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Universidad
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Curso extraordinario Universidad de Zaragoza

**Energía renovable, electricidad e hidrógeno:
presente y futuro de la energía
en el medio rural y la maquinaria agrícola**

Huesca, 30 junio-1 julio 2016

Curso

“Sostenibilidad energética en el sector agropecuario: el caso vitivinícola”

Patrocinadores



Curso

**Energía renovable, electricidad e hidrógeno:
presente y futuro de la energía en el medio rural y la maquinaria agrícola**

Procesos termoquímicos para la valorización de la biomasa residual

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Qué es la biomasa??

Biomass consists of any organic matter of vegetable or animal origin. It is available in many forms and from many different sources e.g. **forestry products** (biomass from logging and silvicultural treatments, process residues such as sawdust and black liquor, etc.); **agricultural products** (crops, harvest residues, food processing waste, animal dung, etc.); and **municipal and other waste** (waste wood, sewage sludge, organic components of municipal solid waste, etc.).

Bioenergy – a sustainable and reliable energy source. A review of status and prospects. IEA, 2009



Criterios de sostenibilidad

- Adhere to the waste hierarchy

The overall waste hierarchy, as set out in the Waste Framework Directive, which is to prefer prevention, re-use, recycling (and composting of materials) over recovery (for example for energy) and, eventually, over disposal (ie landfill or incineration without energy recovery) should be followed in all cases.

- Consider the complete lifecycle GHG emissions that arise from wastes and residues

While the GHG methodology accounts for transport and processing emissions other, potentially significant, emission sources are neglected. In particular, the methodology considers wastes and agricultural residues to be 'zero emission' up to the point of their collection. This ignores the impacts on soil carbon stocks that can be as the extraction of residues increases.

- Mitigate the environmental impacts of certain advanced conversion pathways

The processing of biomass into biofuels via advanced biochemical or thermochemical conversion pathways can require relatively high energy inputs, which are addressed in the GHG methodology. However, other environmental impacts resulting from the processing of biomass through advanced conversion technologies such as water consumption in processing should be investigated and if necessary be addressed by safeguards.

The sustainability of advanced biofuels in the EU. Institute for European Environmental Policy, 2013

Sustainability assessment	Feedstock
Potentially sustainable (contingent on safeguards)	Algae (4x)
	Biomass fraction of mixed municipal waste (4x)
	Biomass fraction of industrial waste (4x)
	Straw (4x)
	Animal manure and sewage sludge (4x)
	Tall oil pitch (4x)
	Palm oil mill effluent and empty palm fruit bunches (4x)
	Bagasse (4x)
	Grape marc and wine lees (4x)
	Nut shells (4x)
	Husks (4x)
	Cobs (4x)
	Used cooking oil (2x)
	Animal fats (Category 1 and 2) (2x)
Likely unsustainable	Bark, branches, leaves, saw dust and cutter shavings (4x)
	Non-food cellulosic material (2x)
	Ligno-cellulosic material except saw logs and veneer logs (2x)
Unclear	Crude Glycerine (4x)

Note: This overview should be read in conjunction with the factsheets (Section 4) that contain information on existing uses and ensuing risks from their potential diversion as well as proposed safeguards to mitigate the risks.

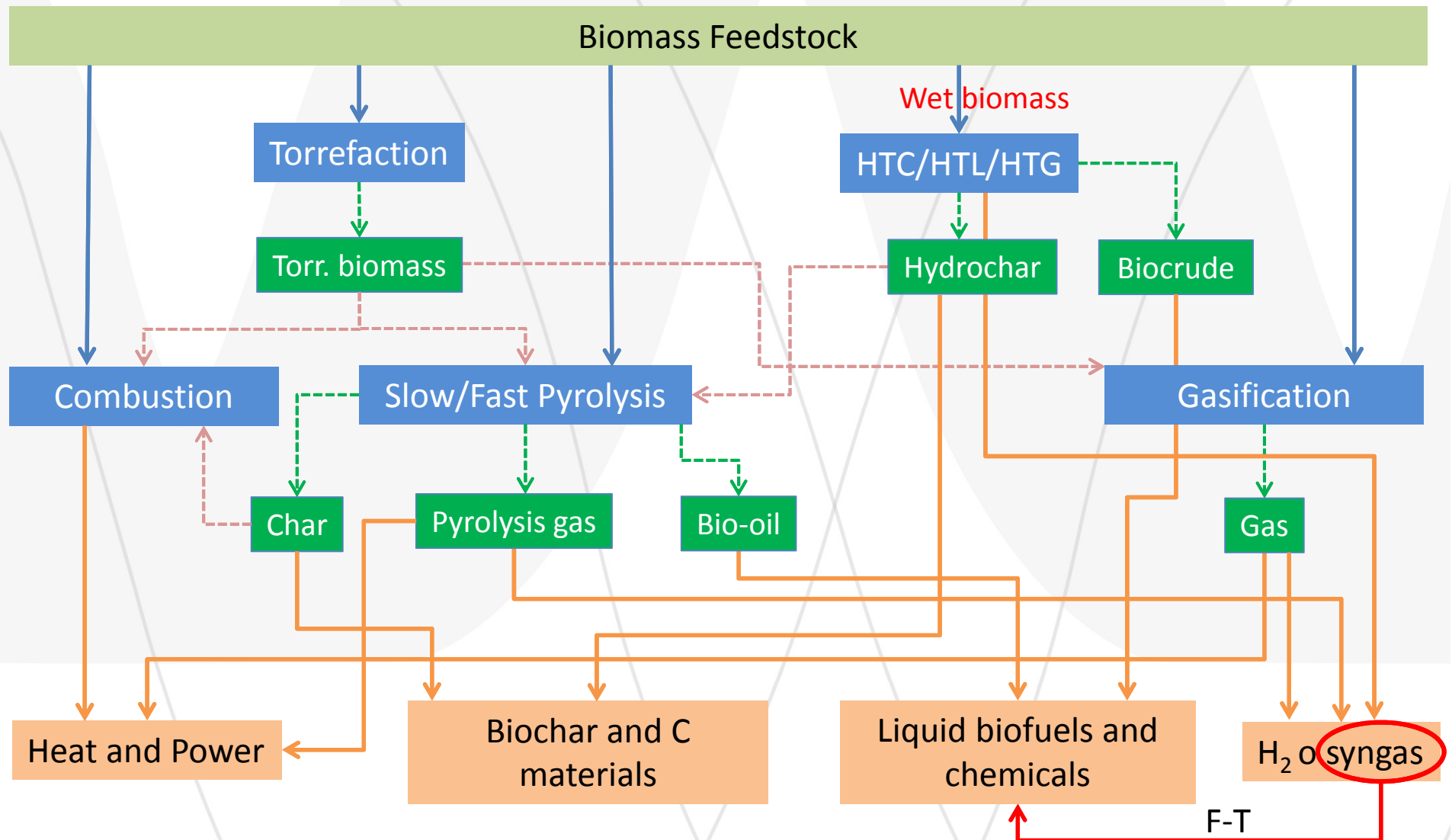
The sustainability of advanced biofuels in the EU. Institute for European Environmental Policy, 2013

¹ Proposal COM(2012) 595 final of 17.10.2012 for a Directive of the European Parliament and of the Council amending Directive 98/70/EC relating to the quality of petrol and diesel fuels and amending Directive 2009/28/EC on the promotion of the use of energy from renewable sources.

Tecnologías de conversión

- **Thermochemical conversion**, by which biomass undergoes chemical degradation induced by high temperature.
- **Physicochemical conversion** is used to produce liquid fuels (biodiesel or vegetable oil) from oil crop (rapeseed, soybean, etc.) by oil extraction possibly followed by a transesterification process.
- **Biological routes** use living micro-organisms (enzymes, bacteria) to degrade the feedstock and produce liquid and gaseous fuels. Biological routes are numerous, key mechanisms being fermentation from sugar (sugar-cane, sugar-beet, etc.), starch (corn/maize, wheat, etc.) and lignocellulosic (grass, wood, etc.) feedstock, anaerobic digestion (mostly from wet biomass), and the more recent bio-photochemical routes (e.g. hydrogen production using algae), which require the action of sunlight.

Procesos de conversión termoquímica



Torrefacción

Raw biomass as a fuel features some drawbacks such as low calorific value due to its high moisture and oxygen contents, high grinding energy requirement due to its rigidity and mechanical strength, and low fluidization properties leading to difficulties in feeding it into boilers (Sarvaramini and Larachi. *Fuel* **2014**, 116, 158-167).

During the torrefaction process, solid biomass is heated in the absence of or drastically reduced oxygen to a temperature of approx. 225-300 °C, leading to a loss of moisture and partial loss of the volatile matter in the biomass. With the partial removal of the volatile matter (about 20%), the characteristics of the original biomass are drastically changed.

Torrefaction increases the **energy density** of biomass and reduces the fibers length and mechanical stability resulting in improved grinding properties (Medic et al., *Fuel* **2014**, 91, 147-154).



