The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
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International Atomic
Energy Agency

ICTP Experts Meeting on "Science & Renewable Energy"
January 15 - 18, 2007

Venue: ICTP Adriatico Guest House - Lundqvist Lecture Hall

310/1905

"Biomass: a Sustainable Energy Source"

P.-U. Foscolo
Università degli Studi di L'Aquila
Italy

University of L'Aquila, Italy

Department of Chemistry, Chemical Engineering and Materials

www.ing.univaq.it foscolo@ing.univaq.it

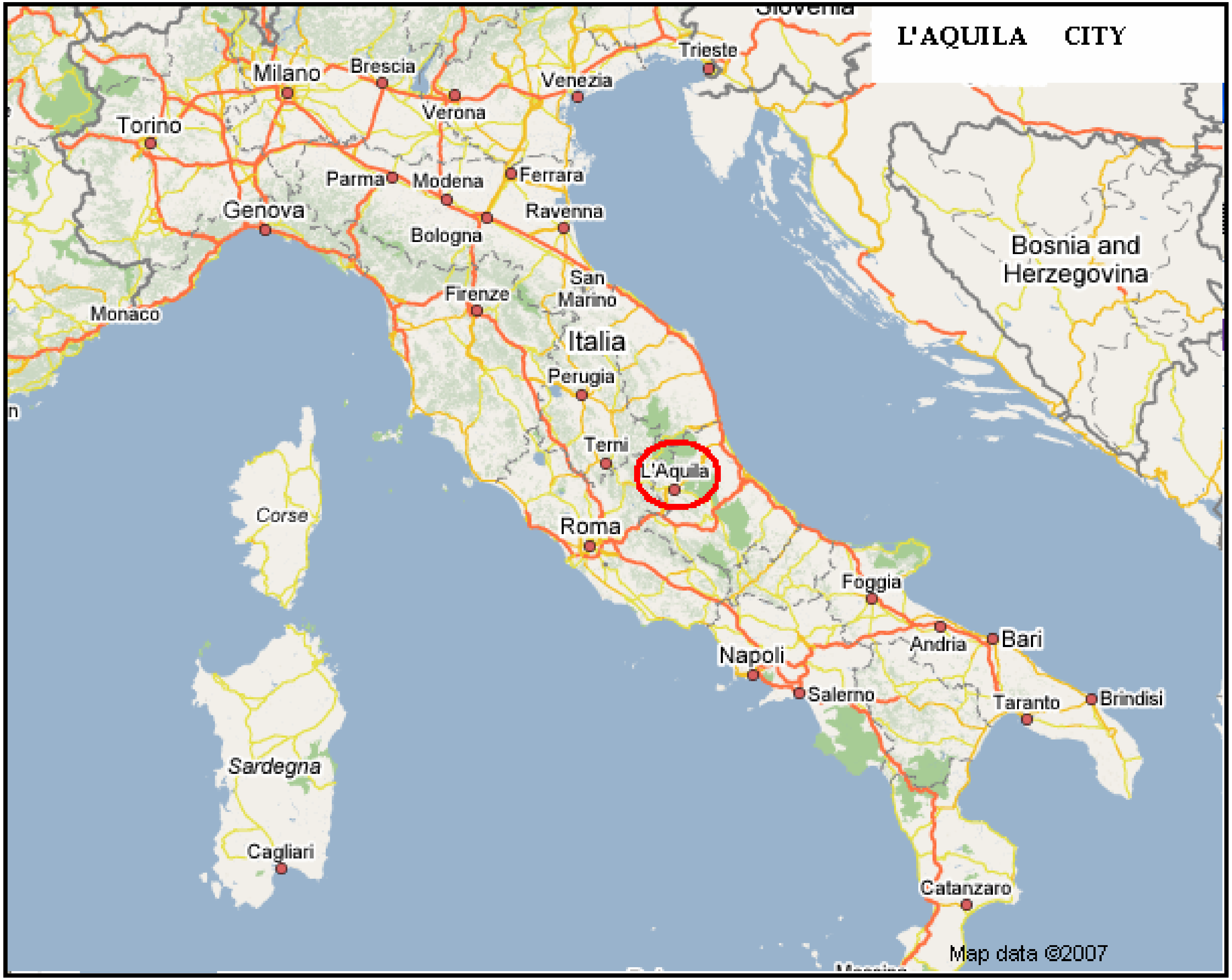
Phone: +39 0862 434214 Fax: +39 0862 434203

BIOMASS

A SUSTAINABLE ENERGY SOURCE

Pier Ugo FOSCOLO

PROF. OF CHEMICAL REACTION ENGINEERING



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Biomass gasification and fluid-dynamics of fluidized bed reactors are actively cultivated in the CRE laboratory at UNIVAQ since more than 25 years, at the level of theoretical and experimental research investigations, including industrial contracts.

Research Group

Prof. Pier Ugo Foscolo, full professor in Chemical Reaction Engineering, author of more than 70 papers in International Scientific Journals and as many Conference presentations;

Prof. Larry Gibilaro, previously employed (as full professor) at University College London. His outstanding experience in *Fluidization-Dynamics* has been recently condensed in a book published by Butterworth-Heinemann;

Prof. Antonio Germanà, part-time professor of Chemical and Process Plant Design. He has a long standing academic and professional experience in plant design, construction and commissioning;

Dr Ing. Nader Jand, assistant professor in Chemical Engineering, with outstanding doctoral and post-doctoral experience in biomass gasification both, at experimental and model developing level;

Post doctoral researchers, PhD students and technical staff

Greatest challenges of sustainability:

- **number one** → **energy**
- **number two** → **clean drinking water**

Source: Nobel Chemist Richard Smalley

"Carbon derived from biomass and then returned to the atmosphere does not add to the accumulation of carbon in the atmosphere, but rather just closes the carbon cycle"

Collective implementation of sustainable solutions:

- **increased energy efficiency in transportation, electricity production and buildings;**
- **use of biofuels and renewable resources;**
- **carbon sequestration**

Source: Pacala and Socolow, *Science*, 2004

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- an abundant and distributed source of energy and chemicals, resulting from storage of solar energy on the earth;

- the biomass production – power generation cycle is characterized by near-zero contribution to the accumulation of green-house gases (sustainable growth);

- the renewable source with the highest potential to contribute to the energy needs of modern society for both the developed and developing economies world-wide.

A FAIRLY DIFFERENT PERSPECTIVE IN RELATION TO FOSSIL ENERGY SOURCES!

FOR A GLOBAL AND WIDESPREAD BREAKTHROUGH OF RENEWABLES (AND BIOMASS AMONG THESE) DIFFERENT SCENARIOS IN THE WORLD ECONOMY NEED TO BE ESTABLISHED

IS THIS A REMOTE HYPOTHESIS?

The world map of the Arab geographer al-Idrîsî, who lived at the court of the Norman King Roger II of Sicily in the middle of the XIIth century, is oriented towards the south, with the Islamic lands in the centre. Another way of looking at the Mediterranean.

Physical and chemical properties of biomass (example)			
Type	**Almond shells**		
Status	**Raw**	**Dry**	**Dry-ash-free (daf)**
Moisture (wt%)	**7.90**	**-**	**-**
Ash (wt%)	**1.16**	**1.26**	**-**
Volatile matter (wt%)	**72.45**	**78.66**	**79.67**
Carbon (wt%)	**46.65**	**50.65**	**51.30**
Hydrogen (wt%)	**5.55**	**6.03**	**6.10**
Oxygen (wt%)	**38.74**	**42.06**	**42.60**
LHV (kJ/kg)	**18350**		
Cellulose (wt%)	**29**		
Hemicellulose (wt%)	**28**		
Lignin (wt%)	**35**		
Density (kg/m^3)	**1200**		

B I O – R E S I D U E S

- **waste-biomass has the potential to provide as much as 330 GW of electric power world-wide, if utilized efficiently;**

- **in Mediterranean countries (because of climate), in Eastern EU countries (because of extensive utilization of land for food crops), and in intensely populated industrial areas, energy crops and virgin biomass are scarce, and costly because of alternative uses;**

- **when agricultural and forestry wastes, by-products of agro-industrial processes or MSW (RDF) are utilized as feedstock, the problem and the cost of disposal are reduced, and this contributes positively to the economic balance of the conversion process to energy or chemicals.**

AN INTERESTING NICHE MARKET!

Physical and chemical properties of biomass (example)			
Type	Olive waste from oil production		
Status	Raw	Dry	Dry-ash-free (daf)
Moisture (wt%)	8.90	-	-
Ash (wt%)	7.74	8.5	-
Volatile matter (wt%)	67.78	74.40	81.31
Carbon (wt%)	43.93	48.22	52.70
Hydrogen (wt%)	6.00	6.59	7.20
Oxygen (wt%)	31.76	34.86	38.10
Nitrogen (wt%)	1.33	1.46	1.60
Sulphur (wt%)	0.05	0.06	0.07
Chlorine	0.34	0.34	0.37
LHV (kJ/kg)		18500	
Bulk density (kg/m^3)	659		

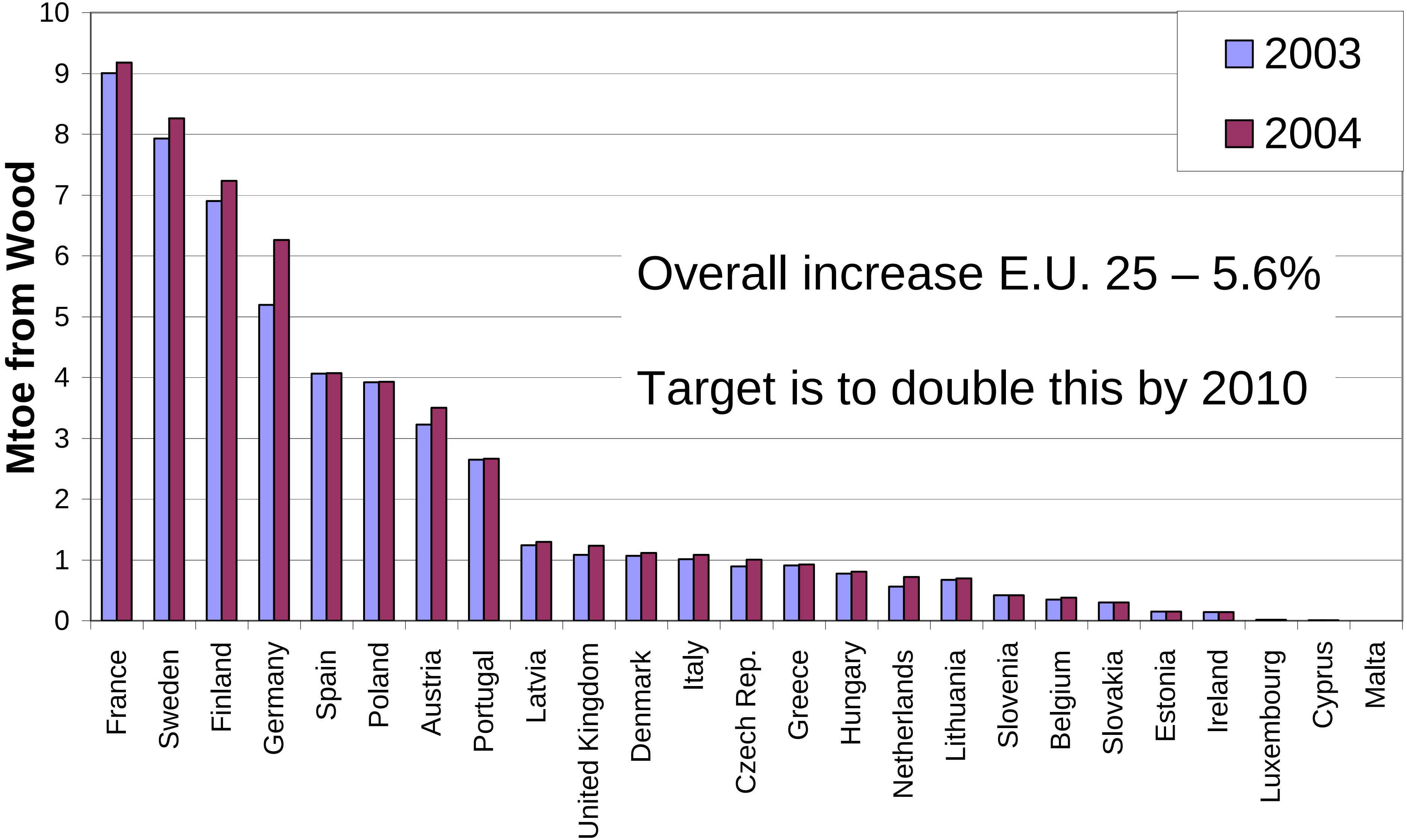
Physical and chemical properties of biomass (example)			
Type	Rice husk		
Status	Raw	Dry	Dry-ash-free (daf)
Moisture (wt%)	6.96	-	-
Ash (wt%)	14.71	15.8	-
Volatile matter (wt%)	66.69	71.71	85.17
Carbon (wt%)	36.25	38.96	46.27
Hydrogen (wt%)	4.75	5.11	6.07
Oxygen (wt%)	35.32	37.96	45.08
Nitrogen (wt%)	2.02	2.17	2.58
Sulphur (wt%)	0.13	0.14	0.17
Chlorine	-	-	-
LHV (kJ/kg)	13544		17290
Bulk density (kg/m^3)	161		

EU Renewables Directive
2001/77/EC

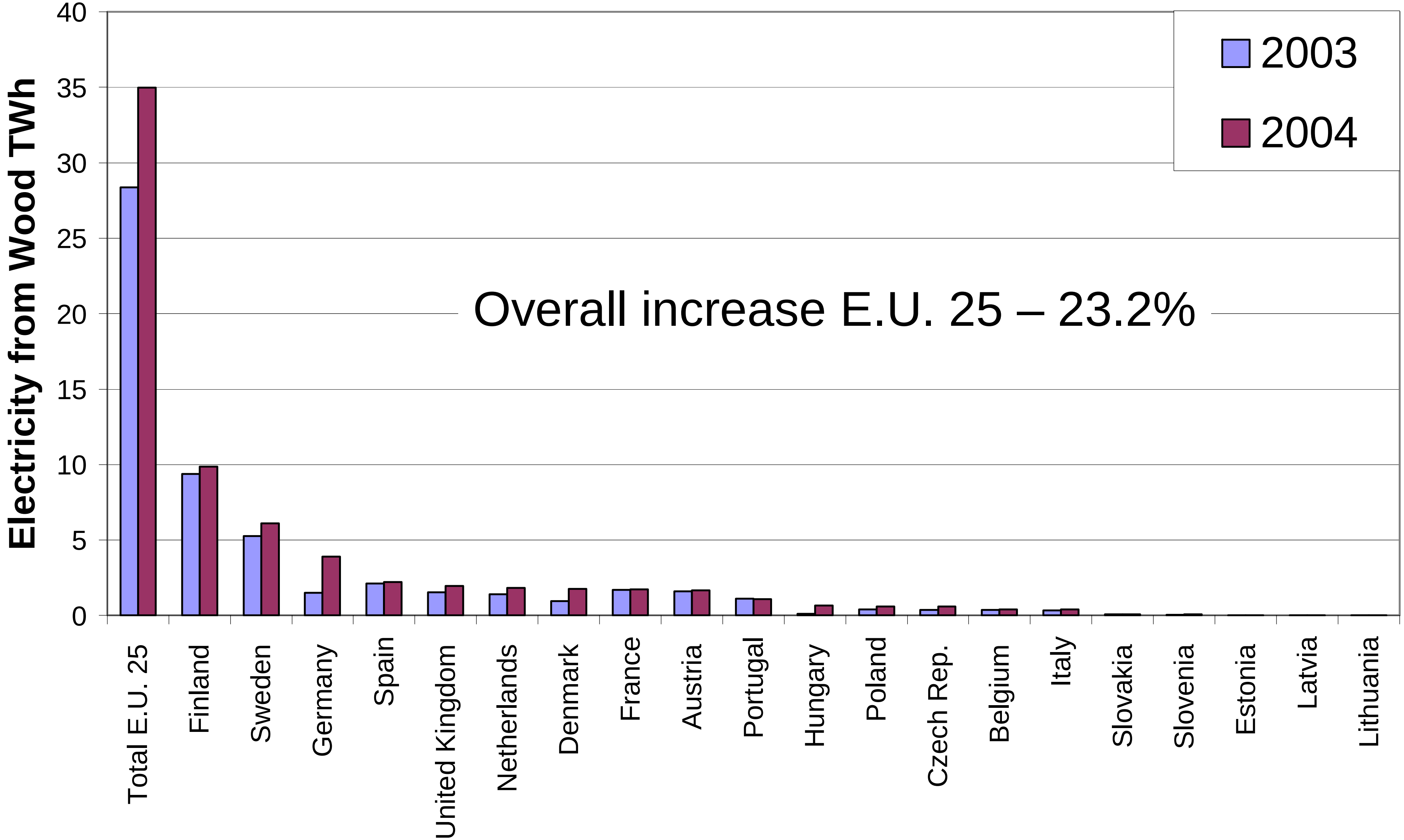
- 12% Energy from renewable sources by 2010.
- EU projections – 75% from Biomass.
- EC proposal 2007: 20% cut in greenhouse gas emissions by 2020

