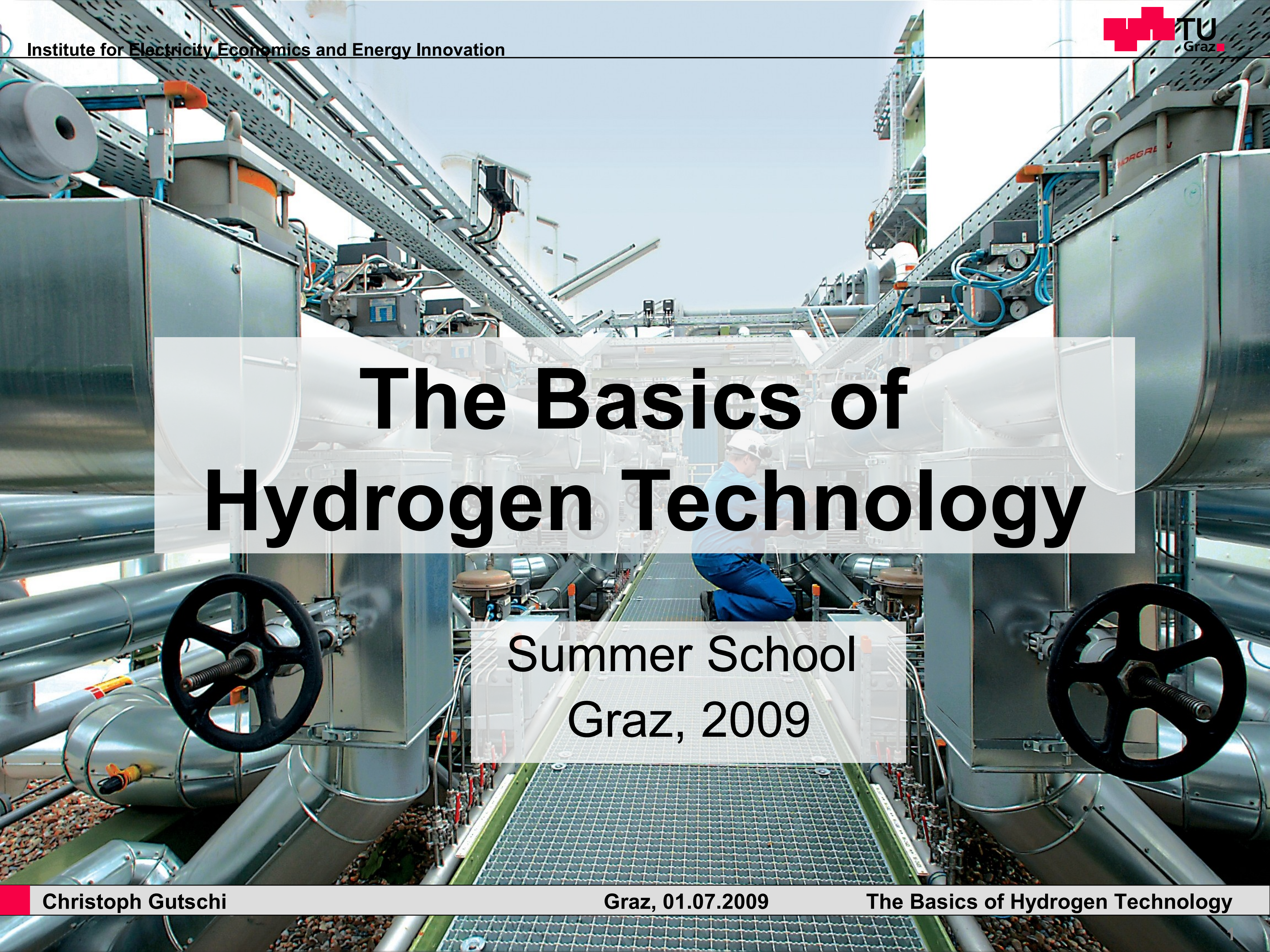


The Basics of Hydrogen Technology

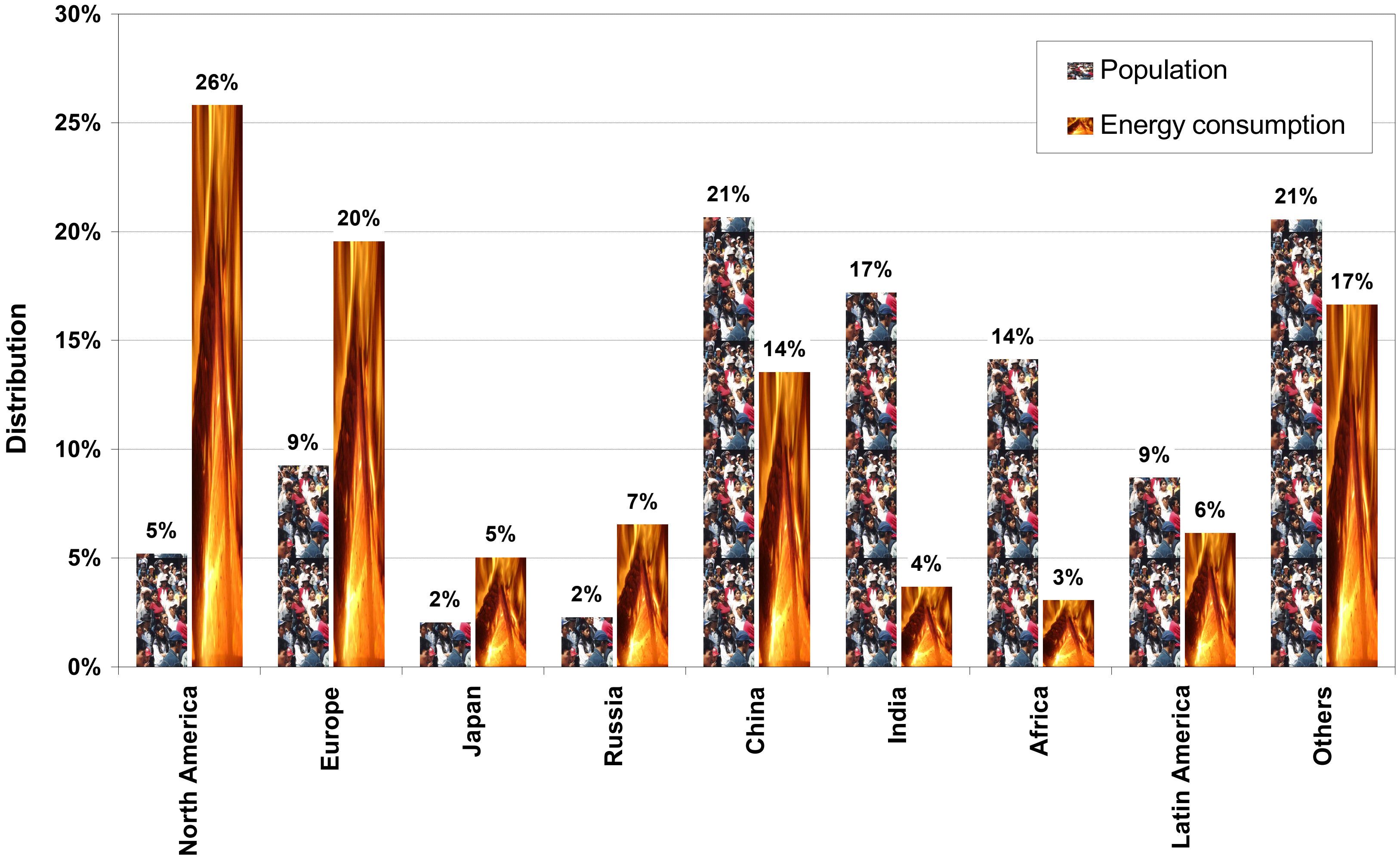
Summer School
Graz, 2009

Why do we need innovations in traffic?

- CO_2 emissions
- EU's Dependency on energy imports
  - some (politically) unreliable suppliers or supply routes
  - influence on trade balance
- Poor efficiency of internal combustion engines
- No practical solution for energy storage in vehicles
- High prices for fossil fuels in the long term

⇒ Can hydrogen technology bring a solution?

Use of primary energy, 2004



Source: BP, World Bank

Content

- Properties of hydrogen
- Production
- Storage
- Transport
- Conversion into mechanical energy
- Advantages & disadvantages, problems
- Overall efficiency

Properties of hydrogen

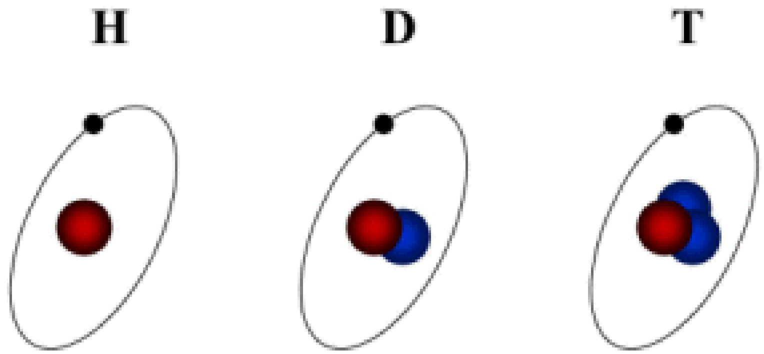
- Net calorific value: 119,97 MJ/kg = 33,33 kWh/kg
- Gross calorific value: 141,89 MJ/kg = 39,41 kWh/kg
- Density: 0,084 kg/m^3 (20 °C, 1.013 hPa)
- Melting point: -259,15 °C
- Boiling point: -252,76 °C
- Odourless, tasteless, invisible, nontoxic, highly volatile, neutral to environment
- One of the nine most common (mass) elements in upper lithosphere, mass fraction: 0,74 %
- Easily flammable, ignition limits: 4-75 $\%_{vol}$
- Flame is invisible but emits UV radiation
- Extremely explosive mixture with air: “oxyhydrogen”

Chemical and physical data

formula	H_2	
molecule mass	2,0159 kg/kmol	
critical temperature	33,19 K	
critical pressure	1,325 MPa	
critical density	30,12 g/dm^3	
critical compressibility factor	0,307	
acentric factor	-0,215	
tripel point	13,957 K	(7,2 kPa)
melting point	13,95 K	(101,3 kPa)
boiling point	20,39 K	(101,3 kPa)
density, liquid	70,96 kg/m^3	(20,39 K, 101,3 kPa)
density, gaseous	1,331 kg/m^3	(20,39 K, 101,3 kPa)
	0,0899 kg/m^3	(0 °C, 101,3 kPa)
enthalpy of vaporisation	899,1 J/mol	(20,39 K, 101,3 kPa)
specific heat, isobaric	28,59 J/molK	(gasförmig, 0 °C, 101,3 kPa)
dynamic viskosity	$8{,}34 \cdot 10^{-6}$ Pas	(gasförmig, 0 °C, 101,3 kPa)
	$13{,}3 \cdot 10^{-6}$ Pas	(flüssig, 20,39 K, 101,3 kPa)
compressibility factor	1,00042	(0 °C, 101,3 kPa)
net calorific value	119,93 MJ/kg	(25 °C, 101,3 kPa)
	10,78 MJ/m^3	(0 °C, 101,3 kPa)
	241,8 kJ/mol	(25 °C, 101,3 kPa)
gross calorific value	141,8 MJ/kg	(25 °C, 101,3 kPa)
	12,74 kJ/m^3	(0 °C, 101,3 kPa)
	285,85 kJ/mol	(25 °C, 101,3 kPa)
diffusion coefficient in air	$0{,}61 \cdot 10^{-4}$ m^2/s	(0 °C, 101,3 kPa)
inversion temperature	193 K	(2,5 MPa)

Sources: Ullmann, Perry, Römpp

Appearance (isotopes, isomers)



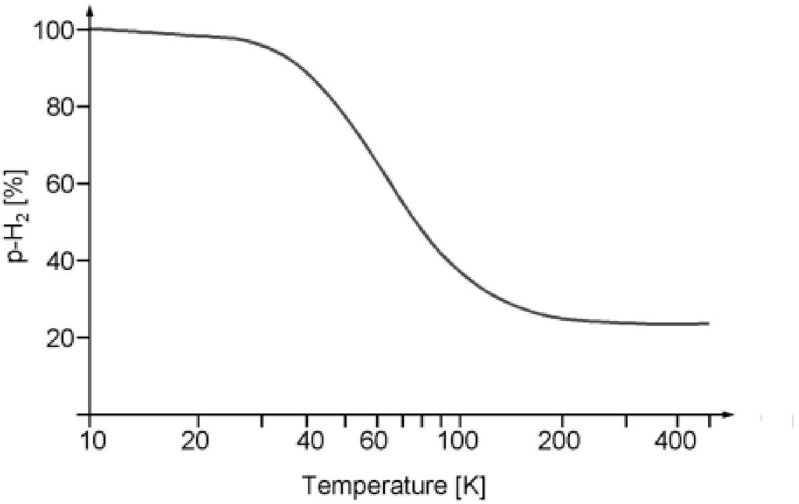
Hydrogen (Protium, ^1H)

Deuterium (D, ^2H)

Tritium (T, ^3H)

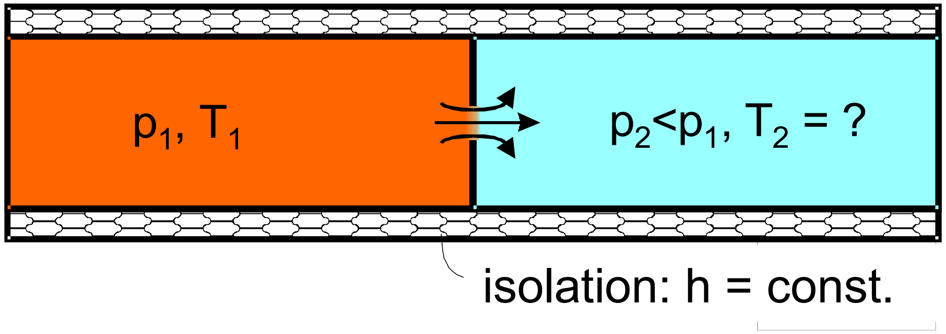
Spin isomers:

- $o\text{-}H_2$ (orthohydrogen)
- $p\text{-}H_2$ (parahydrogen)
- $e\text{-}H_2$ (equilibrium hydro.)
- **$n\text{-}H_2$** (normal hydrogen)

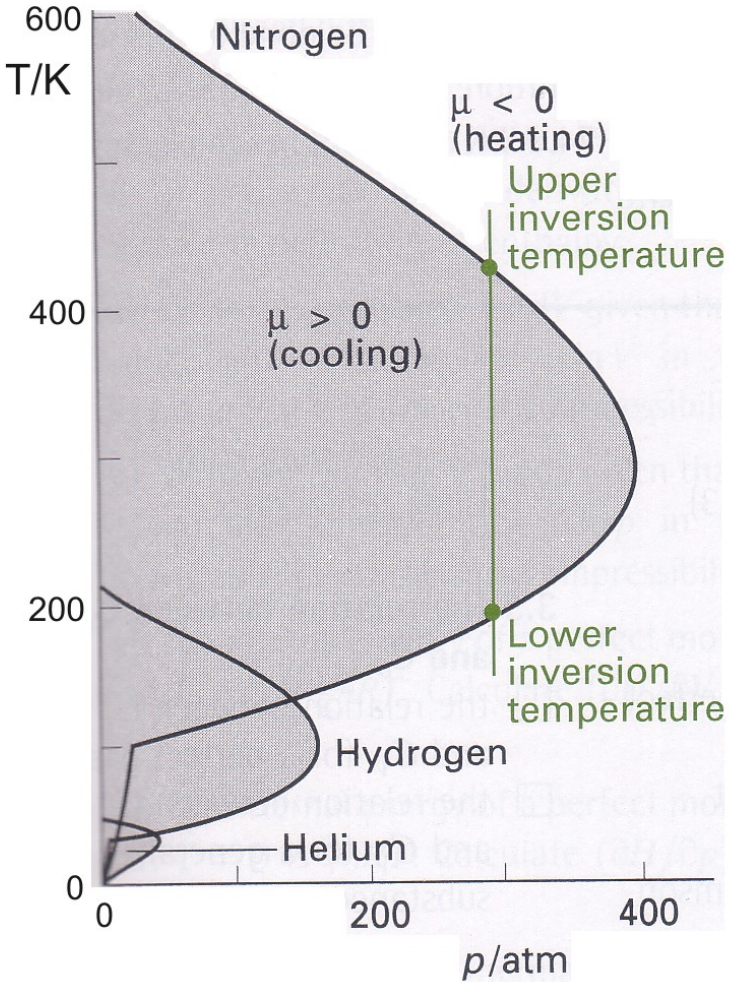


Source: Swiss Hydrogen Association

Joule-Thompson effect



$$\mu = \left(\frac{\partial T}{\partial p}\right)_h$$



At temperatures >202 K H_2-gas is cooling down when compressed!

Source: Atkins

Net and gross calorific value (heating value)

$H_{2\,(g)} + 1/2\ O_{2\,(g)} \rightarrow H_2O_{(g)}$ $\Delta h = 119{,}97$ MJ/kg (H_u)

gaseous product (steam at 25 °C)

$H_{2\,(g)} + 1/2\ O_{2\,(g)} \rightarrow H_2O_{(l)}$ $\Delta h = 141{,}89$ MJ/kg (H_o)

liquid product (water at 25 °C)
... heat of condensation is released!

⇒ gross calorific value > net calorific value

Production of hydrogen

Electrolysis

Steam reforming

Partial oxidation

Gasification process (coal, biomass, lignite)

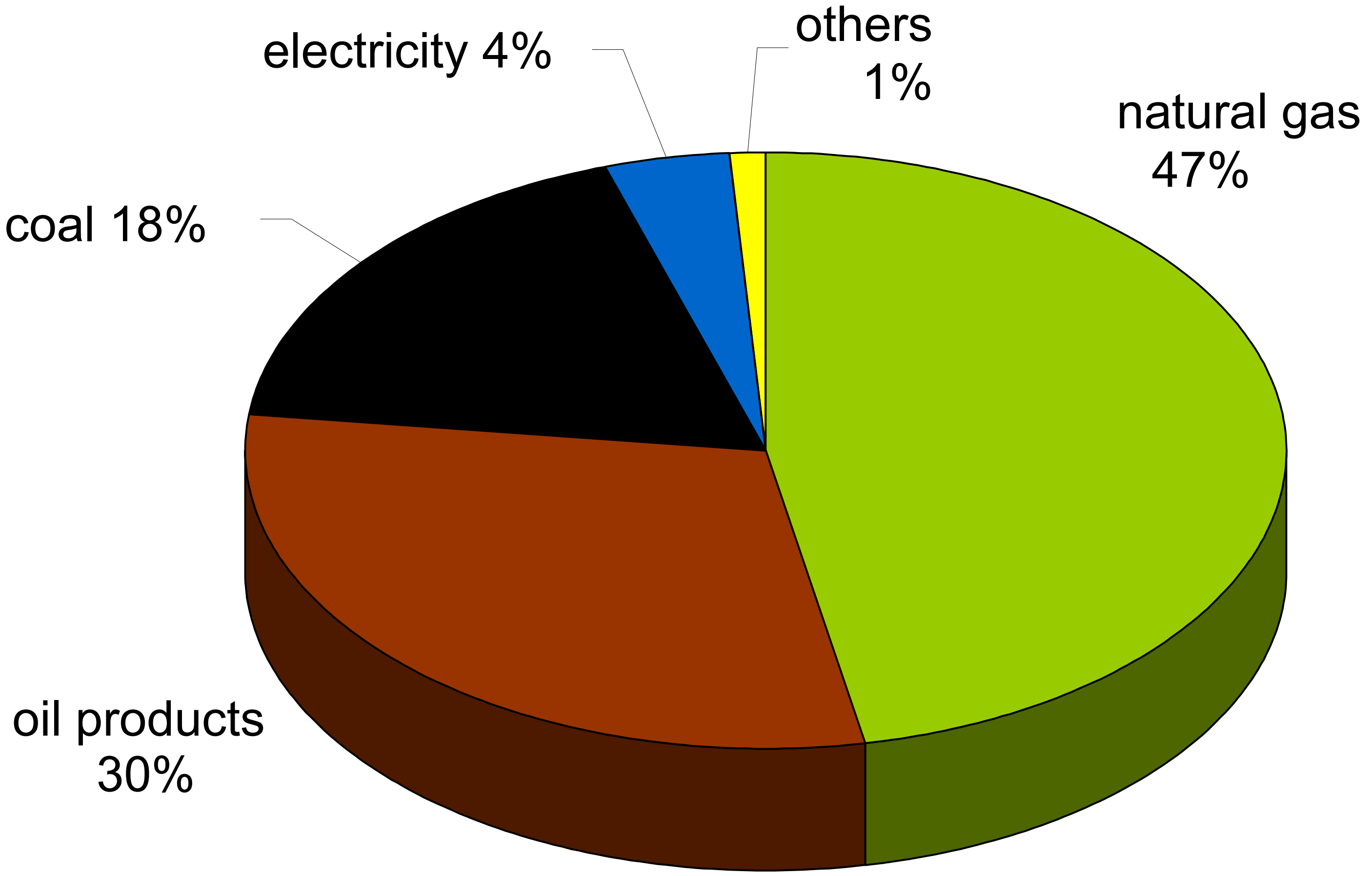
Kvaerner process (CB&H)

Chemical processes (Chloralkali electrolysis, ...)

