Czech Hydrogen Days

Praha, 18 to 20 March 2015

UNIVERSITY OF BIRMINGHAM

Hydrogen from Biomass – A Complex Process

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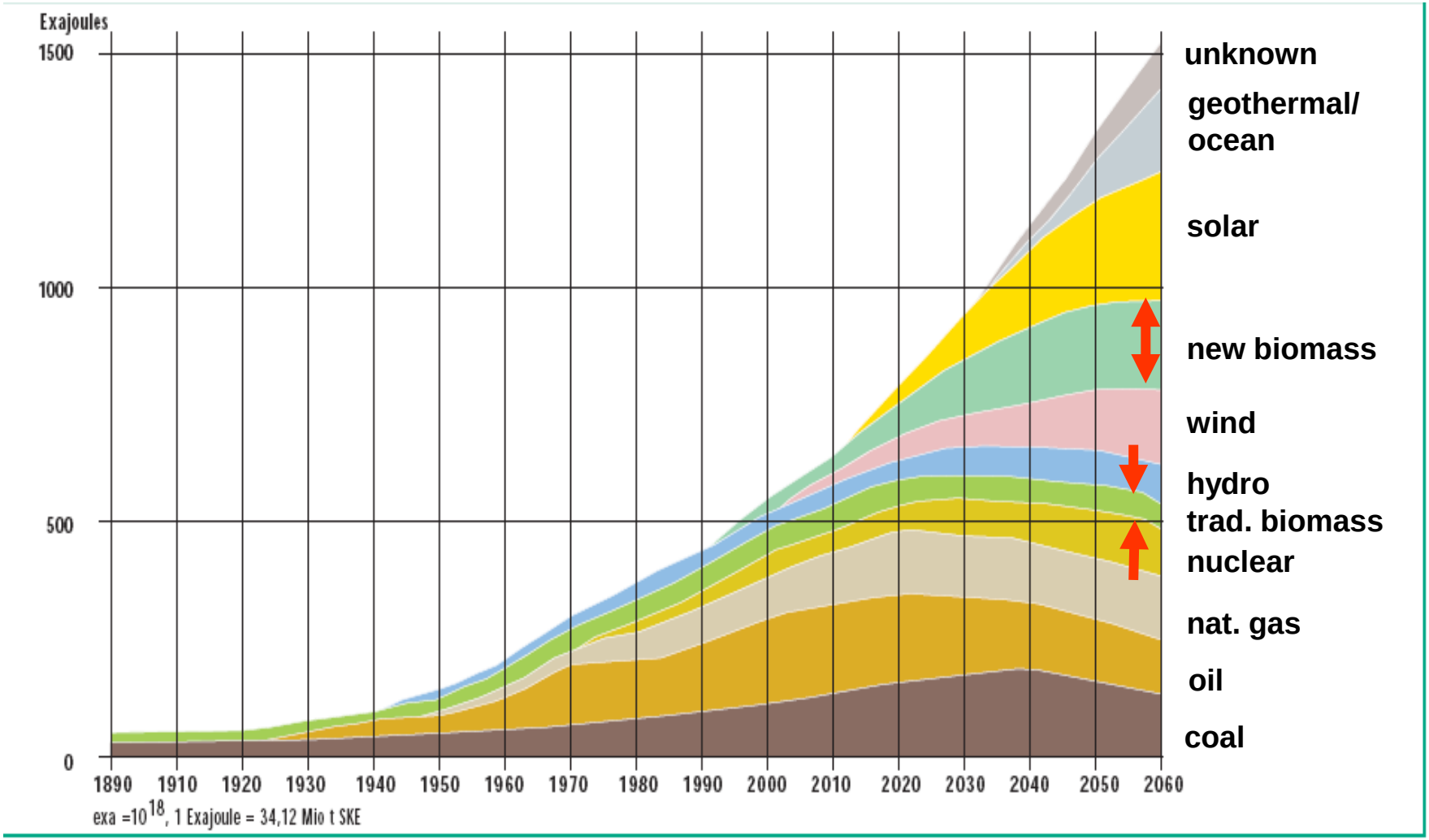
Shell World Energy Scenario (‚thinkable' development)



Source: Deutsche Shell , 1999

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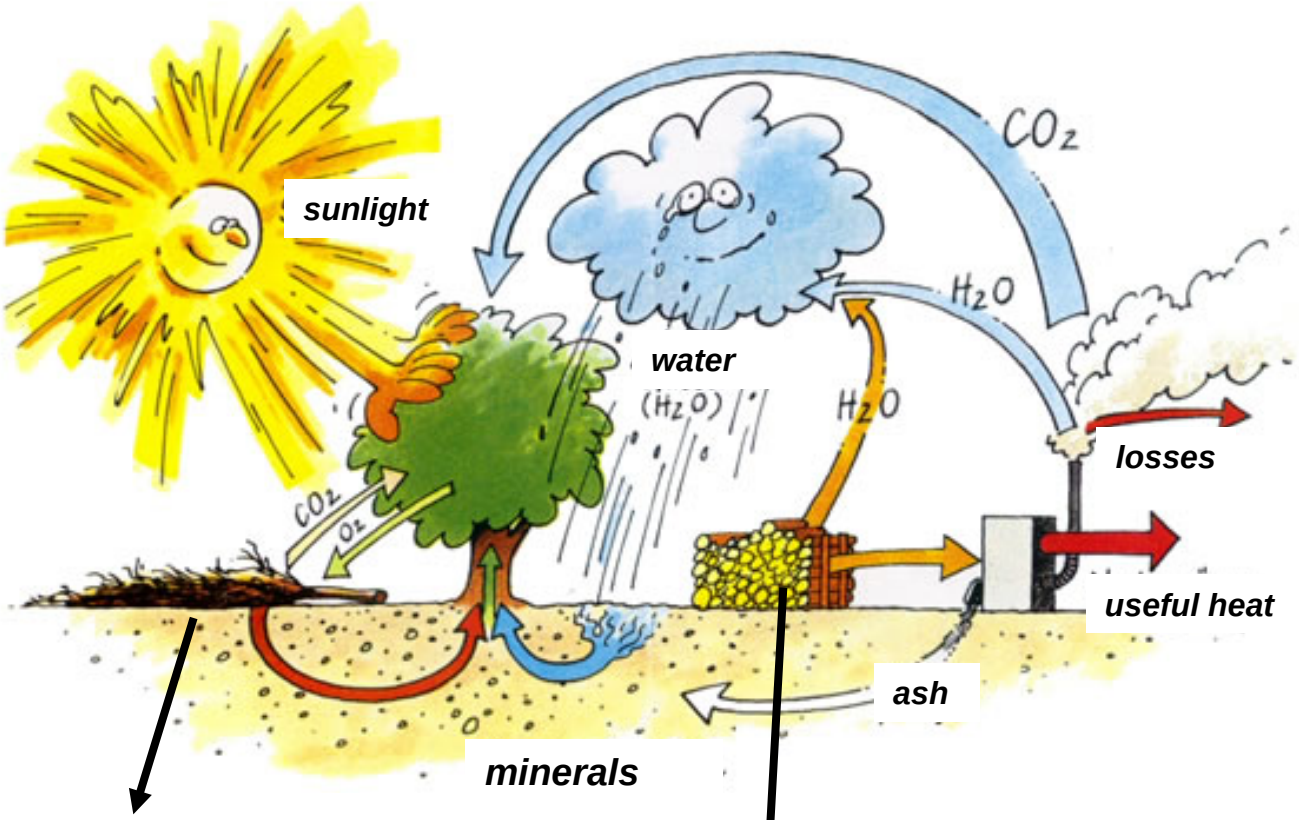
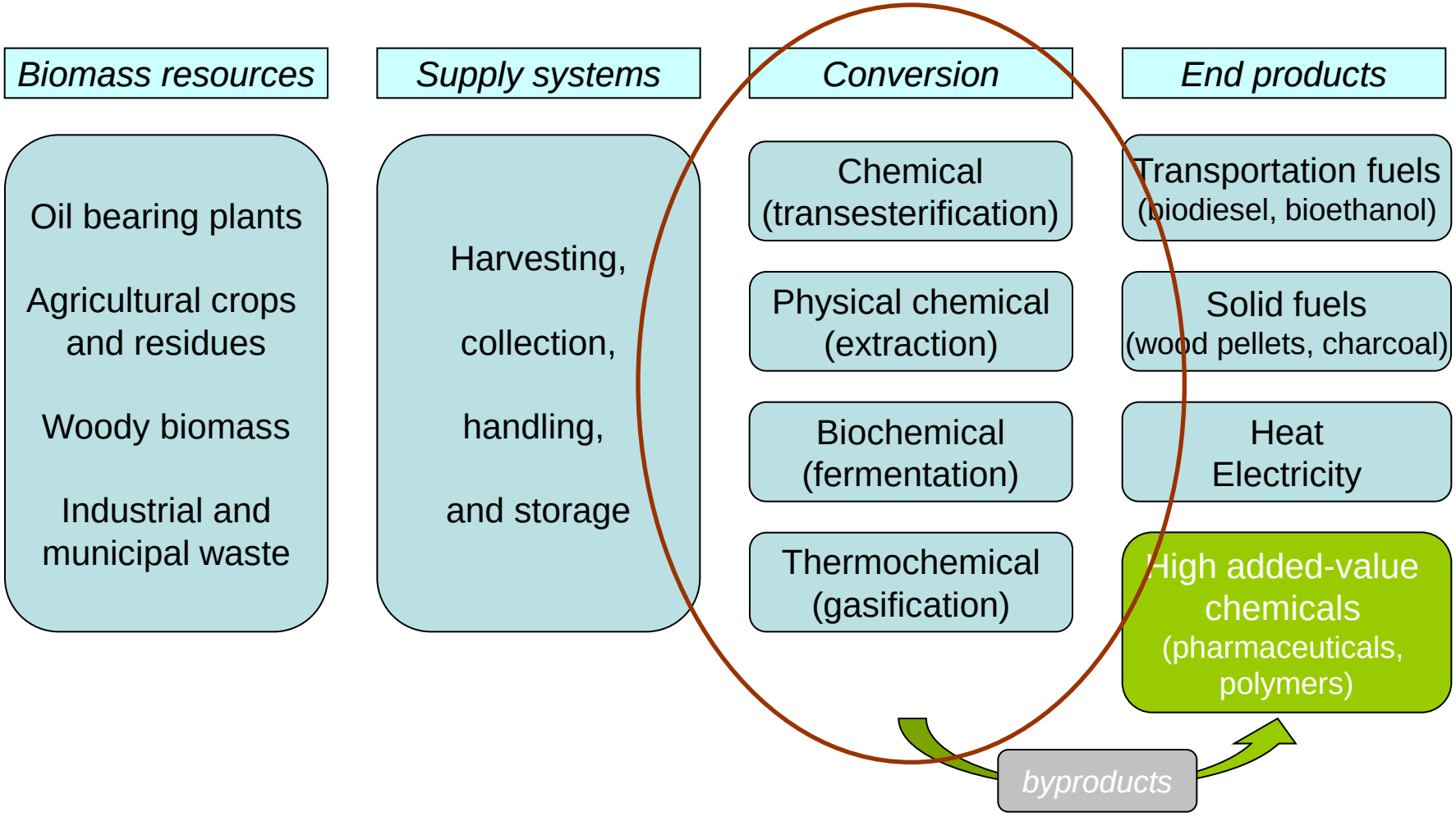
Natural CO_2 Recycling

