3.7	–	0.2
New Zealand	44.2	11.6 (C_2–C_5)	–	–	44.2
Iraq	55.7	21.9	6.5	7.3	3.0
Libya	62.0	14.4	11.0	–	1.1
U.K./Hewett	92.6	3.6	0.9	–	–
U.R.S.S./Urengoy	85.3	5.8	5.3	–	0.4

STEAM METHANE REFORMING

Steam reforming is a chemical process that breaks hydrocarbon molecules, in reaction with water in state of vapor, into syngas, that is a mixture of carbon monoxide and hydrogen:

$$C_nH_m + nH_2O \rightarrow nCO + \frac{2n+m}{2}H_2, \quad \Delta H(298\,K) > 0$$

In the case of methane the reaction is strongly endothermic:

$$CH_4 + H_2O \rightarrow CO + 3H_2\,, \quad \Delta H^0_{298K} = 205.9\,kJ \cdot mol^{-1}$$

And involves several different catalyzed reactions such as:

- the water-gas shift (WGS) reaction:

$$CO + H_2O \rightarrow CO_2 + H_2, \quad \Delta H^0_{298K} = -41\,kJ \cdot mol^{-1}$$

- the Boudouard reaction:

$$2CO \rightarrow CO_2 + C, \quad \Delta H^0_{298K} = -172.4\,kJ \cdot mol^{-1}$$

- the methane decomposition reaction:

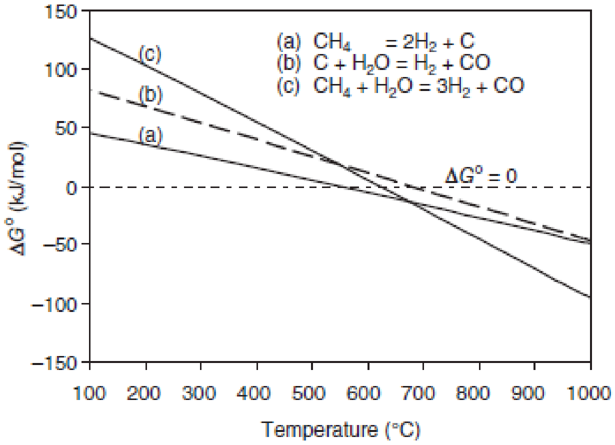
$$CH_4 \rightarrow C + 2H_2, \quad \Delta H^0_{298K} = 74.6\,kJ \cdot mol^{-1}$$

STEAM METHANE REFORMING: THERMODYNAMICS

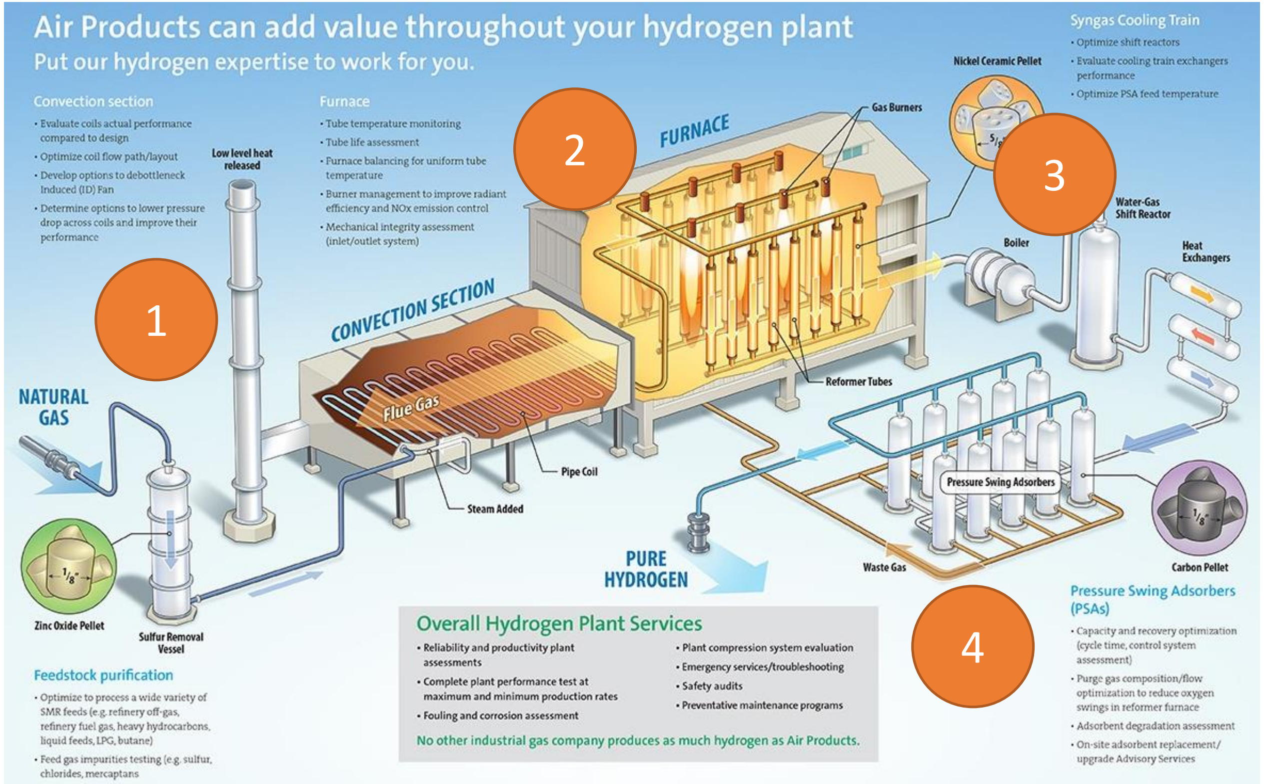
A useful representation for evaluate the ease of reaction is represented by the so-called Ellingham diagram, in which ΔG is displayed in function of reaction temperature.

Since ΔH and ΔS are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines, where ΔS is the slope and ΔH is the y-intercept. The slope of the line changes when any of the materials involved melt or vaporize.

The Ellingham diagram is usually used to evaluate the temperature dependence of the stability of compounds, but it can be also used to investigate the reactions involved in the SMR process. In example, from the Ellingham diagrams it can be observed as the methane decomposition reaction (a), which leads to carbon deposition in the reactor, occurs at about 500°C, while SMR and carbon gasification reaction, take place at higher temperatures. Such a kind of information was important in reactor design (heat transfer does not allow temperature to reduce too much).



STEAM METHANE REFORMING



Air Products can add value throughout your hydrogen plant

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Convection section

- Evaluate coils actual performance compared to design
- Optimize coil flow path/layout
- Develop options to debottleneck Induced (ID) Fan
- Determine options to lower pressure drop across coils and improve their performance

Furnace

- Tube temperature monitoring
- Tube life assessment
- Furnace balancing for uniform tube temperature
- Burner management to improve radiant efficiency and NOx emission control
- Mechanical integrity assessment (inlet/outlet system)

Syngas Cooling Train

- Optimize shift reactors
- Evaluate cooling train exchangers performance
- Optimize PSA feed temperature

Feedstock purification

- Optimize to process a wide variety of SMR feeds (e.g. refinery off-gas, refinery fuel gas, heavy hydrocarbons, liquid feeds, LPG, butane)
- Feed gas impurities testing (e.g. sulfur, chlorides, mercaptans

Overall Hydrogen Plant Services

- Reliability and productivity plant assessments
- Complete plant performance test at maximum and minimum production rates
- Fouling and corrosion assessment
- Plant compression system evaluation
- Emergency services/troubleshooting
- Safety audits
- Preventative maintenance programs

No other industrial gas company produces as much hydrogen as Air Products.

