


**Master of Science in *Energy Engineering
Renewables for Environmental
Sustainability***

<http://beep.metid.polimi.it/>

School of Industrial and Information Engineering
Academic Year 2017-18

Lecture notes for:
Bioenergy and Waste-to-Energy Technologies
Thermochemical conversion processes

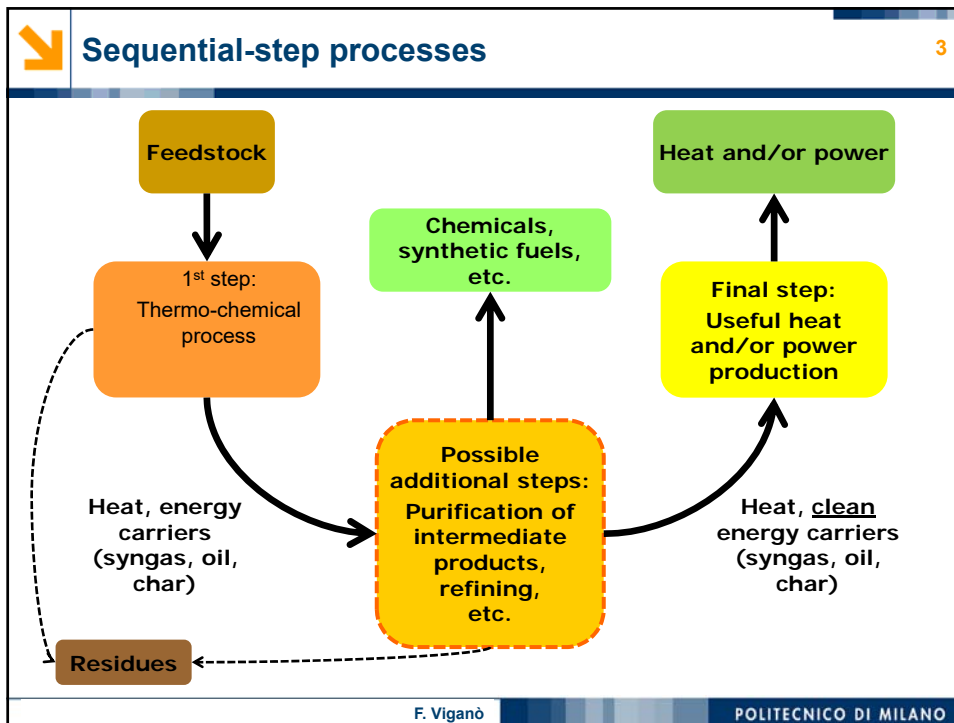
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With the contributions of ing. M. Fantini, ing. E. Martelli, prof. S. Consonni



Lecture outline 2

- **Thermochemical (TC) processes**
- Pyrolysis
- Gasification
- Waste gasification vs. waste combustion
- Reference Books

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Traditional classification of TC processes 4

Thermo-chemical process = Thermal treatment process
i.e. thermal decomposition of the treated material

Typically, thermal treatments are classified according to three basic processes:

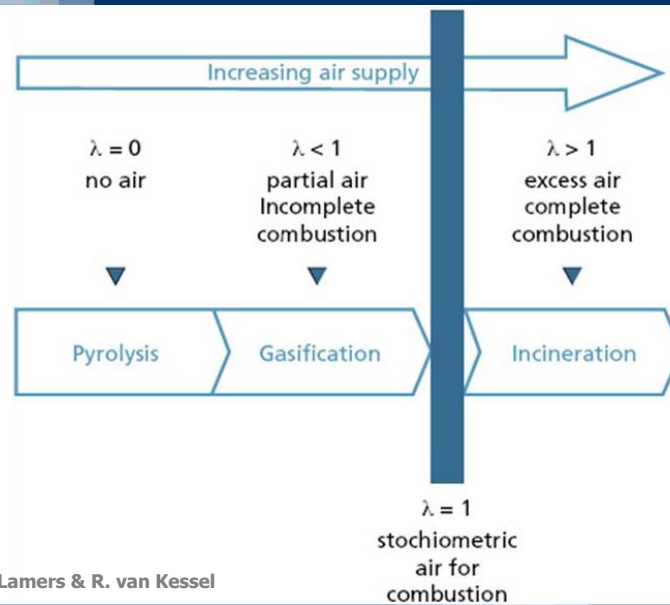
- **PYROLYSIS:** thermal degradation induced by supply of heat with no supply of oxygen; the final product is a mix of solid, liquid and gas fuel materials. In well-designed processes, the overall energy content of the products can be higher than that of the treated material, due to the uptake of the reaction heat.
- **GASIFICATION:** partial oxidation by means of sub-stoichiometric amounts of oxygen; the main product is commonly a syngas (i.e. a synthesis-gas) with an energy content dependent on the type of oxidant and gasification process.
- **COMBUSTION:** complete and fast oxidation of all the suitable atom species with an adequate oxygen excess; final products are heat and fully oxidized species.

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From pyrolysis to combustion

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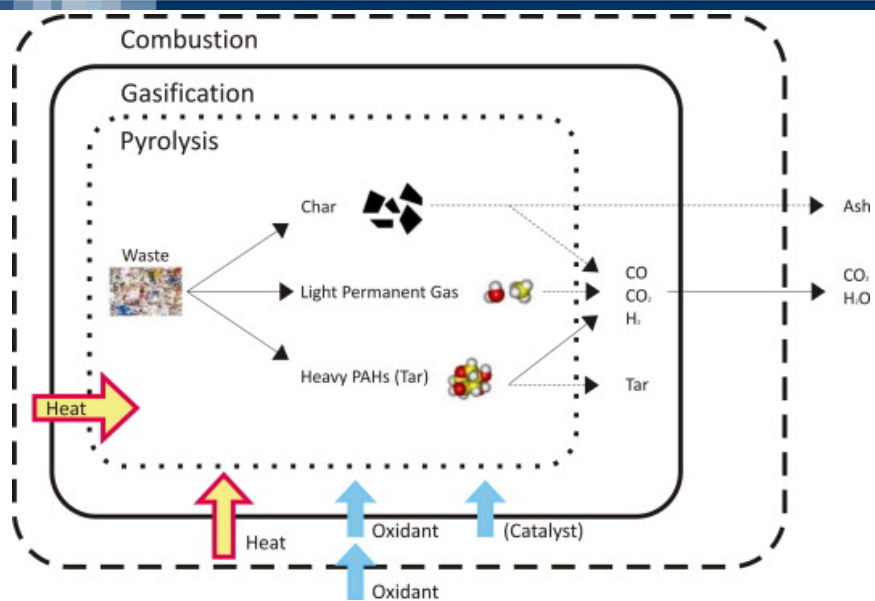
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Pyrolysis, gasification and combustion

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 **Lecture outline**

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- *Thermochemical (TC) processes*
- **Pyrolysis**
- *Gasification*
- *Waste gasification vs. waste combustion*
- *Reference Books*

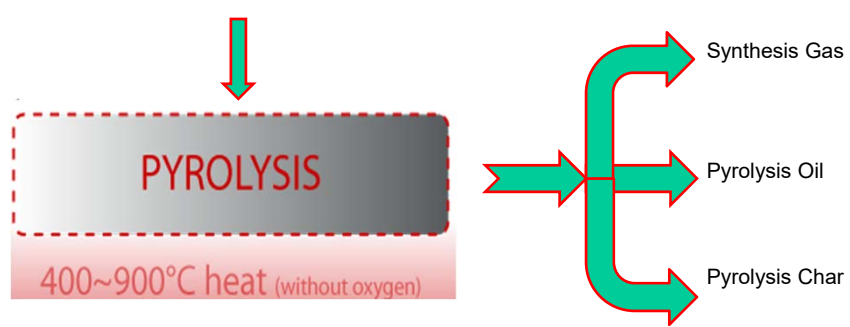
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 **Pyrolysis**

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Thermal degradation induced by supply of heat with no supply of oxygen

Primary energy source
(Coal, Biomass, Waste, etc.)



Synthesis Gas

Pyrolysis Oil

Pyrolysis Char

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Pyrolysis

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Definition:

Pyrolysis is a thermochemical decomposition of an organic material into a range of useful products, either in the total absence of oxidizing agents or with a limited supply that does not allow the complete gasification.

In biomass pyrolysis the molecules (LIGNIN, CELLULOSE and HEMICELLULOSE) break down into simpler molecules ranging from the SOLID to the GAS phase (CHAR, TAR, SYNGAS).

Pyrolysis products are:

- SOLID (mostly char or carbon)
- LIQUID (tars, heavier hydrocarbons and water)
- Gas (e.g. CO₂, H₂O, CO₂)

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Pyrolysis products

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PRODUCTS:

- SYNGAS (i.e. synthesis gas): composed mainly of light hydrocarbons (C₂H₂, C₂H₄, C₂H₆, C₆H₆), carbon oxides, hydrogen and, possibly, volatile pollutants (e.g. HCl, H₂S, NH₃ if the feedstock contains respectively chlorine, sulfur, nitrogen).
- TAR (i.e. oil): composed mainly of heavy hydrocarbons, sometimes partly oxidized.
- CHAR (i.e. solid product): contains the ash (e.g. metals, silicon) of the feedstock, as well as typically large amount of carbon, with little hydrogen and some other species, depending on the nature of the feedstock (it can contain some Cl, S, etc.)

TYPES OF PROCESS:

Slow (conventional), Intermediate, Fast, etc.

- The main classification is based on the heating rate of the treated material. It can range from slow (about 1°C/s) to very high (above 1000°C/s).

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What is TAR ?

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TAR is a complex mixture of condensable hydrocarbons and is a major issue for both biomass pyrolysis and gasification. Many definitions of biomass tar have been given by many institutions working on biomass gasification. Within the European project on standardization of measuring tar a consensus on the definition was agreed, being all organic hydrocarbons higher than benzene (78 kg/kmol).

When biomass is heated the molecular bonds of the biomass break, the smallest molecules are gaseous, the larger are called primary tars. The primary tars, which are always fragments of the original material, can react to secondary tars by further reactions at the same temperature and to tertiary tars at high temperature.

Mixed oxygenates	Phenolic ethers	Alkyl phenolics	Heterocyclic ethers	PAH	Larger PAH
400° C	500° C	600° C	700° C	800° C	900° C

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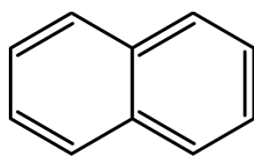
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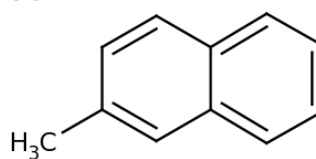
What is TAR ?

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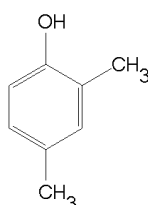
TAR is the name given to heavy aromatic hydrocarbons that are produced by pyrolysis and, sometimes, by gasification.



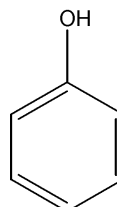
$C_{10}H_8$ - naphthalene
B.P. 217°C



$C_{11}H_{10}$ - 2-methyl naphthalene
B.P. 241°C



$C_8H_{10}O$ - 2,4-dimethyl phenol
B.P. 211°C



C_6H_6O - phenol
B.P. 182°C

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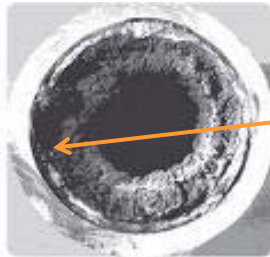
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What is TAR like and what does it ?

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Tar is a black, highly viscous liquid that condenses at relatively high temperatures (it may condense at $T > 300^{\circ}\text{C}!!$). As a consequence, its condensation can cause **CLOGGING** of the gas passages and equipment (pipes, fan, valves, etc). Moreover, tar molecules may damage the catalyst bed of downstream reactor and the components of downstream internal combustion engines/gas turbines.



**obstruction of
pipes cross-
section, corrosion**

**deposits on heat
transfer surfaces
of boilers and on
refractories**



**tar-water mixtures
are difficult to
handle and
contaminate process
residues**

Source: U. Arena, Univ. of Naples

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Pyrolysis yields

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Biomass is decomposed / pyrolyzed by heating it in absence of AIR/OXYGEN:

- At a specific HEATING RATE [K / min]
- Up to a maximum temperature called pyrolysis temperature
- Holding it there for a specific RESIDENCE TIME.

Pyrolysis processes are evaluated on the basis of the following performance indexes:

- MASS YIELD (for LIQUID, GAS and CHAR)

$$\frac{\dot{m}_i}{\dot{m}_{\text{BIOMASS}}}$$

- ENERGY YIELD (for LIQUID, GAS and CHAR)

$$\frac{\dot{m}_i \cdot \text{LHV}_i}{\dot{m}_{\text{BIOMASS}} \cdot \text{LHV}_{\text{BIOMASS}}}$$

Product composition and MASS / ENERGY YIELDS strongly depend on the HEATING RATE, PYROLYSIS TEMPERATURE and RESIDENCE TIME.

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Variants of pyrolysis processes				
Pyrolysis Technology	Vapours Residence Time	Heating rate	Temperature [°C]	Products
Carbonization	days	very low	400	charcoal
Conventional	5-30 min	low	600	oi, gas, char
Fast	0,5 - 5 sec	very high	650	bio-oil
Flash-liquid	< 1 sec	high	< 650	bio-oil
Flash-gas	< 1 sec	high	< 650	chemicals, gas
Ultra	< 0,5 se	very high	1000	chemicals, gas
Vacuum	2 - 30 sec	medium	400	bio-oil
Hydro-pyrolysis ^a	< 10 sec	high	< 500	bio-oil
Methano-pyrolysis ^b	< 10 sec	high	> 700	chemicals
^a pyrolysis with water				
^b pyrolysis with methanol				
Source: D. Mohan, C. U. Jr. Pittman, P. H. Steele, "Pyrolysis of wood/biomass for Bio-oil: A Critical Review. Energy & Fuels, 2006.				
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Pyrolysis physical aspects	
<p>A pyrolysis process entails four main steps:</p> <ol style="list-style-type: none"> 1. DRYING (T < 100°C) Biomass is heated up and the free water/moisture together with some bound water is released. 2. INITIAL STAGE (T from 100°C to 300°C) Bound water and light gases (H₂, CH₄, CO, CO₂) are released from the biomass (where H₂O and gases were trapped) and from the DEHYDRATION of cellulose and hemicellulose molecules. <div style="display: flex; align-items: center;"> <div style="margin-right: 20px;"> <p>DEHYDRATION:</p> <ul style="list-style-type: none"> - T > 250°C cellulose - T > 180°C hemicellulose </div> <div style="font-size: 3em; margin-right: 10px;">}</div> <div> <p>Because of thermal cracking, dehydration begin to loose H₂O and light gases</p> </div> </div> <p>Lignin is not decomposed / dehydrated in this stage because its dehydration takes place at higher temperatures (> 300°C).</p> <p>This stage converts biomass into CHAR and SYNGAS.</p>	
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Pyrolysis physical aspects

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3. INTERMEDIATE STAGE (T from 300°C to 600°C)

It is also called PRIMARY PYROLYSIS. At 300°C lignin dehydration starts, thus, lignin and residual cellulose and hemicellulose are dehydrated into CHAR and SYNGAS.