Torrefaction time 60 minutes

Biomasa torrefactada: un combustible a tener en cuenta

	Wood	Wood pellets	Torrefaction pellets	Charcoal	Coal
Moisture content (% wt)	30 – 45	7 – 10	1 – 5	1 – 5	10 – 15
Lower heating value (MJ/kg)	9 – 12	15 – 18	20 – 24	30 – 32	23 – 28
Volatile matter (% db)	70 – 75	70 – 75	55 – 65	10 – 12	15 – 30
Fixed carbon (% db)	20 – 25	20 – 25	28 – 35	85 – 87	50 – 55
Density (kg/l) Bulk	0.2 – 0.25	0.55 – 0.75	0.75 – 0.85	~ 0.20	0.8 – 0.85
Energy density (GJ/m ³) (bulk)	2.0 – 3.0	7.5 – 10.4	15.0 – 18.7	6 – 6.4	18.4 – 23.8
Dust	Average	Limited	Limited	High	Limited
Hydroscopic properties	hydrophylic	hydrophilic	hydrophobic	hydrophobic	hydrophobic
Biological degradation	Yes	Yes	No	No	No
Grindability	Poor	Poor	Good	Good	Good
Handling	Special	Special	Good	Good	Good
Quality variability	High	Limited	Limited	Limited	Limited

By **pelletizing torrefied biomass**, a number of advantages can be achieved in transport, handling and storage. The compression step increases the volumetric energy density by a factor of 4-8 leading to significant cost savings in shipping and storage.

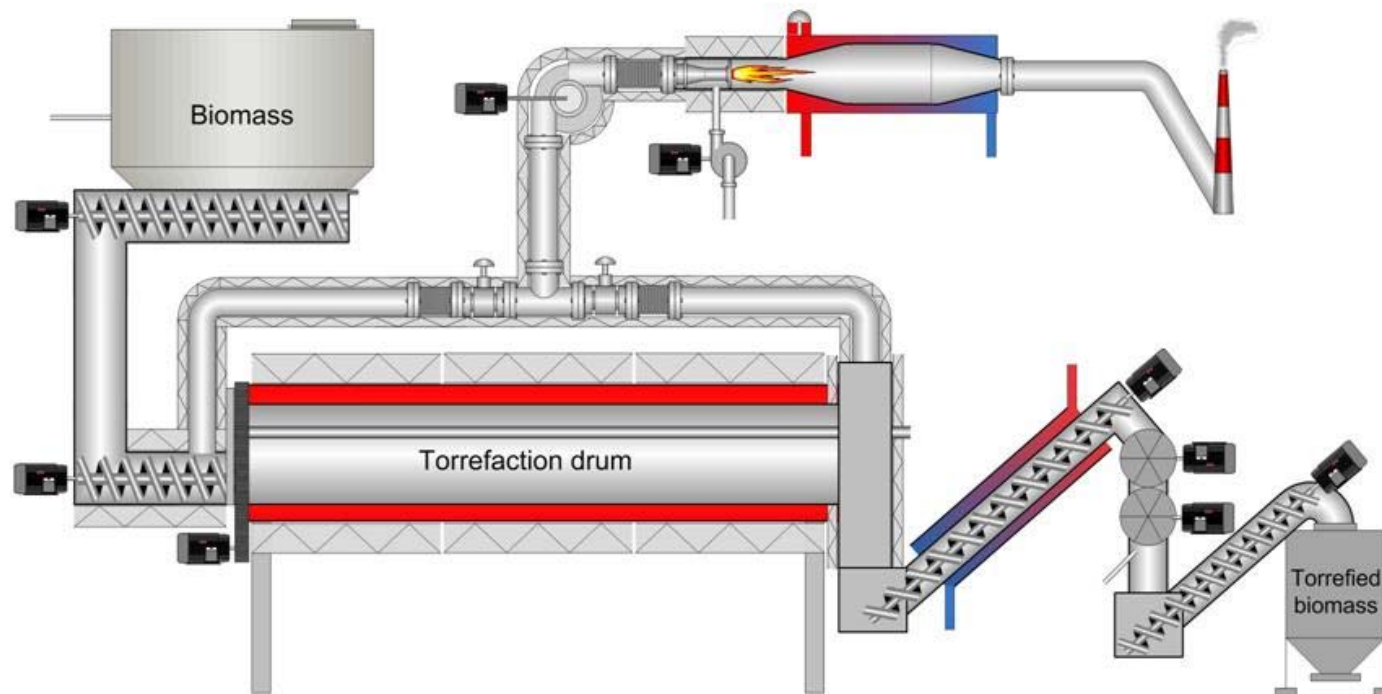
Tecnologías para torrefacción

Reactor technologies	Companies involved
Rotating drum	CDS (UK), Torr-Coal (NL), BIO3D (FR), EBES AG (AT), 4Energy Invest (BE), BioEndev/ ETPC (SWE), Atmosclear S.A. (CH), Andritz , EarthCare Products (USA)
Screw reactor	BTG (NL), Biolake (NL), FoxCoal (NL), Agri-tech Producers (US)
Herreshoff oven/ Multiple Hearth Furnace (MHF)	CMI-NESA (BE), Wyssmont (USA)
Torbed reactor	Topell (NL)
Microwave reactor	Rotawave (UK)
Compact moving bed	Andritz/ECN (NL), Thermya (FR), Buhler (D)
Belt dryer	Stramproy (NL), Agri-tech producers (USA)
Fixed bed	NewEarth Eco Technology (USA)

Status overview of torrefaction technologies. IEA, 2012

Ejemplo: horno rotatorio

The torrefaction process can be controlled by varying the torrefaction temperature, rotational velocity, length and angle of the drum



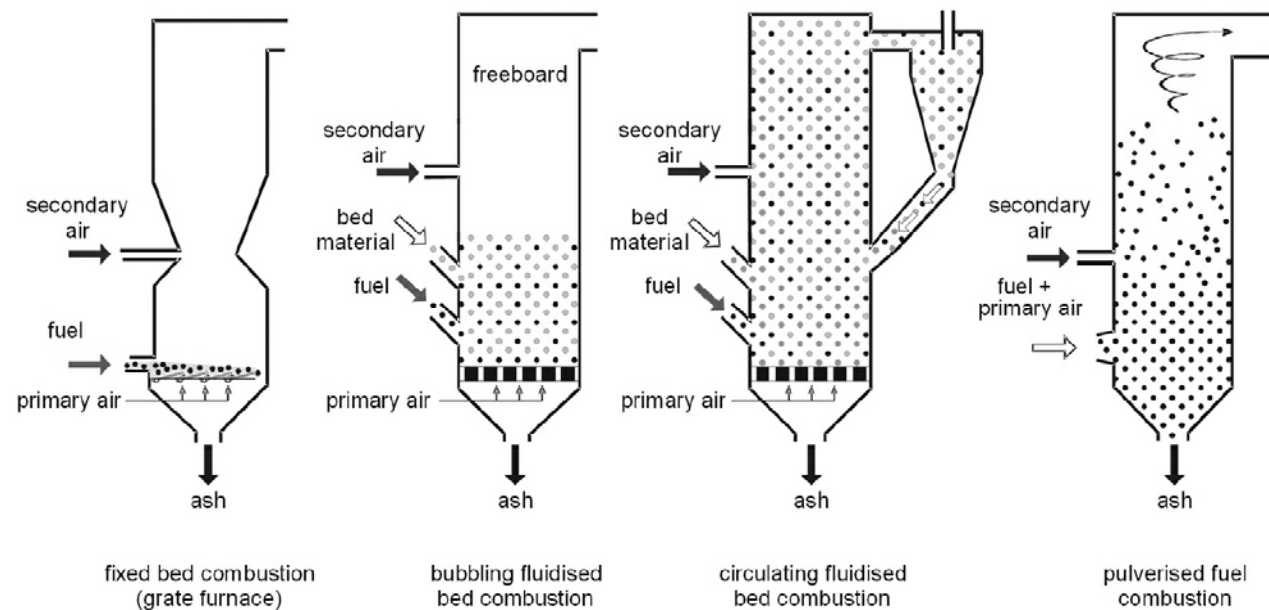
From Umea University, Sweden

Combustión para generación de calor

INDUSTRIAL SYSTEMS

An increasing number of boilers in the 0.5-10 MW_th range are found in industries that consume large amounts of heat and have large volumes of biomass residues at their disposal.