Thermal dissociation (in development)

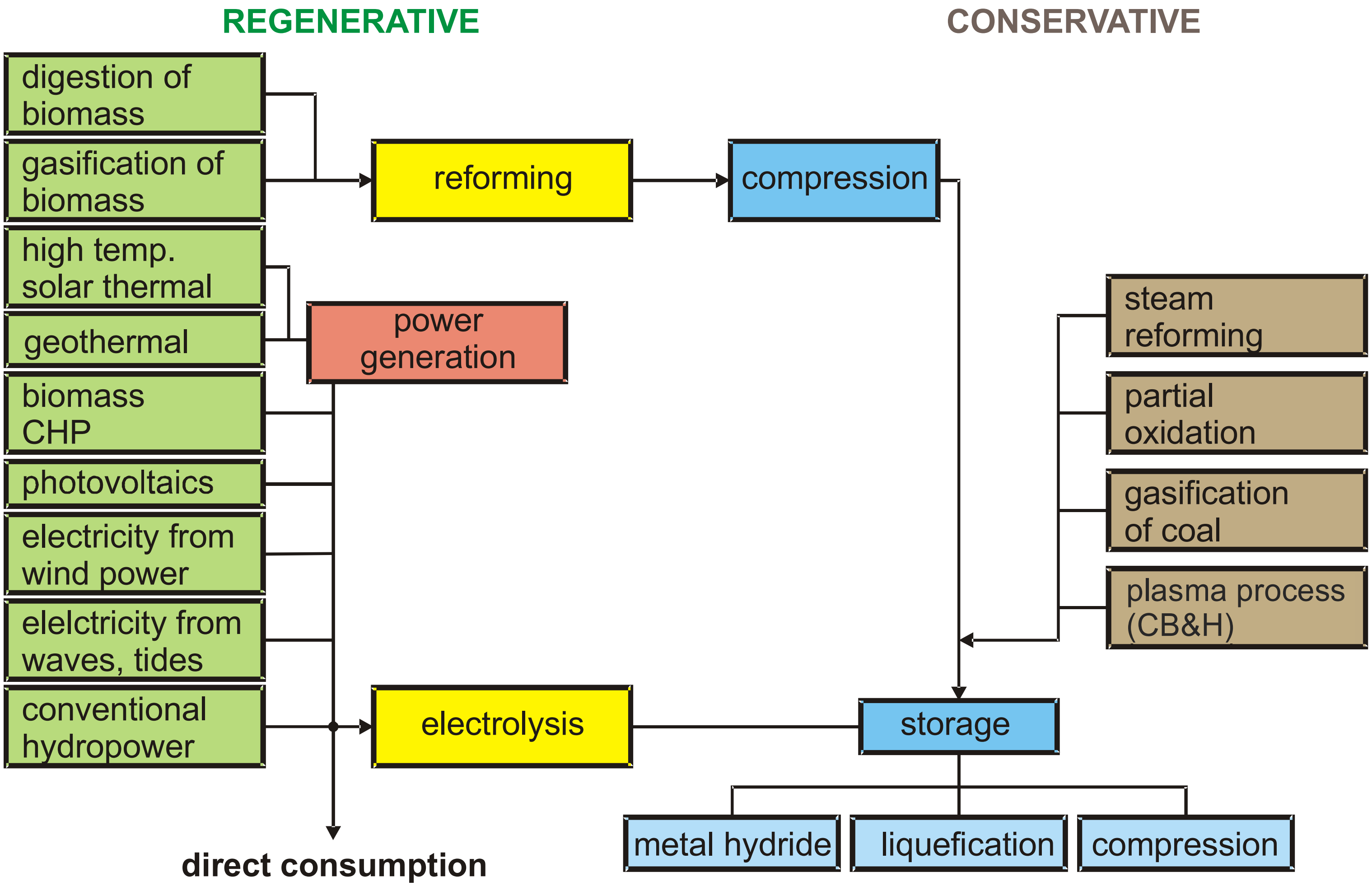
Biological processes (in early development)

Primary energy for production of H_2



Source: Linde

Possible processes for the production of H_2



REGENERATIVE

CONSERVATIVE

digestion of biomass

gasification of biomass

high temp. solar thermal

geothermal

biomass CHP

photovoltaics

electricity from wind power

elelctricity from waves, tides

conventional hydropower

reforming

compression

power generation

steam reforming

partial oxidation

gasification of coal

plasma process (CB&H)

electrolysis

storage

metal hydride

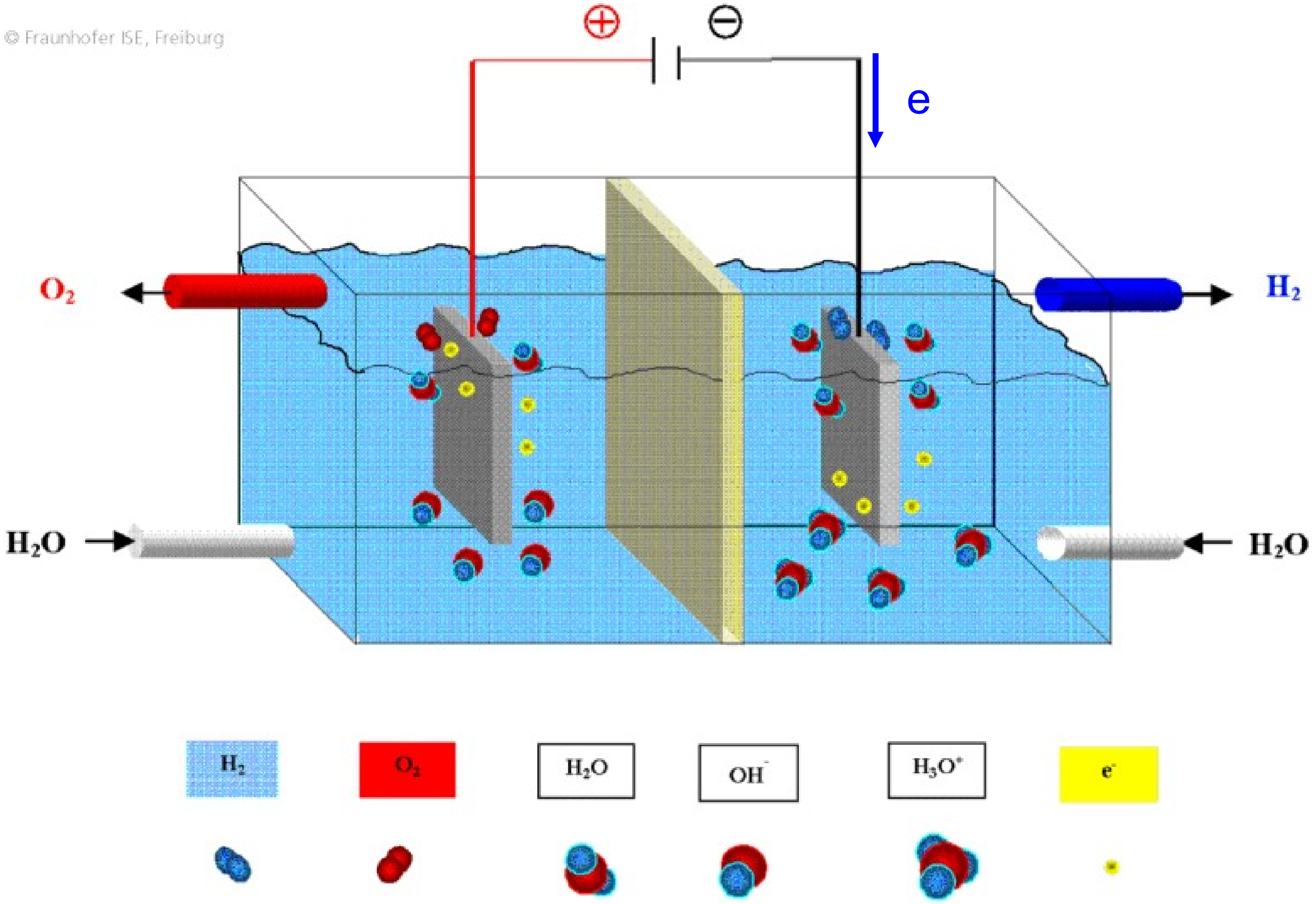
liquefication

compression

direct consumption

Source: dwv

Electrolysis



Source: Fraunhofer ISE

Electrolysis: reactions

Cathode (negative electrode):

$$2\,H_2O_{(l)} + 2\,e^- \quad \rightarrow \quad H_{2\,(g)} + 2\,OH^-_{(aq)}$$

Anode (positive electrode):

$$2\,OH^-_{(aq)} \quad \rightarrow \quad 1/2\,O_{2\,(g)} + H_2O_{(l)} + 2\,e^-$$

Overall reaction

$$H_2O_{(l)} \quad \rightarrow \quad H_{2\,(g)} + 1/2\,O_{2\,(g)}$$

$\Delta H_R = 285{,}8$ kJ/mol (25 °C)

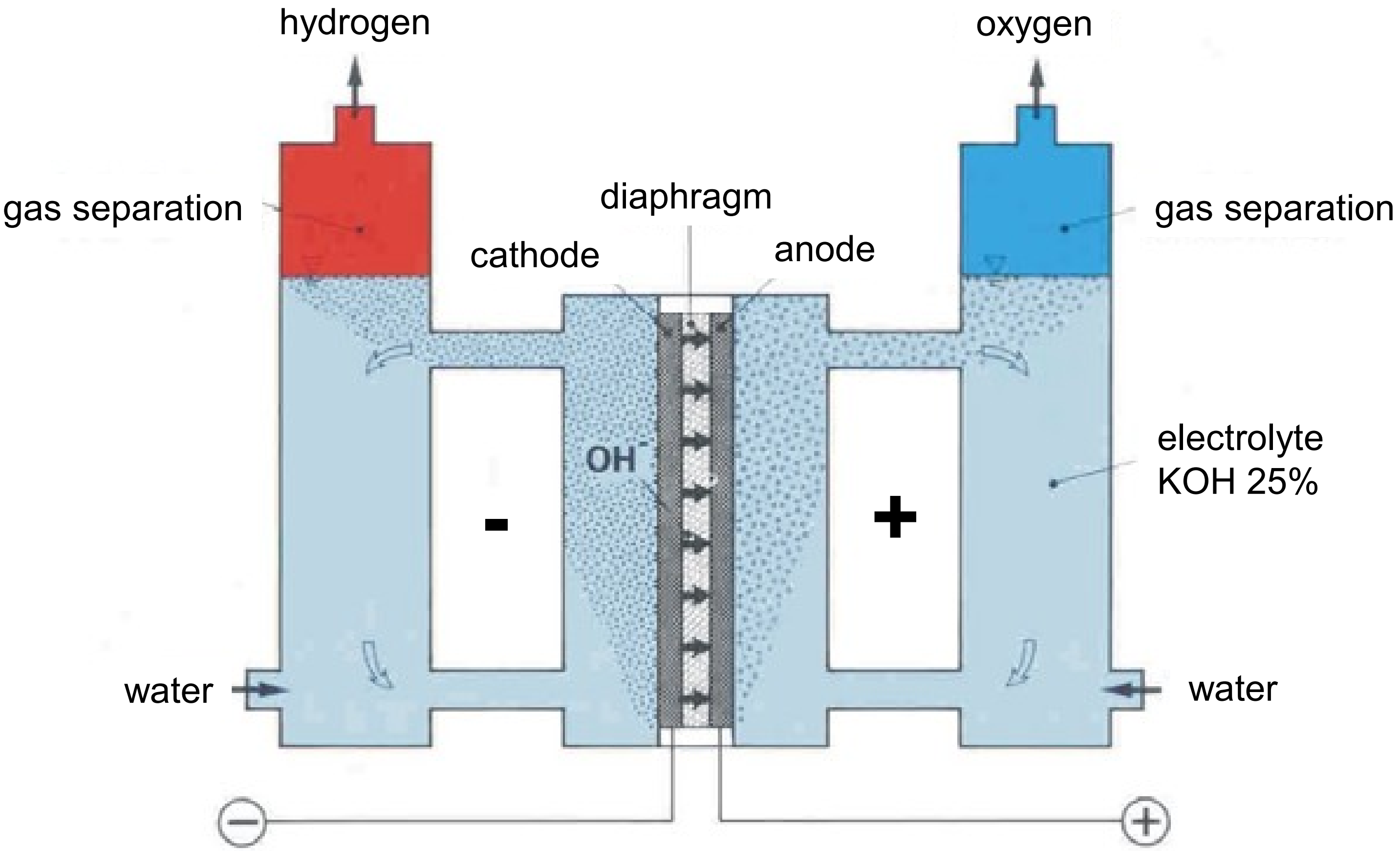
$\Delta G_R = 237{,}1$ kJ/mol

$\Delta S_R = 163{,}3$ J/(mol K)

$$\Delta H = \Delta G + T \cdot \Delta S$$

electricity + heat

Alkaline electrolyser



schematics of an alkaline electrolysis cell

Source: dwv / DLR

Electrolysis: cell voltage

$$\Delta G_R^0 = \mathrm{W}_{\mathrm{el,min}} = \mathrm{F} \cdot \mathrm{n} \cdot \mathrm{U}_{\mathrm{rev}}$$

ΔG_R^0 ..... free enthalpy of reaction / Gibbs free energy of reaction (237,13 kJ/mol)
$\mathrm{W}_{\mathrm{el,min}}$ ... minimum electrical energy for electrolytic separation of water
F .... Faraday constant (96.495 As/mol)
n .... charge number (n = 2)
$\mathrm{U}_{\mathrm{rev}}$ .... reversible cell voltage (cell potential)
T .... temperature of reaction

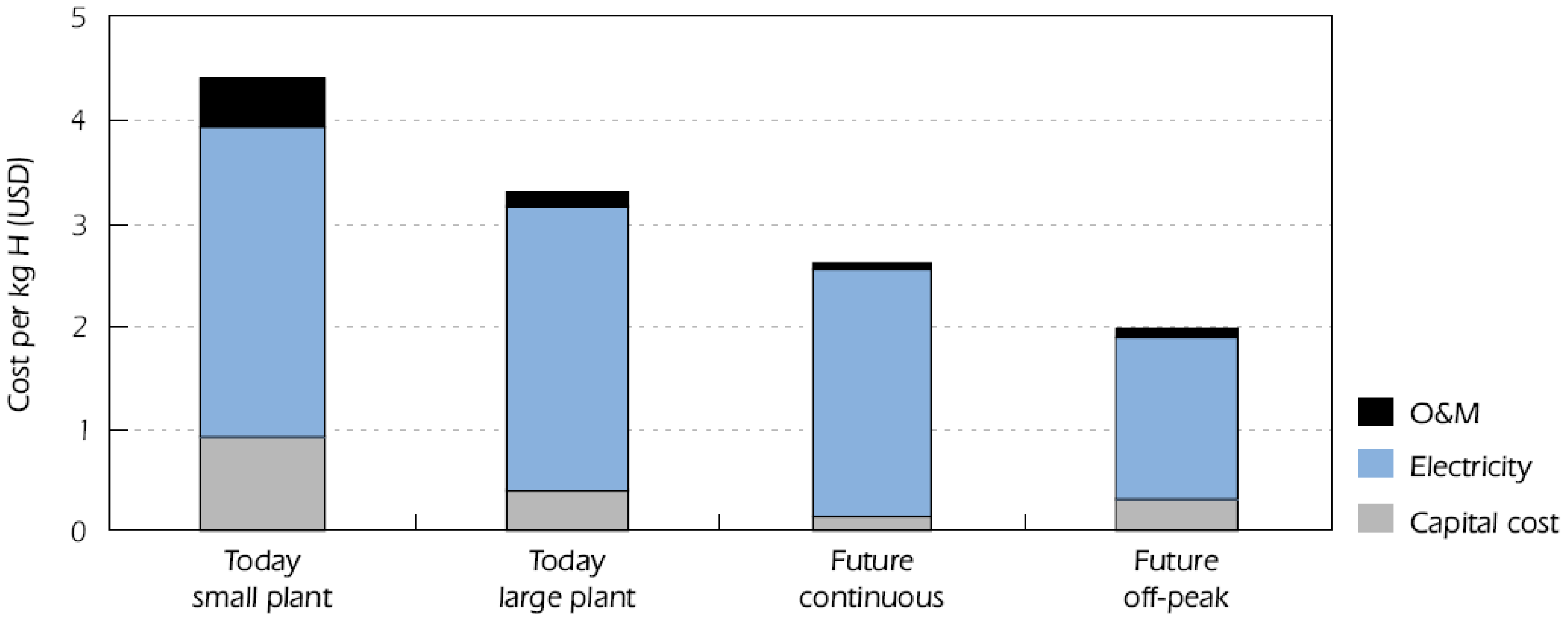
$$U_{th} = \frac{\Delta H_R^0}{n \cdot F} = \frac{\Delta G_R^0 + T \cdot \Delta S_R^0}{n \cdot F} = 1{,}48\,V$$

$$\eta = \frac{U_{th}}{U_{real}}$$

U_{th} .... theoretical cell voltage (cell potential)
T .... temperature of reaction (298 K)

practical voltage:
(1,65) 1,85-2,05 V

Electrolysis: costs



… mainly depending on price for electricity!