Simultaneously, some cellulose molecules are DEPOLYMERIZED into heavy hydrocarbons (condensable species). During DEPOLYMERIZATION, cellulose molecules are split (by thermal cracking) into heavy ($> C_5$) hydrocarbons (TAR). With respect to dehydration, depolymerization is favored at higher temperatures because of its higher ACTIVATION ENERGY (E_a).

4. FINAL STAGE (300°C < T < 900°C)

This phase occurs only if vapors (of hydrocarbons) remain in the reactor at high temperatures for a sufficient residence time.

Hydrocarbon molecules are thermally cracked into char (C atoms that aggregate into solid) and syngas (light species, namely, CH_4 , CO, CO_2 , H_2O and hydrocarbons with $< C_5$).

If vapors generated by pyrolysis is quickly removed from the reactor and cooled down, hydrocarbons are not cracked and condense into the liquid phase (TAR). The shorter the permanence time of the condensable gases in the reactor, the smaller the fraction of cracked hydrocarbons and the higher the liquid yield.

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Pyrolysis products

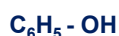
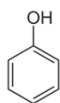
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NOTE: Pyrolysis stages are partially overlapped due to the low thermal conductivity of wood/biomass. External layers may be in the final stage while internal layers are still drying.

1. **CHAR (solid phase):** char is made of carbon, ashes and some oxygen and hydrogen. Its LHV ranges from 30 to 35 MJ/kg.

2. **TAR (liquid phase at ambient temperature/pressure):** it derives from the condensation of the vapors generated during the pyrolysis. It contains:

- About 20% of water
- About 80% of hydrocarbons ($>C_5$), some of them contain also oxygen (they are called PHENOLIC COMPOUNDS, e.g. PHENOL = C_6H_6O , a benzene molecule in which an hydrogen atom is replaced by a hydroxyl group (OH)).



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Pyrolysis products

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Phenol is corrosive for eyes, skin and respiratory tracts and lungs. It may damage liver, lungs and kidneys, then, TAR is very toxic and its handling is subject to severe regulations. TAR also contains lignin mono-molecules which were not completely decomposed into simpler hydrocarbons.

LHV ranges from 13 – 18MJ/kg wet basis.

3. **SYNGAS (non-condensable gases)**: it contains light gases which do not condensate at ambient conditions:

- **PRIMARY SYNGAS**: light gases from dehydration phase CO , CO_2 , H_2 , CH_4 , C_2H_6 , C_2H_4 .
- **SECONDARY SYNGAS**: heavier hydrocarbons generated in the FINAL STAGE C_3H_8 , C_3H_6 , C_4H_{10} , C_4H_8 , C_5H_{18} , C_5H_{10} .

Syngas LHV ranges from 11 to 20 MJ/Nm³.

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Use of pyrolysis products

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Tar (pyrolysis liquid products) is more viscous than fuel oil. It contains much more oxygen and increases its viscosity during time due to the polymerization reactions among the tar molecules.

It is not self-igniting (like diesel) and this is why it cannot be used/blended with diesel for engines.

It is used to generate chemicals_

→ to reduce gasoline (and diesel) via hydrocracking

or

→ to be burned in boilers (but this is not convenient)

Syngas is the most valuable pyrolysis product because it can be used for several applications (Gasification).

Char can be easily milled and burned together with COAL in large power plant (co-gasification, co-firing plants)

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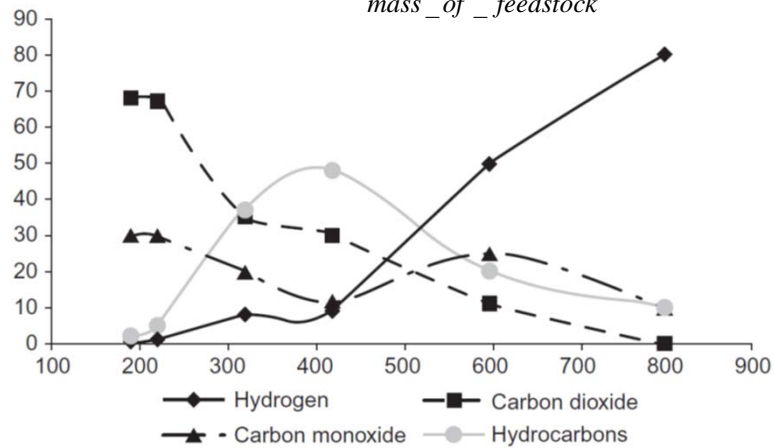


Pyrolysis temperature T_{PY}

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T_{PY} affects both, product yields and composition.

$$YIELD_of_product_i = \frac{mass_of_product_i}{mass_of_feedstock}$$



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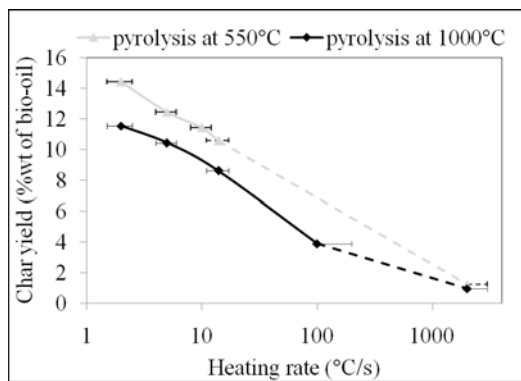
Pyrolysis temperature T_{PY}

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The energy based yield should be preferred since it gives a measure of the conversion efficiency, thus:

$$\eta_i = \frac{mass_of_product_i \cdot LHV_i}{mass_of_feedstock \cdot LHV_{feedstock}}$$

The char yield decreases with T_{PY} because high T_{PY} favors the depolymerization reactions and then the conversion of cellulose, lignin and hemicellulose into GASES. At low temperature, only dehydration takes place and this maximizes the CHAR YIELD.



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Pyrolysis temperature T_{PY}

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The LIQUID YIELD depends on the production of heavy vapors during the polymerization process:

- At LOW temperatures ($< 300^{\circ}\text{C}$) depolymerization does not take place because of its high ACTIVATION ENERGY.
- At HIGH temperatures ($> 600^{\circ}\text{C}$) thermal cracking of vapors causes the conversion of heavy molecules into high gases (SYNGAS).

Then, an optimum T_{PY} which maximizes the liquid YIELD exists. Such optimal T_{PY} is about 500°C .

SYNGAS production is favored at high temperatures to take advantage of the thermal cracking of heavy hydrocarbons.

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Pyrolysis heating rate and residence time

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Heating rate and residence time at final temperature influence the liquid/tar yield because they determine the extent of the FINAL STAGE in which hydrocarbons are cracked into lighter species (TAR species \rightarrow syngas species).


In order to maximize the liquid yield it is necessary to adopt:

1. T_{PY} which causes/favors depolymerization but NOT cracking ($T_{PY} \approx 500^{\circ}\text{C}$) of hydrocarbons with $> C_5$
2. High heating rates (up to $250^{\circ}\text{C}/\text{min}$) so as to have a very short overall residence time in the reactor: in few seconds the biomass is heated up to the final temperature.
3. Very short residence time at the final temperature.

In this way the FINAL STAGE is limited to a short time period.

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Common design rules for pyrolyzers

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MAX CHAR YIELD
("slow pyrolysis", "carbonization")

1. Low final temperature ($T_{PY} \approx 200^{\circ}\text{C}$)
2. Slow heating rate ($< 0.01 - 2^{\circ}\text{C} / \text{s}$)
3. Long residence time (days, hours)

MAX SYNGAS YIELD


1. High T_{PY} temperature ($700 - 900^{\circ}\text{C}$)
2. Slow heating rate
3. Long residence time

MAX LIQUID YIELD
("fast pyrolysis", "flash pyrolysis")

1. Moderate T_{PY} ($\approx 450 - 600^{\circ}\text{C}$)
2. High heating rate ($\sim 250^{\circ}\text{C} / \text{min}$)
3. Short residence time (min, sec)

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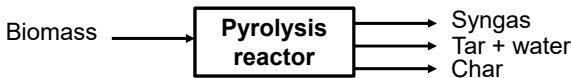
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Energy balance of pyrolyzer reactors

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Pyrolysis is not self – sufficient: it needs the introduction of heat or the combustion of a fraction of the products.



Inside the reactor two classes of reactions may happen:

1. DECOMPOSITION REACTIONS: depolymerization (endothermic reaction) and dehydration (exothermic reaction);
2. REACTIONS BETWEEN PRODUCTS. They take place only at high temperatures ($> \sim 600^{\circ}\text{C}$) due to their high ACTIVATION ENERGY

Methanation _____ $CO + 3H_2 \rightarrow CH_4 + H_2O$

Methanol _ Synthesis _____ $CO + 2H_2 \rightarrow CH_3OH$

Water _ Gas _ Shift _____ $CO + H_2O \rightarrow CO_2 + H_2$

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Energy balance of pyrolyzer reactors

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It results that:

- if T_{PY} is low (200 – 600°C), only endothermic reactions take place and heat must be supplied to sustain them.
- if T_{PY} is high (600 – 900°C) the exothermic reactions take place and they provide heat for the endothermic ones.

The energy balance of the overall reactor can be written as:

$$\dot{Q}_{in} = \sum_i \dot{m}_{out_i} \cdot h_{TCH_i} - \sum_i \dot{m}_{in_i} \cdot h_{TCH_i}$$

or in this equivalent expression:

$$\dot{Q}_{in} = \dot{Q}_{HEAT-UP}^{FEED} + \dot{Q}_{DRYING} + \dot{Q}_{REACTIONS}$$

Thus, in any case, supplying heat to the pyrolysis process is necessary. Reactors must be designed in such a way that heat can be supplied through the walls or in the gas medium.

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Pyrolyzer reactors

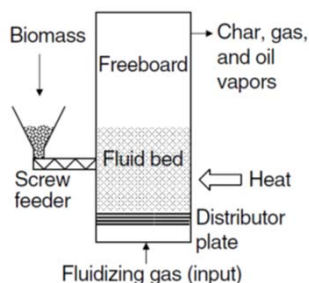
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There are three main configurations:

1. **Fixed or moving beds** – are used for slow pyrolysis processes (carbonization).

Typically fixed bed pyrolyzers are BATCH reactors operating at relatively low temperatures (like OVENS).

2. **Bubbling fluidized beds** – fluidizing gas is needed to provide heat to the process and to keep the bed in the “bubbling regime”.



Operating principle of bubbling beds:

The *Equilibrium condition* of a biomass particle of size (diameter) “d” has to be satisfied.

Thanks to this principle, larger particles automatically tend to stay into the reactor for a longer residence time, until their dimension is decreased (i.e. they are converted into useful products).

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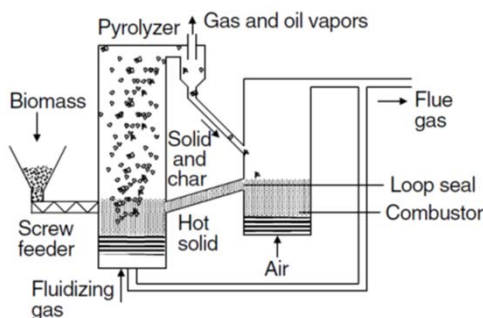
Pyrolyzer reactors

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In bubbling beds an inert material (such as sand) is used to control the bed temperature and provide a high heat transfer of biomass.

The residence time of solids is much longer than that of gases thanks to the bed principle (equilibrium). This helps to obtain high tar yields.

3. Circulating fluidized beds -



Fluidizing gas entrains the biomass particles because the gas velocity is higher than required for the force equilibrium. Solids continuously recycle around on external loop. A portion of char can be burned to supply the reaction heat.

- + high heat transfer
- + good mixing

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General remarks on pyrolysis

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- Feedstock quality has a great influence on the yields of the process (i.e. amounts and qualities of gas, oil and char).
- Once the feedstock is selected and its quality is insured, the process can be tailored to a specific production: favoring the gas yield with respect to the oil or the char yield, etc.
- Slow (or conventional) pyrolysis has been extensively studied in the seventies. It is a process that maximize the production of char. It has been and it is still used to produce activated carbon (the char) from selected materials (typically biomass).
- Fast pyrolysis is the currently most studied process, mainly for the production of chemicals starting from the oil.
- Pyrolysis is studied also for energy purposes, such as:
 - the production of standardized secondary solid fuel (char) with high energy content for industrial or domestic uses;
 - the energy exploitation of difficult materials containing hazardous species: sometimes pyrolysis can allow confining such species into a particular product (e.g. Cr can be confined into char as Cr III).

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Pyrolysis PROS (1/2)

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- In well designed processes, the overall energy content of the products can be higher than that of the treated material, due to the uptake of the reaction heat. Thus, theoretically, pyrolysis can be a good basis for the development of very efficient energy recovery processes.
- Depending on how the process is carried out, the amount and quality of liquid product (oil) can be adjusted. The oil can be the basis for the production of very valuable chemicals.
- Since, theoretically, pyrolysis features no addition of other reagents (like the oxidant in gasification and combustion) than feedstock, the mass of products equals that of the feedstock. Thus, in the presence of contaminating elements, pyrolysis is the process, among all the thermal treatments, which minimizes the amount of contaminated products.
- When a contaminating element is more likely to end up into a specific product (gas, oil or char), pyrolysis concentrates such a contaminant in that product. As an example, chromium (Cr) commonly ends up mostly in the char.

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Pyrolysis PROS (2/2)

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- When hazardous elements end up mainly in the syngas, the concentrations of the species that they form is higher for pyrolysis than for gasification or combustion, because pyrolysis produces always less syngas than the other two families of processes. Thus, the removal of such species can be carried out more easily, thanks to their higher concentrations.
- Due to the theoretically null supply of oxygen, pyrolysis is carried out under strongly reductive conditions, producing only reduced species:
 - typically no dioxin nor furan is produced and, if initially present, they are thermally decomposed into less harmful species;
 - reduced species may be less harmful than the corresponding fully oxidized forms (this is the case of Cr, which ends up mostly in the char as Cr III, instead of being oxidized to Cr VI) and, in some cases, they can be removed more easily from the products than the latter.
- Syngas and oil, whether clean enough, can be used as fuels to run efficient Internal Combustion Engines (ICEs).