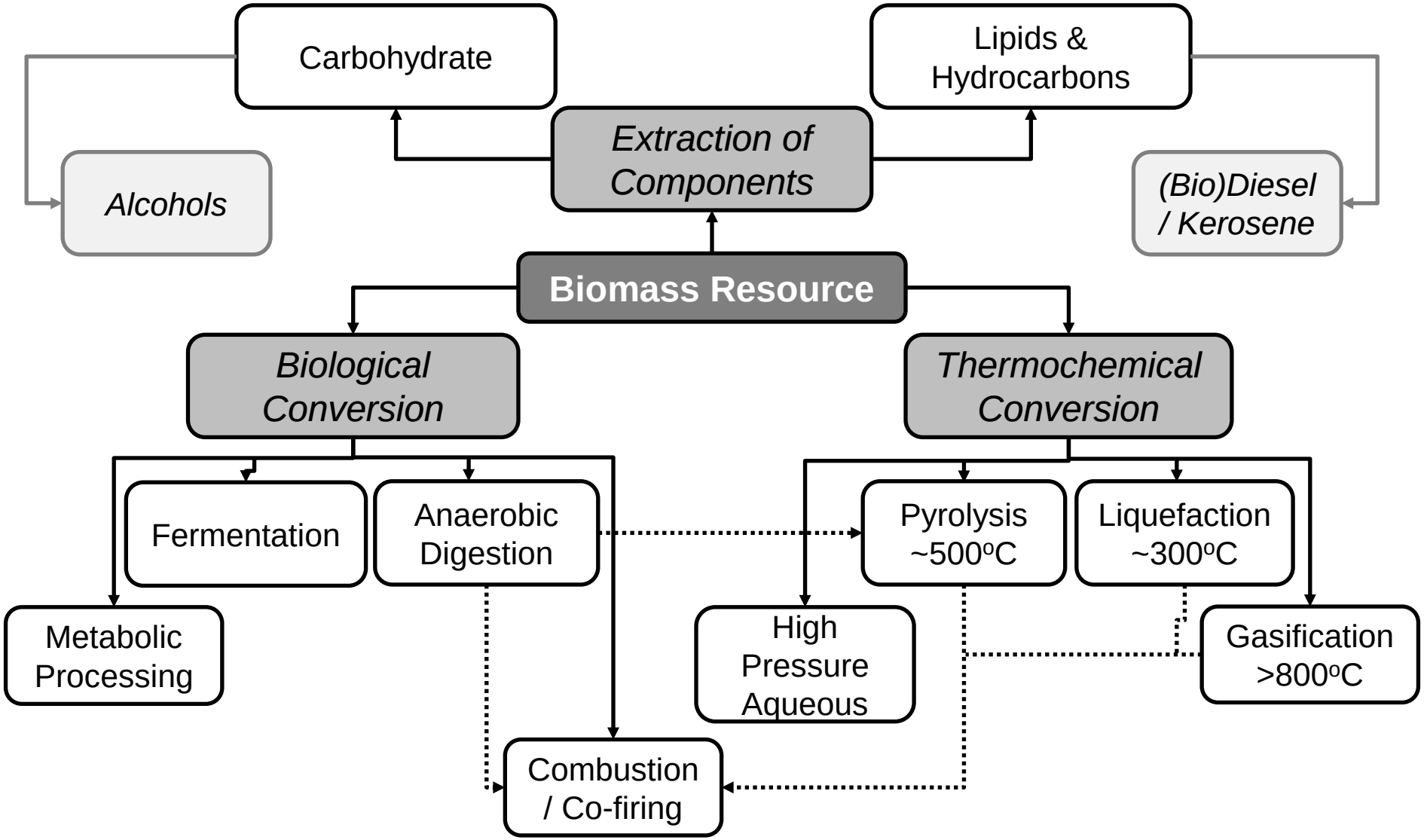


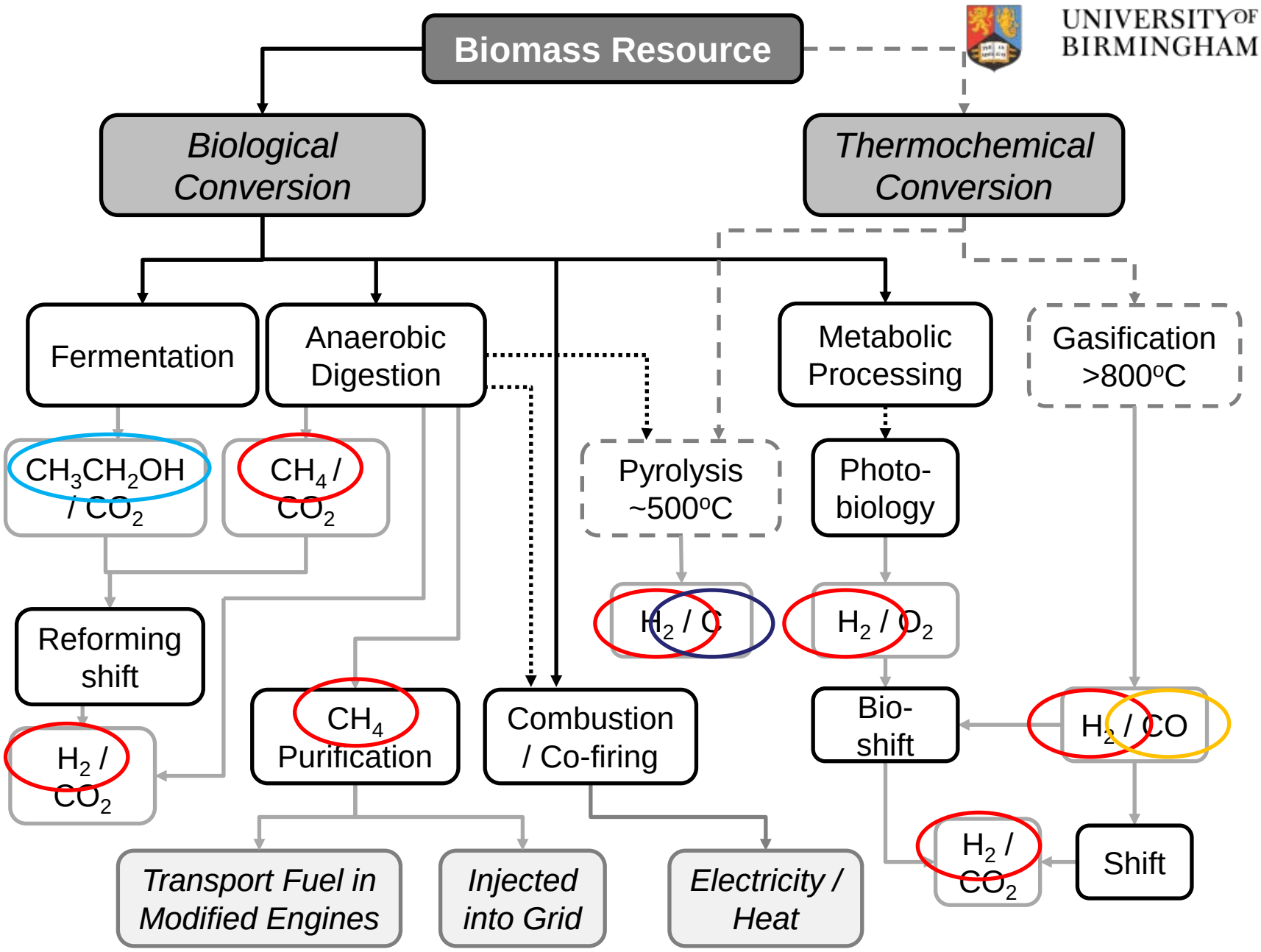
Graphics courtesy MW BaWü

Biomass chain



Biomass Conversion Pathways




Biomass Resource
Biological Conversion
Thermochemical Conversion
Fermentation
Anaerobic Digestion
Metabolic Processing
Gasification >800°C
CH3CH2OH / CO2
CH4 / CO2
Pyrolysis ~500°C
Photo-biology
H2 / C
H2 / O2
Reforming shift
H2 / CO2
CH4 Purification
Combustion / Co-firing
Bio-shift
H2 / CO
H2 / CO2
Shift
Transport Fuel in Modified Engines
Injected into Grid
Electricity / Heat