- 1995 – 3.3% of the EU gross inland energy.
- From 1995 “only” 10-15% growth.
- Need to at least double energy from biomass to meet EU targets.
- Current trend below projections.
- See http://europa.eu.int/comm/energy/

EurObserv'ER 2005 – Energy from Wood

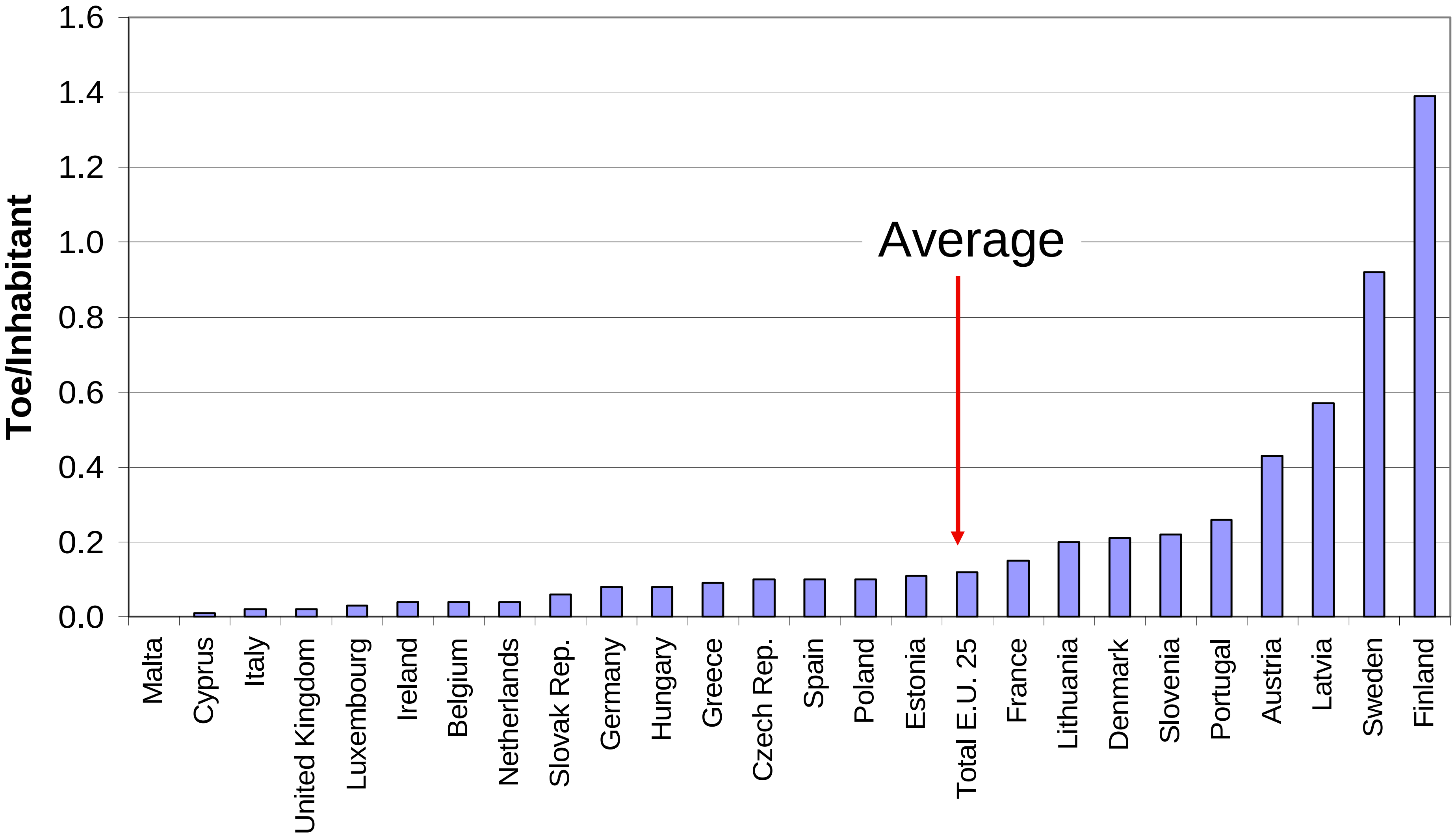


EurObserv'ER 2005 – Electricity from Wood

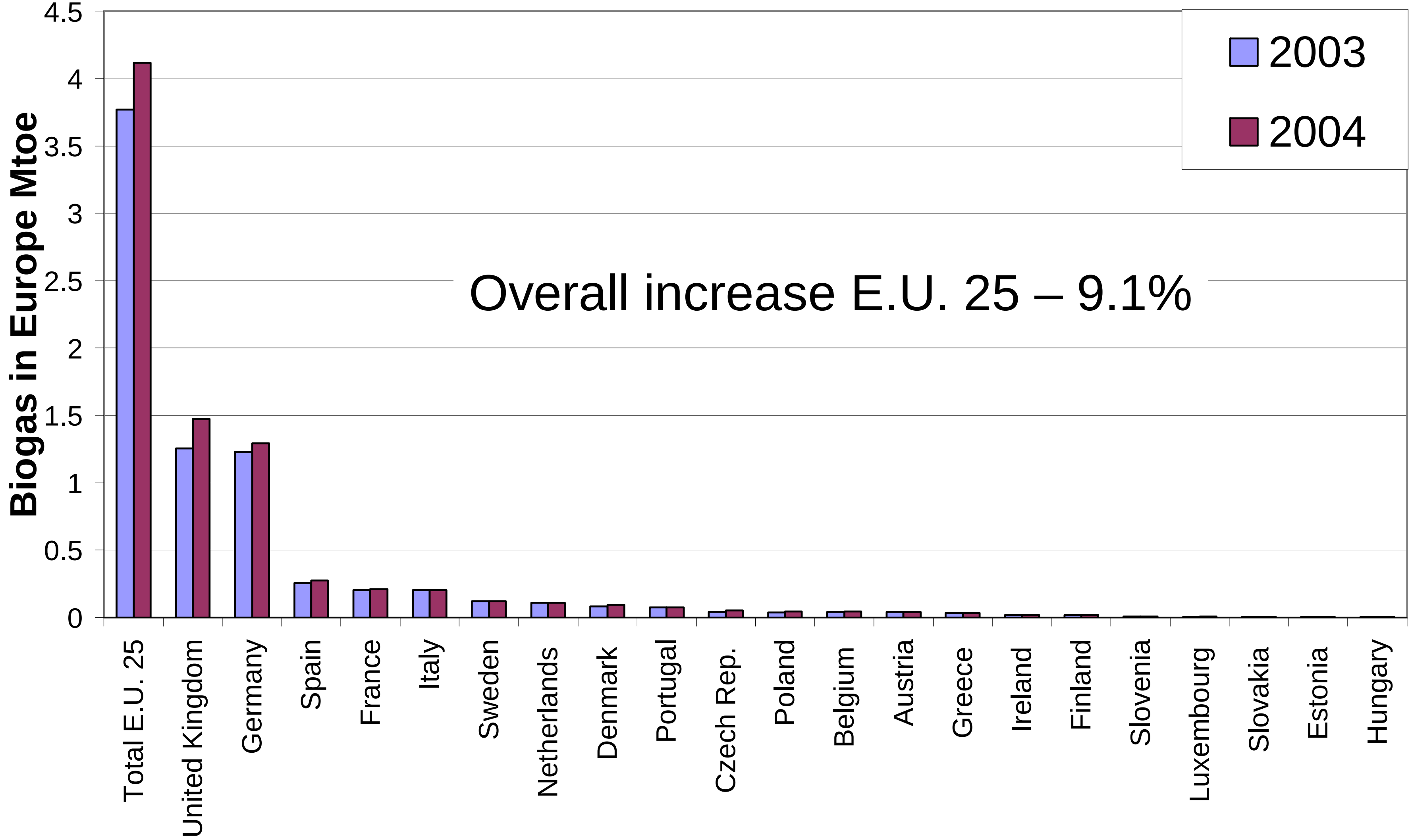


EurObserv'ER 2005 – per capita

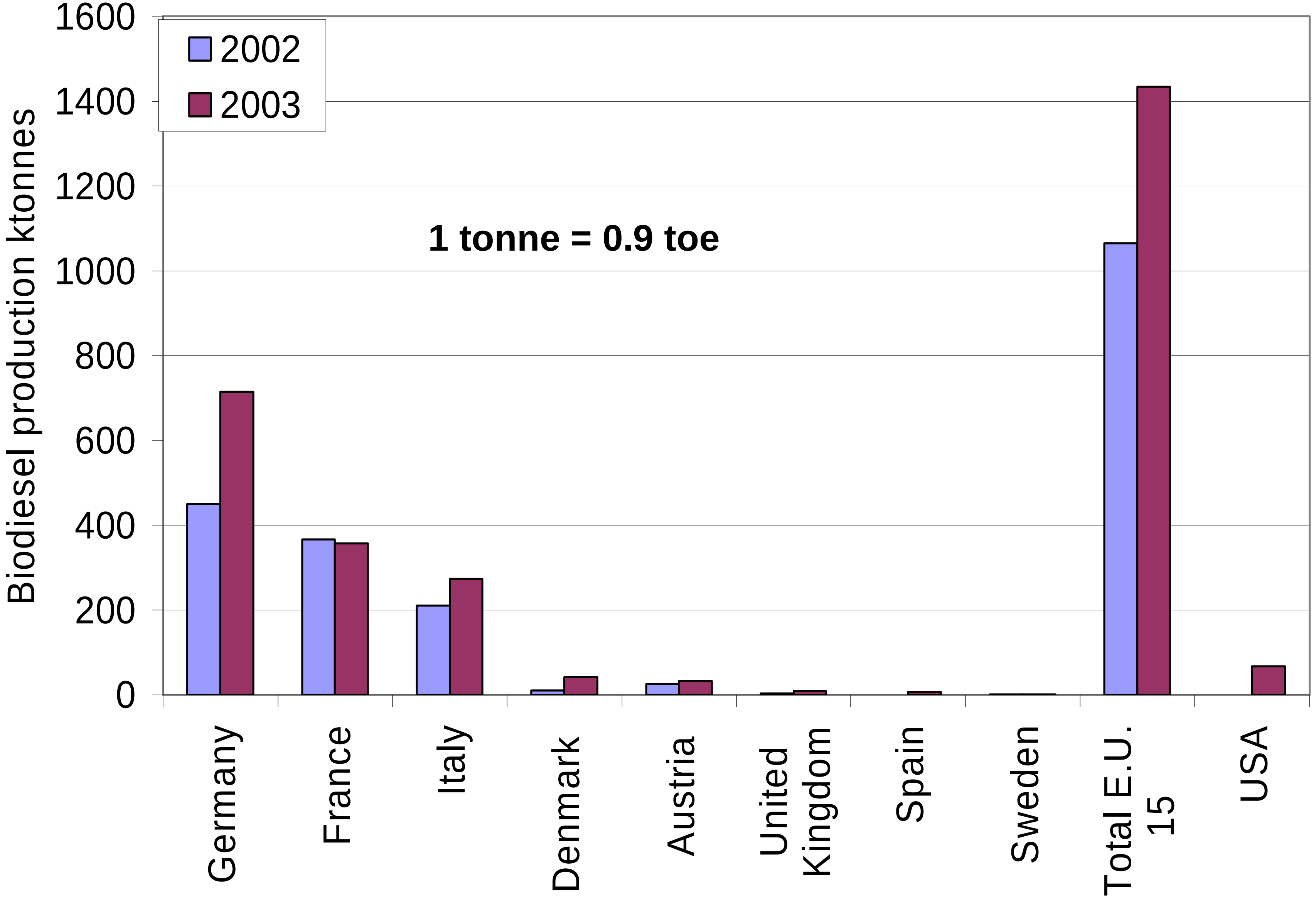
ton of oil equivalent (TOE) = 41.87 GJ or 11.63 MWh – www.wikipedia.org



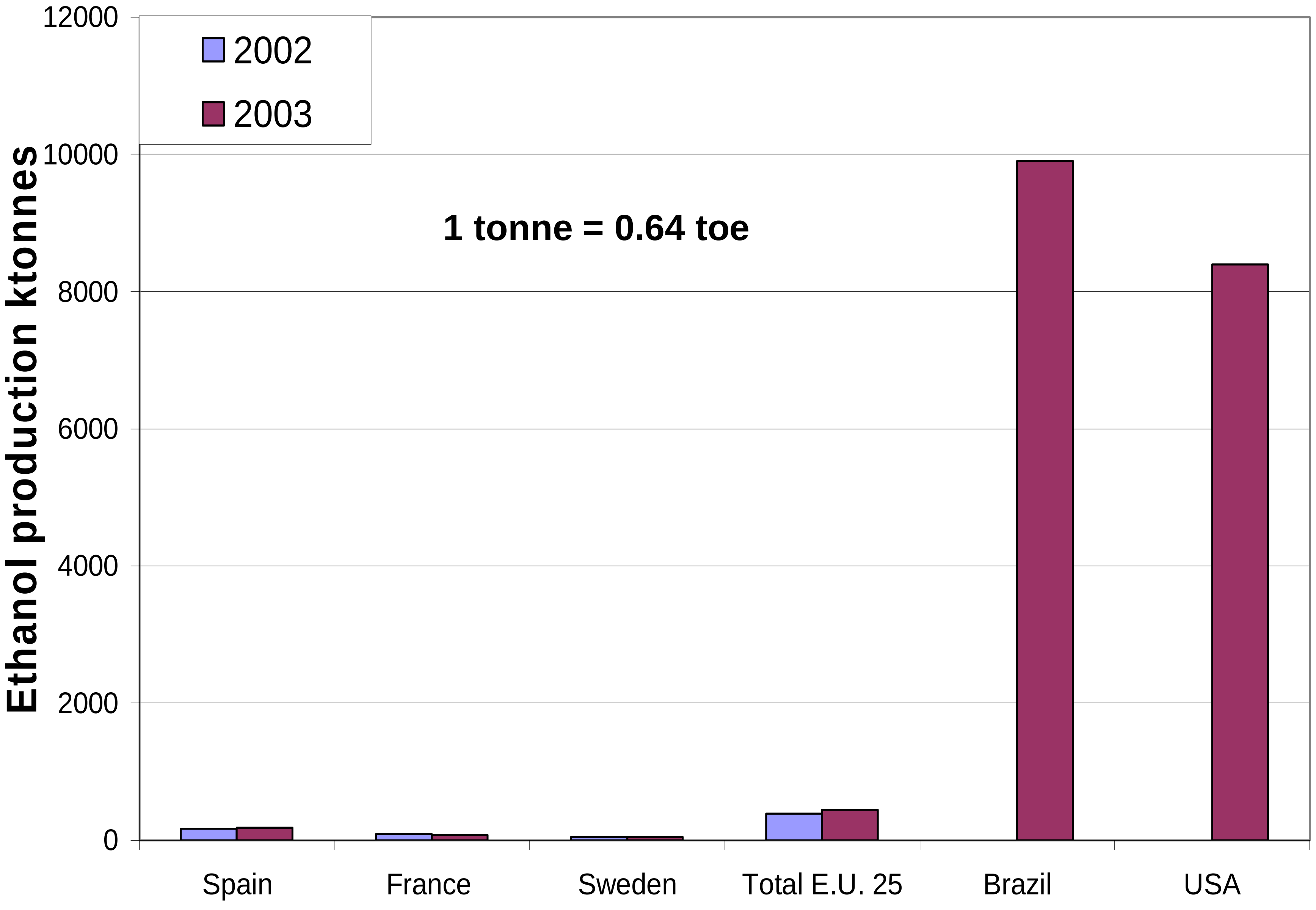
EurObserv'ER 2005 – Biogas



EurObserv'ER 2005 – Biodiesel



EurObserv'ER 2005 – Ethanol



Why the Different Developments?

