2nd Joint European Summer School on
Fuel Cell and Hydrogen Technology
Crete, 17th – 28th Sept. 2012

UNIVERSITY OF BIRMINGHAM

Basic Thermodynamics and System Analysis for Fuel Cells

Prof. Dr. Robert Steinberger-Wilckens
Centre for Hydrogen & Fuel Cell Research
University of Birmingham

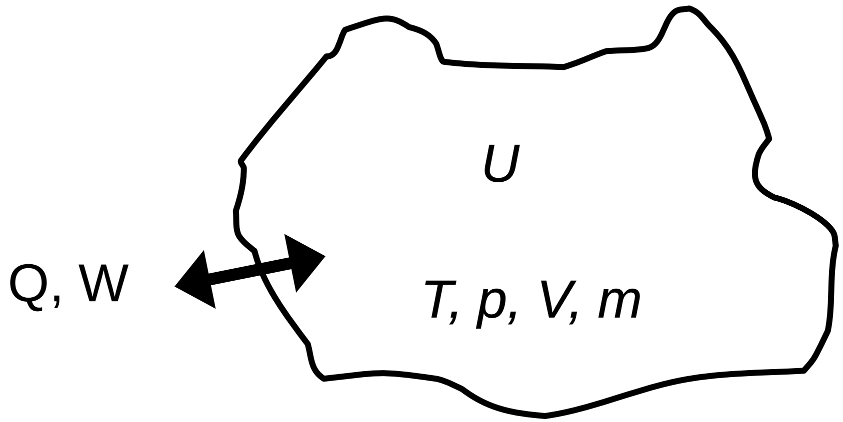
Overview

- Basics of Thermodynamics
- Thermodynamics applied to fuel cells and electrolysis
- System analysis

A very brief Introduction to Thermodynamics

The Model Thermodynamic World

Consider a volume and ist boundary:



system variables:

T temperature

p pressure

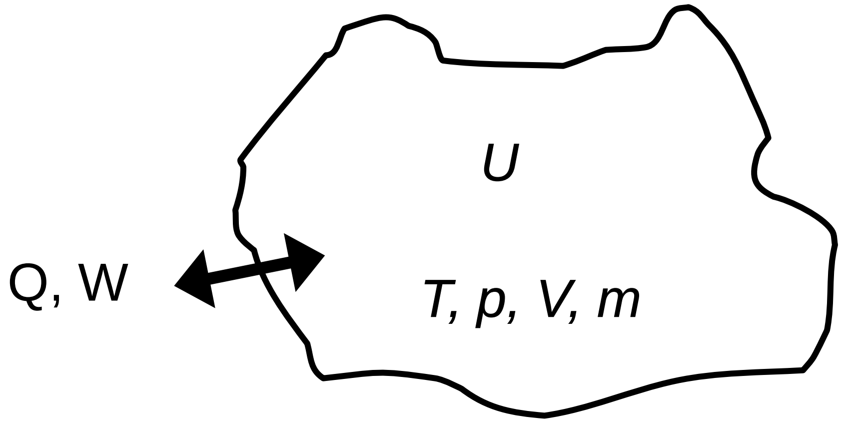
V volume

m mass

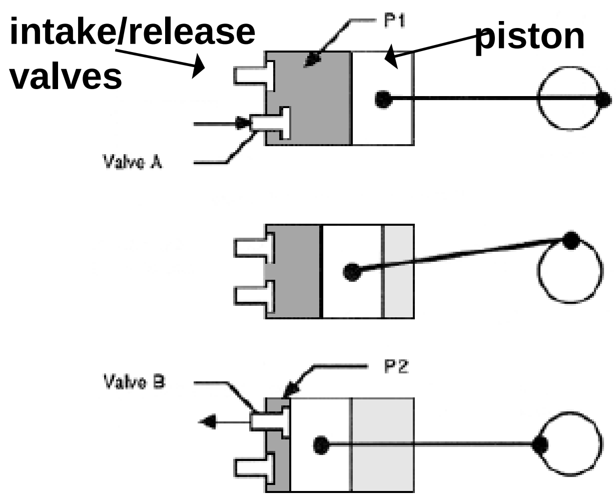
It has a given state of being, quantified by the ‚inner energy state' *U*.

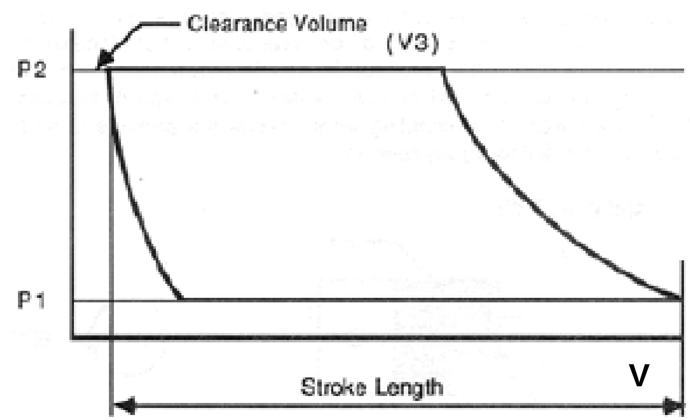
It exchanges activities with the surroundings by transporting mass and energy across the boundary.

Example Representation



system variables:
T temperature
p pressure
V volume
m mass





Ideal gas law:

$$p V = n R T$$

UNIVERSITY OF BIRMINGHAM

The 4 Laws of Thermodynamics

1. Existance of temperature („0th“ Law)
2. Conservation of energy (1st Law)
3. Definition of Entropy (2nd Law)
4. Entropy at T = 0 (3rd Law)

1st Law of Thermodynamics

Any change of inner energy *U* is balanced by the exchange of heat *Q* and work *W*

$$U = Q + W$$

or rather

$$dU = dQ + dW$$

Consequences:

- conservation of energy, $d\,U = 0$ in isolated system
- impossibility of perpetuum mobile of the first kind (delivering work)

Steady State and Transitions

Strictly speaking, all thermodynamic laws are only valid in the steady state (equilibrium).

A transition from one state to another must therefore be calculated in infinitesimal steps. These are assumed to be in balance.

Between two states at times t_1 and t_2 going through a transition, a *process* takes place.

If the process can be reversed and the state at t_1 be achieved again, the process is *reversible*.

2^{nd} Law of Thermodynamics

Every system possesses a property *S* (entropy) that can be calculated from

$d\,S = d\,Q\,/\,T$

In irreversible processes $d\,S \geq d\,Q\,/\,T$

Consequences:

- creation of entropy,
- impossibility of perpetuum mobile of the second kind (converting heat to work)

1^{st} + 2^{nd} Law of Thermodynamics

Combining we get

$$d\,U = d\,W + d\,S \cdot T$$

or

$$d\,W = d\,U - d\,S \cdot T$$

or

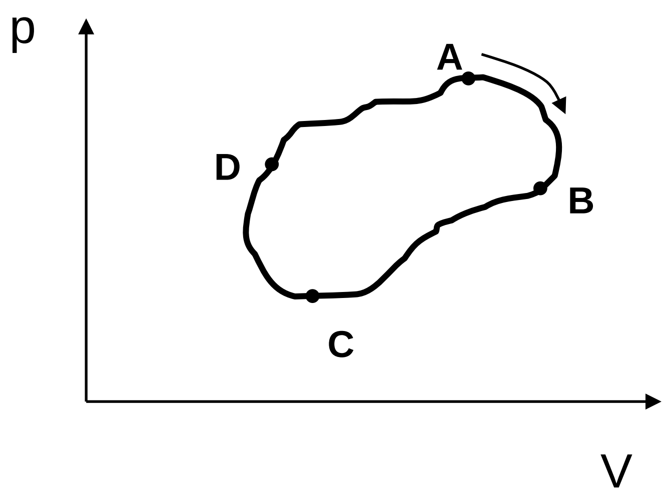
$$\Delta H = \Delta G + T\,\Delta S$$

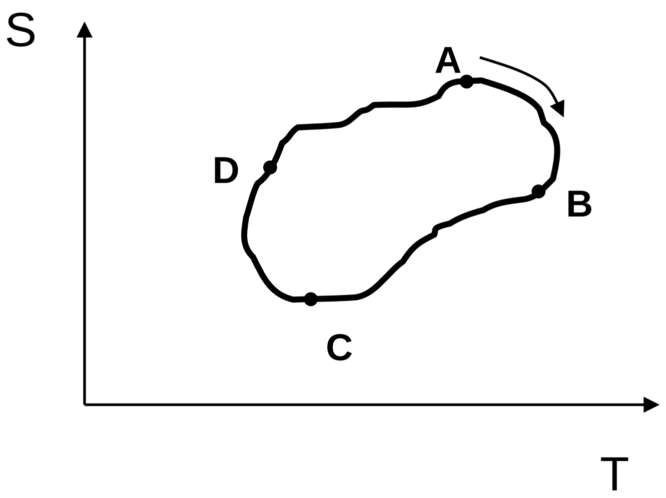
$$\Delta G = \Delta H - T\,\Delta S$$

with H …. ‚enthalpy'
G …. ‚free enthalpy' or ‚Gibb's energy'

Thermodynamic Machines

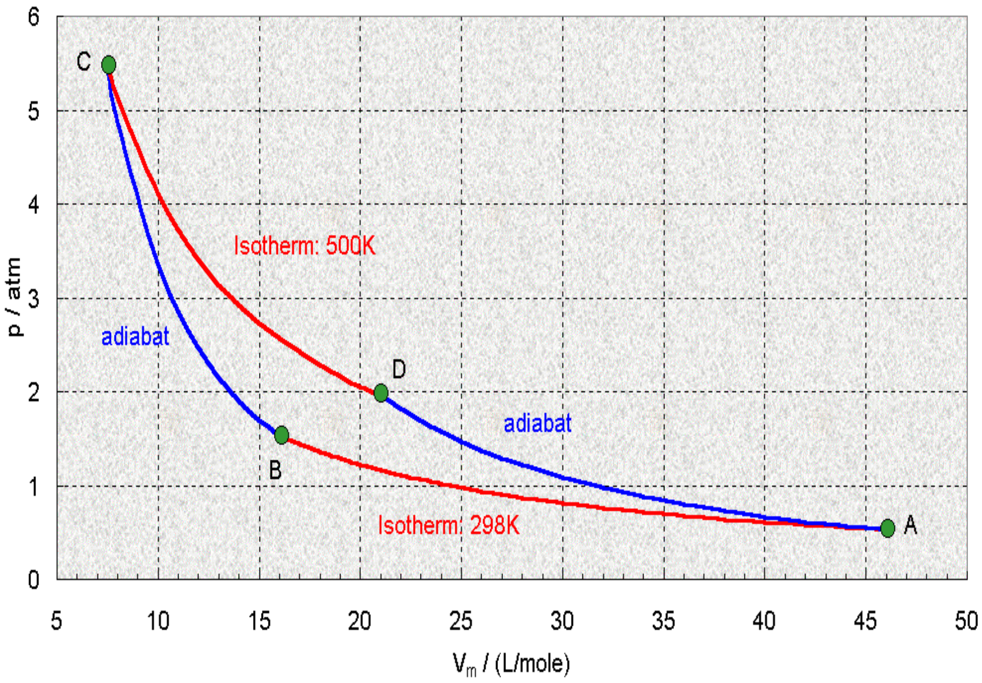
The relevant thermodynamic processes can mostly be considered as circular processes or ‚machines‘.