Sources: Riis, Hagen, OECD/IEA

Steam reforming (allothermal)

$$CH_4 + H_2O_{(g)} + 206\ kJ/mol_{CH4} \overset{cat}{\rightarrow} 3\ H_2 + CO$$

$$CH_4 + 2\ H_2O_{(g)} + 165\ kJ/mol_{CH4} \overset{cat}{\rightarrow} 4\ H_2 + CO_2$$

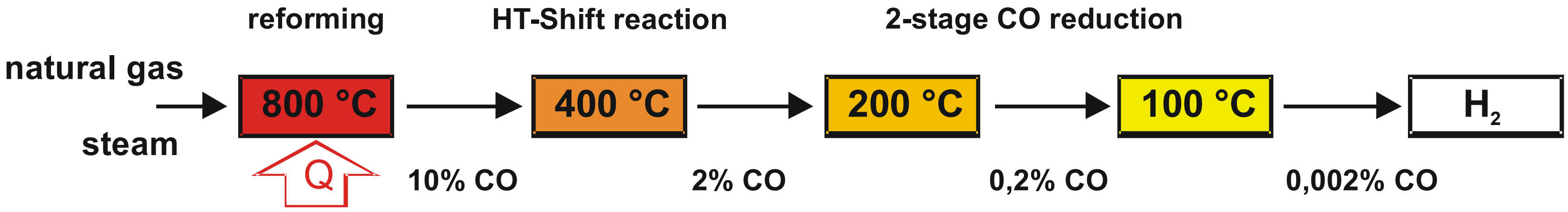
water-gas shift reaction (Dussan reaction):

$$CO + H_2O_{(g)} \overset{cat}{\rightarrow} H_2 + CO_2 + 41\ kJ/mol_{CO}$$

Overall reaction for hydrocarbons:

$$C_nH_m + 2n\ H_2O \rightarrow (2n + m/2)\ H_2 + n\ CO_2$$

Schematics of steam reforming process



reforming | HT-Shift reaction | 2-stage CO reduction

natural gas

steam

800 °C → 400 °C → 200 °C → 100 °C → H_2

Q

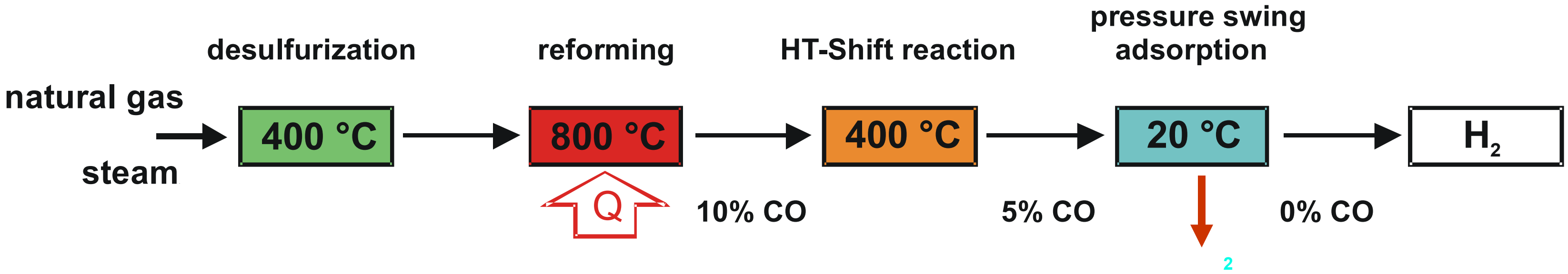
10% CO

2% CO

0,2% CO

0,002% CO

Standard process:



desulfurization | reforming | HT-Shift reaction | pressure swing adsorption

natural gas

steam

400 °C → 800 °C → 400 °C → 20 °C → H_2

Q

10% CO

5% CO

0% CO

endothermic, 15 – 30 bar

process (with modifications) applicable for natural gas, petrol, methanol, ...

Partial oxidation

$$CH_4 + 1/2\,O_2 \quad \rightarrow \quad 2\,H_2 + CO + 36\ kJ/mol_{CH4}$$

$$CH_4 + O_2 \quad \rightarrow \quad 2\,H_2 + CO_2 + 319\ kJ/mol_{CH4}$$

exothermic, 1200-1650 °C, 30-150 bar

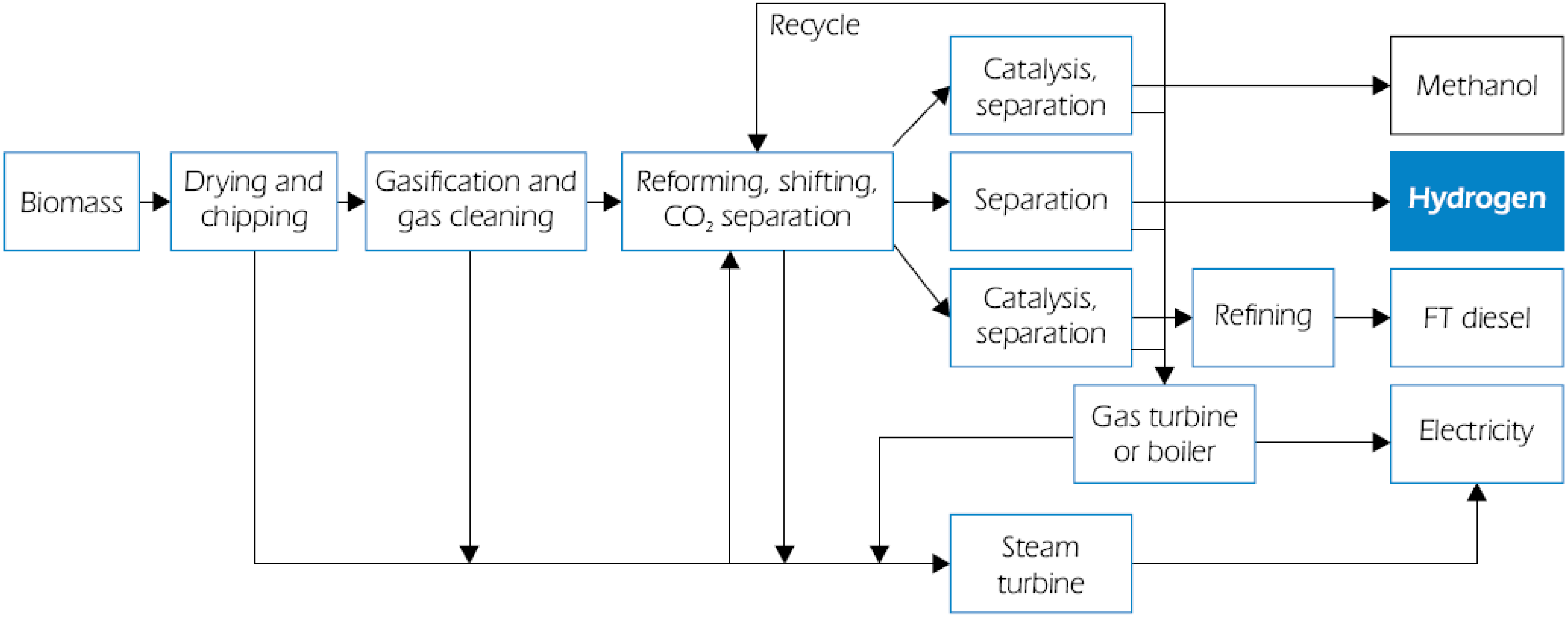
Autothermal reformer

$$4\,CH_4 + O_2 + 2\,H_2O_{(g)} + 85\ kJ/mol_{CH4} \quad \rightarrow \quad 10\,H_2 + 4\,CO$$

Coal gasification

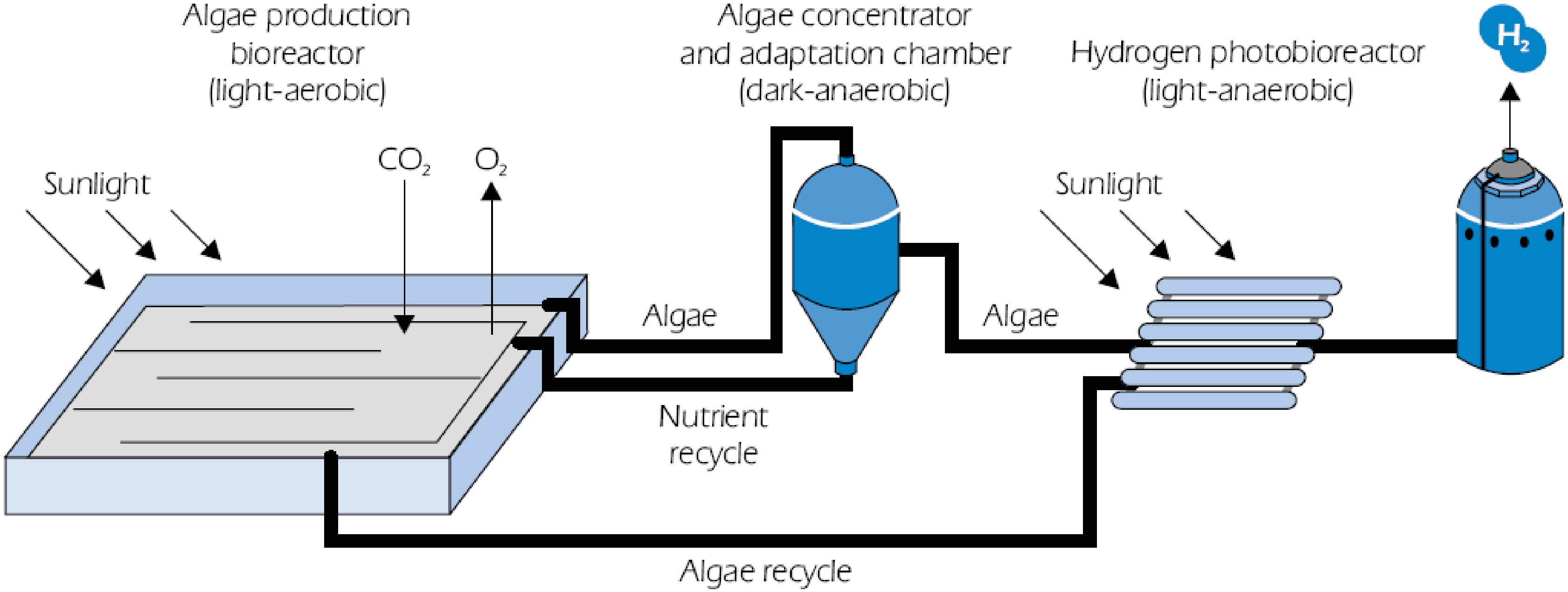
$C + H_2O_{(g)} + 131\ kJ/mol \quad \rightarrow \quad CO + H_2$ (illuminating gas)

Gasification of biomass



Sources: Riis, Hagen, OECD/IEA

Photobiological production of H_2

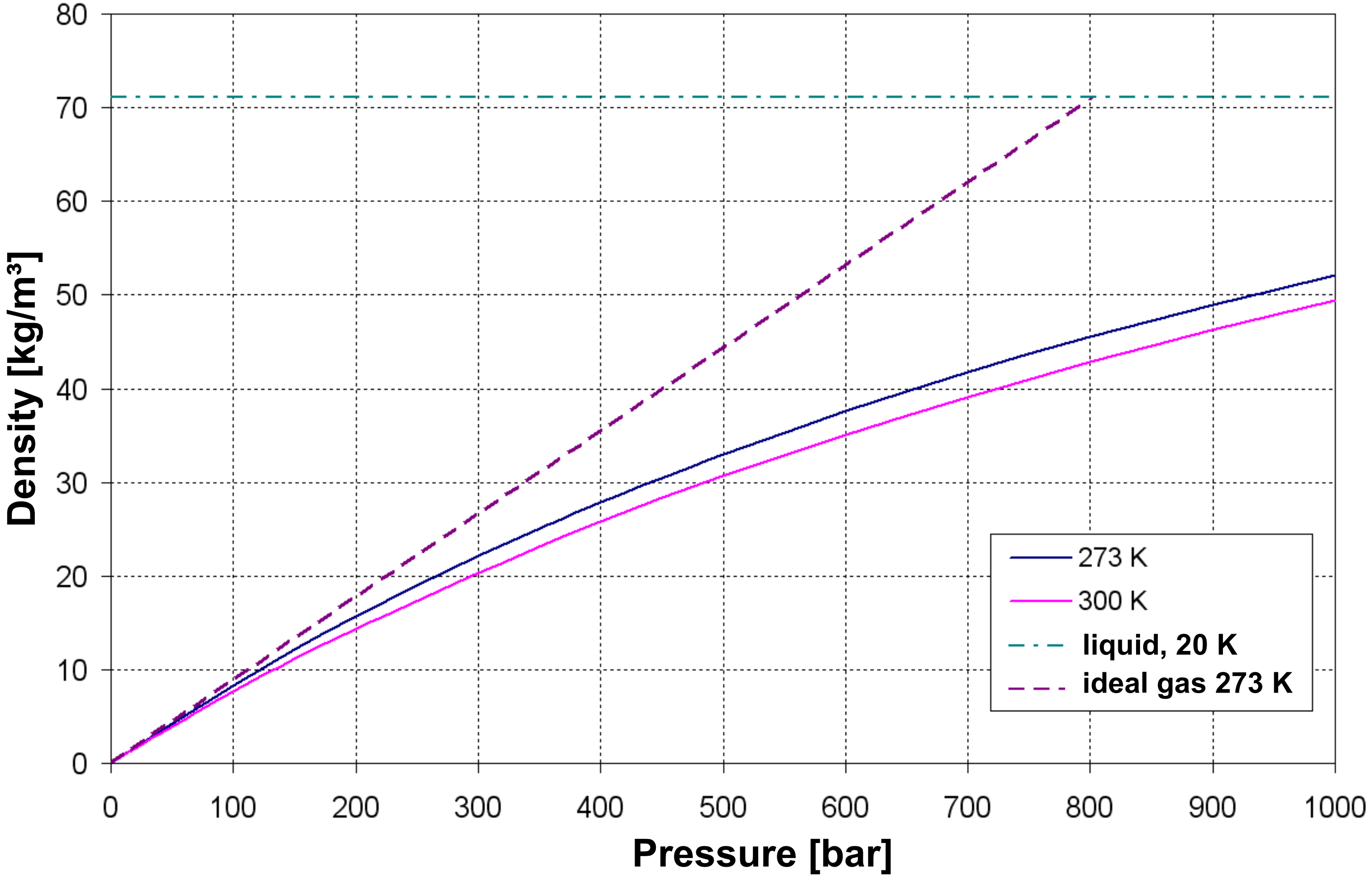


Sources: Riis, Hagen, OECD/IEA

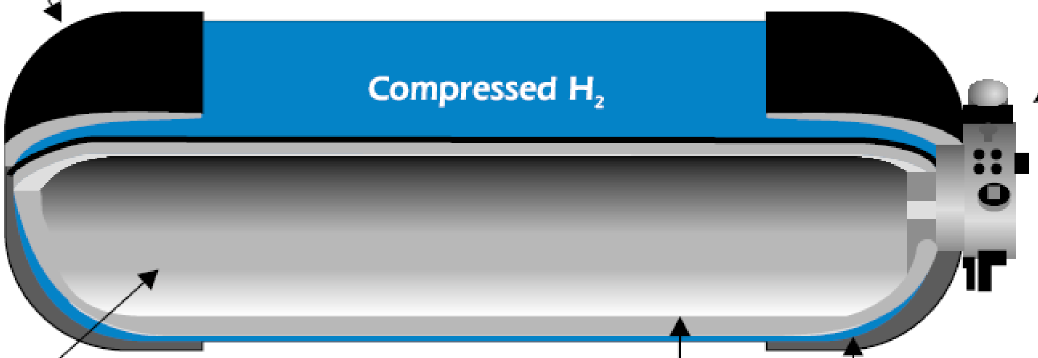
Storage of hydrogen

- **High pressure storage**
- **Cryogenic liquid storage**
- **Metal hydrides**
- (Carbon nanostructures)
- **Chemical compounds (molecules)**

Density of storage



Tank for pressurized hydrogen



Impact-resistant dome
- Light-weight
- Energy absorbing
- Cost-competitive

Manual valve or electrical valve or in-tank regulator

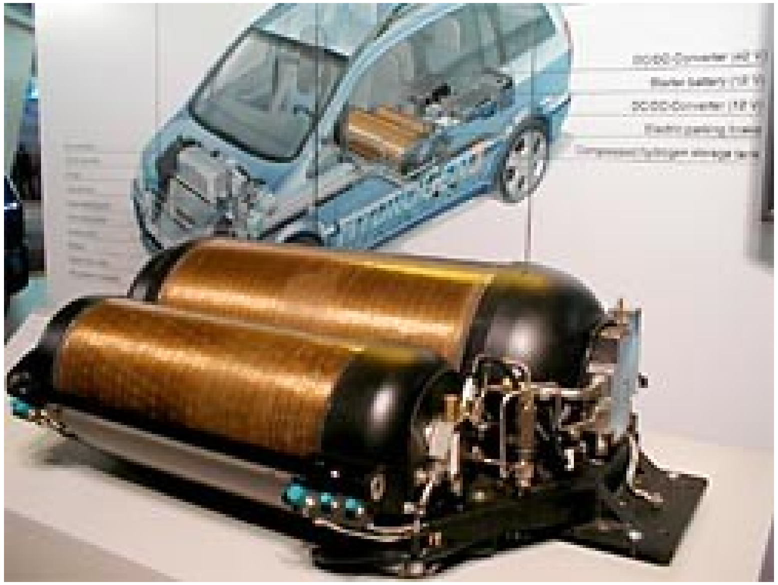
Polymer liner
- Light weight
- Corrosion resistant (hydrogen embrittlement)
- Permeation barrier
- Cost-competitive
- Flexible in size

Carbon-fiber reinforced shell
- Corrosion resistant (acids, bases)
- Fatigue/creep/relaxation resistant
- Light-weight

Reinforced external protective shell
- Gunfire safety
- Impact safety
- Cut/abrasion resistance

Sources: Riis, Hagen, OECD/IEA

Tanks for pressurized hydrogen (2)



