# Thermochemical valorisation of lignocellulosic biomass

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# Agenda

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**Introduction**
→ General context, foreseen trends, key figures, ...

**Raw materials**
→ Sources and characterization

**Thermochemical conversion mechanisms**
→ From pyrolysis to hydrothermal liquefaction

**Technologies**
→ The processes to lead the transformation

**Pespectives**
→ Outlook

# Introduction

# General context - History

Primary energy consumption considerably increased over the passed 45 years:

- 6.10 GTOE in 1973
- 14.0 GTOE in 2017[1]

Mainly driven by fossil fuel use

Which released massive amounts of carbon dioxide

Leading to global warming and climate change

[1] Key world energy statistics. Technical report, International Energy Agency, 2019.

# General context - Outlook

Most agencies around the world foresee and increase in primary energy consumption

Worsening of climate change[2]

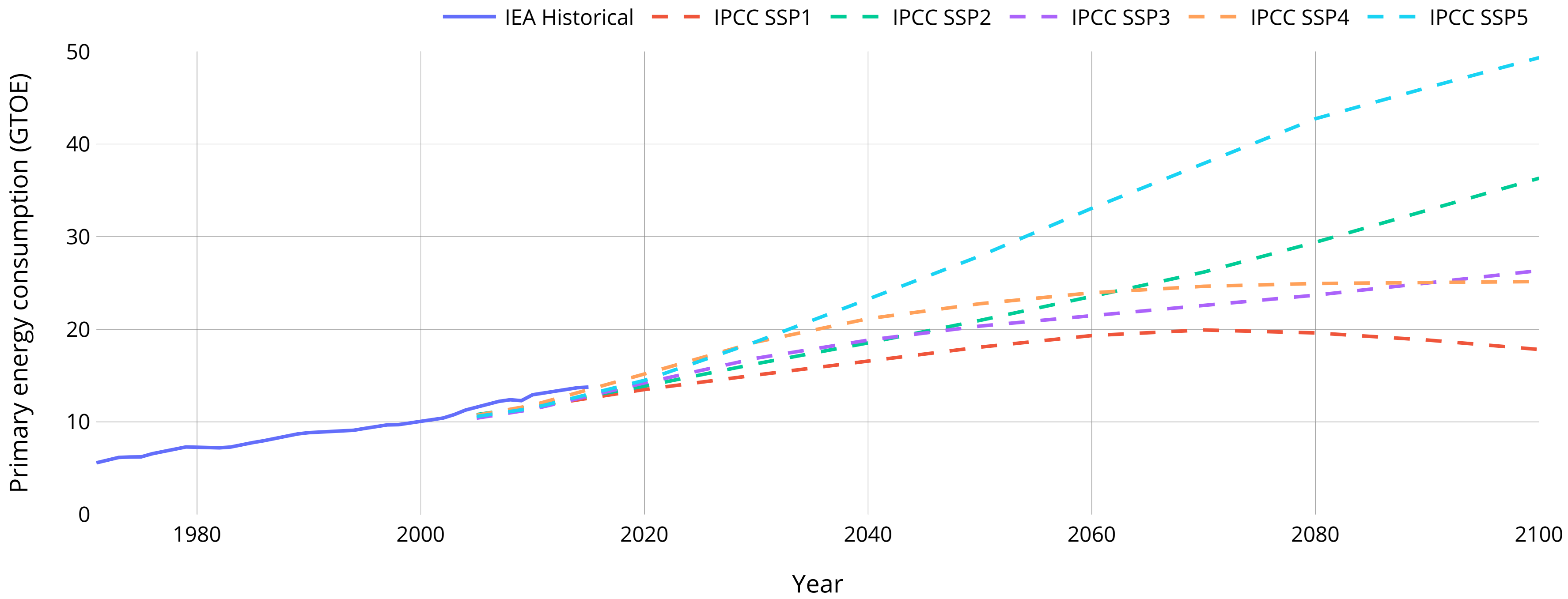


Fig 1 - Historical data and IPCC projections[3]

[2] Climate change 2014 - Synthesis report. International Panel on Climate Change, 2014, Next one in 2022

[3] Global Energy Outlook, Resources for the future data compilation, 2020.

# General context - Mitigation

To mitigate the foreseen negative effects, we should:

- Limit energy consumption
- Trap atmospheric carbon dioxide
- Rely on sustainable energy sources

Lignocellulosic biomass can contribute to these three aspects

Fig 2 - Insulation


Fig 3 - Sequestration


Fig 4 - Biofuel

# This presentation outline

In this context, this presentation will mainly cover the energetic valorisation of lignocellulosic biomass:

- Its place in the global energy context, stocks and regulations
- Conversion mechanisms
- Technologies to lead these transformation

Punctually, we will talk about bio-sourced materials/molecules

Concluded by the perspectives for way of valorisation

# A renewable raw material

Biomass is the first renewable energy (13 % of primary energy consumption).

Mainly used in developing countries for thermal applications[4]

The production of electricity from biomass from biomass is limited to OECD countries

Fig 5 - Cooking purpose

Fig 6 - Heating purpose

[4] WBA Global Bioenergy Statistics 2018

# In more details

In developing countries:

- Biomass accounts for 22 % of the energy mix
- Mainly for cooking and heating
- Combustion stoves have a very poor efficiency (between 5 and 15 %)
  → High potential for improvement (reach 60 to 90%)

In developed countries:

- Biomass represents 3 % of the energy mix
- Mainly for power/heat production

# Stocks

Forests represent 30 % of the land area

- Mainly in Russia, China, Brazil, Canada and USA

As far as energy crops are concerned, arable land is almost all used (12 % of the land area)

- No expansion possible in Asia and North Africa
- 90 % of the growth potential is in Latin America and Sub-Saharan Africa)

# Regulations

The regulation of the biomass market worldwide is described as:

- Opaque
- Not uniform

The regulation on waste is strict (Europe and North America)

The regulation matters a lot

The regulation of biofuels (incentives in favor of bioethanol) led to competition with food-producing culture (among other things) and the 2007-2008 crisis

# Raw materials

# The raw materials

Very diverse origins


Fig 7 - Forests

Fig 8 - Forestry wastes

Fig 9 - Agriculture waste

Fig 10 - Energy crops

Fig 11 - Deconstruction

Fig 12 - Municipal solid wastes

# The raw materials

Because of its origin, biomass has a very variable composition

- For wood, it depends on the species and the conditions of growth
- For waste, it is worse ...

There are three ways to characterize the biomass:

- Its composition in macro molecule
- The composition of its products after pyrolysis (proximate analysis)
- Its atomic composition (ultimate analysis)

# Cellulose / Hemicelluloses / Lignin

Biomass is a structure made of natural polymers[5]

- Cellulose (20 to 50 %)
- Hemicelluloses (20 to 35 %)
  → polymers of sugars
- Lignin (20 to 35 %)
  → polymers of phenols

