Biomass gasification and gas cleaning for diverse applications: CHP & chemical syntheses

(Kyriakos D. Panopoulos)

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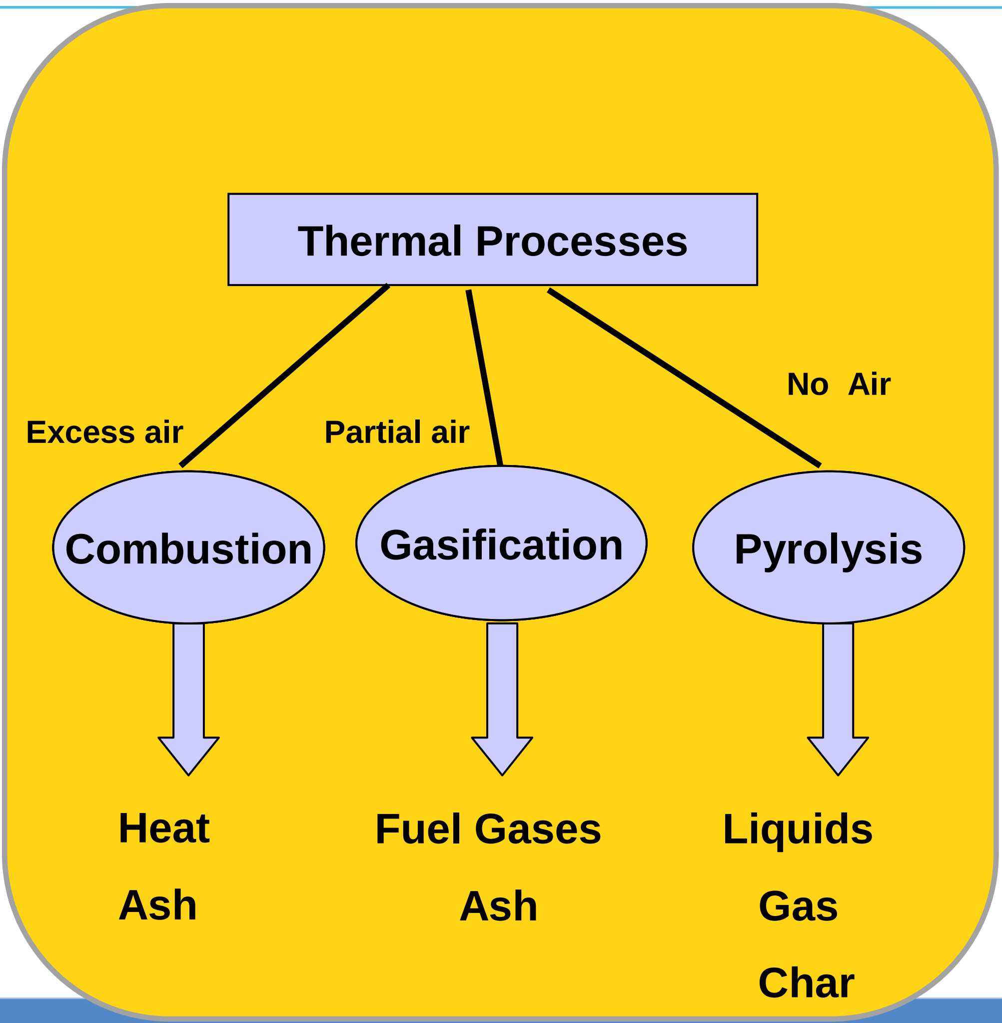
Contents

- Gasification
- Gasification Research
- Applications of product gas
- Gas Cleaning

Thermochemical routes



Thermal Processes

Excess air

Partial air

No Air

Combustion

Gasification

Pyrolysis

Heat

Ash

Fuel Gases

Ash

Liquids

Gas

Char

What is Biomass Gasification?

Thermochemical conversion of a solid or liquid carbon containing fuel into a calorific syngas (H_2, CO, CH_4, CO_2, H_2O, N_2)

Fuels:
e.g. Coal, biomass (wood, straw, power crops, …),
sewage sludge, waste, …

Major steps:
Drying – Pyrolysis – partial oxidation – reducing/reforming

Gasification applications

1. **Heat production (**Utilisation of the gas into furnace/boiler.)
2. **Combined heat and power**
   - i. ICE
   - ii. GT
   - iii. Combined cycle (B-IGCC)
   - iv. Fuels Cells
   - v. Stirling Engines
3. **Liquid fuels and Chemicals**
   - I. MeOH, DME
   - II. Fischer – Tropsch synthesis (hydrocarbons / alcohols)
   - III. SNG
   - IV. H_2
   - V. Chemicals

BAT levels

η

	Technique	Electrical efficiency (net) (%)
Biomass combustion	**Grate-firing**	**Around 20**
	Spreader-stoker	**>23**
	FBC (CFBC)	**>28 – 30**
B- IGCC	**FBG**	**>35**

Gasification process classifications

Depending on the gasification agent

1.Autothermal Gasification

Air: Lower CAPEX , Final product diluted into N2.

O2 or rich O2 , requirement of an ASU

2. Allothermal Gasification

Water Steam

Final product with higher LHV and H_2 και CH_4 contents.

Part of the biomass must be combusted into another vessels and heat must be tranfered to the gasification vessel.

Gasification process classifications

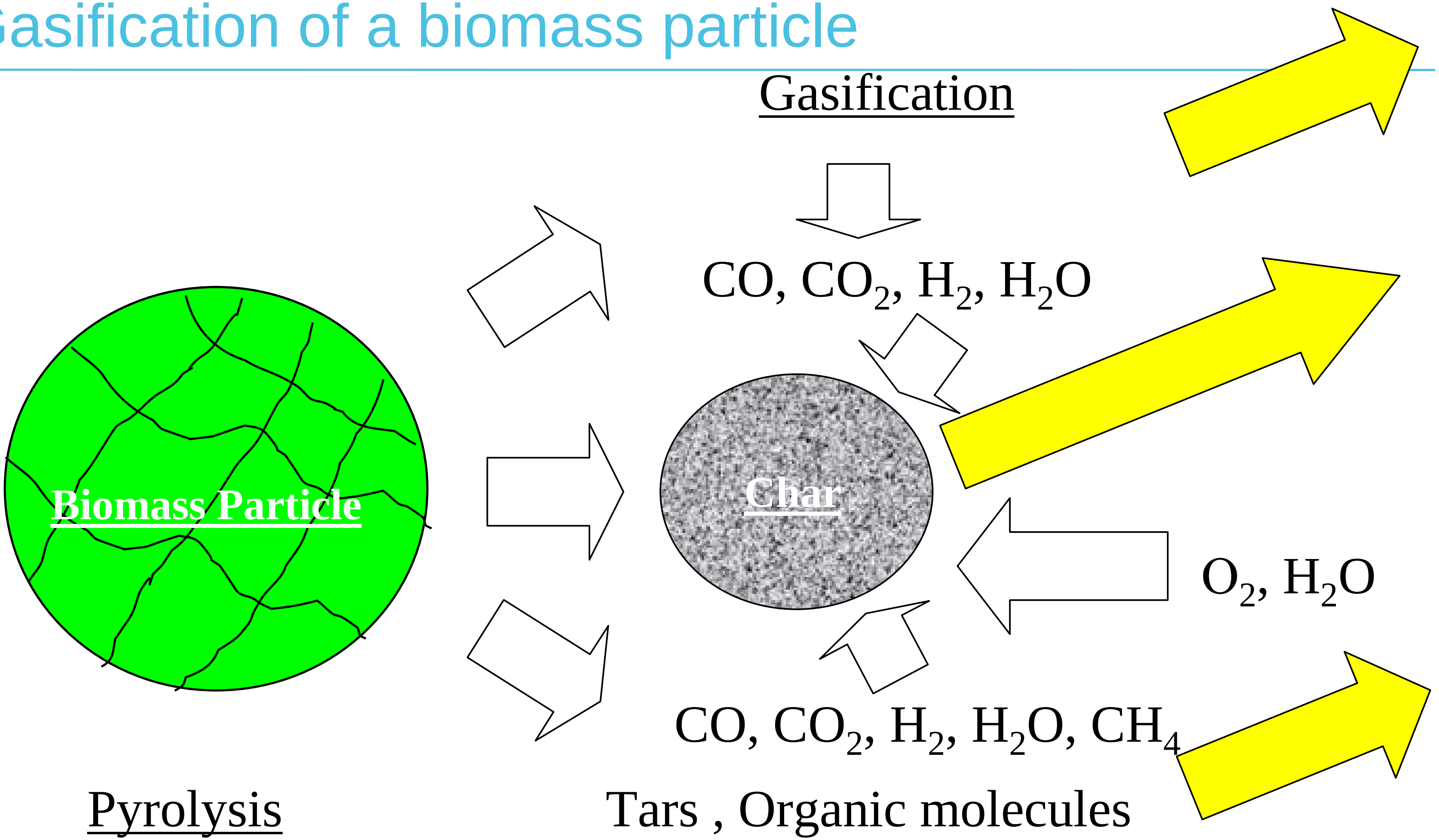
Based on gas flow pattern :

- Fixed Bed Gasifiers
  - ✓ (Updraft)
  - ✓ (Downdraft)
  - ✓(Fluidised Bed)
  - ✓ (Bubling Fluidised Bed)
  - ✓ (Circulating Fluidised Bed)

Based on operating pressure :