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Pyrolysis CONS (1/2)

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FOR THE PRODUCTION OF CHEMICALS:

- The setup of the process is quite complex. Only few companies in the world own well-proven technologies.
- The successful operation of such technologies heavily relies on the insurance of constant-quality feedstock.

FOR ENERGY RECOVERY:

- In this case pyrolysis compares with the other thermal treatment technologies.
- The char, being a solid material, can originate handling difficulties.
- When the feedstock contains contaminants, all the products can be contaminated.
- Some harmful species can present at so high concentrations in the syngas, to make its handling very difficult (e.g. very high concentrations of HCl or HF originate serious corrosion problems to all equipment).
- Oil and – in a larger extent – char, when contaminated can become hazardous residues, which need special care in being disposed of.

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Pyrolysis CONS (2/2)

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- In some cases, the oil may present bad characteristics:
 - instable chemical and physical properties that change in time;
 - very high viscosity or non-Newtonian behavior, with deposit of asphalt residues, etc.
- Some technologies use pyrolysis as the first step of a multiple-step oxidation process, which eventually convert totally or partly the energy content of the feedstock into heat to feed an externally fired power cycle. In such technologies, the potential advantages due to a better control of the oxidation process **must be carefully weighted** against the serious disadvantages of a much higher complexity of the system with respect to a simple, direct combustion scheme:
 - multiple hot reactors vs. a single combustion chamber;
 - flows of high temperature, flammable, explosive and toxic substances (i.e. syngas and oil vapors);
 - problems of sealing to avoid leakages of air / gases, which can lead to explosions, poisoning of people, as well as to control instabilities for the process, etc.

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Lecture outline

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- Thermochemical (TC) processes
- Pyrolysis
- **Gasification**
- Waste gasification vs. waste combustion
- Reference Books

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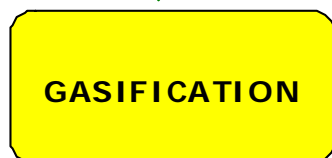


Biomass gasification

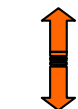
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Partial oxidation by means of sub-stoichiometric amounts of oxygen

Primary Energy source
(coal, biomass, waste, etc.)



Gasifying / Oxidizing agent
(air, O₂, steam, CO₂)



HEAT



CO
H₂
CO₂
H₂O
H₂S
COS
N₂
NH₃
...

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Biomass gasification

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Definition:

Gasification is a chemical process which converts fossil or non-fossil fuels (typically solid or liquid but also gases) into useful gases (CO , H_2 , CH_4). The process requires a controlled amount of reacting oxidizing agent which can be either gas (STEAM , O_2 , AIR , CO_2 ...) or supercritical water ($\text{HYDROTHERMAL GASIFICATION}$).

With respect to pyrolysis which is a thermal degradation process, in gasification the medium takes part in the reactions and it is necessary.

Gasification is carried out for the following reasons:

1. To increase the fuel LHV by rejecting moisture and inert species (H_2O , N_2 , O_2 , ASH);
2. To remove SULPHUR in the gas phase as H_2S by means of cheap processes (COAL GASIFICATION and $\text{TIRES GASIFICATION}$)
3. To increase the H/C ratio of the fuel by adding H_2O in the gasification medium or processing the generated syngas into catalytic gas processes (REFORMING , WATER GAS SHIFT).

The gaseous product is a synthetic or synthesis gas typically called «syngas».

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Gasification basics

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- Gasification is a process aimed at converting the feedstock into a syngas with an appreciable energy content.
- Several processes exist that differ each other by a number of features.
- A first criterion to classify the different processes is the type of oxidizing agent. It can be air, oxygen, oxygen-enriched air, steam, carbon dioxide, etc. Also mixtures of such substances are used.
- The type of oxidizing agent determines whether the process is endothermic (requires heat), exothermic (releases heat) or even autothermic (no uptake, nor release of heat).
- The type of oxidizing agent, in conjunction with the characteristics of the feedstock, determines also the amount and the energy content of the produced syngas.
- Gasification is carried out at temperatures that range from those of pyrolysis ($400\text{-}900^\circ\text{C}$) up to those of mild combustion ($1300\text{-}1600^\circ\text{C}$).
- Since gasification produces only one (syngas) or two (syngas + heat) goods, its design and tuning are much simpler than those of pyrolysis.

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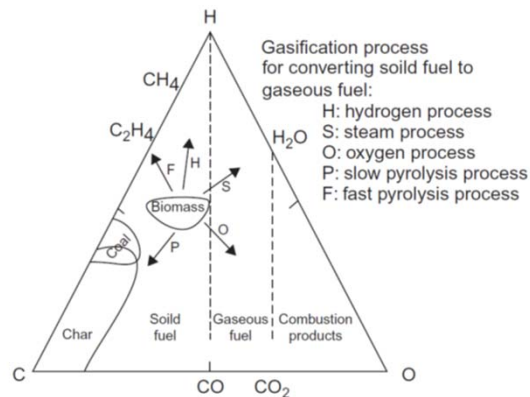


Gasifying agent (medium)

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C – H – O ternary diagram of biomass showing the gasification process.

The ternary diagram can depict the conversion processes....



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Features of gasification

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- Gasification is a chemical process less kinetically controlled than pyrolysis, since the presence of an oxidizing agent speeds up the reactions. Thus, the design of the process is carried out in conjunction with that of the reactor, often called **gasifier**.
- Several gasifiers have been developed, mainly for the gasification of coal. The type of the gasifier is a distinctive feature of each technology.
- A first classification of gasifier types is based on the type of "bed":
 - fixed bed: the solid material stays fixed upon a stationary grate;
 - moving bed: the solid material is moved over a grate;
 - fluidized bed: the solid material is suspended within a reactor by means of high velocity fluid injections;
 - entrained flow: there is no "bed" of solid material, but the feedstock is injected pulverized so to complete most of the condensed phase reactions before a "bed" of material can be formed.

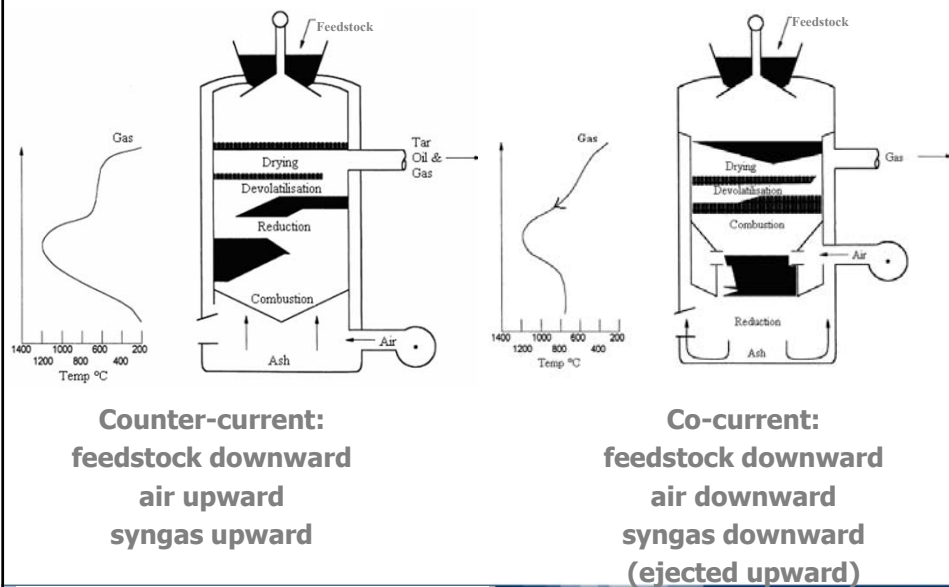
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Fixed or moving bed gasifiers

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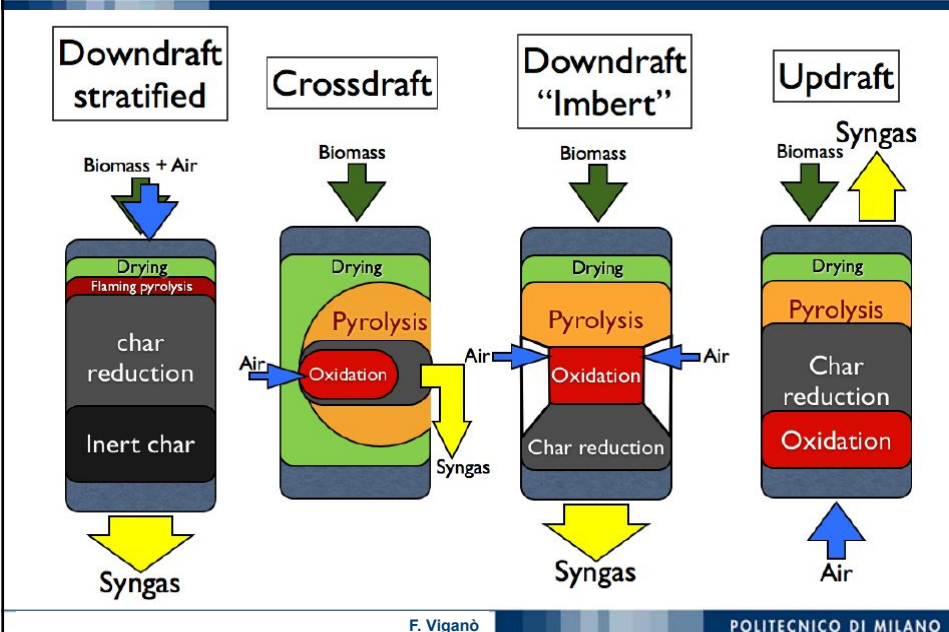
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Types of fixed bed gasifiers

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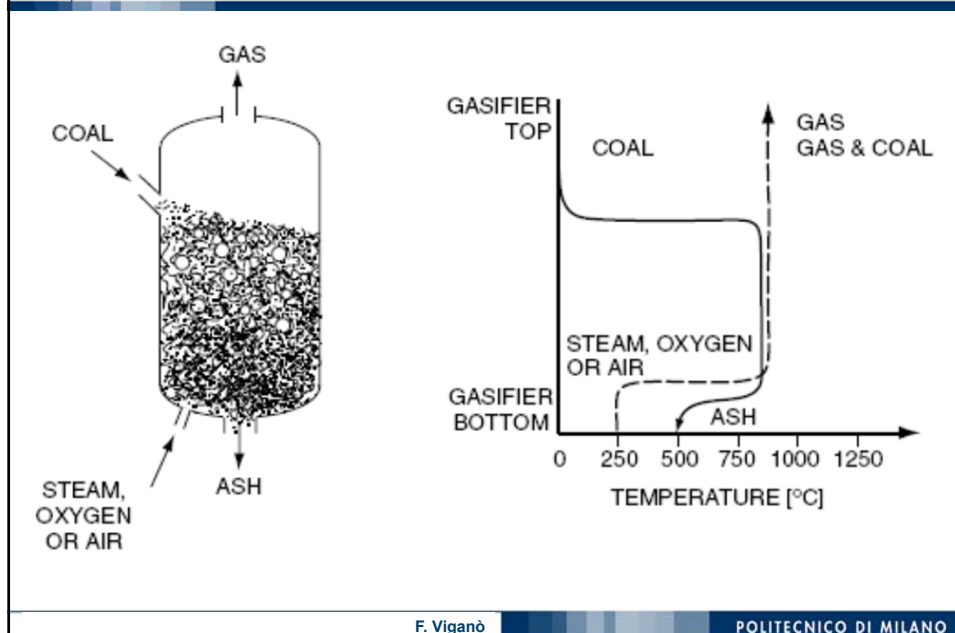
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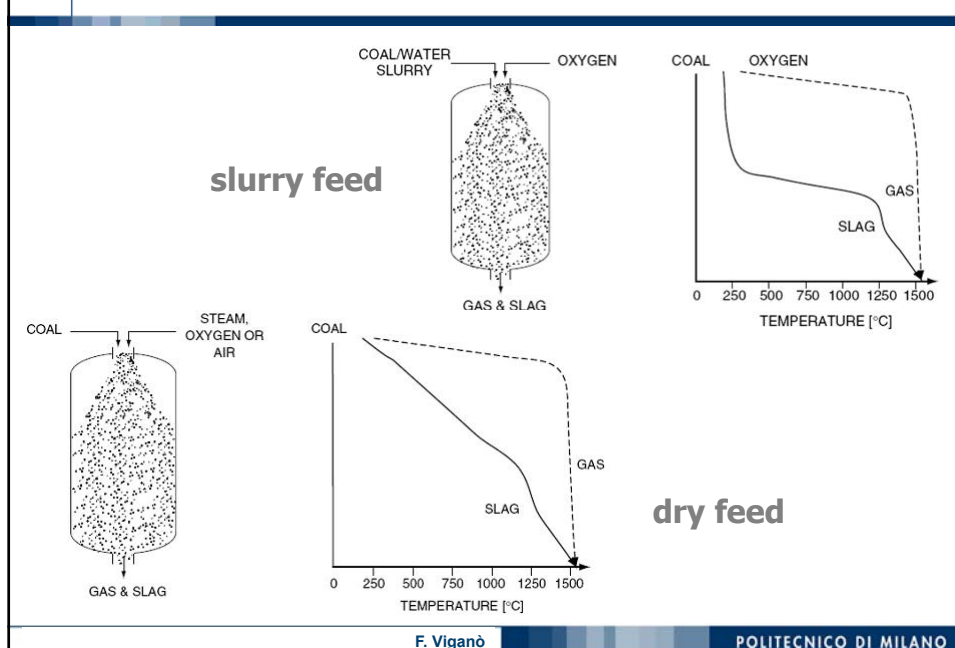
Fluidized bed gasifiers

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Entrained flow gasifiers

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Gasification is NOT a new technology!

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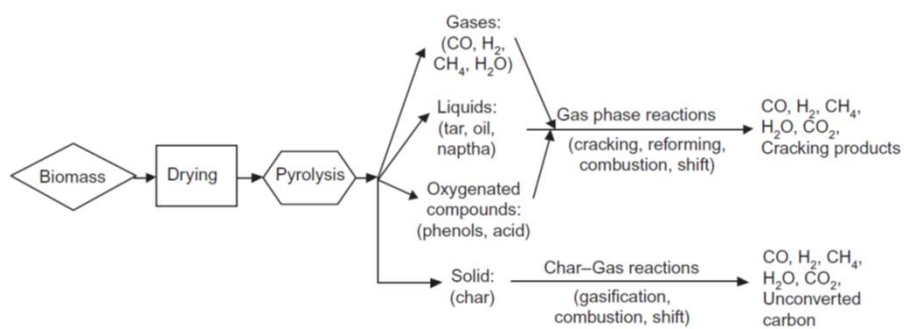


Main gasification steps

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Pyrolysis is not as advantageous as gasification for power generation because of the nasty properties of the pyrolysis oil. Tar cannot be used in gas turbines. Pyrolysis is preferred to gasification only for some specific applications.