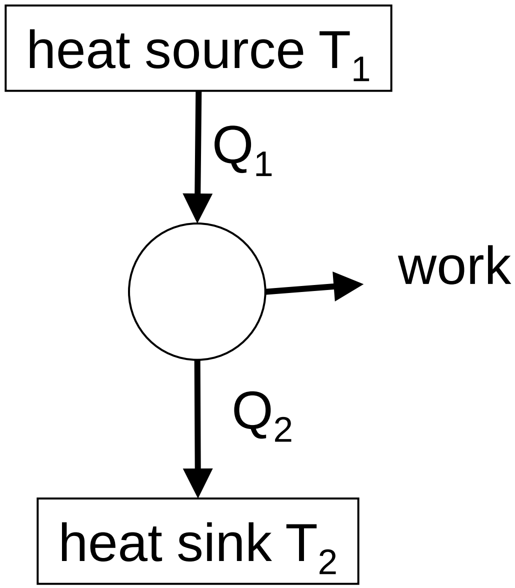


The Carnot Machine: Volume Reaction

1. isothermal compression
2. adiabatic compression
3. isothermal expansion
4. adiabatic expansion



The Carnot Machine (2)



efficiency:

$$\eta_c = W / Q_1$$

from

$$Q_1 - Q_2 - W = 0 \quad (1^{st} \text{ Law})$$

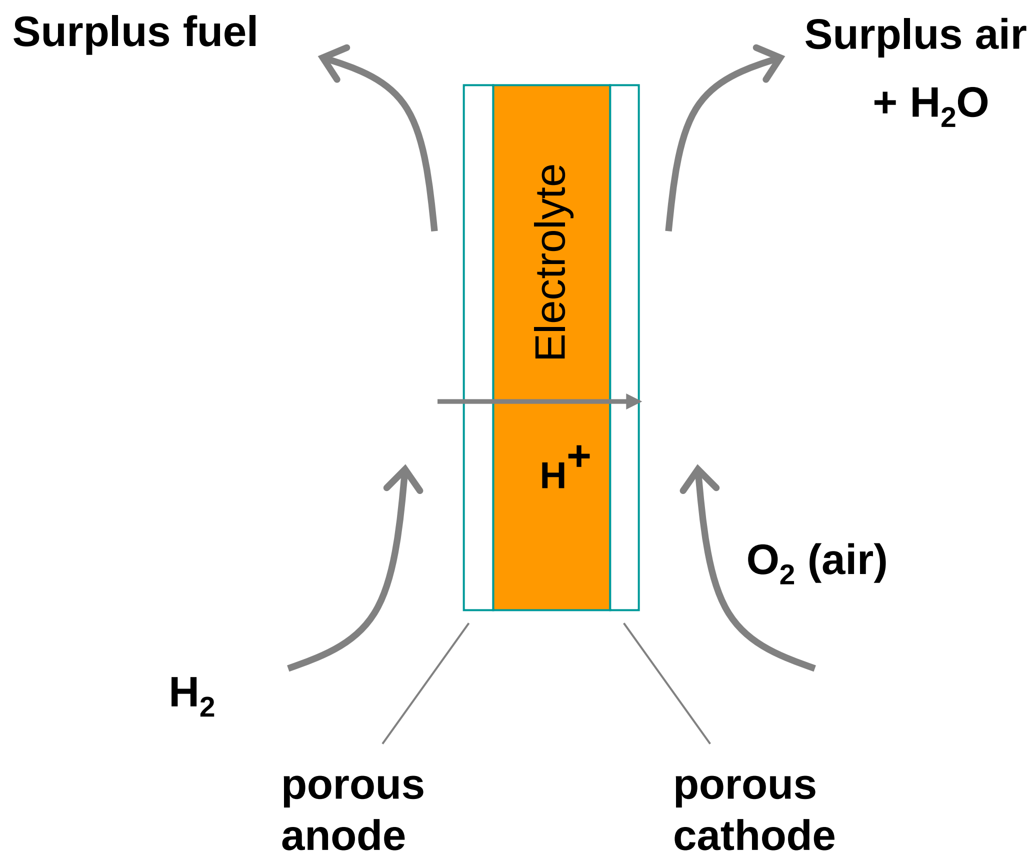
and

$$dS = dQ / T \ (2^{nd} \text{ Law})$$

it follows that

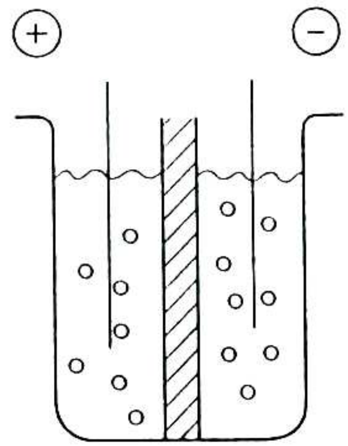
$$\eta_c = 1 - T_2 / T_1$$

Fuel Cell Principle: Surface Reaction



Hydrogen Production: Electrolysis

Splitting of water by electric current



Cathode side	$2H_2O + 2e^-$	$\longrightarrow$	$H_2 + 2OH^-$
Anode side	$2OH^-$	$\longrightarrow$	$1/2\ O_2 + H_2O + 2e^-$
Overall reaction	H_2O	$\xrightarrow[2F]{}$	$H_2 + 1/2\ O_2$

F ... Faraday constant = 96.587 C/mol

Question: Definition of ‚cathode‘ and ‚anode‘?

Electrolysis Thermodynamics

$H_2O \xrightarrow{2F} H_2 + 1/2\ O_2$

Free enthalpy

$\Delta G^o = 237$ kJ/mol (at 25°C, 1 bar = ‚standard‘ conditions)
$= 2F\ U^o_o$

It follows that

$U^o_o = 1{,}23$ V

which is the voltage necessary for water splitting
(ideal case at standard conditions).

Electrolysis Overpotential

Due to kinetic processes and competition of ion reactions at the electrodes the technically necessary Voltage for electrolysis is considerably higher, generally at the order of 1,7 to 1,9 V.

The ideal amount of energy needed per Nm³ H_2 is

$$\Delta G^o / V_N = 237 \text{ kJ/mol} / 22{,}41 \text{ l/mol} = 3 \text{ kWh/Nm}^3$$

Standard electrolysers require about 4,2 to 4,8 kWh/Nm³

Question: lower or higher heating value? (LHV or HHV)

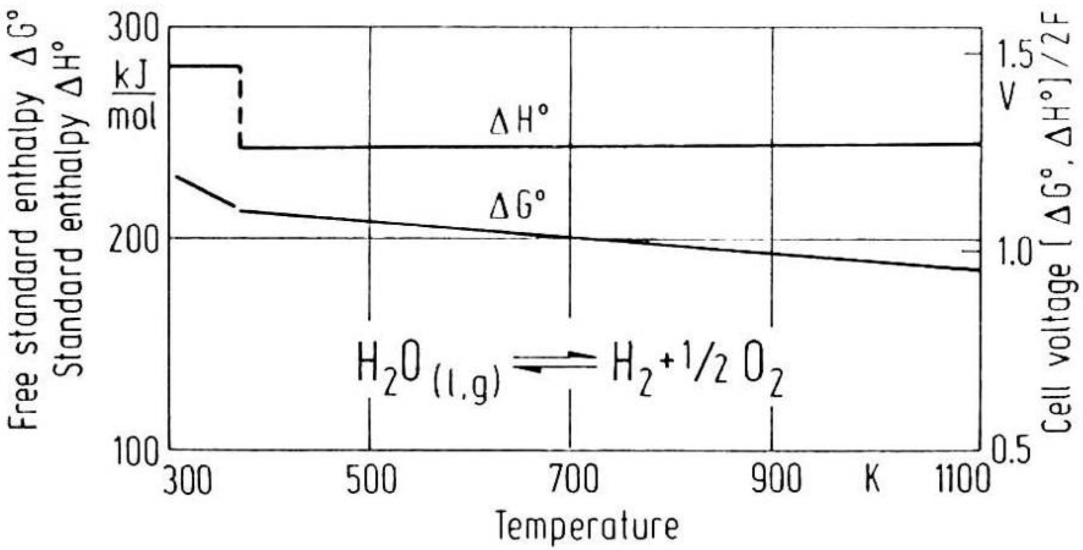
Electrolysis Temperature Dependency

Electrolysis Temperature Dependency

Due to the relationship

$$\Delta G^o = \Delta H^o - T \Delta S$$

The energy for splitting water can also be supplied by heat, not only electricity.



Graphics from Winter/Nitsch,1988

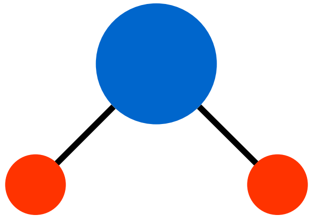
UNIVERSITY OF BIRMINGHAM

Gibbs free energy for H_2 - O_2 reaction

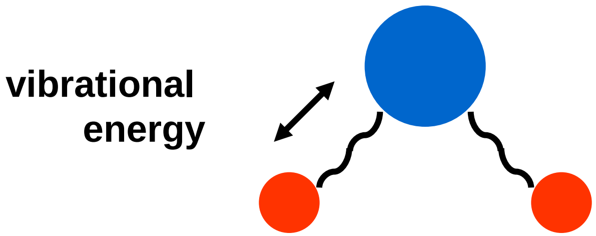
Form of water product	Temperature [°C]	G [kJ/mol]	U_o [V]
Liquid	25	-237,2	1,23
Liquid	80	-228,2	1,18
Gas	80	-226,1	
Gas	100	-225,2	1,17
Gas	200	-220,4	1,14
Gas	400	-210,3	1,09
Gas	1000	-177,4	0,92

Other fuels	Temperature [°C]	G [kJ/mol]	U_o [V]
Methanol	25	-698,2	1,21
Methane	25	-802,7	1,04
Alkali (battery)	25	-277	1,44

Generating Entropy? Loosing Energy?



$T = 0 \qquad \Delta H = \Delta G$



$T > 0 \qquad \Delta H = \Delta G + T\Delta S$

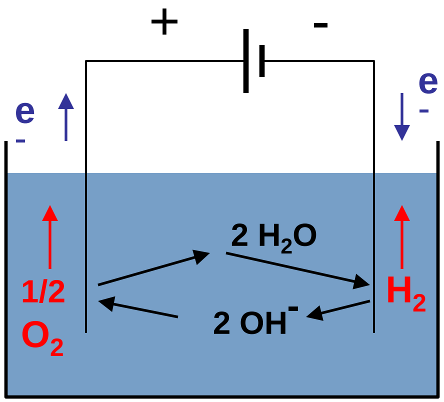
consequence:

- less energy needed for electrolysis
- less energy reclaimed in fuel cell

Electrode Definition

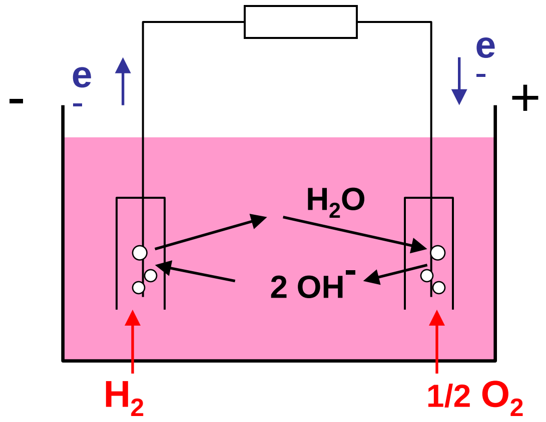
Where are cathode and anode?

Electrolysis



reverse reaction:

Fuel Cell
(=battery!)



Reaction Equilibrium: Fuel Cell Case

Cathode side	$1/2\ O_2 + H_2O + 2e^-$	$\rightarrow$	$2\ OH^-$
Anode side	$H_2 + 2\ OH^-$	$\rightarrow$	$2\ H_2O + 2e^-$
Overall reaction	$H_2 + 1/2\ O_2$	$\rightarrow$	H_2O

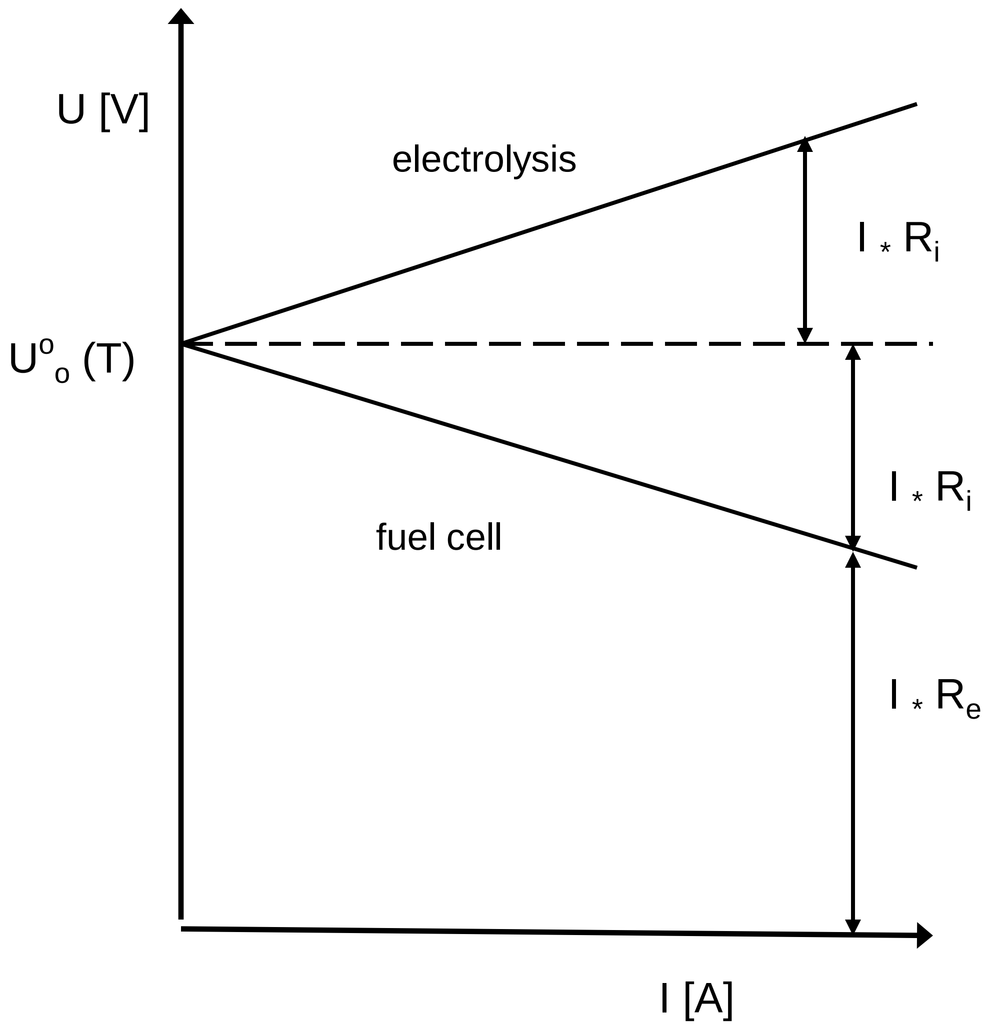
U_o (open circuit) is identical to that of electrolysis (but negative!)

$$\Delta G^o = 2F\ U^o_o = -237 \text{ kJ/mol (at STP, for } H_2 - O_2 \text{ cell)}$$

$$U^o_o = 1{,}23 \text{ V (for convenience, U is not marked as negative)}$$

i.e. energy is <u>released</u>.