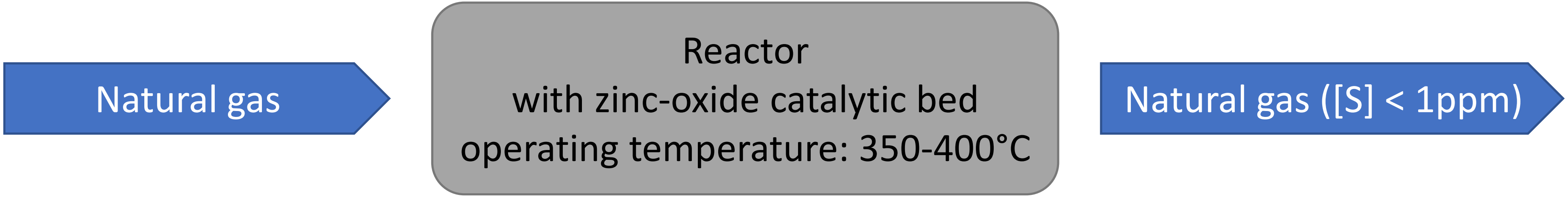
Pressure Swing Adsorbers (PSAs)

- Capacity and recovery optimization (cycle time, control system assessment)
- Purge gas composition/flow optimization to reduce oxygen swings in reformer furnace
- Adsorbent degradation assessment
- On-site adsorbent replacement/ upgrade Advisory Services

1. Pre-treatment
2. Reforming
3. CO shift conversion
4. Final H_2 purification

American Fuel & Petrochemical Manufacturers | 114th Annual Meeting, 2016

STEAM METHANE REFORMING: 1. PRE-TREATMENT



Natural gas

Reactor
with zinc-oxide catalytic bed
operating temperature: 350-400°C

Natural gas ([S] < 1ppm)

STEAM METHANE REFORMING: 2. REFORMING

desulphurised gas

Reactor for steam reforming
Ni-based* catalytic bed for SMR
$T_{op} \approx 500\text{-}900°C$; $P_{op} \approx 20$ bar

Reformed gas

Although the stoichiometry for the reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

suggests that only 1 mol of H_2O is required for 1 mol of CH_4 , the reaction in practice is performed using higher steam-to-carbon (S/C) ratios:

$$\frac{S}{C} = \frac{[H_2O]}{[CH_4]} = 2\ - 4$$

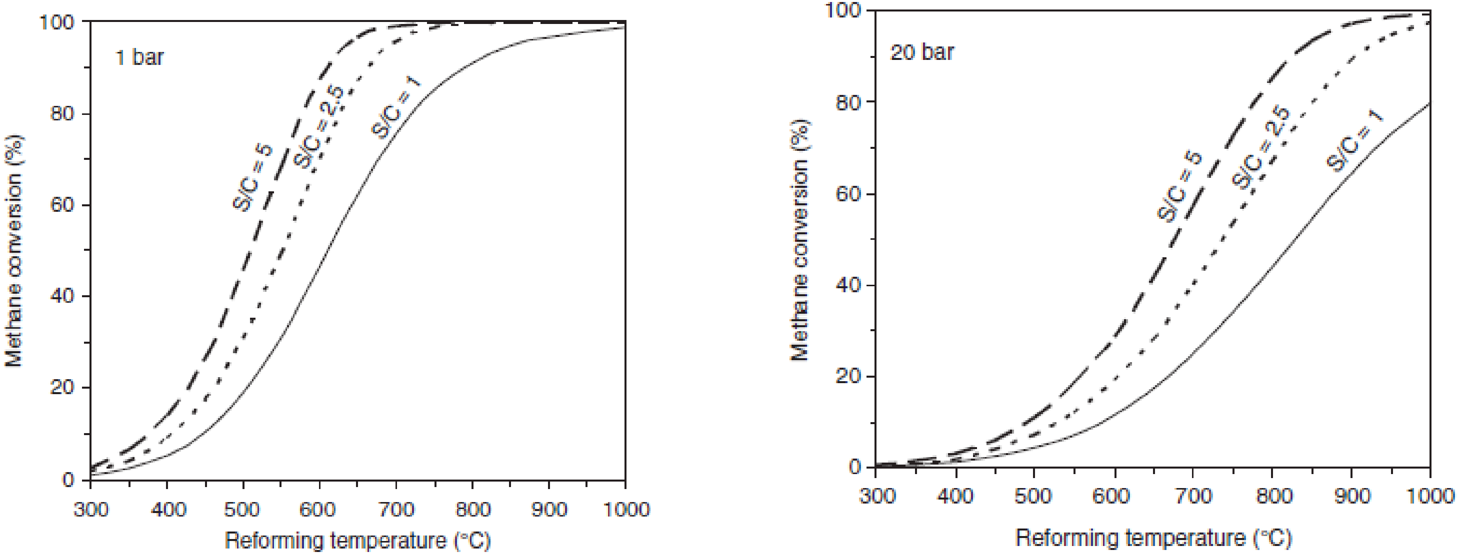
in order to reduce the risk of carbon deposition on the catalyst surface

[*] Catalyst material is used depending on the process; for SMR cobalt and other noble metals can also be used as catalysts but are generally more expensive. Ni has been the favored active metal because of its sufficient activity and low cost. Ni is typically supported on alumina, a refractory and highly stable material.

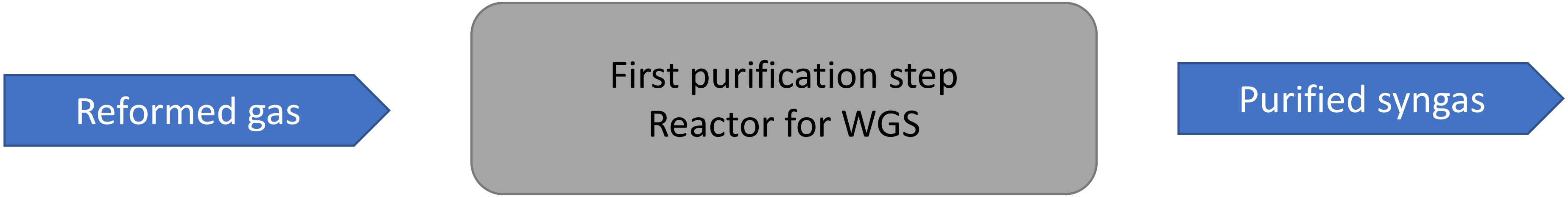
STEAM METHANE REFORMING: 2. REFORMING

By increasing the S/C ratio, it is then possible to reduce the operating temperature of the reactor to maximise the percentage of methane conversion (i.e. at 700°C/1bar or at 900°C/20bar).

As said before, S/C > 1 also allow to reduce/suppress the phenomenon of carbon deposition, which can lead to plant shutdown.