- **Availability of different feedstocks.**
- **Size of farms –**
  - **USA + Brazil very large quantities of biomass from few producers – easier to scale-up – ethanol.**
  - **EU – smaller farms – small to medium scale CHP – biodiesel.**
- **Success stories in biomass use are linked to:**
  - **Tax incentives/guidance from local administrators.**
  - **Availability of waste material from industrial production.**
  - **Optimal use of biomass resource.**

Source: Prof. Ni Weidou, Tsinghua University

- Resources - China
  - Straws and stalks – 300 mil. tce
  - Waste of forest
  - Special plants in deserts

  $\Big\}$ 1.0 billion tce
- Features
  - Highly scattered
  - Collection and transportation will be a big problem
  - Reasonable collection radius – less than 5 km

- For 25 MW power plant with biomass-firing, the radius of collection will be more than 100 km (<u>biomass conversion</u>)

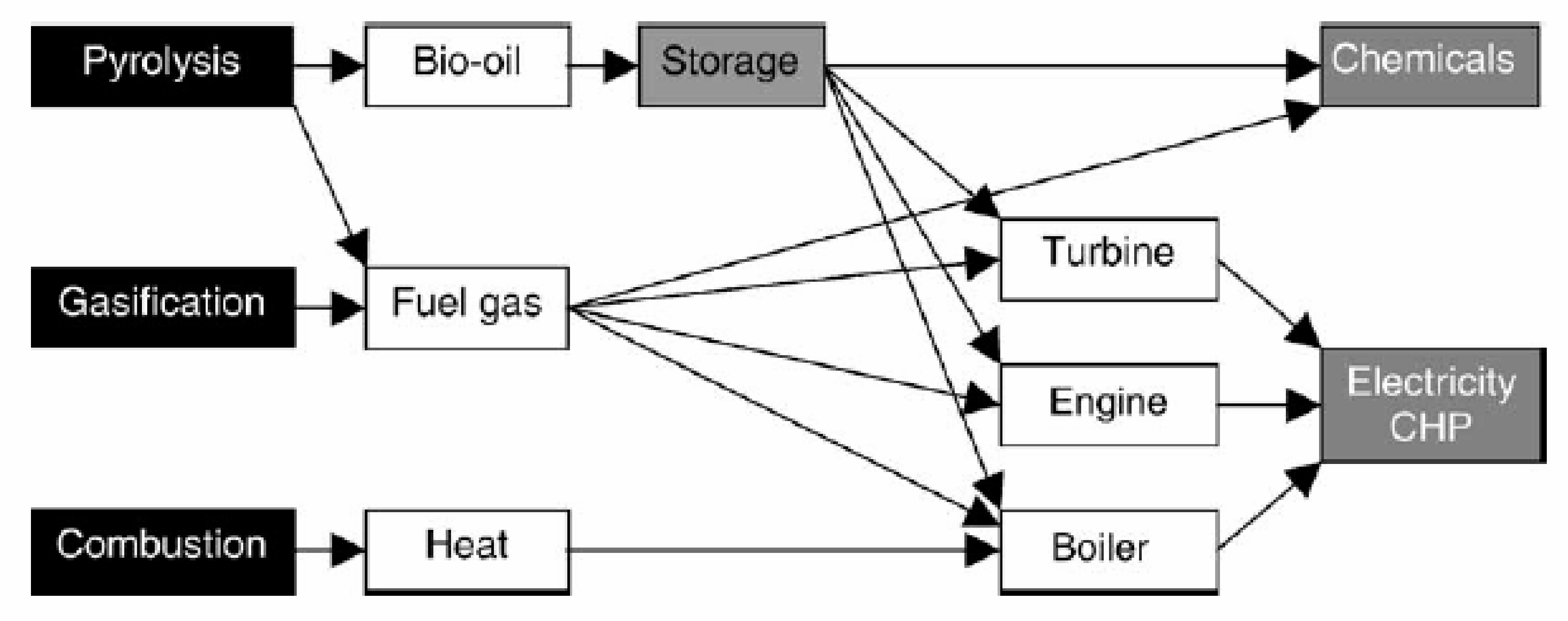
- In China and in parts of the developing world distributed, on-site collection, production and utilization may be more appropriate (<u>small-medium scale plants</u>)

ton of coal equivalent (**TCE**) = 29.3 GJ – www.wikipedia.org

BIOMASS CONVERSION

- Direct combustion or co-firing.
- Gasification – air or steam – to produce syngas.
- Pyrolisis – to produce both liquid and gaseous fuels.
- Cellulose and hemicellulose to basic sugars.
- Biodiesel – ethyl or methyl esters from trans-esterification of vegetable oils.
- Biofuels – produced from syngas.
- Biogas – anaerobic digestion of residues.
- …

BIOMASS THERMAL CONVERSION



Source: Prof. A.V. Bridgewater, 2003

Thermally induced biomass decomposition occurs over the temperature range 250 ÷ 500°C, and the primary pyrolysis (devolatilization) products are

<u>**gases, organic vapours, char**</u>

Their relative yields depend on heating rate and final temperature.

<u>**Combustion:**</u>

The product is heat, to be used immediately for heat and/or power generation.

Overall efficiencies to power ≈ 15% for small plants
up to 30% for larger and new plants

Costs are specially competitive when agricultural, forestry and industrial wastes are utilized.

A well established technology, with a large variety of applications, at small and medium scale.

Flash pyrolysis:

high heating rates (small particles < 2 mm)

moderate pyrolysis reaction temperature (T ≈ 500°C)

short vapour residence time (τ ≤ 2 s)
fluidized bed, and special design reactors

separation of organic vapours from char particles
(cyclones are better than filters)

rapid cooling of pyrolysis vapours to give raw bio-oil

Bio-oil:

a complex mixture of oxigenated hydrocarbons
(about the same elemental composition of biomass)

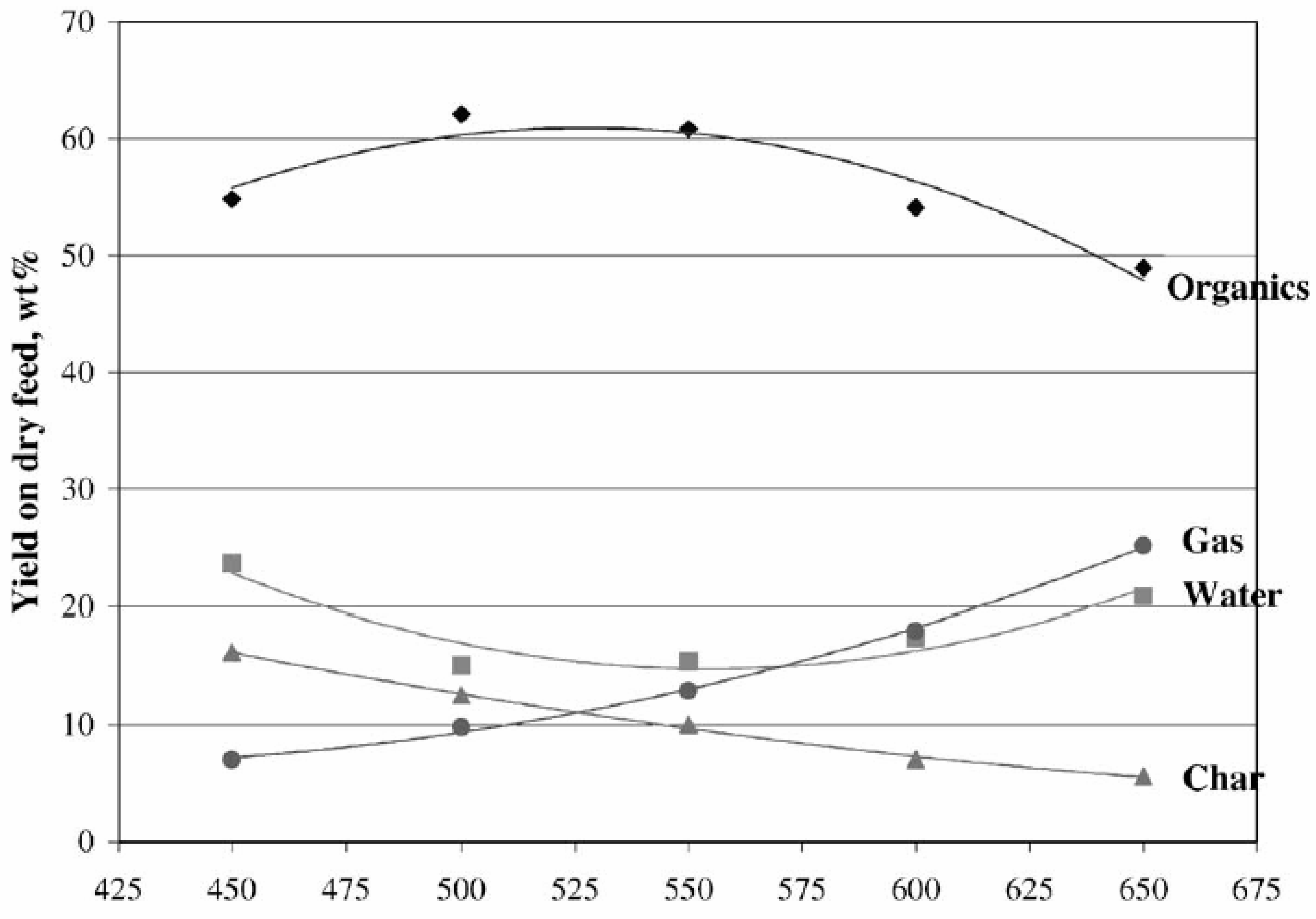
yield: up to 75% by weight of the original fuel on dry basis

LHV ≈ 17 MJ/kg (40% of conventional fuel oil diesel)

does not mix with hydrocarbon fuels

upgrading: hydrotreating, catalytic cracking (costly!)

Variation of products with temperature in a flash pyrolysis process



Source: Prof A.V. Bridgewater, 2003

Gasification:

fuel gas (CO, CO_2, H_2, CH_4) is obtained by partial oxidation and steam or pyrolytic reforming of vapours and char (air/O_2/steam gasification)

$T \leq 850°C$, to avoid ash sintering phenomena

$\tau > 2$ s, to allow enhancement of heterogeneous reactions

fixed and fluidized bed gasification reactors

primary and downstream catalytic treatments improve gas quality

up to 85% by weight of the original dry biomass is converted in gas

LHV: from 4 MJ/Nm^3 (air gasification) to 12 MJ/Nm^3 (O_2/steam gasification)

hot gas efficiency up to 95% (total energy in raw gas/energy in the feed)

cold gas efficiency up to 80% (raw gas/biomass feedstock heating value)

Gasification:

the closest to industrial exploitation from among the available conversion options, for efficient power generation and synthesis of commodity chemicals;

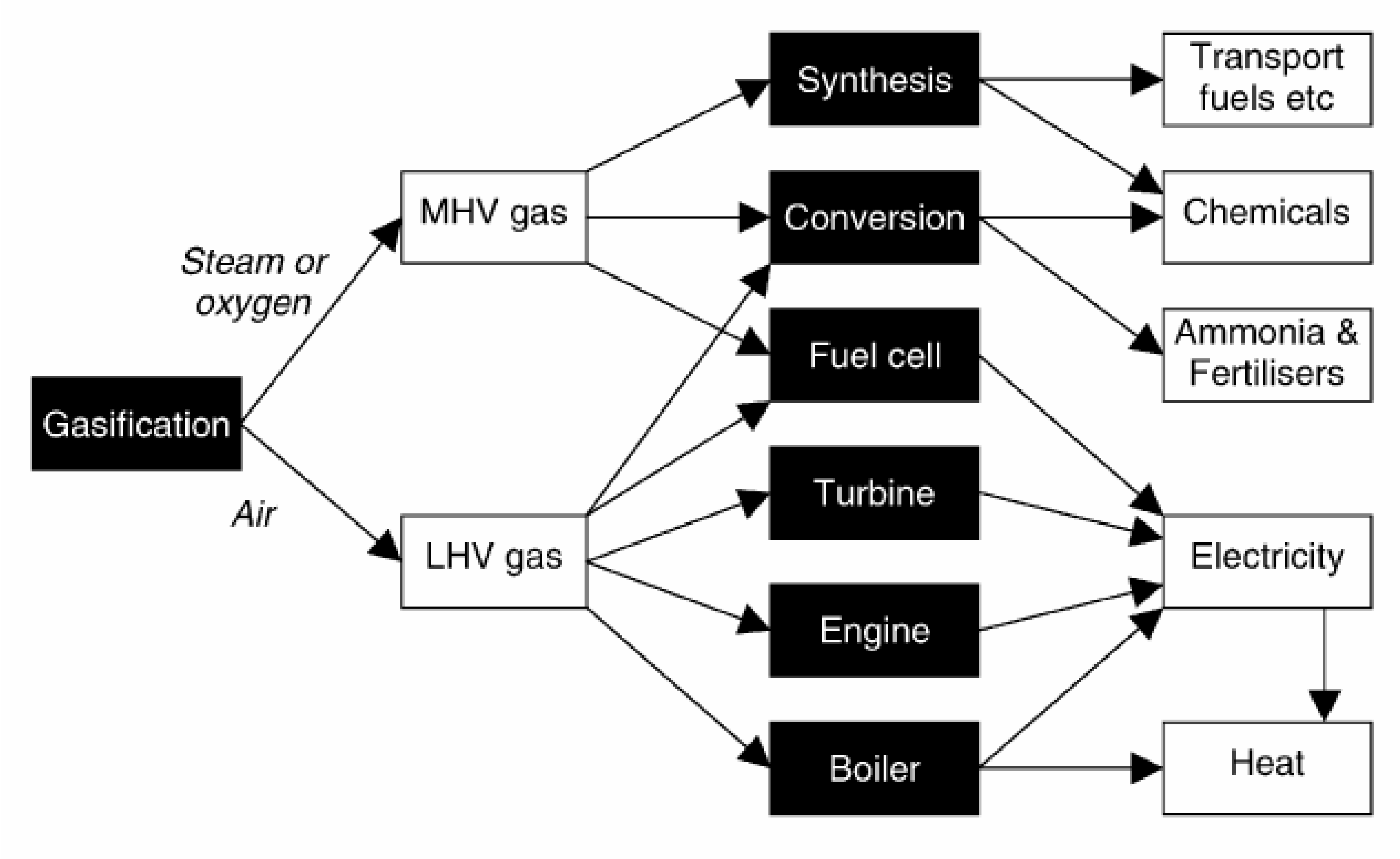
it can be well integrated with MCFC or SOFC (molten carbonate and solid oxide fuel cells accept syn-gas as a fuel because operate at high temperature), and FC + turbine or gas turbine + steam turbine combined cycles for stationary power generation, with net electric efficiencies > 40% (pressurized gasification);

it is a source of hydrogen: a pure H2 energy vector is obtainable by combining biomass gasification with a CO2 sorption process (for instance, with calcined dolomite) for a variety of utilities and applications;

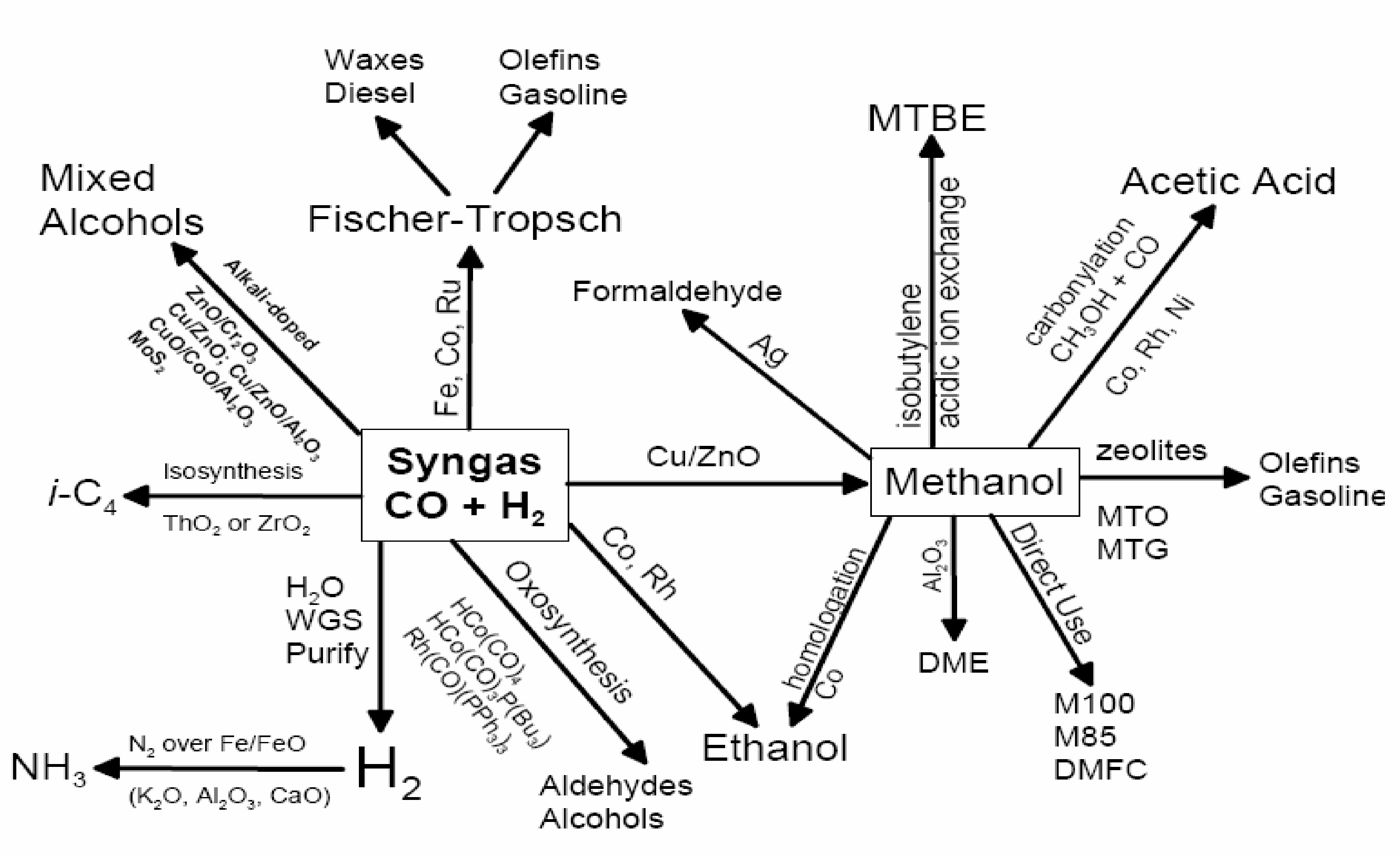
the technologies to obtain chemicals from the producer gas are commercially available. Major obstacles are: Large scale operation and High gas quality;

gasification will be able to better penetrate di energy markets if it is completely integrated into a biomass system.