A typical gasification process generally follows the sequence of steps below:



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Main gasification steps

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DRYING: When biomass particles enter into a gasifier, the first part of the residence time is spent to evaporate both free and bound water.

The process continues up to 200°C.

PYROLYSIS: Cellulose, hemicellulose and lignin molecules are broken into heavy hydrocarbons in a cracking process. No gasification reactions with the gaseous medium (steam, O₂, air) takes place because the heating rate is much faster than the reaction rate of the gasification reactions. Thus, initially, biomass molecules are cracked as in pyrolysis process and not gasified. Pyrolysis produces light gases (syngas made of H₂O_g, CO₂, CO, H₂, CH₄) and heavier hydrocarbons (tar) and char (rich of carbon).

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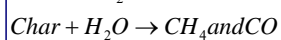
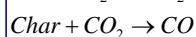
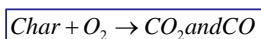
Main gasification steps

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CHAR GASIFICATION REACTIONS: Biomass char is more porous (larger number of pores) than coke produced through high temperature carbonization of coal because biomass volatile fraction is larger: pores are generated as gases and moisture leave the solid particle.

The porosity of biomass char is in the range of 40 – 50% while that of coal char is 2 - 18%. The pores of biomass char are much larger (20 - 30 µm) than those of coal char. Thus, its reaction behavior is different from that of chars derived from coal, lignite, etc. For this reason biomass char is more reactive than coke (pores increase the contact surface between gas and solid where reactions take place).

Main reactions involved:



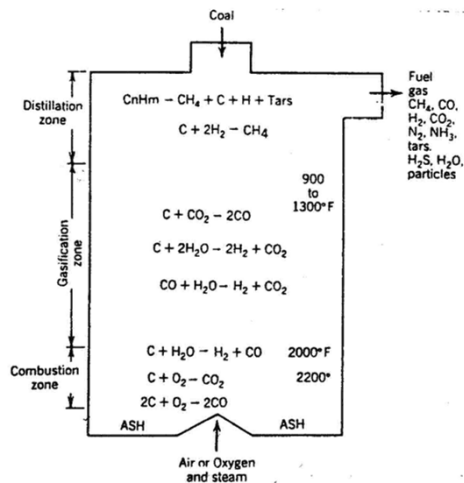
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Gasification reactions

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The various reactions take place in different zones of the reactors.

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Gas phase gasification reactions

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R1	Boudouard	$C + CO_2 \rightarrow 2CO$	$\Delta H^\circ = 172 \text{ kJ/mol}$
R2	Water - gas	$C + H_2O \rightarrow CO + H_2$	$\Delta H^\circ = 131 \text{ kJ/mol}$
R3	Hydrogasification	$C + 2H_2 \rightarrow CH_4$	$\Delta H^\circ = -74,8 \text{ kJ/mol}$
R4		$C + \frac{1}{2}O_2 \rightarrow CO$	$\Delta H^\circ = -111 \text{ kJ/mol}$
R5		$C + O_2 \rightarrow CO_2$	$\Delta H^\circ = -394 \text{ kJ/mol}$

The first four are "carbon reactions" and the fifth one is part of the so classified "oxidation reactions".

The main (those with the highest reaction rate) gas phase reactions are:

R6	Tar	Cracking	
R7	Water - gas	shift	$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H^\circ = -41,1 \text{ kJ/mol}$
R8	CO	Combustion	$CO + \frac{1}{2}O_2 \rightarrow CO_2$ $\Delta H^\circ = -284 \text{ kJ/mol}$
R9	Methanation		$CO + 3H_2 \rightarrow CH_4 + H_2O$ $\Delta H^\circ = -206 \text{ kJ/mol}$

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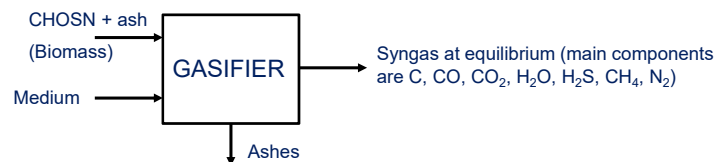
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Simple Thermodynamic model

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To determine the syngas composition under the full chemical equilibrium assumption it is sufficient to consider a limited number of reactions.



5 atomic species \longrightarrow 5 atomic balances equations

8 unknown variables (molar flow rate of product species)

\longrightarrow 3 equations needed

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Simple Thermodynamic model

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A possible choice is R1 – R2 – R3:

$$R1_Boudouard \quad K_{R1}(T) = \frac{X_{CO}^2}{X_{CO_2}} \cdot p$$

$$R2_Water - gas \quad K_{R2}(T) = \frac{X_{CO} \cdot X_{H_2}}{X_{CO_2}} \cdot p$$

$$R3_Hydrogasification \quad K_{R3}(T) = \frac{X_{CH_4}}{X_{H_2}^2 \cdot p}$$

This simple equilibrium model can give a good approximation of the syngas composition if the gasifier temperature is high ($> 1500\text{ K}$). The equilibrium condition is verified for entrained flow gasifiers but not for fluidized bed and fixed bed reactors in which the tar content is much higher than the value predicted by the equilibrium calculation. This is due to the low reaction rate of the cracking reactions.

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Kinetic model

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A more sophisticated and accurate model can be developed by considering the chemical kinetics of the gasification reactions.

In this model you need to take into account:

- T and species distribution in the reactor bed
- T and species distribution in biomass particles
- Biomass particle porosity (number of active sites)
- Gas phase reactions
- Char gasification reactions

The model is a set of Partial Derivative Equations which is very difficult to solve.

Based on their activation energy and reaction mechanism, it's possible to state that the slowest reactions are:

- Char gasification reactions
- Tar cracking reactions

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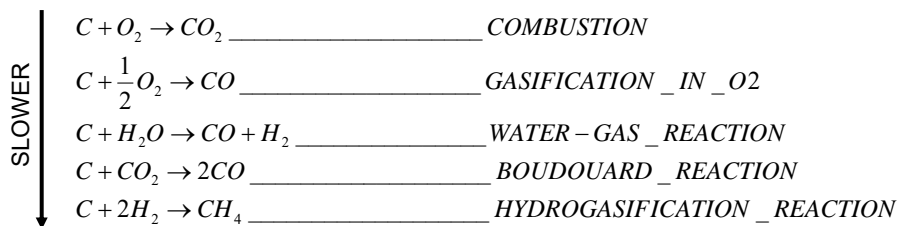


Kinetic model

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Thus, a kinetic model should predict a higher tar content and a lower C conversion efficiency with respect to the full equilibrium model.

KINETIC OF CHAR REACTIONS:



The first two reactions are the fastest ones. If O_2 is present in the gasification medium, it reacts to oxydize and gasify the carbon atoms of the char. The combustion reaction is 15 – 50 times faster than the gasification reaction.

The combustion reaction, having a large ΔH° (enthalpy of reaction) and being exothermic, provides heat to the other (endothermic) gasification reactions.

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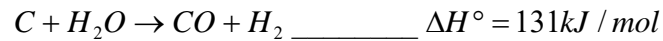
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Kinetic model

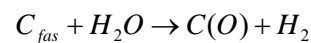
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The water – gas reaction is the most important gasification reaction because generates H_2 and its reaction rate is sufficiently high.

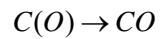


Reaction model / chain:

The steam molecule approaches an active site of carbon " C_{fas} " and dissociate into H_2 and $C(O)$ (SURFACE OXIDE).



In the second step the surface oxide becomes a carbon oxide



The reaction is endothermic. For this reason, if steam is used as gasification medium, heat must be provided to the gasifier.

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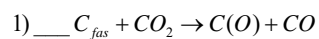
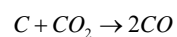
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Kinetic model

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The Boudouard's reaction model describes the carbon gasification in CO_2 :

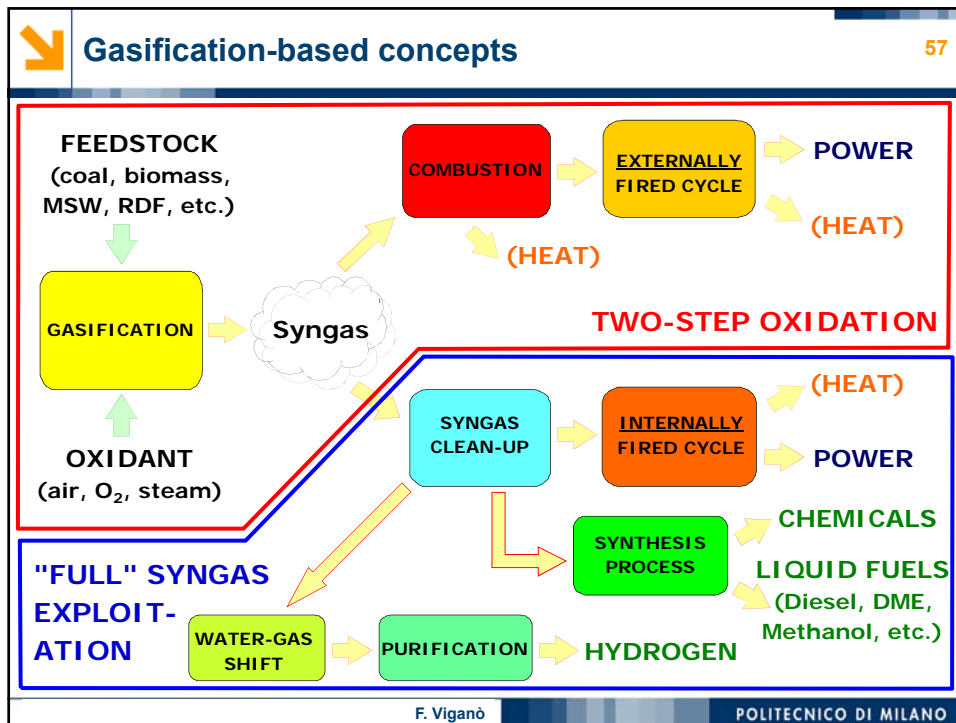


Having a large activation energy, its reaction rate is negligible below 1000K.

The hydrogasification reaction $C + 2H_2 \rightarrow CH_4$ has a very low reaction rate and then its effect on the syngas composition is limited. It is strongly desired when syngas is converted into SNG = Substitute Natural Gas (CH_4).

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Gasification PROS (1/2): 58

- Syngas can potentially be exploited in more efficient ways than solid/liquid fuels can. After purification, syngas can be used as fuel for internal combustion engines (e.g. reciprocating engines, gas turbines, combined cycles), which are inherently more efficient than externally-fired power cycles.
- The combustion of a gaseous fuel is more controllable (e.g. premixed combustion), leading to higher combustion efficiencies due to:
 - less need for oxidant excess (less stack losses);
 - more complete combustion (less losses for incomplete combustion);
 - zero ash content (zero losses for ash discharge).
- A more controllable combustion (e.g. premixed combustion) can also lead to easier limitation of pollutants formation.
- Some chemical species (pollutants or precursors of pollutants) can potentially be removed from syngas more easily or by means of cheaper processes than what can be done on the feedstock or on its combustion products.

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Gasification PROS (2/2):

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- Sometimes, some pollutants or precursor of pollutants can be removed in less hazardous forms from the syngas than they can from combustion products.
- The volume flow of syngas is typically appreciably lower than that of combustion products and this circumstance can make cheaper the treatments for pollutant removal.
- Syngas can potentially be used directly or as intermediate chemicals:
 - as town gas (this was one of the first applications of coal gasification);
 - as the basis for the production of liquid synthetic fuels (e.g. methanol, DME, Fischer-Tropsch);
 - for the production of hydrogen, to be used in industrial processes or as fuel for transportation (in the future);
 - as the basis for the production of many other chemicals (e.g. ammonia, urea);
 - as reducing agent in the production of glass or metals.

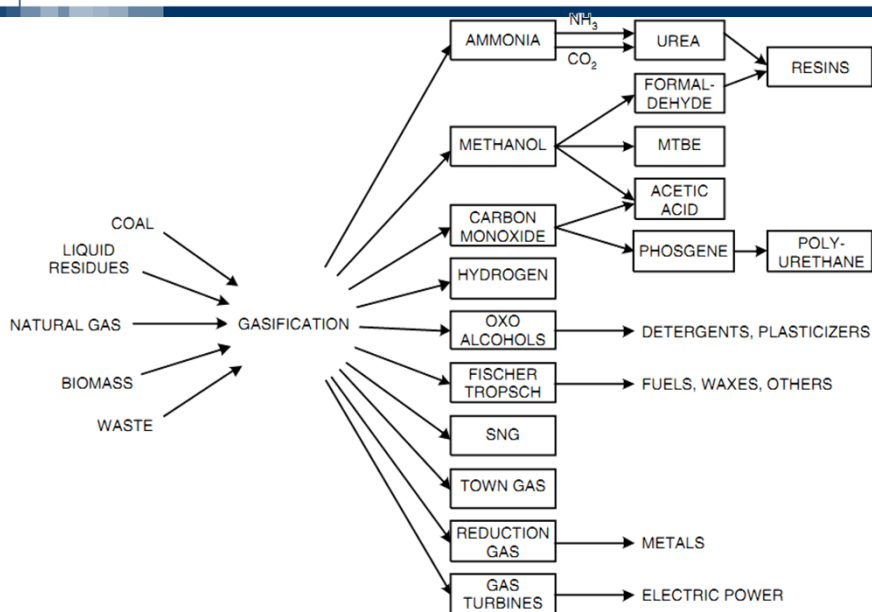
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Potential syngas applications

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Gasification CONS:

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- Syngas is typically toxic, flammable and explosive. Its handling raises several safety concerns.
- Some pollutants potentially contained in the feedstock can originate very corrosive / aggressive / hazardous compounds during gasification, making syngas handling and treatment very challenging.
- Syngas treatment (cooling, purification, etc.) is complex and can become very costly especially at small scales.
- Losses associated with syngas treatment can reduce significantly the potential benefits of gasification in terms of energy efficiency.
- Gasification-based technologies are much more complex than combustion-based technologies and, thus, more capital intensive.
- Their reliability is negatively affected by their complexity (more components, more things that can break).
- Plant control and regulation are very resource demanding.
- Startup, shutdown and load variations of gasification-based plants are very difficult operations.