Schematic Voltage Characteristics: Electrolysis and Fuel Cell



internal resistance
due to non-ideal conductibility
resulting in heat produced a.o.

work delivered to external circuit

Fuel Cell Efficiency

1. Efficiency = useful output / total input

$$\eta = Q_{el} / -\Delta H$$

2. Ambiguity: HHV or LHV?

3. Maximum possible efficiency (thermodynamic efficiency)

$$\eta = \Delta G / \Delta H$$

assuming that all change in Gibbs free energy can be transformed to electricity

alternative: $\eta = U / U^o_o$ (since $U = -\Delta H / 2F$)

Compare to Carnot efficiency $(T_1 - T_2) / T_1$ ($T_{1,2}$ in [K]) and Betz efficiency (58%)

Maximum Efficiency as Function of Temperature

Form of water product	Temperature [°C]	G [kJ/mol]	U_o [V]	η
Liquid	25	-237,2	1,23	83%
Liquid	80	-228,2	1,18	80%
Gas	80	-226,1		
Gas	100	-225,2	1,17	79%
Gas	200	-220,4	1,14	77%
Gas	400	-210,3	1,09	74%
Gas	1000	-177,4	0,92	62%

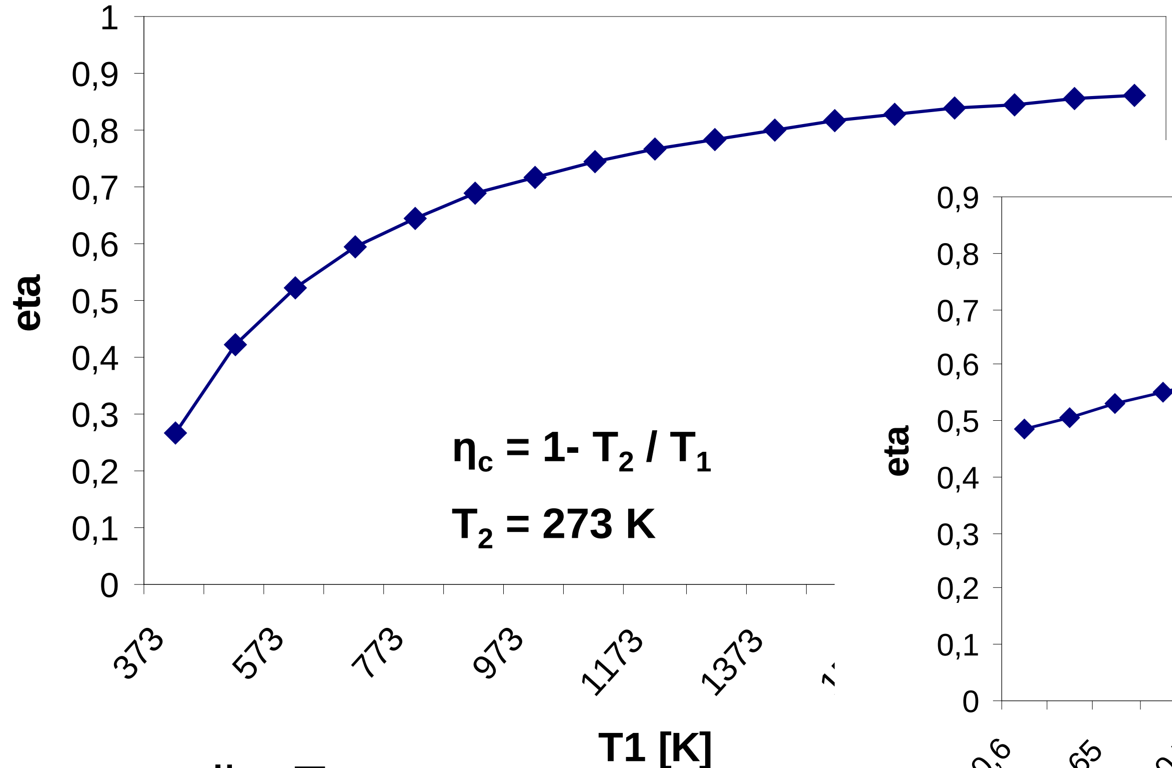
Some Fuel Cell Principal Properties

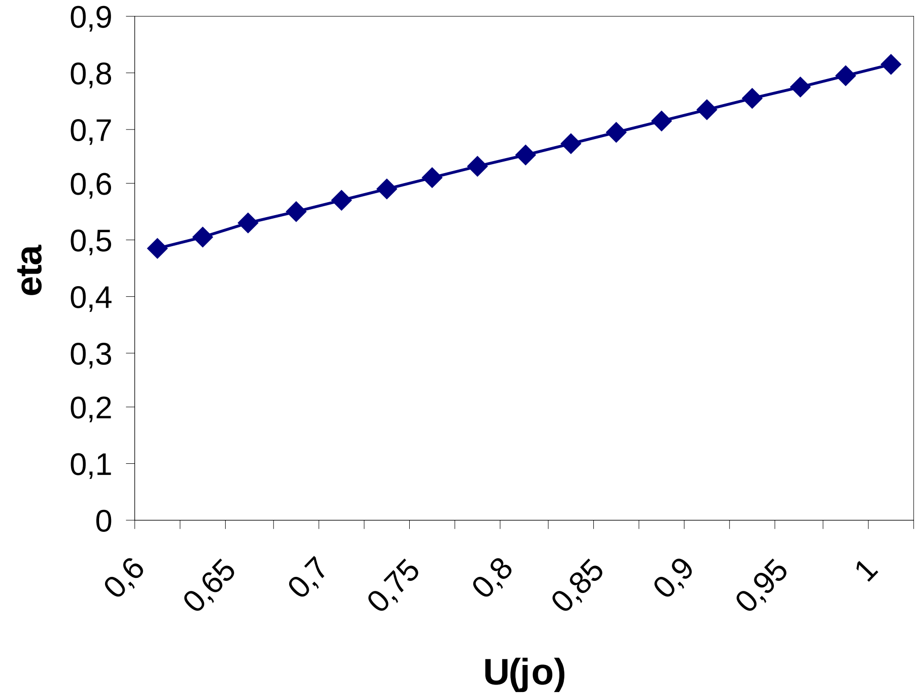
1. not limited by Carnot efficiency (~ $(T_1-T_2)/T_1$),
   only by electrochemical, kinetic and ohmic losses
2. modular
3. low noise
4. exhaust emission predominantely water (and maybe CO_2)
5. no moving parts

ergo:

- efficient and low-emission energy conversion technology

Increasing Efficiencies



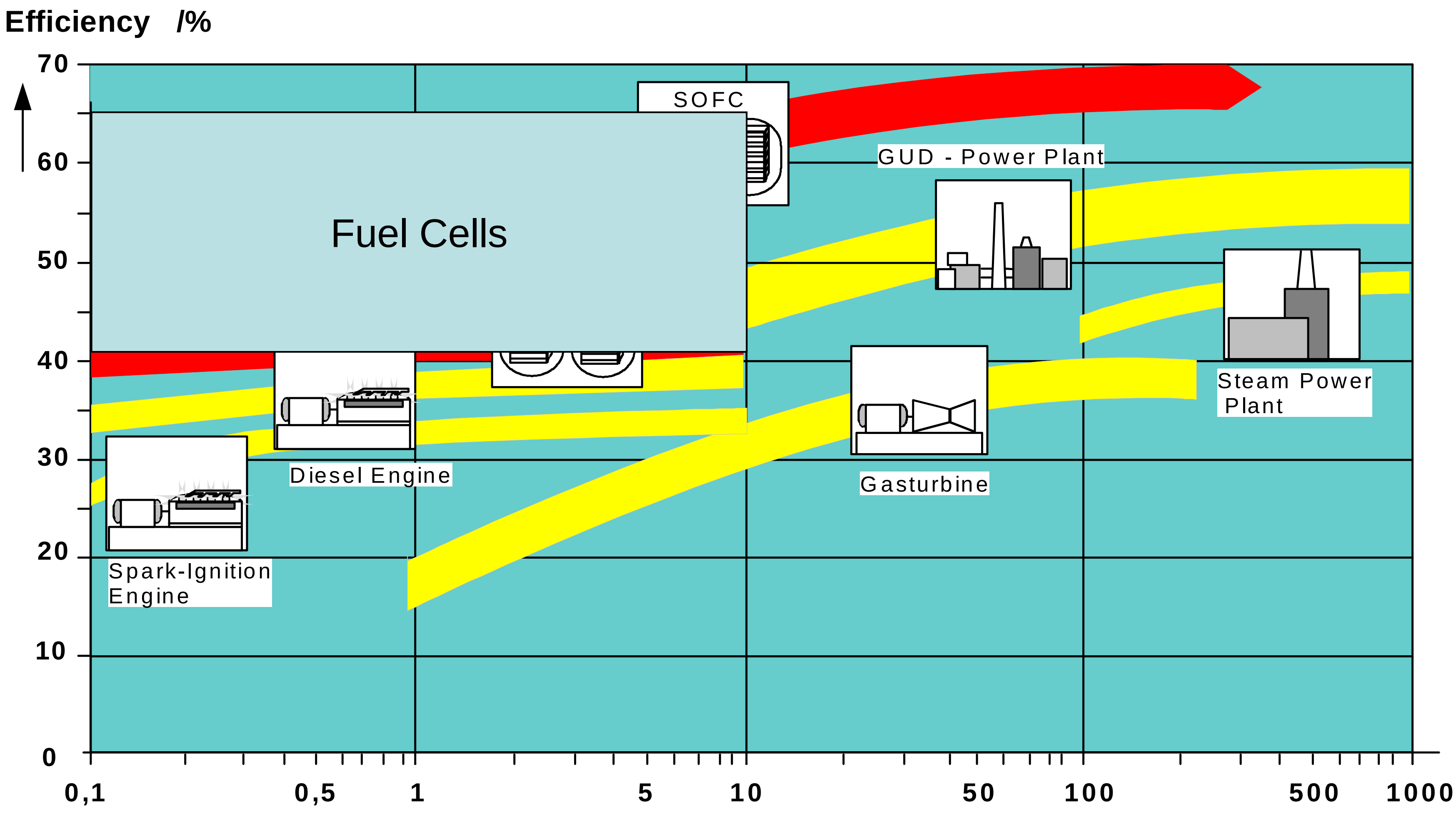


$\lim T_1 \to \infty$

$\lim T_2 \to 0$

$\lim U \to U^o_o$

High Efficiency Electricity Production



Upper Limiting Curve: Future Technology.
(Development tendency: GT / GUD: 2000 ; SOFC: 2010).
Lower Limiting Curve: Actual Technology.