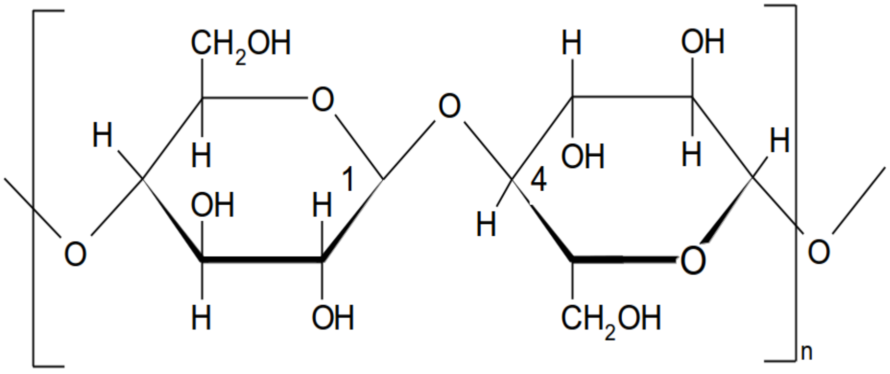


Fig 14 - Cellulose

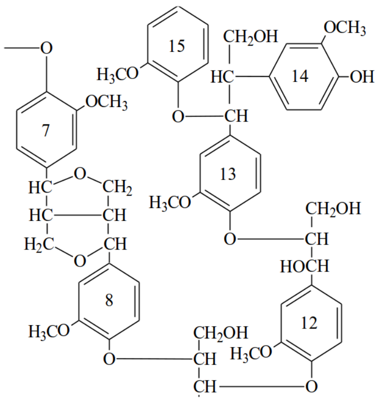


Fig 13 - Lignin

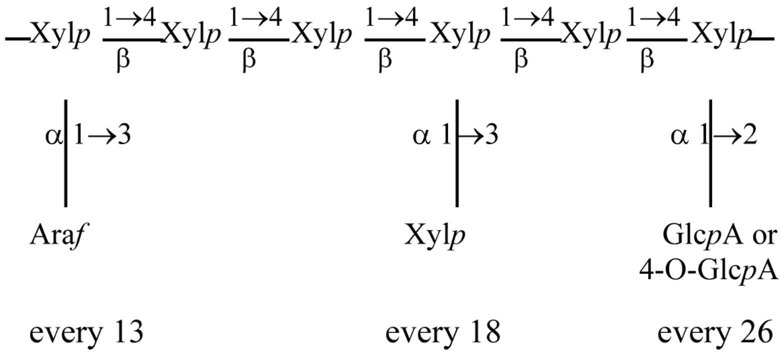


Fig 15 - Hemicellulose

[5] Valorisation énergétique de biomasse par voie thermochimique - Aspects théoriques - S. Salvador

# Proximate analysis

The water content of the biomass is determined (for wood, it goes from 9 to 50 %wwb)

Then the biomass is pyrolyzed (under standard conditions) to determine the volatile matter (light gases + tars) and the solid (char)

Finally, the char is oxidized to determine the amount of ash

Tab 1 - Various lignocellulosic biomass proximate analysis

# Ultimate analysis

The composition in C, H, N and S (plus ash) is determined by oxidation under $O_2$

O is determined by pyrolysis, in the presence of a catalyst to crack the tars and obtain only CO

Tab 2 - Various lignocellulosic biomass ultimate analysis[6]

[6]Thermal Data for Natural and Synthetic Fuels", S. Gaur and T. Reed, Marcel Dekker, 1998.

# Conversion mechanisms

# Conversion pathways

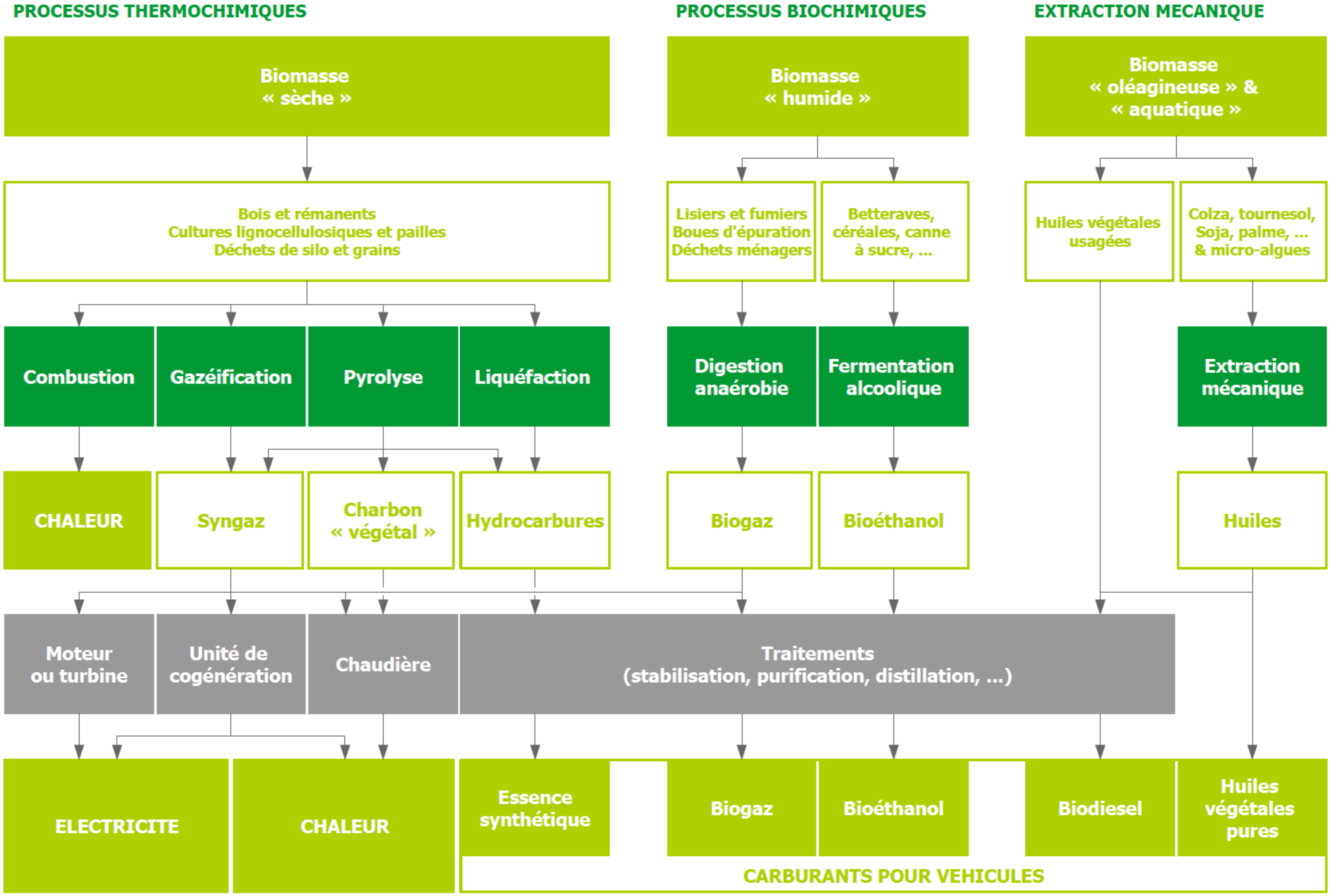


Fig 16 - Lignocellulosic biomass conversion pathways[7]