Principal types of combustion reactors



The Handbook of Biomass Combustion and Co-firing. Earthscan: London, 2008)

Advantages

Disadvantages

Grate furnaces

- low investment costs for plants $< 20\text{MW}_{\text{th}}$
- low operating costs
- low dust load in the flue gas
- less sensitive to slagging than fluidized bed furnaces
- usually no mixing of wood fuels and herbaceous fuels possible (only special constructions can cope with such fuel mixtures)
- efficient NO_x reduction requires special technologies (combination of primary and secondary measures)
- high excess oxygen (5–8vol%) decreases efficiency
- combustion conditions not as homogeneous as in fluidized bed furnaces
- low emission levels at partial load operation require a sophisticated process control

BFB furnaces

- no moving parts in the hot combustion chamber
- NO_x reduction by air staging works well
- high flexibility concerning moisture content and kind of biomass fuels used
- low excess oxygen (3–4 Vol%) raises efficiency and decreases flue gas flow
- high investment costs, interesting only for plants $> 20\text{MW}_{\text{th}}$
- high operating costs
- reduced flexibility with regard to particle size ($< 80\text{mm}$)
- utilization of high alkali biomass fuels (e.g. straw) is critical due to possible bed agglomeration without special measures
- high dust load in the flue gas
- loss of bed material with the ash without special measures

Advantages

Disadvantages

CFB furnaces

- no moving parts in the hot combustion chamber
- NO_x reduction by air staging works well
- high flexibility concerning moisture content and kind of biomass fuels used
- homogeneous combustion conditions in the furnace if several fuel injectors are used
- high specific heat transfer capacity due to high turbulence
- use of additives easy
- very low excess oxygen (1–2vol%) raises efficiency and decreases flue gas flow

- high investment costs, interesting only for plants > 30MW_{th}
- high operating costs
- low flexibility with regard to particle size (< 40mm)
- utilization of high alkali biomass fuels (e.g. straw) is critical due to possible bed agglomeration
- high dust load in the flue gas
- loss of bed material with the ash without special measures
- high sensitivity concerning ash slagging

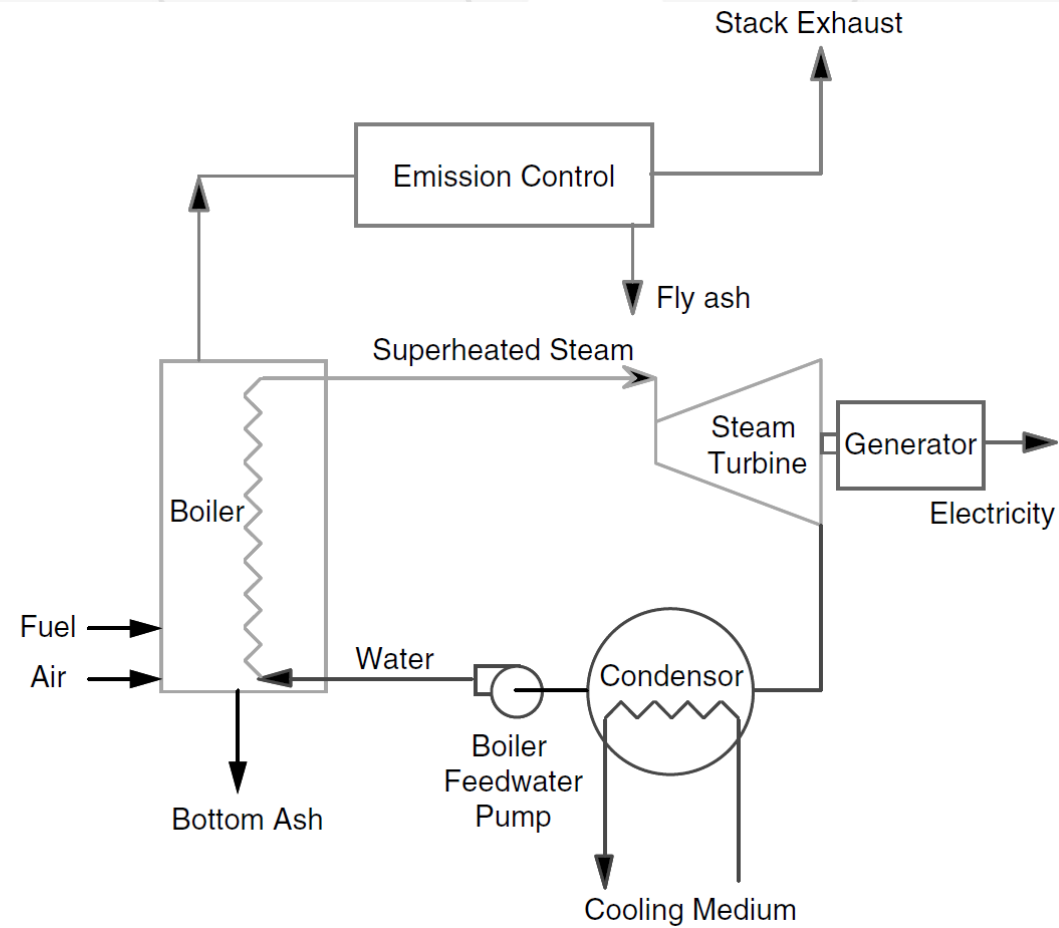
Pulverized fuel combustion

- low excess oxygen (4–6vol%) increases efficiency
- high NO_x reduction by efficient air staging and mixing possible if cyclone or vortex burners are used
- very good load control and fast alteration of load possible

- particle size of biomass fuel is limited (< 10–20mm)
- high wear rate of the insulation brickwork if cyclone or vortex burners are used
- an extra start-up burner is necessary

Combustión para generación de electricidad

Ciclo de Rankine



Technology	Efficiency ^a	Cost of electricity (cUSD/kWh)	Scale of plant	General issues	Development state
Combustion + steam cycle	15–30%	7–9 ^b 5–18 ^e 10.4–21.7 (large) ^d 6.9–24.3 (medium) ^d 11.3–37.3 (small) ^d	Viable for large scale (30–100 MW) Recent development of small scale applications	Reliable technology Difficult biomass procurement for large scale	Commercial
Combustion + Stirling engine	Around 30%	15–24 ^b	Micro scale application (10–100 kW)		Demonstration
Combustion + ORC	16–20%	11–25 ^b	Small scale (0.5–2 MW)	Few ORC plants operate on biomass Need to improve efficiency and reliability, and to reduce costs	Demonstration/ Early commercial
CHP plants (biomass based)	High Overall 70–90%	7.5–13 ^b 6.5–25 ^e	Scale is limited by heat demand and its seasonal variation	Need to find an economic application for waste heat	Commercial
Direct co-firing	35–45% (at 10% biomass on energy base)	3–5.5 ^b 2.9–5.3 ^c 6.9–12.2 ^d 3.5–12 ^e	Cost-effective	Because of biomass varying characteristics, there are limits to the amount of biomass that can be co-fired Possible impacts on plant operation and lifetime	Commercial



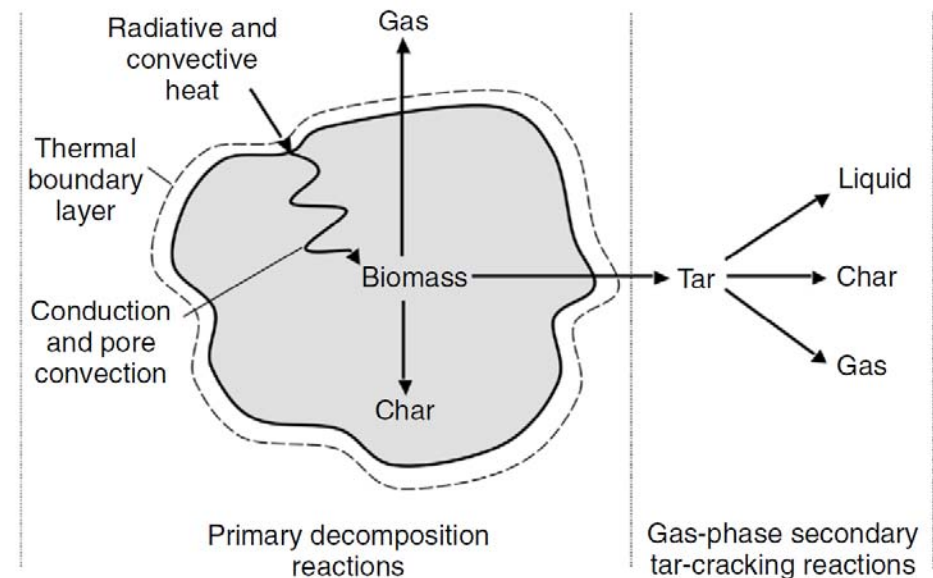
Fiorese et al. *Energy Policy* 2014, 65, 94-114

Pirólisis

Biomass pyrolysis includes thermal degradation of its polymer constituents cellulose, hemicellulose, lignin, peptides and lipids. The biomass polymer fragments (volatiles) formed are driven out of the biomass particle due to the pressure that is being built up inside the particle.

They are widely distributed in molecular weight, and partly still in the liquid phase (aerosols). The intrinsic pyrolysis reactions are very fast, but in practice heating of the biomass particles and mass transfer limitation delays the pyrolysis process significantly.