An Introduction to Energy and Efficiency

Overview of Indicators

- Efficiency
  * of a single process
  * of a process chain
  * of energy services
- Primary energy consumption
  * direct
  * cumulative energy
- Fossil energy consumption
- Direct emissions
- Direct & indirect emissions (LCA)
- Energy payback (harvest factor)
- Externalities

Energy Efficiency Definitions

∢ = (desired) energy output / (necessary) energy input

conventional:

energy input given as lower heating value (LHV)

result (example): out of 1 Nm^3 of natural gas equivalent to 10 kWh, 1 kWh is disregarded

reason: 10% of the combustion energy is contained in the exhaust gas as water vapour and not sensible heat

→ ∢ is calculated approx. 10% higher than corresponds to the factual chemical energy content of the fuel

Energy Efficiency Definitions /2

correct (but unconventional):

energy input given by higher heating value (HHV)

→ ≺ corresponds to the factual chemical energy content of the fuel and gives the full picture of the conversion technology

≺ = energy output / energy input (HHV)

Efficiency and Efficiency Chains

PE primary energy
UE useful energy
CO combustion

Conventional boiler

1 PE → **CO** → η_{LHV} = 0,90 UE (heat)

CO → η_{HHV} = 0,81 UE (heat)

CO ↓ CO_2 NO_x

Condensing boiler

1 PE → **CO** → η_{LHV} = 1,05 UE (heat)

CO → η_{HHV} = 0,95 UE (heat)

CO ↓ CO_2

η_{therm} = 105 % LHV

η_{therm} = 95 % HHV

Efficiency and Efficiency Chains /2

PE primary energy
UE useful energy
EG electricity generation

Coal or Nuclear power plant

1 PE $\longrightarrow \boxed{\textbf{EG}} \longrightarrow$ 0,33 UE

$\downarrow CO_2$ $\downarrow NO_x$

Combined Cycle power plant

1 PE $\longrightarrow \boxed{\textbf{EG}} \longrightarrow$ 0,42 UE

$\downarrow CO_2$ $\downarrow NO_x$

Renewable Energy power plant

$\boxed{\textbf{EG}} \longrightarrow$ 1 UE (= 1 PE)

Efficiency and Efficiency Chains /3

PE primary energy
UE useful energy
EG electricity generation

Average German Electricity Grid

$$1\ \text{PE} \rightarrow \boxed{\textbf{EG}} \rightarrow 0{,}33\ \text{UE}$$

$\downarrow CO_2$ $\downarrow NO_x$

reference case

Gas Engine CHP

$$1\ \text{PE} \rightarrow \boxed{\textbf{CHP}}$$

$\downarrow CO_2$ $\downarrow NO_x$

$\nearrow$ 0,6 UE heat $\leftarrow$ 0,7 PE **condensing boiler**

$\searrow$ 0,3 UE electricity $\leftarrow$ 0,91 PE **electricity grid**

$\sum = 1{,}61$ PE

Efficiency and Efficiency Chains /4

PE	primary energy
UE	useful energy
FC	fuel cell
FP	fuel processing

Natural Gas PEFC Residential System

1 PE → **FP** ($\eta = 0,85$) → CO_2 → **FC** ($\eta = 0,87$) → H_2O

0,41 UE heat

0,34 UE electricity

reference case

← 0,43 PE **cond. boiler**

← 1,03 PE **electricity grid**

$\sum$ = 1,46 PE

Natural Gas SOFC Residential System

1 PE → **FC** ($\eta = 0,80$) → H_2O, CO_2

0,33 UE heat

0,50 UE electricity

reference case

← 0,35 PE **cond. boiler**

← 1,51 PE **electricity grid**

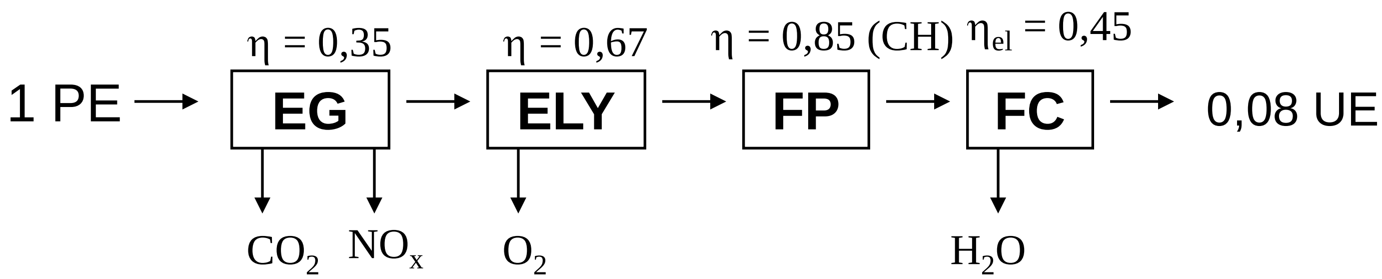
$\sum$ = 1,86 PE

Efficiency and Efficiency Chains /5

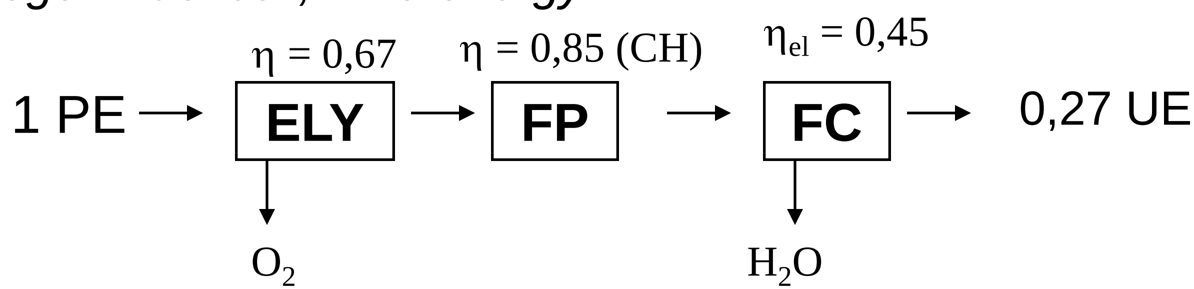
UNIVERSITY OF BIRMINGHAM

PE	primary energy
UE	useful energy
EG	electricity generation
FP	fuel processing
CH	compressed hydrogen

Hydrogen Fuel cell, grid electricity



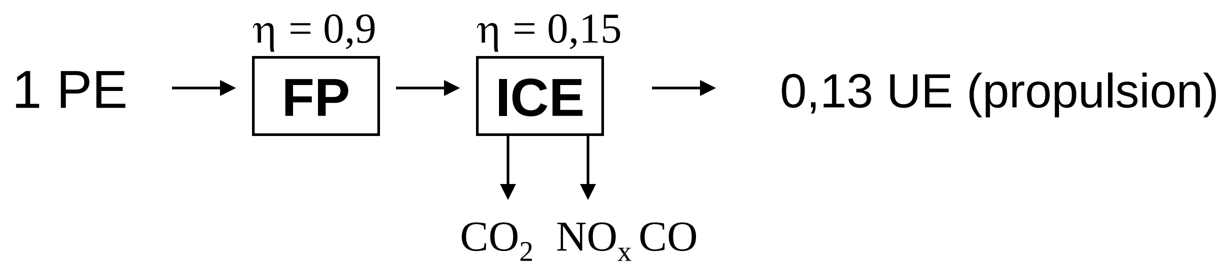
Hydrogen Fuel cell, wind energy



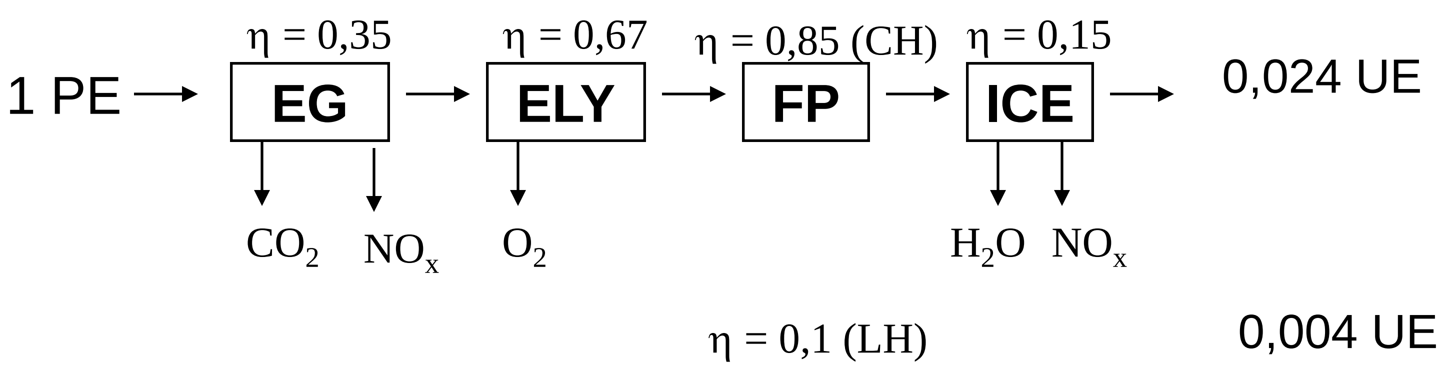
Efficiency and Efficiency Chains /6

PE primary energy
UE useful energy
EG electricity generation
ICE internal combustion engine
FP fuel processing
CH compressed H_2
LH liquid H_2

Internal combustion motor



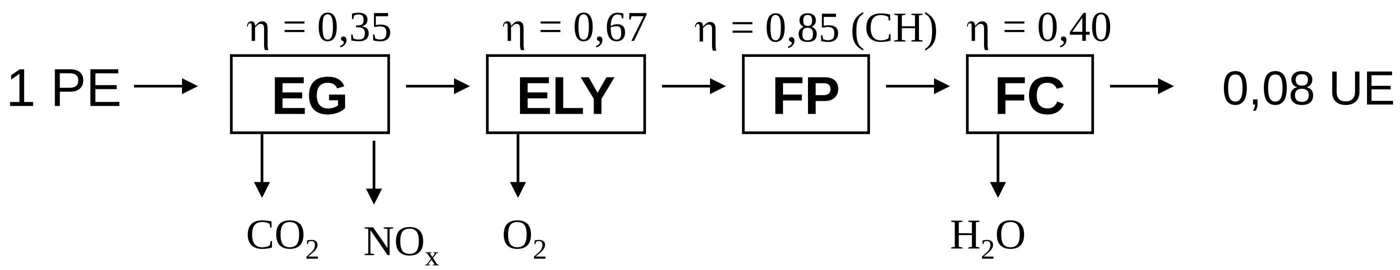
H_2 Internal combustion motor, grid electricity



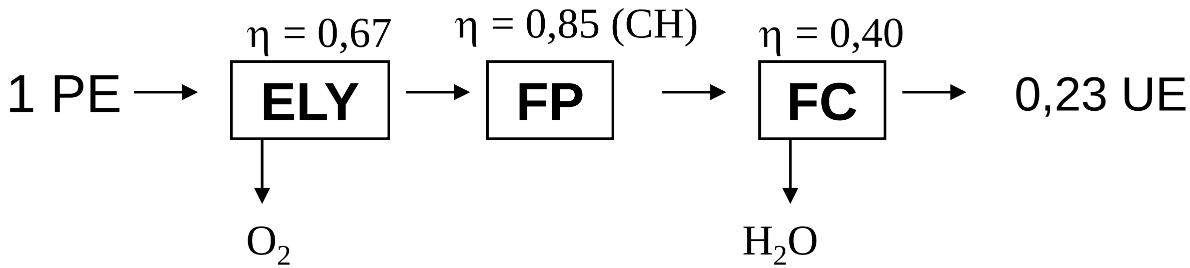
Efficiency and Efficiency Chains /7

PE	primary energy
UE	useful energy
EG	electricity generation
FC	fuel cell
FP	fuel processing
CH	compressed H_2