STEAM METHANE REFORMING: 3. PURIFICATION VIA CO SHIFT CONVERSION



Reformed gas

First purification step
Reactor for WGS

Purified syngas

After SMR, the reacted gas is mainly composed by:

- H_2
- CO, which is further processed to increase the H_2 concentration in the mixture via the Water-Gas Shift reaction :

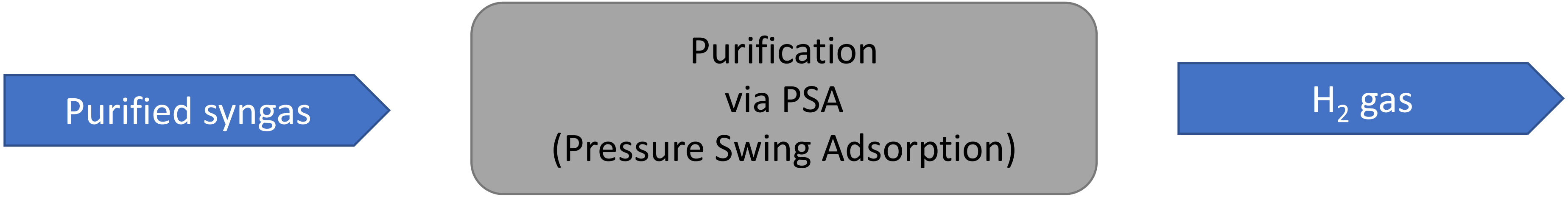
$$CO + H_2O \rightarrow CO_2 + H_2, \quad \Delta H^0_{298K} = -41\ kJ \cdot mol^{-1}$$

- Unreacted CH_4, which is feed back to the SMR reactor

The WGS develops in two steps:

1. High Temperature Shift (HTS): T_{op} ≈300-500°C; [CO] < 2 v%
2. Low Temperature Shift (LTS): T_{op} ≈150-250°C; [CO] < 0.2 v%

STEAM METHANE REFORMING: 4. PURIFICATION VIA PSA



Purified syngas

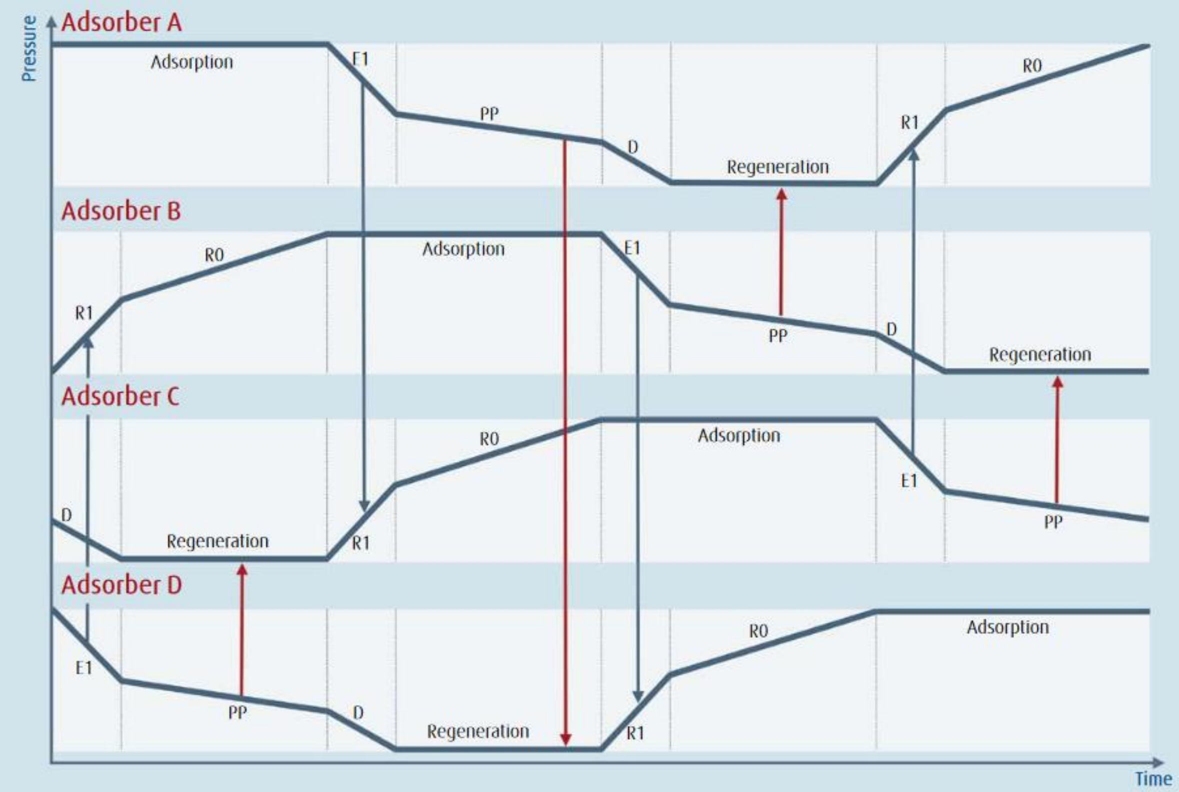
Purification
via PSA
(Pressure Swing Adsorption)

H_2 gas

PSA is based on the phenomenon that different gases are characterized by different adsorptions pressures onto solid surfaces, and that different gases desorb surfaces at different pressures.

As solid phase highly porous materials are used, such as activated carbon or zeolites.

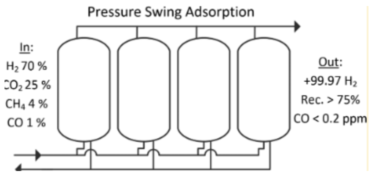
STEAM METHANE REFORMING: 4. PURIFICATION VIA PSA



PSA develops along four steps:

1. Adsorption
2. Depressurization
3. Regeneration
    a. Pressure Equalization (PE)
    b. Provide Purge (PP)
    c. Pressure Dump (D)
    d. Purging
4. Repressurization

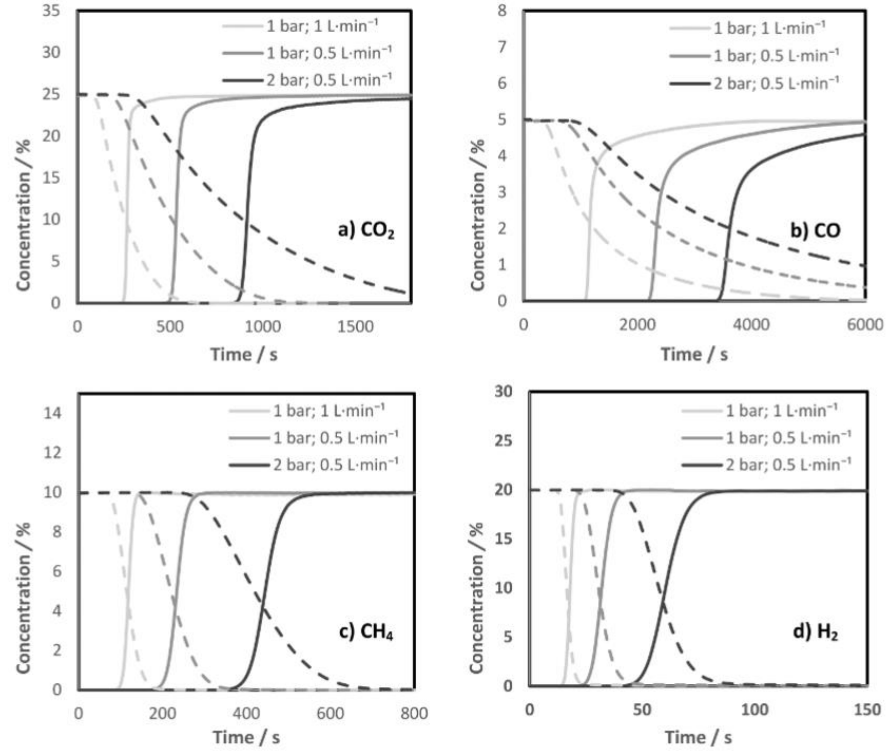
Four reactors are continuously fed with gas and iteratively commute among the four steps to guarantee continuous gas flow, to minimize hydrogen losses and maximize the hydrogen recovery rate.