Fuel Processing – Reactions

Steam reforming

- $C_xH_yO_z + (x-z)\ H_2O \rightarrow x\ CO + (x-z+y/2)\ H_2$
- $CH_4 + H_2O \leftrightarrow CO + 3\ H_2$

Water gas shift reaction

- $CO + H_2O \leftrightarrow CO_2 + H_2$

CPO “Catalytic Partial Oxidation”

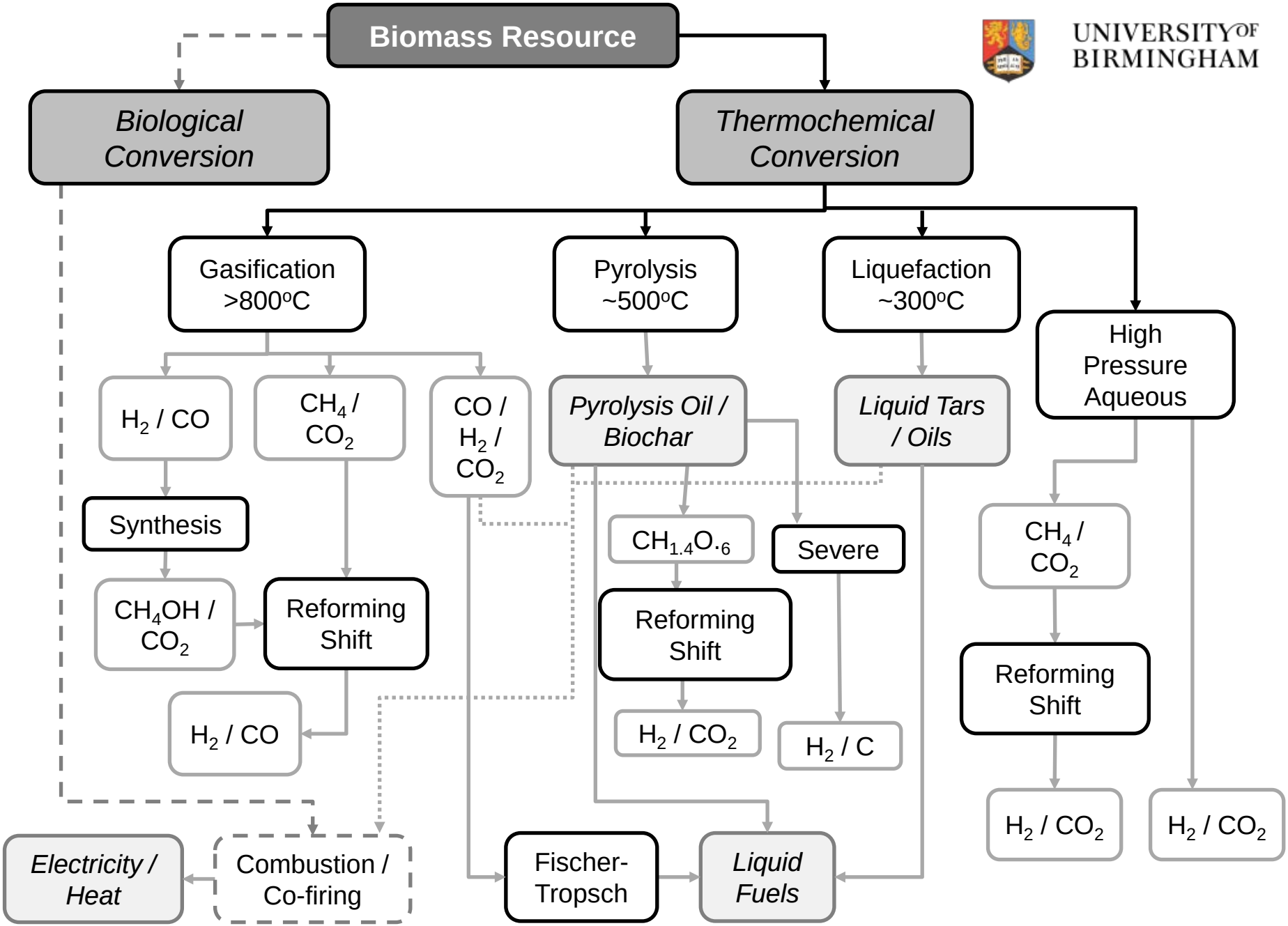
- $C_xH_yO_z + (x-z)/2\ (O2+3.76\ N_2) \rightarrow x\ CO + y/2\ H_2 + 3.76(x-z)/2\ N_2$

ATR “Autothermal Reforming”

- $C_xH_yO_z + n(O2+3.76\ N_2) + (x-2n-z)\ H_2O \rightarrow x\ CO + (x-2n-z+y/2)\ H_2 + 3.76n\ N_2$

Dry reforming

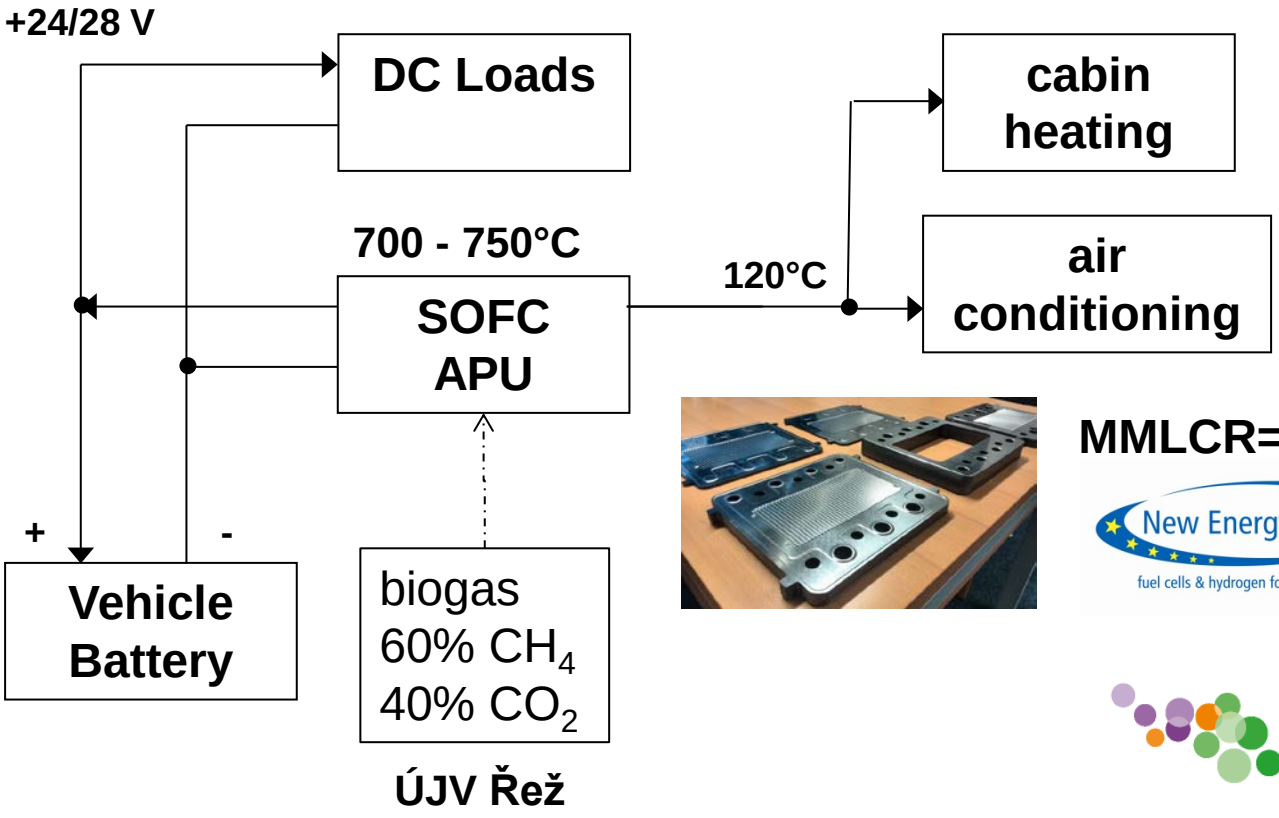
- $CH_4 + CO_2 \leftrightarrow 2CO + 2\ H_2$