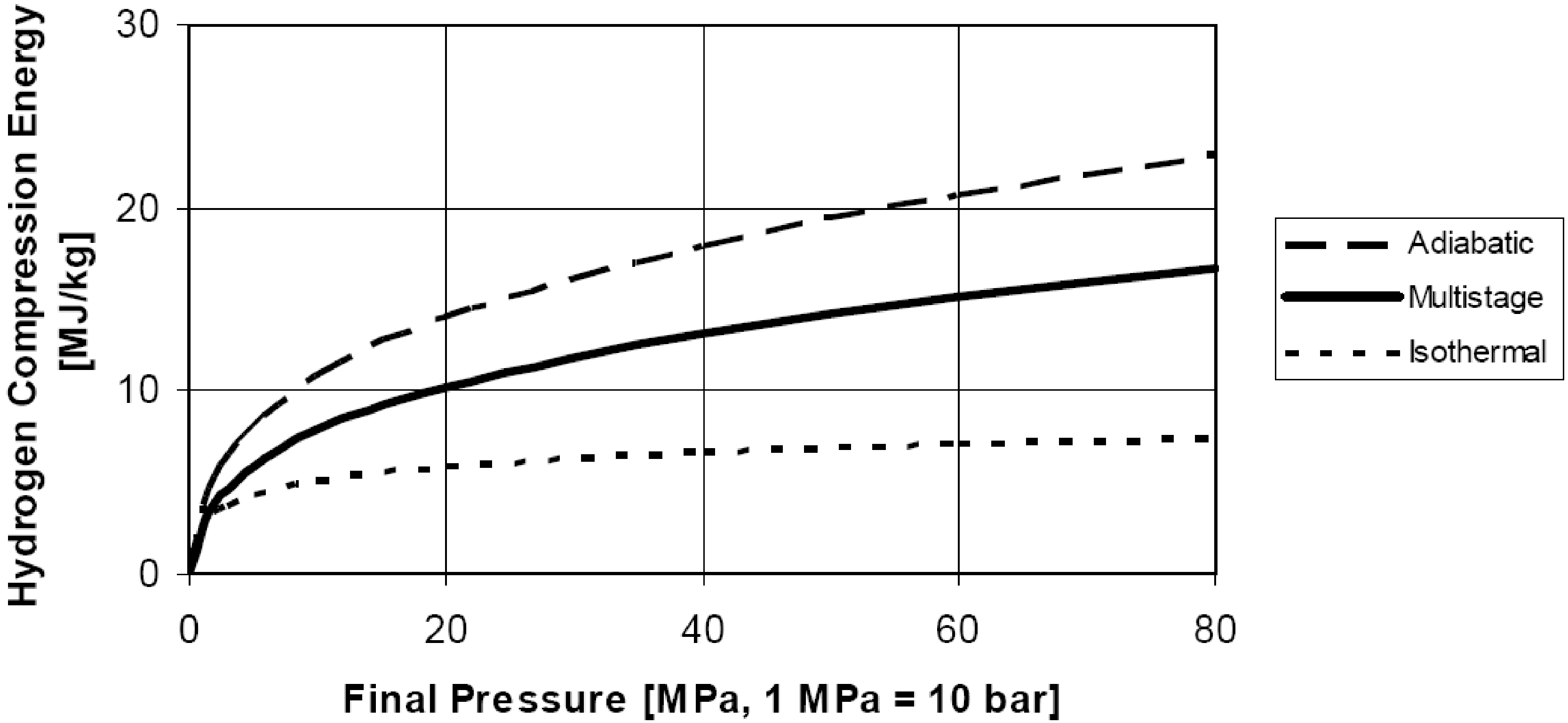
Source: www.HFPeurope.org

Theoretical work of compression

$$W_{1,2} = p_1 \cdot V_1 \cdot \ln \frac{p_2}{p_1} = \frac{m}{MG_{H2}} \cdot R \cdot T \cdot \ln \frac{p_2}{p_1}$$

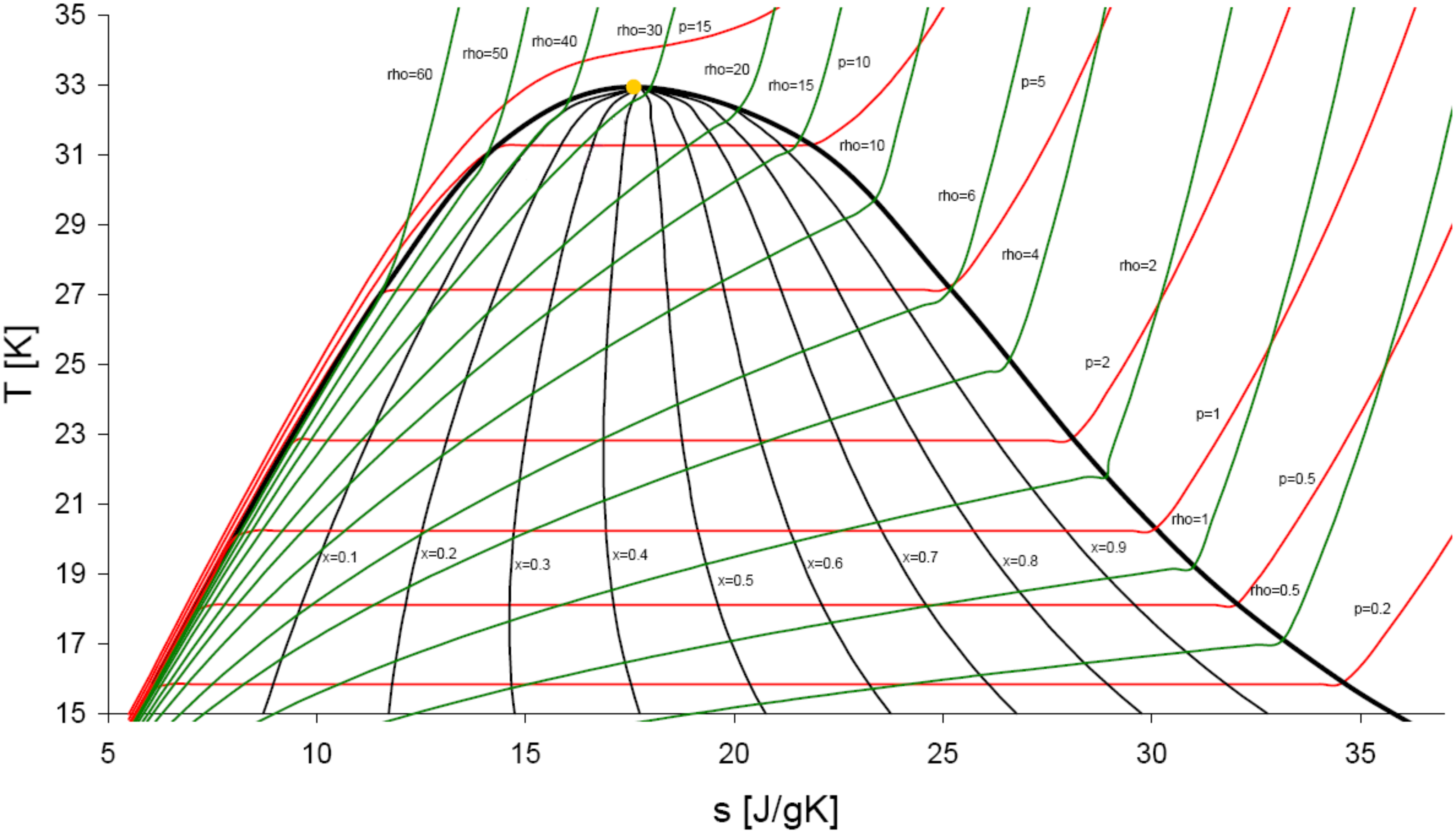
$W_{1,2}$	work for **isothermal compression** of an ideal gas from pressure p1 to pressure p2
p_1	initial pressure
p_2	final pressure
V_1	initial volume
m	mass of gas
R	gas constant
T	temperature
MG_{H2}	molecular weight

Energy demand for compression



Source: Bossel

Liquid hydrogen



Source: Klell

Vessels for liquid hydrogen

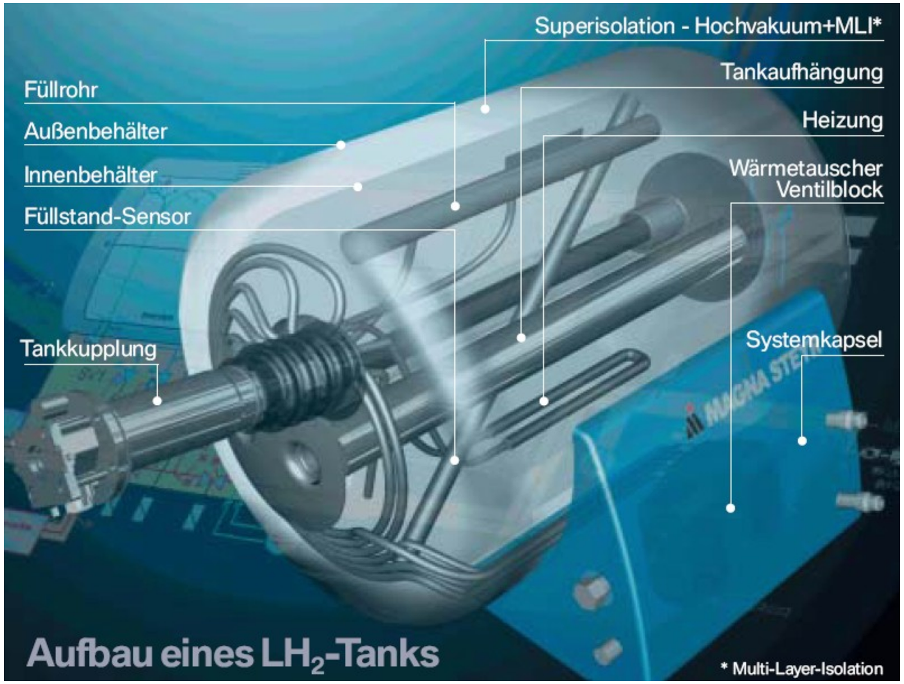
Sources: Magna, Linde, NASA

Liquefaction plants in Western Europe

operator	city	start of operation	capacity
Air Products	Rozenburg (Netherlands)	1987	5,0 t/d
L'Air Liquide	Wazier (France)	1988	10,5 t/d
Linde	Leuna (Germany)	2007	5,0 t/d
Linde	Ingolstadt (Germany)	1992	4,4 t/d
		total	**24,9 t/d**

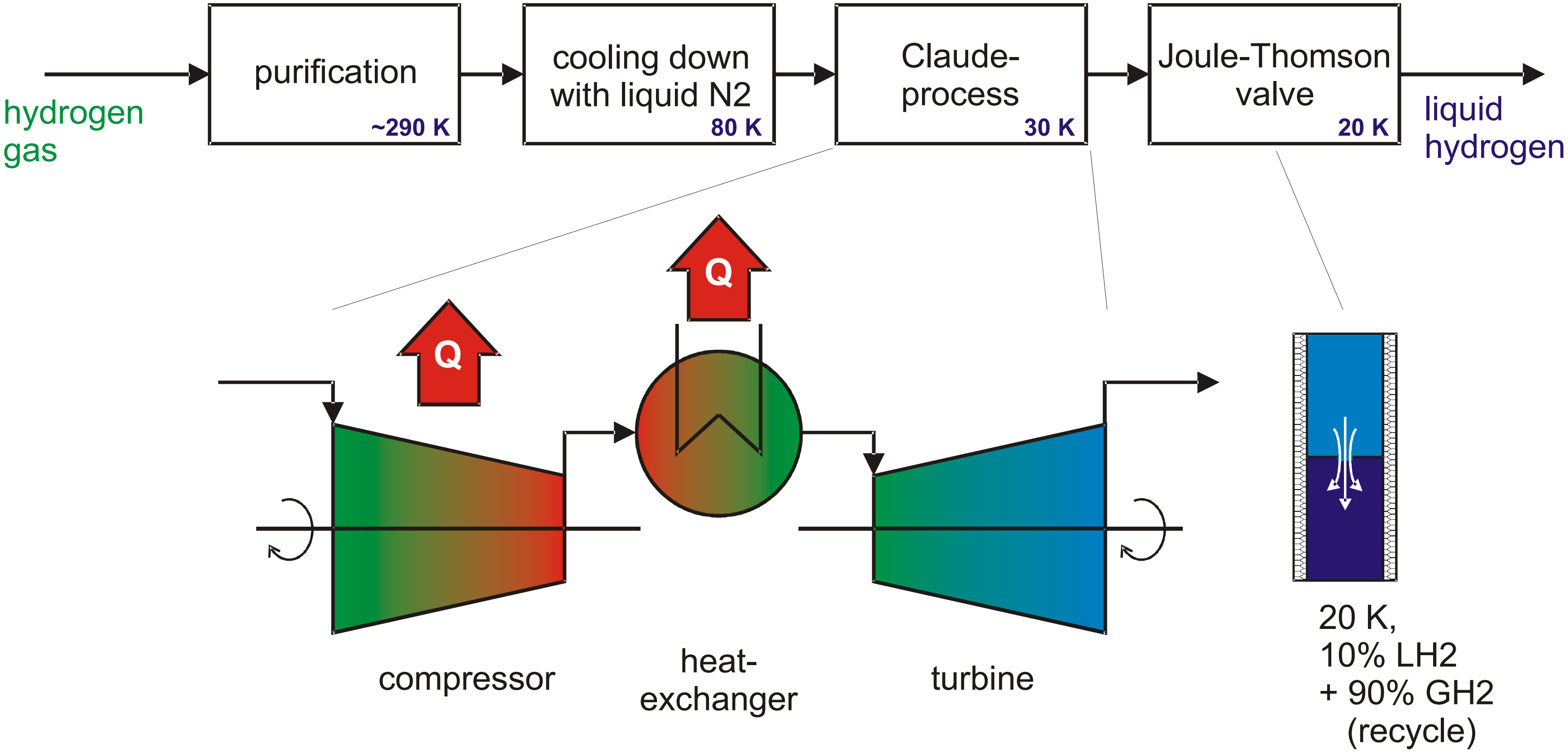
Source: Linde

LH2 Tank



Source: Magna Steyr

Liquefaction of hydrogen



hydrogen gas

purification ~290 K

cooling down with liquid N2 80 K

Claude-process 30 K

Joule-Thomson valve 20 K

liquid hydrogen

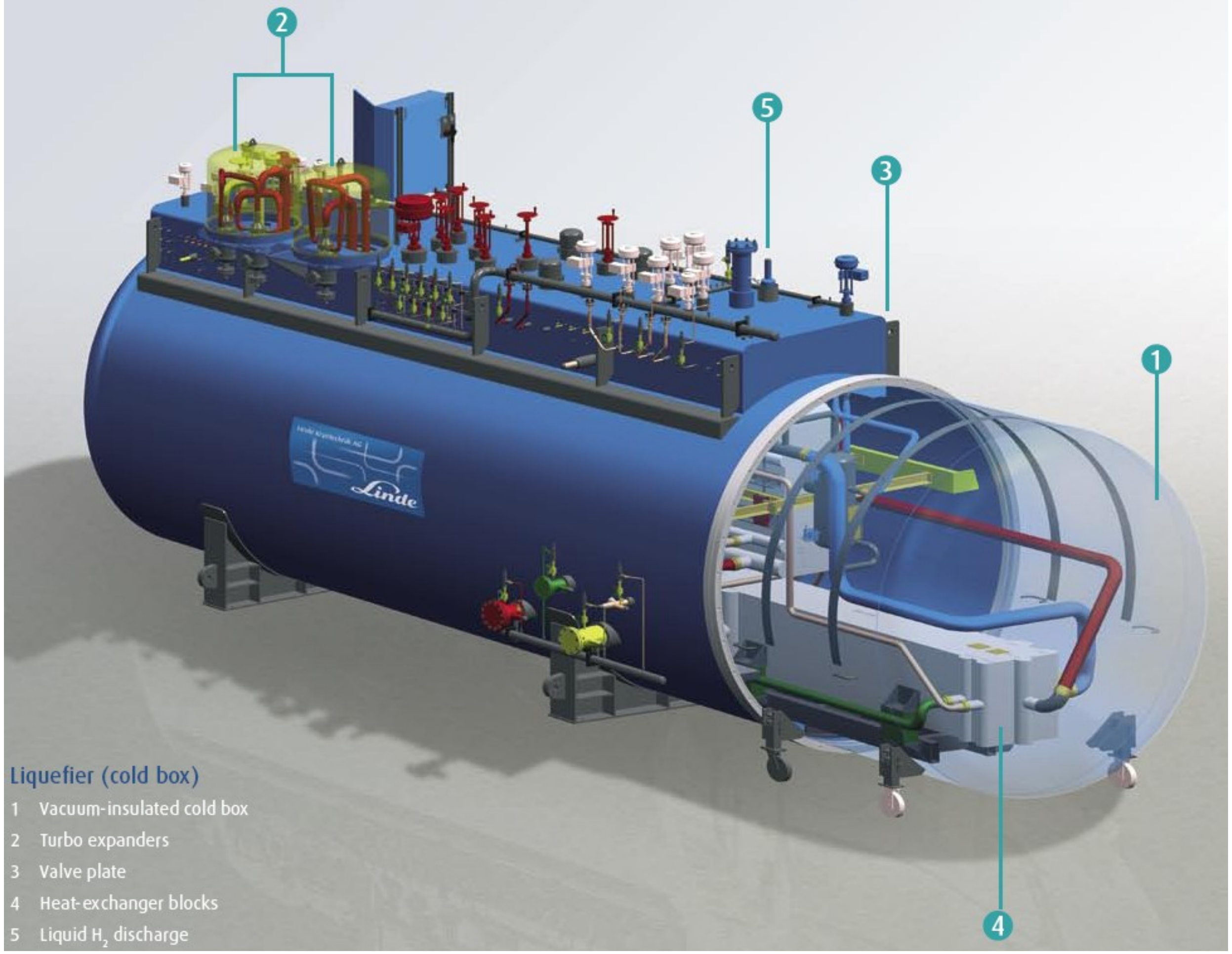
compressor

heat-exchanger

turbine

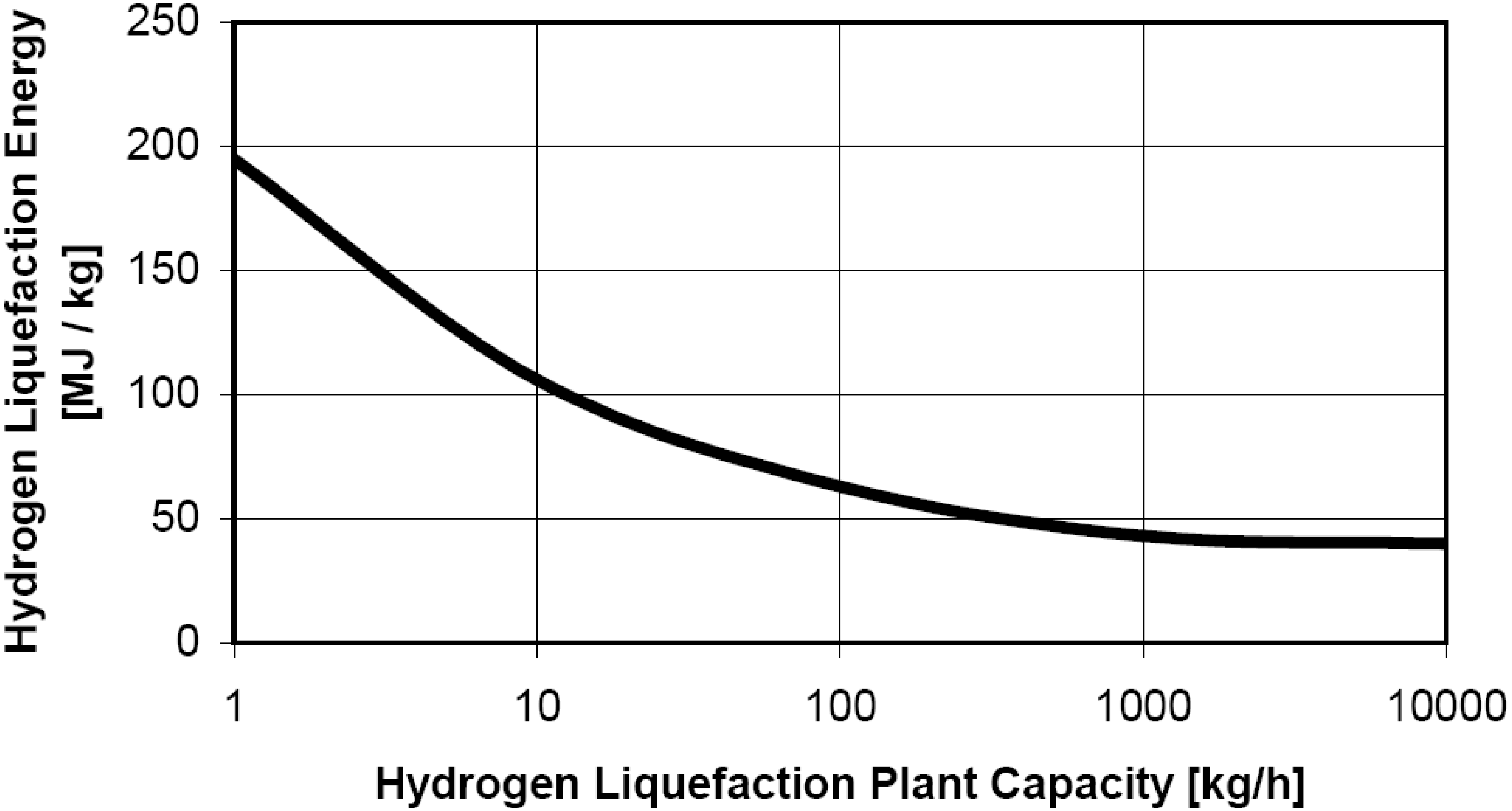
20 K,
10% LH2
+ 90% GH2
(recycle)