H_2 FC vehicle, grid electricity



H_2 FC vehicle, wind energy

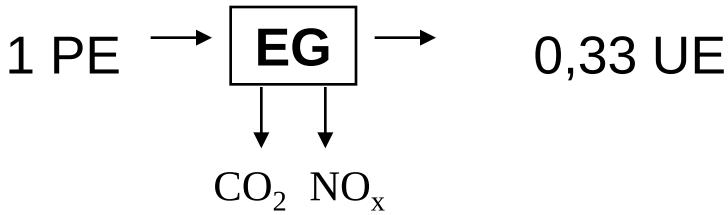


Efficiency and Efficiency Chains

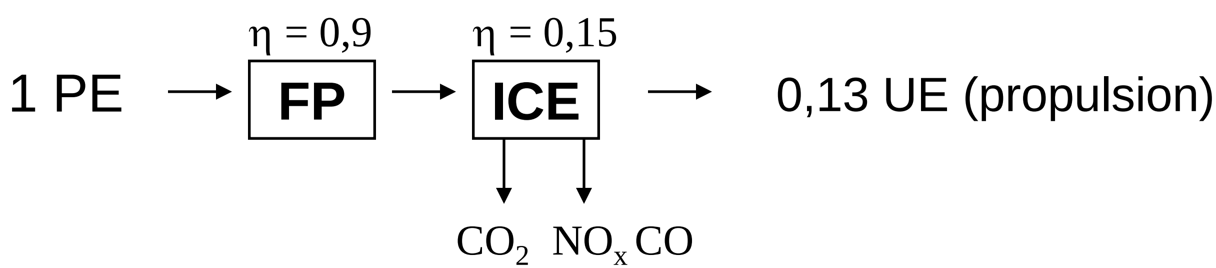
PE primary energy
UE useful energy

EG electricity generation
FP fuel processing
ICE internal combustion engine

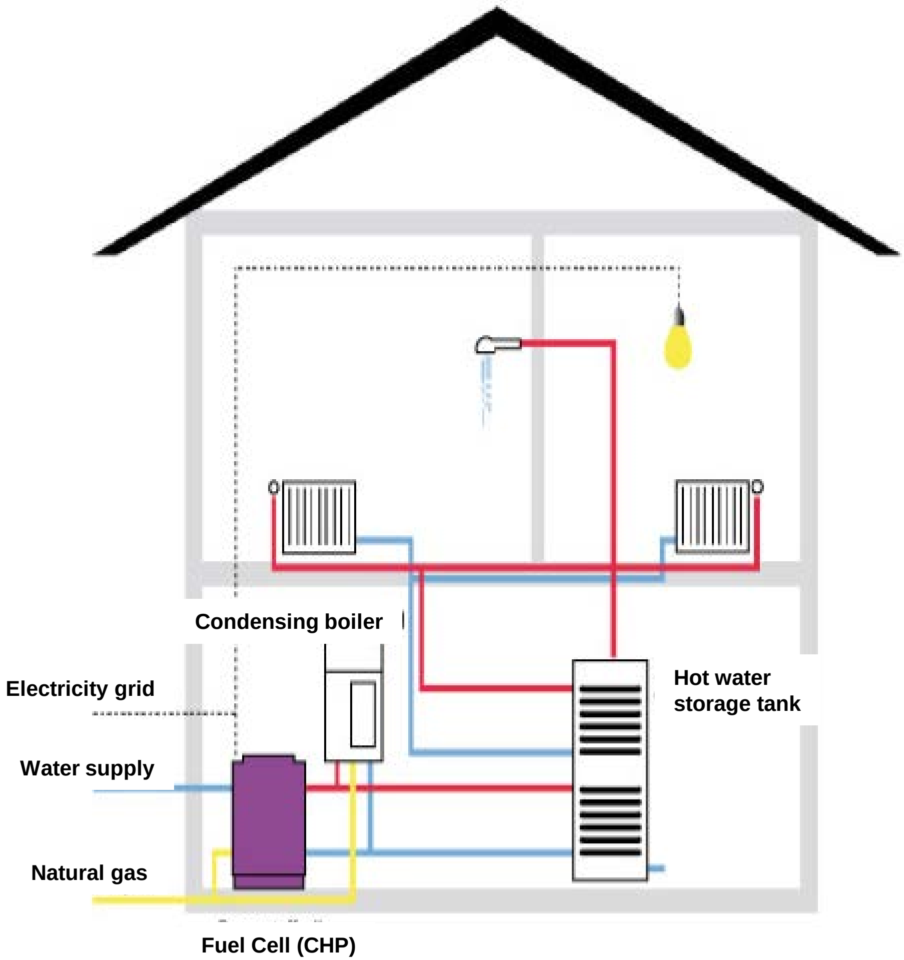
Coal or Nuclear power plant + grid



Internal combustion engine



Combined Heat and Power (CHP)

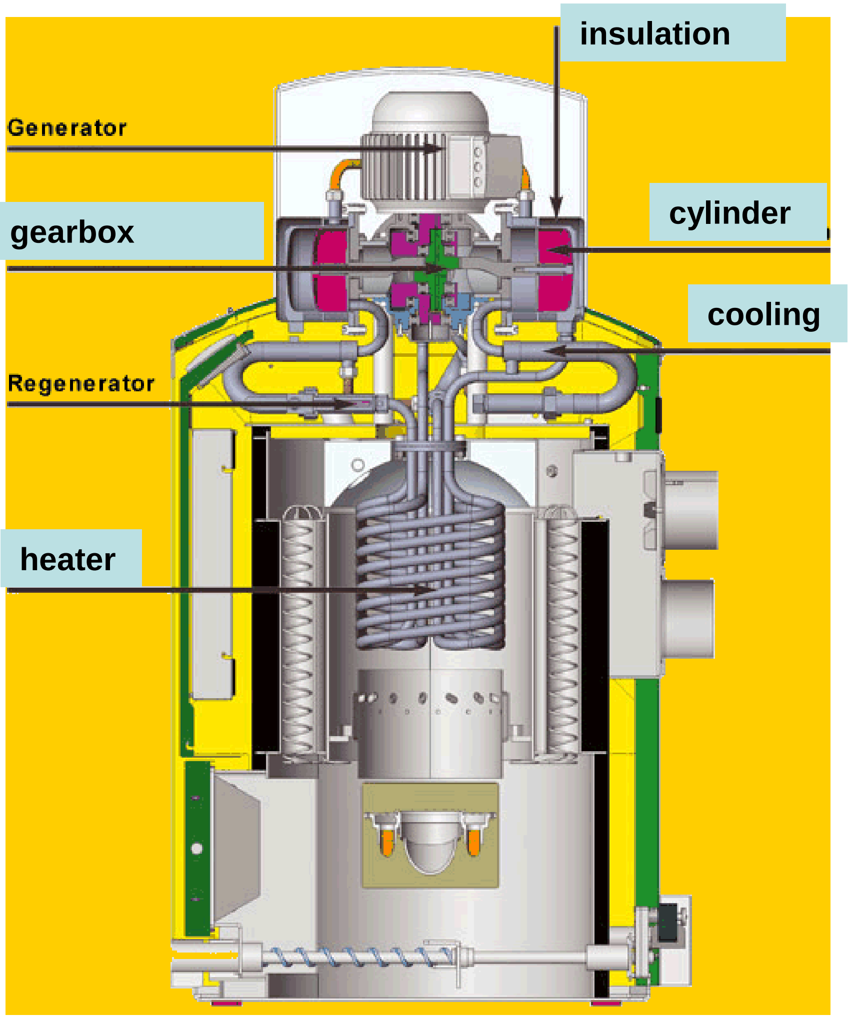


use of waste heat from electricity generation for heating purposes etc.

SenerTec ‚Dachs'
Hot water storage and buffer

photographs courtesy SenerTec

Micro-CHP – Stirling engine



graphics courtesy KWB

UNIVERSITY OF BIRMINGHAM

Efficiency and Efficiency Chains /2

PE	primary energy
UE	useful energy
EG	electricity generation

Gas Engine CHP

reference case

$\eta = 0{,}90$

1 PE → **CHP** → 0,6 UE heat ← 0,7 PE **condensing boiler**

CHP → 0,3 UE electricity ← 0,91 PE **electricity grid**

CHP ↓ CO_2 NO_x

$\sum$= 1,61 PE

Natural Gas SOFC Residential System

reference case

$\eta = 0{,}83$

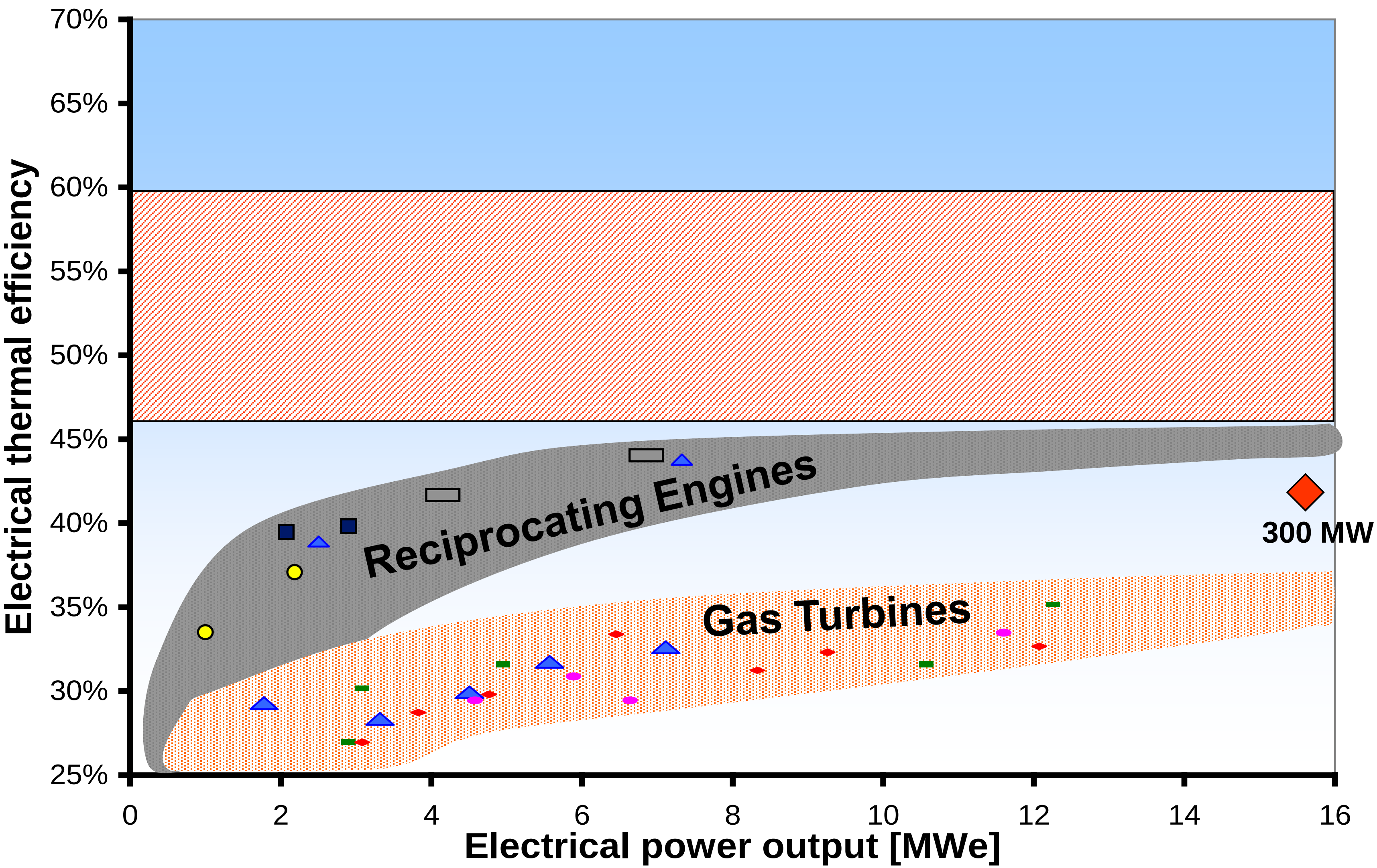
1 PE → **FC** → 0,33 UE heat ← 0,35 PE **cond. boiler**

FC → 0,50 UE electricity ← 1,51 PE **electricity grid**

FC ↓ H_2O CO_2

$\sum$ = 1,86 PE

CHP Unit Efficiencies

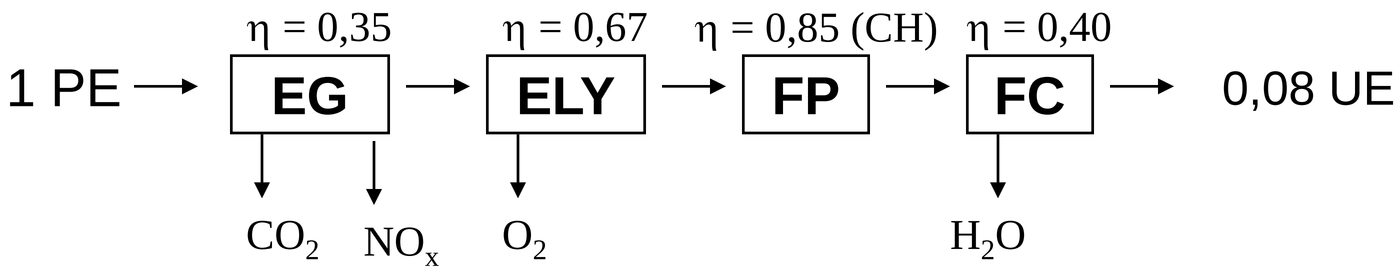


graph courtesy of RollsRoyce FCS

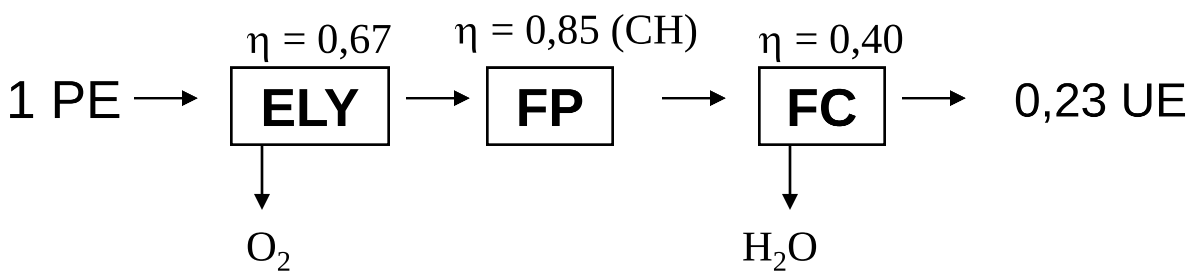
Efficiency and Efficiency Chains /3

PE primary energy
UE useful energy
EG electricity generation
FC fuel cell
FP fuel processing
CH compressed H_2