https://www.linde-engineering.com/en/images/HA_H_1_1_e_09_150dpi_NB_tcm19-6130.pdf

Revals F. et al., Ind. Eng. Chem. Res.2018, 57, 5106−5118; DOI:10.1021/acs.iecr.7b05410

STEAM METHANE REFORMING: 4. PURIFICATION VIA PSA



Revals F. et al., Ind. Eng. Chem. Res.2018, 57, 5106−5118; DOI:10.1021/acs.iecr.7b05410

STEAM METHANE REFORMING: THE REACTION CHAMBER

Pre-heated gas mixture (methane + steam) is fed in the reaction chamber

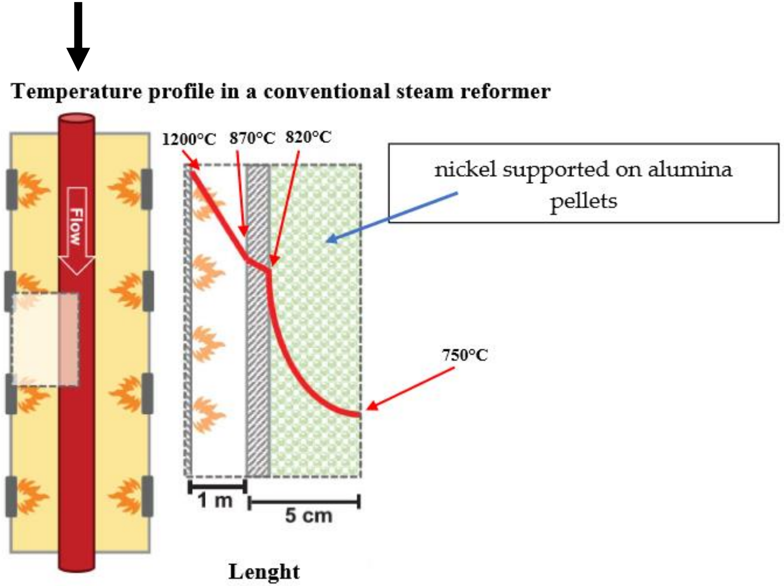


Figure 4. Temperature profile in a conventional steam reformer.

Meloni E. et al., Catalysts 2020, 10(3), 352

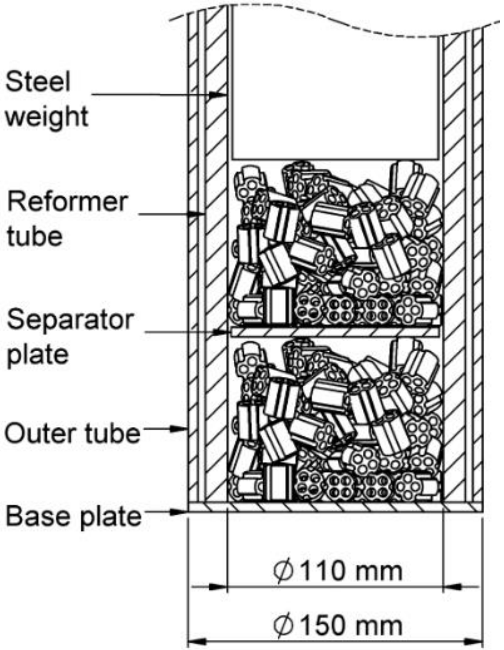


FIGURE 2 Illustration of bulk thermal cycling test rig with two catalyst pellet types loaded in a section of reformer tube

Young A. et al., Int J Appl Ceram Technol.2018;15:74–88

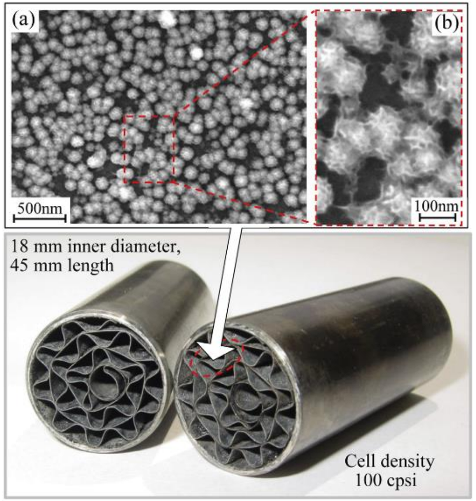


Fig. 1. Overview of the prepared honeycomb-type catalyst and (a),(b) SEM photographs for the typical surface of the stainless fin substrate.

C. Fukuhara et al. / Applied Catalysis A: General 468 (2013) 18–25

STEAM METHANE REFORMING: THE REACTION CHAMBER

Temperature profile in a conventional steam reformer

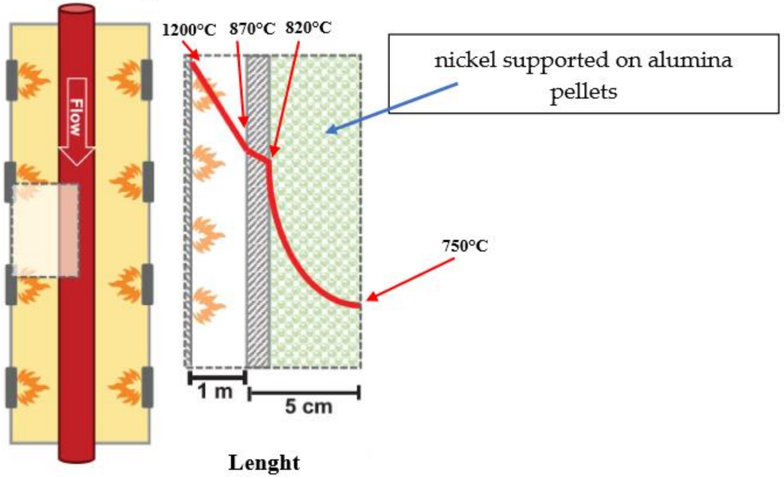


Figure 4. Temperature profile in a conventional steam reformer.

Meloni E. et al., Catalysts 2020, 10(3), 352

Heat transfer is critical to ensure fast kinetics as the reaction moves forward. To enhance SMR reaction, two main approaches can be employed:

- Improve the process efficiency by integrating the SMR reaction and the products separation steps to shift the equilibrium and enhance the reaction rate in the forward direction.
- Improve the reactor design by optimizing both the mass transport and heat transfer in reactor; this also helps in facilitating reaction kinetics and decreasing energy consumption, and contemporary containing reactor size and costs.