Liquefaction unit



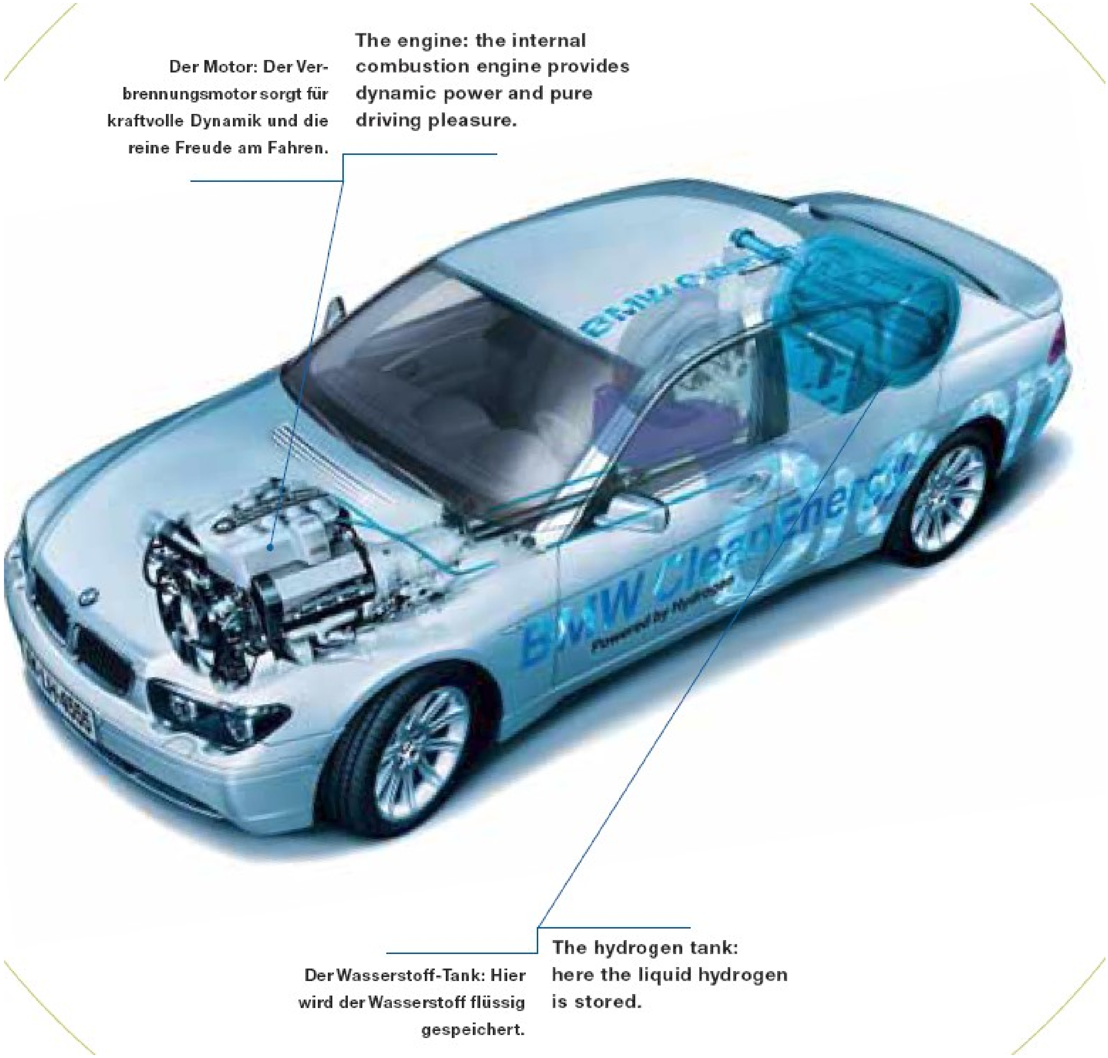
Source: Linde Kryotechnik

Energy demand for liquefaction



Source: Bossel

LH2 powered vehicle



Der Motor: Der Verbrennungsmotor sorgt für kraftvolle Dynamik und die reine Freude am Fahren.

The engine: the internal combustion engine provides dynamic power and pure driving pleasure.

Der Wasserstoff-Tank: Hier wird der Wasserstoff flüssig gespeichert.

The hydrogen tank: here the liquid hydrogen is stored.

Source: BMW

Comparison: LH_2 vs. GH_2

Name: **HydroGen3**

Type: Opel Zafira Minivan with fuel cell (electric power train)

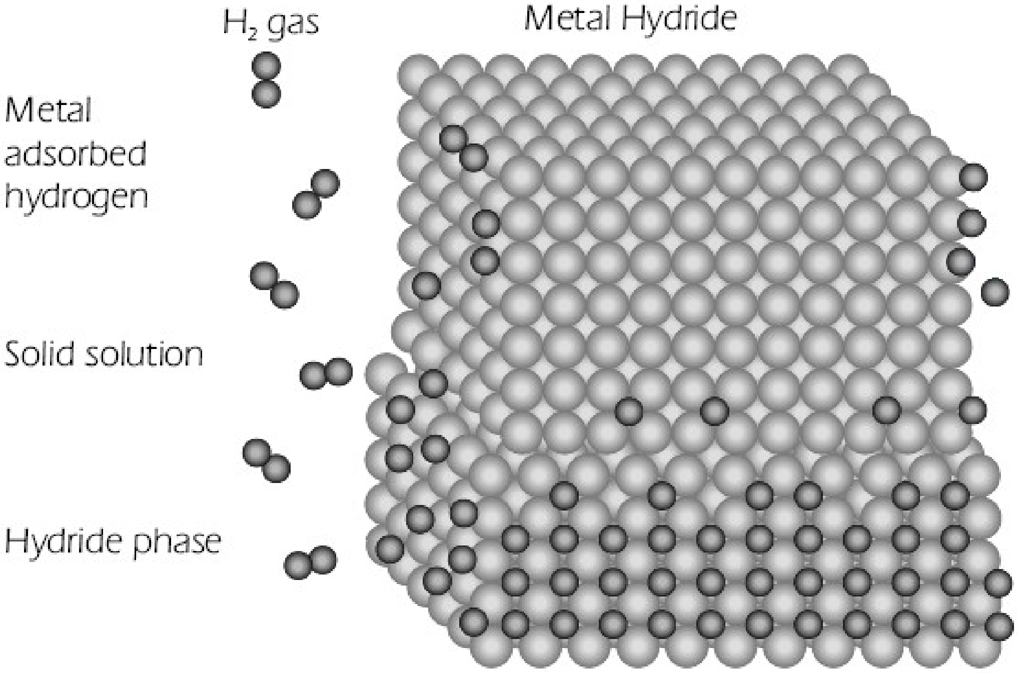
Seats: 5

Velocity: 160 km/h

Tank system: **4,6 kg LH (20 K)** **3,1 kg CH_2 (700 bar)**

Source: General Motors

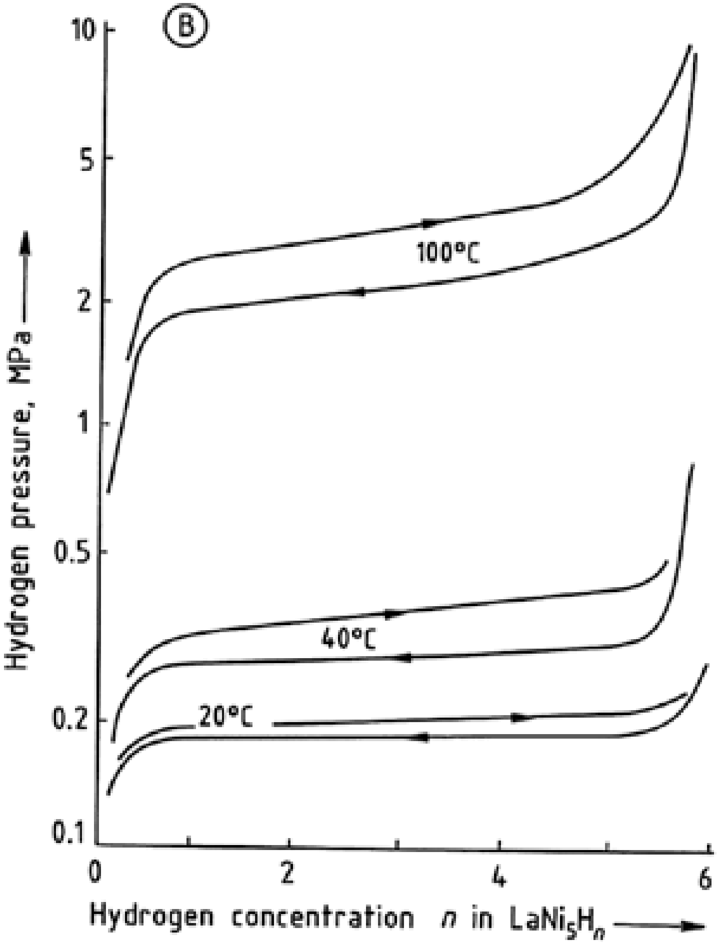
Metal hydrides

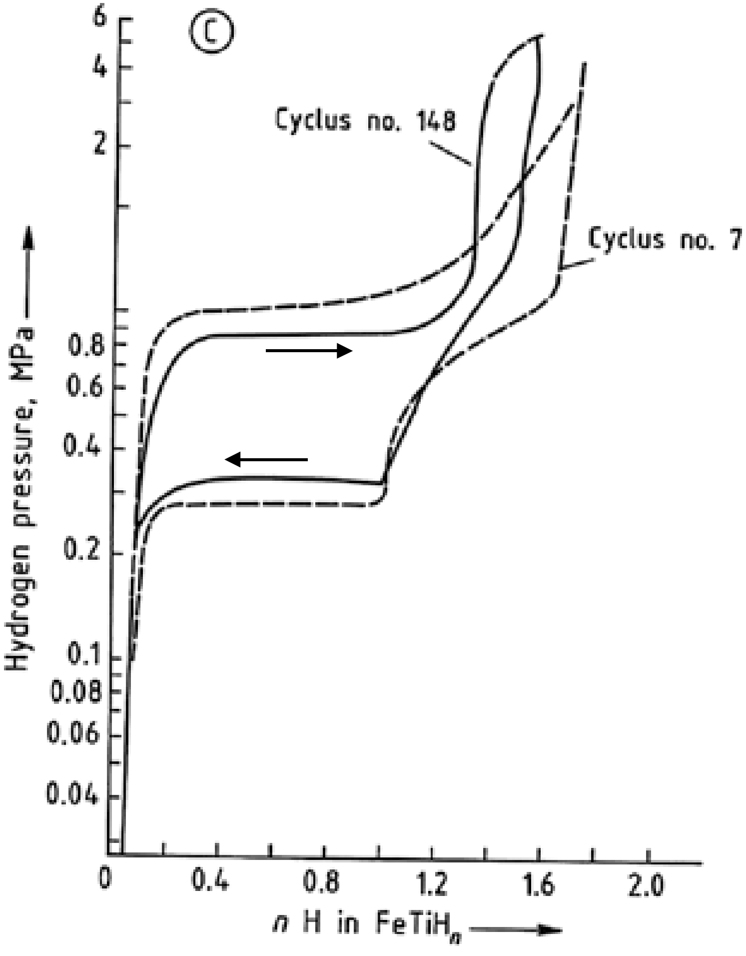


$$M + x/2\ H_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} MH_x + \text{heat}$$

Source: Schlappach, Züttel

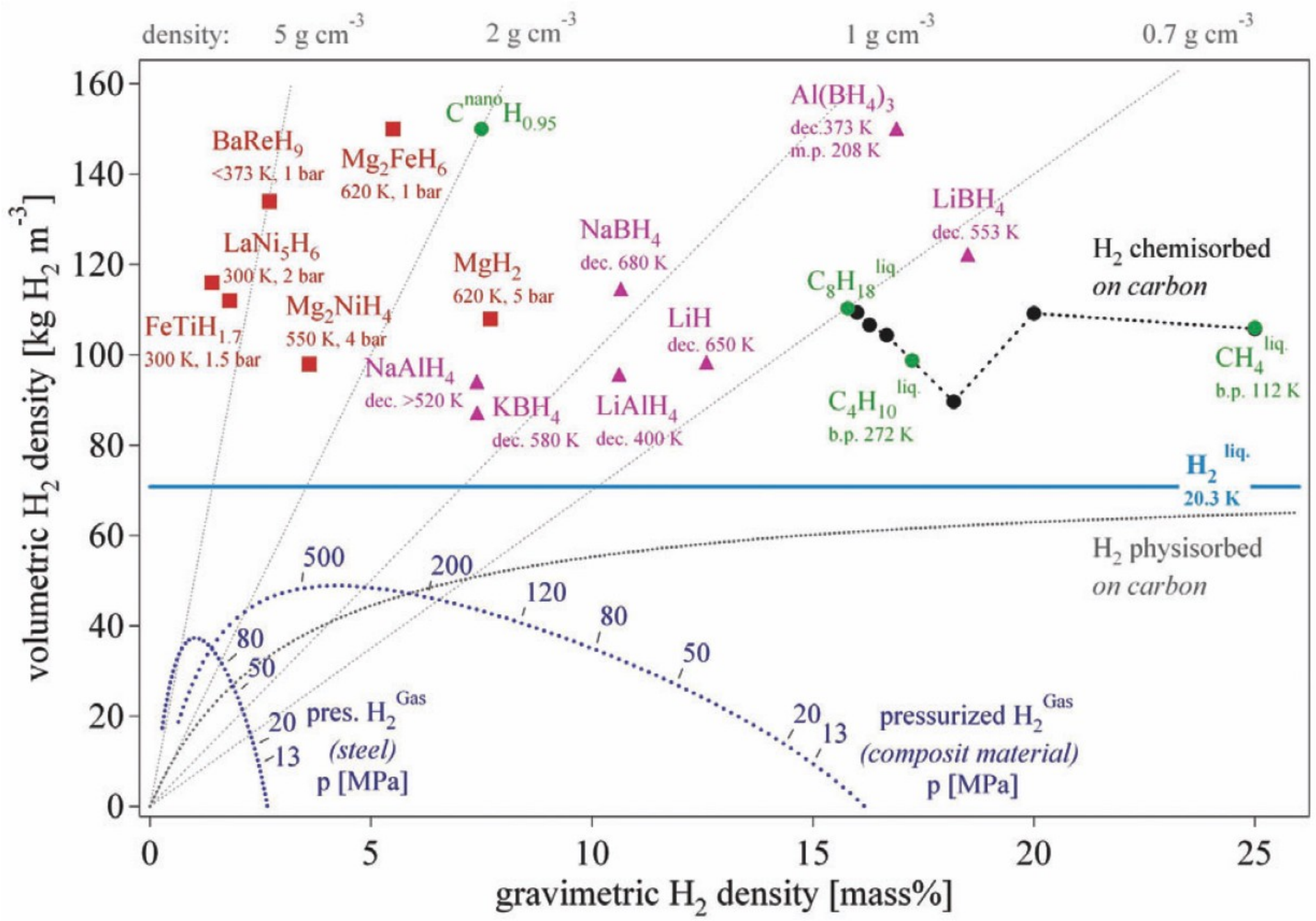
Metal hydrides: charging and discharging