Biomass Resource
Biological Conversion
Thermochemical Conversion
Gasification >800°C
Pyrolysis ~500°C
Liquefaction ~300°C
High Pressure Aqueous
H2 / CO
CH4 / CO2
CO / H2 / CO2
Synthesis
CH4OH / CO2
Reforming Shift
H2 / CO
Pyrolysis Oil / Biochar
CH1.4O.6
Reforming Shift
H2 / CO2
Severe
H2 / C
Liquid Tars / Oils
CH4 / CO2
Reforming Shift
H2 / CO2
H2 / CO2
Electricity / Heat
Combustion / Co-firing
Fischer-Tropsch
Liquid Fuels

Fuel Cell Fuel Purity Requirements

Type	CO	CO_2	N_2	H_2S	Cl	particles
PEFC	<10 ppm	tol.	tol.	0	<0,05 ppm	0
PAFC	<2%	tol.	<2%	<50 ppm	<1 ppm	<1 mg/m³
MCFC	tol.	tol.	tol.	<0,1 ppm	<1 ppm	<1 µm
SOFC	tol.	tol.	tol.	<1 ppm	<1 ppm	<1 mg/m³

Use of Biogas with an SOFC APU



MMLCR=SOFC

- no gas processing
- high electrical efficiency >50%

www.balticbiogasbus.eu

Methane from Renewable Energy Sources

Realistic sources:

- fermenter gas
- sewage gas
- landfill gas
- mine gas

at development stage:

- gasification of biomass
- gasification of household wastes

new ‘hype’:

- methane synthesis (power to gas)

Anaerobic digestion

In absence of air converts animal or plant waste into methane

- Typical Wastes
  - Manure (feed lots, pig farms, poultry)
  - Olive oil mill waste
  - Potato processing waste

- Typical Products
  - Biogas (CH_4, CO_2)
  - Fibre or digestate (solid residue similar to compost)
  - Fertilizer (liquid fraction)

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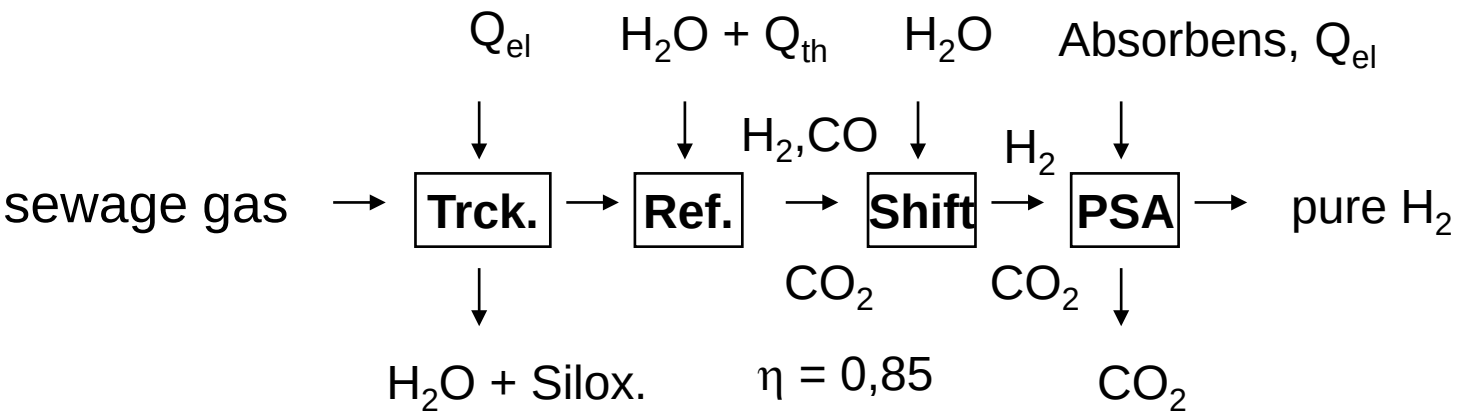
Gases from Biomass Digestion

Typ	CO	CO_2	N_2	H_2S	Cl	others	particles
Biogas	0	30 – 40%	(2%)	yes	(yes)	NH_3	0
Sewage gas	0	25 – 35%	(2%)	yes	yes	Siloxane	0
Land fill gas	0	30 – 45%	0	yes	yes		0

Gas Treatment: Sewage Gas - PEFC

Waste Water Plant Cologne

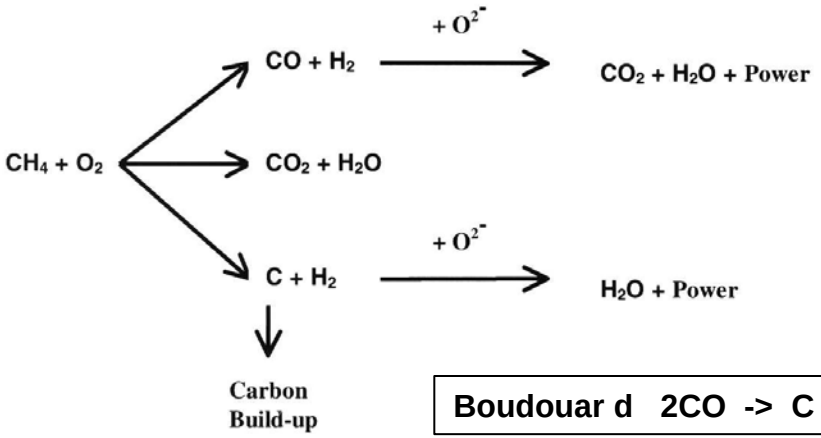


problems:

- many process steps with possibility of failure
- high energy demand for PSA

Carbon Formation Reactions

carbon build-up due to hydrogen and oxygen mismatch



Boudouar d 2CO -> C + CO_2

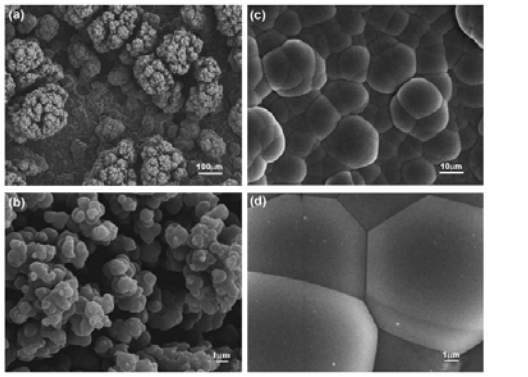
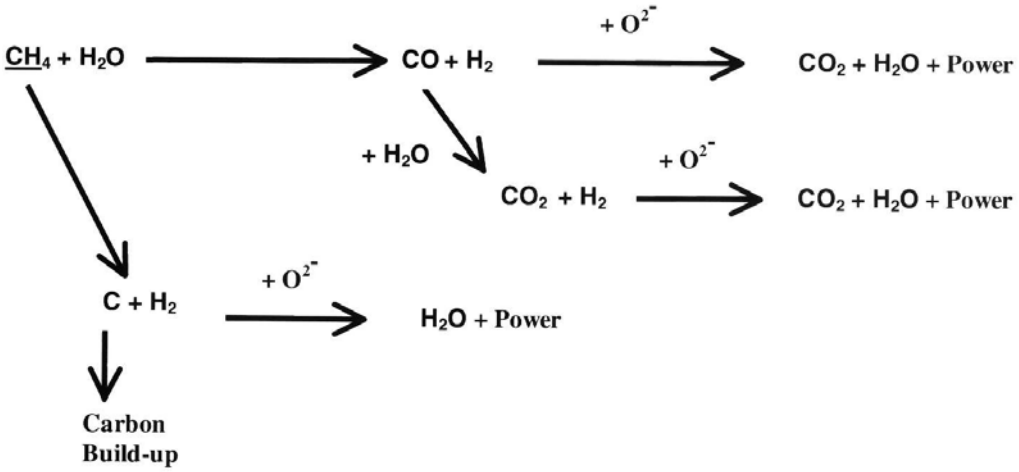
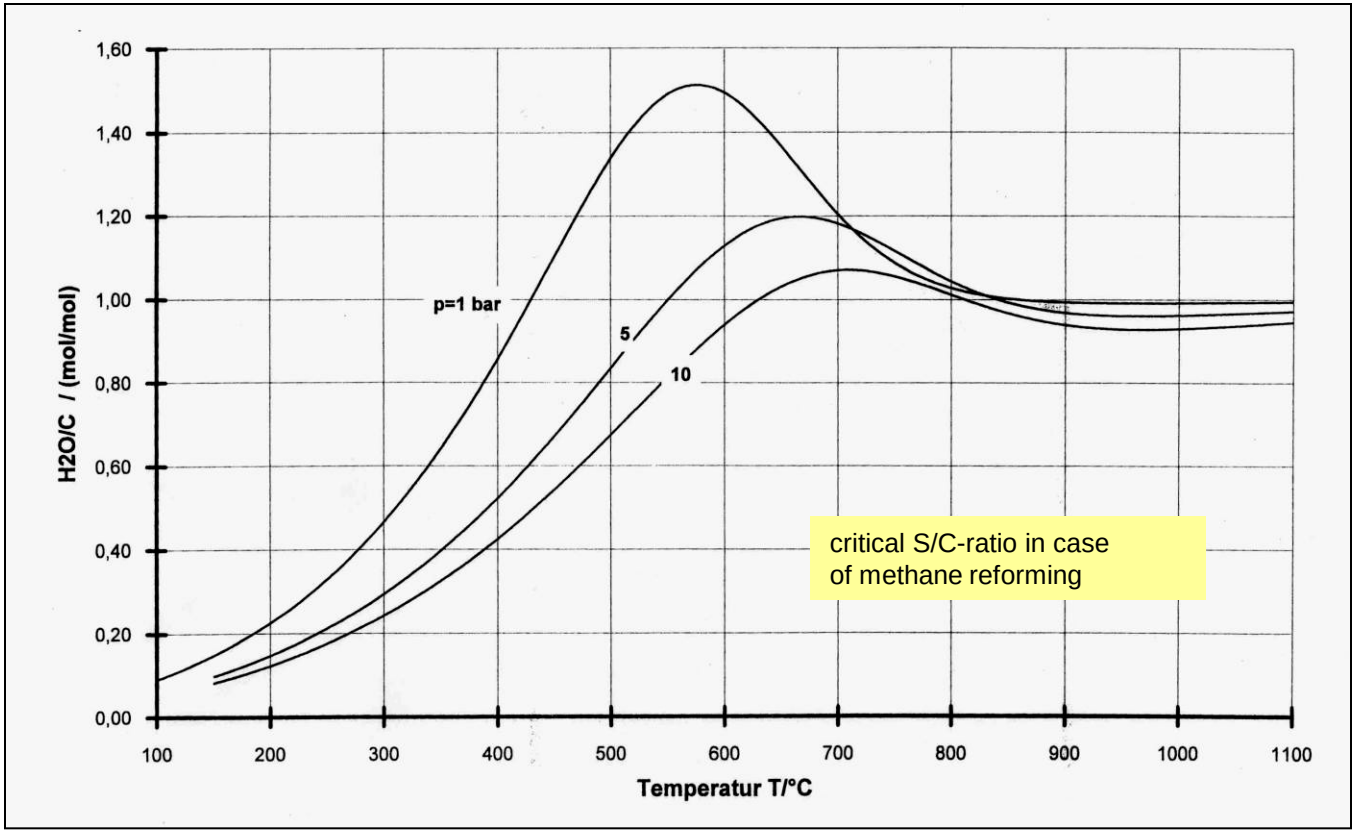