H_2 FC vehicle, grid electricity

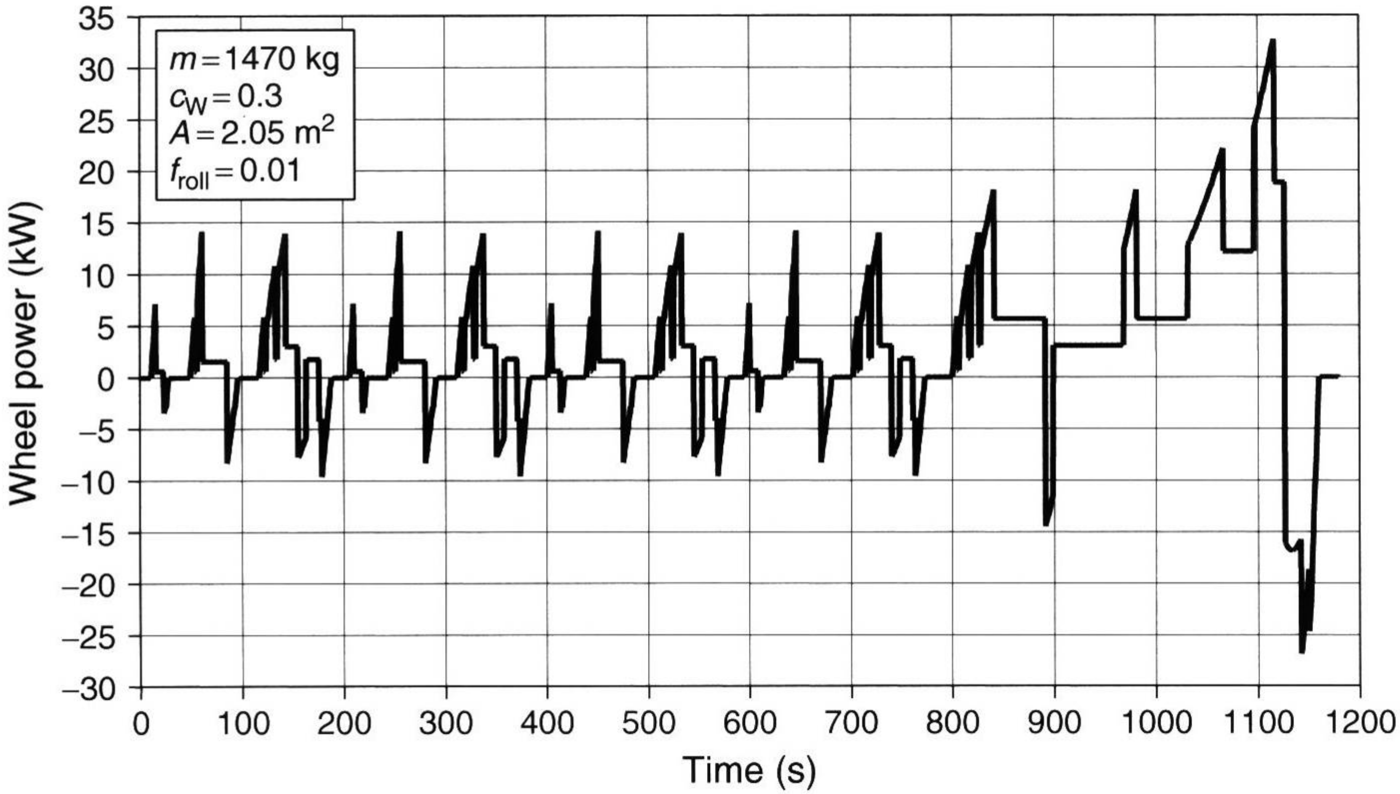


H_2 FC vehicle, wind energy



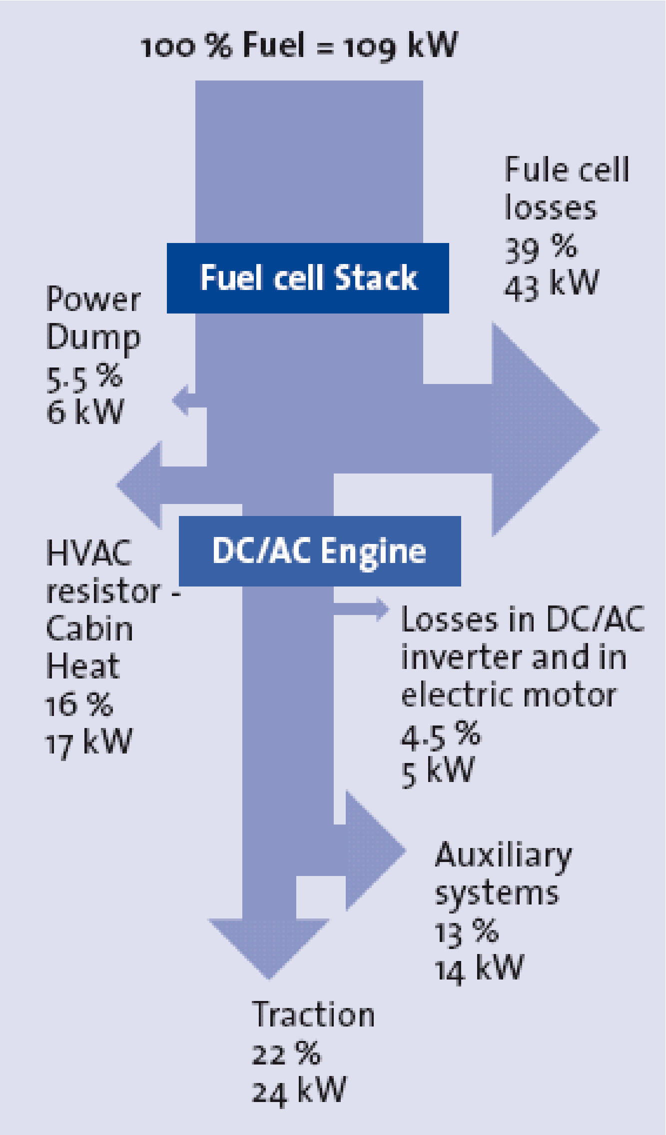
Vehicle Requirement Profile

New European Driving Cycle example



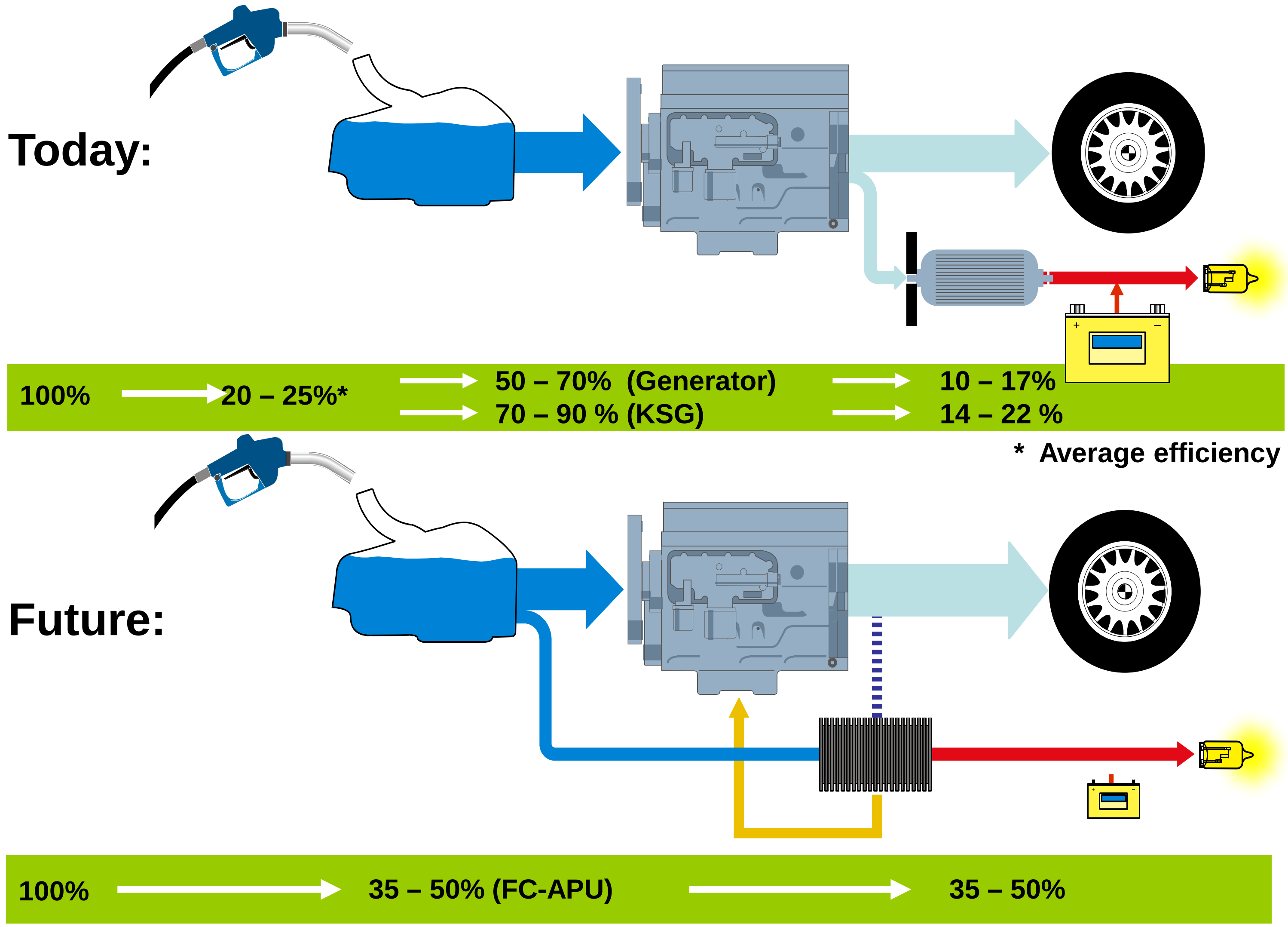
source: EU

CUTE Results: Total system efficiency



source: CUTE

Change in On-Board E-Power Generation



Graph: BMW

Cumulative Energy: Definitions

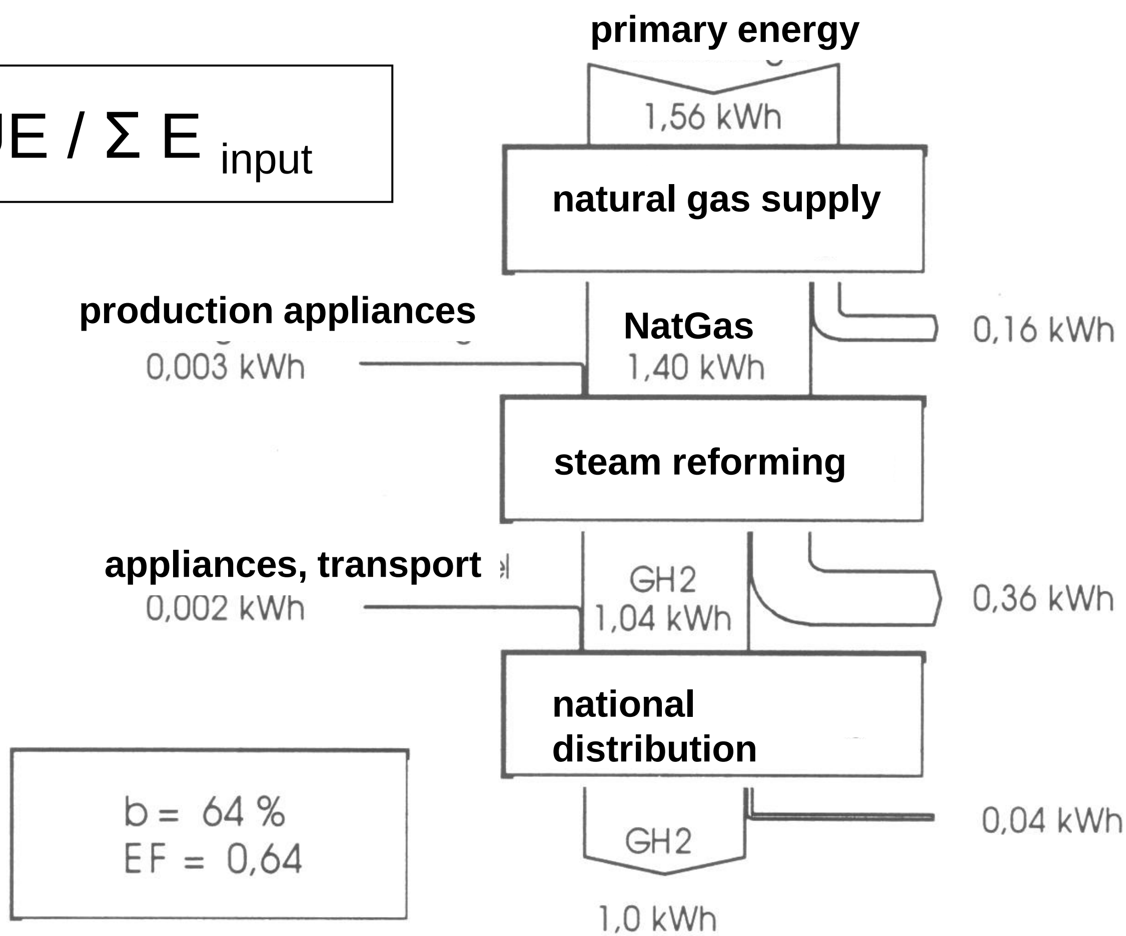
b = total chain energy efficiency
= (end) energy output / (primary) energy input

‚Energy input‘ includes all input, i.e. not only for operating the system, but also for building it.