- Atmospheric or Near atmospheric operation
- Pressurized

Gasification of a biomass particle



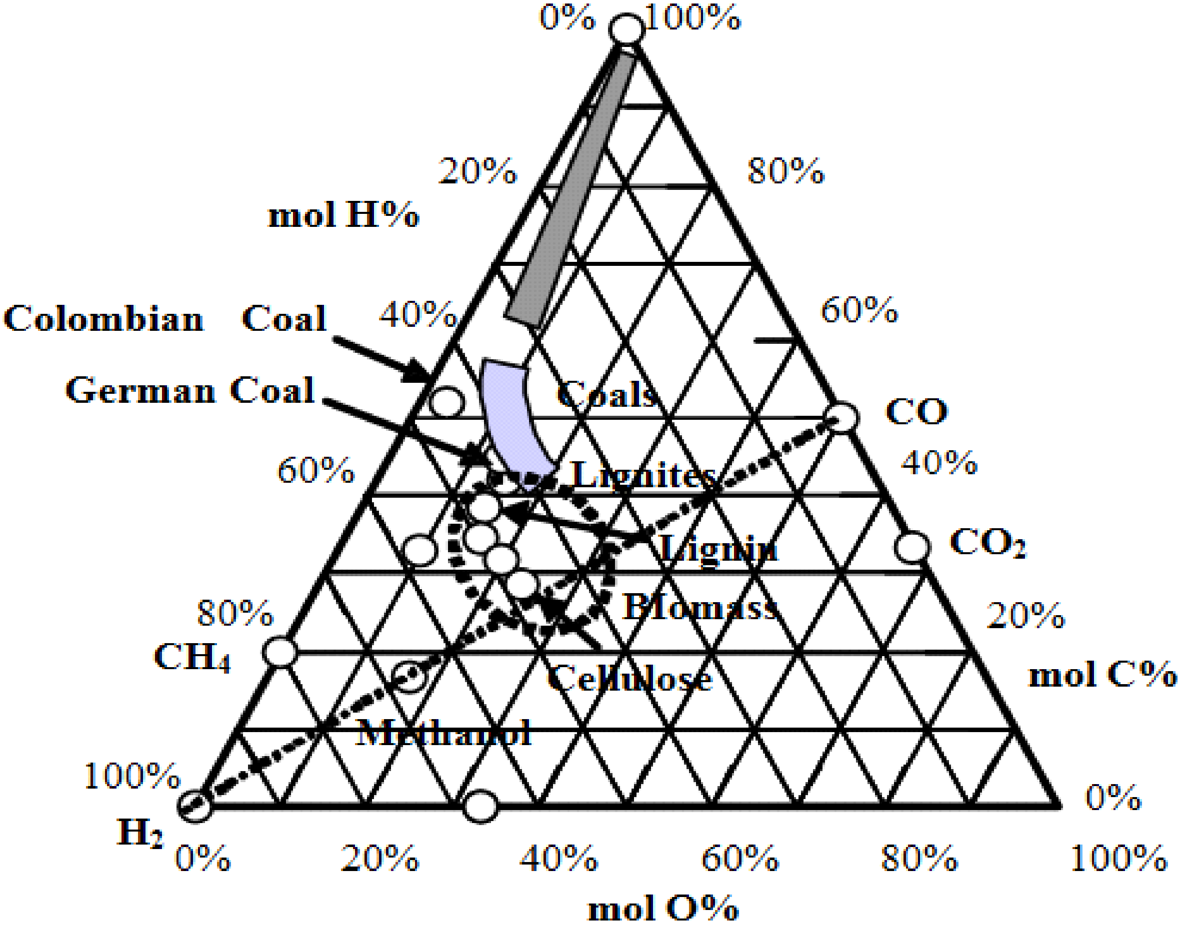
Gasification chemistry

Table 1: Gasification Reactions

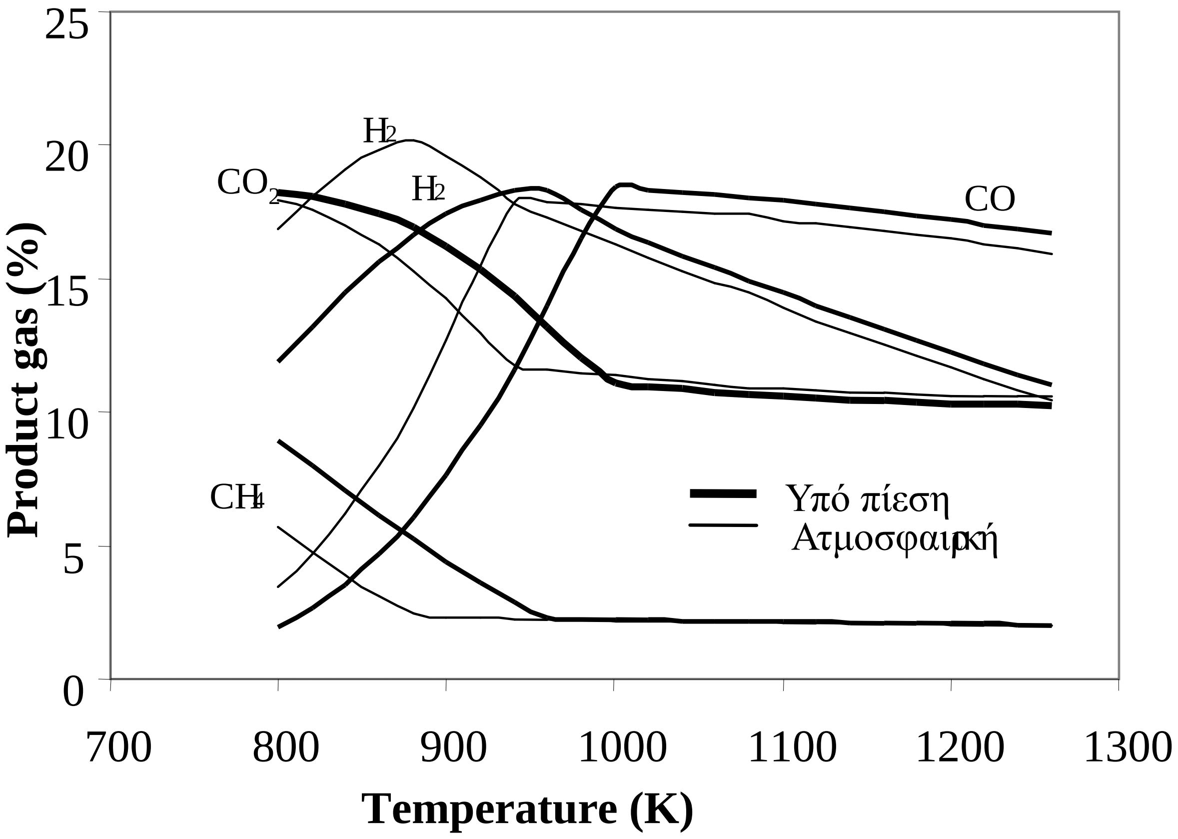
Exothermic Reactions:		
$C_{(s)} + O_2 \leftrightarrow CO_2$	$\Delta H_R = -393$ kJ/mol	Combustion Reactions
$C_{(s)} + 1/2O_2 \leftrightarrow CO$	$\Delta H_R = -110$ kJ/mol	
$H_2 + 1/2O_2 \leftrightarrow H_2O$	$\Delta H_R = -242$ kJ/mol	
$CO + 1/2O_2 \leftrightarrow CO_2$	$\Delta H_R = -283$ kJ/mol	
$C_{(s)} + 2H_2 \leftrightarrow CH_4$	$\Delta H_R = -75$ kJ/mol	Hydrogenation
$CO + H_2O \leftrightarrow CO_2 + H_2$	$\Delta H_R = -42$ kJ/mol	Shift Reaction
Endothermic Reactions:		
$C_{(s)} + CO_2 \leftrightarrow 2CO$	$\Delta H_R = +173$ kJ/mol	Boudouard Reaction
$C_{(s)} + H_2O \leftrightarrow CO + H_2$	$\Delta H_R = +132$ kJ/mol	Water – gas Reaction
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	$\Delta H_R = +206$ kJ/mol	Steam–methane reforming Reaction

+ Fate of Sulphur and Nitrogen

Gasification basics - CHO

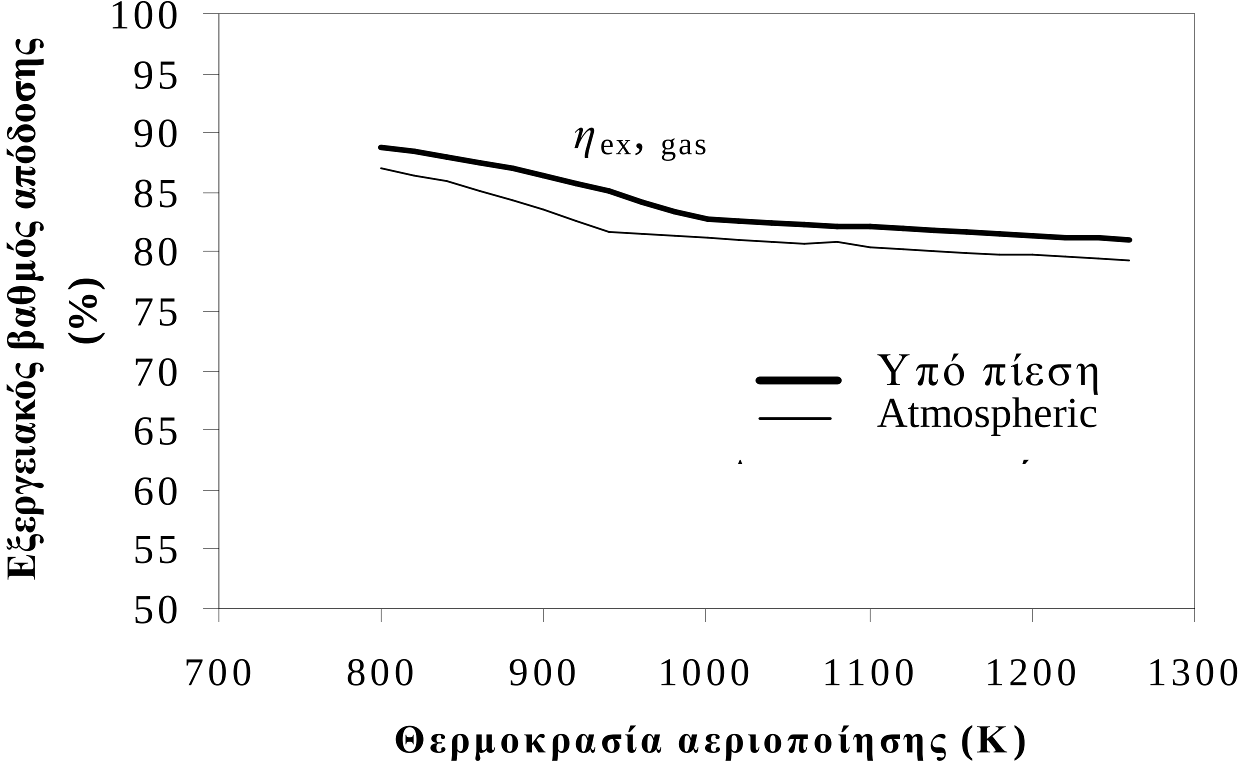


Air Gasification



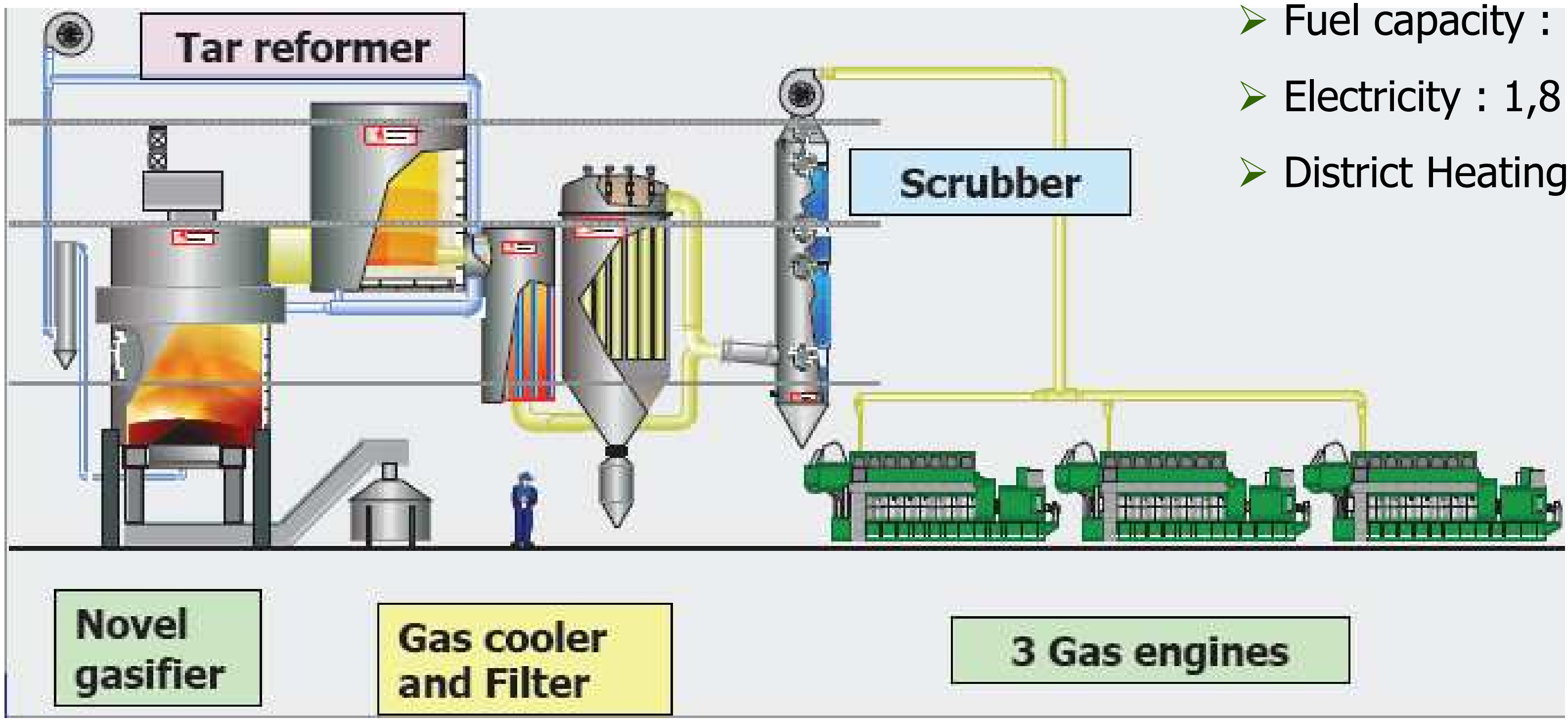
Air Gasification

Additional air increases the $T_{gasifier}$ & dilutes the product gas



$$\eta_{ex,gas} = \frac{E_{gas} + E_{char}}{E_{biomass} + E^{Q}_{Tgas} + E_{air}}$$

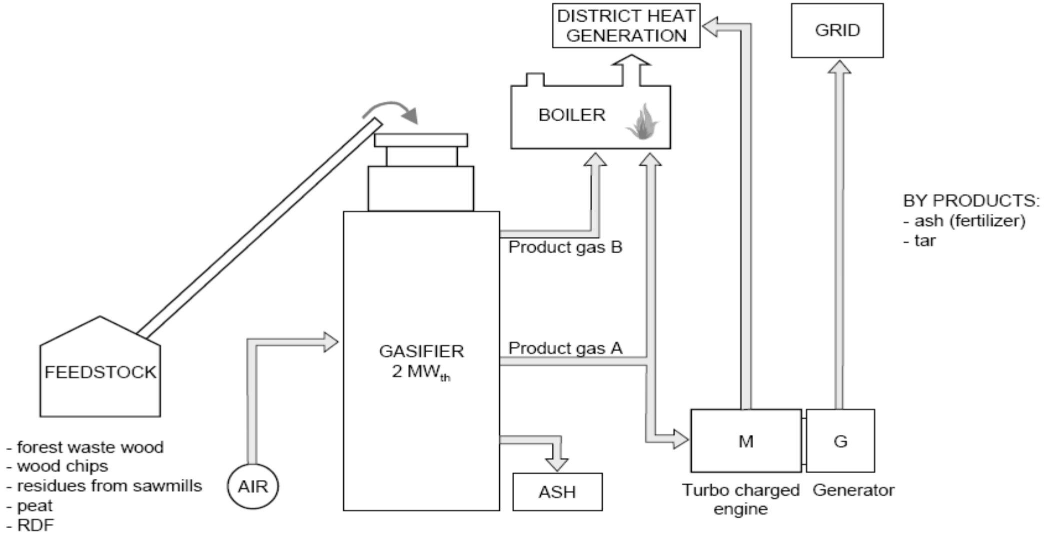
Gasifier applications



Kokemaki - Finland

- Fuel capacity : 7,2 MW_{th}
- Electricity : 1,8 MW_{el}
- District Heating : 4,3 MW_{th}

Gasifier Applications

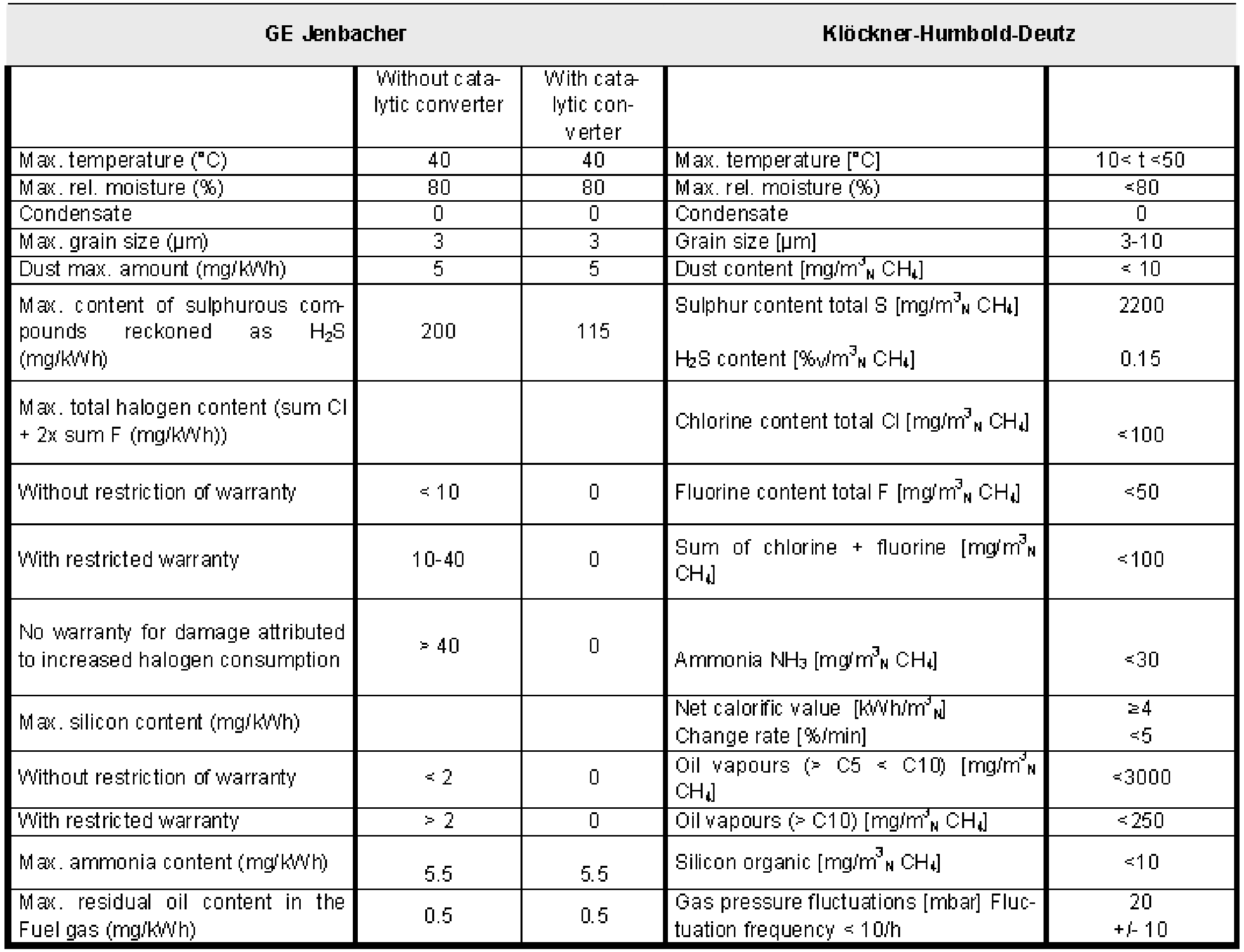


Tervola - Finland

- Fuel : 2,0 MW_{th}
- Electricity : 0,45 MW_{el}
- District heating : 1,1 MW_{th}