Fig. 4. The morphology of carbonaceous deposits on the surface of an anode containing 10 wt.% CeO_2 and 20 wt.% Cu after long-term testing in n-butane at 1173 K.



Source: Larminie/Dicks

Methane Reforming: Carbon formation



Elemental carbon can develop at and below the curves indicated. Technically the steam-to-carbon ratio is therefore generally chosen as 2,5 to 3 [mol/mol].

source: A. Gubner

Updraft Gasifier

$CH_{1.4}O_{0,6} \rightarrow CO + C + (CH)_x + H_2O$

$C + CO_2 \rightarrow CO$

$C + H_2O \rightarrow CO + H_2$

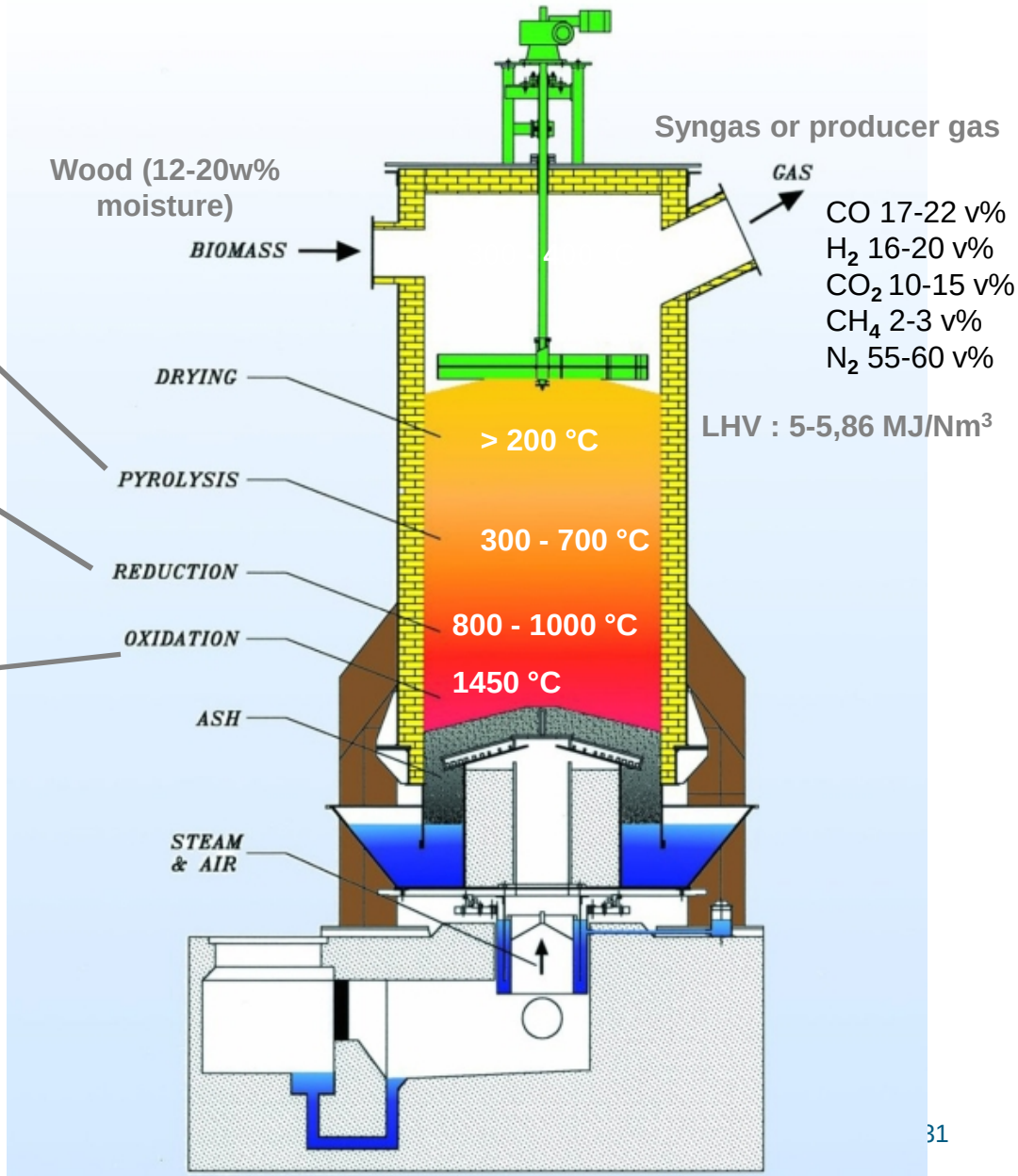
$CO + H_2O \rightarrow CO_2 + H_2$

$CH_{1.4}O_{0,6} + O_2 \rightarrow CO_2 + H_2O$

The methane concentration can be increased by pressure increase

$CO + 3\,H_2 \Leftrightarrow CH_4 + H_2O$

$2\,C + 2\,H_2 \Leftrightarrow CH_4$



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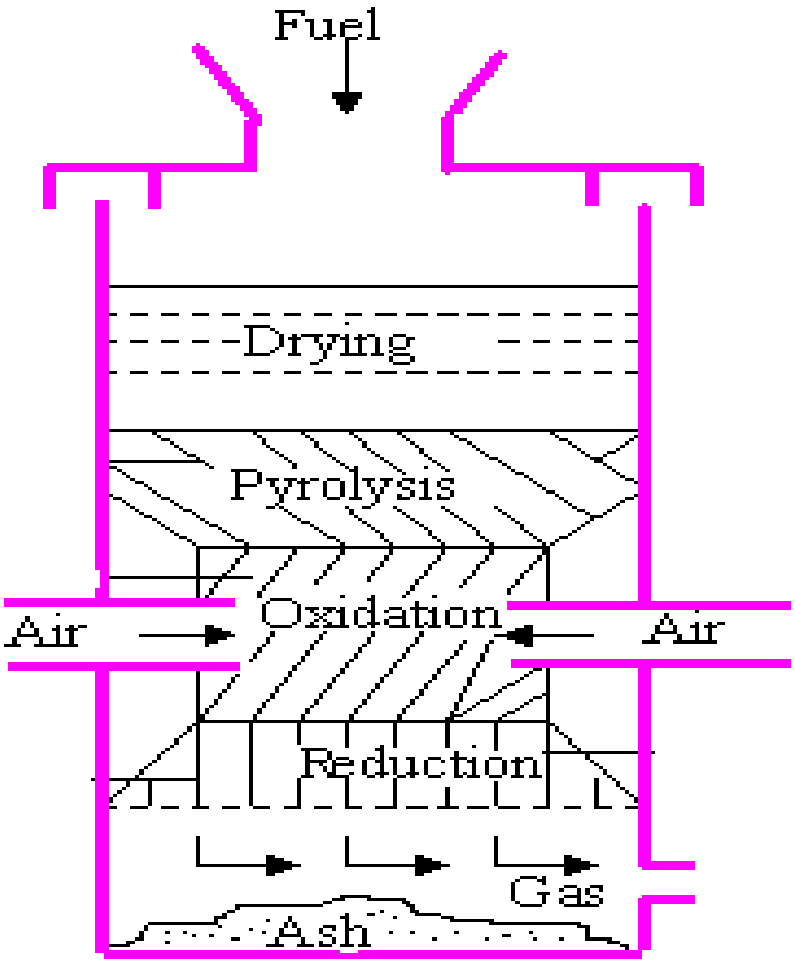
Downdraft Gasifier