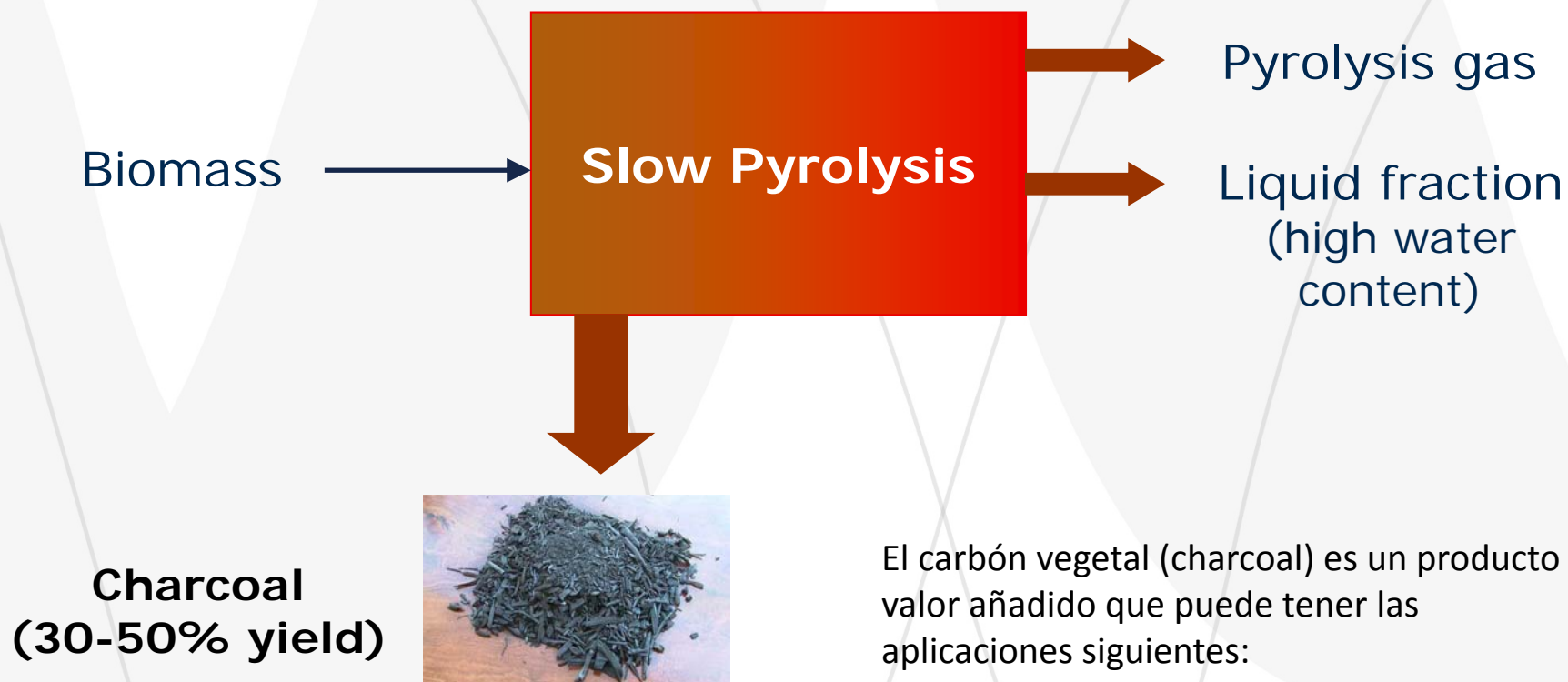
Pyrolysis in a biomass particle



P. Basu. *Biomass Gasification and Pyrolysis (Practical Design and Theory)*. Academic Press: Burlington, MA, 2010

Pirólisis lenta (carbonización)

velocidad de calentamiento $1-100\text{ }^{\circ}\text{C min}^{-1}$



El carbón vegetal (charcoal) es un producto de valor añadido que puede tener las aplicaciones siguientes:

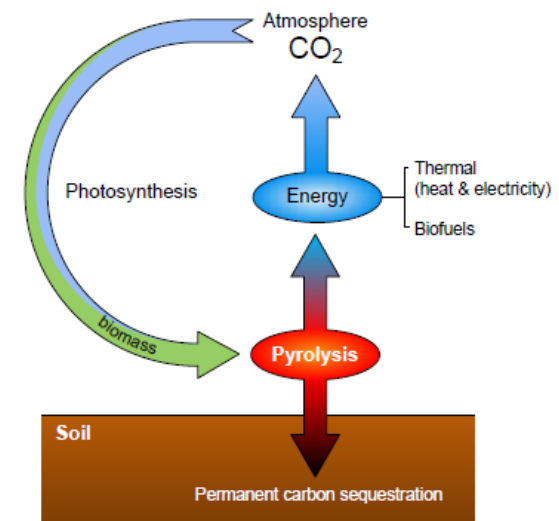
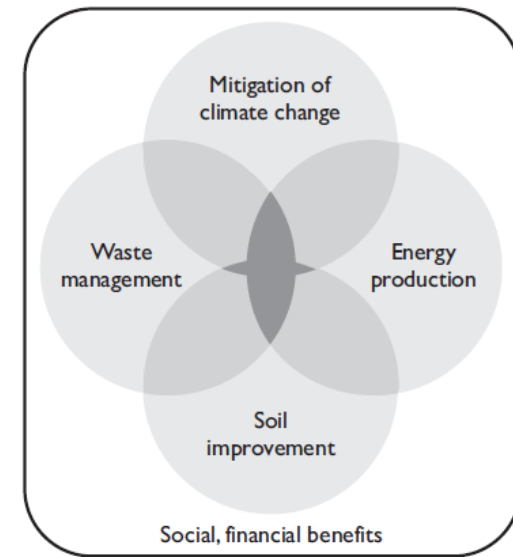
- 1) Combustible
- 2) Agente reductor en altos hornos
- 3) Material adsorbente y soporte de catalizadores metálicos
- 4) **BIOCHAR**

Biochar

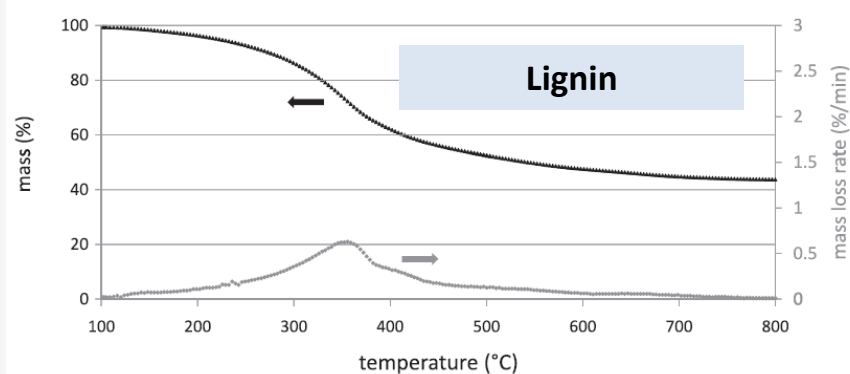
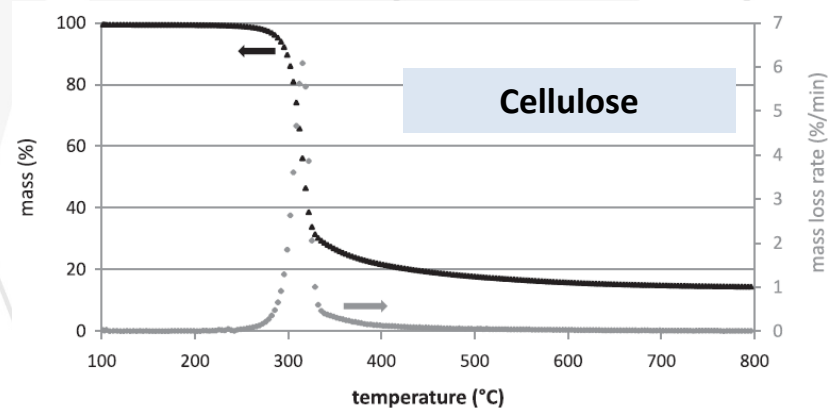
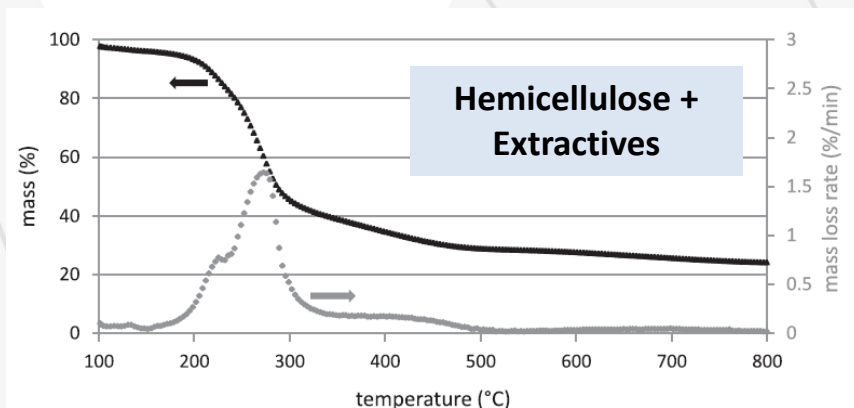
Emerging during the last decade is the use of charcoal, derived from wood and many other biomass types, as a soil amendment and carbon sequestration material. It is then called biochar.