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Syngas purification in a coal gasification plant

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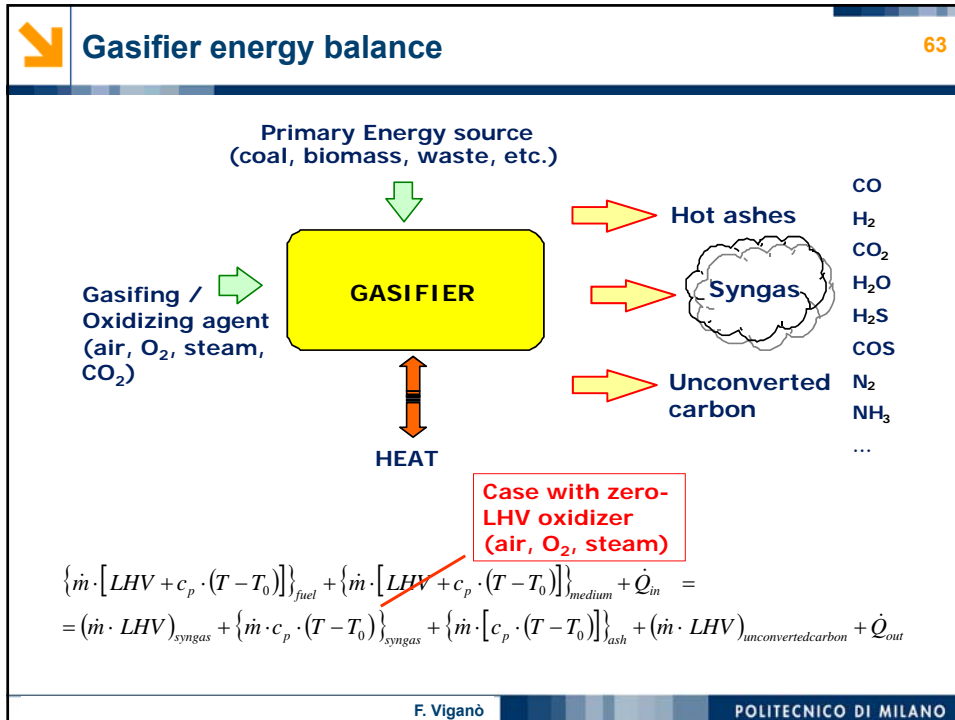


Urea production in Coffeyville, Kansas. IGCC with GE quench gasifier (former Cool Water)



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Performance indicators 64

Hot Gas Efficiency (HGE) accounts for chemical + thermal energy in the syngas

$$HGE = \frac{(\dot{m} \cdot LHV)_{syngas} + \left\{ \dot{m} \cdot c_p \cdot (T - T_0) \right\}_{syngas}}{(\dot{m} \cdot LHV)_{fuel}}$$

Cold Gas Efficiency (CGE) accounts for the amount of energy that remains as chemical energy in the syngas.

$$CGE = \frac{(\dot{m} \cdot LHV)_{syngas}}{(\dot{m} \cdot LHV)_{fuel}}$$

CGE measures the performance of the gasifier in converting the chemical power of the fuel into the chemical power of syngas.

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Performance indicators

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Substituting the expression of the energy balance:

$$CGE = 1 + \frac{c_p \cdot (T - T_0)_{fuel}}{(LHV)_{fuel}} + \frac{\{\dot{m} \cdot c_p \cdot (T - T_0)\}_{medium}}{(\dot{m} \cdot LHV)_{fuel}} + \frac{\{\dot{m} \cdot c_p \cdot (T - T_0)\}_{ash} + \{\dot{m} \cdot [LHV + c_p \cdot (T - T_0)]\}_{syngas}}{(\dot{m} \cdot LHV)_{fuel}} - \frac{(\dot{Q})_{thloss}}{(\dot{m} \cdot LHV)_{fuel}}$$

CGE is favored by:

- High carbon conversion efficiency
- Low heat losses
- Low syngas temperature
- Low inert content (O₂ better than air)
- High medium temperatures
- Low moisture content of biomass
- Low ash content

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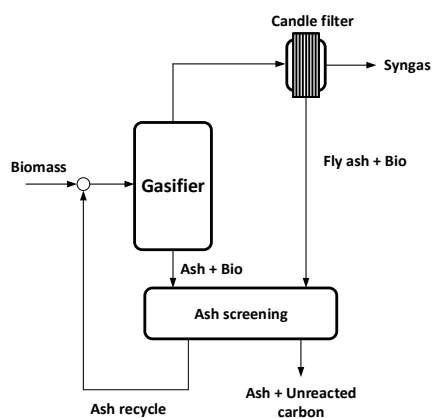


Performance indicators

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Carbon conversion:

$$\varepsilon_c = \frac{\text{Moles of carbon atoms converted into SYNGAS species}}{\text{Moles of carbon at inlet (feedstock)}}$$



A fraction of the inlet carbon remains in the solid state within the solid particles (char). These are entrained by the gas flow and collected in the gas cleaning unit (called fly ASH) or extracted from the gasifier as ASH (bottom ash, or slag).

Many gasifiers, in order to increase the carbon conversion, mill the ash and the fly ashes and recycle them back to the gasifier.

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Main operating parameters

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Main operating parameters:

- Gasification temperature (T_G)
- Gasification pressure (P_G)
- Oxidant purity
- Residence time (t_G)
- O/C Oxygen to Carbon Ratio
- S/C Steam to Carbon Ratio

Determined / chosen on the basis of:

- Type of feedstock (e.g. black coal, lignite, biomass);
- type of reactor (i.e. gasifier);
- type of feeding system;
- type of oxidant;
- type of moderating agent;
- use of syngas.

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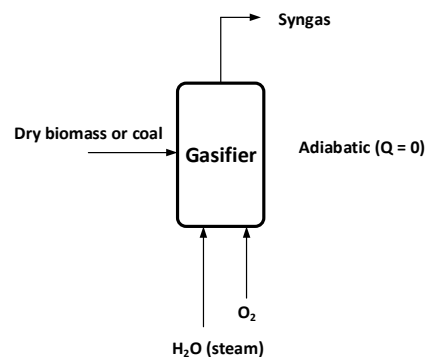
Optimal operating point

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In a gasifier (coal or biomass) it is necessary to determine the optimal operation variables which maximize the CGE:

- O_2 or AIR mass flow rate
- H_2O (steam/water) mass flow rate
- Feedstock moisture content

Considering a general gasification process, the optimal feed moisture content from an “efficiency” point of view is ZERO, as determined by the energy balance. So, leaving this variable aside from the analysis and considering a perfect dry – biomass, we have:



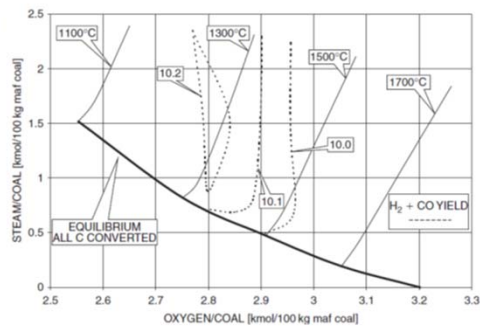
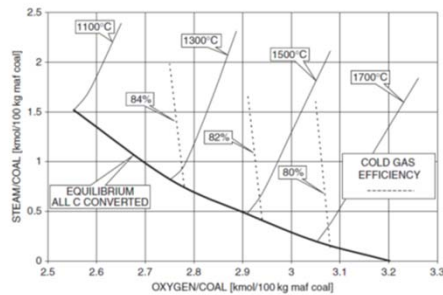
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Optimal operating point

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Optimal operating point

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We can state that:

1. Gasification temperature is set by:
 - Gasifier kinetics
 - Ash melting point
 - TAR conversion into SYNGAS
2. For a desired gasification temperature, the oxygen and steam mass flow rates must be chosen close to the BOUNDARY line of complete carbon conversion so as to maximize CGE. Since wood and other fibrous biomasses contain an already high amount of H atoms and MOISTURE, steam is not strictly necessary (steam mass flow rate = 0). There exists only a minimum amount of O₂ to realize the complete carbon / char conversion. Instead, for coal gasification, some steam or water must be added to reach the optimal operative parameters (max CGE).

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Basic technologies of gasifiers

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Gasifiers for biomass and similar feedstock (coal, residues and waste) can be classified into three main categories:

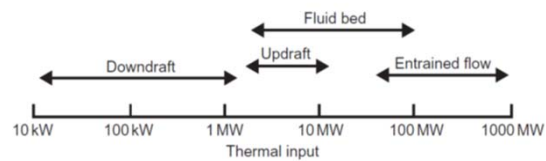
➤ FIXED (or MOVING) BED GASIFIER

- ✓ up-draft
- ✓ down-draft
- ✓ cross-draft

➤ FLUIDIZED BED GASIFIER

- ✓ bubbling
 - atmospheric
 - pressurized
- ✓ circulating

➤ ENTRAINED FLOW GASIFIER



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Basic technologies of gasifiers: fixed bed

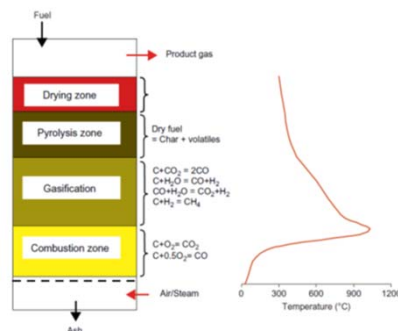
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Biomass particles lie over a grate (either fixed or moved by a mechanism) and the gasification medium is forced across the particle bed.

Fixed bed reactors are subdivided into 3 classes:

- ✓ up-draft: gas flows from the bottom to the top
- ✓ down-draft: gas flows from the top to the bottom
- ✓ cross-draft: gas flows from one to the other side of the gasifier (horizontally).

UPDRAFT



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Basic technologies of gasifiers: fixed bed

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UPDRAFT

The maximum temperature is reached in the combustion zone, at the gas inlet, where O_2 oxidizes biomass particles and heats up the gas.

Thanks to the countercurrent layout, the hot syngas generated in the combustion and gasification zone is used to pyrolyze and dry the fresh biomass particles. As a result, syngas leaves the gasifier at very low temperatures ($\sim 100^\circ\text{C}$) and this maximizes the COLD GAS EFFICIENCY of the gasifier. However, on the other hand, the generated syngas entrains significant amount of TAR generated in the pyrolysis zone.

CGE $\approx 90\%$ (LHV basis)

Tar content in syngas \approx

30 – 150 g/Nm³ (very high)

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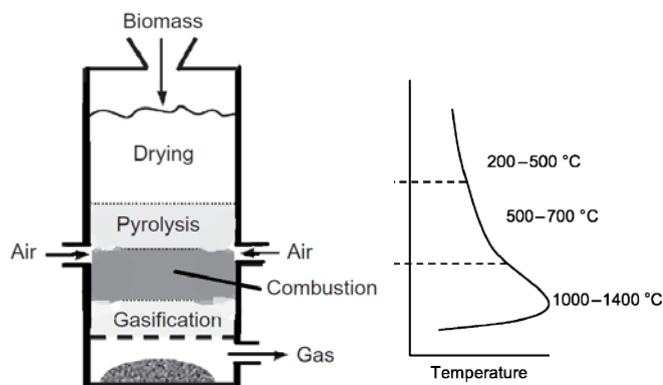


Basic technologies of gasifiers: fixed bed

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DOWNDRAFT

The advantage of downdraft gasifier with respect to updraft arrangements is the lower production of tar ($< 3 \text{ g / Nm}^3$) because the vapors generated in the pyrolysis zone must pass through the combustion zone responsible ($T > 1000^\circ\text{C}$) for the cracking of heavy hydrocarbons



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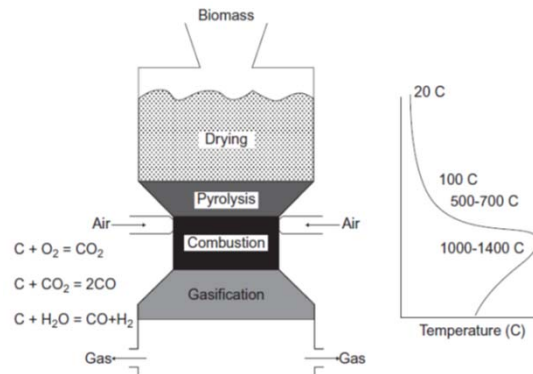
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Basic technologies of gasifiers: fixed bed

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Using appropriate geometries, temperature can be increased:



On the other hand, syngas leaves the reactor at high temperatures compared with UPDRAFT gasifiers. As a result, its CGE is lower ($\approx 85\%$ on LHV basis).

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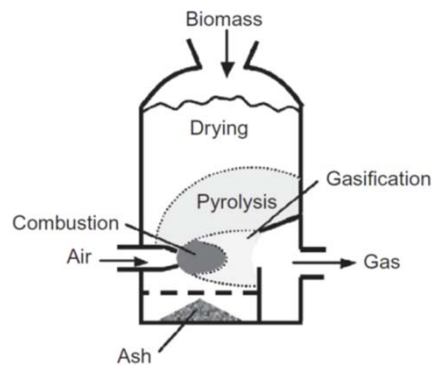


Basic technologies of gasifiers: fixed bed

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CROSSDRAFT

Thanks to very high temperature which is reached in the combustion zone (where all the syngas must pass through), syngas is almost tar free ($< 0,1 \text{ g/Nm}^3$). However, typical CGE values for crossdraft gasifiers are quite low (80%) compared to those of UPDRAFT and DOWNDRAFT.



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Basic technologies of gasifiers: fixed bed

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Advantages of fixed bed gasifiers

This type of gasifiers must be preferred to entrained-flow and fluidized-bed gasifiers for the following features:

1. Capability of accepting feedstocks with high moisture contents (up to 60%) while preserving a good CGE. For instance UPDRAFT gasifiers can use 60% moisture content biomass without the requirement of a DRYER because biomass particles are automatically dried by the generated syngas. On the other hand, and entrained-flow or fluidized-bed gasifier would require a dryer to reduce the biomass moisture content (in order to reach a sufficiently good CGE);
2. Capability of accepting particles with large sizes (up to 5 cm) and diverse size distribution;
3. Easy operation and control.