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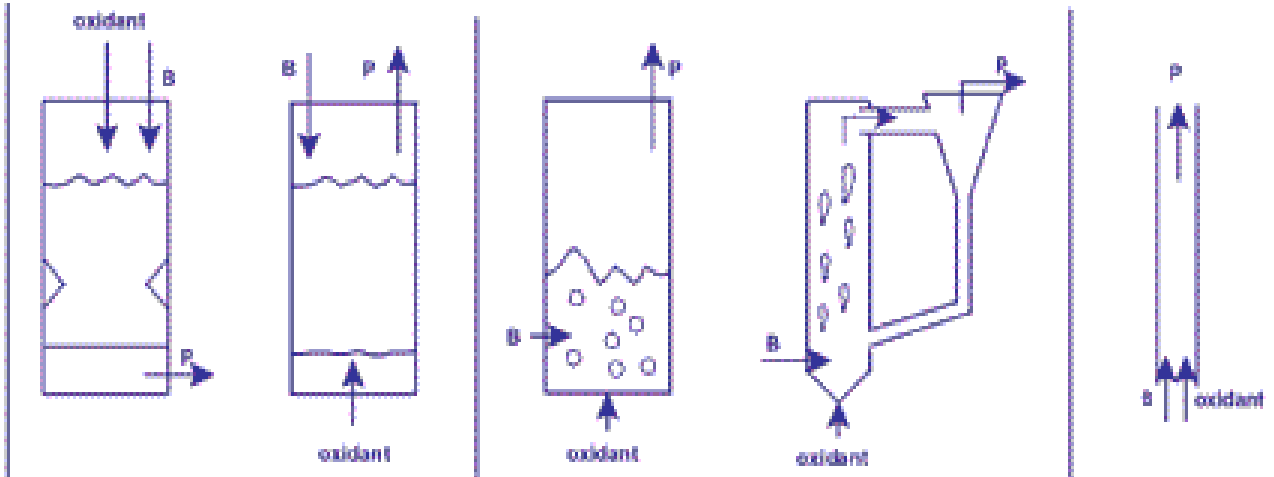
Biomass Gasification: Gasifier types



	Moving bed / fixed bed		Fluid beds		Entrained beds
	Co-current	Counter current	dense	circulating	
T°C	700-1200	700-900	< 900	< 900	1500
tars	low	very high	intermediate	intermediate	absent
control	easy	very easy	intermediate	intermediate	very complex
scale	< 5 MW_t	< 20 M_t	10<MW_t<100	20<MW_t<?	> 100 MW_t
feedstock	very critical	critical	less critical	less critical	very fine particles

source: BTG

Biomass Gasification: Product gas quality

Type	H_2	CO	CO_2	CH_4	N_2	Tar	Particles
						g/m³	
Upstream/ Fxb./steam	30%	30%	10%	10%	20%	**100**	>
Downstream / Fxb./ steam	50%	25%	20%	10%	n.d.	**1**	>
Circ. Fluidised	30%	25%	25%	10%	10%	**10**	>>
Circ. Fluidised/ 2-phase	20%	20%	10%	0%	41%	**low**	>>

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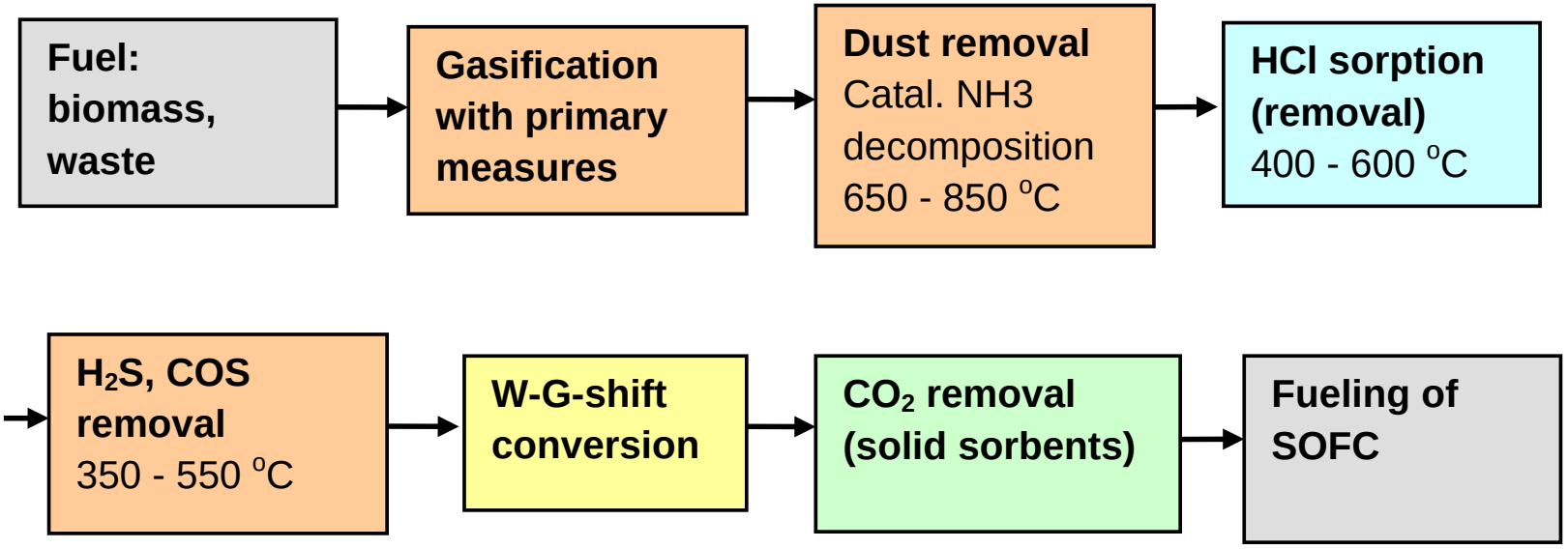
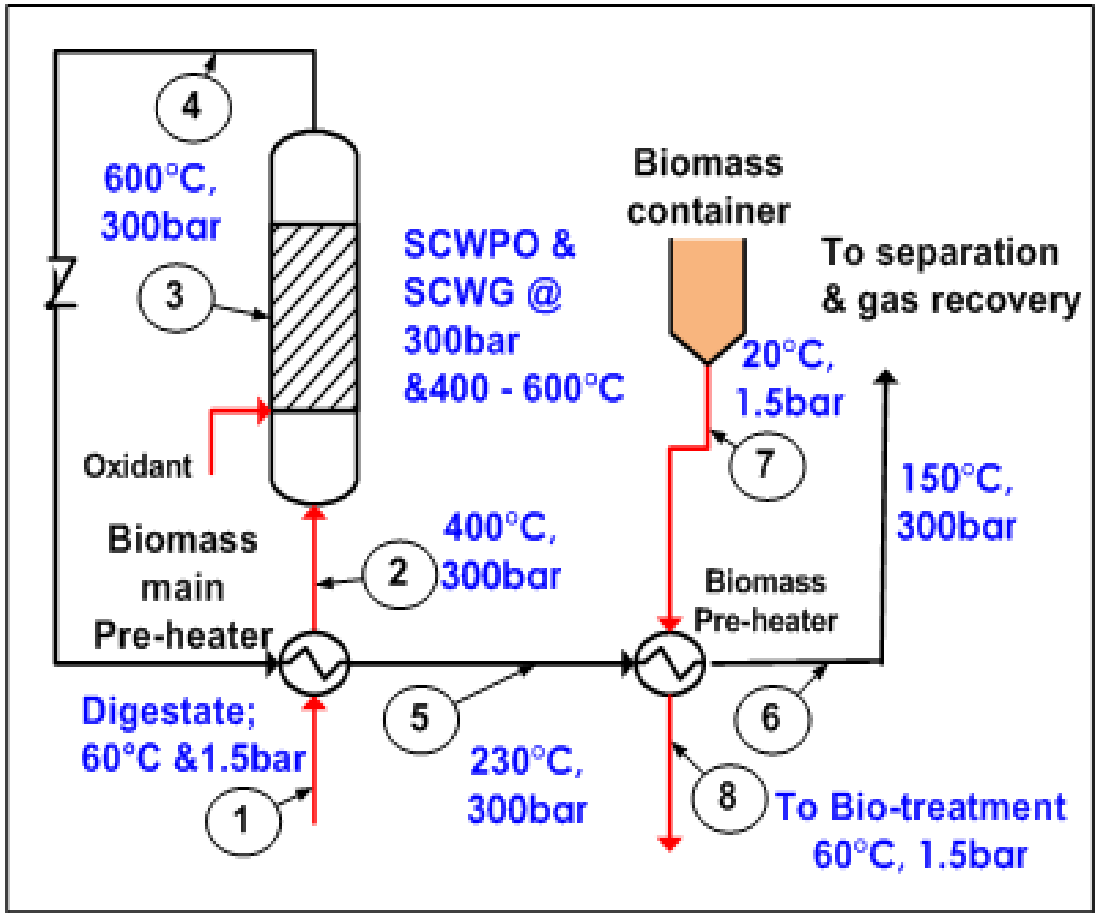
Gas Cleanup