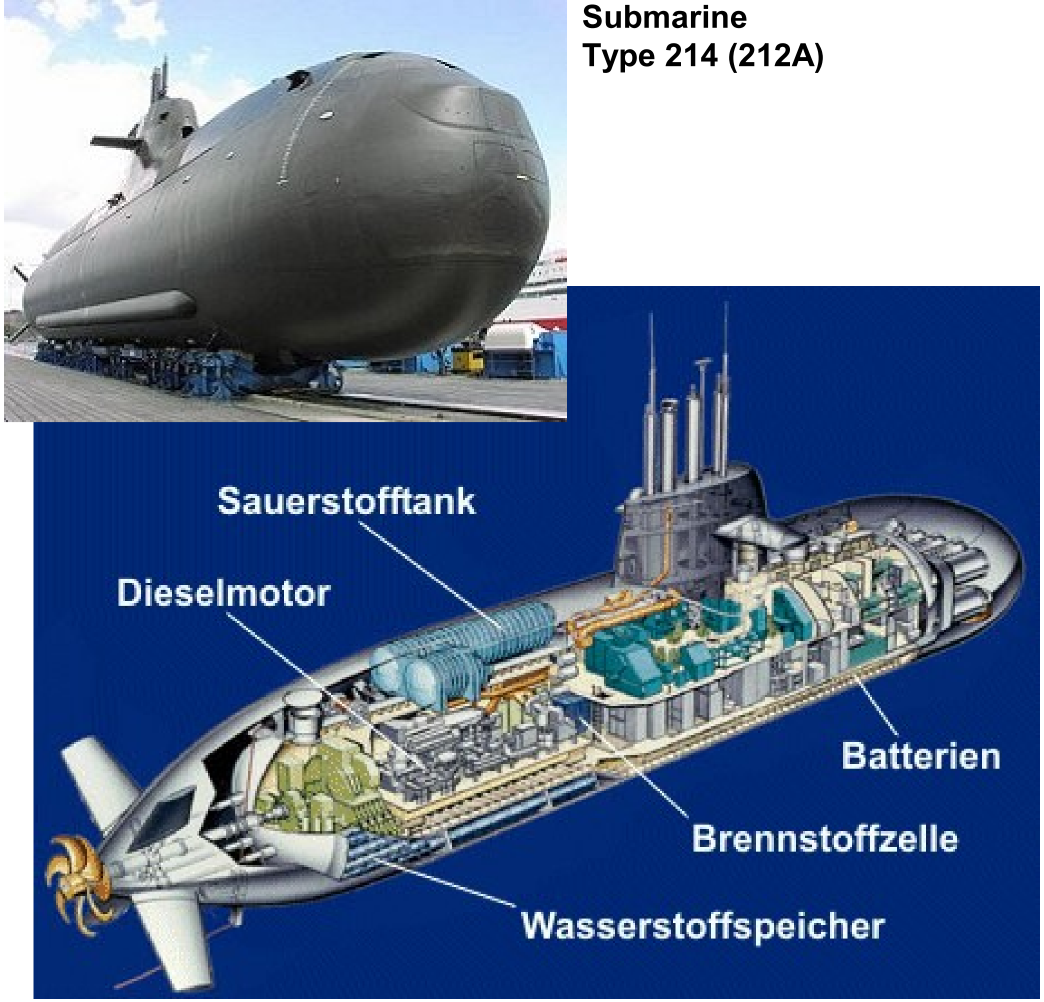
Source: Ullmann

Metal hydrides: Storage density



Source: Schlappach, Züttel

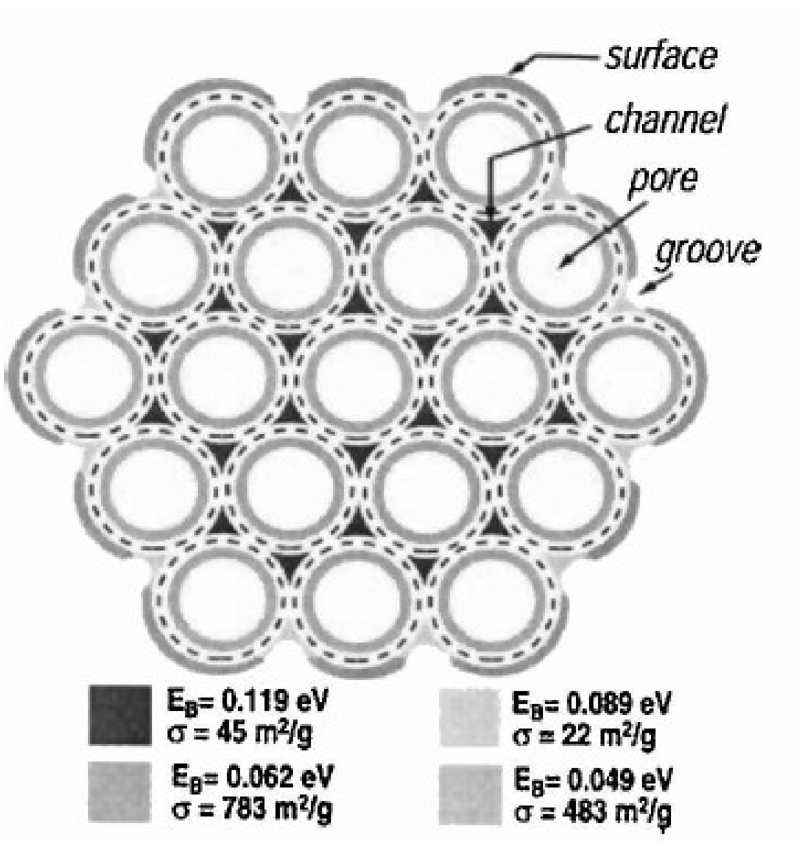
Metal hydrides: application

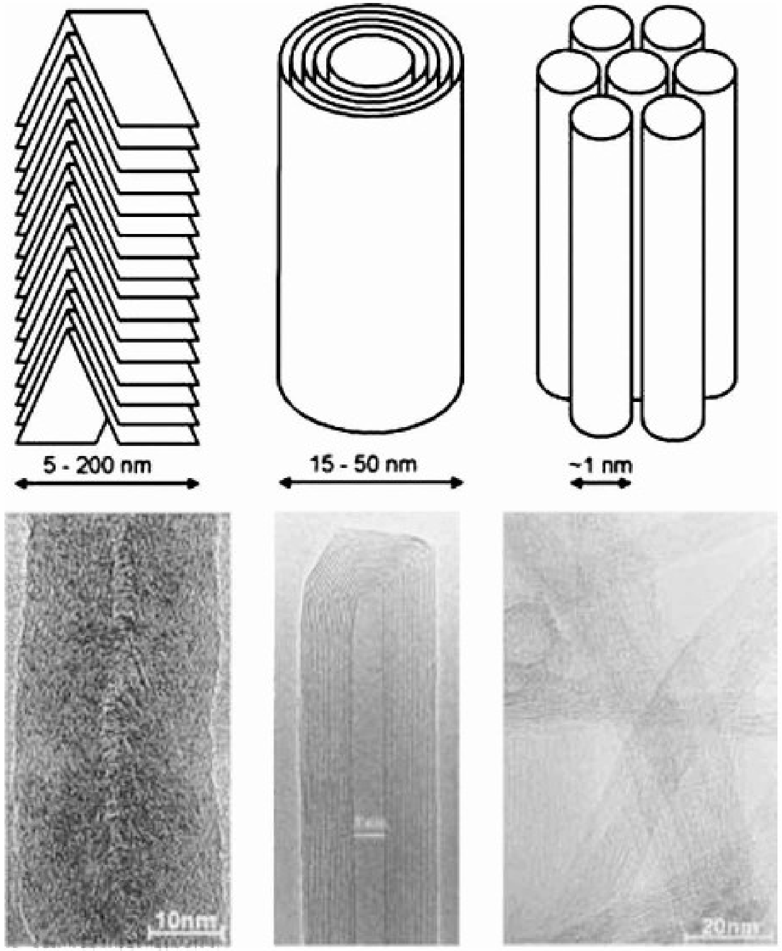


Submarine
Type 214 (212A)

Sources: Udomi, www.hfpeurope.org, HDW

Carbon nanostructures





still under development …

Source: Hirscher, Becher

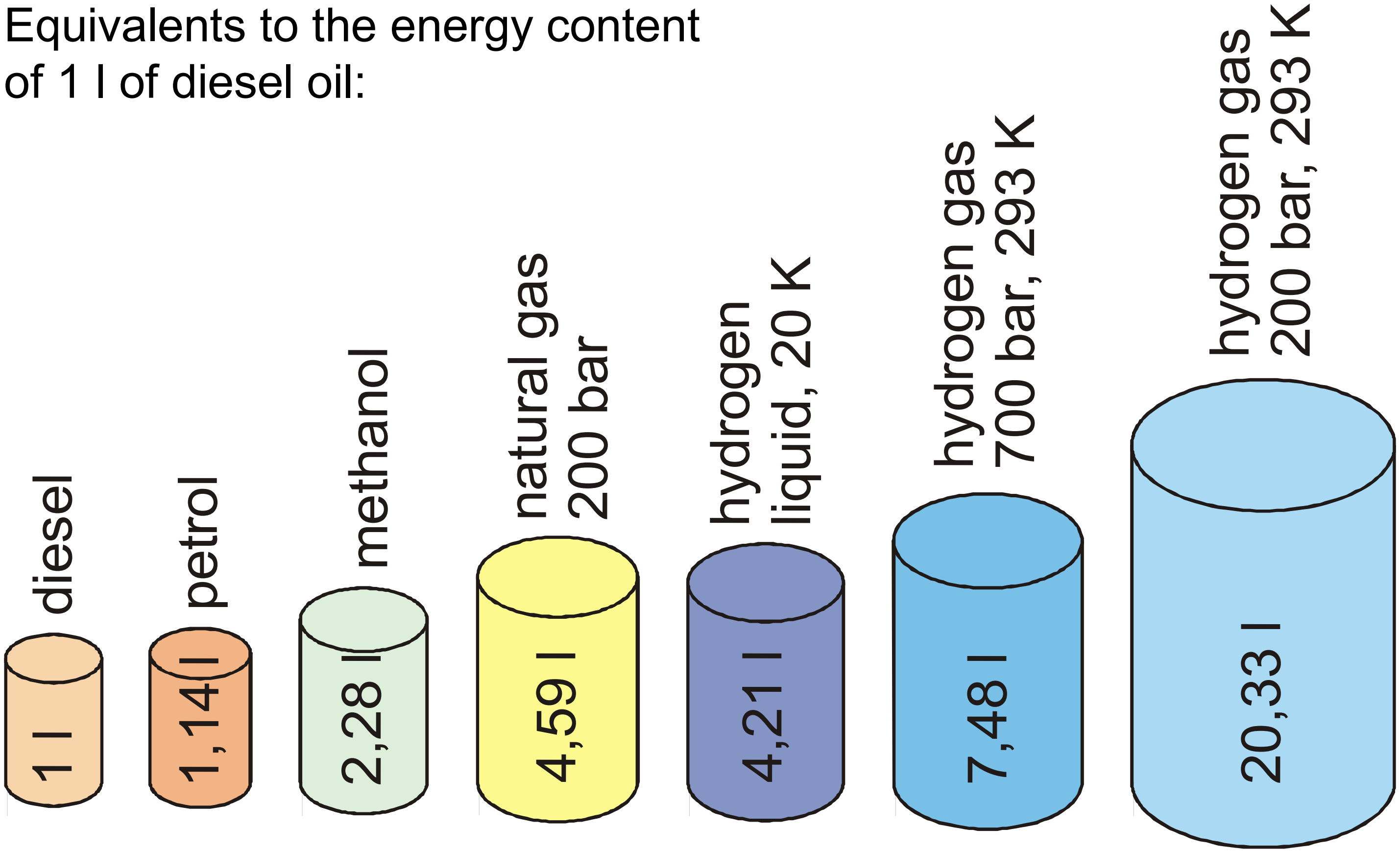
Storage of H_2 in chemicals

Chemical	Formula	H_2-fraction	Density	Vol. for 1 kg H_2	Comments
		[$\%_{gew}$]	[kg/dm^3]	[dm^3/kg_{H2}]	
Liquids					
hydrazine	N_2H_2	12,58	1,011	7,8	highly toxic, carcinogenic
ammonia	NH_3	17,76	0,67	9,3	toxic, corrosive
methane, liquid	CH_4	25,13	0,415	9,6	cryogenic, -175 °C
ethanol	C_2H_5OH	13,0	0,79	9,7	
Methanol	CH_3OH	12,5	0,79	10,0	toxic
Hydrogen, liquid	H_2	100	0,07	14,0	cryogenic, -252 °C
Sodium borohydride, sol. 30 %	$NaBH_4+H_2O$	6,3	1,06	15,0	expensive
Hydrides					
Titanium hydride	TiH_2	4,4	3,9	5,8	
Lithium hydride	LiH	12,68	0,82	6,5	corrosive
Aluminium hydride	AlH_3	10,80	1,3	7,1	
Beryllium hydride	BeH_2	18,28	0,67	8,2	highly toxic
Calcium hydride	CaH_2	5,0	1,9	11,0	corrosive
Silane	SiH_4	12,55	0,68	12,0	instabile, toxic
Sodium hydride	NaH	4,3	0,92	25,9	corrosive, cheap
Potassium hydride	KH	2,51	1,47	27,1	corrosive
Complex hydrides					
Lithium borohydride	$LiBH_4$	18,51	0,666	8,1	corrosive
Sodium borohydride	$NaBH_4$	10,58	1,0	9,5	toxic, corrosive
Titanium iron hydride	$TiFeH_2$	1,87	5,47	9,8	
Aluminium borohydrid	$Al(BH_4)_3$	16,91	0,545	11,0	
Palladium hydrid	Pd_2H	0,47	10,78	20,0	

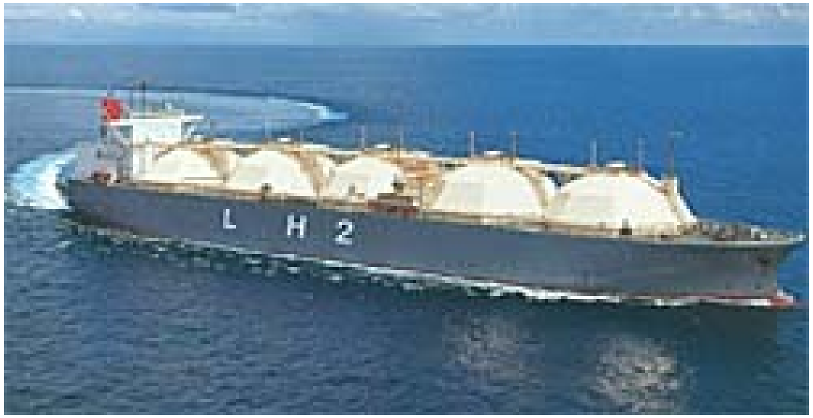
Source: Larminie

Comparison of storage density

Equivalents to the energy content of 1 l of diesel oil:

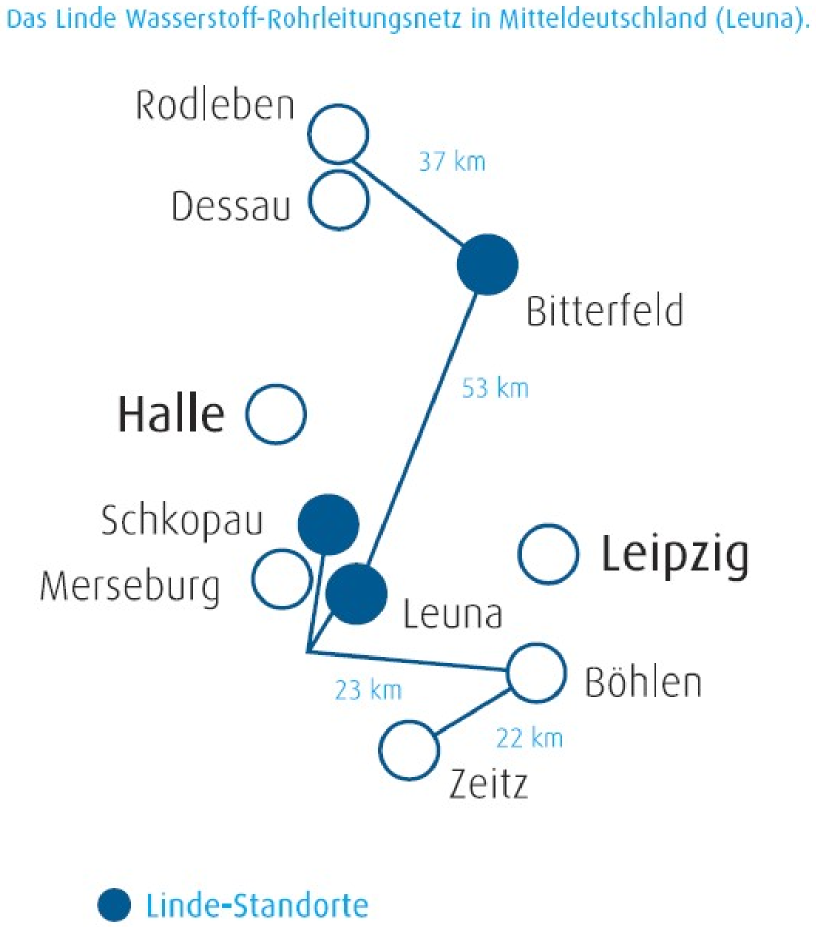


Transport of hydrogen



Source: www.HFPeurope.org

Hydrogen transport in pipelines


Das Linde Wasserstoff-Rohrleitungsnetz in Mitteldeutschland (Leuna).

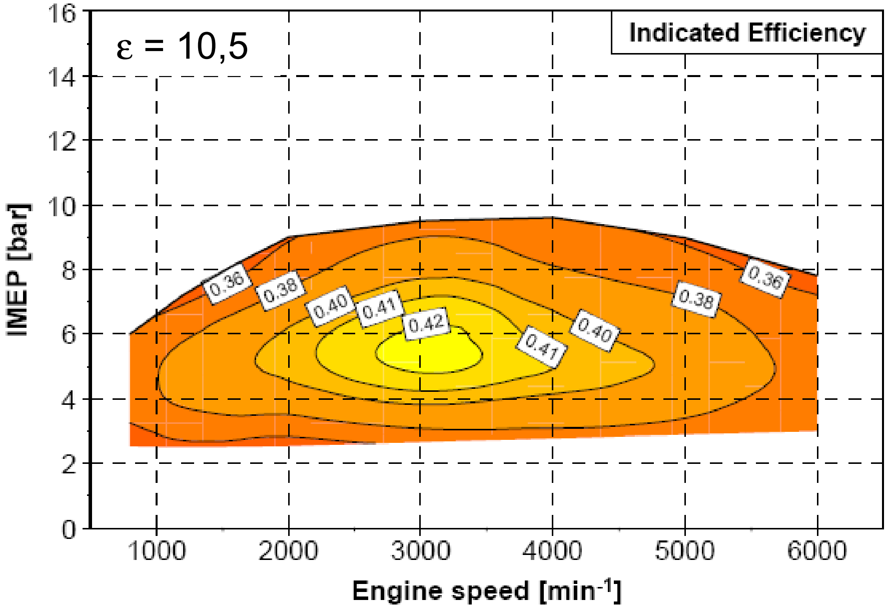
Source: Linde

Hydrogen engine

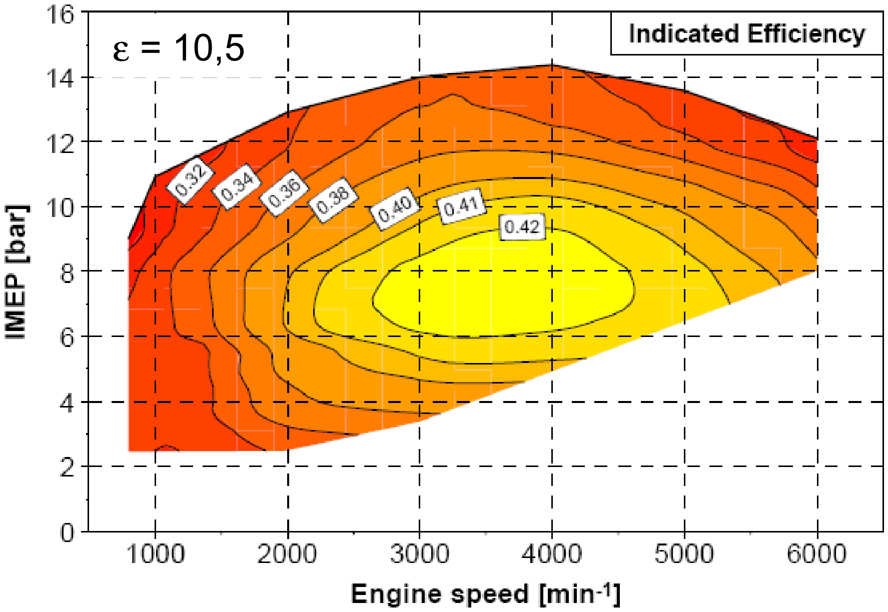
Source: BMW

Efficiency of hydrogen in engines

mixture in suction tube:
(Otto engine)