STEAM METHANE REFORMING: THE REACTION CHAMBER

Reactors can be further characterized according to the flow rate of the gas passing through the reactor and the volume of the reactor itself. The ratio among these two quantities is defined as space velocity:

$$SV = \frac{\dot{V}}{V}$$

Due to the fact that temperature and pressure of the reacting species can change the volumetric flow rate at any location in the reactor, the nonreacted reactor inlet conditions are often used as a flow rate.

In defining the volumetric flow rate, the flow of the reactant can be considered only, because the reactant is the only part in the mixture which is supplying energy. Thus the steam can be neglected, disentangling the SV from the steam-to-carbon ratio.

As a reactor volume the total volume of the reacting chamber is usually accounted for.

STEAM METHANE REFORMING: THE CATALYST

Catalysts are characterized by the following characteristics:

- **Activity**: it is a measure of how fast the reaction(s) proceeds in the presence of the catalyst. It is mainly influenced by temperature, concentration of the chemical species, pressure, and residence time. It is limited by mass transfer, heat transfer, and reaction kinetics. They are fully coupled with one another, and improving the control of the catalyst temperature helps to improve catalyst activity and the overall performance.
- **Selectivity**: it is the measure of the amount of the desirable product obtained from the reacted quantity of the feedstock. It is often less than unity because of the presence of secondary reaction pathways creating undesirable by-product(s), reducing the overall efficiency. This leads to the need in adding subsequent purification steps to the process. In example, in reformation, CO is undesirable because it can poison the electrode of a proton exchange membrane fuel cell (PEMFC). Carbon formation or coke can also degrade the catalyst.

STEAM METHANE REFORMING: THE CATALYST

- **Lifetime (stability)**: it is the measure of withstanding to the degradation process which are limiting catalyst lifetime. When a hydrocarbon finds an active site on a catalyst, it breaks down the chemical bonds and reassembles, and it consumes heat and reduces the catalyst and fuel temperature in the process. During operation catalysts do undergo physical and chemical changes which are limiting its lifetime. Thus, the chemical, thermal, and mechanical stability of the catalyst determine the operation life of the reactor. To date catalyst lifetime is around 50 000 hours of operation (5 years).

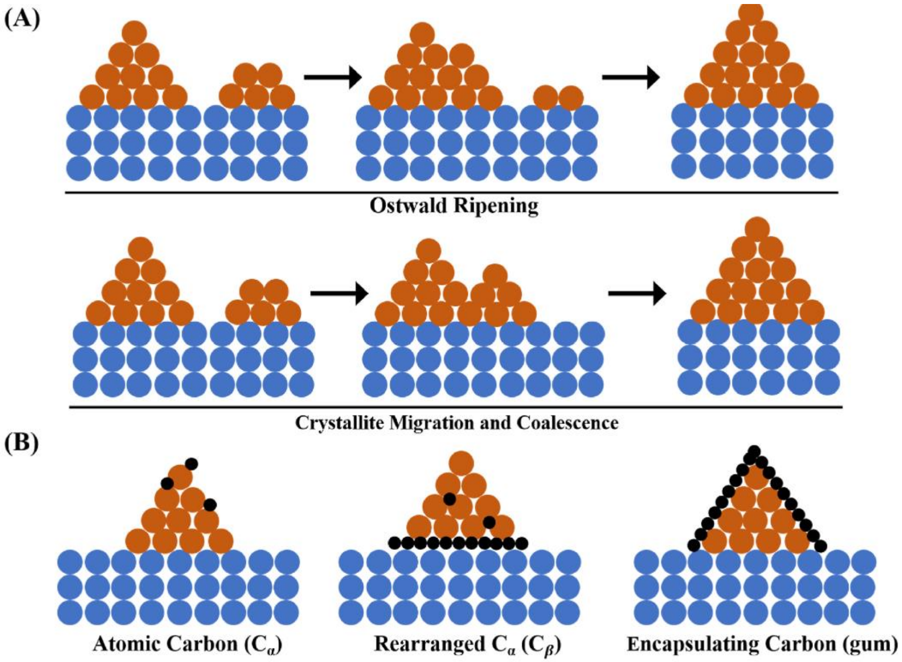


Fig. 2. Schematic illustrations of the (A) sintering and (B) coking issues of an SRM catalyst.

H. Zhang et al., R enewable and Sustainable Energy Reviews 149 (2021) 111330

STEAM METHANE REFORMING: SUMMARY

Advantages:

- To date, is the cheapest hydrogen production method
- It is characterized by high efficiency (70 -80%)
- High hydrogen yield
- Stable process
- If performed on-site it allows to exploit the larger volumetric densities of alternative fuels

Disadvantages:

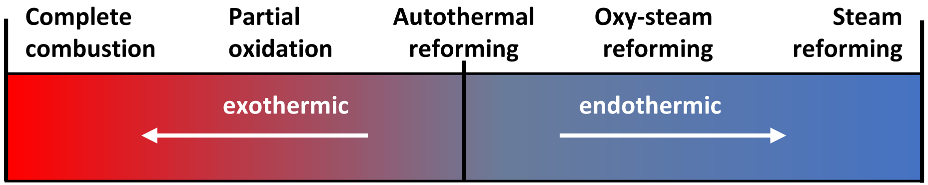
- Slow start-up
- Complex system
- Poor scalability to smaller sizes
- Hydrogen purification required

3. ADDITIONAL (REFORMING) PROCESSES

PARTIAL OXIDATION

Partial Oxidation (POX) is an alternative to SMR and is generally employed with higher hydrocarbons or if pure oxygen is available. POX is an exothermic reaction:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2\,, \quad \Delta H = -36\; kJ \cdot mol^{-1}$$



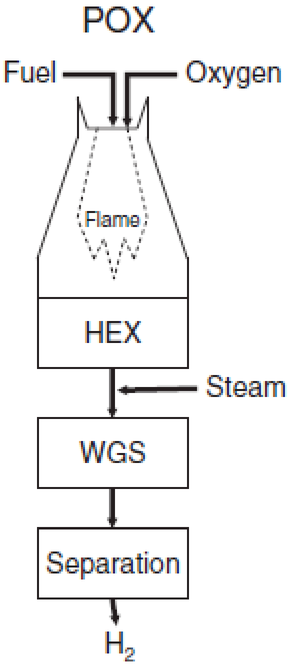
Adapted from : Mosinska, M. et al., *Catalysts* 2020, *10*, 896.

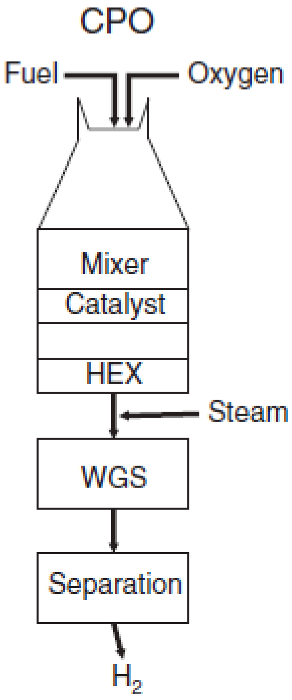
And, the amount of enthalpy variation (thus the degree of exothermicity) depends on the reactant-to-oxygen concentration ratio:

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2\,, \quad \Delta H = -319\; kJ \cdot mol^{-1}$$

As a result, it is possible to reduce reformer start-up times by increasing the temperature rapidly; that is achieved by increasing the air (or oxidant)-to-fuel ratio. The O2/C is used to express O_2 concentration.