EF = energy harvest factor
= energy output / fossil energy input

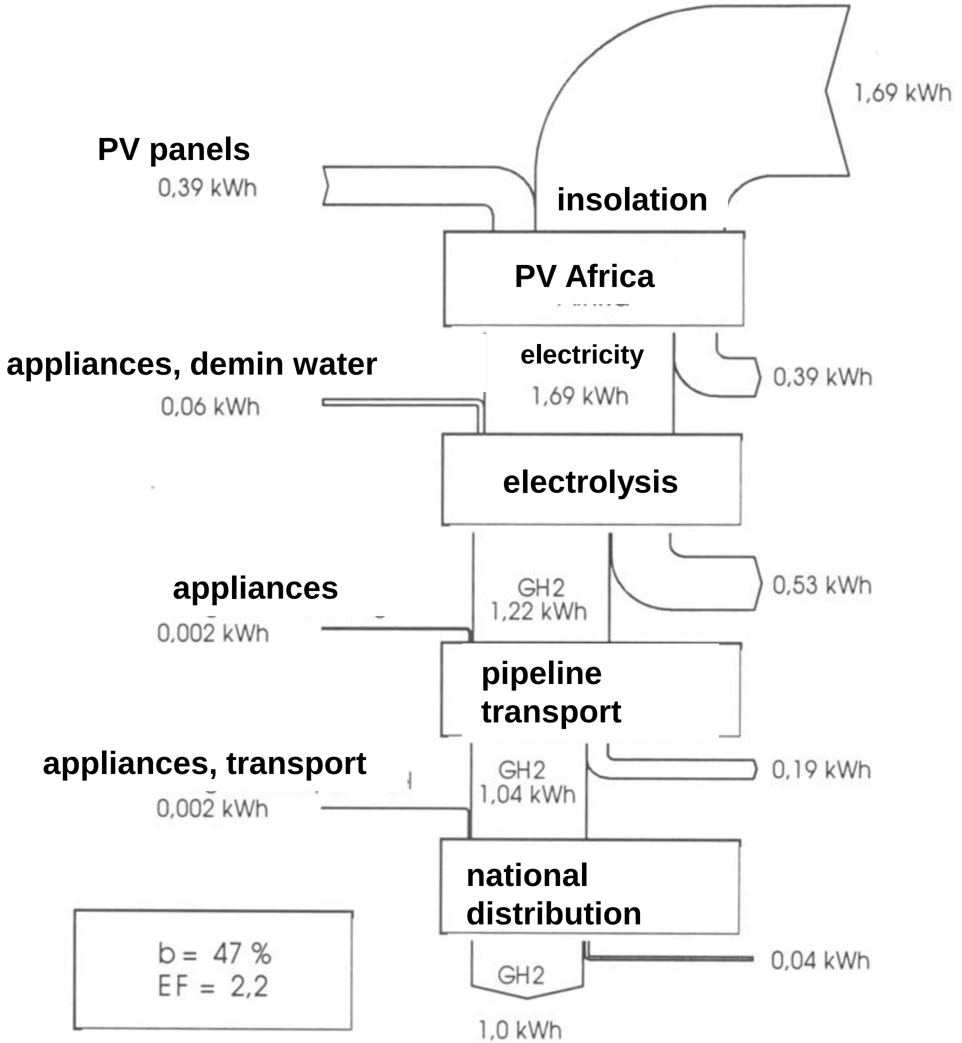
Cumulative Energy: NG Steam Reforming

$$b = UE / \Sigma E_{input}$$



source: FfE

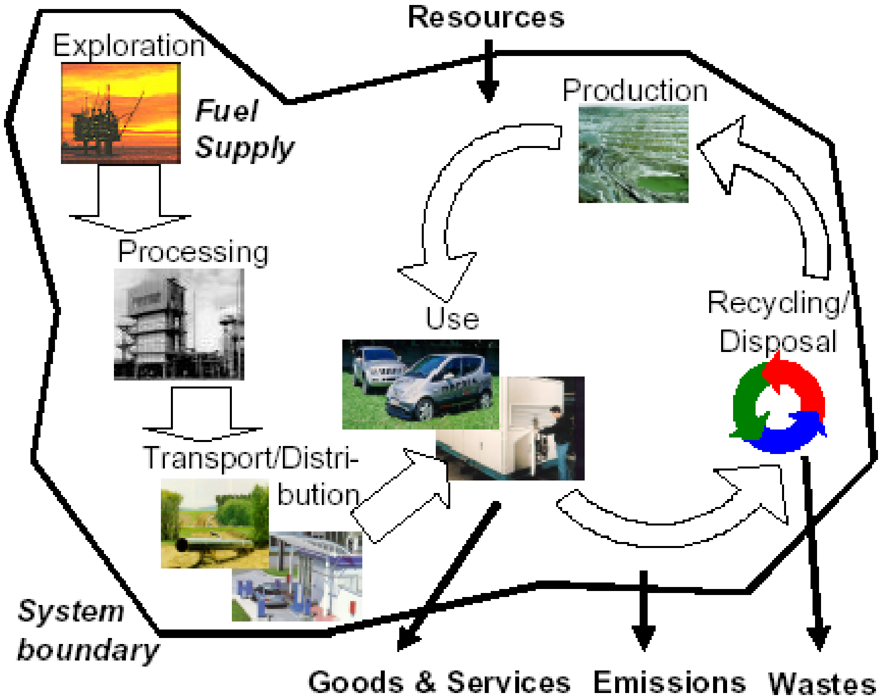
Cumulative Energy: PV-Hydrogen production



source: FfE

LCA Elements

Definition of boundaries



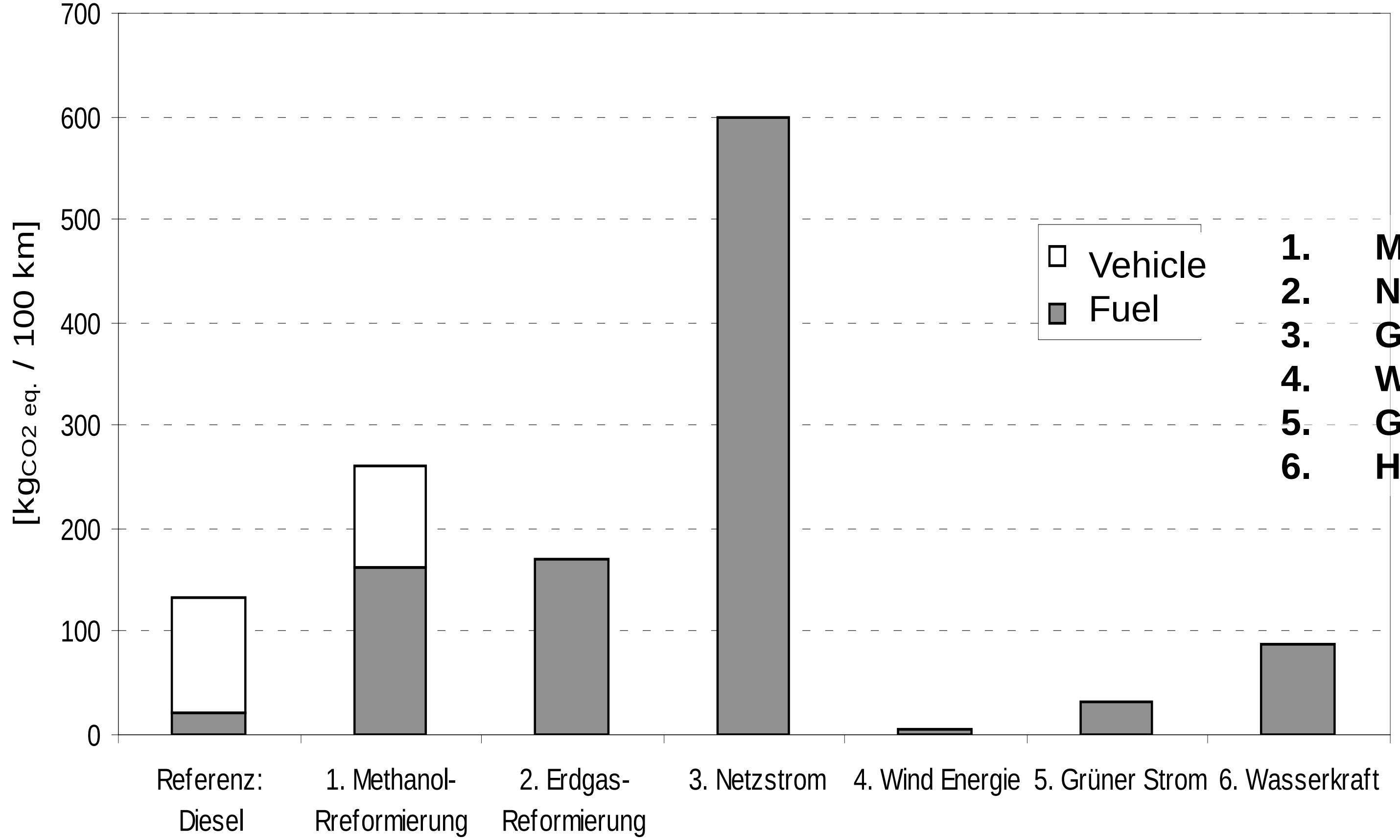
LCA Procedure

- Analysis of all process steps involved
- Cumulation of all specific emission and impact factors, i.e.
  kg CO_2 / kWh energy
  kg CO_2 / kg of building material
  kg SO_2 / kWh energy
  etc.
  Detail given by inclusion or omission of secondary, tertiary etc. sources (system boundary).

Goal: Comparison of base case with alternative variants

Well-to-Wheel Analysis (1)