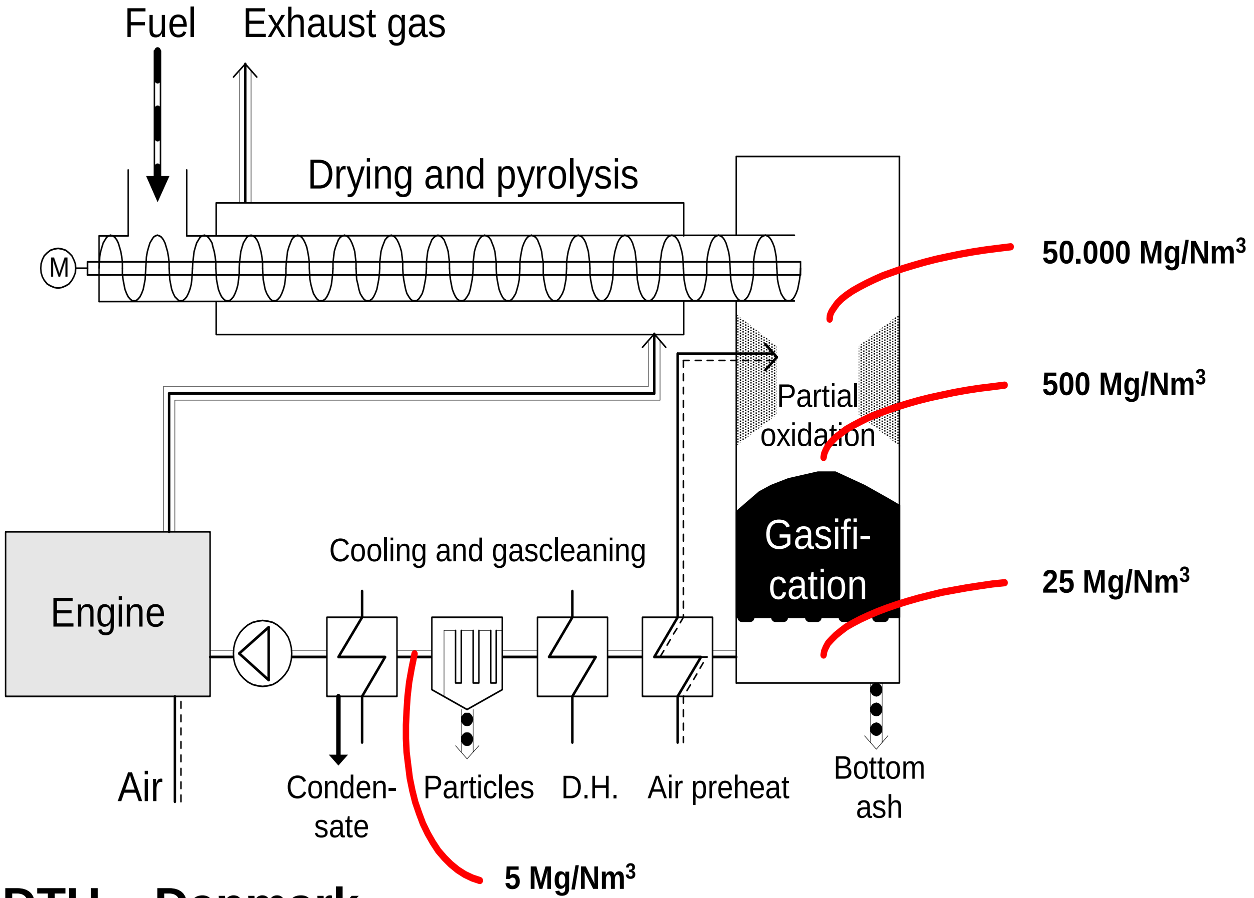
	Raw gas values (optimised downdraft gasifier) mg / m^3_n	Clean gas requirements for engine applications mg / m^3_n
Particle	100 – 1,000	At least < 50 If possible < 5
Tar	100 - 500	At least < 50 If possible < 25

Gasifier Applications – Specifications



GE Jenbacher			Klöckner-Humboldt-Deutz	
	Without catalytic converter	With catalytic converter		
Max. temperature (°C)	40	40	Max. temperature [°C]	10< t <50
Max. rel. moisture (%)	80	80	Max. rel. moisture (%)	<80
Condensate	0	0	Condensate	0
Max. grain size (µm)	3	3	Grain size [µm]	3-10
Dust max. amount (mg/kWh)	5	5	Dust content [mg/m^3_N CH_4]	< 10
Max. content of sulphurous compounds reckoned as H_2S (mg/kWh)	200	115	Sulphur content total S [mg/m^3_N CH_4] H_2S content [%v/m^3_N CH_4]	2200 0.15
Max. total halogen content (sum Cl + 2x sum F (mg/kWh))			Chlorine content total Cl [mg/m^3_N CH_4]	<100
Without restriction of warranty	< 10	0	Fluorine content total F [mg/m^3_N CH_4]	<50
With restricted warranty	10-40	0	Sum of chlorine + fluorine [mg/m^3_N CH_4]	<100
No warranty for damage attributed to increased halogen consumption	> 40	0	Ammonia NH_3 [mg/m^3_N CH_4]	<30
Max. silicon content (mg/kWh)			Net calorific value [kWh/m^3_N] Change rate [%/min]	≥4 <5
Without restriction of warranty	< 2	0	Oil vapours (> C5 < C10) [mg/m^3_N CH_4]	<3000
With restricted warranty	> 2	0	Oil vapours (> C10) [mg/m^3_N CH_4]	< 250
Max. ammonia content (mg/kWh)	5.5	5.5	Silicon organic [mg/m^3_N CH_4]	<10
Max. residual oil content in the Fuel gas (mg/kWh)	0.5	0.5	Gas pressure fluctuations [mbar] Fluctuation frequency < 10/h	20 +/- 10

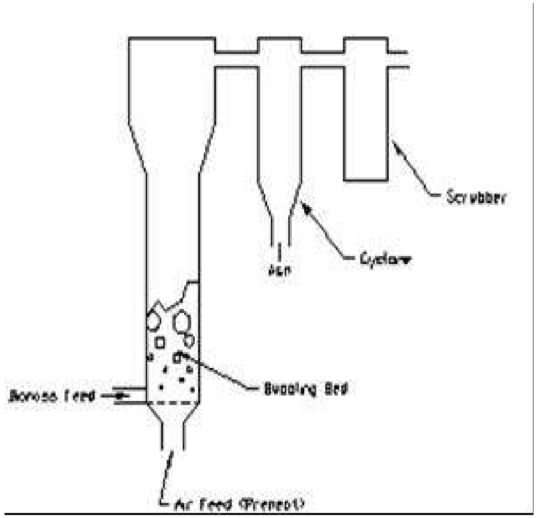
2-stage downdraft gasifier*

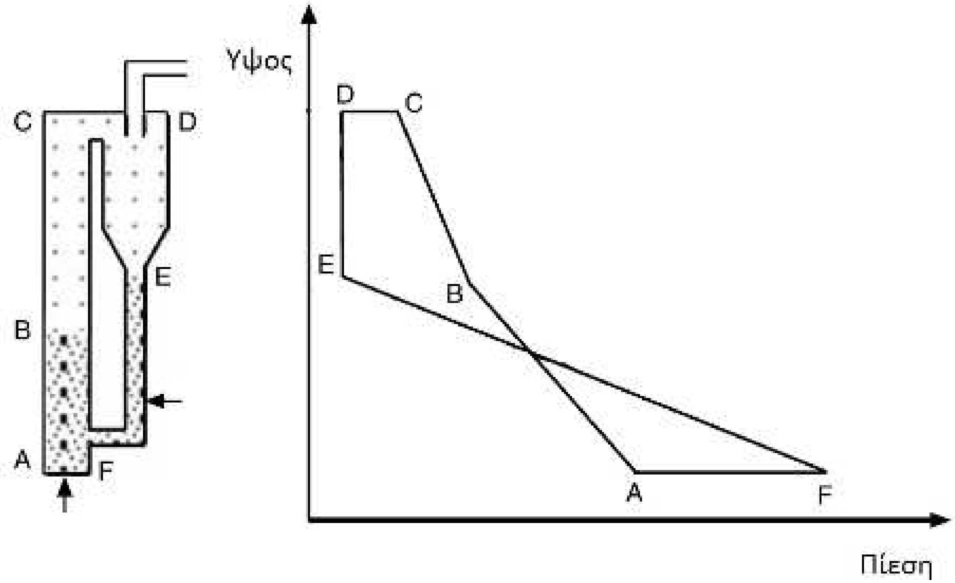


***Viking Gasifier – DTU – Denmark**

Fluidized bed gasification

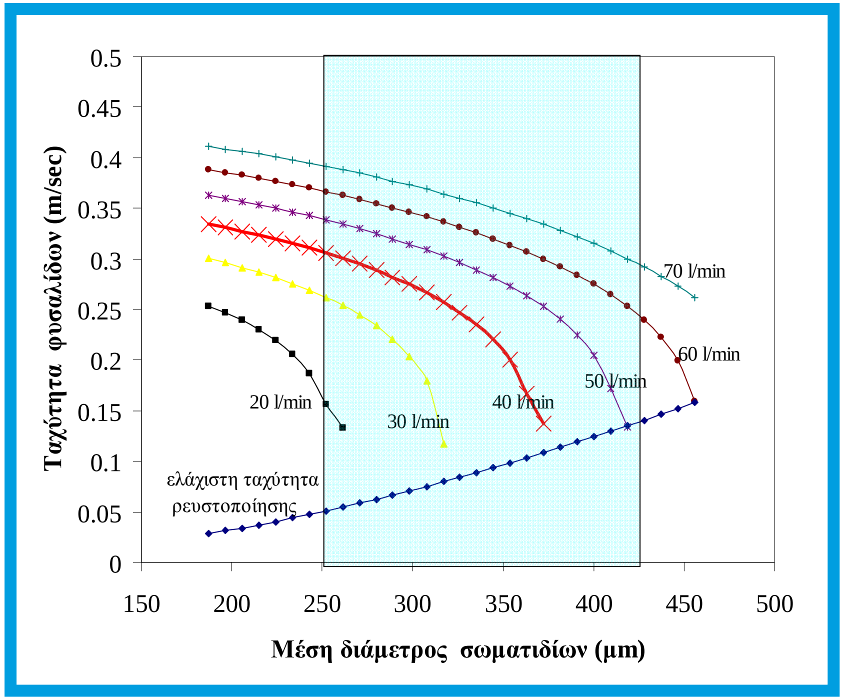
- Diverse solid fuels , Up- scalling , Large particle carryover

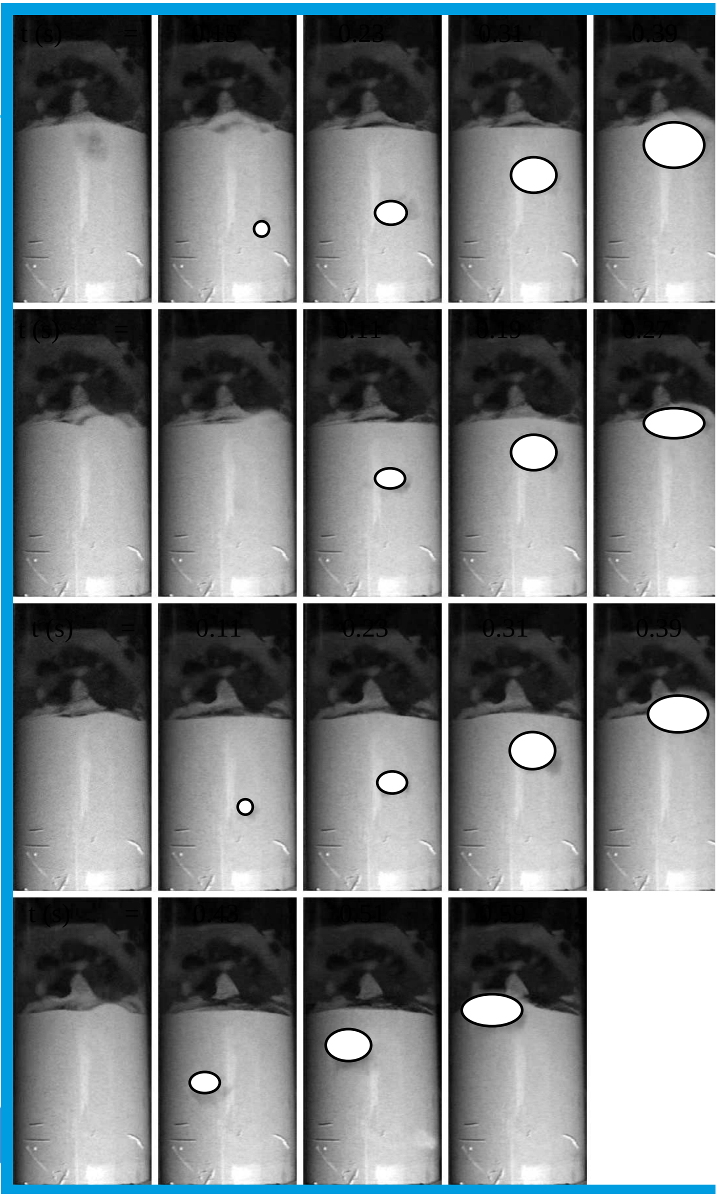




Conditions for Circulation Fluidization		
	UNIT	VALUE
Superficial velocity of gasifier	m/s	3 – 6
Conditions for Bubbling Fluidization		
Superficial velocity of gasifier	m/s	0.21 – 2