Utilization of gas from biomass gasification



Source: Prof A.V. Bridgewater, 2003



Source: Spath & Dayton, 2003 - NREL/TP-510-34929
http://www.eere.energy.gov/biomass/pdfs/34929.pdf

The global reactive process occurring in a biomass gasifier can be characterized as follows:

$$C_{a_C} H_{a_H} O_{a_O} N_{a_N} + x_1 H_2 O_{(l)} + x_2 H_2 O_{(g)} + x_3 \left(O_2 + \gamma N_2\right) \Rightarrow \quad z_1 H_2 +$$

$$z_2 CO + z_3 CO_2 + z_4 CH_4 + z_5 N_2 + z_6 NH_3 + z_7 H_2 O_{(g)} + z_8 C_{10} H_8 + z_9 C_{(s)}$$

the g-atoms of carbon, hydrogen, oxygen and nitrogen in the biomass raw formula are given by the fuel elemental analysis,

x_1 is given by the fuel humidity,

(x_1+x_2) is fixed by the steam/biomass ratio, SBR,

x_3 by the value of the equivalence ratio, ER,

γ is chosen according to the nature of the gasification agent (air, enriched air or pure oxygen).

The list of chemical species on the RHS of the above equation has been restricted to the most significant ones.

Devolatilizazion takes place while the fuel particle is heated up, at temperatures above 300°C:

Biomass $\Longrightarrow$ **Organic vapours + Gas + Char**

At the gasification temperature (> 800°C):

Organic Vapours $\xrightarrow{\text{cracking, steam reforming}}$ **CO, CO_2, H_2, H_2O; light hydrocarbons (mainly CH_4)**

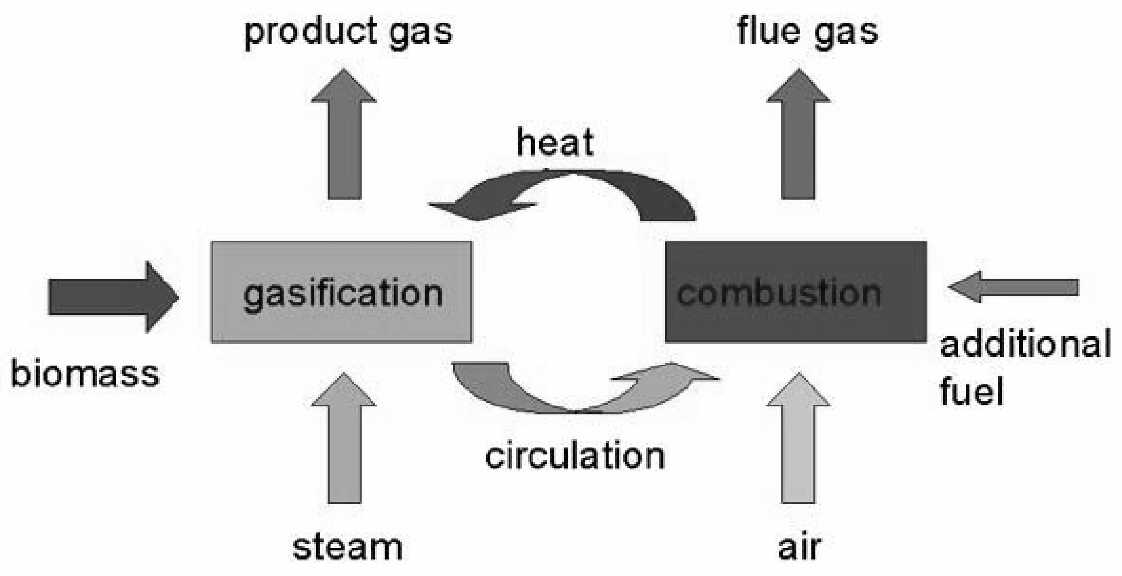
Organic Vapours $\xrightarrow{\text{polymerisation}}$ **high molecular weight organics (tar)**

Char + H_2O, CO_2 $\Longrightarrow$ **CO, H_2**

Overall, an endothermic reaction process

How to supply the energy needed by the gasification process:

- **addition of air/oxygen-enriched air/oxygen, to burn part of the solid fuel;**
- **circulation of reactor bed inventory between separate gasification and combustion zones (solid particles act as an heat carrier);**
- **circulation of bed inventory + an additional, exothermic reaction which helps furnishing the necessary thermal energy: solid circulation allows the regeneration of the reactant.**



Source: Prof Hermann Hofbauer, Vienna University of Technology, Austria

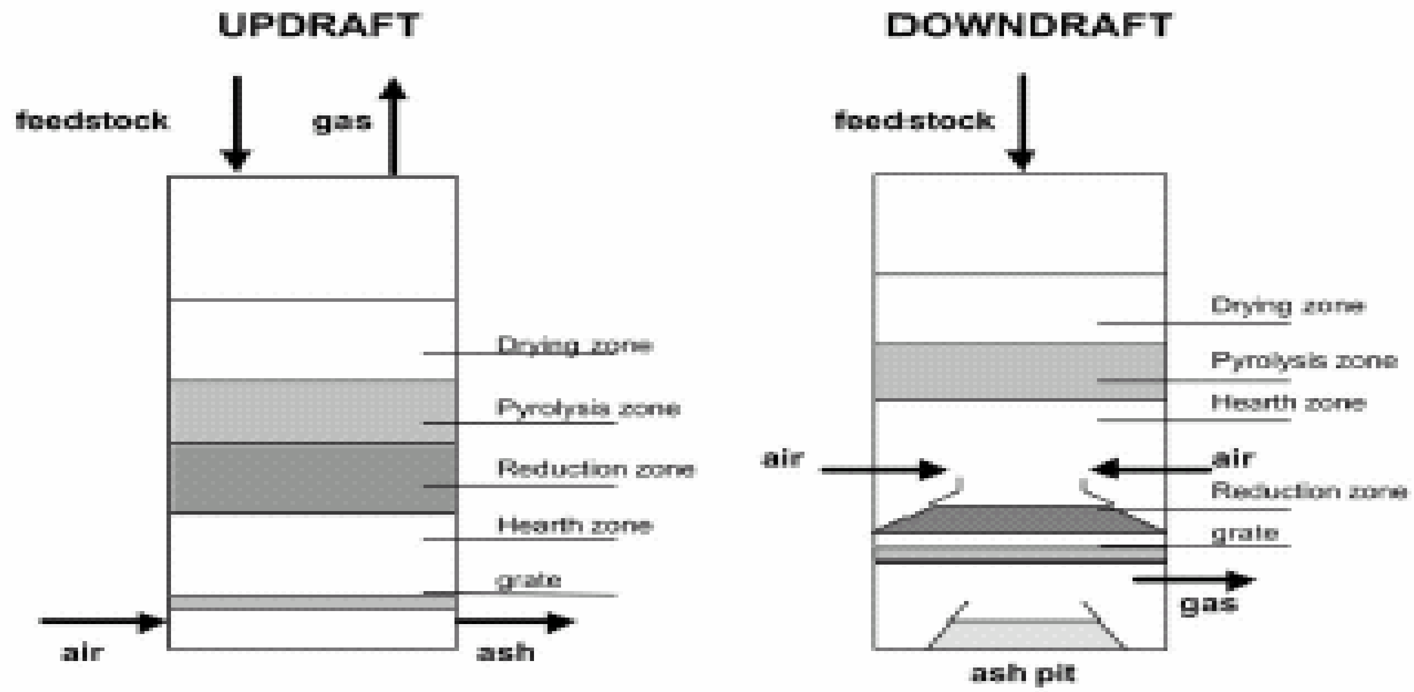
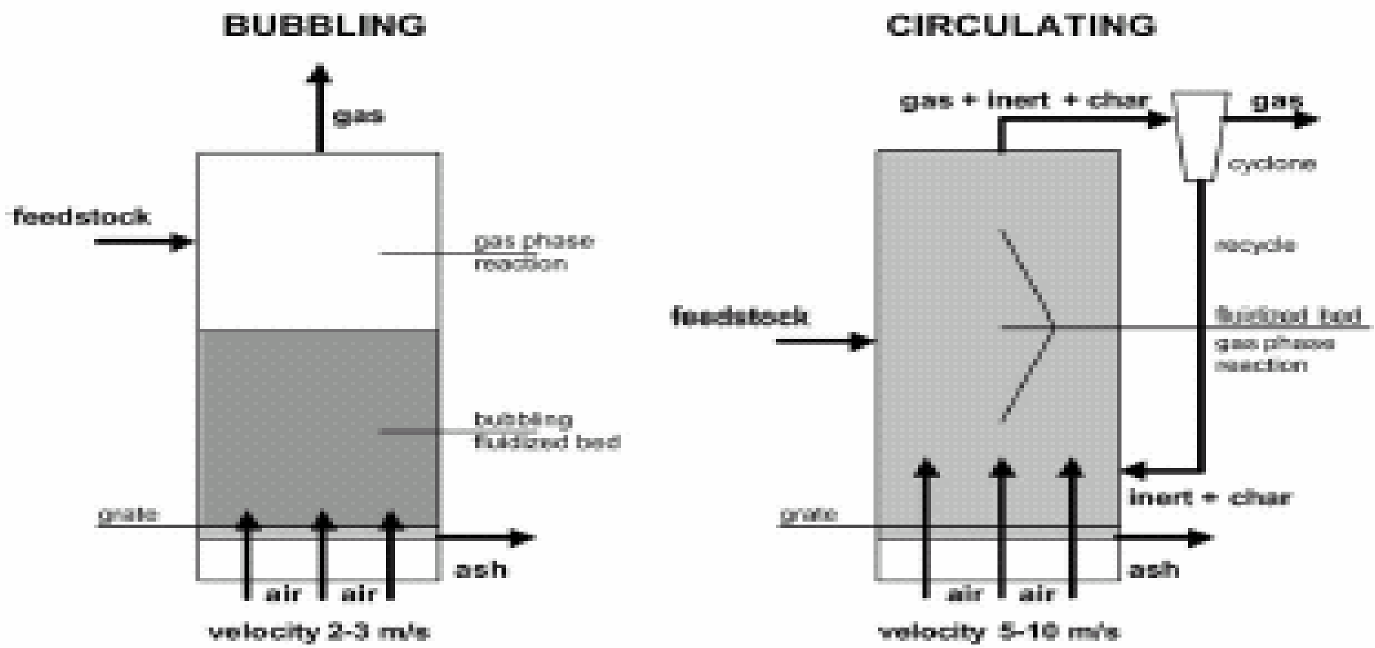


Fig. 5. Fixed bed gasifiers (Quaak et al., 1999).



FLUIDIZED BED GASIFIERS

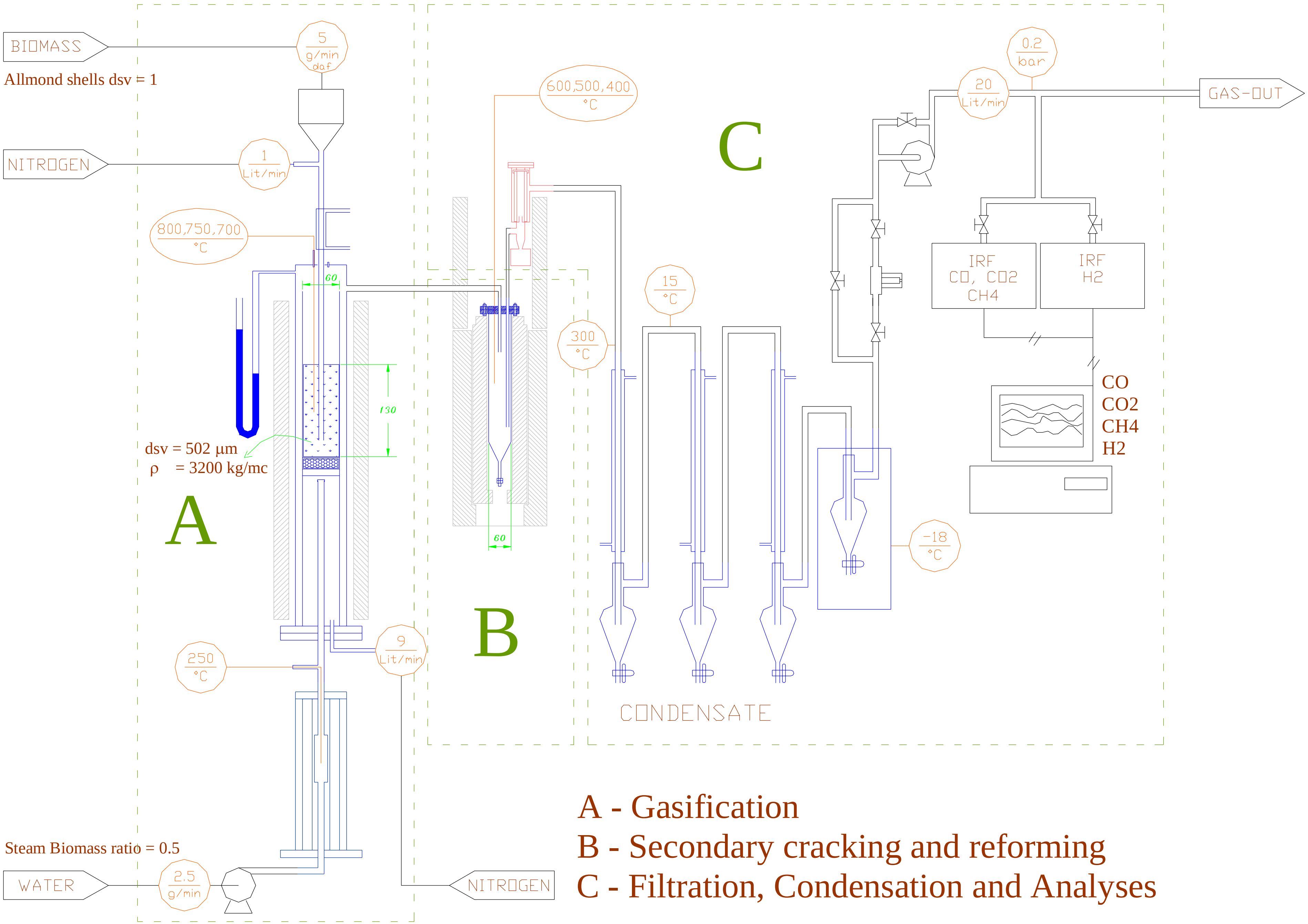
Advantages:

- very good mixing of the bed inventory;
- temperature homogeneity;
- high heat-up rates of the feedstock particles;
- possibility to add a catalyst to enhance yield of permanent gases;
- internal circulation of the bed inventory to help mixing of particles of different densities;
- external circulation of the bed inventory (fast fluidized beds).

Disadvantages:

- entrainment of fine particles (char, ash) by the product gas;
- feedstock of controlled size, very smooth feeding rates;
- careful design and operation.