[7] Solen-Energy.be

# Pyrolysis - Role

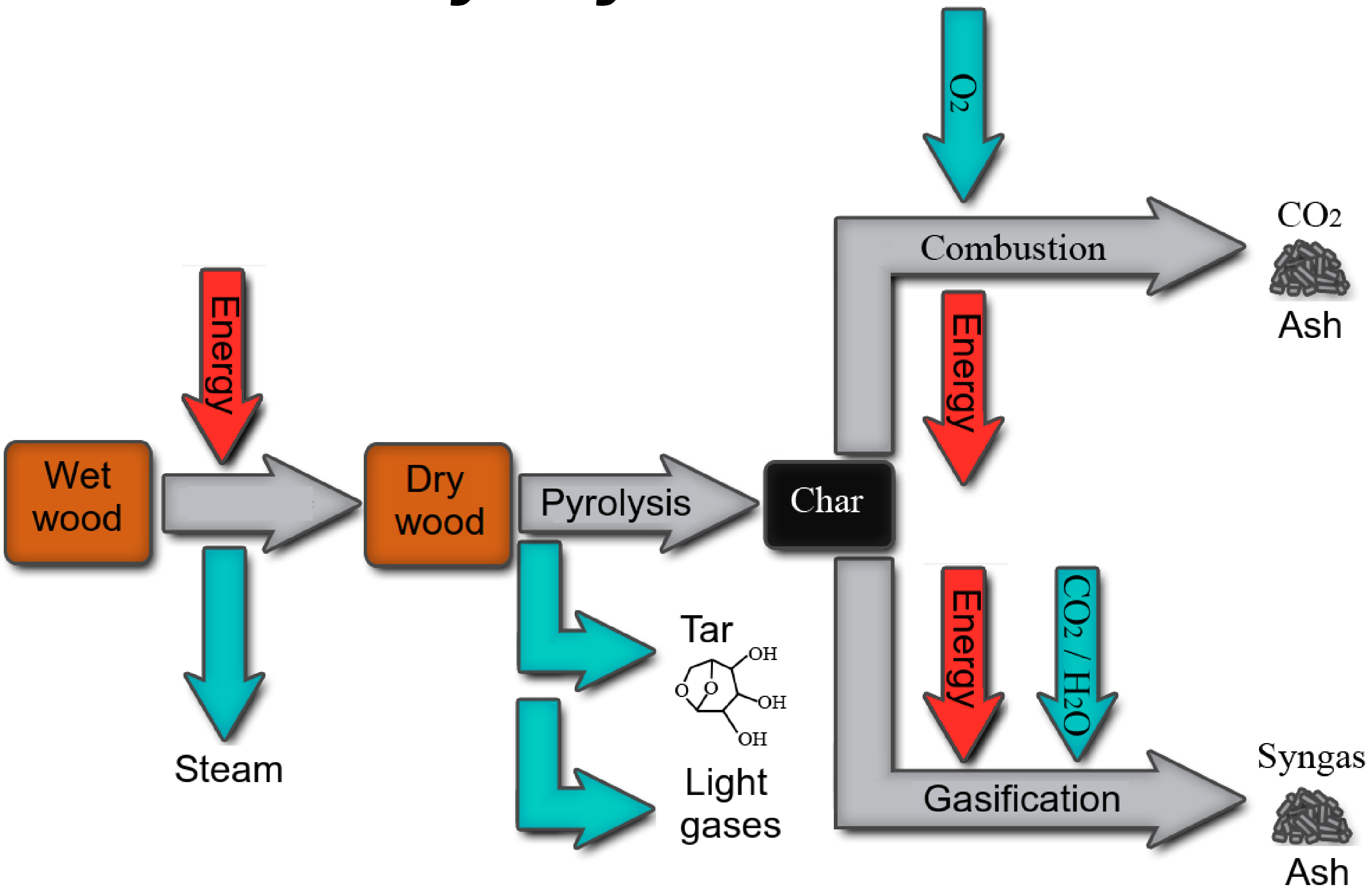


Fig 17 - Pyrolysis and its key role as intermediate reaction

# Pyrolysis - Products

The distribution of the products depends on the conditions of the pyrolysis

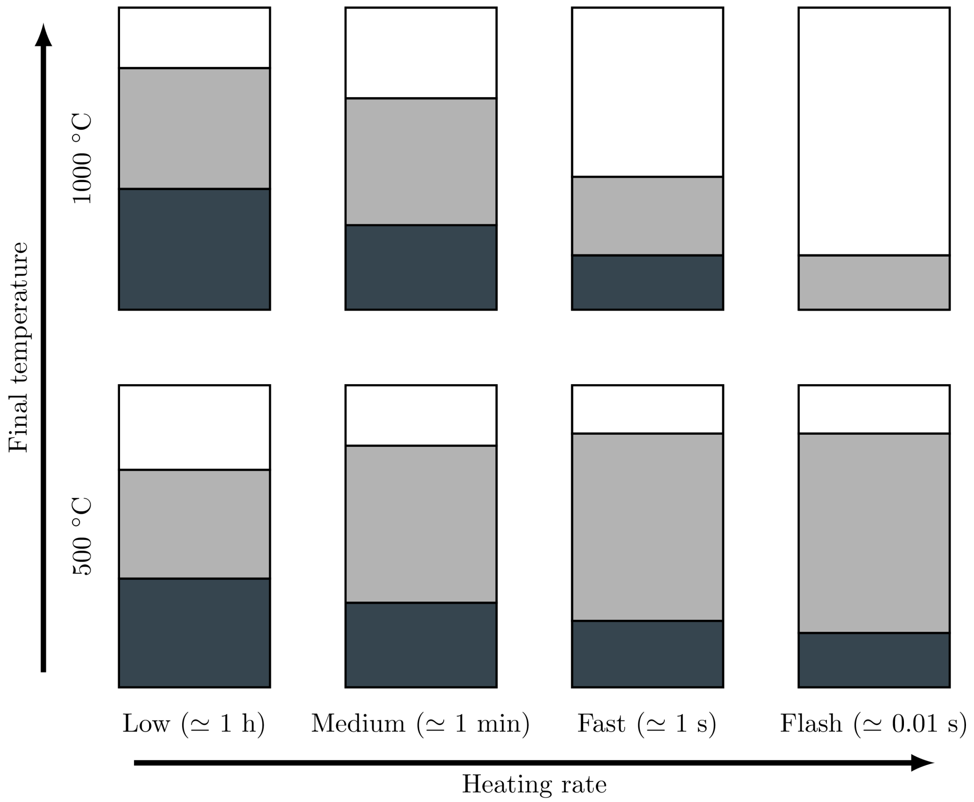


Fig 18 - Pyrolysis and products distribution[8]

[8] Bois énergie. Techniques de l'ingénieur. X. Deglise, A. Donnot

# Hydrothermal conversion

Water at high pressure (> 50 bar) and high temperature (> 200 °C) attacks the structure of the biomass

The oils produced are different from those obtained by pyrolysis

Like pyrolysis, a range of operating conditions (pressure / temperature) give a range of products