Bubbling Fluidized bed Mode



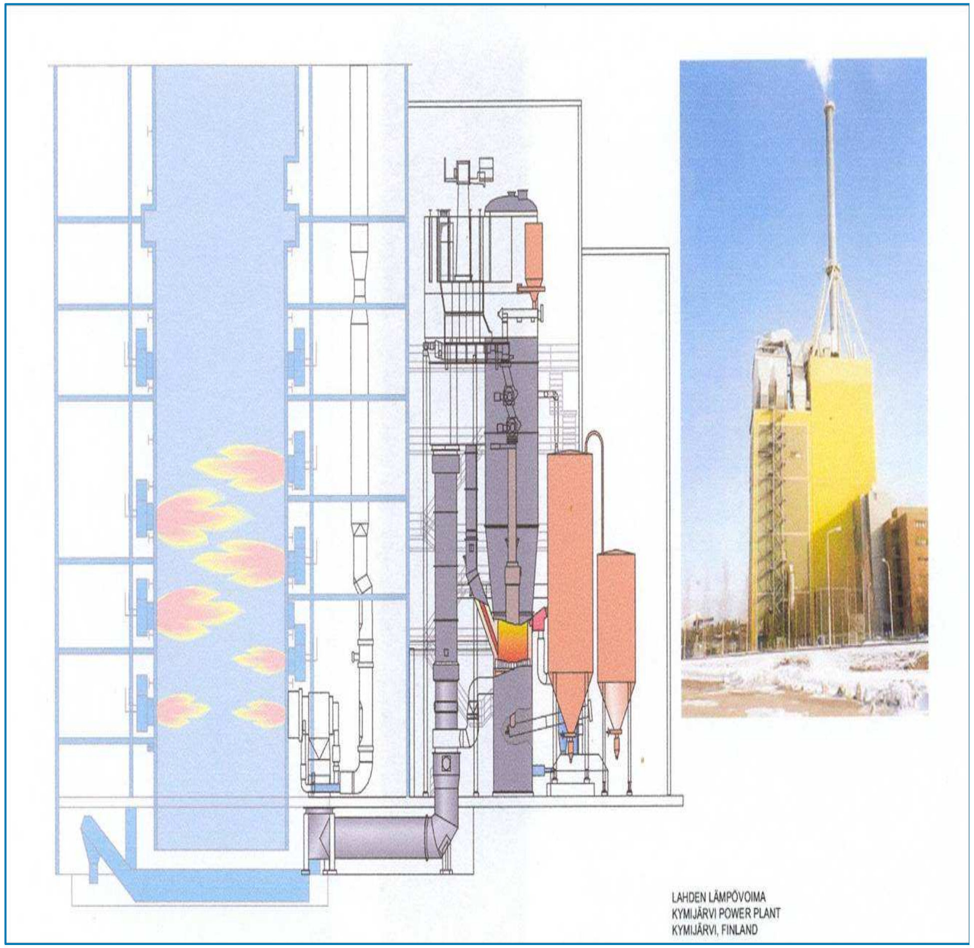


Fluidized bed gasification applications

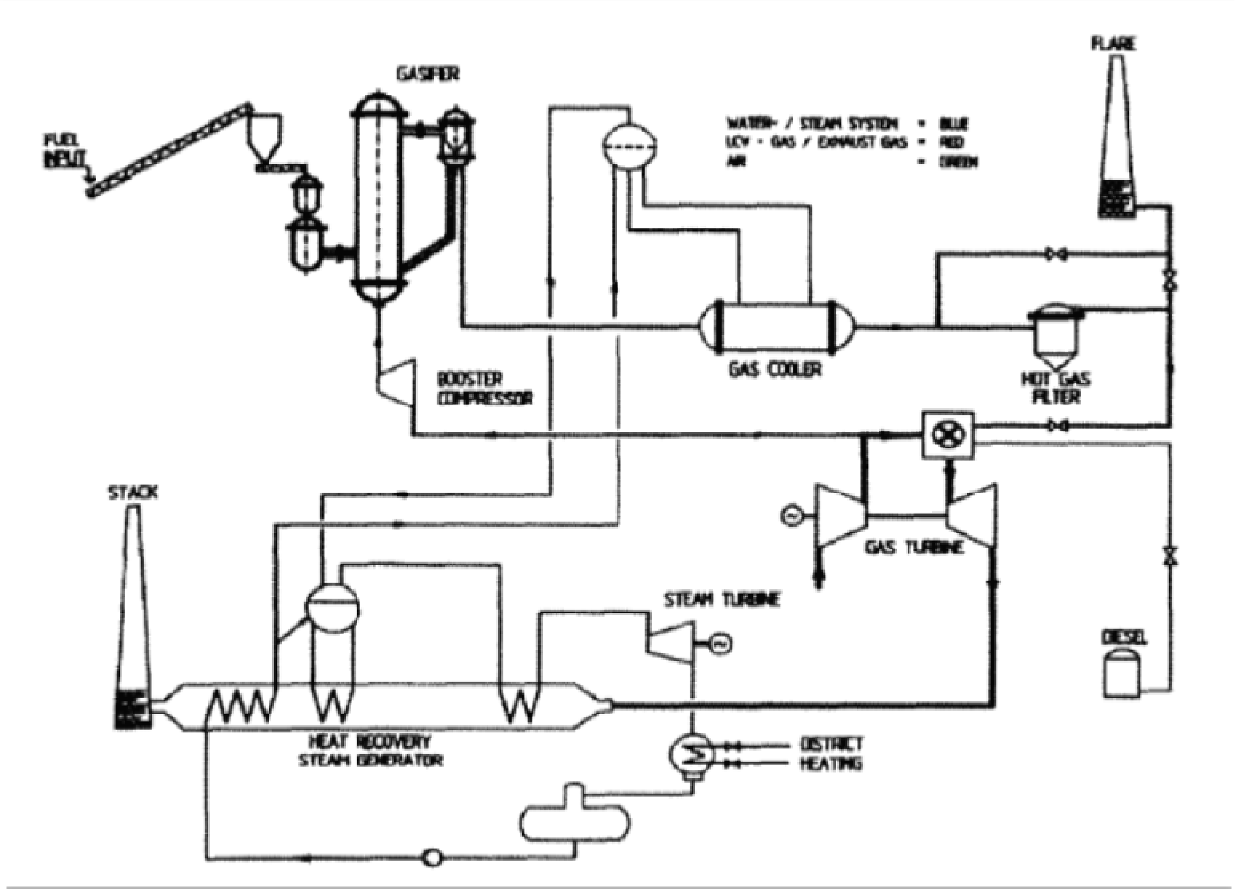
- Gasifier integrated with coal based combustion unit / **Kymijarrvi, Lahti Finland**

- 300 GWh per annum biomass & RDF - Fossil fuel replacement

- Cheap solution – direct use in existing boiler – avoiding co-feeding solid biomas and coal.



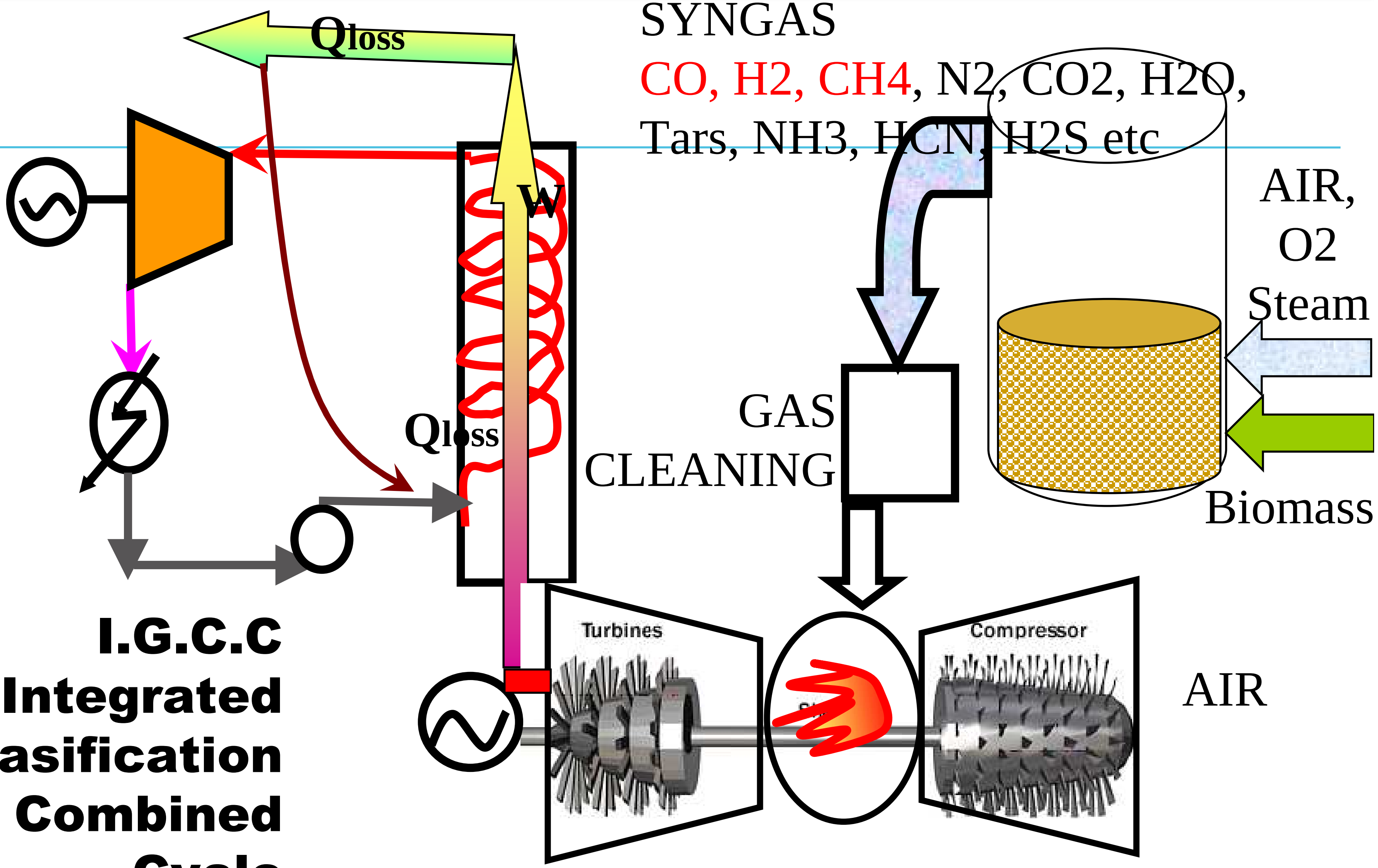
Fluidized bed gasification applications



Varnamo IGCC- Sweden

- 18 barg / 950 - 1000 ^{o}C
- Hot gas cleaning
- LHV = 5 MJ / Nm^3
- Fuel : 18,0 MW$_{th}$
- Power : 6,0 MW$_{el}$
- Heat : 9,0 MW$_{th}$

I.G.C.C Integrated gasification Combined Cycle



RAW SYNGAS

CO, H_2, CH_4, N_2, CO_2, H_2O, Tars, NH_3, HCN, H_2S etc

Qloss

W

Qloss

GAS CLEANING

AIR, O_2 Steam

Biomass

AIR

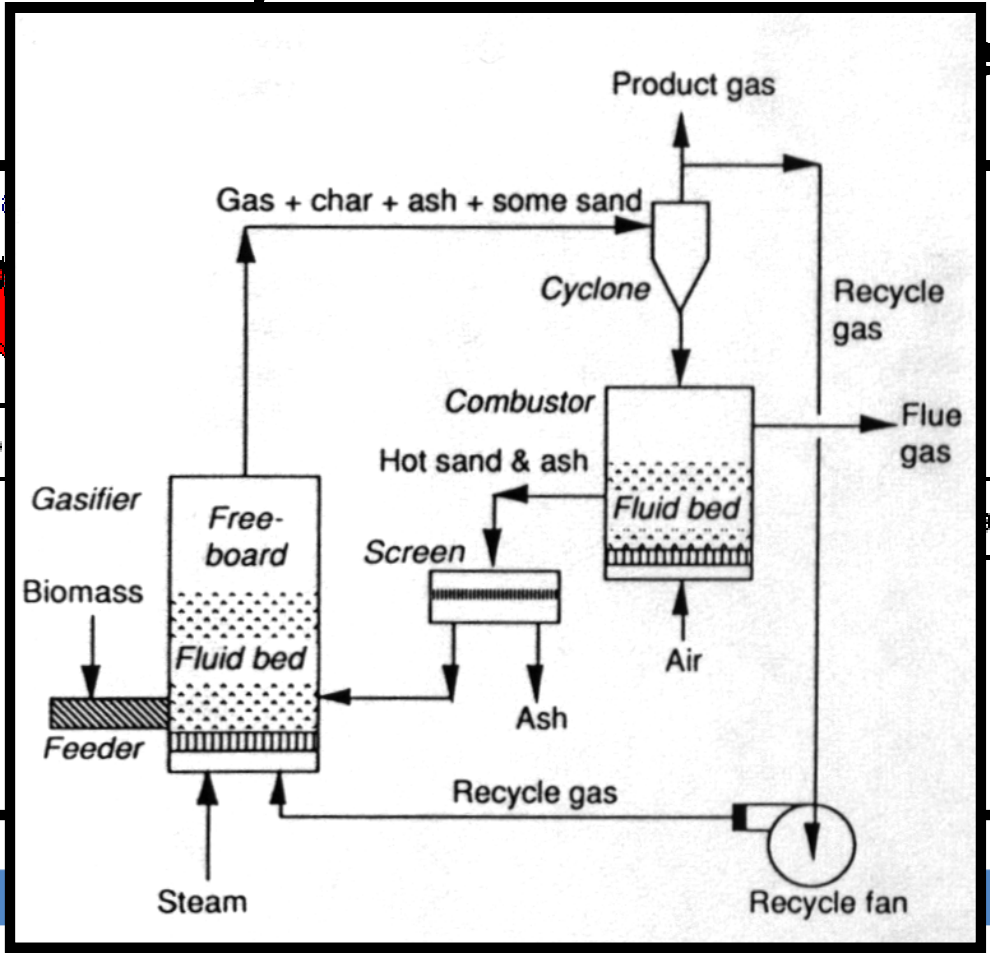
Allothermal Gasification
1) Twin Bed Reactor