Laboratory, fluidized bed steam gasification facility



A - Gasification

B - Secondary cracking and reforming

C - Filtration, Condensation and Analyses

Steam gasification of almond shells with Ni/Olivine bed inventory (d_P=500μm)

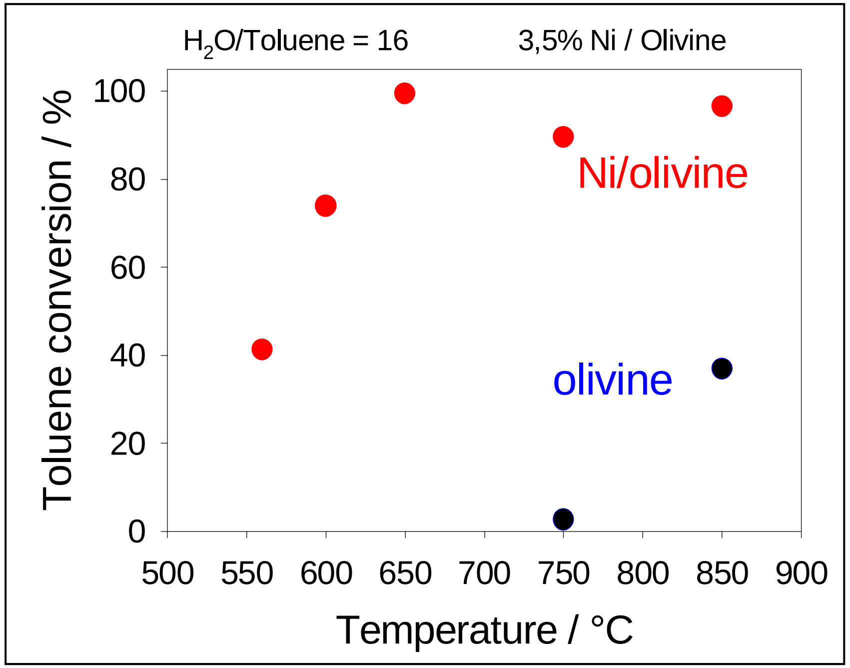
Gasifier temperature, °C	820	820	820	750	700
Steam / biomass dry	1	1	0.5	0.5	0.5
Water conversion, %	45.0	45.5	59.0	43.0	26.0
Gas yield, Nm^3dry/kg daf	1.83	1.88	1.77	1.32	0.99
Tar content, g/Nm^3 dry	0.5	0.4	0.2	1.8	17.7
Char residue, g/kg daf[1]	37.3	31.6	45.2	127.1	170.1
Carbon conversion, %	92.5	93.7	91.2	75.5	63.5
H_2 (%vol. dry gas)	51.8	52.4	50.8	45.5	38.8
CO (%vol. dry gas)	24.4	24.1	34.4	27.9	26.5
CO_2 (%vol. dry gas)	19.2	19.2	10.6	19.8	24.0
CH_4 (%vol. dry gas)	4.7	4.3	4.2	6.9	10.8
$[H_2]*[CO_2]/([CO]*[H_2O])$	1.07	1.14	1.08	1.19	0.75
Kp water gas shift	0.98	0.98	0.98	1.31	1.65

[1]calculated by imposing the closure of the carbon mass balance.

Tar reforming

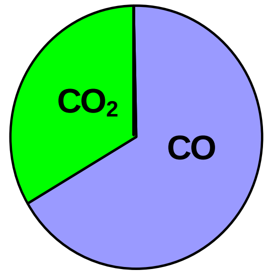
Steam reforming of toluene

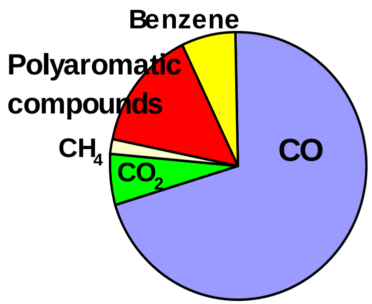
$$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2 \quad \text{and} \quad CO + H_2O \rightleftarrows CO_2 + H_2$$



- high activity of **Ni/Olivine** in toluene reforming at 800°C
- stability (no deactivation) after 7 h on stream

Selectivity 850°C





- total toluene conversion to permanent gases CO_2, CO and H_2 with **Ni/Olivine** catalyst

Source: Prof A. Kiennemann, University of Strasbourg

CHP in Güssing Austria

Source: Dr Reinhard Rauch, TUV

CHP in Güssing Austria

Start up of gasifier	November 2001
Start up of gas engine	April 2002
Fuel	wood chips
Fuel Power	8000 kW
Electrical output	2000 kW
Thermal output	4500 kW

Güssing Austria – Reasons for Success

- 40% of region is covered by forest.
- In early '90s the Major decided to change the energy supply of the city to local renewable sources.
- District heating now supplies 95% of users
- 2 MW production covers the city's demand for electricity.
- Biodiesel is produced from a RME plant built in 1990.

R&D Projects at pilot scale

- **Direct coupling of biomass gasification and fuel cell**

funded in part by EC (JOR3-CT97-00196 and ENK5-CT2000-00314) and by the Italian Goverment (FISR, GU n° 146, June 24, 2004).

- **Electricity generation from wood scraps and rice husk**

a bilateral project between Italy and China, involving the Liaoning Institute for Energy Resources (LIER), ENEA (Trisaia Research Centre) and the University of L'Aquila.

Construction and Operation of an Integrated Pilot Plant

- **500 kWth fast internally circulating fluidized bed (FICFB) gasifier for catalytic biomass steam-gasification.**
- **Hot gas clean-up system for acid compounds removal by adsorption on a basic powder, and ceramic candle fine particle filtration.**
- **125 kWe Molten Carbonate Fuel Cell (MCFC)**

Accompanying Research Tasks

- **Development of a low-cost Ni-olivine catalyst for hydrogen enhancement and tar reduction.**
- **Laboratory scale experimentation for gasification kinetics.**
- **CFD model of the gasifier.**
- **Flowsheet simulation tool of the whole system, to develop optimal operation and control strategies.**

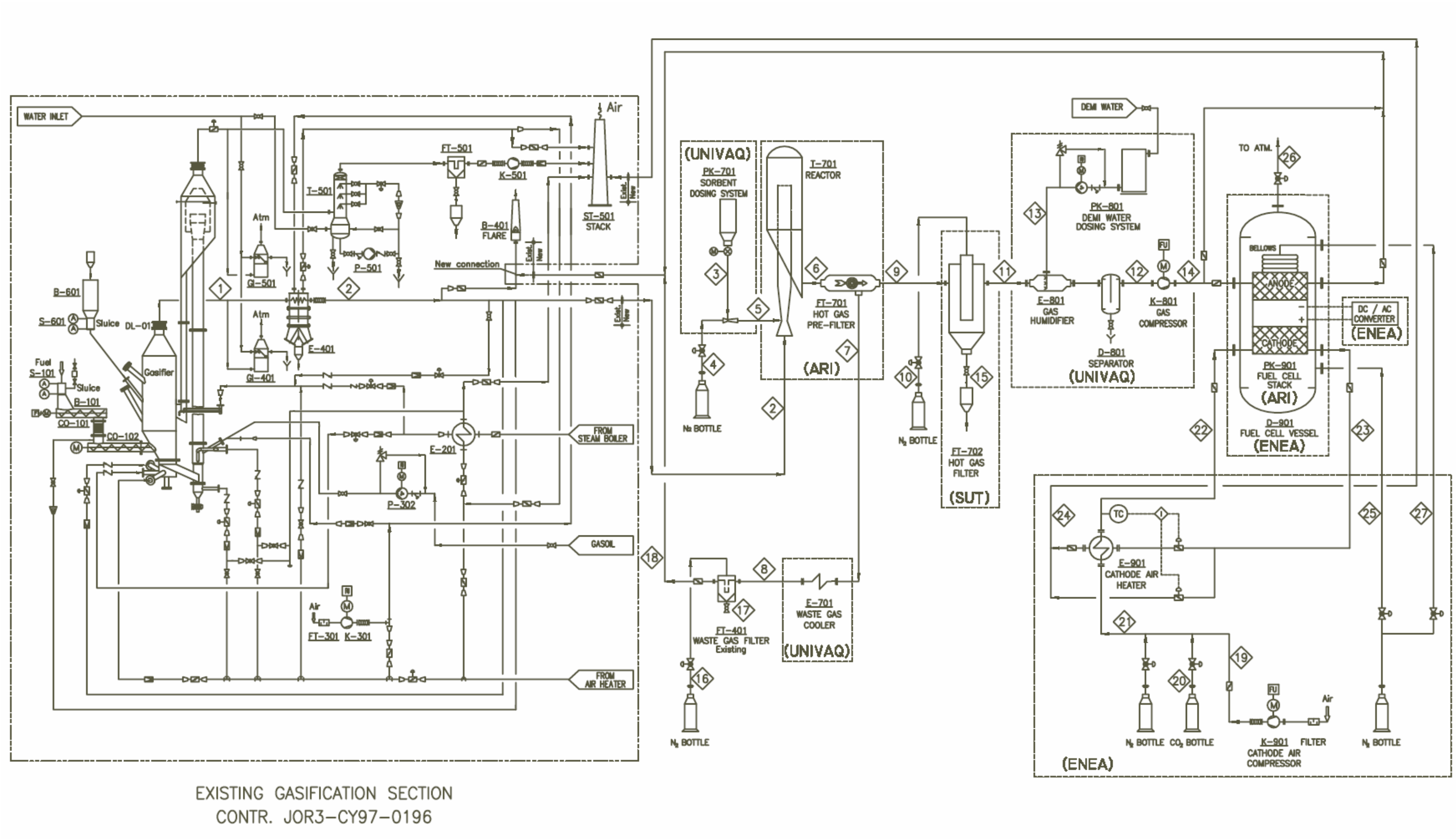
Project structure

Participant Name	Main Functions
University of L'Aquila Italy	Coordination, Pilot plant integration and catalytic gasification studies
Technical University of Vienna Austria	System simulation, catalyst performance in 100 kWth gasifier
University College London United Kingdom	Cold modeling and CFD simulation of the gasifier
University of Strasbourg France	Development, characterization and preparation of Ni-olivine catalyst
Ansaldo Ricerche Srl Genova – Italy	Hot gas clean-up system: acid gas removal
Pall Schumacher GmbH Crailsheim – Germany	Hot gas clean-up system: fine particles filtration
ENEA – Research Agency for New Technology, Energy and Environment – Italy	Pilot plant assembly and operation
Ansaldo Fuel Cells SpA Genova – Italy	MCFC stack design and supply