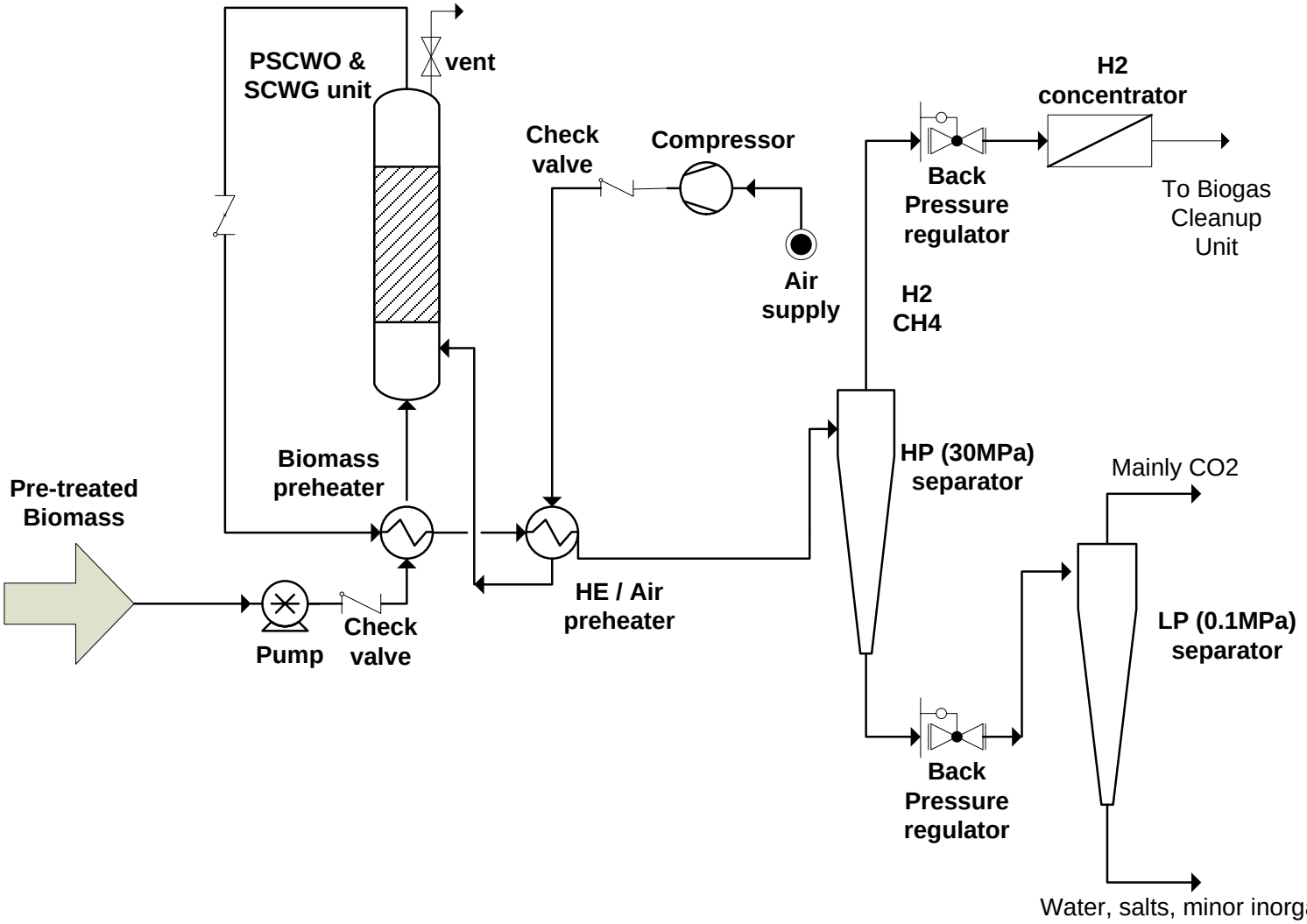
source: BioCleanGas

Supercritical Water Gasification



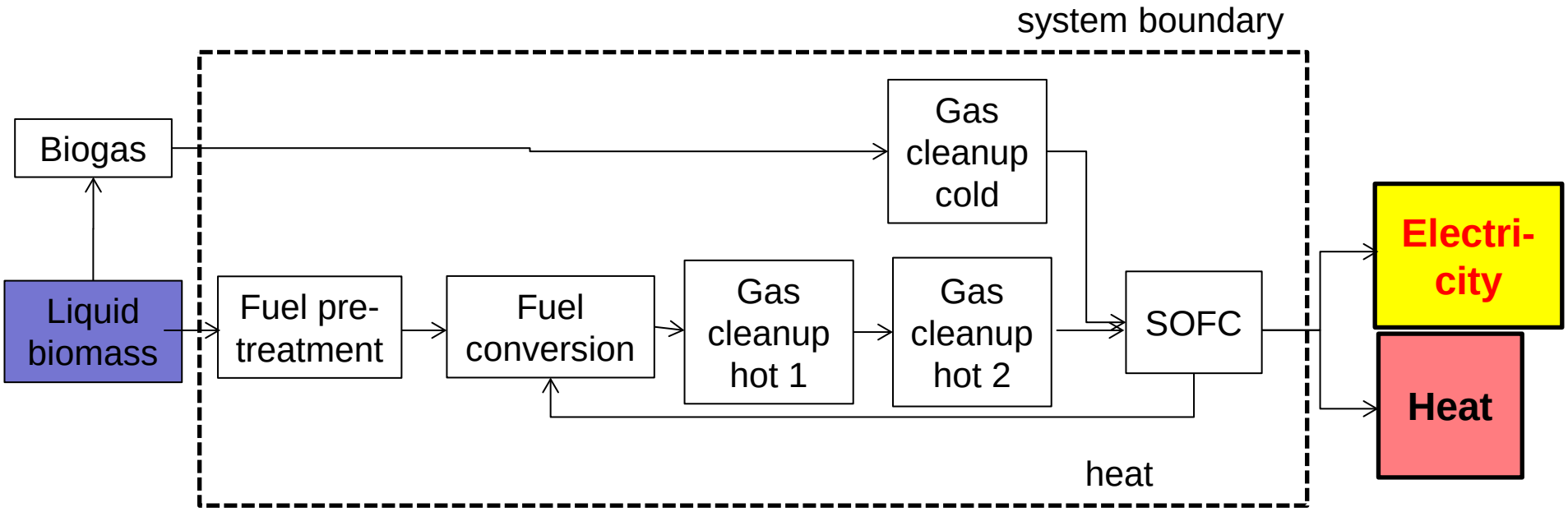
source: Bushra Al-Duri

Supercritical Water Gasification (2)

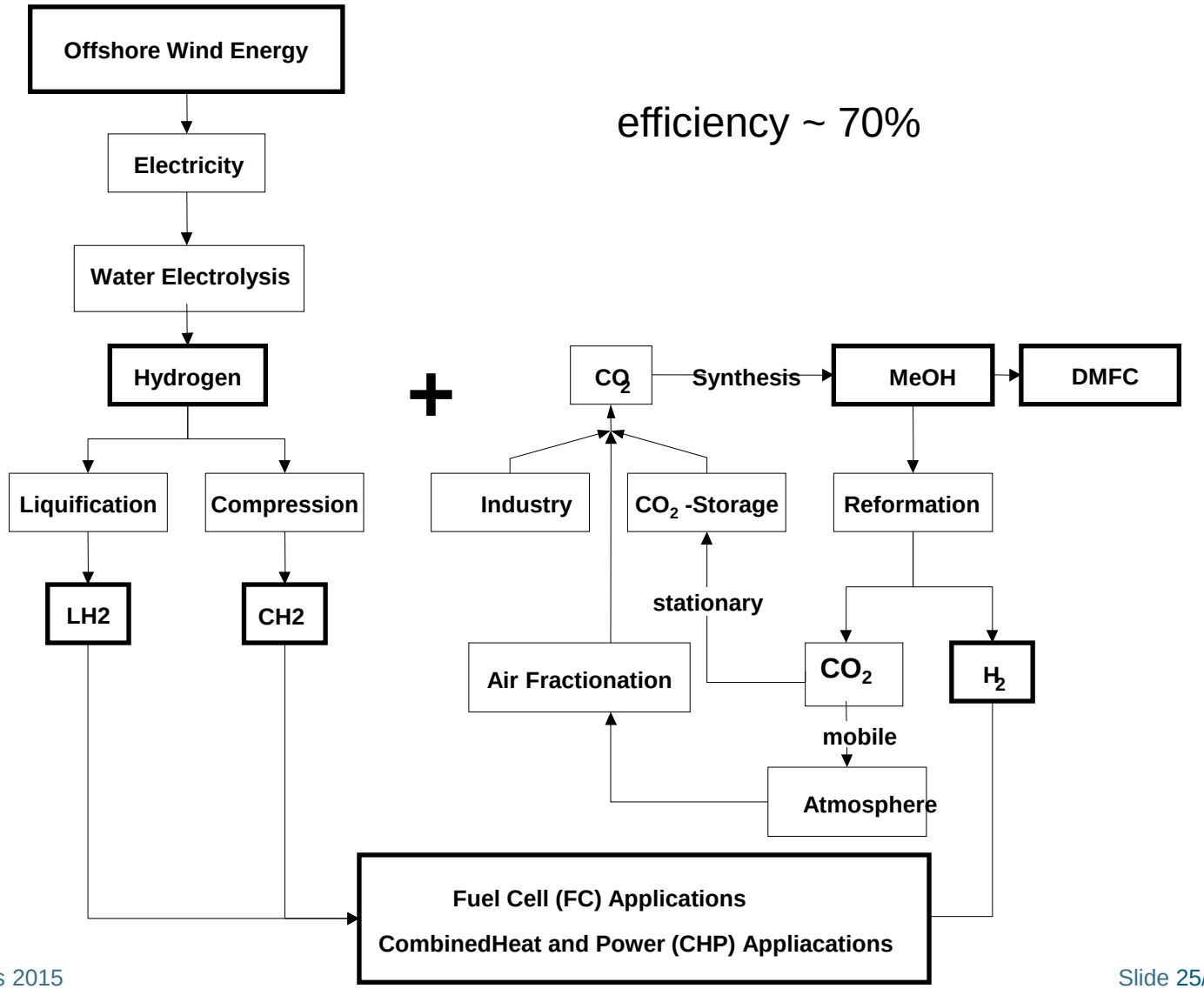


source: Bushra Al-Duri

Hybrid Conversion System



Liquid Product: Methanol Synthesis



efficiency ~ 70%

Biomass Infrastructure

- 8 MW gasifier requires about 35 km radius collection of biomass
- trade-off between transport energy expense and energy yield
- energy density of biomass transport is questionable – rather transport product gas than the raw material