PARTIAL OXIDATION: THE REACTOR





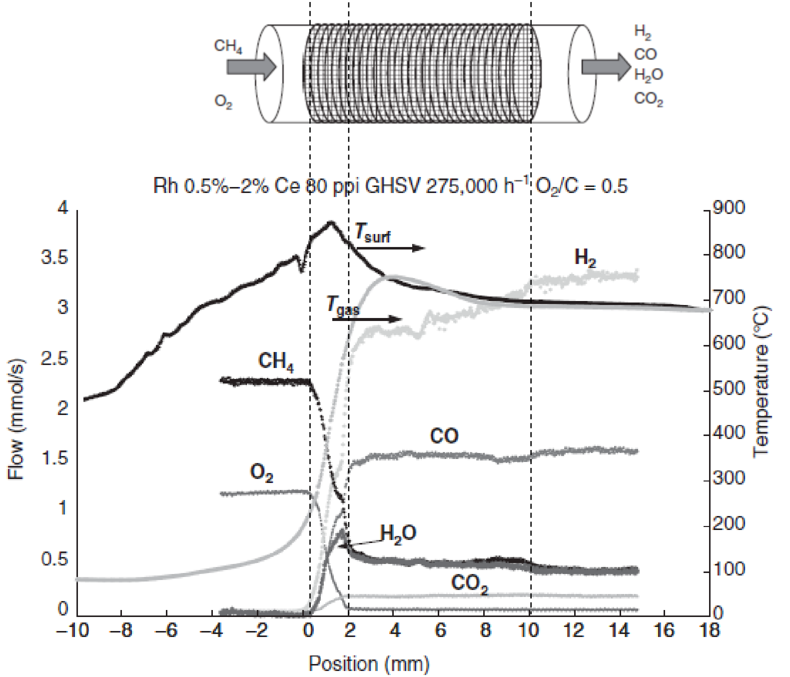


Figure 3.8. Measured temperature and concentration profile of a typical CPO catalyst bed. 0 mm indicates the start of the catalyst, whereas 10 mm denotes the end. Prior to and after the 0–10 mm range are two blank monoliths that act as heat shields.

PARTIAL OXIDATION AND AUTOTHERMAL REFORMING: SUMMARY

Advantages:

- Compact design due to the lack of external heat supply

Disadvantages:

- Less process efficiency (due to the occurrence of undesired and unpredictable reaction paths) leads to a reduced hydrogen production with respect SMR
- Susceptible to coke formation, thus higher operating temperatures (with respect SMR) are required
- Expensive, because of the need to add a post treatment of the raw syngas to remove carbon and acid gases and purify the produced hydrogen.

AUTOTHERMAL REFORMING

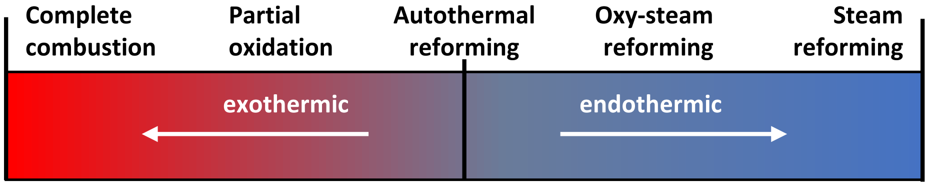
Autothermal reforming (ATR) is defined as the combination between SMR and CPOX, taking place into close thermal contact by placing them into a single catalytic reactor in order to maximize heat transfer.

$CH_4 + O_2 + H_2O$

Reactor for ATR
$T_{op} \approx$ 900-1100°C; $P_{op} \approx$ 1-50 bar

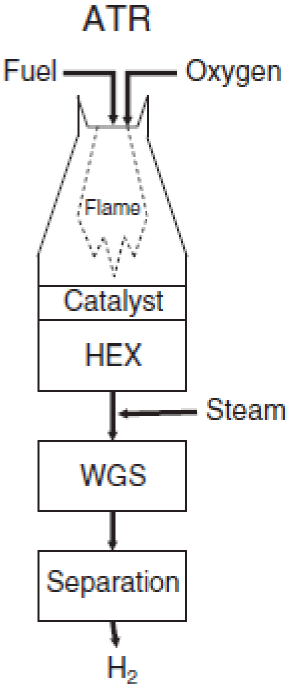
H_2 rich syngas

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
$$CH_4 + O_2 \rightarrow CO_2 + 2H_2$$



Adapted from : Mosinska, M. et al., *Catalysts* 2020, *10*, 896.

AUTOTHERMAL REFORMING



ATR merges the advantages of both reactions, showing a high yield of produced hydrogen, a favorable H2/CO ratio for downstream usage in chemical synthesis, and adequate response to dynamic loads.

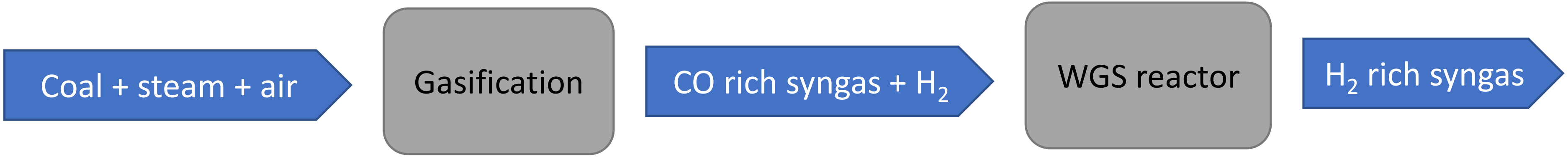
Ideally, the heat generated from the exothermic POX reaction is used for rapid start-up and supplying the heat needed for the endothermic SR reaction during operation. Reactors are smaller than reactors for SMR but bigger than reactors for POX

With a higher temperature due to the oxidation step, ATR is also capable of reforming multiple fuels, a necessary characteristic if alternative hydrocarbon feedstocks are reformed.

ATR is usually fed with higher S/C ratios than POX in order to facilitate the occurrence of MSR and WGS reactions.

COAL GASIFICATION

Gasification is the process with which coal is partially or completely converted to a syngas containing CO, H_2, CO_2, CH_4, and impurities (such as H_2S and NH_3). The composition of the obtained syngas is strongly dependent on the feedstock used for gasification.



Coal + steam + air

Gasification

CO rich syngas + H_2

WGS reactor

H_2 rich syngas

Coal gasification is a very complex process (based on pyrolysis) where both coal or biomasses can be used as a feedstock. Hydrogen is produced by means of the steam gasification reaction:

$$C_{(S)} + H_2O \rightarrow CO + H_2$$

But, being CO the main product of the gasification process (also the following reactions occur during gasification process: $C_{(S)} + O_2 \rightarrow CO_2, C_{(S)} + 0.5H_2O \rightarrow CO$, $C_{(S)} + CO_2 \rightarrow 2CO$), a WGS reactor is needed to convert CO into H_2.