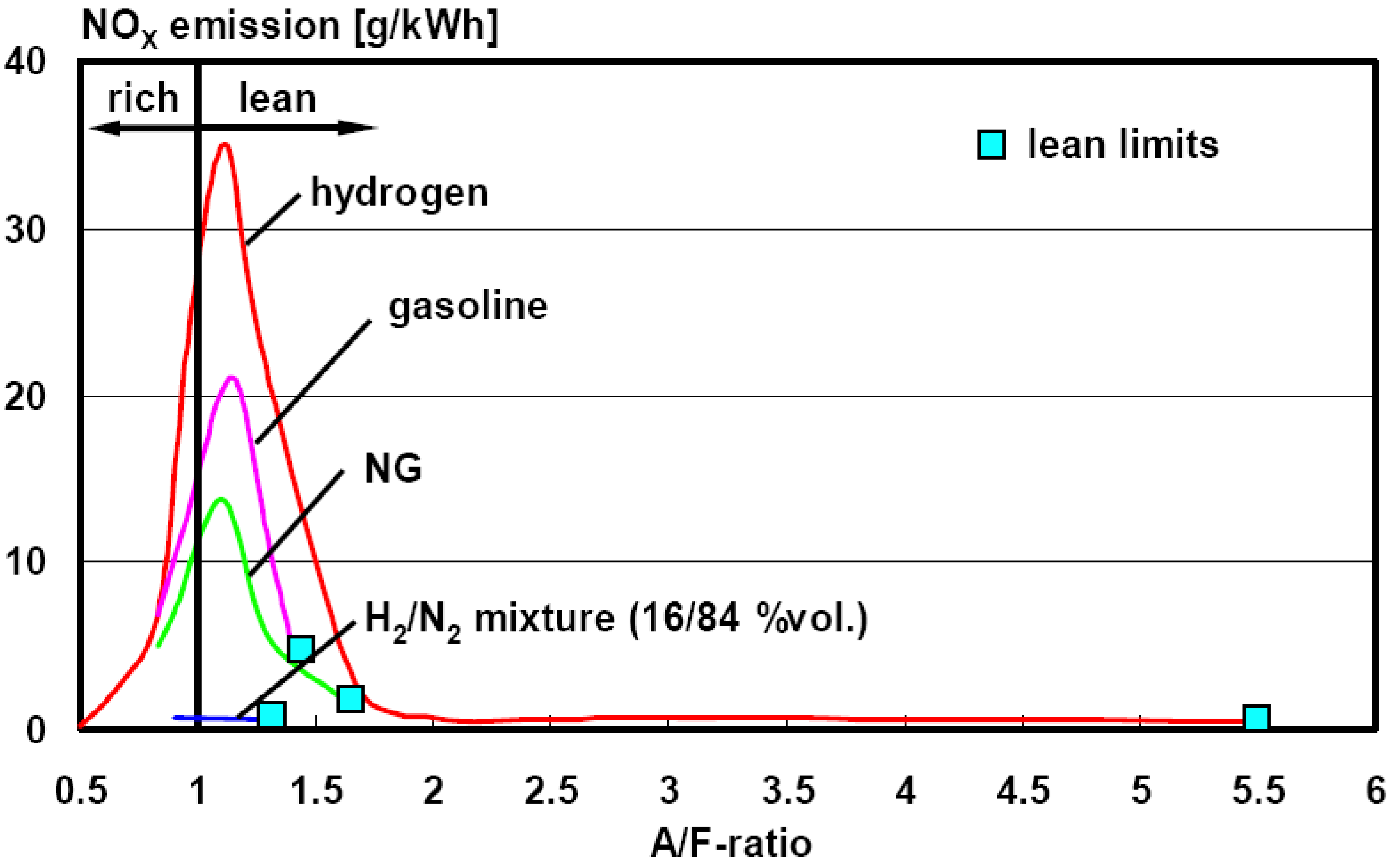


direct injection:
(Diesel engine)



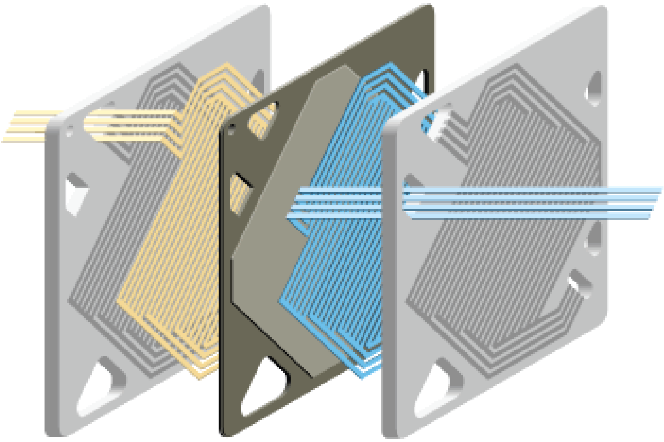
Source: Grabner et al. (TU Graz, BMW)

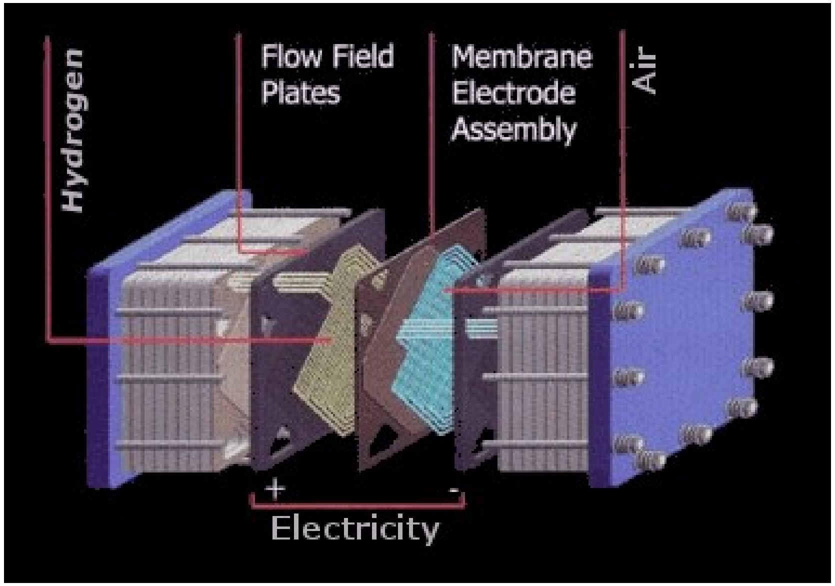
Emissions in engines

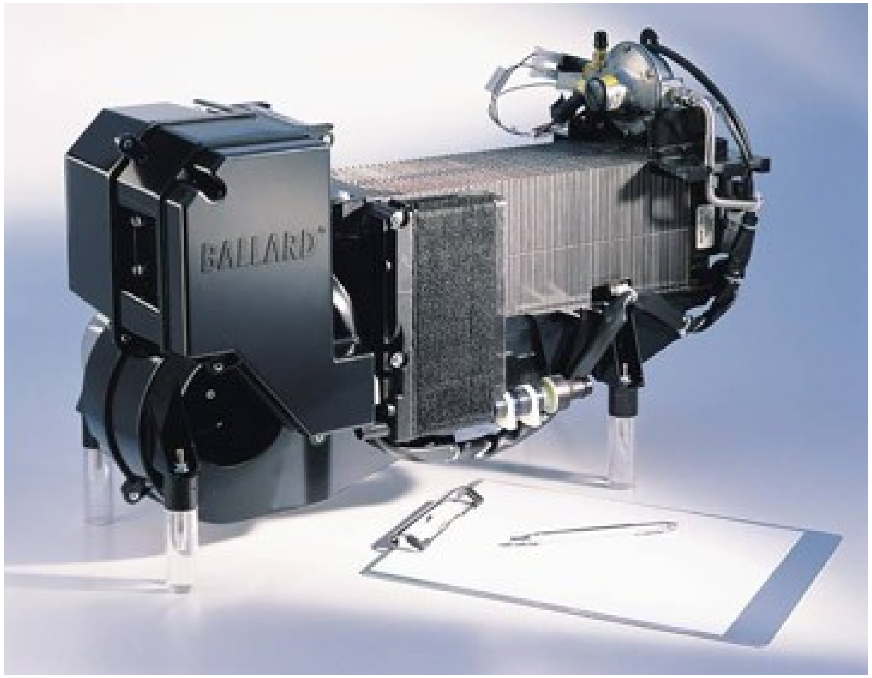


Source: Herdin (Jenbacher)

Fuel cell stack

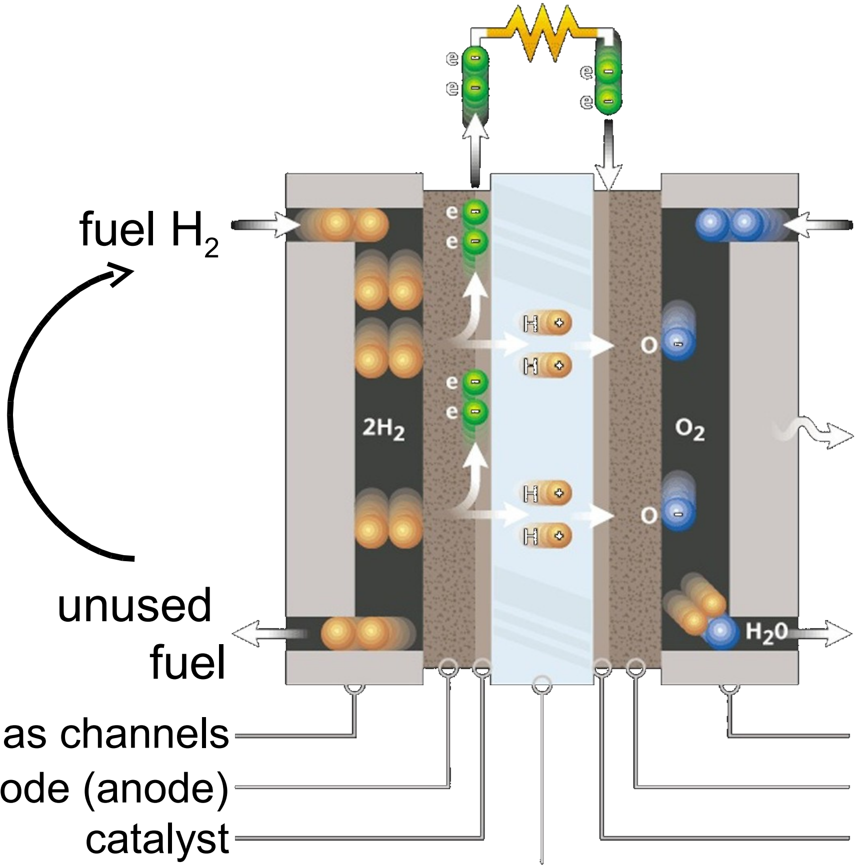






Source: Ballard

Function of a PEM fuel cell



electric circuit

fuel H_2

fuel recycle

unused fuel

O_2 from air

heat (85 °C)
water- or air cooling system

air + steam

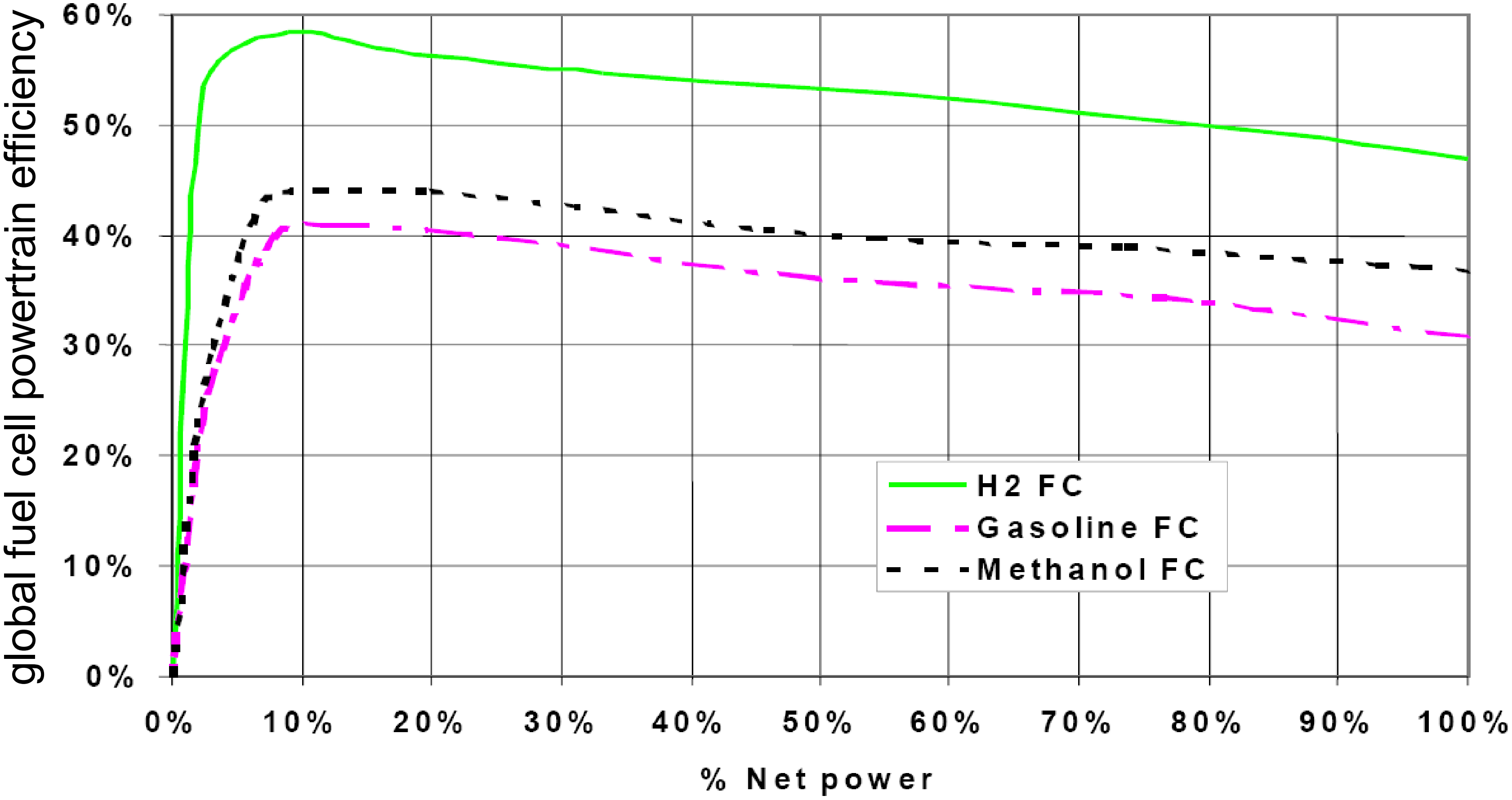
bipolar plate with gas channels
gas diffusion electrode (anode)
catalyst

bipolar plate with gas channels
gas diffusion electrode (cathode)
catalyst

„Proton Exchange Membrane“ (PEM)

Source: Ballard

Efficiency of fuel cells



Source: EUCAR, GM

Properties of fuel cells

Advantages

\+ very high efficiency

\+ good part load behaviour

\+ very low emission levels

\+ only few rotating parts

\+ (theoretical) potential for low maintenance units

Disadvantages

\- high specific costs [€/kW]

\- efficiency decreases with operation hours

\- sensible for impurities in fuel and air

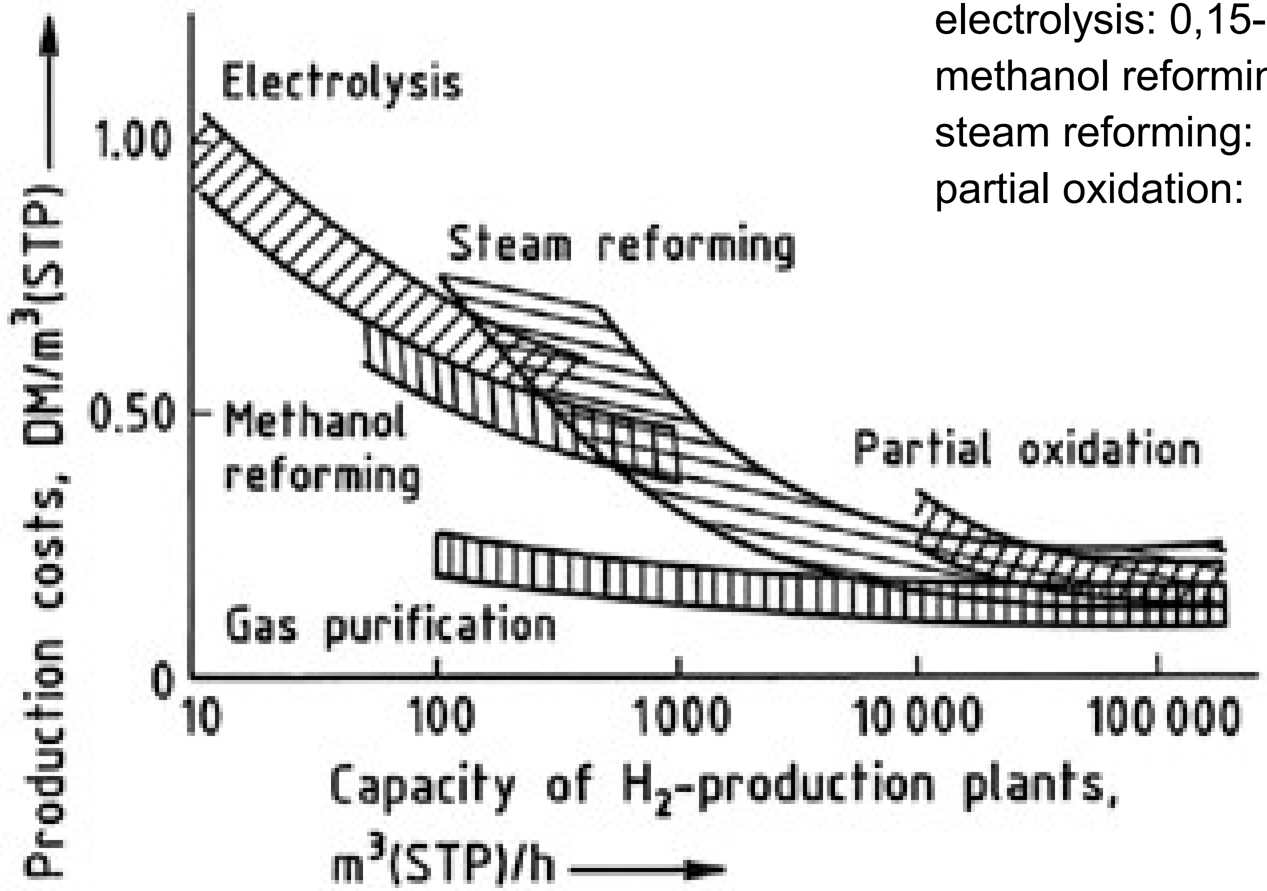
\- lifetime still too short

\- reasonable availability not demonstrated yet

\- only few producers of stacks

\- marketability not reached yet

Costs of hydrogen production



cost limits:

electrolysis: 0,15-0,09 DM/kWh

methanol reforming: 525–400 DM/t

steam reforming: naphtha – natural gas

partial oxidation: HFO 300 DM/t, residue 100 DM/t

year: **1983, BRD**

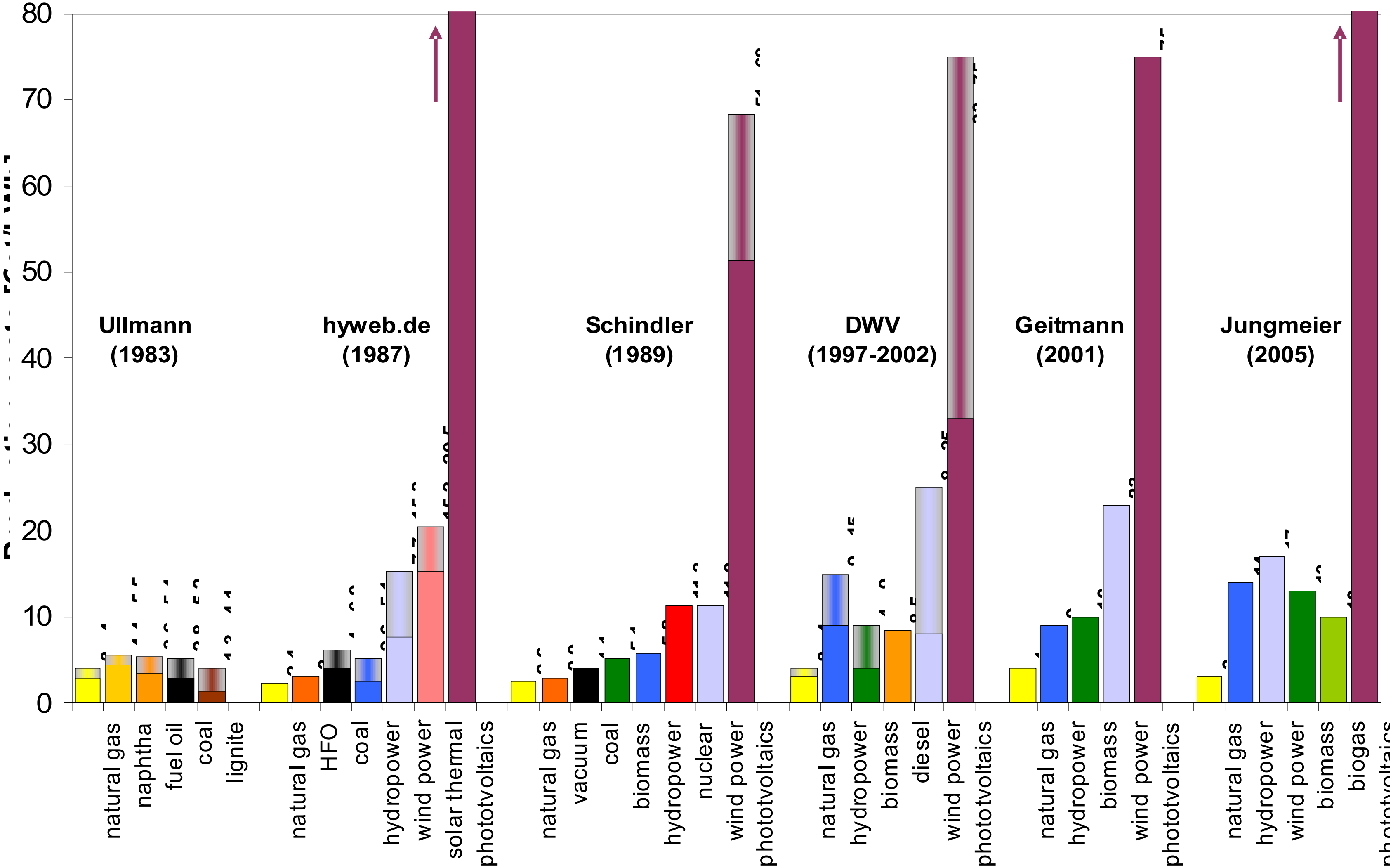
natural gas: 8,5 DM/GJHHV

electricity: 0,09-0.15 DM/kWh

naphtha: 650 DM/t

Source: Ullmann

Costs of hydrogen production (2)



Safety risks of hydrogen?