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Basic technologies of gasifiers: fixed bed

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Limitations of fixed bed gasifiers

In respect to fluidized bed and entrained flow gasifiers:

1. Limited carbon conversion efficiency: a significant fraction of the inlet carbon is not gasified but it leaves the reactor together with the ash due to the limited availability of O_2 in certain zone of the bed. Indeed, due to the fact that the bed is fixed, it may happen that some zones of the reactor bed are not reached by the proper flow rate of O_2 /air (imperfect distribution of O_2 over the bed).
2. Low productivity or low specific thermal power expressed as $[MW/m^3] \frac{\dot{m}_{BIO} \cdot LHV_{BIO}}{V_{REACTOR}}$ that is directly proportional to $\frac{1}{RESIDENCE_TIME}$. A fixed bed reactor requires a longer residence time because of:
 - Its lower average temperature (350 – 600°C)
 - Imperfect distribution of O_2 over the particle bed.
3. High tar content in the syngas

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Basic technologies of gasifiers: fixed bed

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For these reasons, fixed bed reactors are used only for small plants

UPDRAFT	from 1 to 10 MW
DOWNDRAFT	from 10 kW to 1 MW

Typical syngas composition

N ₂	40%
H ₂	15 – 20%
CO	10 – 15%
CO ₂	10 – 15%
CH ₄	3 – 5%

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Basic technologies of gasifiers: fluidized bed

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The basic idea is improving the mixing and temperature uniformity of the bed. A fluidized bed is made of granular solids, called bed material, that are kept in a semi-suspended condition (fluidized state) by the passage of the gasifying medium at appropriate velocities.

The large thermal inertia of the bed makes fluidized bed reactors quite insensitive to fluctuations of fuel composition and moisture content.

Fluidized bed reactors are subdivided into 2 classes:

- ✓ bubbling
 - atmospheric
 - pressurized
- ✓ circulating

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Basic technologies of gasifiers: fluidized bed

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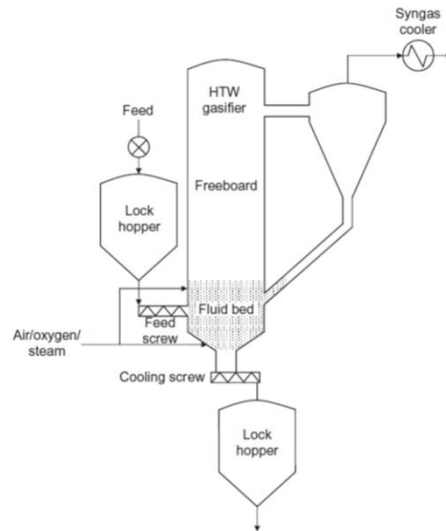
Bubbling fluidized beds

Gas velocity is chosen close to the value which ensures biomass particle equilibrium:

- $F_D = F_W$, that is, $v_{GAS} = 0,5 \div 1$ m/s.

Features:

- Bed of particles (BIOMASS, ASH, SAND)
- Freeboard = empty zone above the bed
- Bubbles of gas cross the bed of solids causing a continuous mixing of particles.
- Smallest particles are entrained and leave the bed of solids, the medium ones fall back on the bed, the largest ones ($d > d^*$) tend to stay in the lower section of the bed.



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Basic technologies of gasifiers: fluidized bed

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- The freeboard is needed to allow entrained particles to come down to the bed and to provide additional residence time for the gas phase reactions (mainly, tar cracking reactions)
- Heat released by char combustion at the inlet of the gas is quickly distributed to the bed thanks to the continuous mixing
- Particles are extracted from the bottom of the bed. These particles may be ash – rich particles (completely gasified) or large fresh biomass particles (not properly milled) which tend to stay at the bottom of the bed. Thus, unreacted particles are extracted and this causes a loss of cold gas efficiency. To improve the CGE it is possible to adopt a screening system (a sieve) to divide the largest particles (which are supposed to be those of fresh biomass) and recycle them back into the reactor bed.

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Basic technologies of gasifiers: fluidized bed

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Bubbling (and circulating) beds are operated at **temperatures** in the range of 800 – 1000°C.

- *Not above* 1000°C in order to avoid ash melting and agglomeration with other bed particles
- *No lower* than 800°C in order to not penalize reaction rates and cause an oversizing of the reactor or an incomplete gasification with an excess of tar production. In addition, lower temperatures are not enough to cause the thermal cracking of tar molecules.

The **tar** content in syngas is in the range of 1 – 3 g/Nm³.

Fluidized bed reactors can accept particles with a relatively wide size distribution because larger particles tend to stay at the bottom of the bed and are not entrained by the gas flow.

Typical values of **CGE** are between 90% and 95%, depending on the medium.

The **fluidization gas velocity** is low, about 0,5 – 1 m/s.

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Basic technologies of gasifiers: fluidized bed

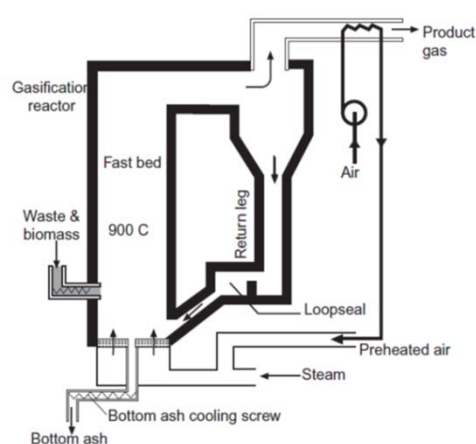
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Circulating fluidized bed gasifiers (CFBG)

The fluidization gas velocity is set to a high value (3,5 – 5,5 m/s) so as to entrain the particles. Particles are entrained by the gas flow and exit the reactor. A cyclone separates solid from syngas, so, solid particles are recycled back to the reactor inlet.

Ash are extracted from the recycle flow and NOT directly from the bed.

Compared to the bubbling fluidized beds, CFBG improves the carbon conversion efficiency.



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Basic technologies of gasifiers: fluidized bed

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Many industrial plants prefer CFBG to BFB because of the following advantages:

1. Higher Carbon Conversion Efficiency thanks to a better selection of the extracted particles;
2. Higher turbulence of the bed which guarantees an improved heat transfer rate between gases and particles and then uniformity of the temperature distribution. These effects translate into a higher C conversion efficiency and tar conversion into CO and H₂.
3. Higher turbulence of the bed leads to a more homogeneous distribution of O₂ and other species in the bed and then an improved kinetics and conversion of biomass into useful species.

The main disadvantages are:

1. Erosion of the reactor walls due to the high gas velocities
2. High electric consumption of the fan required to pressurize the gas medium.

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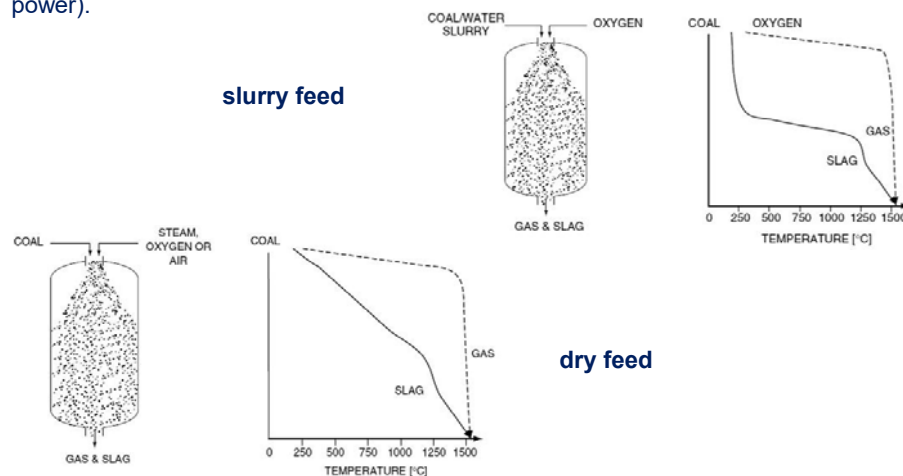
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Basic technologies of gasifiers: entrained flow

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Entrained flow gasifiers are today widely used for COAL gasification. They are industrially proven, reliable and available at large sizes (up to > 100MW of thermal power).



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Basic technologies of gasifiers: entrained flow

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- They are combustors operating in scarcity of oxidant. Feedstock and oxidant are typically arranged in co-current configuration.
- Temperature of syngas is appreciably higher than ash melting point → limited CGE (about 75%), especially with feedstock of low-grade. To reach such high temperatures in fact, the fuel chemical power must be converted into heat via the char combustion reactions and this reduces the syngas chemical power. For this reason, entrained flow gasifiers require:
 - ✓ Low moisture feed (water must be evaporated)
 - ✓ Low ash content fuels (ash must be heated up)

CGE falls in the range of 75 – 85% depending on the gasification medium (air or O₂) and feeding system. Ashes leave the bottom of the reactor as slag (liquid state) thanks to the high enough gasification temperature (1300 – 1500°C) to melt the ash.

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Basic technologies of gasifiers: entrained flow

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- Due to the high operating temperature there is no presence of tar.
- However, high consumption of oxidant (typically almost pure oxygen) is required to reach such high operating temperatures.
- To allow an acceptable carbon conversion with so limited residence times, the feedstock needs to be finely grinded (particle size < 100 μm): this is easy for coal, but practically impossible for raw biomass.
- Residence time of few seconds allows building very compact gasifiers. Most of the gasifiers (especially for coal) so far built are of the entrained flow type. Due to the short residence time, fuel particles must be:
 - ✓ Fine (small size): < 1 mm for reactive biomass (wood)
< 100 μm for coal
 - ✓ Dry (low moisture content), otherwise the residence time is not enough to carry out the drying phase, pyrolysis and gasification. Particles may leave the reactor as “fly ash”, rich of unconverted carbon.

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Basic technologies of gasifiers: entrained flow

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Entrained flow gasifiers are not commonly adopted for biomass because of:

- High moisture content of biomass;
- Biomass particles are not small enough and the size distribution is not well controlled;
- High corrosion level of melted ash from biomass.

A state of the art practice to use biomass in entrained flow gasifiers developed for coal powder is the “torrefaction”. Torrefaction is a biomass pre-treatment which makes the biomass fibrous structure easier to mill into fine particles (100 μm). However, torrefaction consumes part of the biomass LHV to heat it up at the process temperature (300°C).

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Effect of pressure on Gasification Processes

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Pressure influences the equilibrium condition of gasification reactions. More in detail, according to the chemical equilibrium theory, a pressure increase is unfavorable to:

- All the char gasification reactions
- The tar cracking reactions

... but such pressure increase favors:

- The methanation reaction $\text{CO} + 3\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CH}_4$
- The hydrogasification reaction $\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$

As a result of these considerations, a pressure increase leads to:

- A lower C conversion efficiency (-)
- A higher tar content in the generated syngas (-)
- A higher CH_4 content in the syngas:
 - (+) if SNG (Substitute Natural Gas) must be generated from syngas
 - (-) if other chemical products must be generated.

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Pressure selection Criteria

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- Pressurization reduces significantly the volume of the plant equipment (thus costs), since it reduces the specific volume of the gas streams. Pressurized gasifiers have a higher productivity. Moreover, pressurized syngas allows to decrease the size of the downstream equipment (pipes, reactors etc.). Limit: 100 bar
- Pressurization has only a marginal effect on the chemical equilibria of most of the gasification reactions
- For dry feed gasifiers pressurization is much more costly
- The production of pressurized syngas allows directly feeding several devices (e.g. gas turbines, ICEs)
- Pressurizing the syngas requires more energy than pressurizing the gasification medium and the biomass because the syngas stream has a larger volumetric flow than that of reactants

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Pressure selection Criteria

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If a pressurized gasifier is adopted, a feeding system for biomass pressurization is needed. While atmospheric gasifiers can be equipped with simple devices such as rotary screw and rotary valve feeder, pressurized gasifier need a more sophisticated system capable of pressurizing the SOLID STREAM of BIOMASS. The most common options are:

- Lock – hoppers + metering bin + injection screw
- Lock – hoppers + pneumatic transport
- Plug – feeders + injection screw

These systems are more expensive than rotary valve feeders and they may cause many issues such as clogging etc. ...

Feeding systems can operate up to 40 – 60 bar depending on the type.

Gasifiers can be designed for pressures ranging from 1 to 60 bar.

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Gasifier pressure criteria

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The gasifier pressure is chosen on the basis of:

- End-use pressure requirements
- Effect on the size of the gas line and cost
- Limits of the feeding system

If the end – user is:

- | | | |
|--|---|-------------------------|
| a. Internal combustion engine | } | Atmospheric |
| b. Boiler | | |
| c. Gas turbine | } | Pressurized 10 – 40 bar |
| d. Chemical process for fuel synthesis | | |

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Air vs O₂ gasification and steam

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Gasification process can be either air-blown or oxygen blown or steam-blown or can use a mixture of these gases.

Steam blown gasifiers are not common and not commercially available because they must be INDIRECTLY HEATED. In fact, being no O₂ available, oxidization reactions cannot take place. Mainly, endothermic reactions take place:



The overall reaction is endothermic and heat must be provided by Indirectly heating the medium or the gasifier.

- (-) high capital costs (heat exchange surface)
- (-) product gas is rich in hydrocarbons (C₂H₂, C₂H₄ and CH₄) which, in some applications, must be reformed to CO and H₂
- (-) gasification complexity

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Air vs O₂ gasification and steam

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Advantages:

- (+) syngas is richer of H₂ and CH₄ which is an advantage if it is used for H₂ production or CH₄ production
- (+) high CGE

Air blown gasifiers are preferred for power generation at small scale because:

- (+) they do not need an ASU (Air Separation Unit)
- (+) syngas dilution with N₂ is not an issue since syngas is fed into a gas engine, even better, some N₂ is required to lower the stoichiometric flame temperature in the syngas combustor, thus, N₂ content is desired.

Oxygen blown gasifiers are competitive at large scale (> 100 MW) because it increases the CGE. For chemical plants (Biomass to liquids, fuels and chemicals), O₂ gasification is REQUIRED or strongly recommended. N₂ content is strongly not recommended.

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Feeding systems

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The feeding system must prevent unwanted introduction of air. This aspect can be a serious issue, in particular when the gasifier is pressurized. The pressurization of a solid feedstock can be done only by means of a transport fluid. On the basis of the state of the transport fluid, two systems can be identified:

- Slurry feed (for entrained flow reactors): the transport fluid is liquid and it is mixed with the feedstock at atmospheric pressure so to reach a mud-like state, which allow pumping by means of reciprocating pumps.
- Dry feed: the transport fluid is a pressurized (inert) gas that is used to pressurize the feedstock through a series of chambers separated by "valves". These devices are called lock-hoppers.

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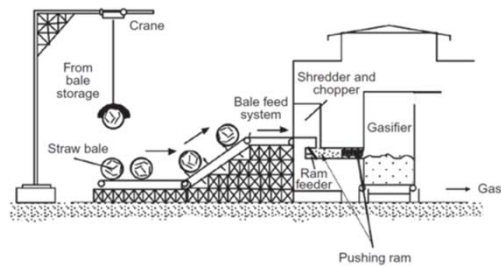
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Feeding systems

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...for baled biomass...