GASIFICATION: AN OUTLOOK

Coal gasification

Advantages:

- Cheap
- Good efficiency (about 60%)
- Mature process

Disadvantages:

- Characterized by very high greenhouse gases emissions

Biomass gasification

Advantages:

- Based on a sustainable feedstock
- Decentralized
- Suitable to be adapted to industrial needs

Disadvantages:

- Scarsicity of available and sustainable biomass
- Expensive (because decentralized)
- Reduced efficiency (about 50%)

FINAL REMARKS ON REFORMING

The most appropriate production method to be selected is dependant on the application: for example, in combustion applications, high concentrations of CO and/or unconverted fuel are not typically problematic, yet in fuel cell applications, there are significant requirements for fuel purity.

SMR is characterized by the advantage of producing a relatively high hydrogen concentration in the product gas, which makes it suitable for being used in fuel cell systems.

However, the endothermic nature of this process makes it evolve slower than POX, and it can be a problem if reforming it is meant to be used for mobile applications (as in example installed on-board on a ship). Its slow dynamic response makes it suitable for operating at loadings as much constant as possible, while if directly used to supply a fuel cells system, sudden load decrease might lead to unwanted reactor heating up and consequent possible catalyst sintering, while in case of sudden increase in load demand, the reformer would not be able to the required hydrogen to the fuel cell system.

Because of this, and due to its slow start-up and shut-down times, SMR is considered more suitable for centralized, large scale, hydrogen production.

Hydrogen and fuel cells
Prof. Marco Bogar

FINAL REMARKS ON REFORMING

On contrary, POX reactors, are characterized by a fast start-up, as to increase temperature it is simply needed to increase the oxygen concentration.

For the same reason, it is extremely well equipped to handle transient loads.

While POX reactors are compact, POX produces more CO than SMR and WGS reactors are needed to convert CO to H_2, which increases the size of the production plant.

Heat transport must be carefully designed, operative temperature of POX reactors can overcome 1000°C. Moreover, nonuniform mixing can lead to temperature hot spots formation and cause catalyst sintering.

The major drawback of POX is the low concentration of hydrogen in the product gas.

FINAL REMARKS ON REFORMING

ATR operates ideally at a thermoneutral point. This gives ATR a higher efficiency and hydrogen concentration than POX and, at the same time, a better dynamic response than SR and the flexibility to accommodate multiple fuels. Rapid start-up is possible because of the ability to produce heat within the catalyst bed rather than transferring heat from the surroundings. Hot spots are reduced because of the addition of steam in the reforming reaction.

For these reasons, ATR has great potential in applications that require a lightweight, compact reactor capable of reforming multiple fuels, such as for transport applications, providing a rapid response to hydrogen demand with short start-up times, high efficiencies, and fuel flexibility.

4. NOVEL THERMOCHEMICAL TECHNOLOGIES

HYDROGEN PRODUCTION: METHANE PYROLYSIS

In a methane pyrolysis process, heat is added to the methane molecules to decompose them into hydrogen gas and solid carbon.

CH_4

High temperature pyrolysis

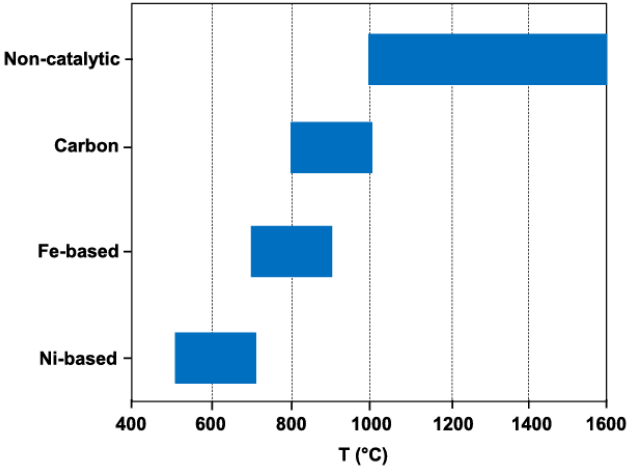
H_2 + carbon black

The methane pyrolysis process is endothermic:

$$CH_4 \rightarrow C_{(S)} + 2H_2\ , \quad \Delta H^0 = 74.91\ kJ \cdot mol^{-1}$$

It is currently under investigation because it can produce hydrogen at a low cost and with low- or near-zero emissions and can be thus more efficient in reducing green house gases emissions.

As solid catalyst materials Fe, Ni, Co and C can be used.



S.R. Patlolla et al. Renewable and Sustainable Energy Reviews 181 (2023) 113323

HYDROGEN PRODUCTION: METHANE PYROLYSIS

Advantages:

- No/low CO_2 emissions
- Solid C and H_2 as direct products of reactions
- Theoretical efficiency of 78%

Disadvantages:

- No industrial standard present
- External heat required

Open challenges:

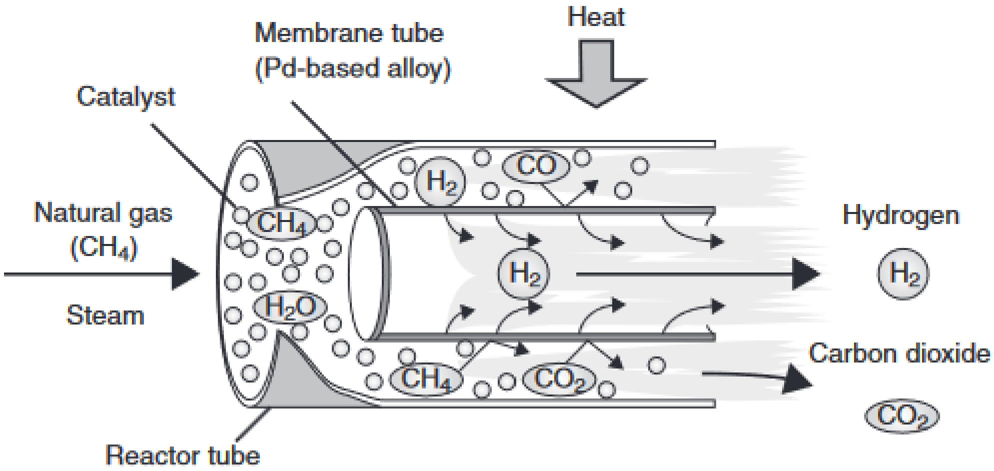
Reaction mechanism, kinetics, and elementary steps are still to be unrevealed: this lack of knowledge is at the basis of the still limited H_2 yields of the process.

A reactor standard has not been developed yet and lot of reactor types are still under prototyping and investigation.

Safety and reliability of commercial systems, and the safe storage and upcycling of solid carbon still need to be faced.

HYDROGEN PRODUCTION AND PURIFICATION: MEMBRANE SEPARATION

The membrane technology merges SMR with hydrogen separation and purification process in one device. the reactor hosts catalyst pellets promoting SMR reaction and a membrane tube conveys the produced hydrogen towards the exit



12.1 Conceptual diagram of membrane reformer.

Shirasaki, Y. (2013). *Handbook of Membrane Reactors || Membrane reactor for hydrogen production from natural gas at the Tokyo Gas Company: a case study. , (), 487–507.* doi:10.1533/9780857097347.2.487

HYDROGEN PRODUCTION AND PURIFICATION: MEMBRANE SEPARATION

Pd is used because it possesses a high hydrogen permeability without being subjected to drastic embrittlement phenomenon.

Pd-based membranes are dense, they are sustained by a ceramic (Yttria-stabilized zirconia) substrate and operate at about 300-500 °C. diffusion is driven by pressure difference.