Biochar added to the soil

- stores atmospheric carbon permanently
- reduces the N_2O greenhouse gas emissions from N-fertilizers
- increases the soil organic matter
- improves soil aeration and water retention
- increases cation exchange (nutrient retention)
- improves soil microbial activity



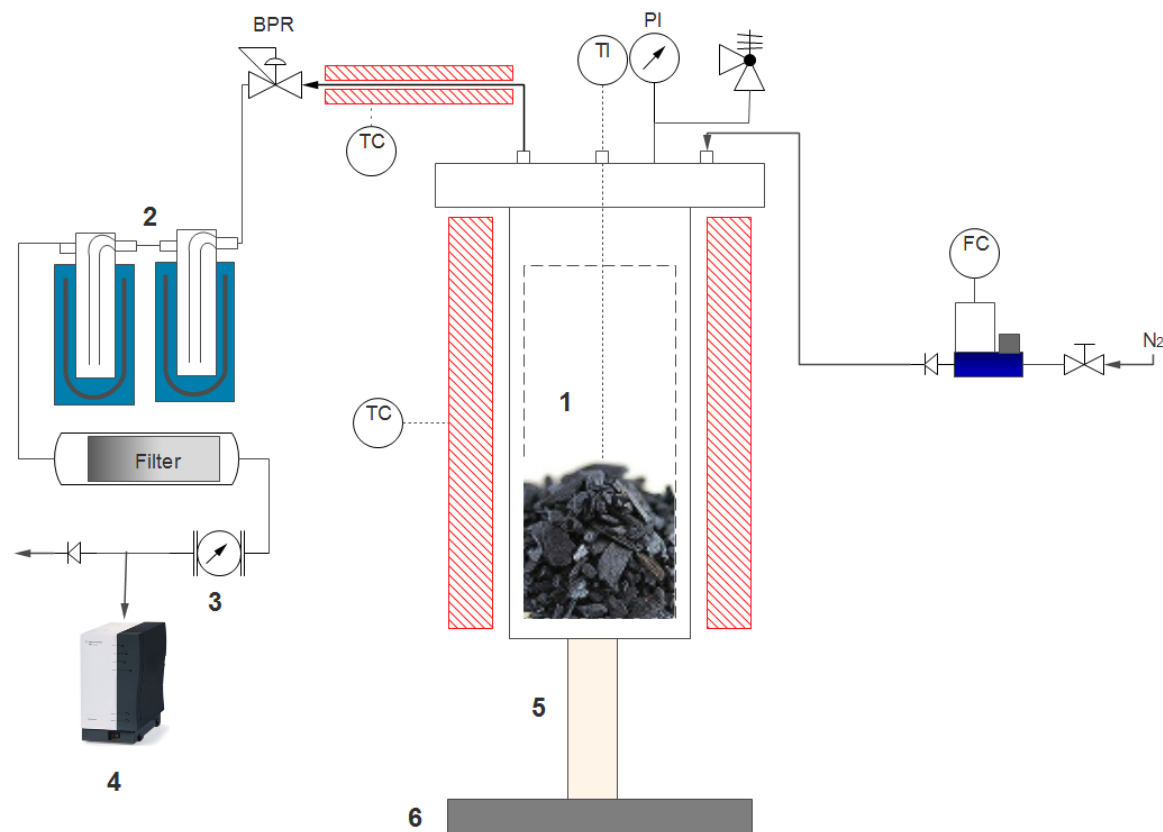
Pirólisis lenta (efectos de la composición de la biomasa)



F. X. Collard, J. Blin. *Renew. Sustain. Energy Rev.* 2014, 38, 594–608

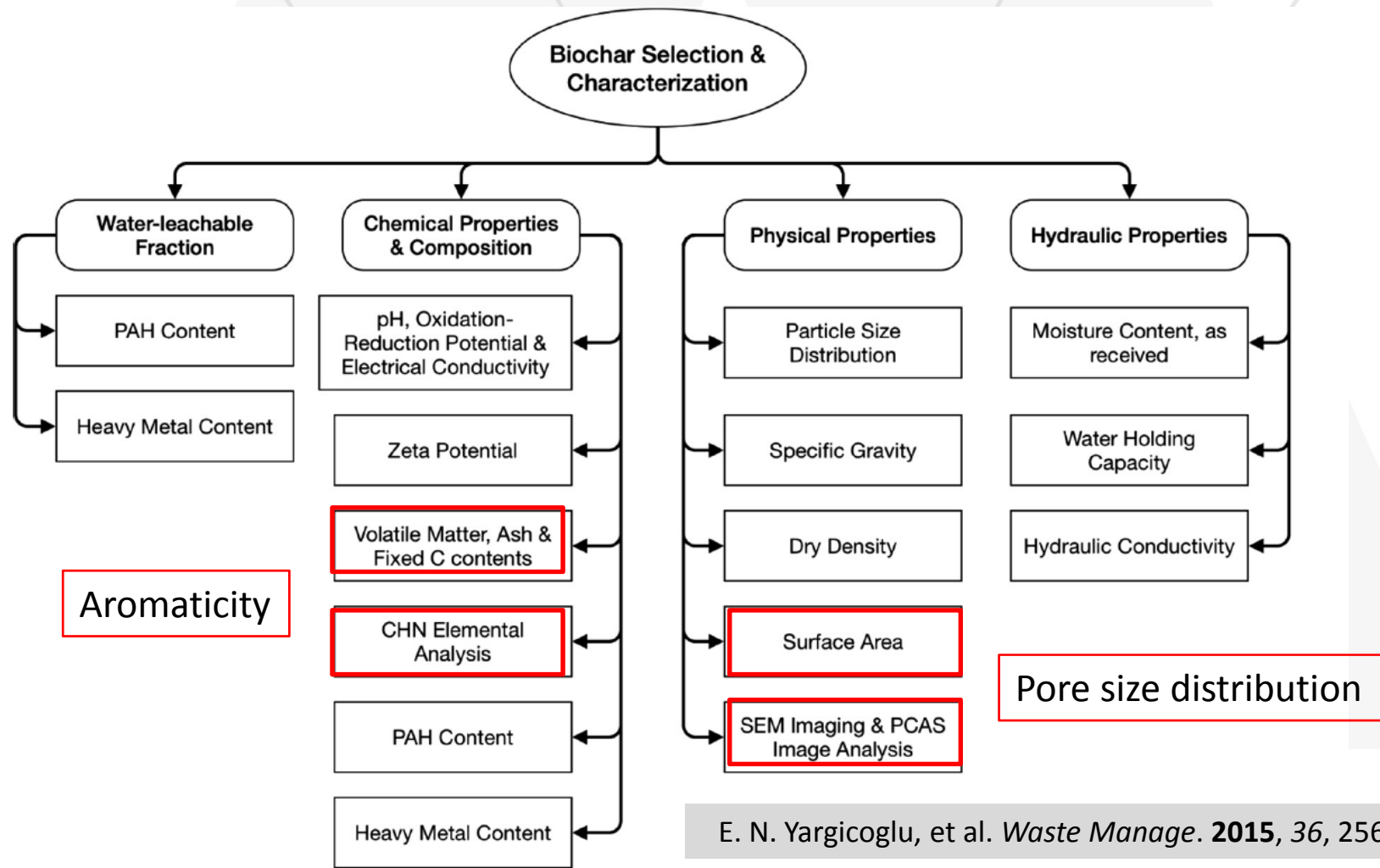
biomass	C	H	N	S	extractives (%)	hemicellulose (%)	cellulose (%)	lignin (%)	ash (%)
wood chips	46.4	5.9	0.085	0	4.6	31.8	31.8	19.0	0.45
wheat straw	43.6	6.2	0.30	0.08	7.4	27.3	27.3	16.4	5.5
olive husks	50.9	6.3	1.37	0.03	8.7	18.5	18.5	28.0	2.8
grape residues	47.9	6.2	2.11	0.09	15.6	17.2	17.2	30.4	5.1
rice husks	40.3	5.7	0.30	0.03	8.0	24.3	24.3	14.3	15.3

Pirólisis lenta (parámetros de operación)