Source: NASA, www.yale.edu

Ignition behaviour

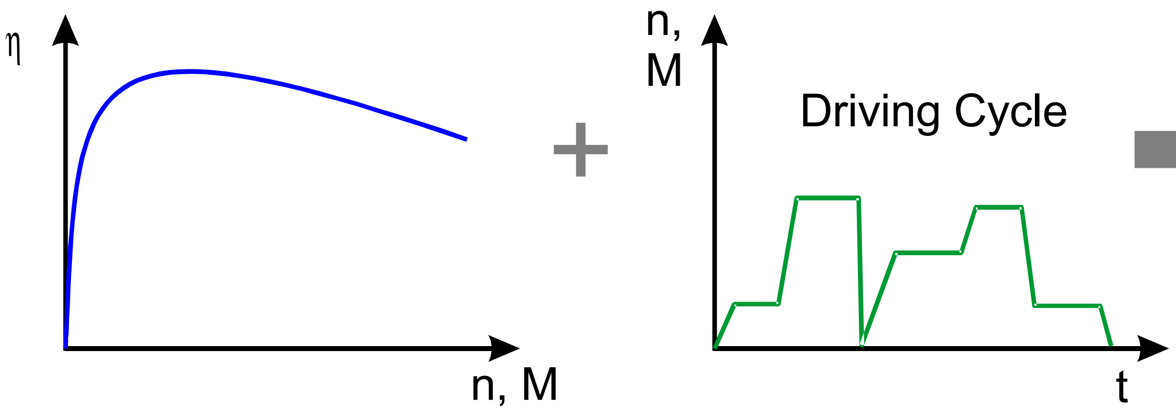
	Hydrogen	Methane	Propane	Gasoline
Density of gas at stand. cond., kg/m^3 (STP)	0.084	0.65	2.42	4.4
Heat of vaporisation, J/g	445.6	509.9	376.2	250–400
Lower heating value, kJ/g	**119.93**	50.02	46.35	44.5
Higher heating value, kJ/g	**141.8**	55.3	50.41	48
Thermal conductivity of gas at stand. cond., mW cm^{-1} K^{-1}	1.897	0.33	0.18	0.112
Diffusion coefficient in air at stand. cond., cm^2/s	0.61	0.16	0.12	0.05
Flammability limits in air, vol %	**4.0–75**	5.3–15	2.1–9.5	1–7.6
Stoichiometric composition in air, vol %	29.53	9.48	4.03	1.76
Minimum energy for ignition in air, mJ	**0.02**	0.29	0.26	0.24
Autoignition temperature, K	858	813	760	500–744
Flame temperature in air, K	2318	2148	2385	2470
Maximum burning velocity in air at stand. cond., m/s	**3.46**	0.45	0.47	1.76
Detonation velocity in air at stand. cond., km/s	1.48–2.15	1.4–1.64	1.85	1.4–1.7
Energy of explosion, mass-related, gTNT/g	**24**	11	10	10
Energy of explosion, volume-related, gTNT/m^3 (STP)	2.02	7.03	20.5	44.2

Source: Ullmann, Perry

Assessment of total system efficiencies

Production, storage, distribution ⇒ **WTT**

„Well-to-Tank“

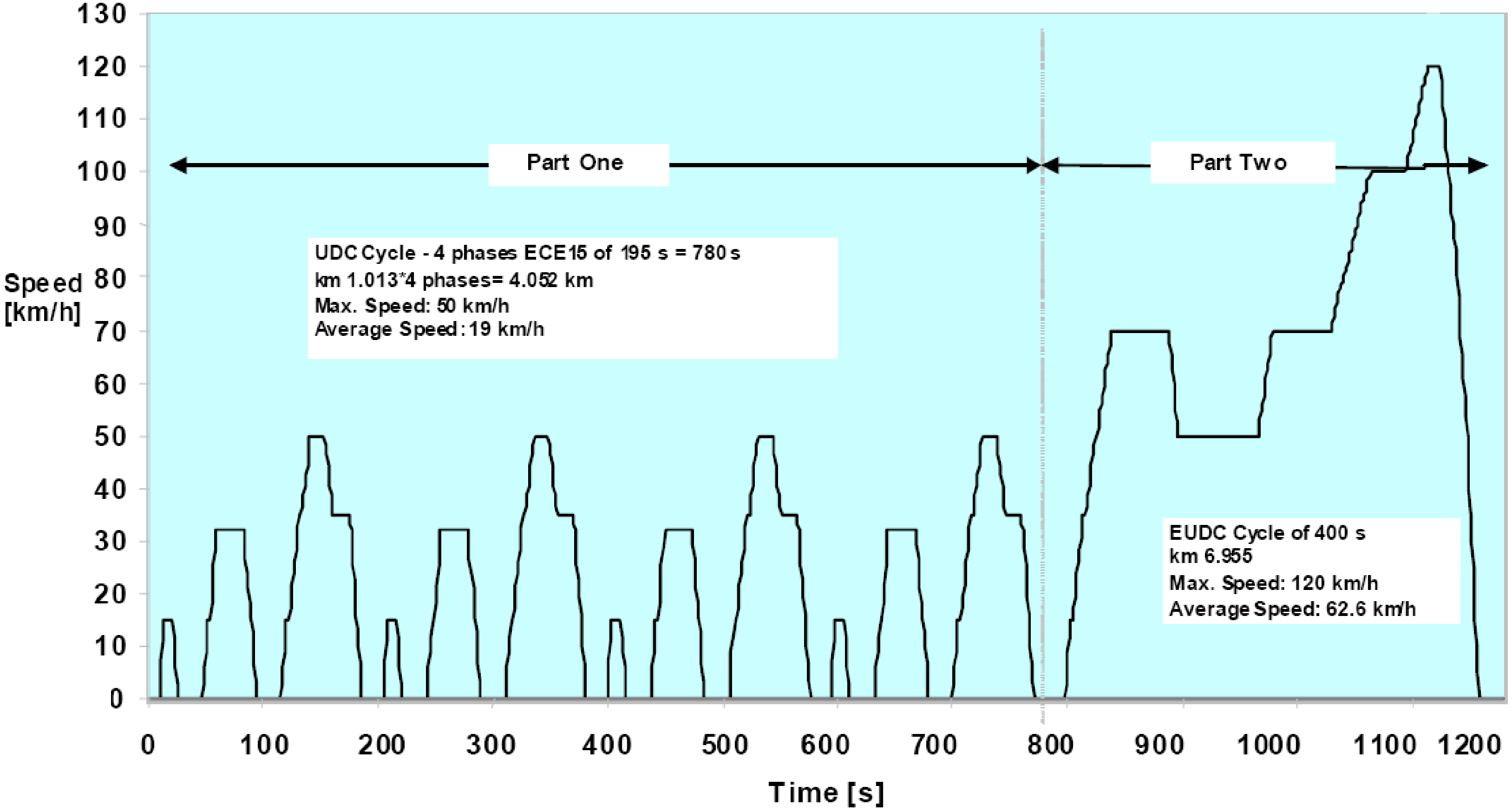


➡ **TTW**

„Tank-to-Wheels“

WTT · TTW = WTW „Well-to-Wheels“

New European Driving Cycle (NEDC)



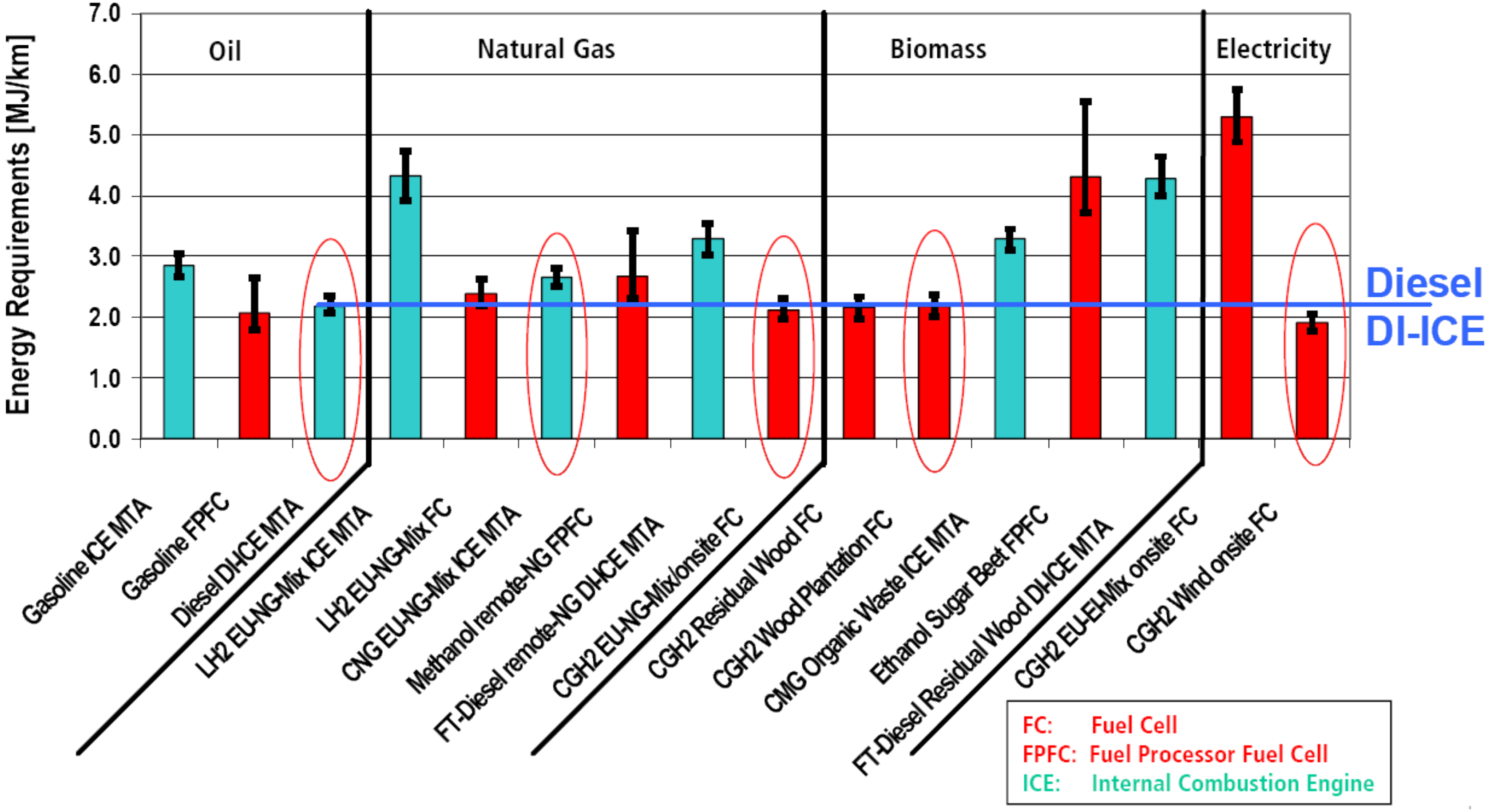
UDC Cycle - 4 phases ECE15 of 195 s = 780 s
km 1.013*4 phases= 4.052 km
Max. Speed: 50 km/h
Average Speed: 19 km/h

EUDC Cycle of 400 s
km 6.955
Max. Speed: 120 km/h
Average Speed: 62.6 km/h

Source: EUCAR

Example: efficiency WTW

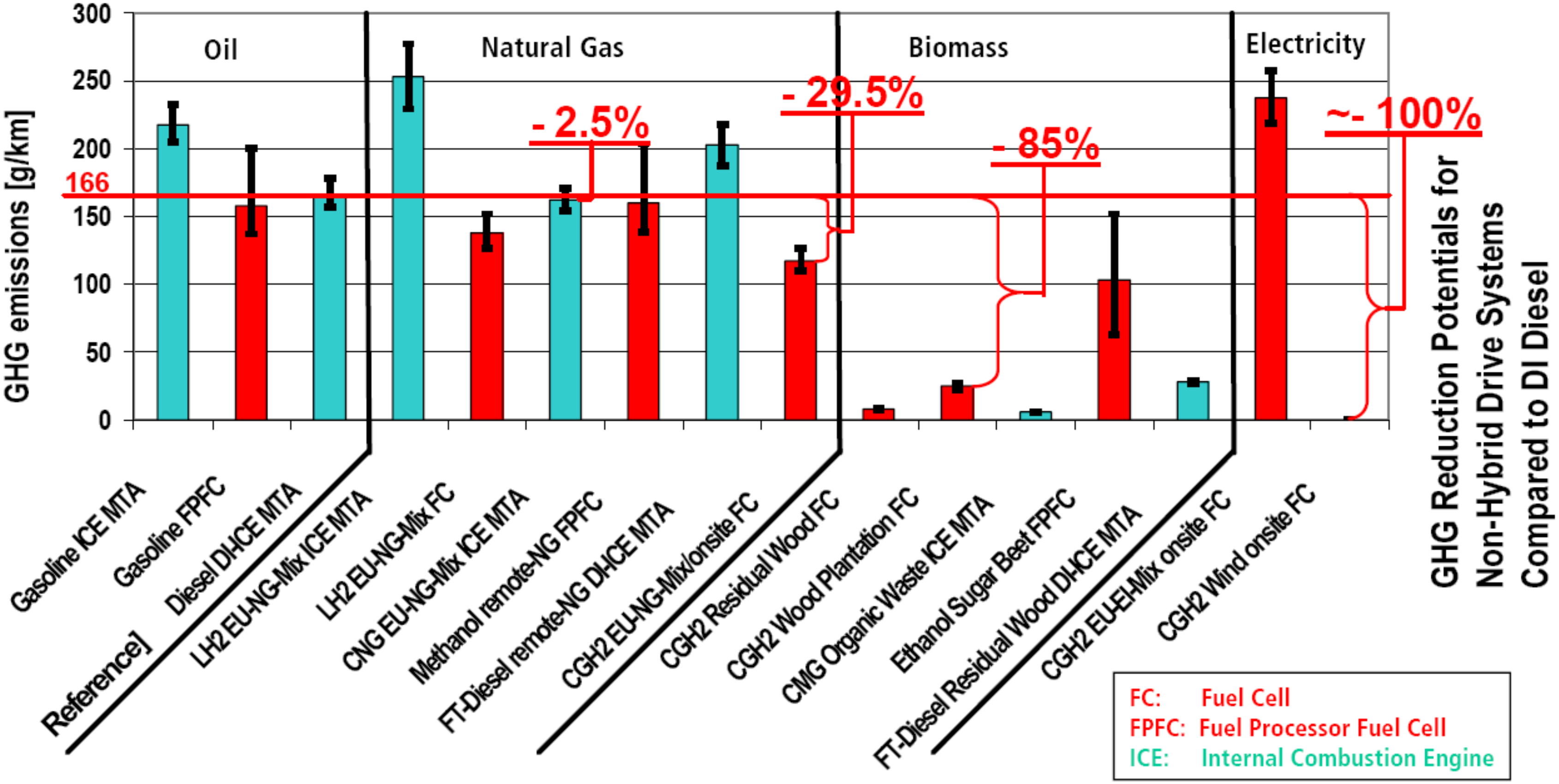
Vehicle: Opel Zafira



Source: LB-Systemtechnik

Example: GHG-emissions WTW

Vehicle: Opel Zafira



FC: Fuel Cell
FPFC: Fuel Processor Fuel Cell
ICE: Internal Combustion Engine

Source: LB-Systemtechnik

Is hydrogen technology a reasonable option?

Overall efficiency:

electrolysis → storage → fuel cell

- high pressure storage:

  η**ges** $= \eta_{El} \cdot \eta_{Sp} \cdot \eta_{Br} = 0{,}85 \cdot 0{,}9 \cdot 0{,}55 =$ **42 %**

- cryogenic storage:

  η**ges** $= \eta_{El} \cdot \eta_{Sp} \cdot \eta_{Br} = 0{,}85 \cdot 0{,}7 \cdot 0{,}55 =$ **32,7 %**

problems:

- **storage**
- **production**
- missing infrastructure
- safety

Hydrogen technology: Conclusions

Advantages

+ might be produced from renewable sources
+ CO_2-free production from fossil sources possible
+ high efficiency in fuel cells
+ no local CO_2 emissions
+ nearly emission free traffic might be possible

Disadvantages/Problems

- mainly produced from fossil sources in the mid-term
- purification of fuel (desulfurization)
- **storage**
- availability of **fuel cells**
- **overall efficiency**
- production costs
- safety

Recommended literature

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- Jungmeier G., ***Wasserstoff aus erneuerbarer Energie in Österreich – Ein Energieträger der Zukunft?***, Berichte aus Energie und Umweltforschung 40/2006, Bundesministerium für Verkehr, Innovation und Technologie, 2006.
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- Groß R., Otto W., Patzelt A., Wanner M., ***Flüssigwasserstoff für Europa – die Linde-Anlage in Ingolstadt***, Linde AG, Berichte aus Technik und Wissenschaft 71/1994.
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- Bossel U., ***The Physics of the Hydrogen Economy***, European Fuel Cell News, Vol. 10, No. 2, Juli 2003.
- www.hyweb.de.

Thank you for your attention!