Fig 19 - Lab-scale batch autoclaves

# Hydrothermal conversion

Hydrothermal gasification → mainly $H_2$, $CO_2$ and $CH_4$

Hydrothermal liquefaction → mainly oil

Hydrothermal carbonisation → mainly char

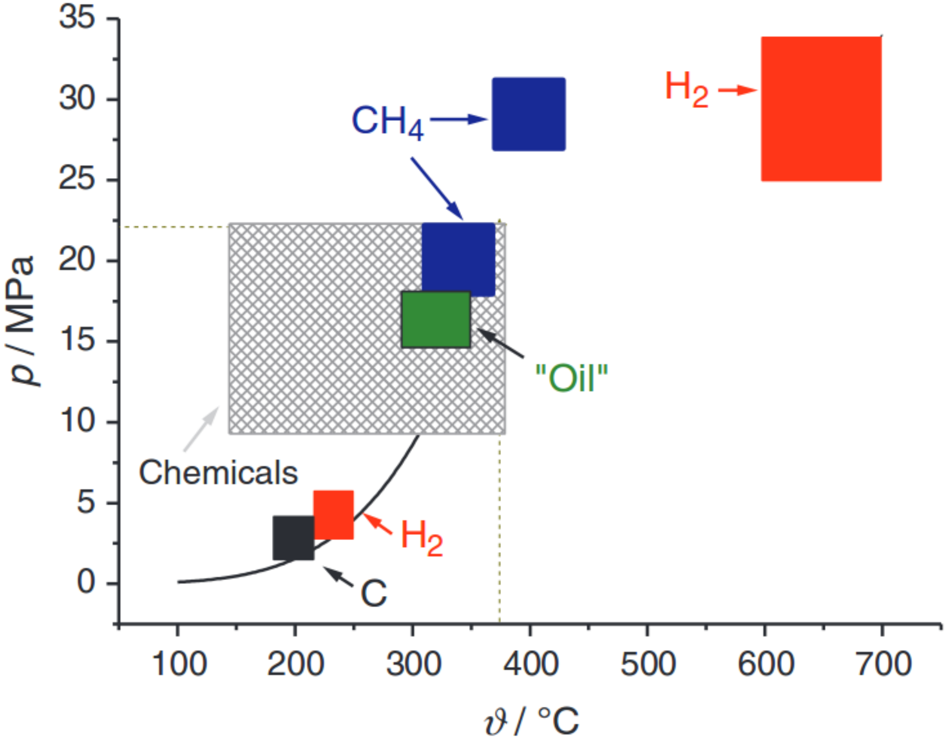


Fig 20 - Hydrothermal conversion products distribution[9]

[9] Kruse, A. (2009). Hydrothermal biomass gasification. The Journal of Supercritical Fluids, 47(3), 391-399.

# The char

The solid product of those reactions is:

- Called *char*
- A porous matrix made of carbon (95%) and ash (5%)
- Coming from the degradation of lignin

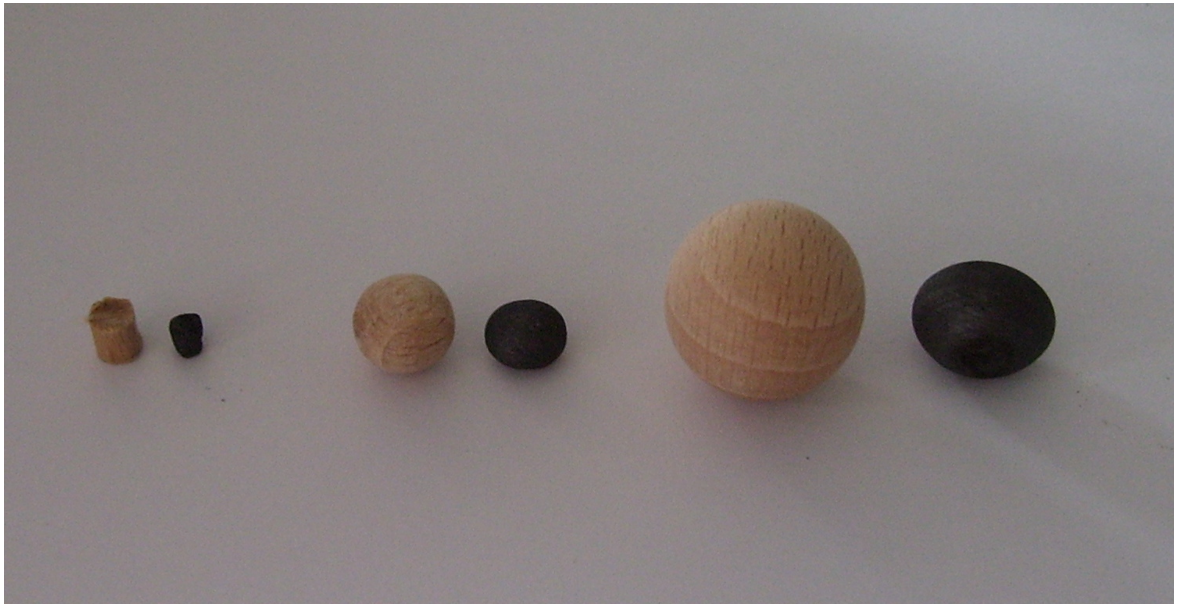

Fig 21 - Fresh samples and their charred counterparts

# The char

Char is a very good catalyst:

- Very porous (high specific surface)
- Support of mineral salts (wood ashes)
- Use for the abatement of gaseous pollutants
- It can also be used as a fertilizer

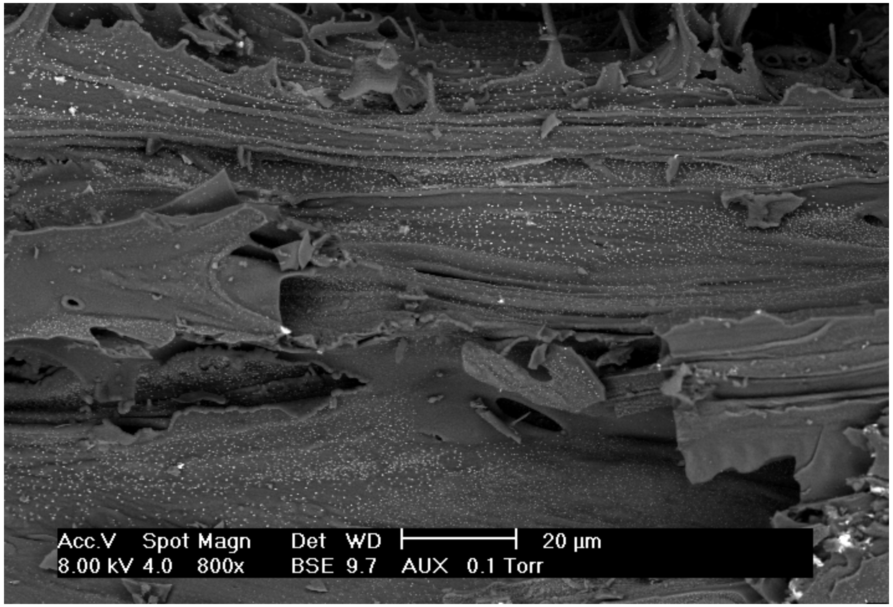

Fig 22 - SEM view of char

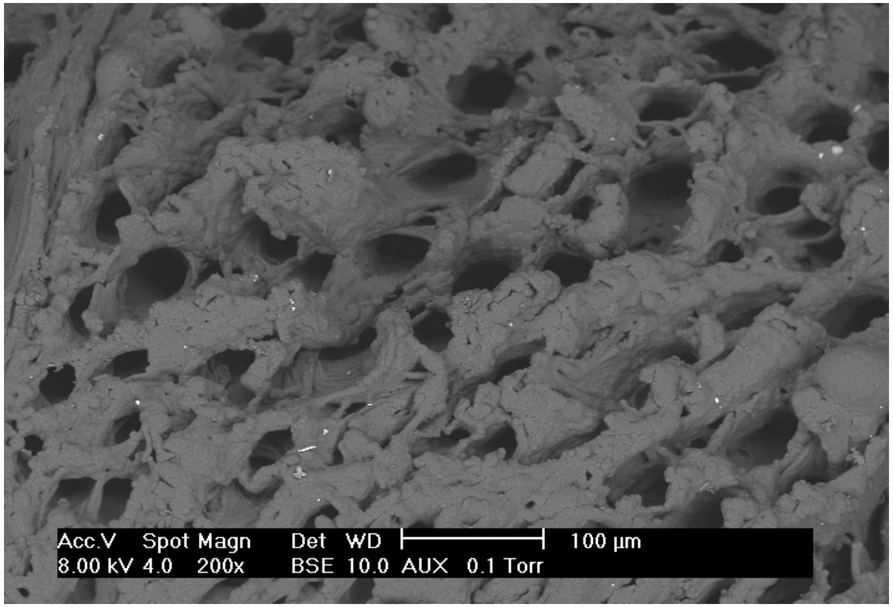

Fig 23 - Another SEM view of char

# Tar / Oils

The liquid products of those reactions are:

- Called *tar* or *oil*
- Composed of more than 300 organic molecules
- Gaseous at pyrolysis temperature, liquid at room temperature
- Classified according to two scales:
  → Molecular weight: light, medium and heavy
  → Degree of cracking: primary, secondary and tertiary

Fig 24 - Different tar fractions

# Light gases

The gaseous products of those reactions are:

- Called *light gases*
- Molecules ranging from $H_2$ to $C_3H_8$
  $\rightarrow$ mainly $H_2$, CO, $CO_2$ and $CH_4$
- Gaseous at room temperature

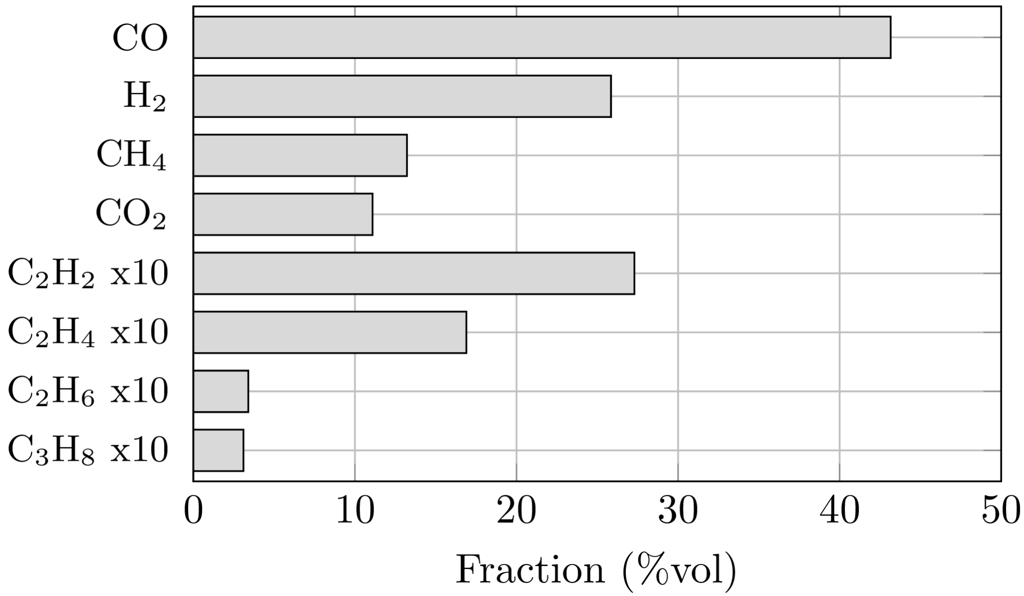


Fig 25 - Example of light gases distribution

# Conversion technologies

# The processes and their products

Depending on the conditions, pyrolysis and hydrothermal conversion produce different compounds

It is thus possible to direct the transformation of biomass towards:

- A desired product (gas, liquid and solid)
- The composition of the desired product (richness in $H_2$, type of oil, ...)

There are therefore different thermochemical conversion processes depending on the desired goal

Two processes can produce the same product, but certainly not at the same price

# The pretreaments

It is most often necessary to pre-treat the biomass before processing it

The purpose of the pretreatment is to improve the characteristics (homogeneity, flowability, size distribution, ...) of the raw material

Drying:

- Energy intensive
- Water modifies the conditions of pyrolysis as well as its products (different tars)
- Lightens the raw material (transport)

Torrefaction:

- Improves grindability and flowability
- Reduces hygroscopicity
- Protects against microorganisms

# The pretreaments

Grinding:

- Homogenizes the raw material (waste)
- Improves flowability
- Gives the desired size distribution (transfers, flow, ...)

Pelletizing:

- Standardizes the product

Fig 26 - Picture of pellets

# Pure biomass combustion

The biomass is pretreated (drying, grinding) before being burned

The goal is to produce heat that can be used to:

- To make electricity (not very profitable alone)
- To make mechanical power/heat

The most interesting process is to produce power and some electricity with an ORC (150 kWe, at $55/MWh)

The cost of a new installation is high

Levelised cost of electricity: about 100 $/MWh[10]

Averaged end-consumer price in the EU: 21 €/MWh[11]

[10] IEA - Projected Costs of Generating Electricity 2020
11EuroStat 2020 - Electricity price statistics

# Pure biomass combustion

Staged combustion boiler:

- 1, 2 and 3 - staged injections
- 4 - end of combustion
- 5 - evacuation

Problem of clogging of the exchanger tubes by ashes

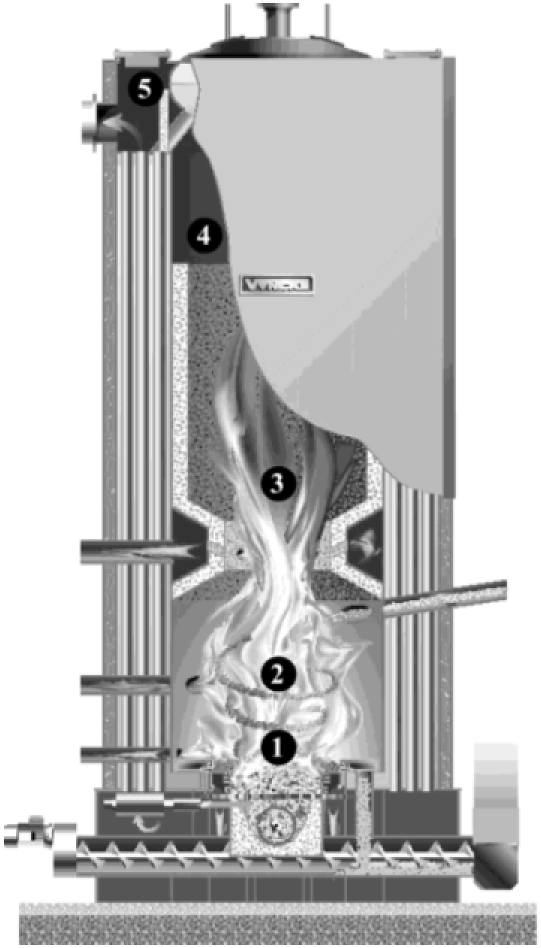


Fig 27 - Classical modern burner[12]

[12] Combustion and Co-combustion of Biomass: Fundamentals, Technologies, and Primary Measures for Emission Reduction, T. Nussbaumer, 2003

# Co-firing

An alternative is co-firing (coal/biomass mix, natural gas/biomass)

The advantages are numerous:

- Up to 20% biomass
- Existing plants are flexible (different types of coal and gas are available)
- Low capital investment

The process can produce electricity incorporating a fraction of biomass at competitive costs for large capacities (150 MWe, at $59/MWh)

# Carbonisation

Produce charcoal:

- Fuel
- Catalyst
- Fertilizer

The process is a slow pyrolysis at low temperature

The yield is quite good

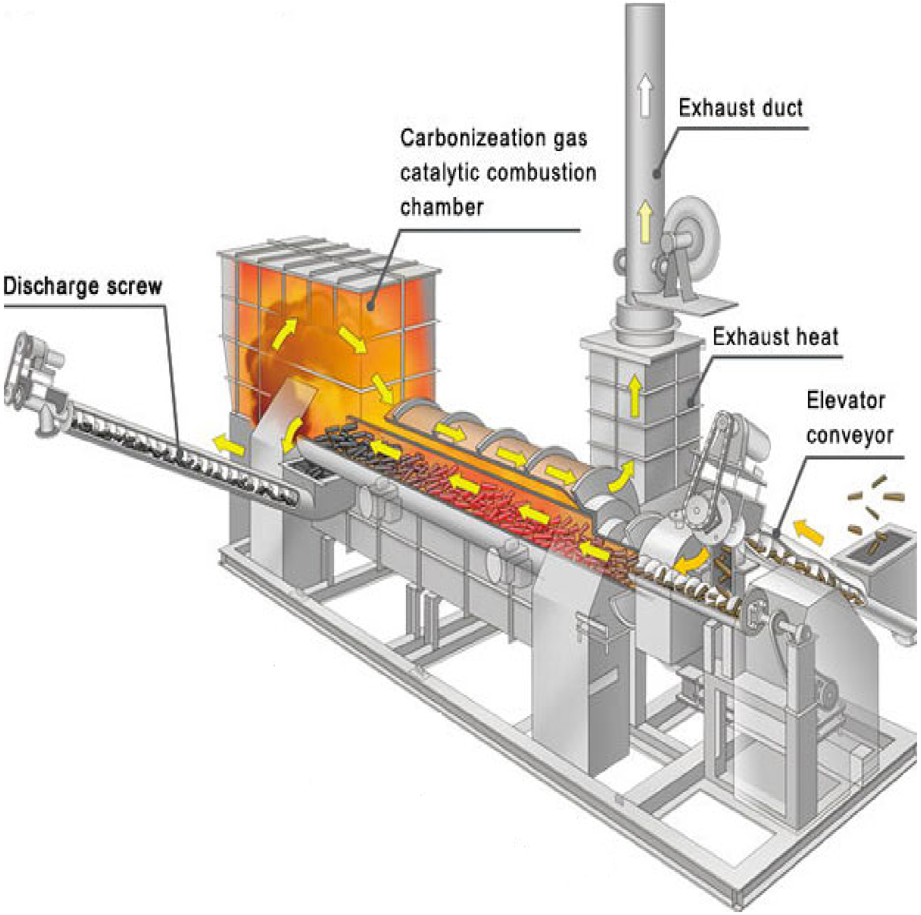


Fig 28 - Carbonisation reactor

# Liquefaction

There are three thermochemical routes to produce liquid fuels from lignocellulosic biomass:

- Oil production by fast pyrolysis followed by upgrading
- Oil production by hyrothermal liquefaction followed by an upgrade
- Syngas production by gasification followed by Fischer-Tropsh synthesis

# Liquefaction - Flash pyrolysis

Requires high heating rates:

- Finely ground biomass
- Reactor with very good gas/solid contact (fluidized beds, vortex reactor, ...)

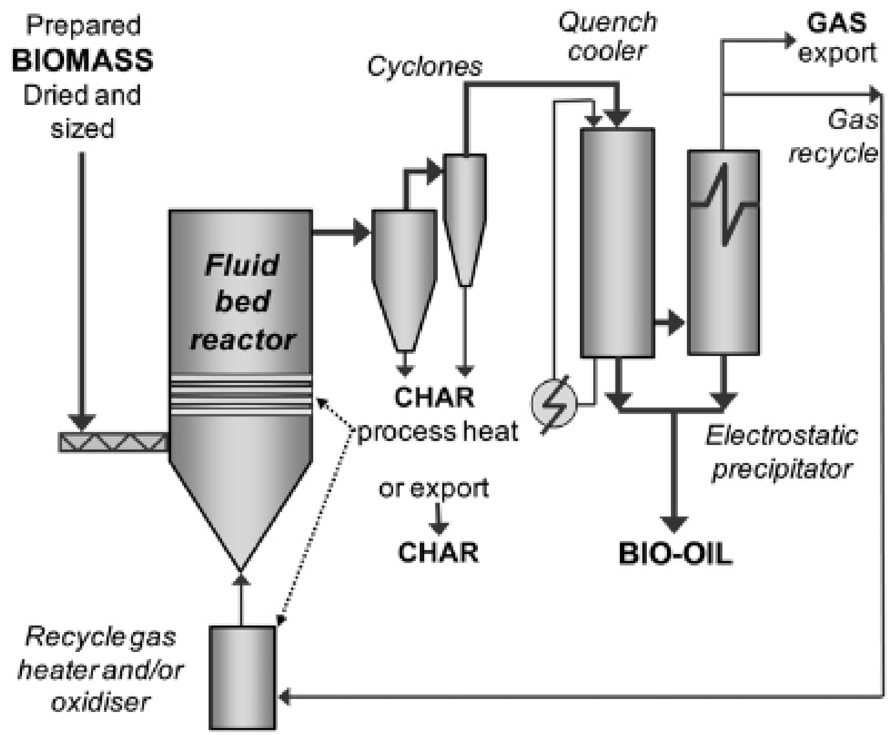


Fig 29 - Fluidized bed flash pyrolysis process[13]

[13] Combustion and Co-combustion of Biomass: Fundamentals, Technologies, and Primary Measures for Emission Reduction, T. Nussbaumer, 2003

# Liquefaction - HTL

Very interesting for algal biomass:

- Does not require drying of the biomass

This technology can also be used for lignocellulosic biomass

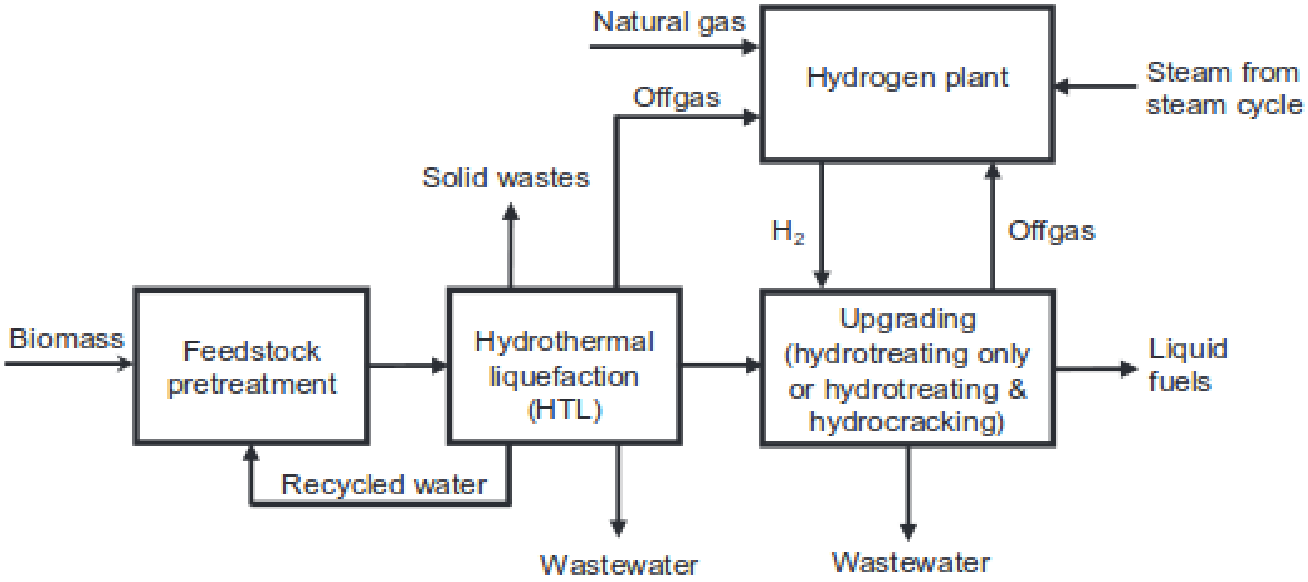


Fig 30 - Hydrothermal liquefaction workflow[14]