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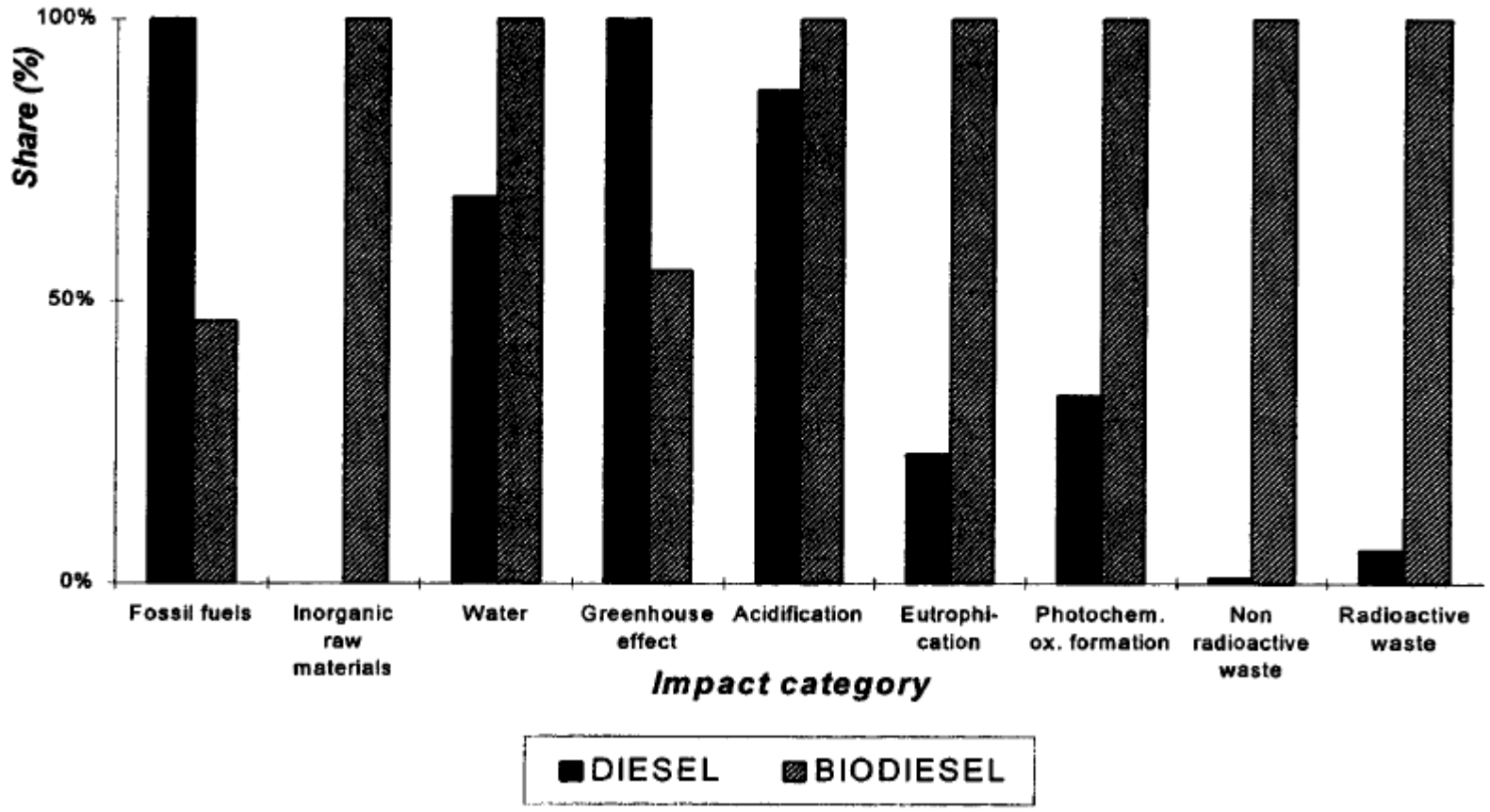
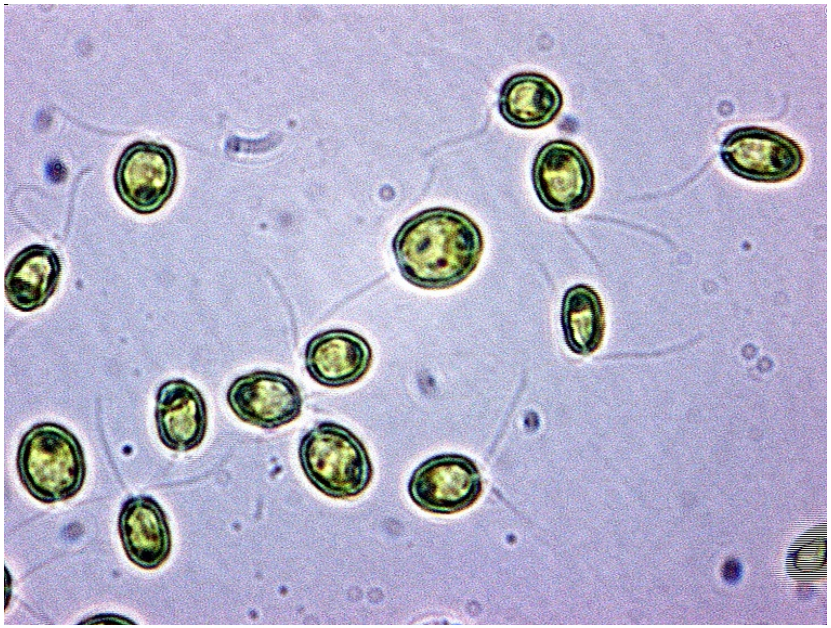
Biomass Environmental Impact

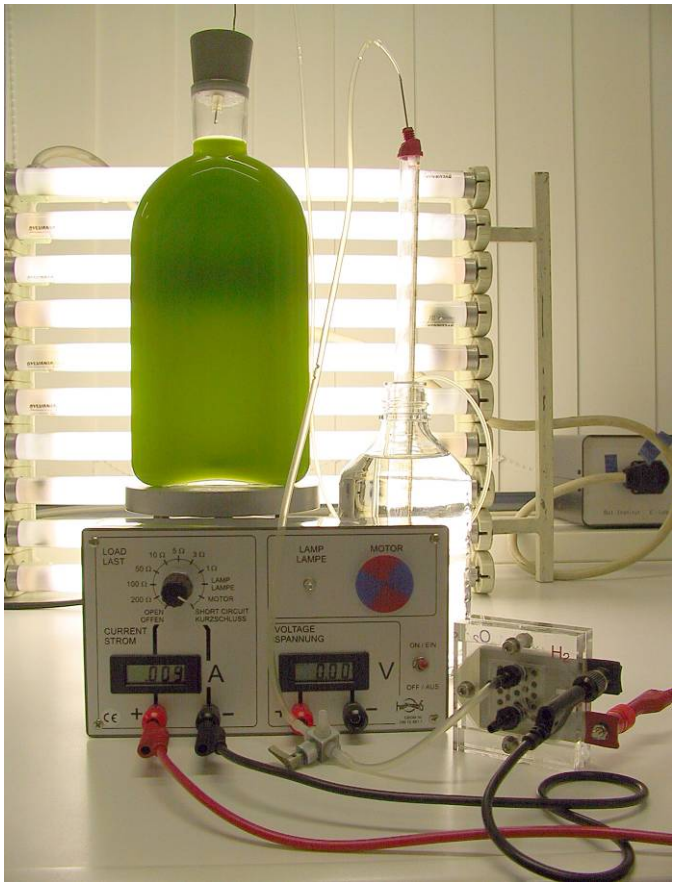


Food vs. Energy?

- is there an ethical dilemma?
- competition for resources:
  - not in Europe – agricultural over-production can be channelled into the energy market
- at a global scale:
  - potential competition has to be closely monitored – energy crops have to be grown as such and food crops not converted to energy crops – at the bottom line, though, the markets decide
- crop growing:
  - cultivation of energy crops releases N_2O_2 – but so would food production

Free Hydrogen Production: Algae and Bacteria





not quite for free: light and heat required, yield is limited

source: University of Bonn

Summary

- a huge number of options exist to turn biomass into fuel gases suitable for SOFC
- this creates a high flexibility both of fuel supply and fuel use
- the product gases can be used for energy conversion, but also as chemical raw products, adding another degree of freedom
- issues of transport and distribution and scale of conversion need to be kept in mind
- a competition of food and energy use of biomass can be negated for the situation in Europe

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Thank you for your attention!

... and any questions?