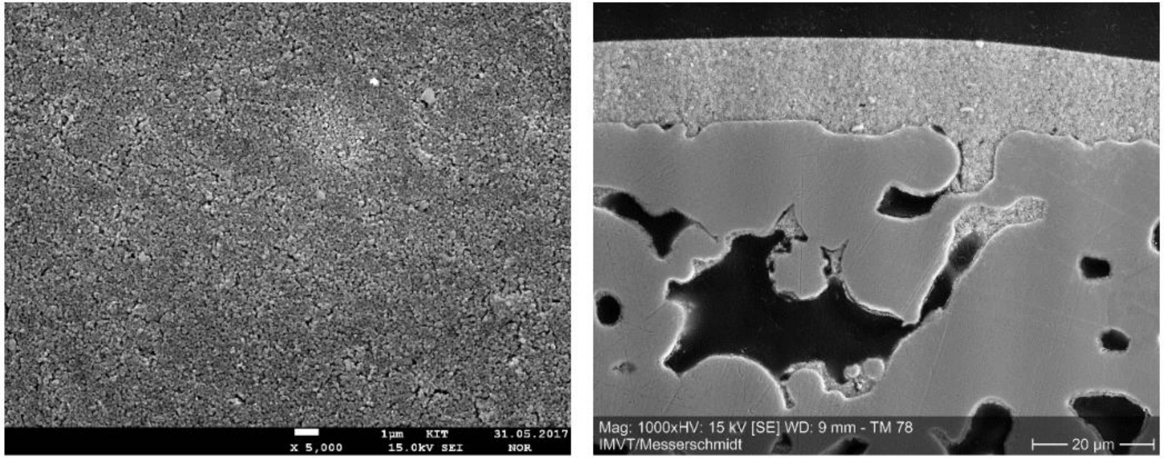


Figure 5. Surface (**left**) and cross-sectional view (**right**) of substrates currently fabricated at IEK-1 in Jülich and Institute for Micro Process Engineering (IMVT) in Karlsruhe.

Wunsch A. et al.,
Membranes 2018, 8, 107

HYDROGEN PRODUCTION AND PURIFICATION: MEMBRANE SEPARATION

Operating principle: solution-diffusion mechanism driven by a difference of pressure

(1) Transport to the surface and adsorption

(2) Dissociation into atomic hydrogen ($H_2 \rightarrow 2H^+$) via chemisorption

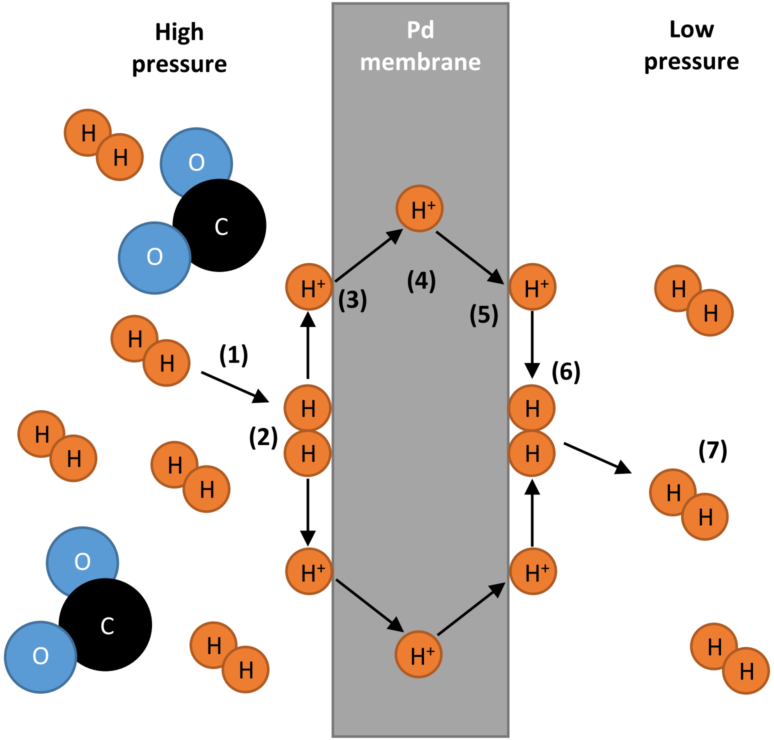
(3) Diffusion of the atomic hydrogen into the membrane

(4) Diffusion through the palladium lattice

(5) Diffusion of the atomic hydrogen to the membrane surface

(6) Recombination to molecular hydrogen ($2H^+ \rightarrow H_2$)

(7) Desorption



HYDROGEN PRODUCTION AND PURIFICATION: MEMBRANE SEPARATION

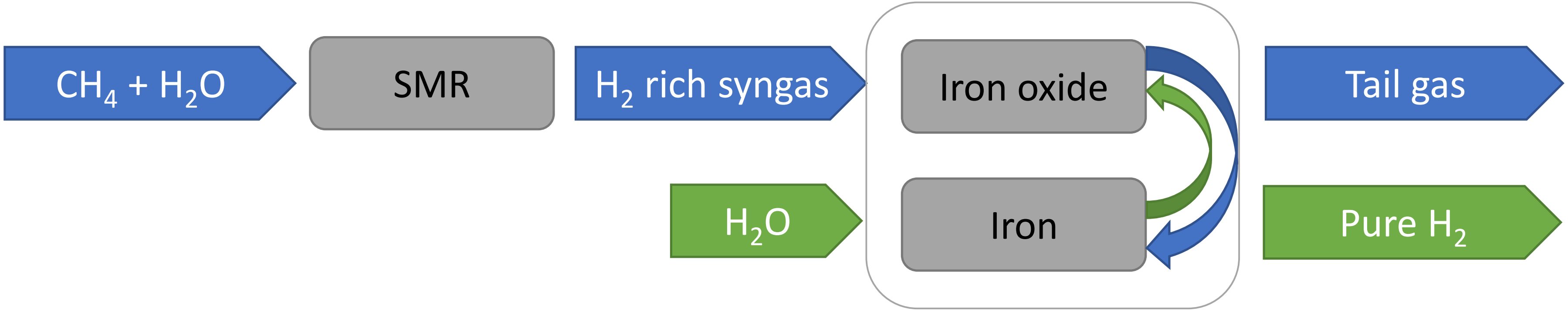
Advantages:

- It is a single step process
- Suitable for decentralized systems
- Pd-membranes: increased hydrogen production when integrated in SMR plants
- Pd-membranes: highly selective (theoretically 100% hydrogen purity is achievable)

Disadvantages:

- Still limited durability (not applicable at industrial level)
- Pd-membranes: costs and subjected to embrittlement on the long term.

HYDROGEN PRODUCTION AND PURIFICATION: CHEMICAL LOOPING



Syngas conversion: $CO + H_2 + FeO_x \rightarrow CO_2 + H_2O + Fe$

Steam addition and hydrogen production: $x \cdot H_2O + Fe \rightarrow H_2 + FeO_x$

HYDROGEN PRODUCTION AND PURIFICATION: CHEMICAL LOOPING

Advantages:

- Suitable to be fed with different syngas compositions
- Suitable for decentralized systems
- High efficiency (65 – 75 %)
- High hydrogen purity (>99.999%)
- No downstream hydrogen purification required
- CO_2 separation is possible (for carbon capture and storage)

Disadvantages:

- Still at the early stages of development, not extensively explored yet.

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