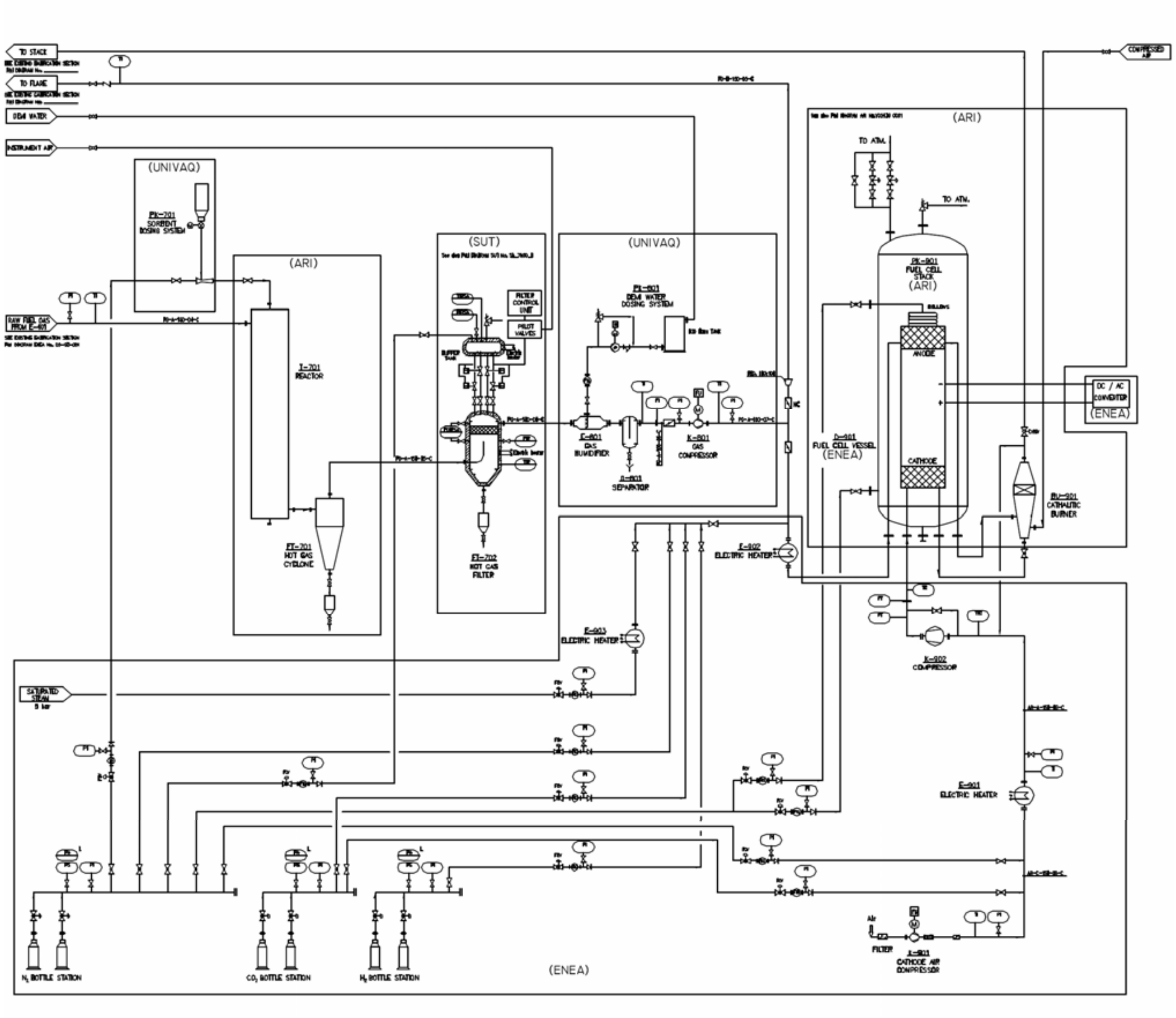
Enea's Trisaia Site

Enea research centres

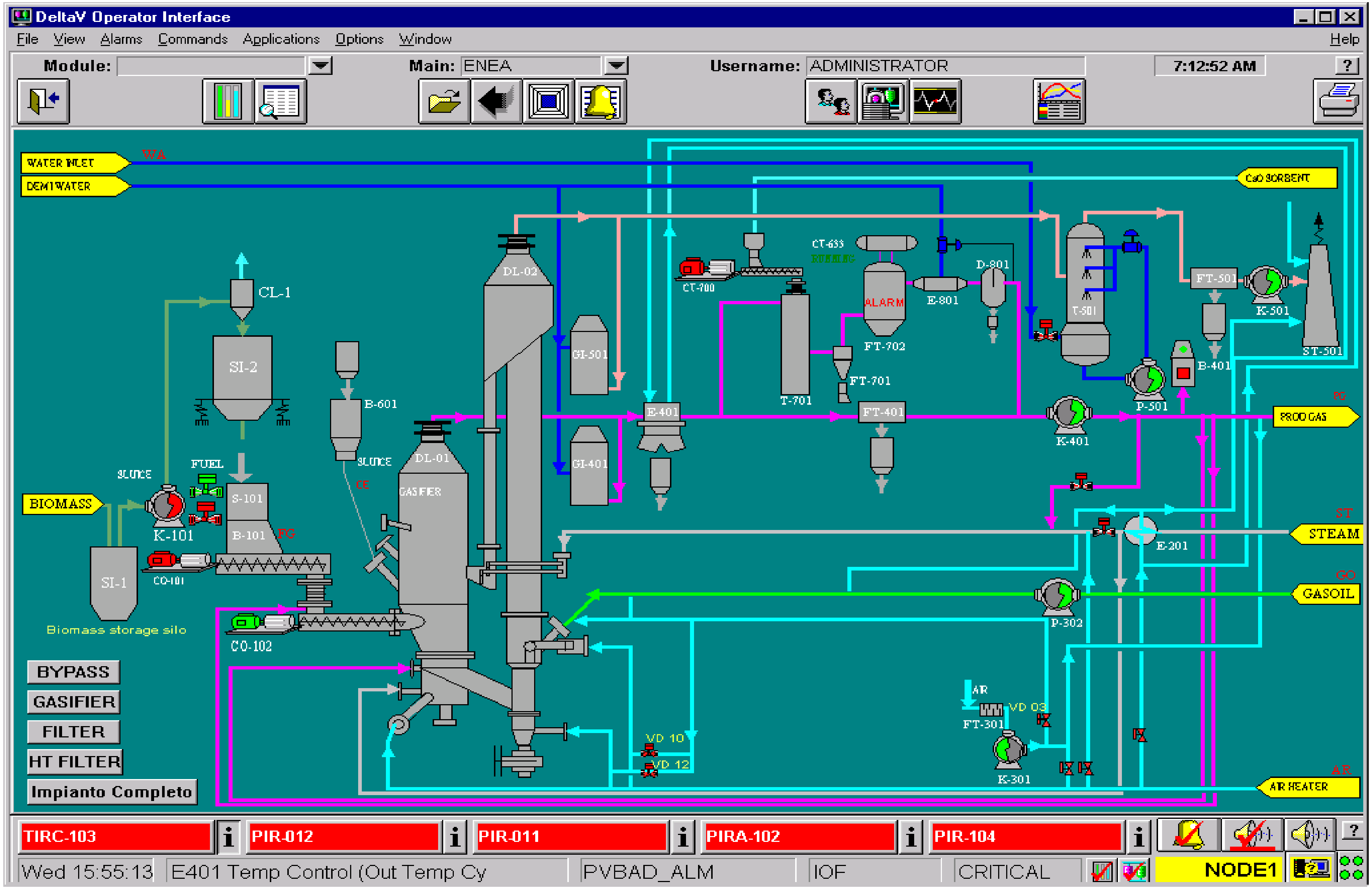
Plant Flowsheet



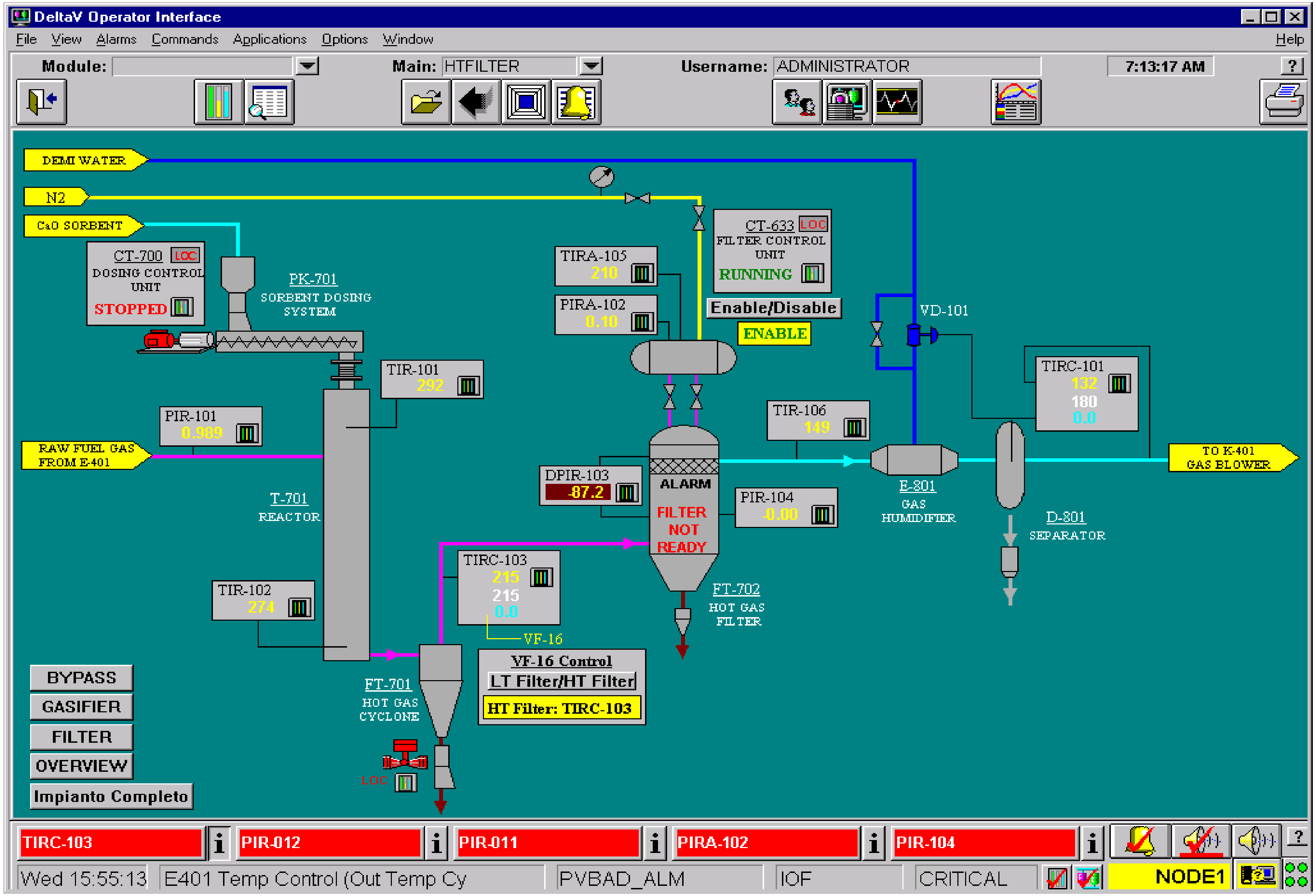
Gas Clean-up and Fuel Cell Section



The Fast Internally Circulating Fluidized Bed (FICFB) Gasifier, developed by Vienna University of Technology.



The hot gas clean-up section of the Trisaia integrated plant

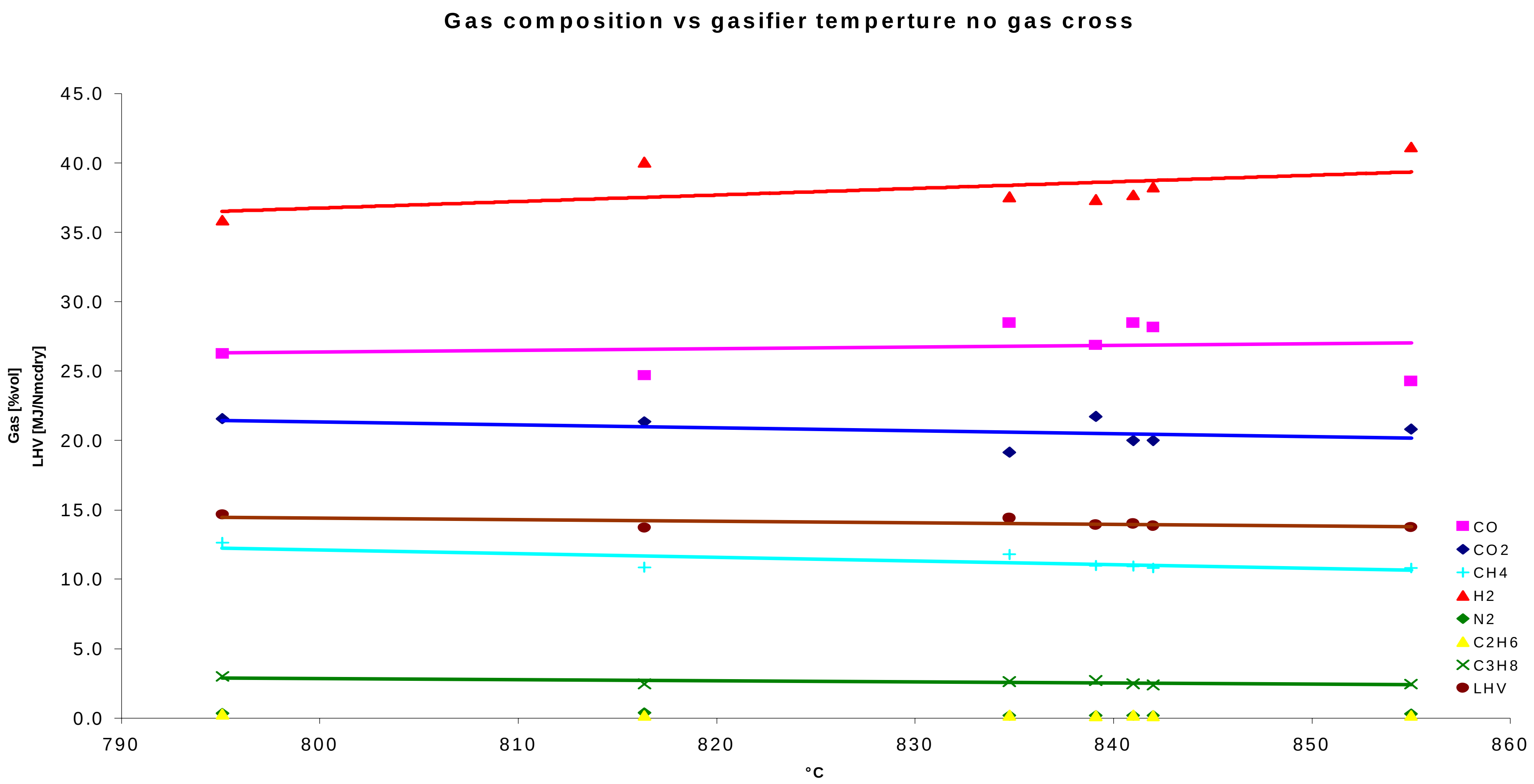


Trisaia Pilot Plant (I)

Trisaia Pilot Plant (II)

Molten Carbonate Fuel Cell

Fuel gas quality (Olivine bed inventory)



Dry gas yield: up to 1.4 Nm^3/kg of biomass d.a.f.

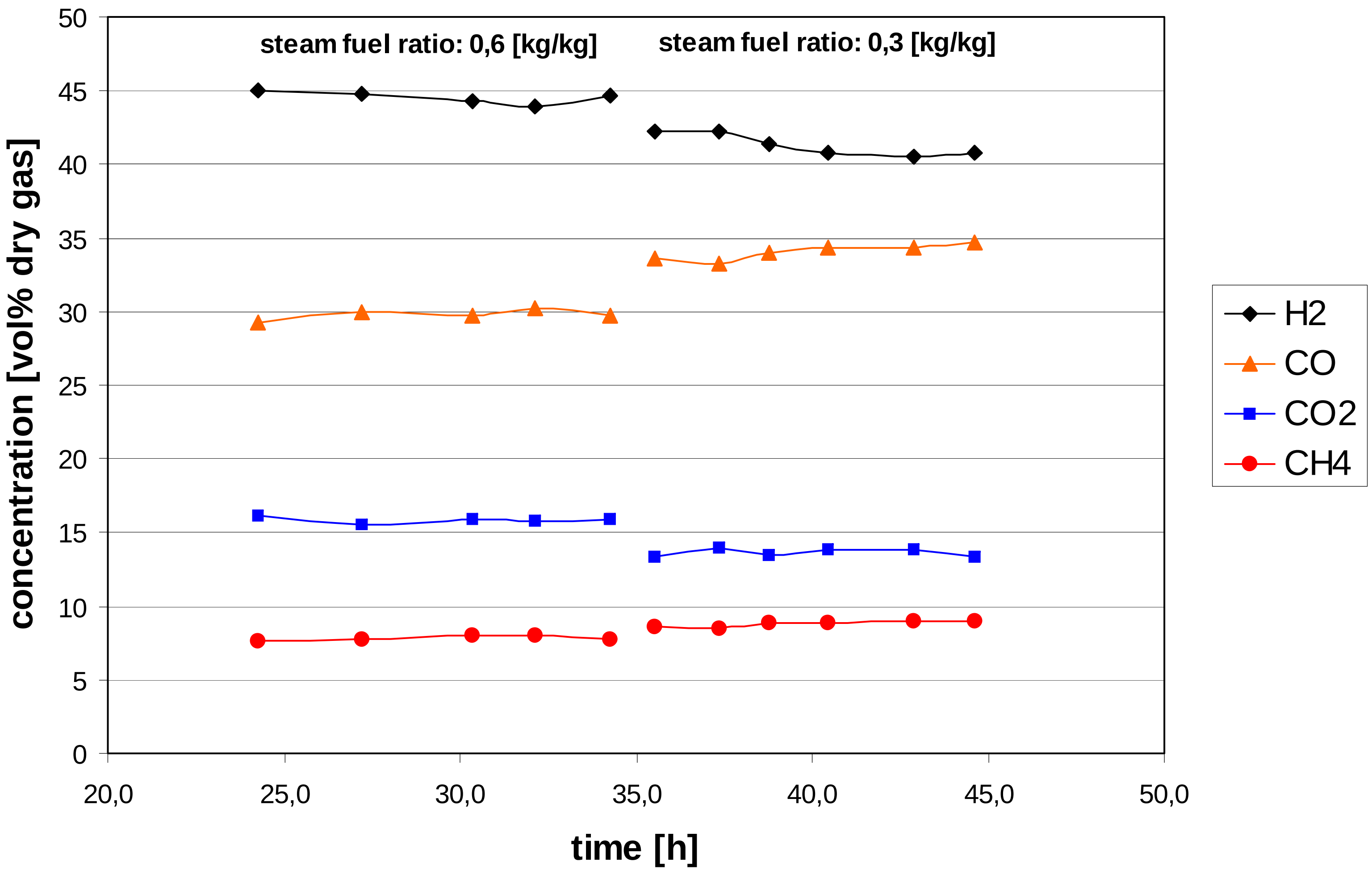
Tar content: 3 – 6 g/Nm^3 dry gas

Gasifier chemical efficiency: up to 72%

Gasifier thermal efficiency: up to 95%

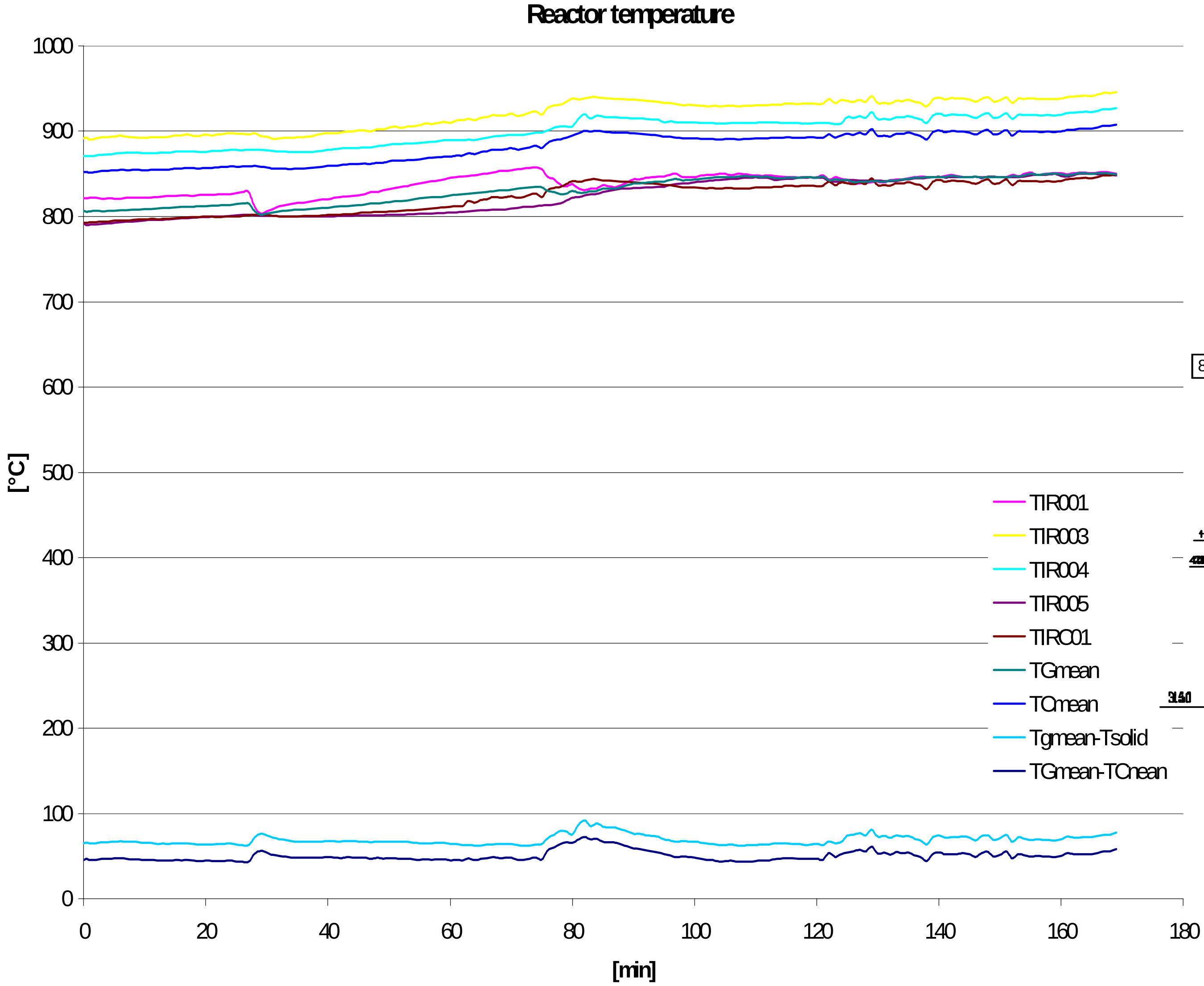
Fuel gas quality with the Ni-Olivine catalyst in the gasifier bed