[14] Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading. Y. Zhu et al., 2014

# Liquefaction - Gasif. & Fischer-Tropsh

The successive steps:

- Pretreatment of biomass (grinding, drying, torrefaction)
- Pyro-gasification (fluidized bed, ...)
- Separation of the products (solids and gas)
- Gas purification
- $H_2$/CO ratio adjustment
- Synthesis of fuels

# Liquefaction - Gasif. & Fischer-Tropsh

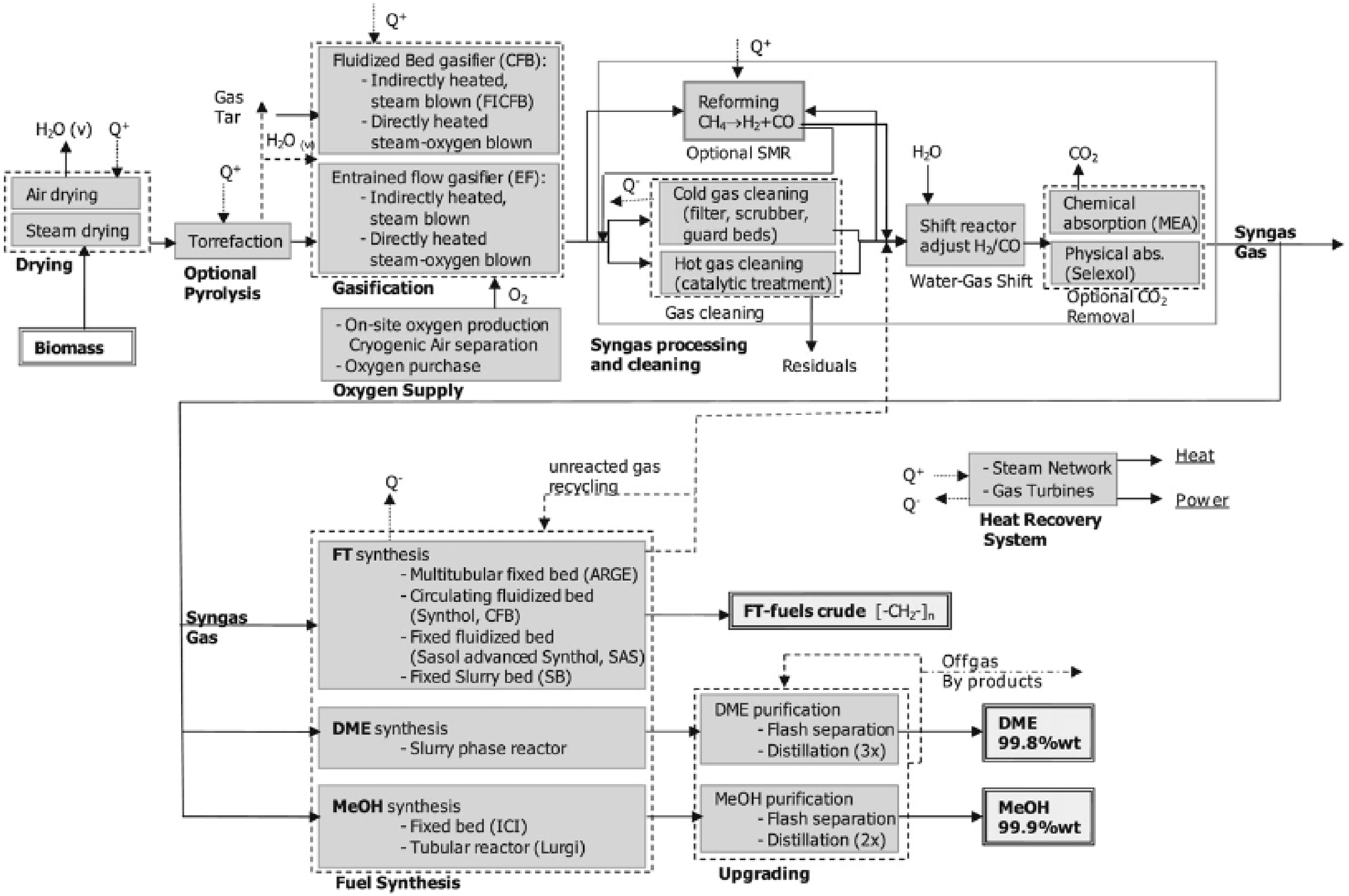


Fig 31 - Gasification & Fischer-Tropsh workflow [15]

[15] Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis. L. Tock, et al, 2010

# Liquefaction - Final product price

In the end, the price of a liter of fuel depends strongly on the process:

- Flash pyrolysis followed by an upgrade: 0.56 - 0.98 $/l
- Hydrothermal conversion followed by an upgrade: 1.29 $/l
- Gasification followed by synthesis: 1.05 - 1.64 $/l (one study reports 0.60/l)

Gas purification step penalizes gasification

Organic carbon to carbon fuel yield penalizes hydrothermal conversion

# Gasification

It allows to produce molecules of interest:

- $H_2$ needed for other applications (synthesis of liquid fuels, ...)
- Methanol, ethanol, ammonia