...screw feeder



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Lecture outline

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- Thermochemical (TC) processes
- Pyrolysis
- Gasification
- **Waste gasification vs. waste combustion**
- Reference Books

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- **Motivations shared with gasification of fossil fuels:**
 - generation of high-quality energy carrier
 - adoption of internal combustion engines
 - syngas clean-up ahead of combustion
 - production of highly-valued chemicals
 - production of liquid fuels / hydrogen
- **Additional motivations:**
 - reducing conditions limit generation of dioxins/furans (although emissions depend on processes downstream)
 - production of inert solid residues
 - gas-phase combustion easier to control and operate
- **Problems:**
 - feedstock size --> mechanical pre-treatment
 - sensitivity to feedstock properties --> reliability, operability
 - (very) low heating value of feedstock
 - small scale --> oxygen-blown gasification very costly

potential advantage / benefit of gasification vs. combustion		related drawbacks / issues that hinder the benefit of gasification
1	combustible gas generated by gasification (syngas) is easier to handle, meter and control than MSW	a) syngas is highly toxic and explosive --> major security concerns and sophisticated control equipment; b) feedstock is oxidized/converted in two steps (gasification + syngas combustion/conversion) --> complex and costly plants, difficult O & M, low reliability
2	reducing conditions in the gasifier (i) improve quality of solid residues, particularly metals; (ii) reduce generation of dioxins, furans and NO _x	actual production of pollutants depends on how syngas is processed downstream of the gasifier; if syngas is eventually oxidized, dioxins, furans and NO _x may still be an issue
3	syngas can be used, after proper treatment, in highly efficient internally-fired cycles (gas turbines and combined cycles, Otto engines)	a) required syngas treatment is costly and causes significant energy losses b) due to the losses of gasification and syngas clean-up, overall energy conversion efficiency is typically lower than that of combustion plants; c) at the small scale typical of waste treatment plants, efficiency of internally-fired systems is low (especially if gas turbine-based)

Waste gasification vs. waste combustion		101
potential advantage / benefit of gasification vs. combustion		related drawbacks / issues that hinder the benefit of gasification
4	syngas can be used, after proper treatment, to generate high-quality fuels (diesel fuel, gasoline or hydrogen) or chemicals	a) required syngas treatment very demanding and costly b) at the small scale typical of waste treatment plants, fuel/chemicals synthesis is extremely expensive
5	gasification at high pressure enhances the opportunities to increase energy conversion efficiency and reduce costs	pressurized waste gasification poses formidable challenges and has not been attempted by any technology developer

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A comparative evaluation

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Technology:	Conventional WtE with grate combustor	Fluidized bed (Ebara) + syngas combustion	Grate gasifier (Energos) + syngas combustion
Distinctive aspects	-	vitrified solid residues	NO _x control
Thermal treatment	Direct combustion	Two-step oxidation	Two-step oxidation
Oxidant	Air	Air	Air
Gasifier	-	Fluidized bed, Adiabatic	Grate, Adiabatic
Combustion conditions	heterogeneous, solid-gas	heterogeneous, solid-gas	homogeneous, gas-phase
Combustor	Cooled by boiler tube banks	Cooled by stand-alone circuit	Adiabatic
Flame temperature	below ash melting	above ash melting	below ash melting
Boiler	Integrated with combustor	Heat Recovery Steam Generator (HRSG)	Heat Recovery Steam Generator (HRSG)
Power cycle	steam Rankine cycle	steam Rankine cycle	steam Rankine cycle
Cycle parameters	variable with plant size	p_{ev} 30 bar T_{sh} 325°C	variable with plant size
Syngas cleanup	-	Not desirable	Not applied but potentially applicable

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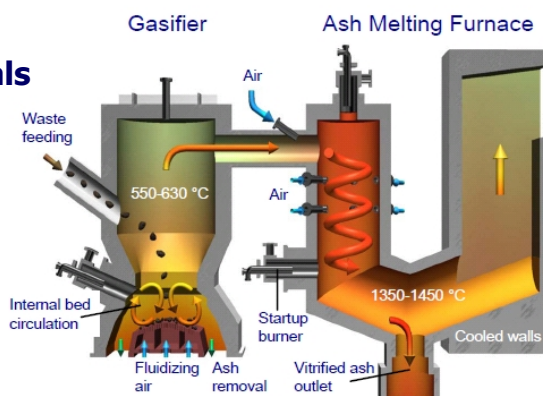
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Fluidized bed: Ebara technology

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- 1) Fluidized bed gasification at $\sim 600^{\circ}\text{C}$
- 2) Adiabatic combustion of syngas (+solids) at $\sim 1400^{\circ}\text{C}$
- 3) Heat Recovery Steam Generator (HRSG)
- 4) Flue gas treatment downstream of HRSG
- 5) Heavy ashes and metals discharged from gasifier
- 6) Vitrified slag discharged from combustor
- 7) Medium-small scale: 10-100.000 tonn/anno



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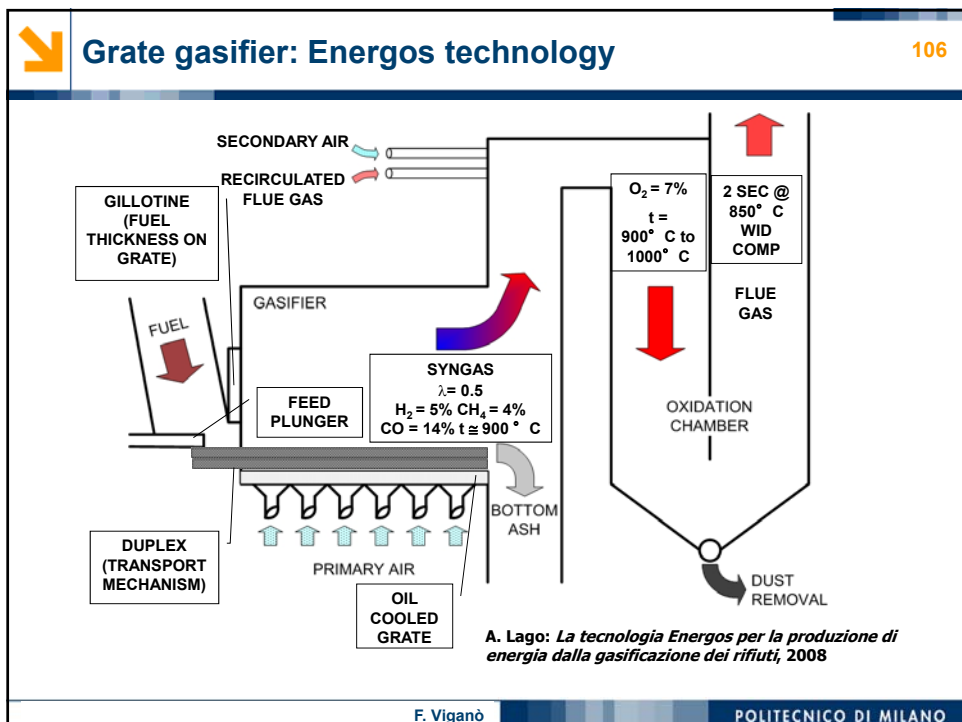
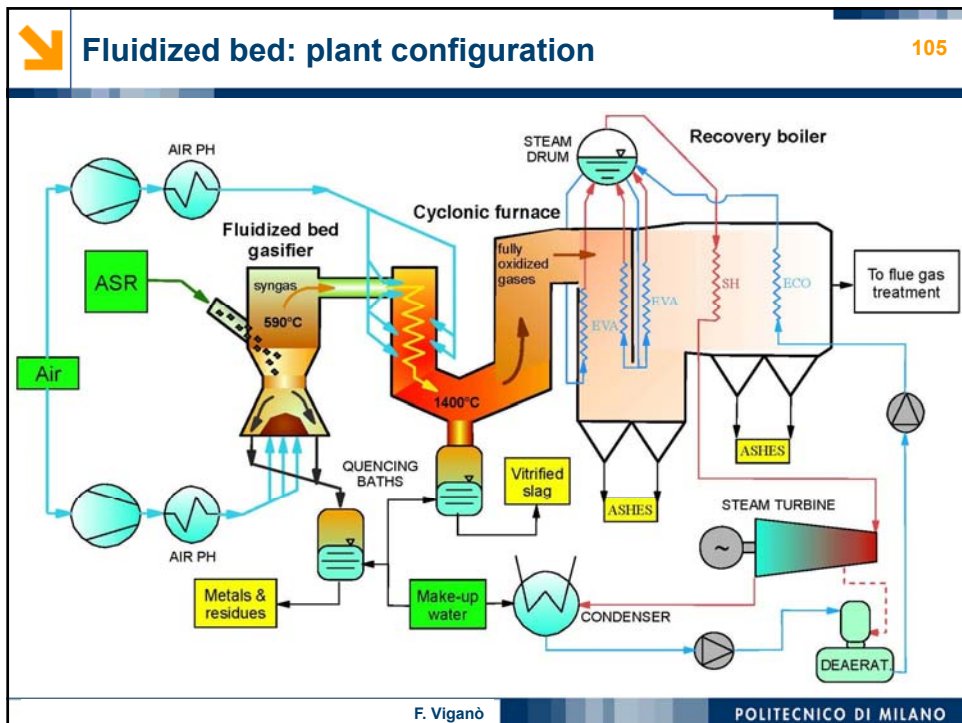
Ebara plants

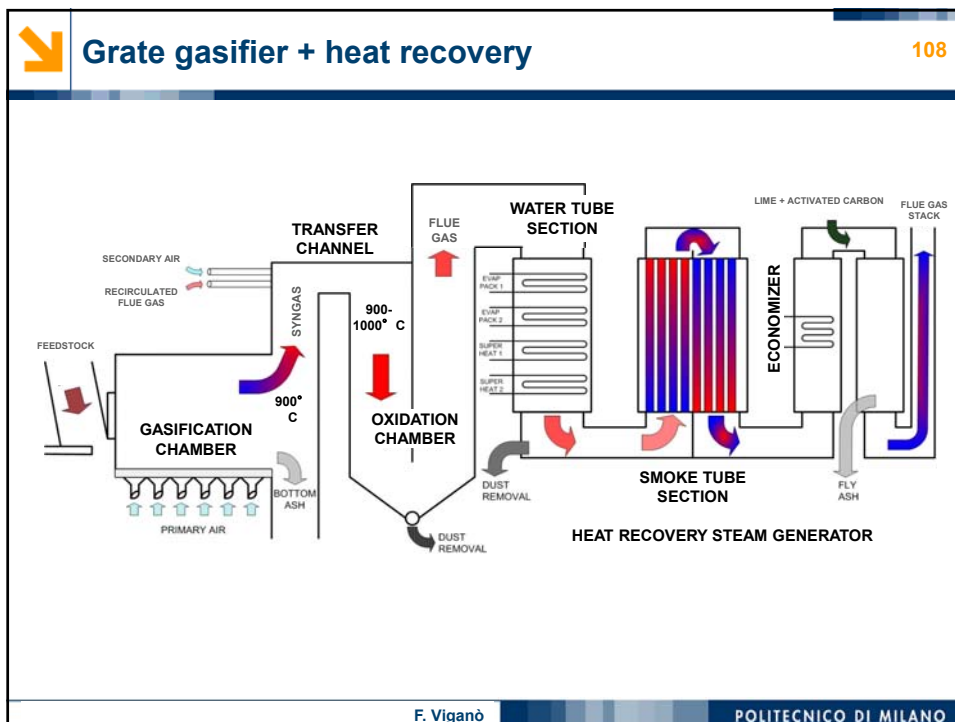
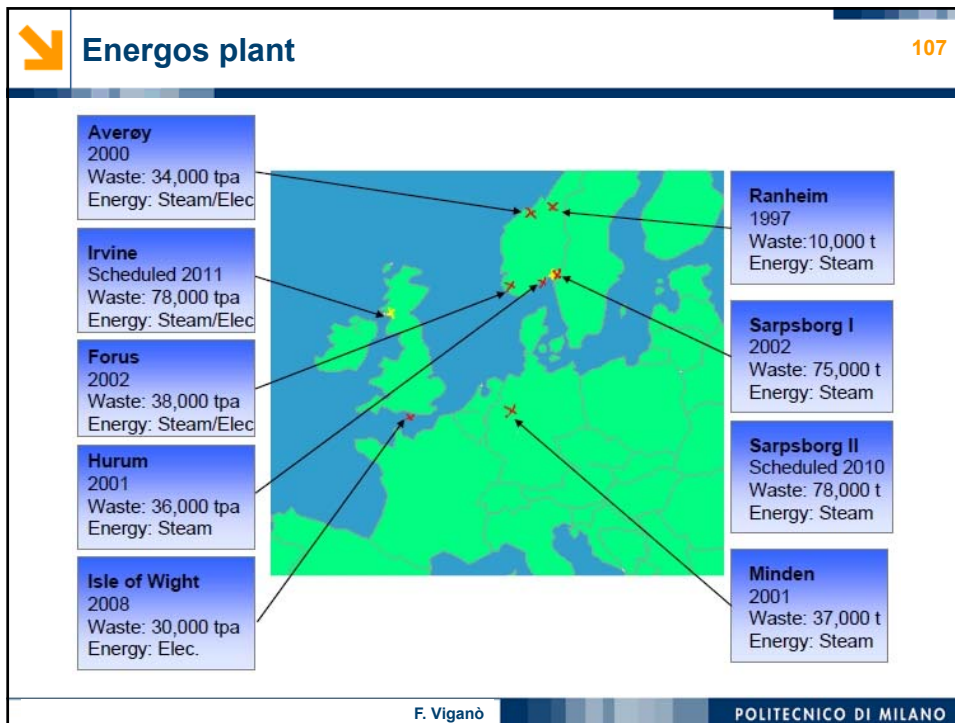
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Plant	Commissioning Date	Type of Waste	Treatment capacity		Thermal Capacity [MW]
			Tonn/day	LHV [MJ/kg]	
Aomori, JP	Feb. 2000	ASR, Sewage Sludge	2 x 225	14,3	2 x 40
Joetsu City, JP	Mar. 2000	Dry Sludge, Waste Plastic	15,7	12,3	2,2
Kurobe, JP	Dec. 2000	ASR, Waste Plastic	63	10,2	7,4
Sakata Area, JP	Mar. 2002	MSW	2 x 98	10,9	2 x 12,3
Kawaguchi, JP	Nov. 2002	MSW	3 x 140	13,0	3 x 21
Ube City, JP	Nov. 2002	MSW	3 x 66	12,5	3 x 9,5
Chuno Union, JP	Mar. 2003	MSW	3 x 56	11,3	3 x 7,3
Minami-Shinshu, JP	Mar. 2003	MSW	2 x 46,5	8,4	2 x 4,5
Nagareyama City, JP	Feb. 2004	MSW	3 x 69	11,7	3 x 9,3
Tokyo Rinkay Corp., JP	Aug. 2006	Industrial Waste	2 x 275	13,0	2 x 41,4
Hino City, JP	Apr. 2007	MSW	3 x 60	7,5	3 x 5,2