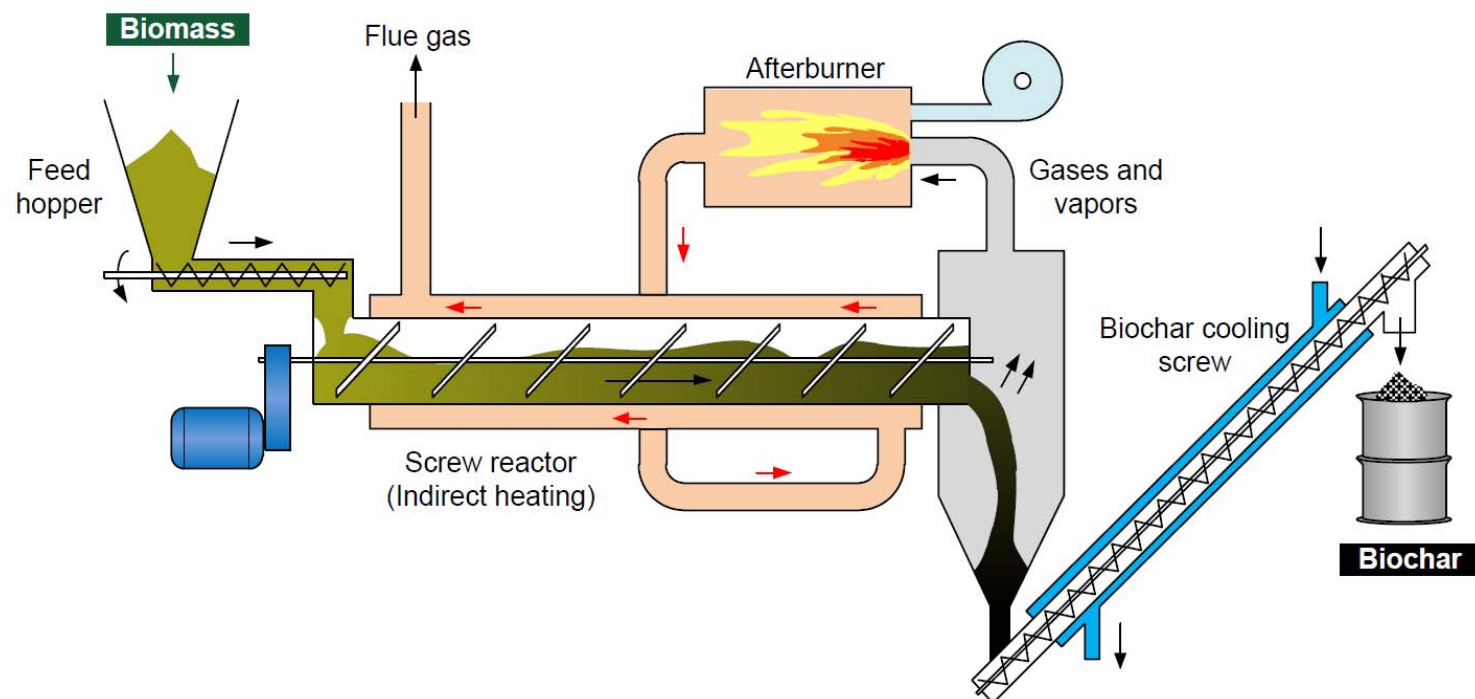
Peak Temperature?
Pressure?
Particle size?
Residence time?

Caracterización del biochar



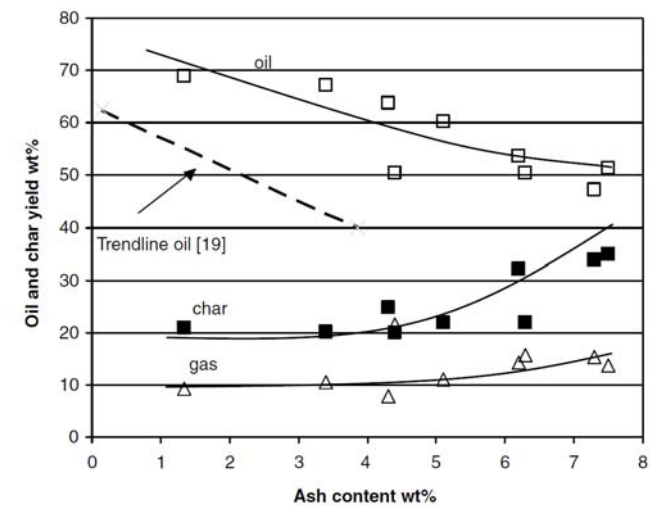
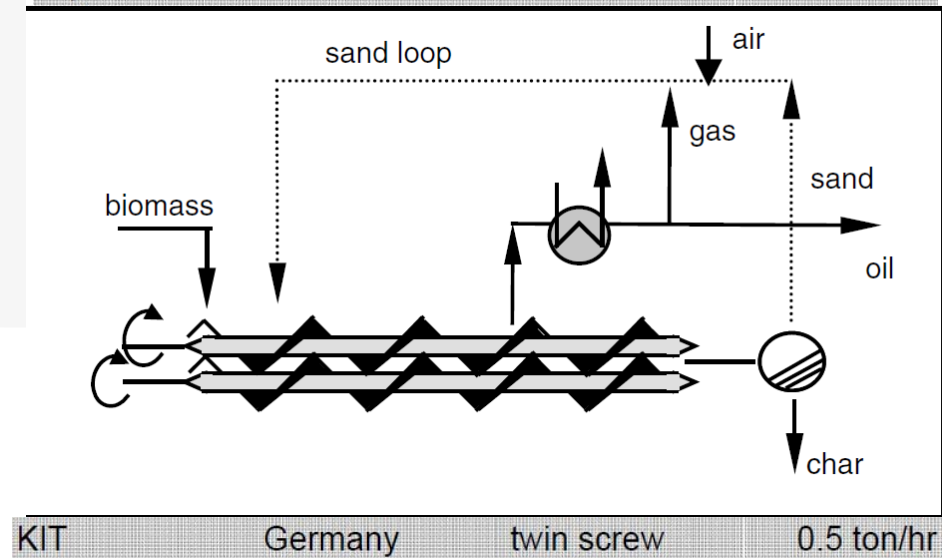
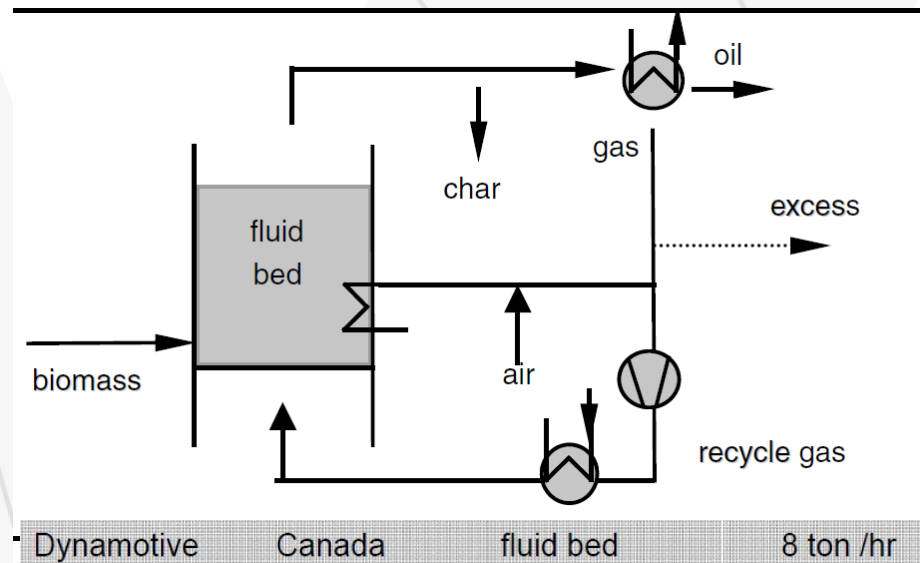
E. N. Yargicoglu, et al. *Waste Manage.* **2015**, 36, 256–68

Pirólisis lenta (proceso continuo)



Screw pyrolyzer from Pyreg
(Germany)

Pirólisis rápida (bio-oil)



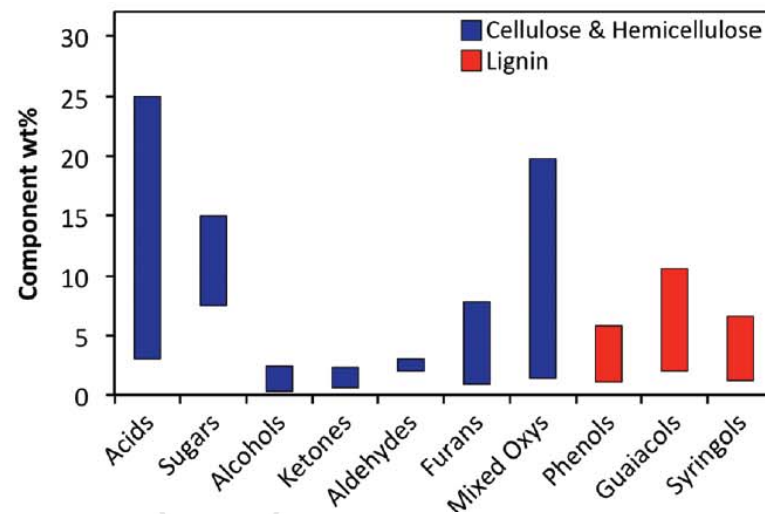
Bio-oil Upgrading

Pyrolysis oil cannot be directly used as a transportation fuel and it cannot be “dropped-in” to existing petroleum refinery processes. Of particular note, raw bio-oil has properties of (i) low heating value, (ii) incompatibility with conventional fuels due to high oxygen content, (iii) high solids content, (iv) high viscosity, and (v) chemical instability.