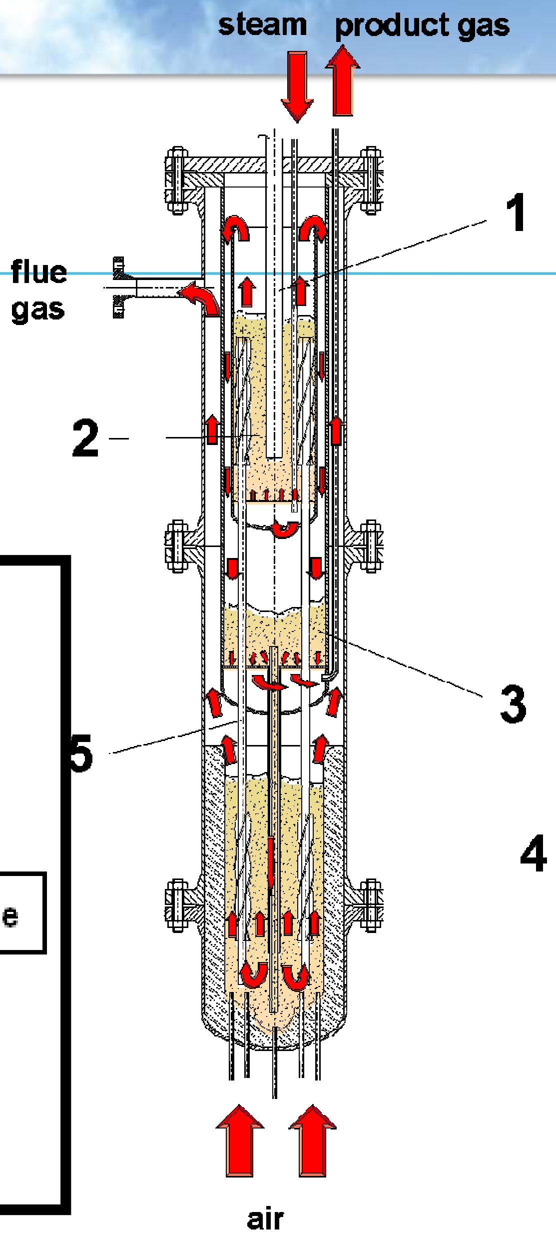
eat

he

co

ation zone

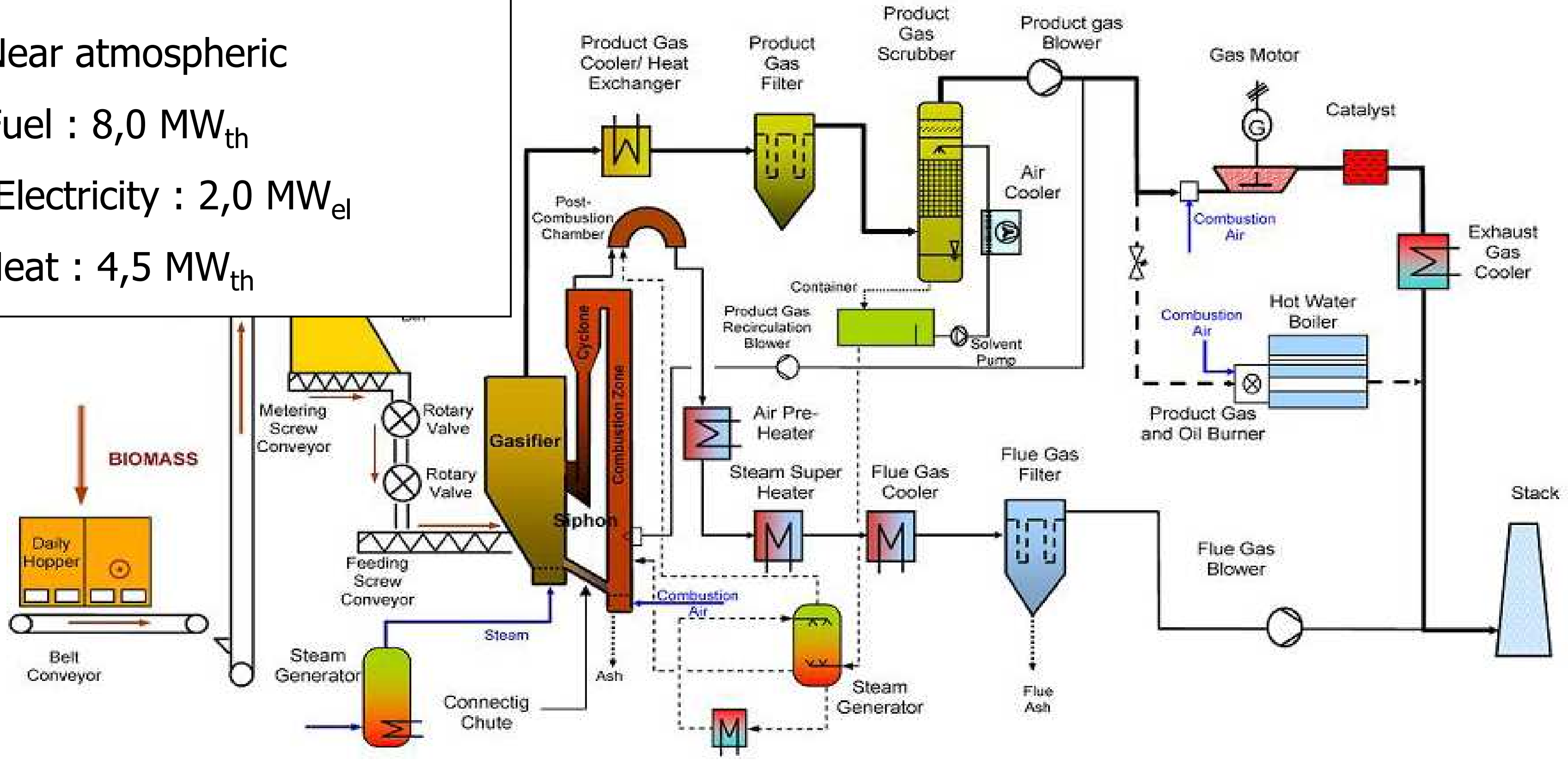




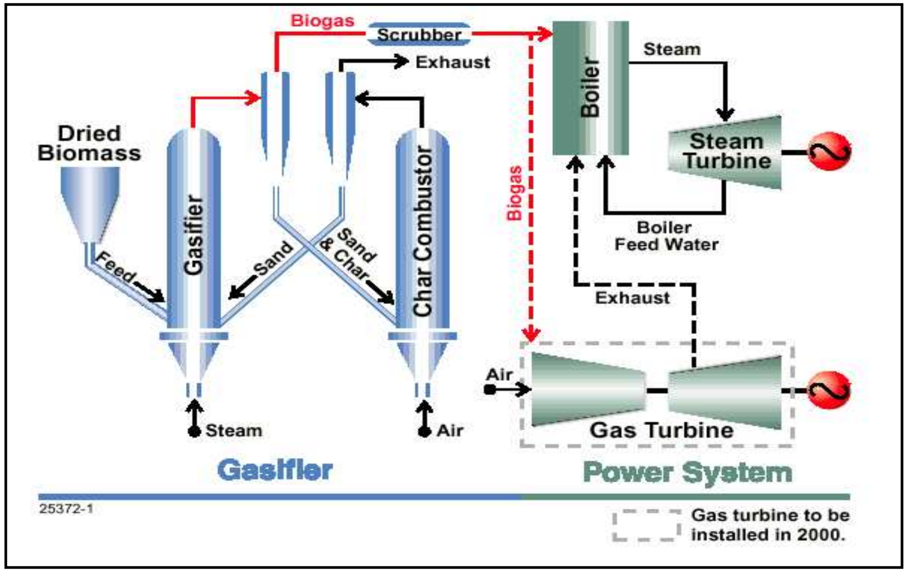
Fluidized bed gasification applications

Gussing - Austria

- FICFBC Gasifier
- Near atmospheric
- Fuel : 8,0 MW_{th}
- Electricity : 2,0 MW_{el}
- Heat : 4,5 MW_{th}



Fluidized bed gasification applications



Vermont IGCC- USA

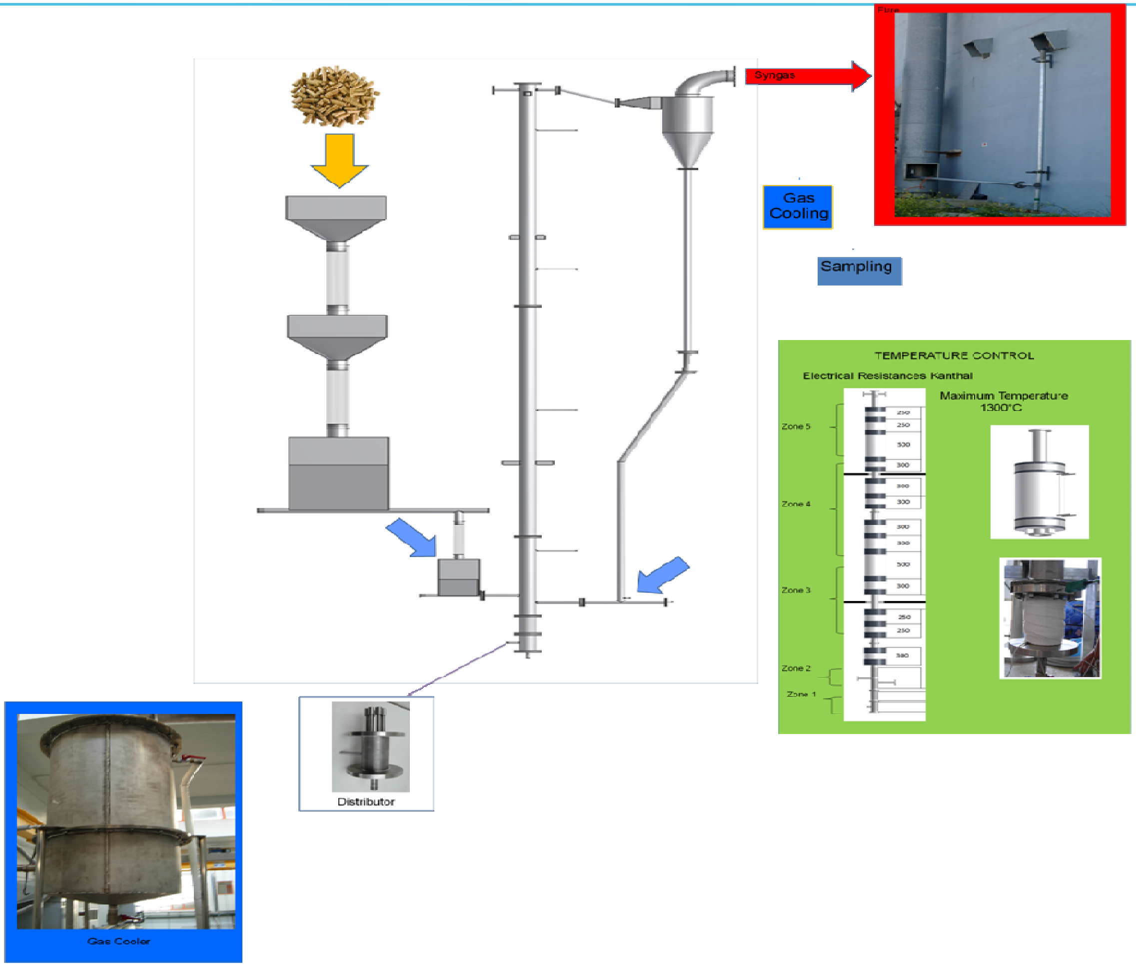
- Allothermal Pressurized
- HHV = 11-14 MJ / Nm^3
- Diverse fuels – 200 tn/d

Different gasifiers – Different product gases

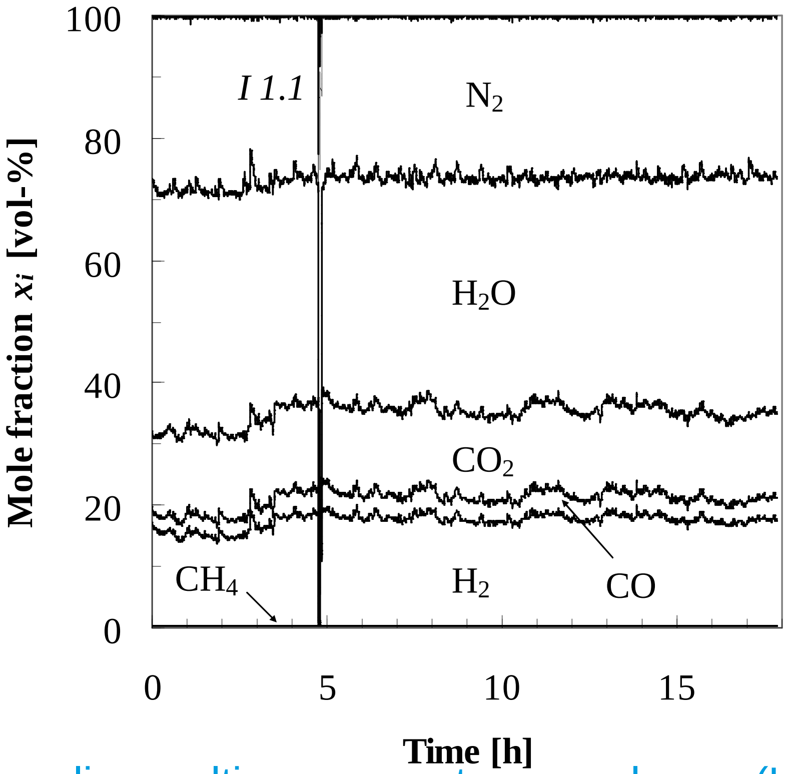
Table 2: Composition of product gas for different reactor types [2]

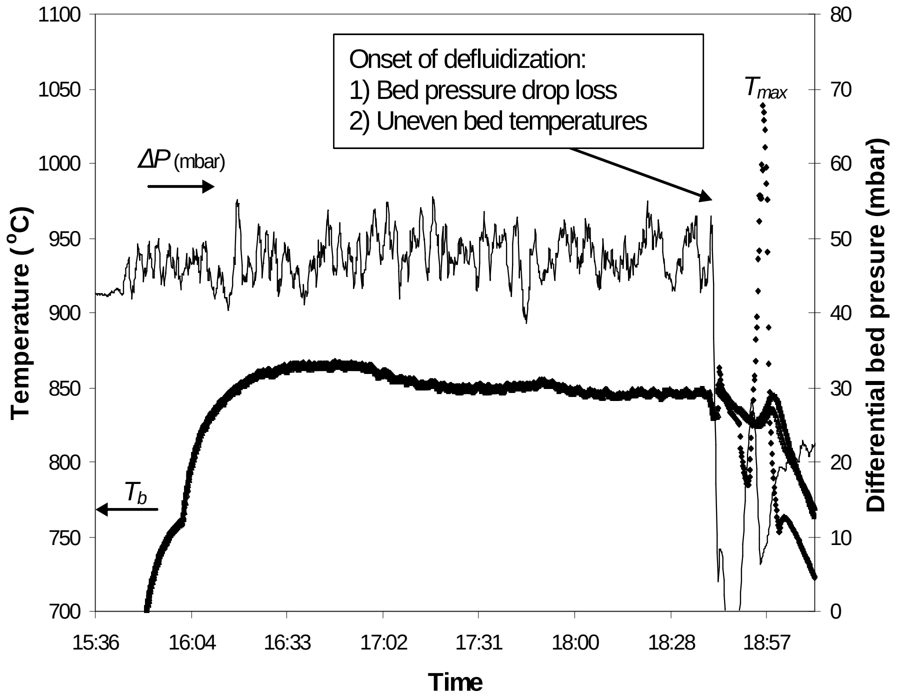
Type of reactor	H_2	CO	CO_2	CH_4	N_2	HHV (MJ/m^3)	Quality of Syngas	
							Tar	**Dust**
Fluidized bed / air	9	14	20	7	50	5.4	Fair	Poor
Updraft / air	11	24	9	3	53	5.5	Poor	Good
Downdraft / air	17	21	13	1	48	5.7	Good	Fair
Downdraft/oxygen	32	48	15	2	3	10.4	Good	Good
Dual fluidized bed	31	48	0	21	0	17.4	Fair	Poor
Pyrolysis	40	20	18	21	1	13.4	Fair	Good