CO_2 equiv. per 100 km

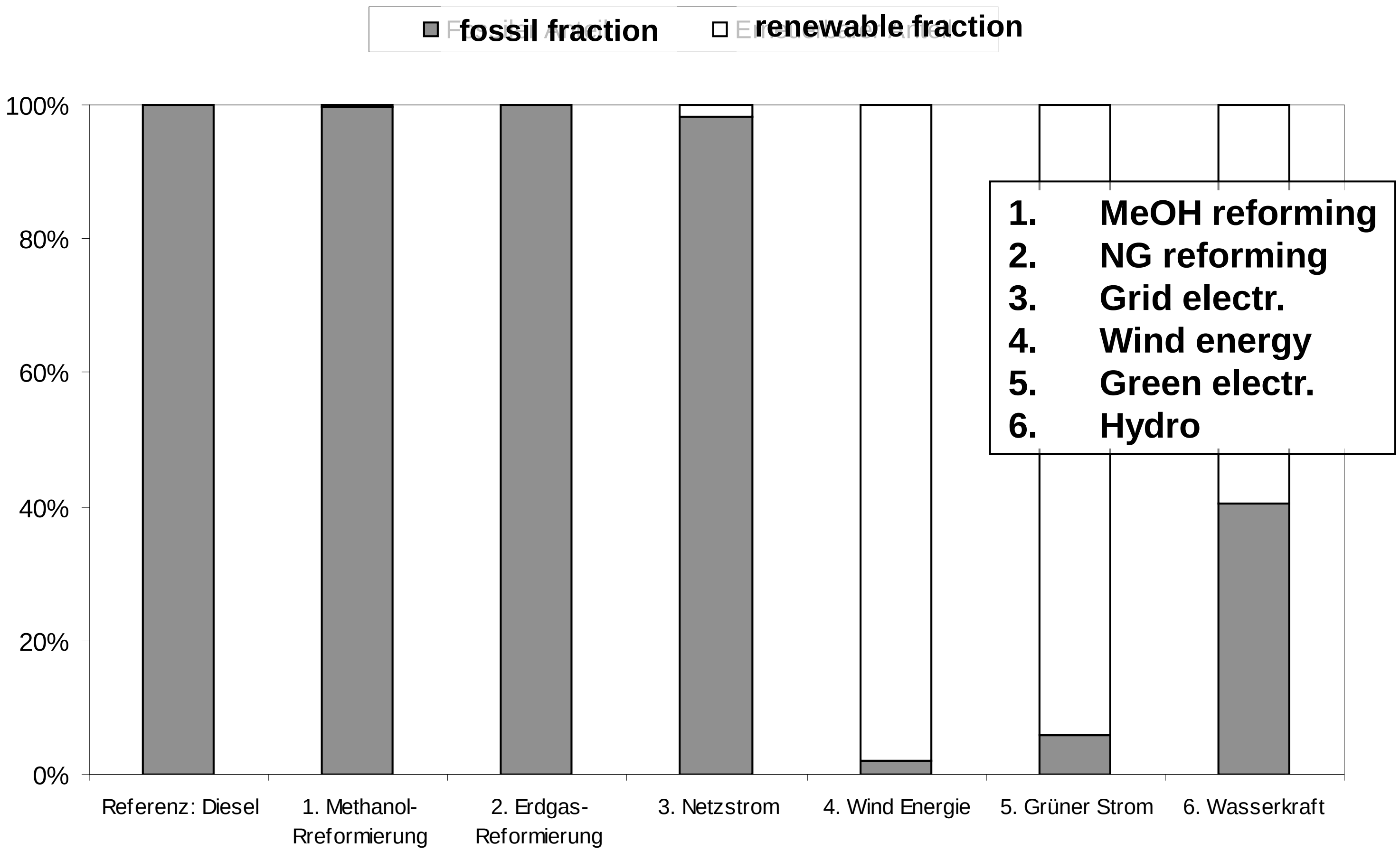


1. MeOH reforming
2. NG reforming
3. Grid electr.
4. Wind energy
5. Green electr.
6. Hydro

FC vehicle, various hydrogen production paths, base case: Diesel

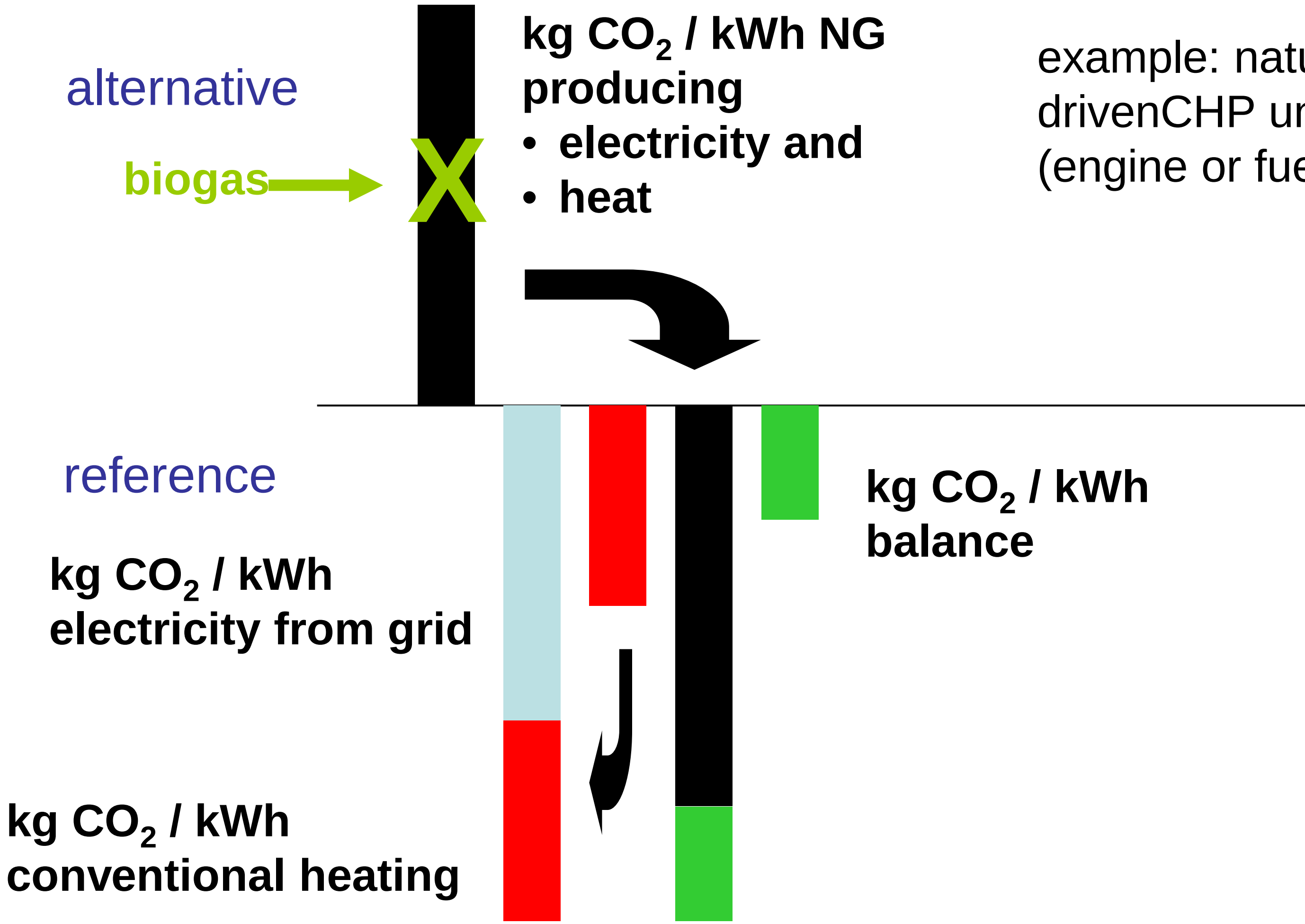
Well-to-Wheel Analysis (2)

Fossil fraction of energy



FC vehicle, various hydrogen production paths, base case: Diesel

Total Balance of Conversion: kg CO_2 / kWh



example: natural gas drivenCHP unit (engine or fuel cell)

Internal versus External Costs
examples for vehicle traffic

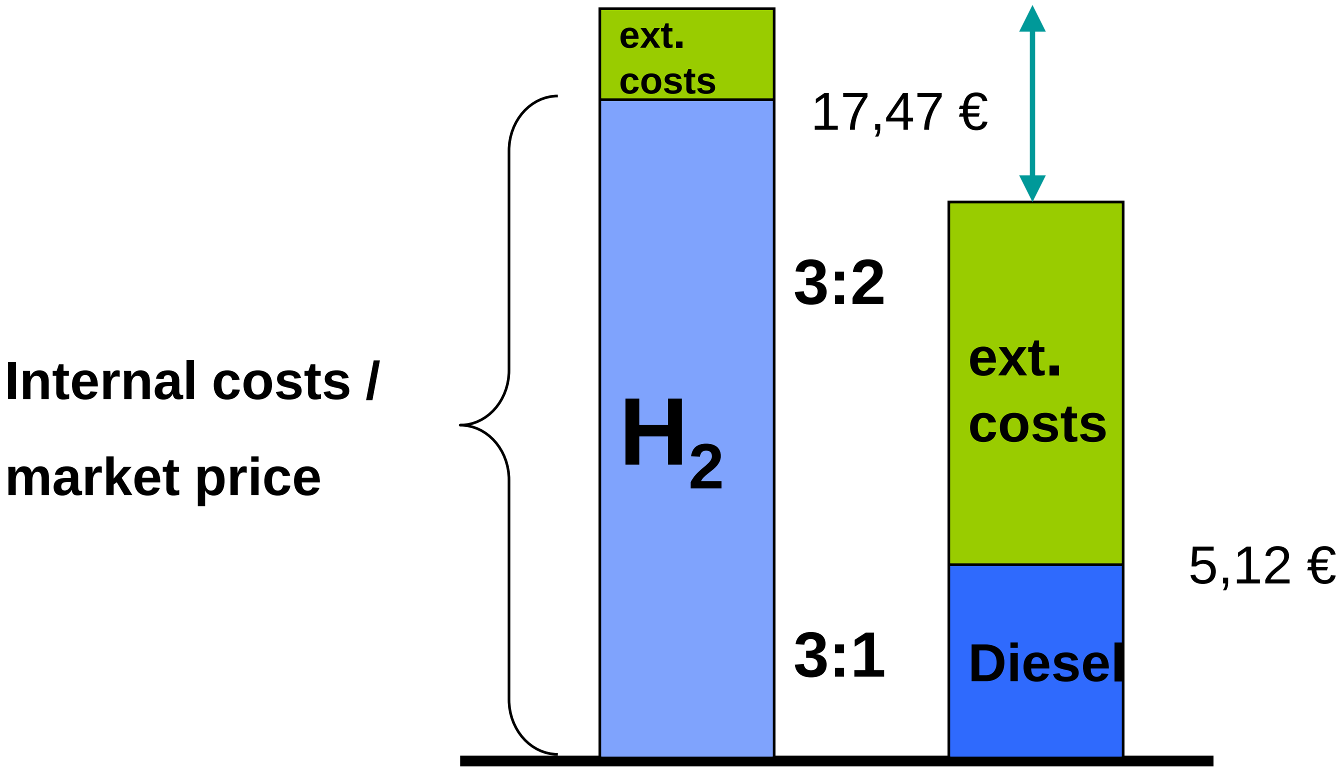
Internal costs:

- costs of production and delivery of vehicles and fuels
- taxes and levys
- market price (as a sum of the above plus company profit)

External costs

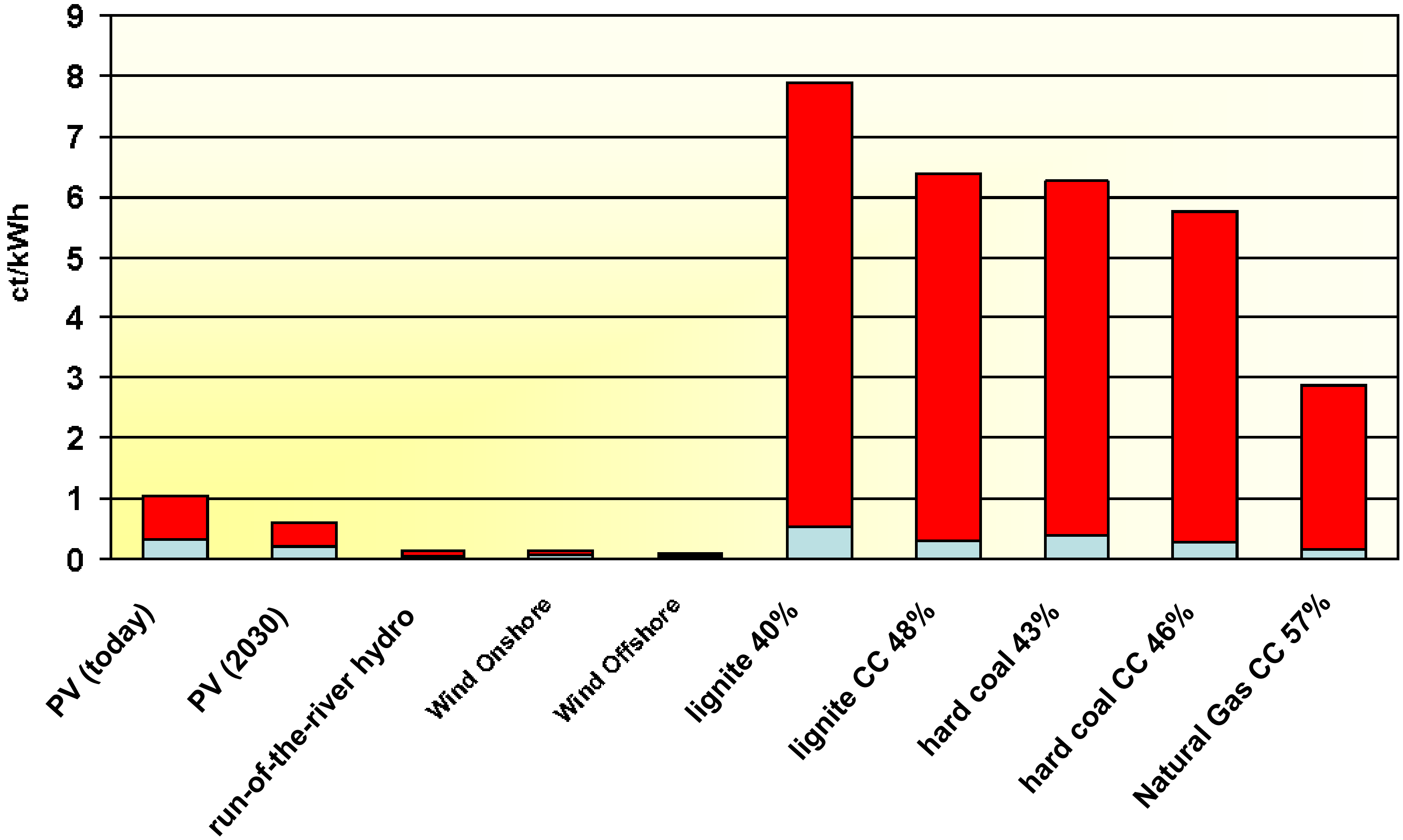
- costs caused for the society, but not attributed or attributable to single products or services
- health services due to environmental pollution
- health and other services due to noise pollution
- public services in safety, accident prevention etc.
- general costs of land use, rain run-off management etc.

Including External Costs



UNIVERSITY OF BIRMINGHAM

External Costs of Electricity Generation



source: DLR

Thanks for your Attention!

Any Questions?