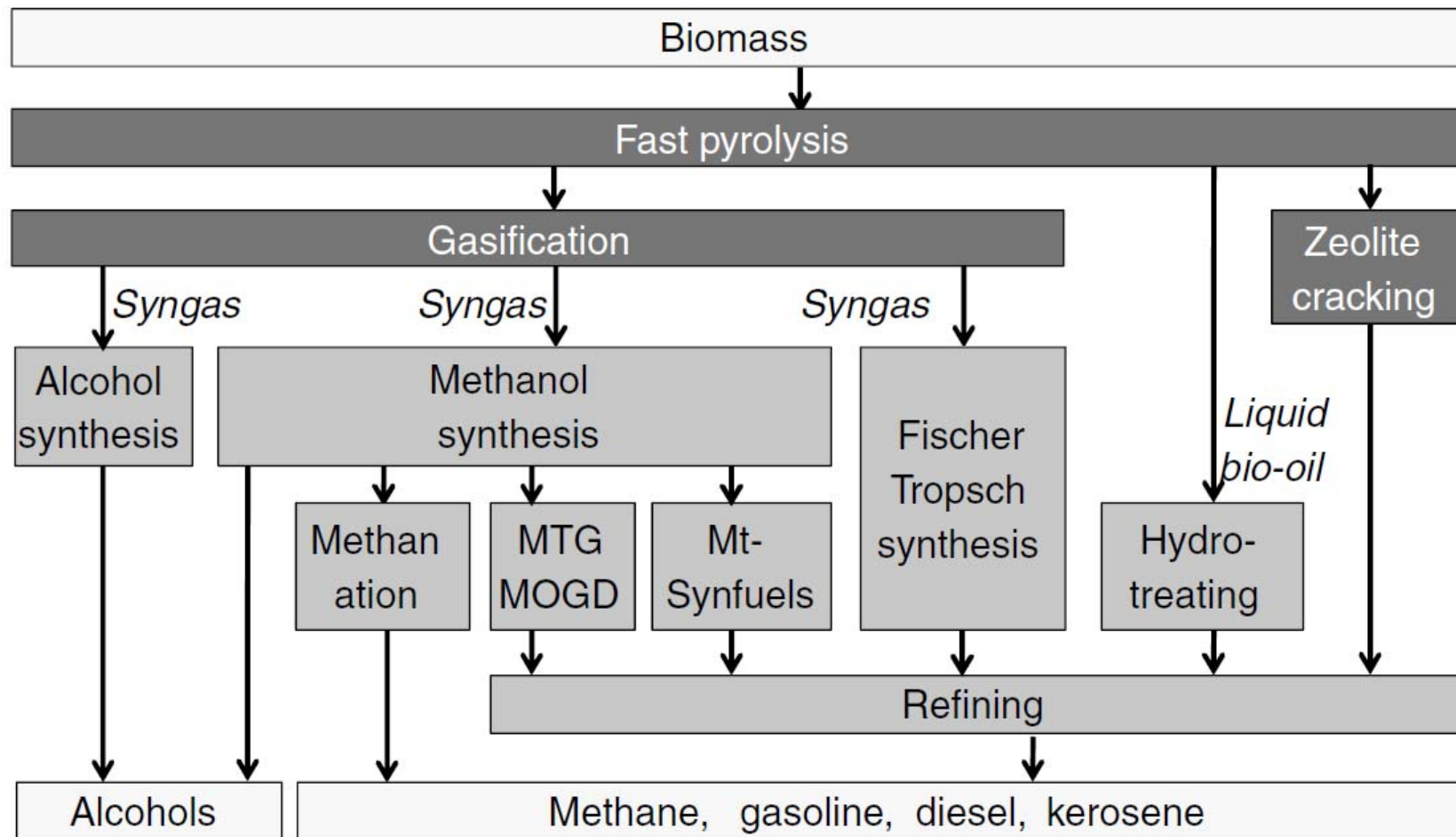
Table 1 Elemental composition and water content ranges of crude petroleum oils compared to pyrolysis bio-oils^{23–25}

	Petroleum crude oil (wt%)	Pyrolysis bio-oil (wt%)
C	83–86	55–65
H	11–14	5–7
O	<1	30–50
N	<4	<0.1
S	<1	<0.05
Water	0.1	20–30

D. A. Ruddy, et al. *Green Chem.* **2014**, *16*, 454

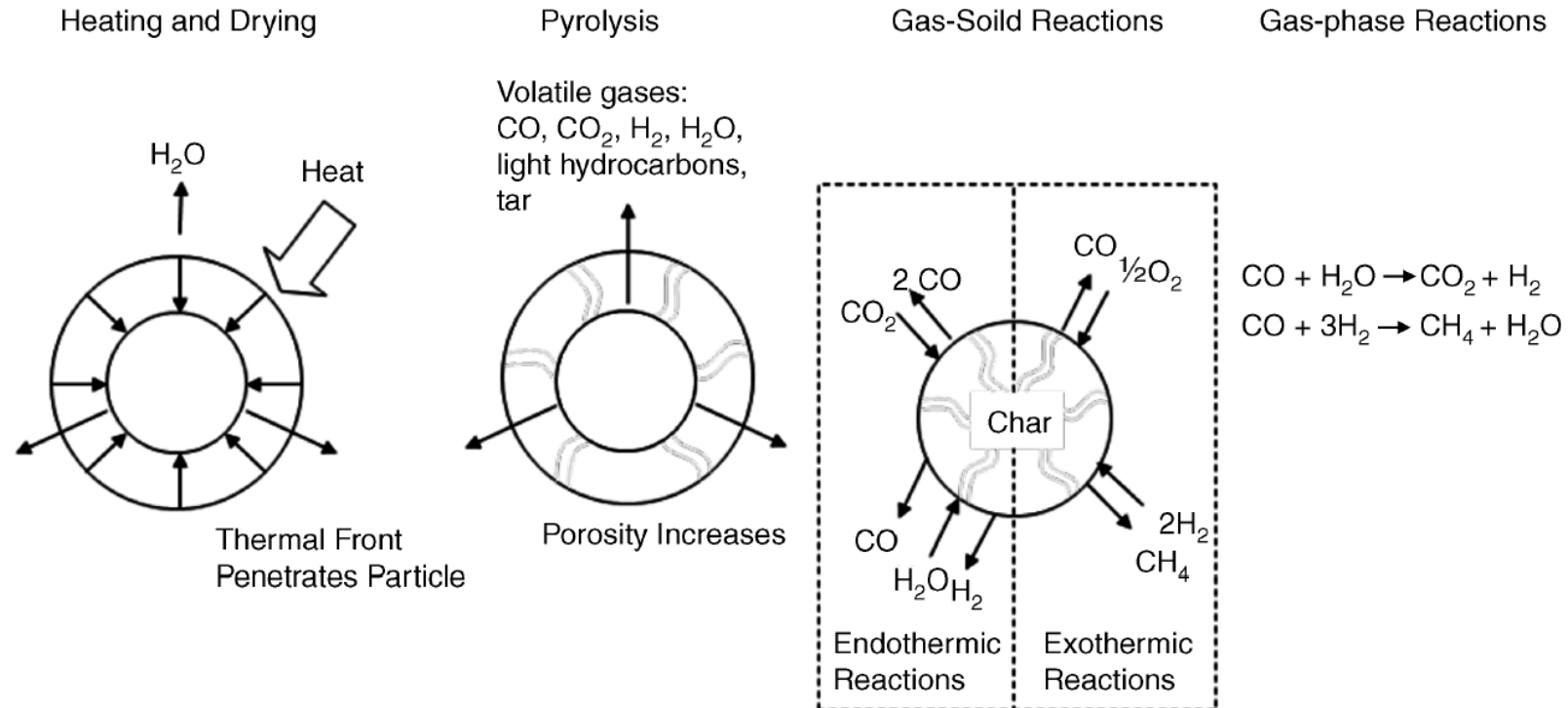


Algunos posibles métodos



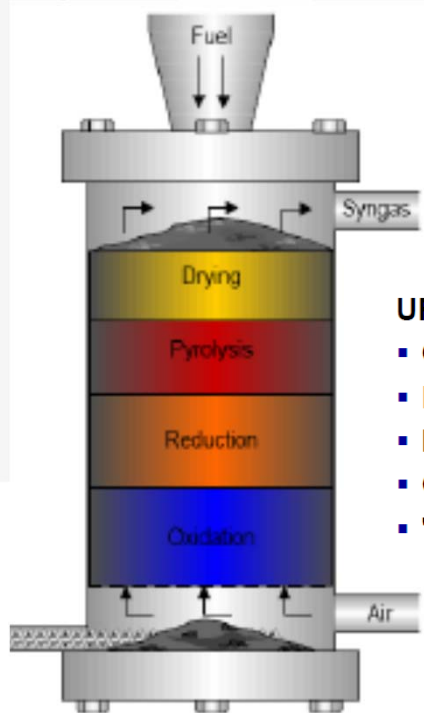
A. V. Bridgwater. In: Thermochemical Processing of Biomass; Ed. Robert C. Brown; Wiley, 2011.