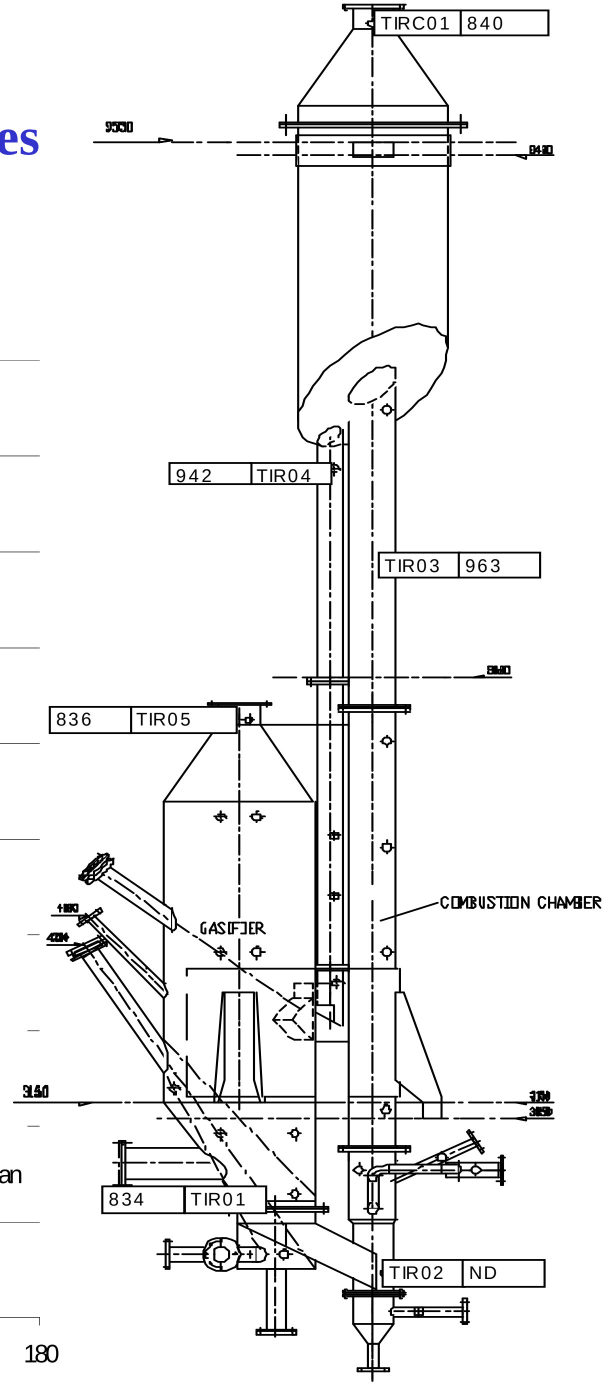
(Kiennemann, Petit, Courson, Foscolo, Rapagnà and Matera, PCT Patent, 2001)



Tar content = 0.5 g/Nm^{3}dry when the bed inventory is 50% Ni-Olivine

Temperature level in gasification and combustion zones



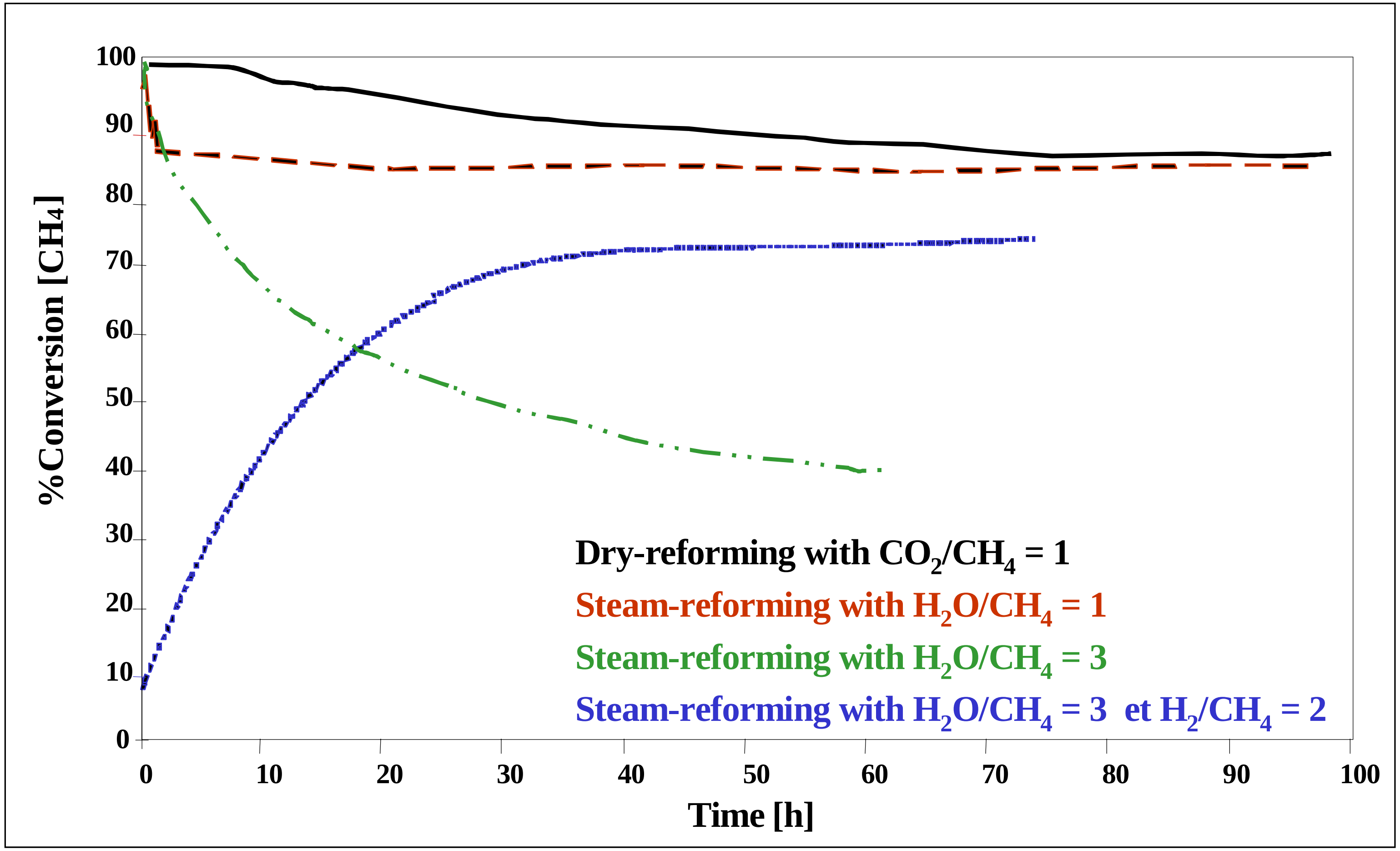


Catalyst optimisation Ageing

- **Dry- and Steam-reforming of methane**

$$\begin{cases} CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \\ CH_4 + H_2O \longrightarrow CO + 3H_2 \end{cases}$$

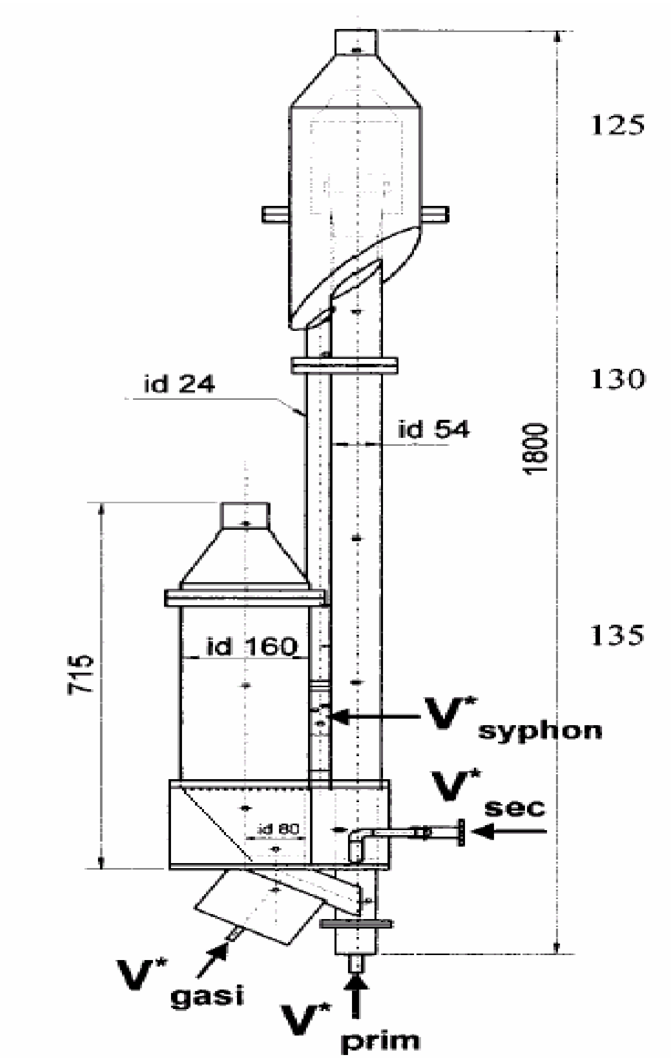
F(total) = 7.5 NL/h/$g_{catalyst}$, F(CH_4) = 0.75 NL/h/$g_{catalyst}$, T = 800 °C



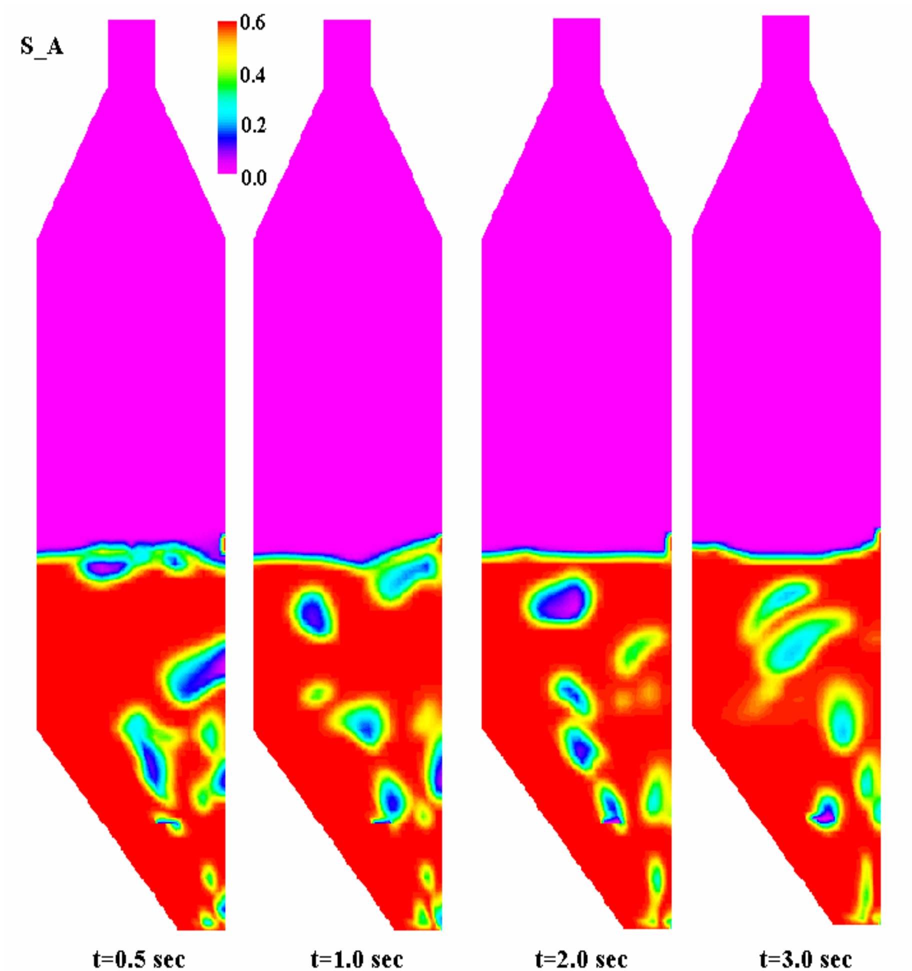
Simulation of the fluidized bed gasifier

(Brandani and Zhang, AIChE Symp. Series, 2004)

Cold Model



CFD



Two gas inlets with solid circulation

Source: Prof. S. Brandani, University College London

Performance of the entrained flow reactor for fuel gas deacidification

(Ansaldo Ricerche srl)

T_{in} [°C]	508
T_{out} [°C]	476
CaO [kg/h]	0.57
Ca/(Cl+S) [molar]	4.3
H_2S_{in} [ppmv]	250
HCl_{in} [ppmv]	105
H_2S_{out} [ppmv]	40
HCl_{out} [ppmv]	36
SR [%]	84
ClR [%]	66

Performance of the ceramic candle filter

(Pall Schumacher Germany GmbH)

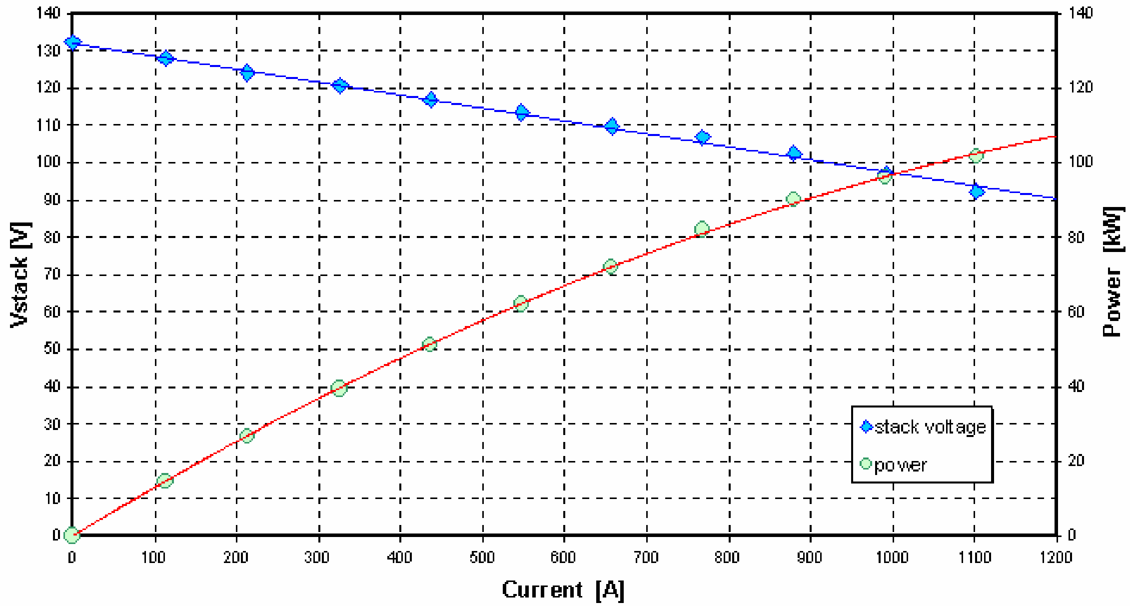
Gas flow rate [Nm^3/h]	**140**
Tin [°C]	**460**
Tout [°C]	**430**
ΔP [mbar]	**12**
N_2 temperature [°C]	**210-220**
$Particulate_{in}$ [g/Nm^3]	**6.4**
$Particulate_{out}$ [mg/Nm^3]	**2.1**

Performance of the 125 kW molten carbonate fuel cell

(Ansaldo Fuel Cell SpA)

(WP8) Simulated Biomass-derived gas - Results

V vs. I curve



simulated mix (*)

ANODE:

H_2	40.4 %MOL
CO_2	24.8 %MOL
STEAM	27.8 %MOL
N_2	7.0 %MOL

CATHODE:

O_2	12.9 %MOL
CO_2	5.0 %MOL
STEAM	13.7 %MOL
N_2	68.4 %MOL

(*) The same planned for the TRISAIA Plant

power

stack voltage = 92.4 V

stack current = 1102 A

100kW has been demonstrated

By courtesy of

Ansaldo Fuel Cell SpA

GASIFICATION OF WOOD SCRAPS AND RICE HUSK

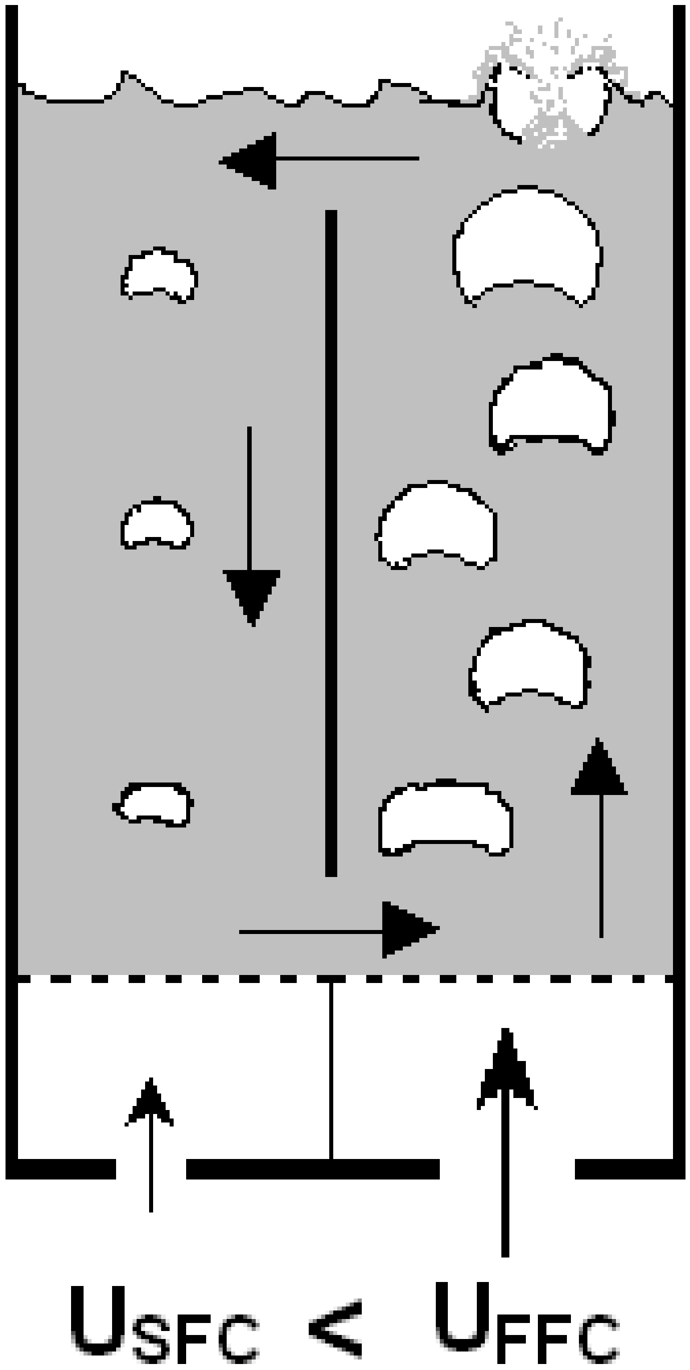
YINGKOU, LIAONING, CHINA

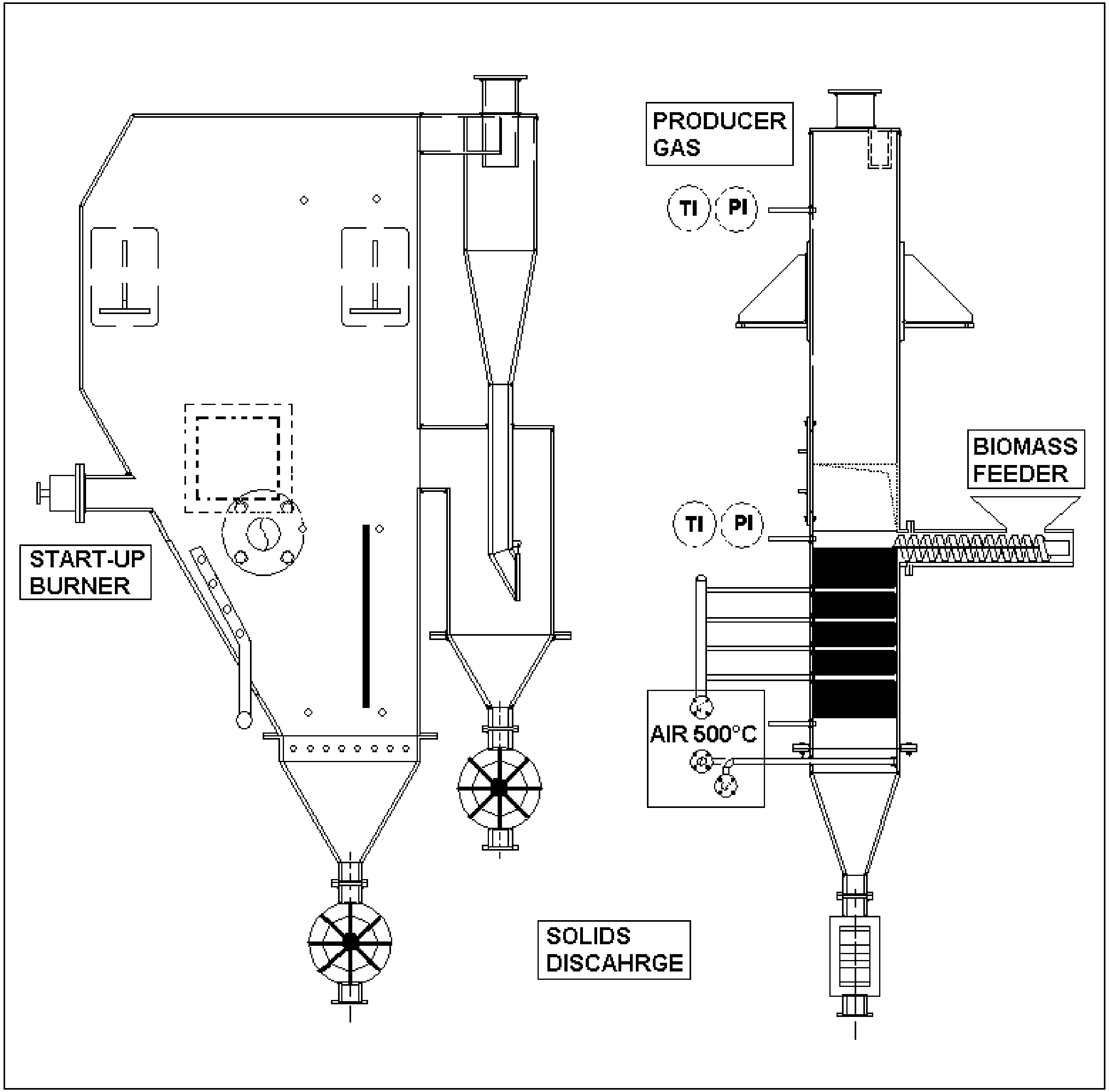
Solid circulation between two interconnected fluidized beds (IFB)

The circulation system is made of two granular beds fluidized at different gas velocities, and interconnected by means of an overflow baffle and an orifice. The overall bed inventory should allow a bubbling bed height just above the upper tip of the baffle.

The driving force for solid circulation is provided by the difference in pressure, ΔP, between the two beds, at their bottom level; as it occurs in liquid-like systems, ΔP is in turn linked to the difference in the average density of the particle suspensions on both sides of the baffle, determined by the bubble fraction associated to the respective fluidizing velocity.

Both fluidized beds are contained in the same vessel, so that the gaseous streams coming from both sides of the baffle are mixed together before leaving the reactor.




PRODUCER GAS
TI
PI
BIOMASS FEEDER
TI
PI
START-UP BURNER
AIR 500°C
SOLIDS DISCAHRGE

Cold model testing

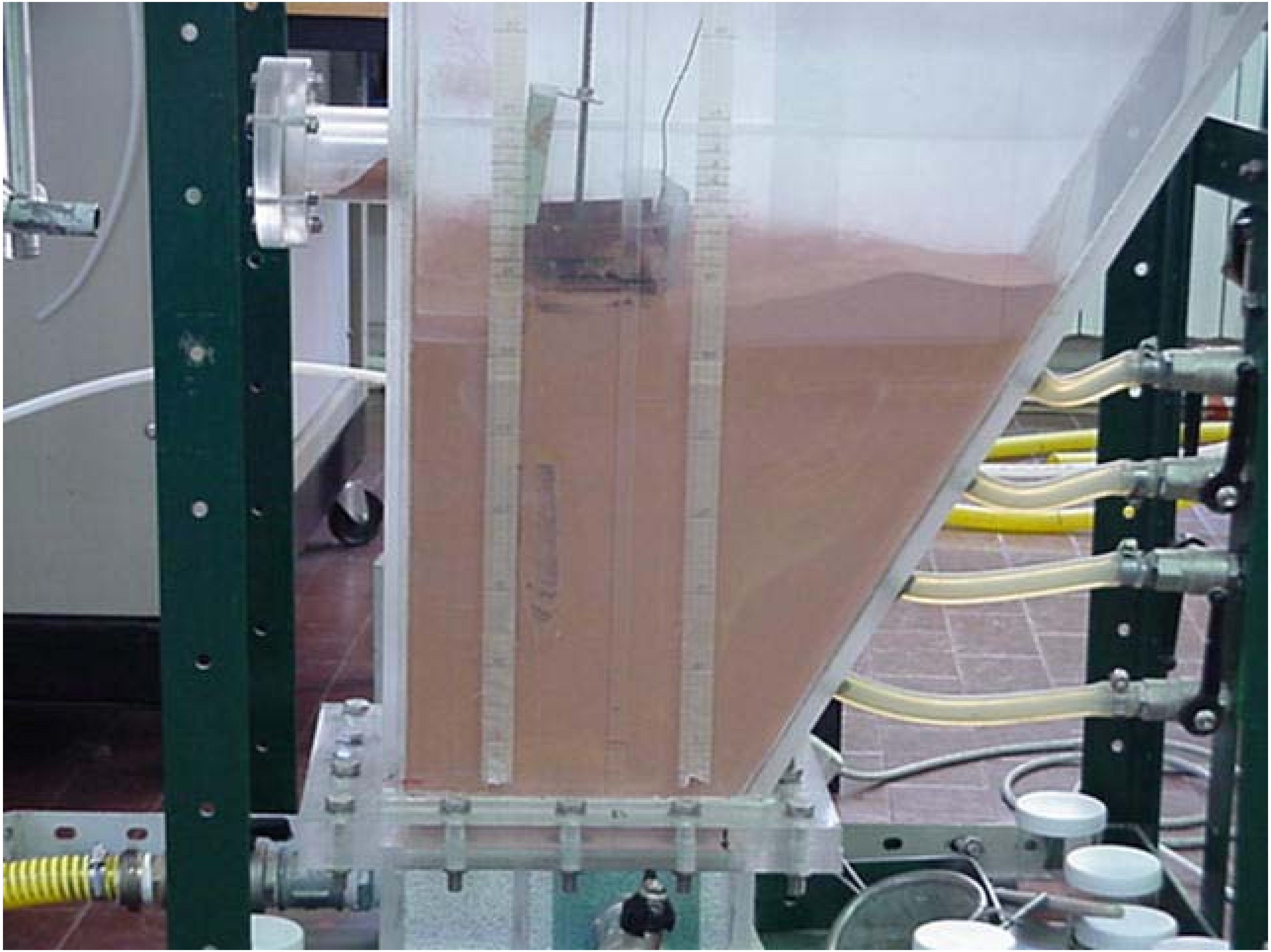
Scaling rules are based on the equations of change for fluidization, which define a set of dimensionless numbers: systems characterized by similar values for the corresponding dimensionless quantities, exhibit similar dynamic behaviour.

In addition to the requirement of geometric similarity, which should include also particle average size, shape and size distribution, further fluid dynamic requisites are given by the equality of each one of the following quantities, between the reactor and its cold model:

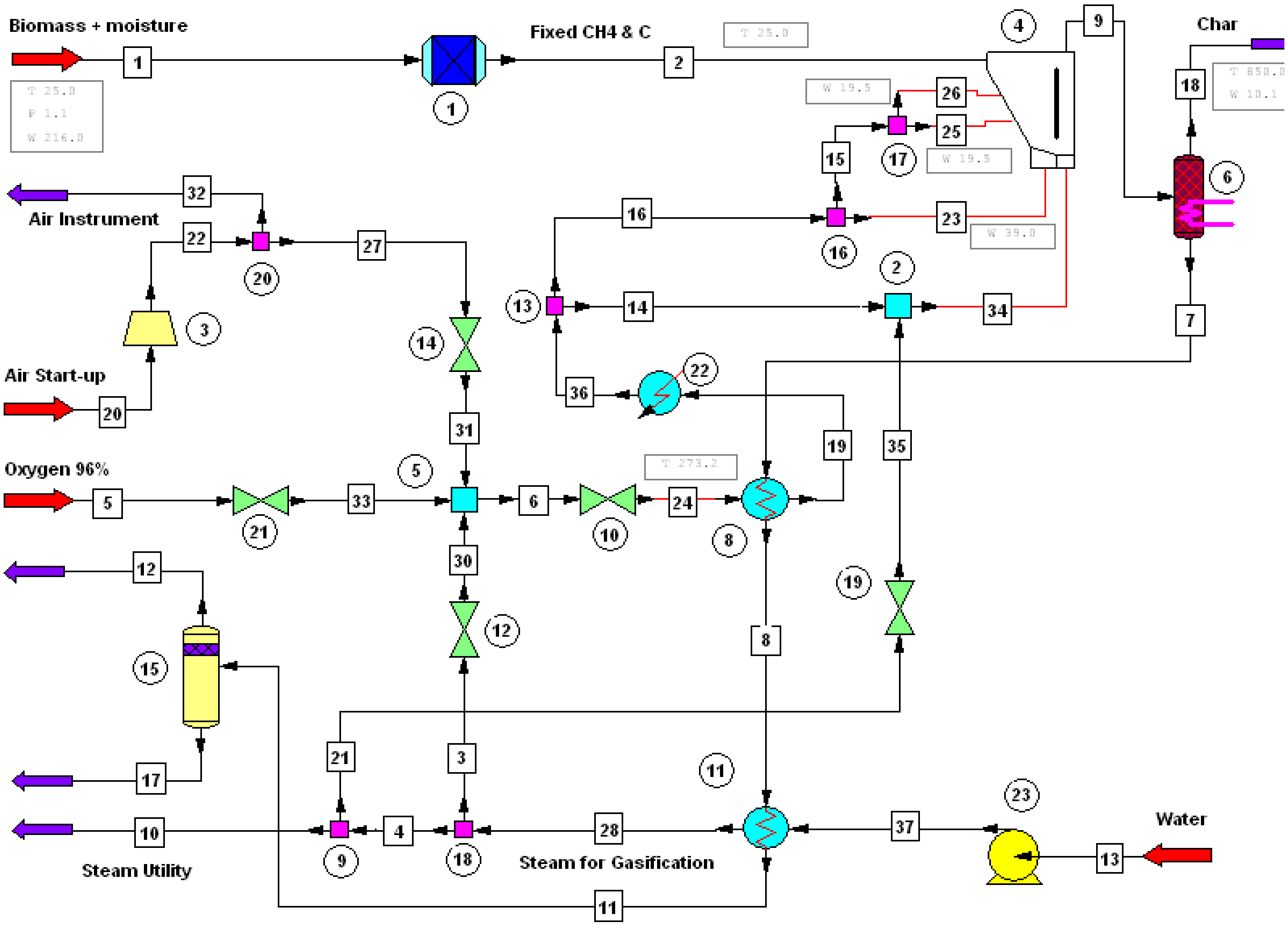
$$De = \frac{\rho}{\rho_P}$$

$$Ar = \frac{d_P^3\,\rho_P\left(\rho_P - \rho\right)g}{\mu^2}$$

$$Fr = \frac{U_0}{\left(g\,D_R\right)^{1/2}}$$



Flow sheet of a 1 MWth steam/O_2 gasification pilot plant



Fuel gas quality (estimated)

Quantity	Value	Unit
Gas yield	1.34	Nm^3 dry gas/kg biomass daf
LHV	10	MJ/Nm^3 dry gas
P.M.	23	g/mol (average molecolar weight dry gas)
Gas composition		
H_2	32.5	% in volume
CO	24.1	"
CO_2	29.5	"
CH_4	8.8	"
N_2	1.3	"
H_2O	3.9*	"
Char+tar**	51	g / kg biomass daf
η chemical	0.735	- (gassification efficiency)
E.R.	0.27	O_2 in the feed stream / O_2 needed for combustion
G.R.	0.91	kg (O_2 + H_2O) / kg biomass daf
O_2/H_2O	0.43	- (molar ratio)

* equilibrium humidity at 30°C