Fluidized Bed Gasification research - CERTH



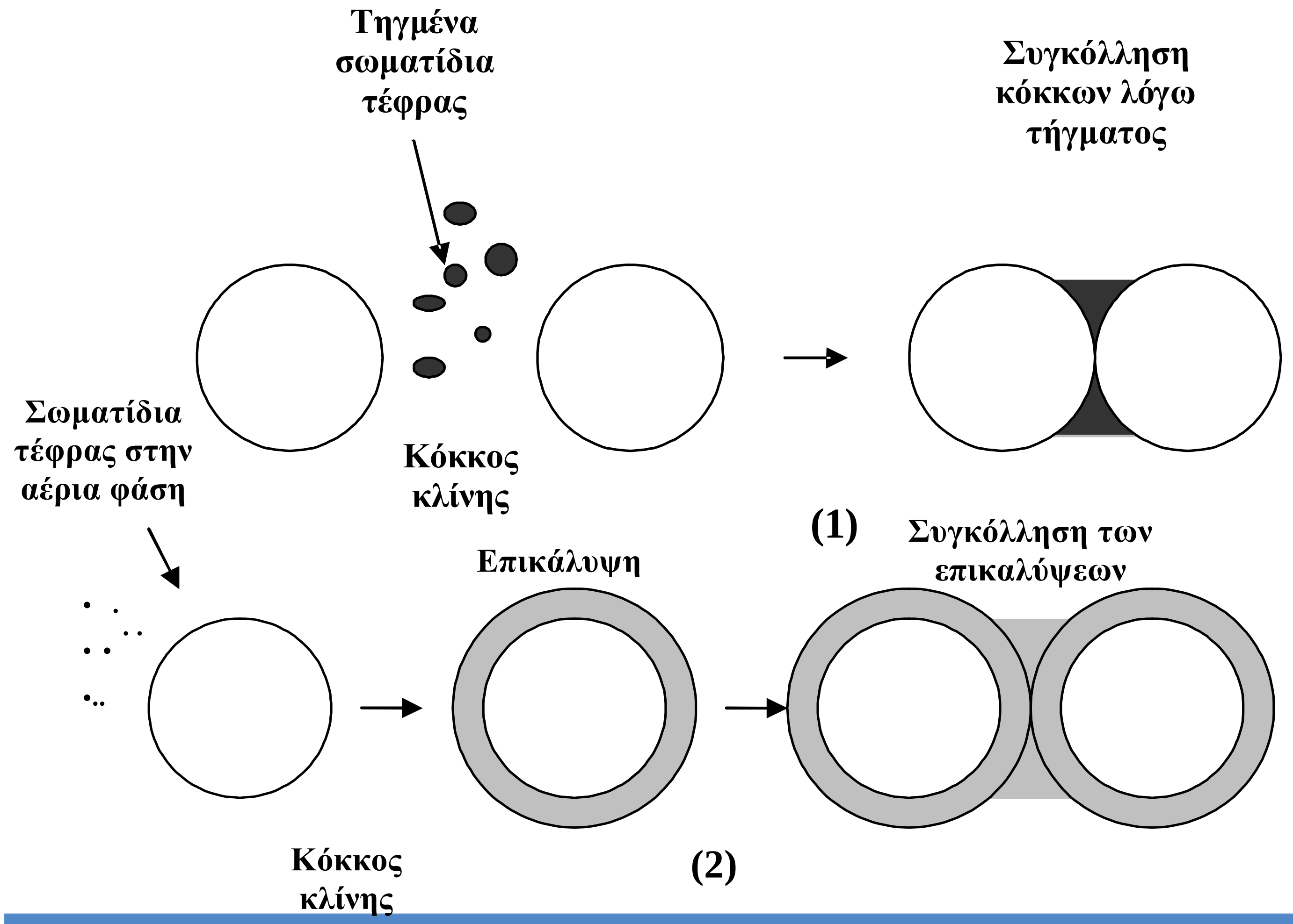
Various Technical RTD Aspects





on line multi-component gas analyzers (H_2, CO, CO_2, CH_4, O_2/N_2), Tar Protocol, FTIR, metal sampling system (Cd), (TI), (Hg), (Sb), (As), (Pb), (Cr), (Co), (Cu), (Mn), (Ni), (V), (Sn)

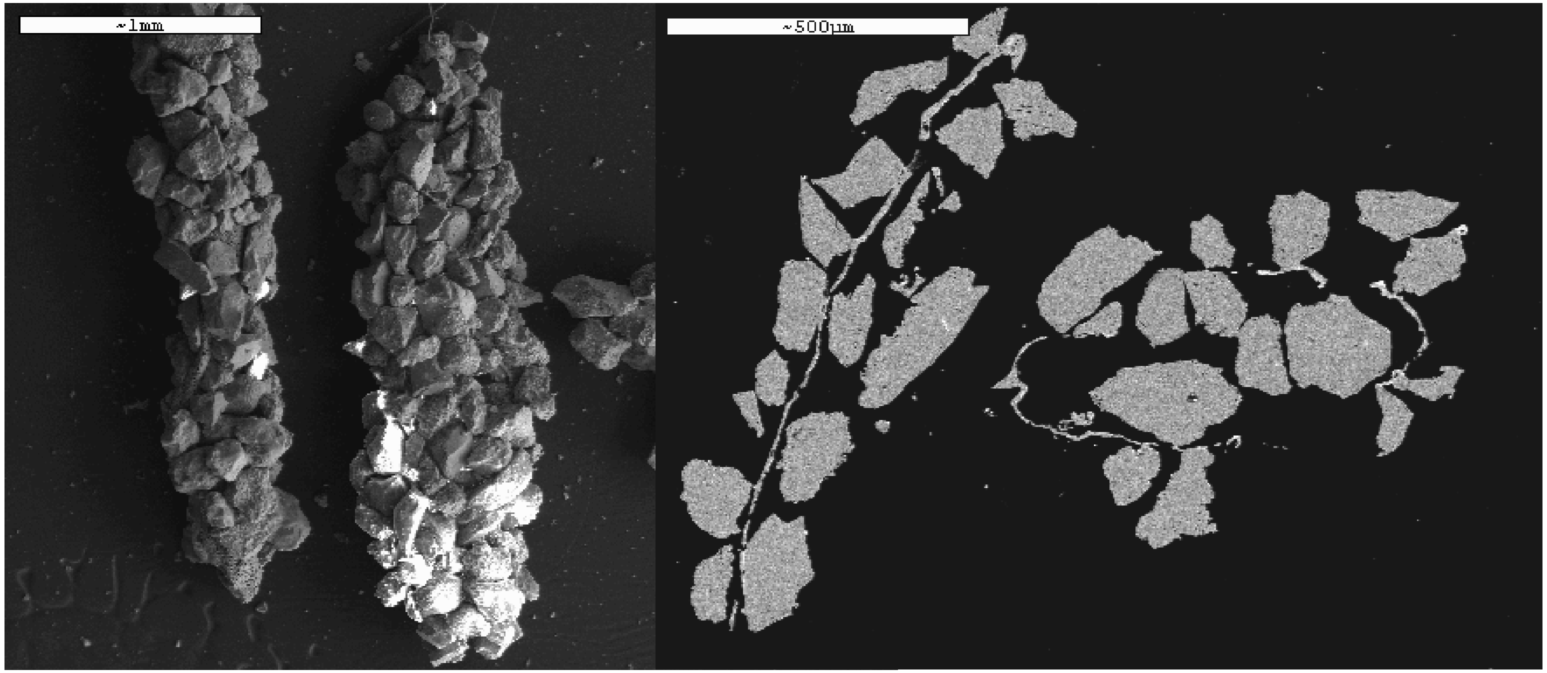
Various Technical RTD Aspects



Bridging between bed inventory particles

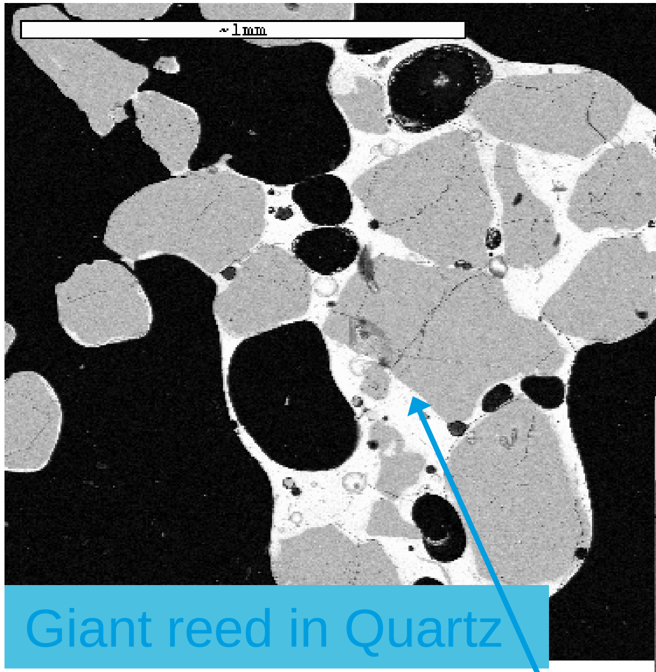
Full coverage of bed inventory particles.

Examples of agglomerates



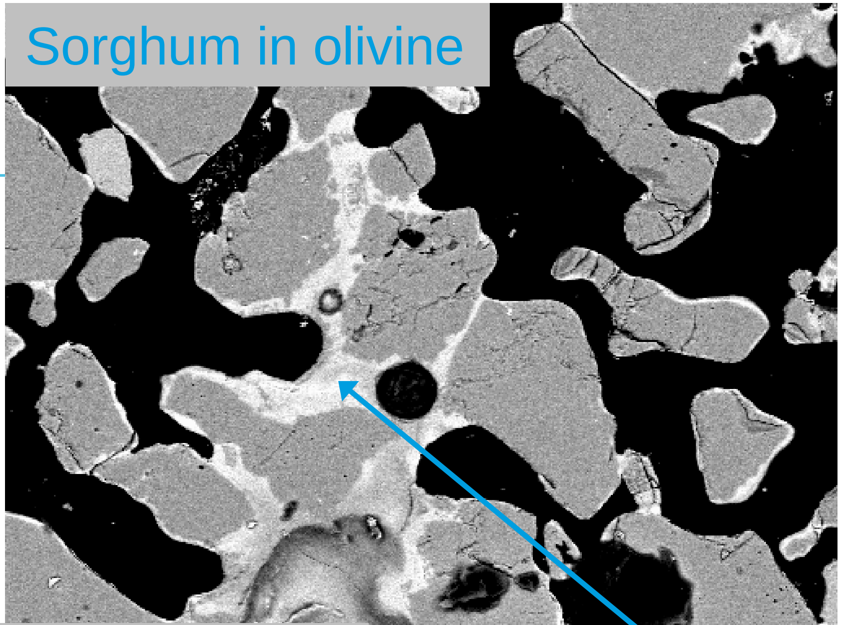
Arundo Donnax

Examples of agglomerates



Giant reed in Quartz

SiO_2, K_2O



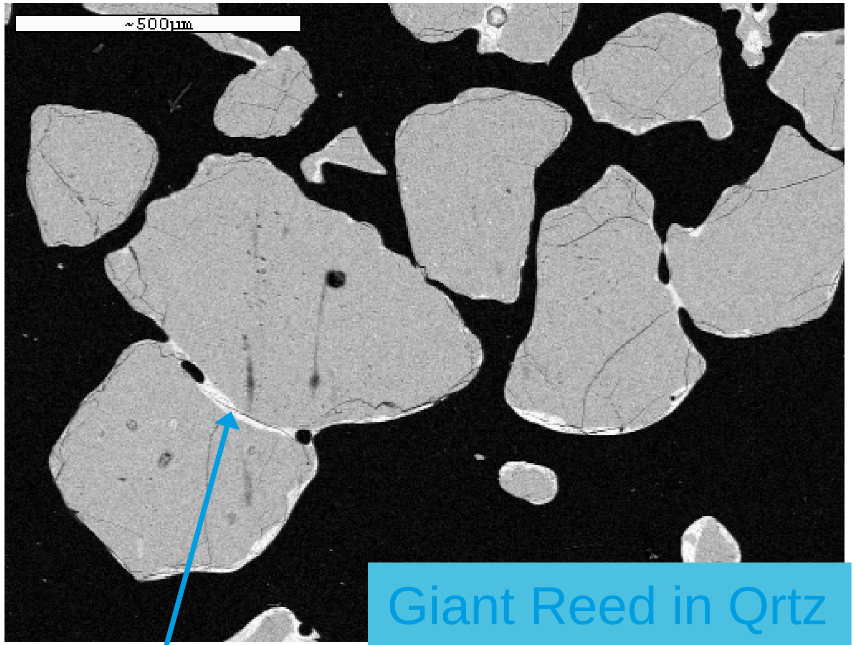
Sorghum in olivine

SiO_2, K_2O

Olive baggase in olivine

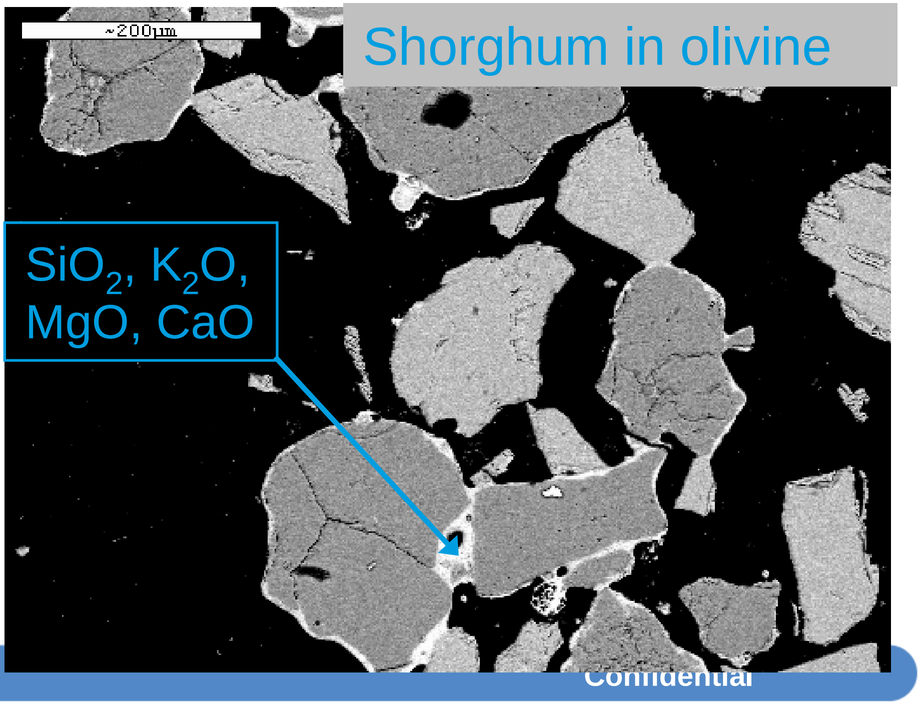
SiO_2, K_2O, MgO, CaO

Examples of agglomerates



Giant Reed in Qrtz

SiO_2, K_2O



Shorghum in olivine

SiO_2, K_2O, MgO, CaO

Characterization of impurities – Tars

1. Primary products: characterized by cellulose-derived products such as levoglucosan, hydroxyacetaldehyde,and furfurals; analogous hemicellulose-derived products; and lignin-derived methoxyphenols;
2. Secondary products: characterized by phenolics and olefins;
3. Alkyl tertiary products: include methyl derivatives of aromatics, such as methyl acenaphthylene, methylnaphthalene, toluene, and indene;
4. Condensed tertiary products: show the PAH series without substituents: benzene, naphthalene, acenaphthylene, anthracene/phenanthrene, pyrene.