The produced gases can feed a gas turbine and produce mechanical power

Residual char is very porous, it is a very good catalyst

# Reactor technologies

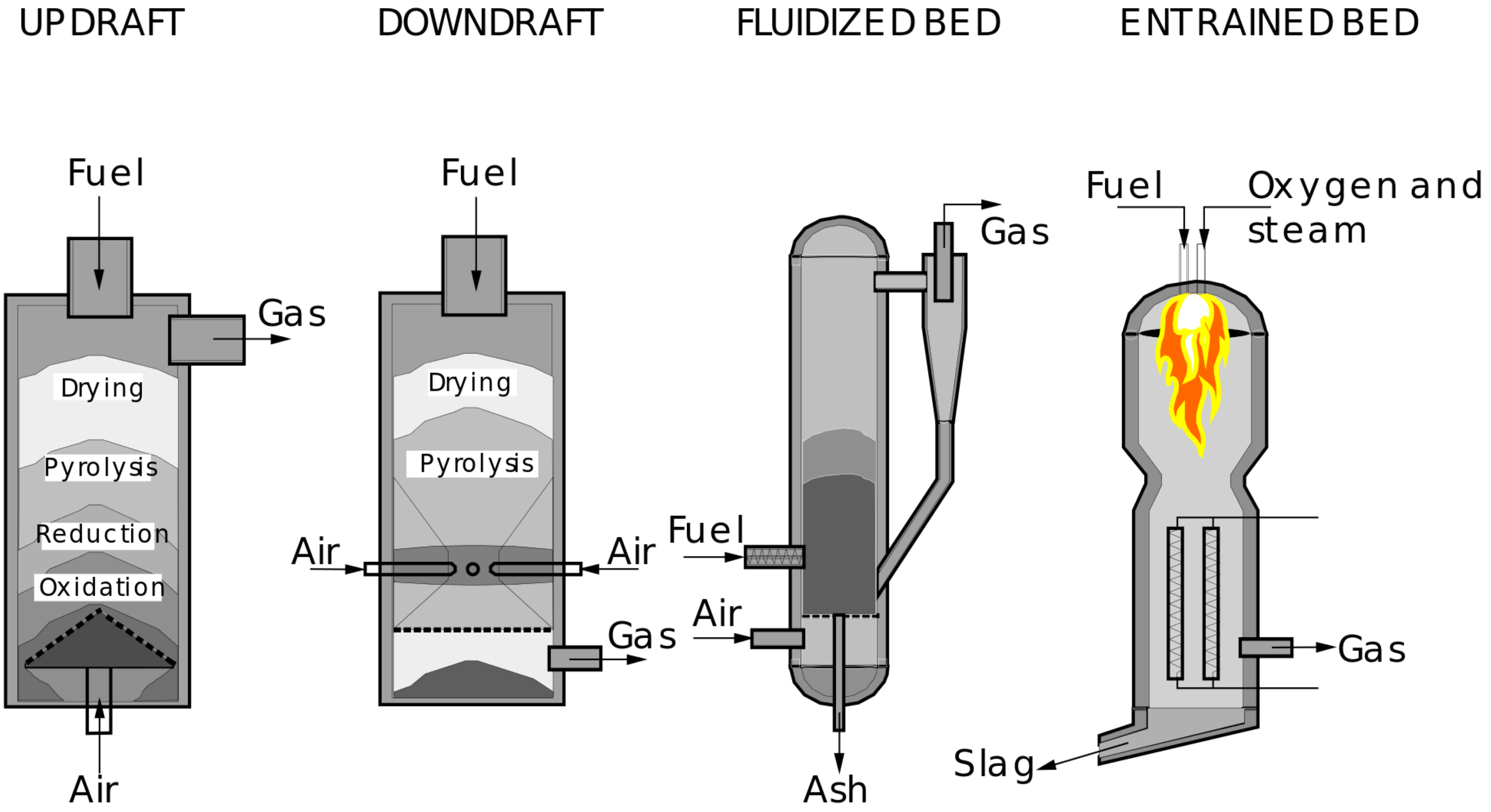


Fig 32 - Most classical reactor types[16]

[16] Wikipedia

# Economies of scale as perspectives

To be competitive, industrial processes need:

- Repeatable raw material inputs
- Large volumes
- Maximum operability (ideally 24/7)

It is therefore necessary to standardize raw materials and operate the processes continuously

# Processes & Products - Summary

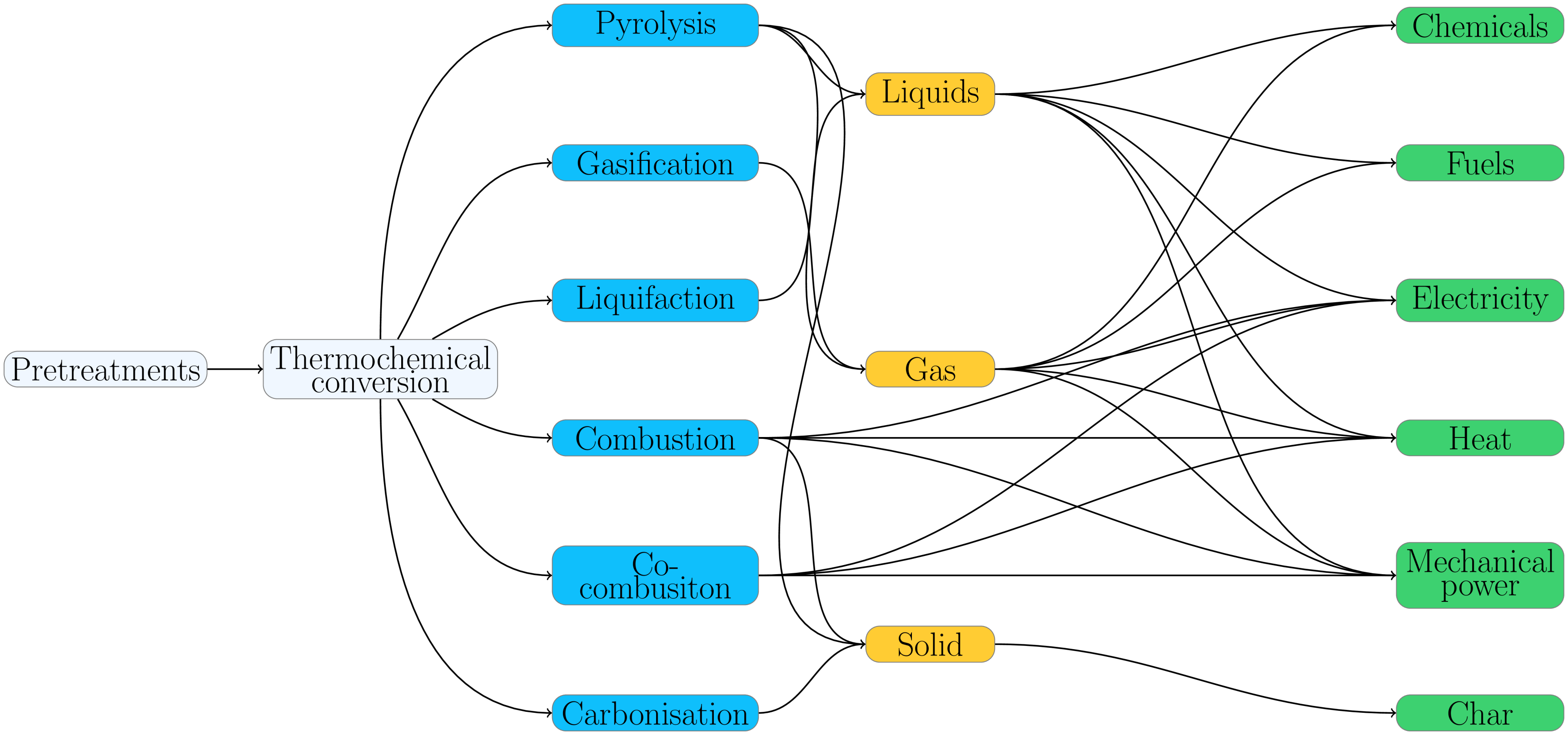


Fig 33 - Processes and products flowsheet

# Pespectives

# Potential for the future

Reasonable forecasts predict between 4.8 and 12.0 GTOE/year in 2050 of energy from biomass

For a consumption between 15.8 and 26.4 GTOE/year

About a third would come from waste (forest, agriculture, MSW)

The rest would come from dedicated crops (energy crops)

- This raises the question of the land on which the biomass would be would be cultivated

# Growth opportunities

Growth in biofuel (mobility) needs

- Multiplication of consumption by a factor of 10 to 20 by 2030 (but on a rather low basis, 1.5% of the fuel used today)

Growth in the need for heat and mechanical power in industry:

- Doubling of power by 2050

Electricity generation:

- From 1.3% to 2.4 - 3.3% of electricity produced on biomass basis by 2030

# The technologies

Current technologies (the result of many years of R&D) are competitive:

- Yields have been improved
- Especially if the biomass input is cheap (waste)

The main areas of progress are:

- Liquid fuels
- Small scale heat production

# Social acceptability

Food crisis of 2007-2008:

- Low stocks
- Use of cereals to make fuel
- Volatility of financial markets

The issue of competition of energy crops with food crops is taken seriously

- Positive effect $\rightarrow$ absorb surplus

Land dedicated to biomass cultivation must be chosen carefully:

- No competition with food
- Low impact on water resources

# For the industry as a whole

The future depends strongly on the choices made by governments

- Legislation (EU voted: minimum share of renewable energy 35% (total consumption) and 12% in transport, by 2030)
- Subsidies / Incentives
- Carbon price
- Greenhouse gas emission reduction targets

Be careful with energy crops

Land dedicated to biomass cultivation must be chosen carefully:

- Do not compete with food crops, but synergize (EU voted: less than 7% must come from food crops for transport sector)

# Thank you for your attention

Our partners

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