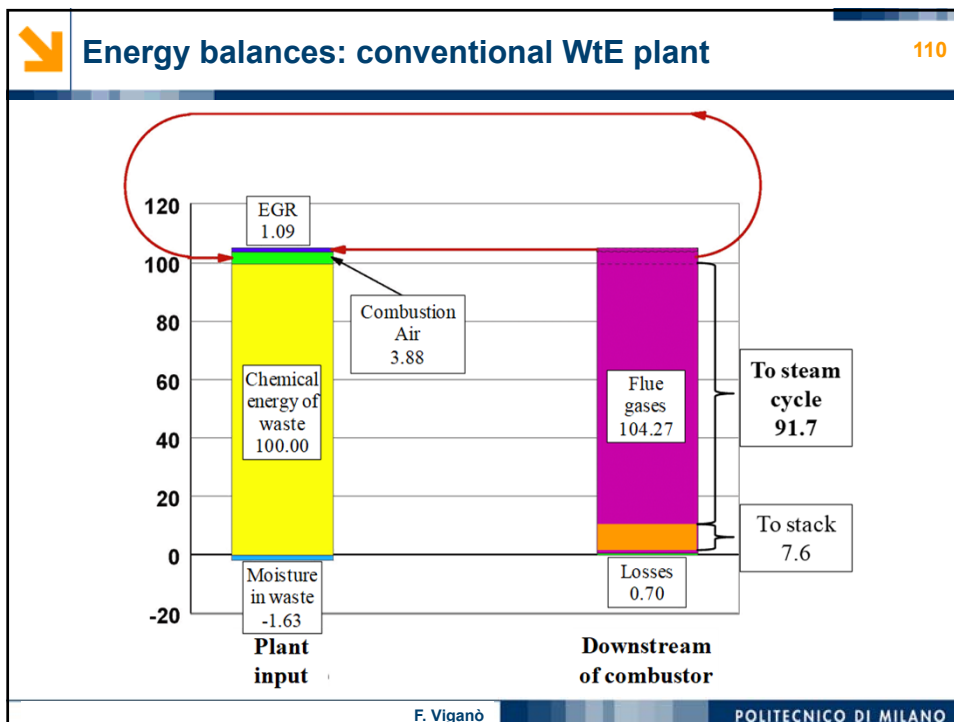
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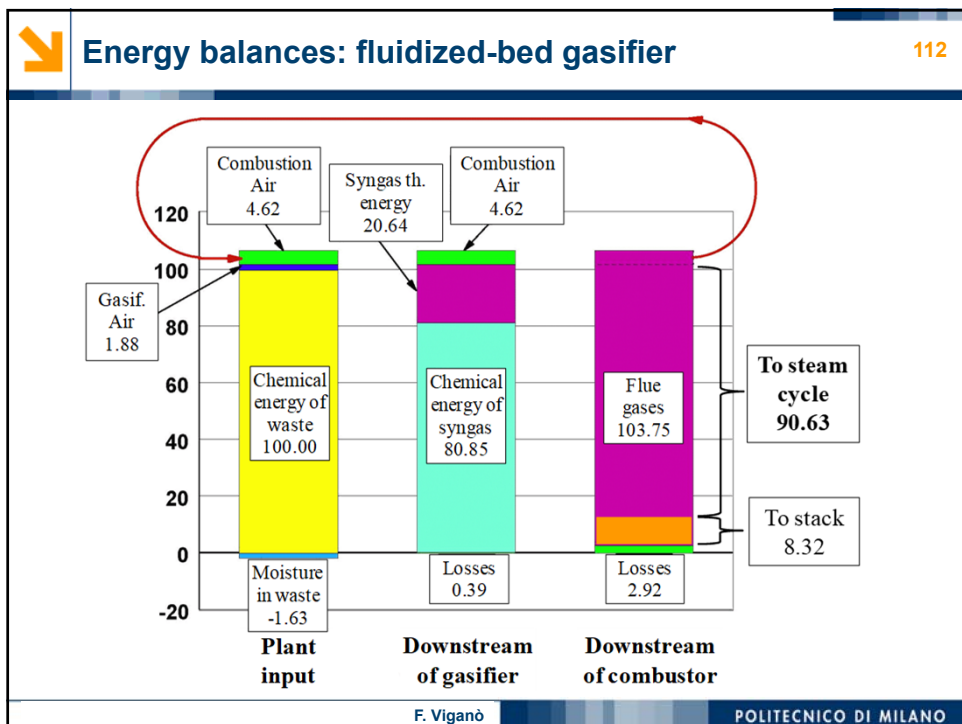
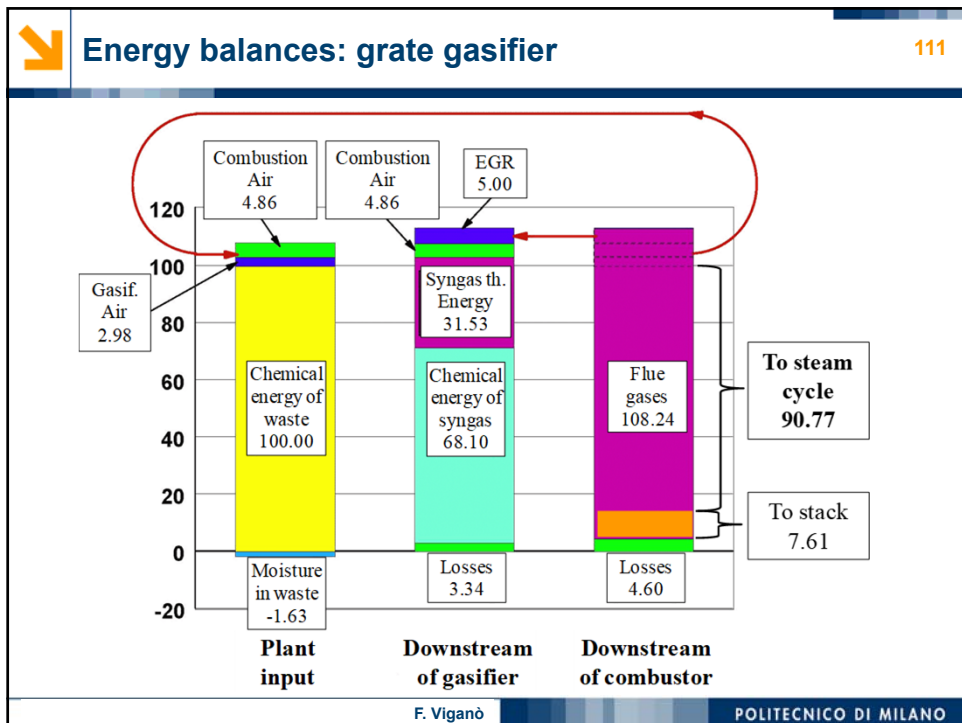
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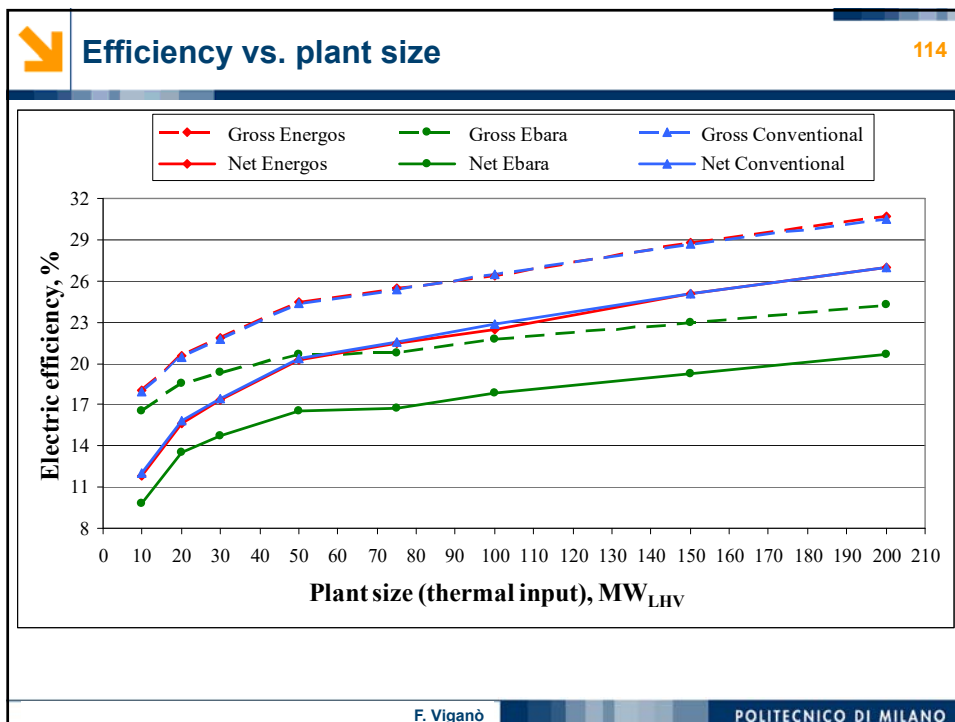
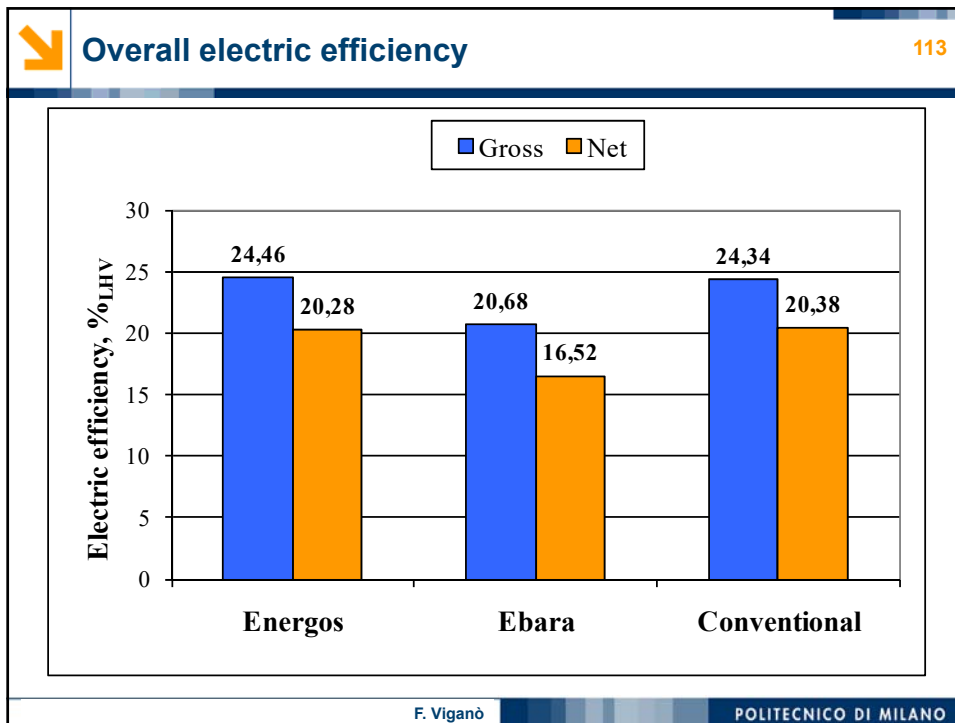













Assumptions		109
Reference plant	Treatment capacity, t/y	135.000
	Design LHV, MJ/kg	10,34
	Design yearly operating hours, h/y	7.800
	Nominal thermal input, MW _{LHV}	50
	Energy production	only electricity
Variations with scale		
		Gross electric power, MW _E
		2,5 5 10 20 50 75
Boiler	Evaporation pressure, bar	30 35 40 45 65 70
	Superheat temperature, °C	350 380 400 420 440 450
	Flue gas temp. at economizer exit, °C	180 180 180 180 180 180
Steam cycle	Final heat recovery from flue gas	No No Yes Yes Yes Yes
	LP regenerative condensate preheater	No No Yes Yes Yes Yes
	Condensing pressure, bar	0,12 0,10 0,09 0,08 0,07 0,06
	Feedwater temperature at boiler inlet, °C	120 120 140 140 140 140
Other	Stack temperature, °C	~180 ~180 135 135 135 135
	Primary / secondary air preheating, °C	120 120 120 120 120 120
	O ₂ content in flue gas at boiler exit, % _{vd}	7,0 7,0 6,5 6,0 6,0 5,5
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Environmental impact				115
	Energos	Ebara	Conventional	
NOx	Homogeneous combustion, high EGR 	High combustion temperature 	Heterogeneous combustion, moderate EGR 	
Dioxins / Furans	Short cooling time in HRSG (??) 	High combustion temperature 	Intermediate combustion temperature 	
Bottom ash	may need treatment, reduced species 	Vitrified, recyclable 	may need treatment, oxidized species 	
In all cases, heavy flue gas treatment is mandatory. Emissions and environmental impact depend on features of flue gas treatment				
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Conclusions - 1		116
<ul style="list-style-type: none"> •Much more than for the gasification of solid fuels, the prospects of waste gasification are subject to a number of technical/economic uncertainties •Additional motivations with respect to the gasification of fossil fuels: <ul style="list-style-type: none"> – easier combustion / emission control – more favorable characteristics of solid residues •However, there are additional issues: <ul style="list-style-type: none"> – sensitivity to feedstock characteristics – small scale – complexity/cost of syngas clean-up – low conversion efficiencies 		
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- Technologies offered by Energos ed Ebara consist of two-step oxidation --> performances are very similar to the ones of conventional combustion plants
- Similarly to grate combustion plants, energy performance
 - is determined by the parameters of the steam cycle
 - crucially depends on plant size
- Emissions are mainly determined by the characteristics of the flue gas treatment system
- Specific advantages of the two technologies analyzed are
 - relatively good NO_x control (Energos grate gasification)
 - production of solid residues as inert, vitrified slag (Ebara fluidized bed gasification)




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 **Lecture outline** 119

- *Thermochemical (TC) processes*
- *Pyrolysis*
- *Gasification*
- *Waste gasification vs. waste combustion*
- *Reference Books*

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 **Reference Books** 120

- 1) **GASIFICATION**, C. Higman and M.J. Burgt, second edition.
- 2) **HANDBOOK BIOMASS GASIFICATION**, second edition.
- 3) **BIOMASS GASIFICATION AND PYROLYSIS**, Prabir Basu.
- 4) **BIOMASS AS A SUSTAINABLE ENERGY SOURCE FOR THE FUTURE, FUNDAMENTALS OF CONVERSION PROCESSES**, W. de Jond and R. van Ommen, Wiley edition.

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