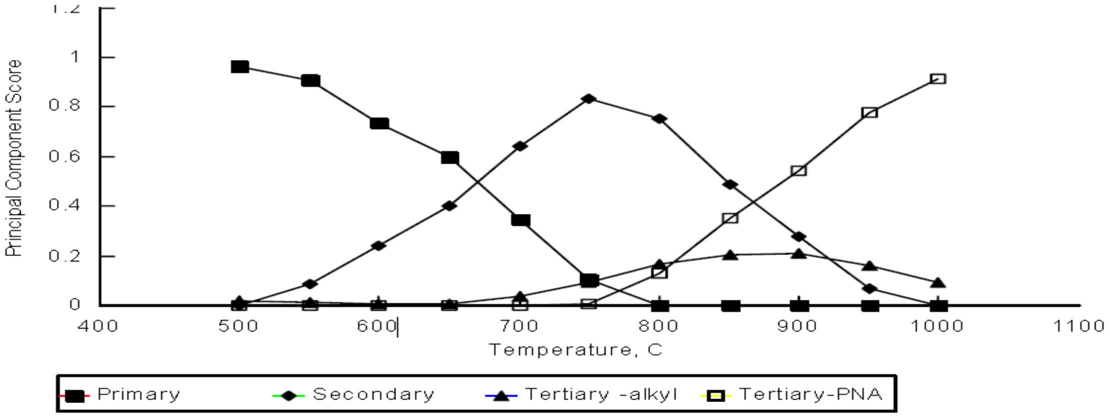
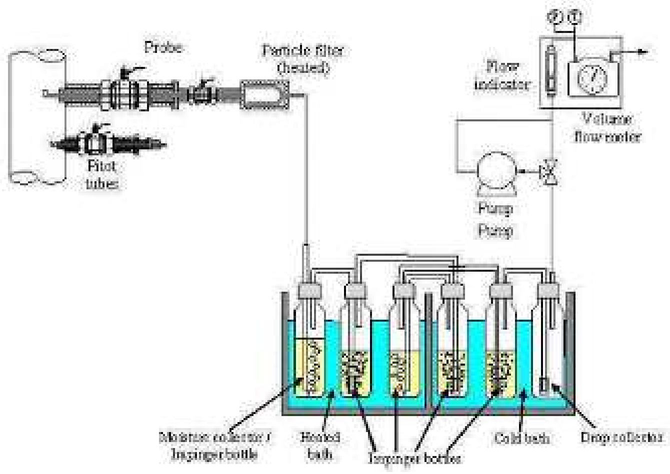
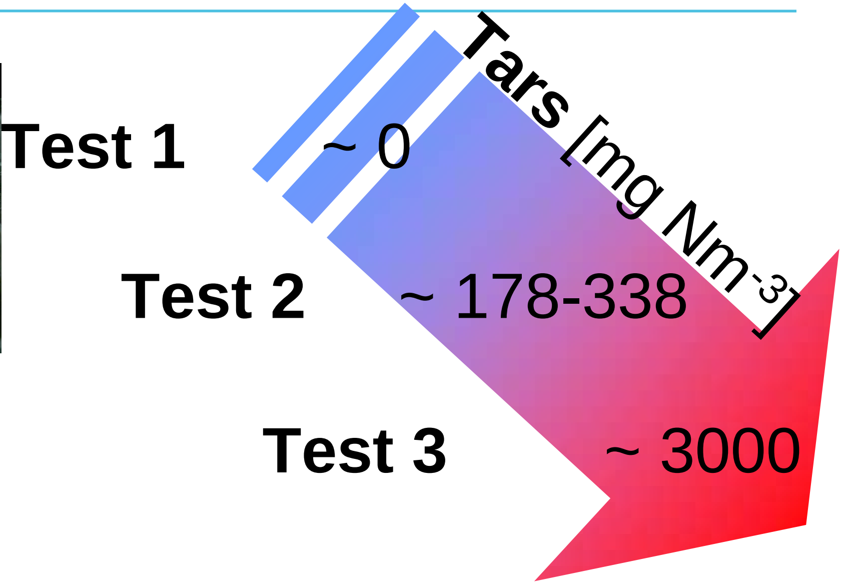


Figure 2.4. The distribution of the four "tar" component classes as a function of temperature at 300 ms (0.3 s) gas-phase residence time (reprinted from Evans and Milne 1997)

Characterization of Impurities – Tars and their effect



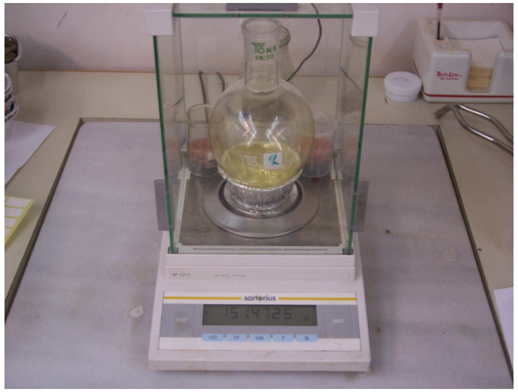


Tars [mg Nm^{-3}]

Test 1 ~ 0

Test 2 ~ 178-338

Test 3 ~ 3000



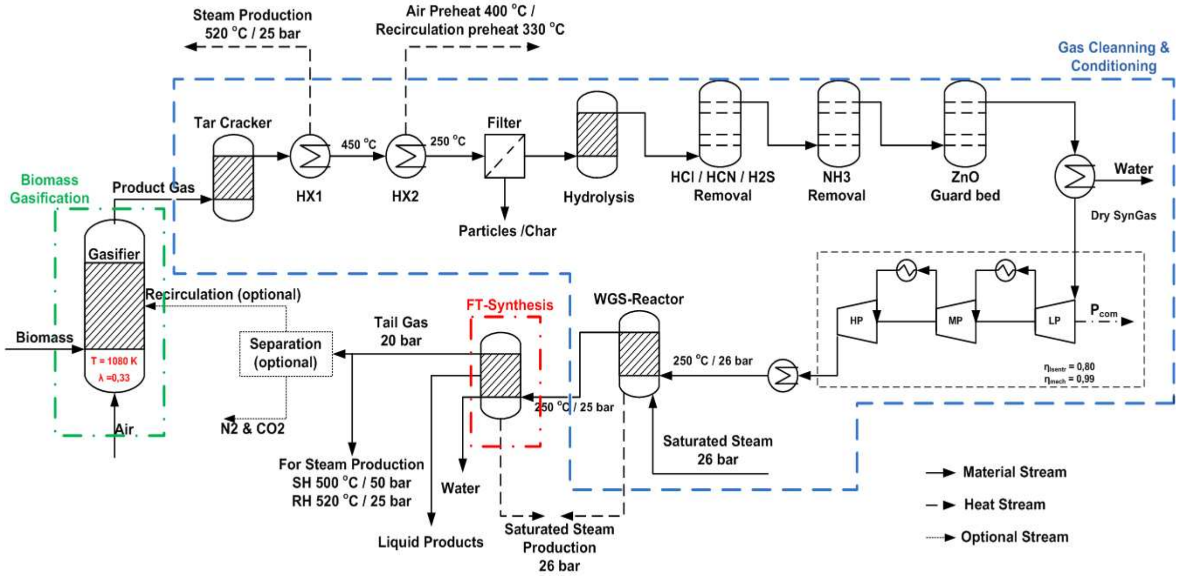
Gas cleaning Requirements for power – CHP applications

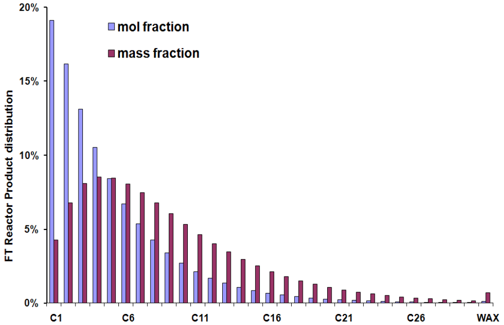
	Upper limit		
	SOFC	**ICE**	**GT**
Particles (ppmw)	0.1	**50**	**1**
NH_3 (ppmv)	5000	**-**	
H_2S (ppmv)	1	**-**	**1.0**
Halogens (ppmv)	1	**-**	**0.5**
Alkalis (ppmw)	-	**-**	**0.1**
Tars (ppmw)	-	**100**	**0.5**

Potential Syntheses of Fuels and Chemicals

- Fischer – Tropsch
- MeOH - DME
- H2 (for example for H_2O_2)
- bioSNG

FT-synthesis plant





Main reactions	
Alkanes	$n\mathrm{CO} + (2n+1)\mathrm{H_2} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O}$
Alkenes	$n\mathrm{CO} + 2n\mathrm{H_2} \longrightarrow \mathrm{C_2H}_{2n} + n\mathrm{H_2O}$
Water-gas shift	$\mathrm{CO} + \mathrm{H_2O} \rightleftarrows \mathrm{CO_2} + \mathrm{H_2}$
Side reactions	
Alcohols	$n\mathrm{CO} + 2n\mathrm{H_2} \longrightarrow \mathrm{H(-CH_2-)}_n\mathrm{OH} + (n-1)\mathrm{H_2O}$
Boudouard reaction	$2\mathrm{CO} \longrightarrow \mathrm{C} + \mathrm{CO_2}$

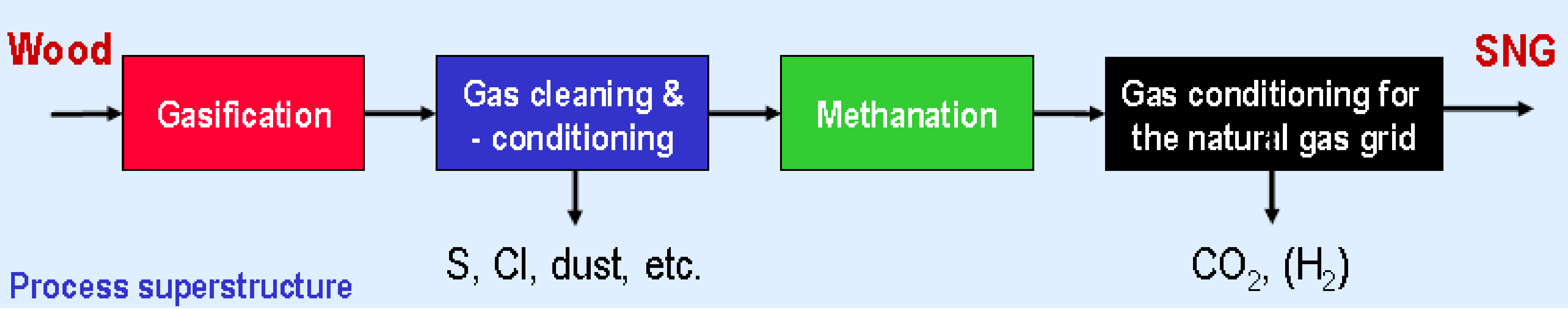
Syntheses

Process	Catalyst	Process Conditions			% conv (CO basis)	Products	Sectivity
		T [ºC]	P [bar]	H_2/CO			
FT Synthesis	Fe	300-350	10-40	1,7	50-90% with recycle	a-olefines gasoline	ASF-48% (max) 15-40% actual
	Co	200-240	7-12	2,15		Waxes diesel	ASF – 40% max
	Ru					Waxes	
MeOH synthesis	ZnO/Cr_2O_3	350	250-350	3	99% (25% max/pass – 4-7% Actual pass)	Methanol	>99% with recycle
	$Cu/ZnO/Al_2O_3$	220-275	50-100				

Gas cleaning requirements

Process	Contaminant	Level	Source/Comments
FT Synthesis	Sulfur	200 ppb	[1]
		1000 ppb	[2]
		60 ppb	[3]
		10 ppb	[4] – [5]
	Halides	10 ppb	[2]
	Nitrogen	10 ppm NH3 0.2 ppm NOX 10 ppb HCN	[3]
		20 ppb	[4] –[5]
	Solids	0 ppm	[1]-[5]
MeOH synthesis	Sulfur (not COS)	<0.5 ppmv (<0.1 ppb HCN)	[6]
	Halides	0.001 ppmv	[7]
	Fe and Ni	0.005 ppmv	[6]

bioSNG production



Wood

Gasification

Gas cleaning & - conditioning

Methanation

Gas conditioning for the natural gas grid

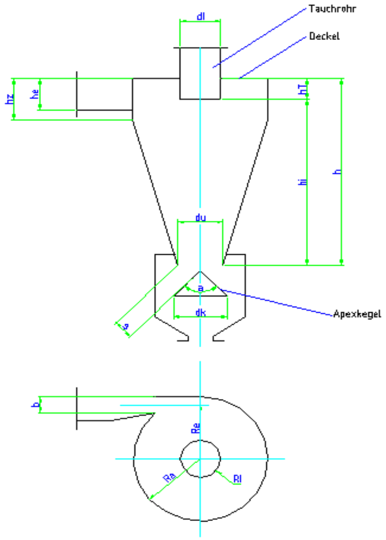
SNG

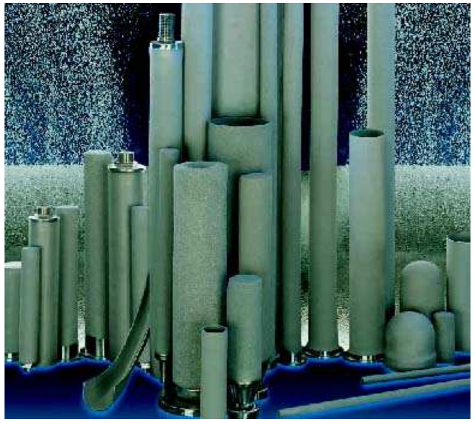
S, Cl, dust, etc.

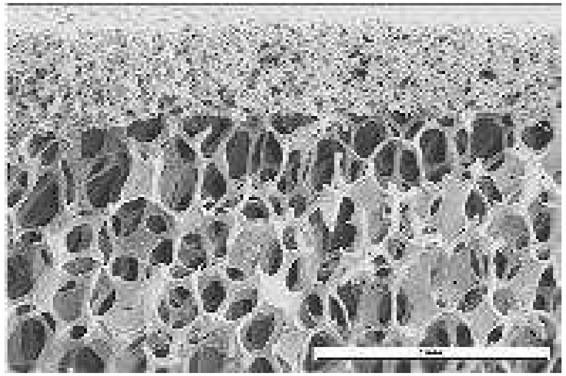
CO_2, (H_2)

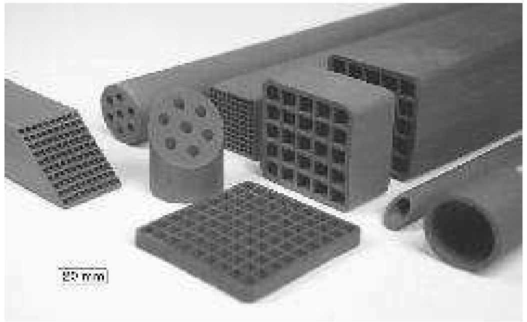
Process superstructure

Particle Removal

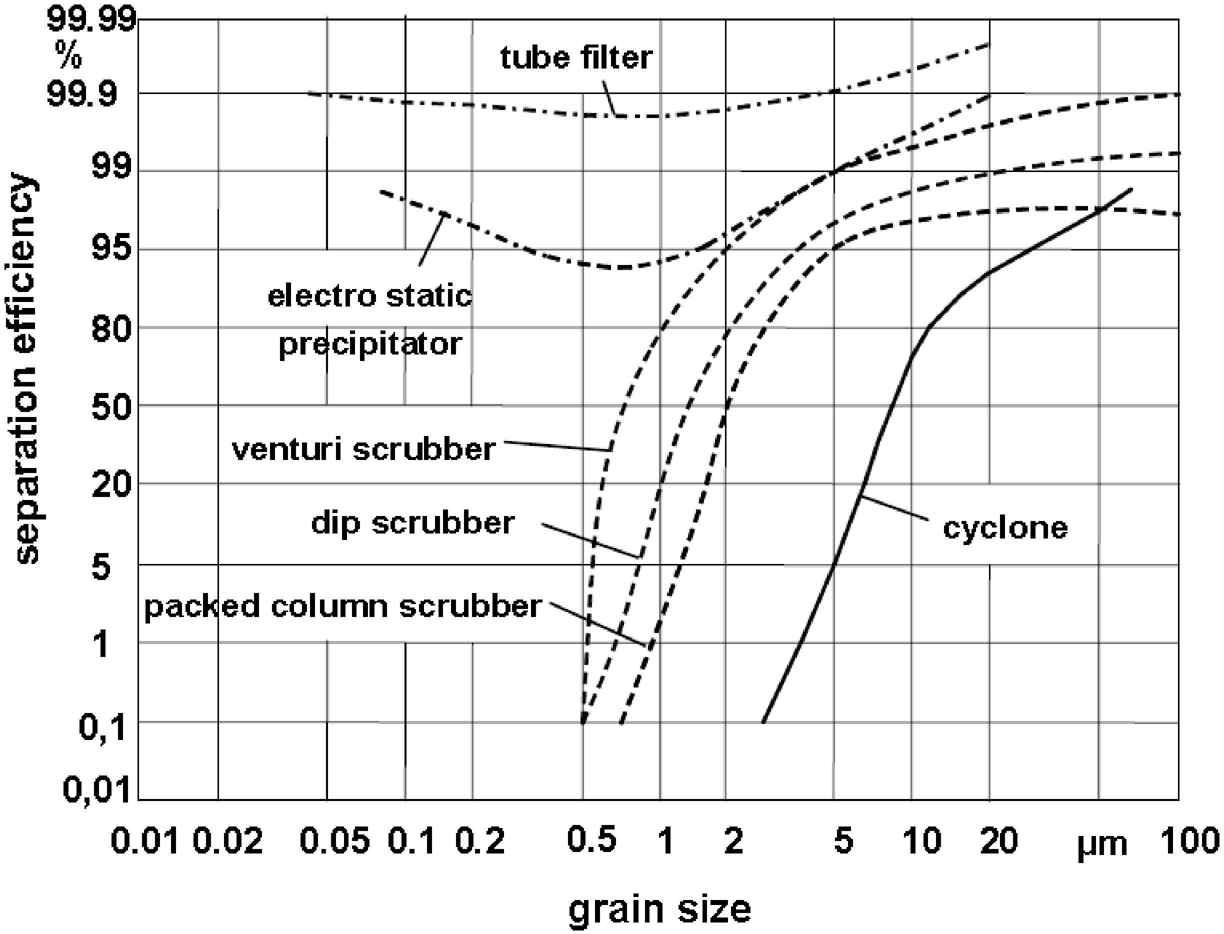




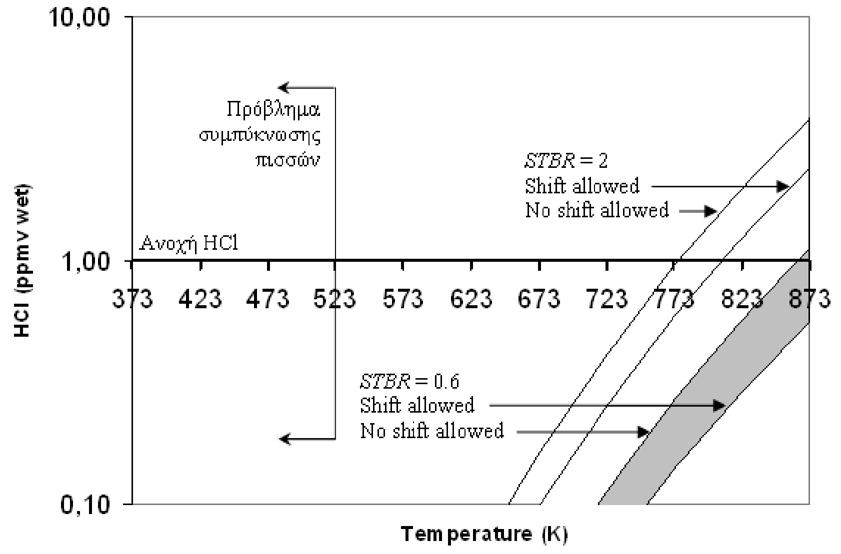




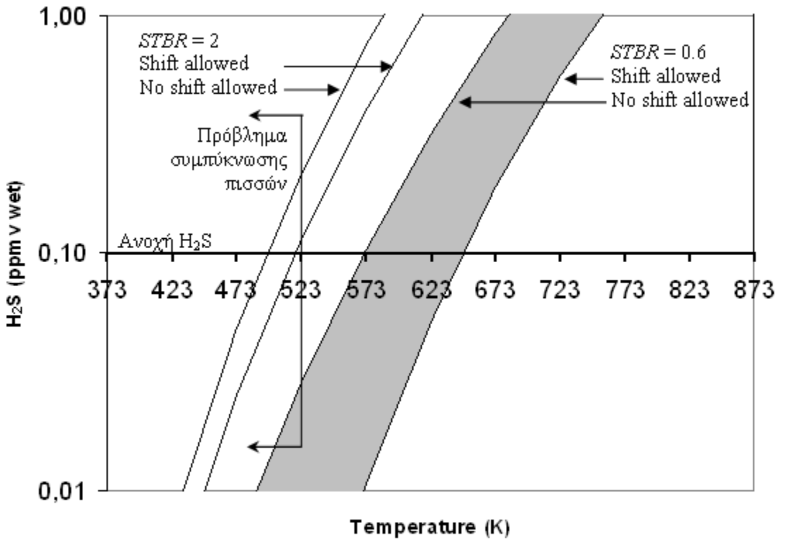
Effectiveness in particle removal



Gas species cleaning with solid phase sorbents



Σχήμα 6.9. Πρόβλεψη της συγκέντρωσης εξόδου HCl από προσροφητική κλίνη Na_2CO_3 συναρτήσει της θερμοκρασίας, για διάφορα *STBR*, με και χωρίς την αντίδραση μετατόπισης σε ισχύ.



Σχήμα 6.10. Πρόβλεψη της συγκέντρωσης εξόδου H_2S από προσροφητική κλίνη ZnO συναρτήσει της θερμοκρασίας, για διάφορα *STBR*, με και χωρίς την αντίδραση μετατόπισης σε ισχύ.

$Na_2CO_3 + HCl \leftrightarrow NaCl + CO_2 + H_2O$

$$K_p = P_{H_2O} P_{CO_2} / P_{HCl}$$

$ZnO_{(s)} + H_2S \leftrightarrow ZnS_{(s)} + H_2O$

$$K_p = P_{H_2O} / P_{H_2S}$$

Shift : $CO + H_2O \leftrightarrow CO_2 + H_2$

Tar elimination techniques

Thermal tar treatment

Thermal tar treatment systems work on the basis of partial oxidation of producer gas loaded with tarry contaminants situated after the gasifier. Partial oxidation converts tar on the expense of calorific value in the producer gas. Thermal tar treatment is rather unusual in gas cleaning – this type of tar treatment presents itself rather as a possible process step for the reduction of the tar release potential in gas production through primary measures.

Catalytic tar treatment systems

Catalytic tar treatment is based on the principle of tar cracking through thermochemical reactions supported by catalysts. The cracking or reforming process leads to a decomposition of tarry compounds which results in the successive formation of permanent gasphases and lighter tar compounds.

Use of special Solvents

Use of Activated Carbon

Mapping of Gas Cleaning T, P, application etc

	Particles Removal	**Akali species**	**Sulfur species**	**Halogen species**	**Tars**	**Nitrogen species**
HOT	Cyclones, Barrier-Ceramic Candle Filters	Aluminosilicates (kaolin, bauxite and clay)	Solid sorbents (Zn, Ce, Co,Fe)		Particle Removal techniques Thermal cracking Catalysts (Ni-Fe-dolomite)	Catalysts (Ni-Fe-dolomite)
WARM	Electrostatic Filters Barrier-Metallic Candle Filters	Particle Removal techniques	Catalysts (Al-Co-Mo, etc)	Ca, Na, K carbonate based sorbents	Particle Removal techniques Activated Carbon	
COLD	Wet Scrubbers	Wet scrubbers	Chemical absorption (alkaline/ water or alkaloamines)	CRI catalyst dioxine reduction	Particle Removal techniques	Wet scrubbers (water)
		Particles Removal techniques	Physical absorption (Rectisol, Selexol)	Wet scrubbers (water/alkali solution/olga)	Wet scrubbers (water/oil) Activated Carbon	Activated Carbon

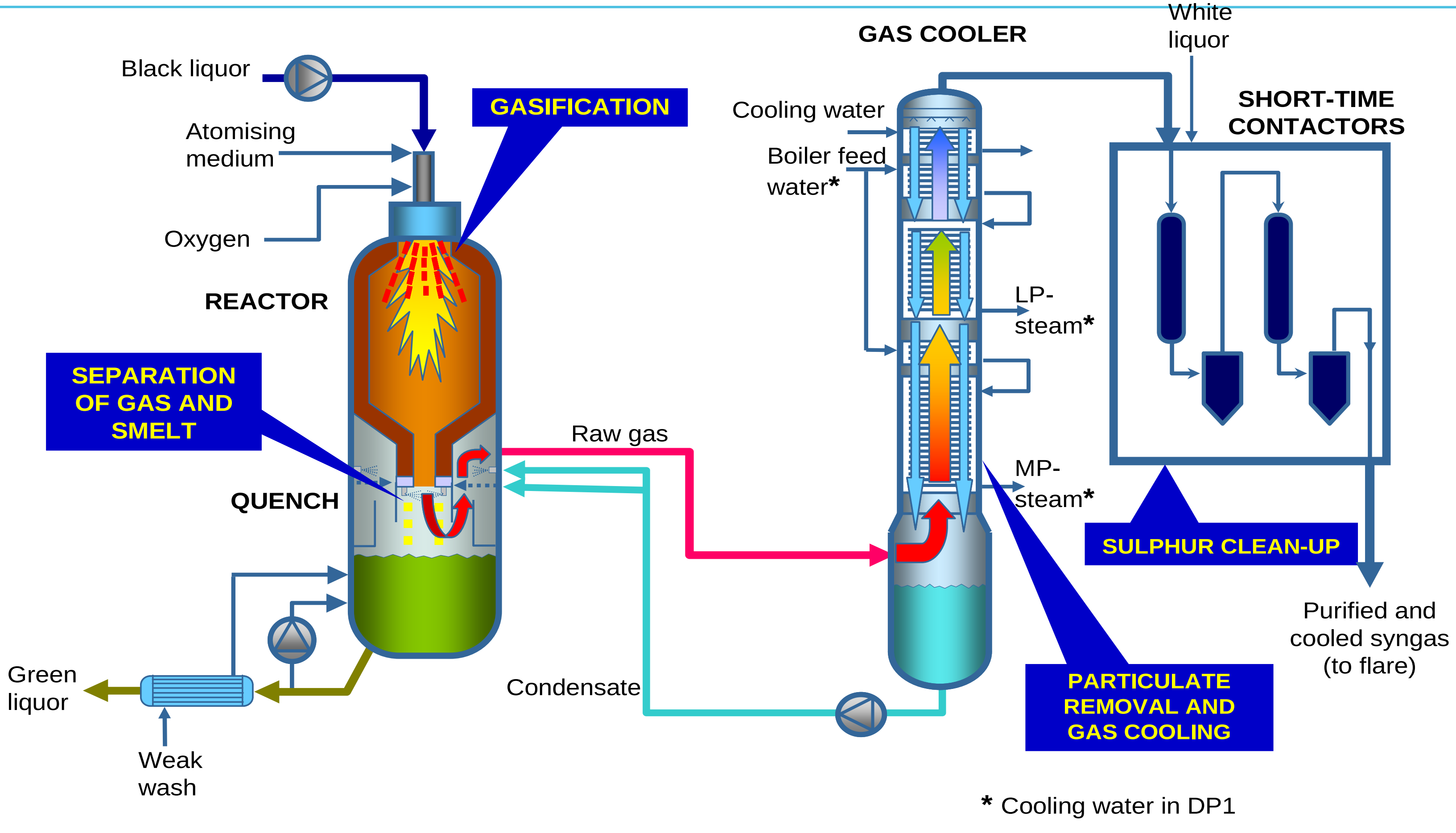
Entrained flow gasification

Examples :

Liquid biomass: black liquor , pyrolysis oil
Or fine-grained ground solid biomass (torrefied) < 0.1 mm (10 µm)

- Usually use of oxygen.
- The retention time is only a few seconds, and so gasification has to take place quickly at temperatures between 1200 and 1500℃.
- The high temperatures ensure a complete conversion of the hydrocarbon compounds resulting from pyrolysis of the fuel.
- The reactivity of the fuel regarding the heterogeneous gas/solid reactions is of secondary importance because the boundary layer determines the speed of the entire process.
- The ash melts and accumulates after adequate cooling as slag.

Black Liquor gasification*



* Cooling water in DP1

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Physical / Chemical Solvents*

- Chemical solvents for acid gas removal, such as MDEAs (methyldiethanolamine) form chemical bonds between the acid gas (H2S,CO2) and the solvent.
- Physical solvents for instance Selexol or Rectisol remain chemically non-reactive with the gas, and salts formation is avoided.
- Chemical solvents are favourable at low acid-gas partial pressures, whereas physical solvents are favoured at high acid-gas partical pressures [13].

- The Selexol process is a dominant acid-gas removal system in gasification projects [13]. The process solvent is a mixture of dimethyl ethers of polyethylene glycol [CH3(CH2CH2O)*n*CH3] , *n* is between 3 and 9.
- Rectisol, which uses methanol for absorption, can remove H2S to lower concentrations than Selexol. Since downstream catalysts in biorefineries for DME and for FT synthesis require H2S concentrations of the order of 0.1 ppmv to prevent sulfur poisoning [7], the Rectisol® is chosen.
- State-of-the-art Rectisol process involves the cryogenic process in a methanol scrubber at -70℃ up to room temperature, thus reheating the product gas for higher alcohol syntheses brings inevitable high energetic loss.
- For synthesis of mixed alcohols, the catalyst is a molybdenum-sulfide based material that has a much higher tolerance for sulfur (at least 100 ppmv), so Selexol® is more appropriate.

Thank you for your attention!

ANY QUESTIONS ?