Gasificación



R. L. Bain, K. Broer. In: Thermochemical Processing of Biomass; Ed. Robert C. Brown; Wiley, 2011.

GASIFICATION METHOD	AIR	OXYGEN	INDIRECT steam + oxygen/circulating bed material
GAS HEATING VALUE	3 - 7 MJ/m ³ n	7 - 15 MJ/m ³ n	7 - 15 MJ/m ³ n
SIZE RANGE	small - medium < 100 MWth	large > 100 MWth	medium - large > 50 MWth
FEEDSTOCK	reactive: biomass, refuse derived fuel (RDF)	coal, bottom oils	biomass
APPLICATIONS	CHP	syngas, power, (CHP)	syngas

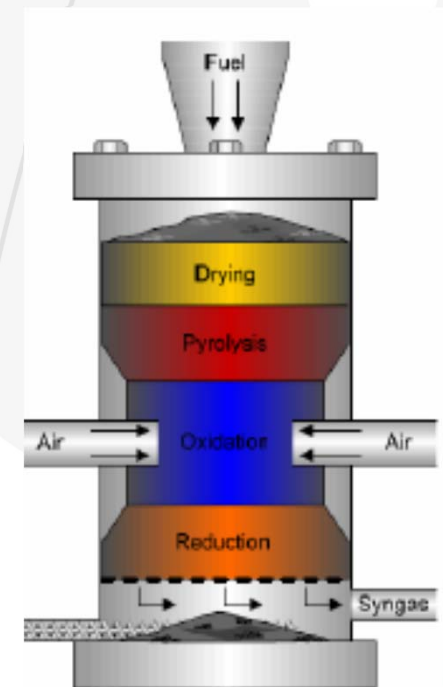


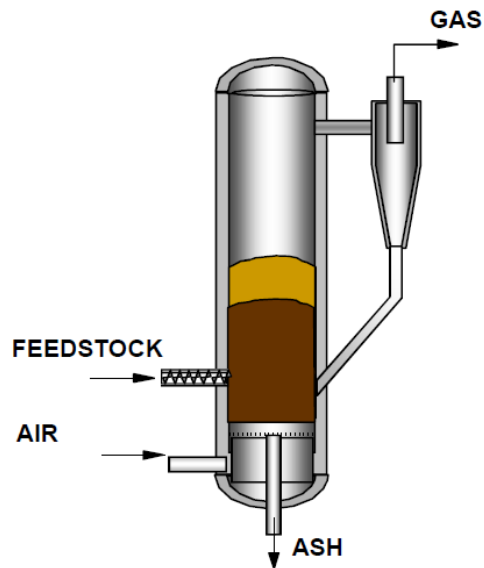
UPDRAFT

- Output < 10 MWth (biomass)
- Feedstock size 10 - 100 mm
- Moist feedstock < 50 p-%
- Gas temperature < 300 °C
- "Dirty" gas

DOWNDRAFT

- Output < 2 MWth
- Feedstock size 10 - 100 mm
- Dry feedstock < 20 p-%
- Gas temperature < 800 °C
- Clean gas
- The most common gasifier type





FLUIDIZED BED

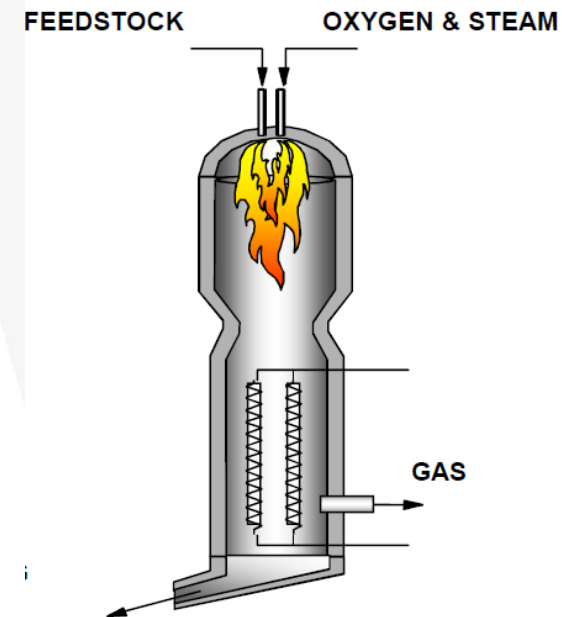
- Output > 20 MWth
- Feedstock size < 10 mm
- Gas temperature < 800 °C

BUBBLING FLUIDIZED BED (BFB)

- Fluidizing velocity 1 - 3 m/s
- Long residence time

CIRCULATING FLUIDIZED BED (CFB)

- Fluidizing velocity 3 - 10 m/s
- Higher output/diameter
- Reactive feedstocks

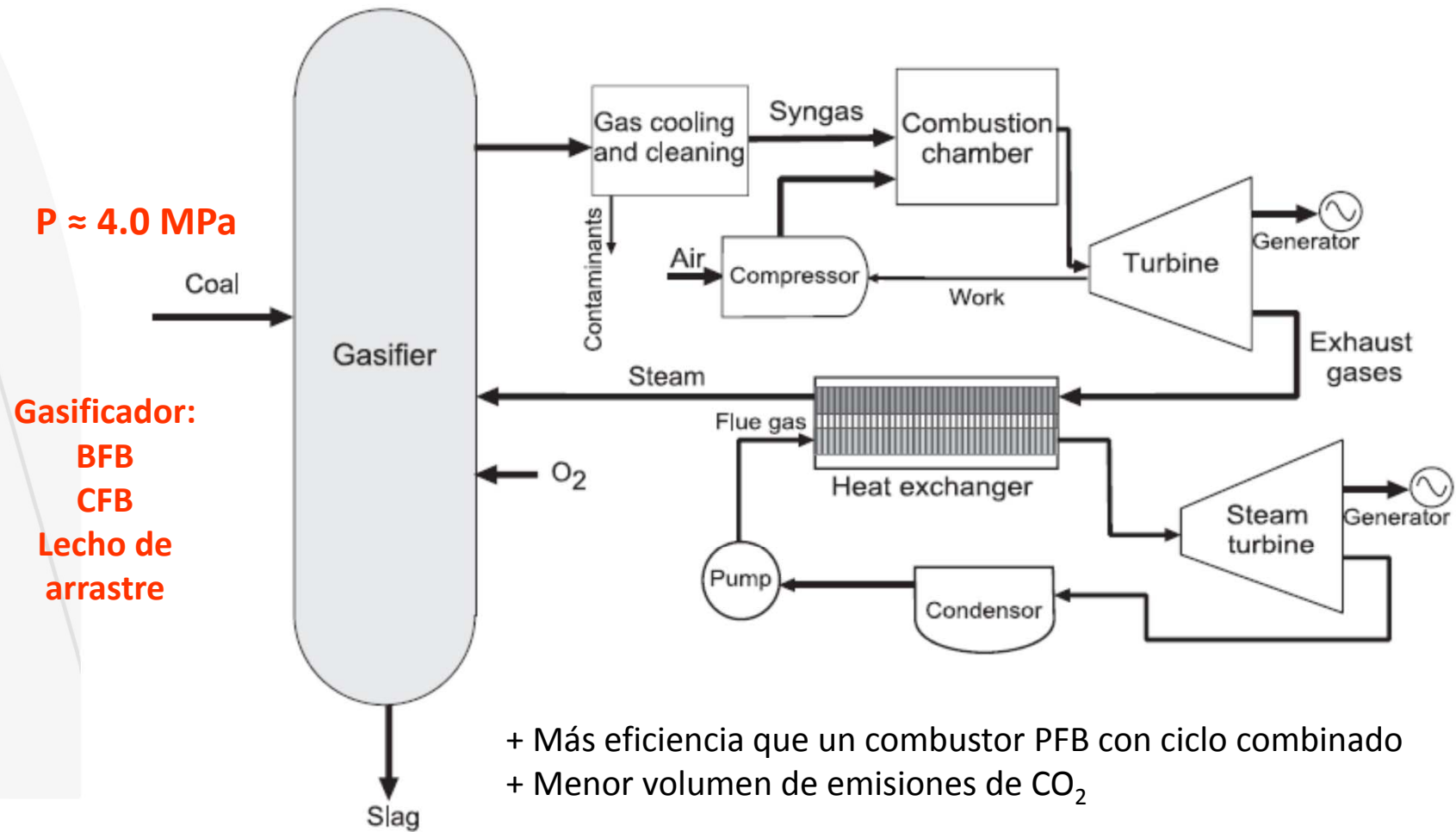


ENTRAINED FLOW

- Output > 100 MWth
- Feedstock size < 0.1 mm
- Coal, oxygen gasification
- Gasification temperature 1300 - 1700 °C
- Usually pressurised reactors
- Texaco, Shell, Prenflo

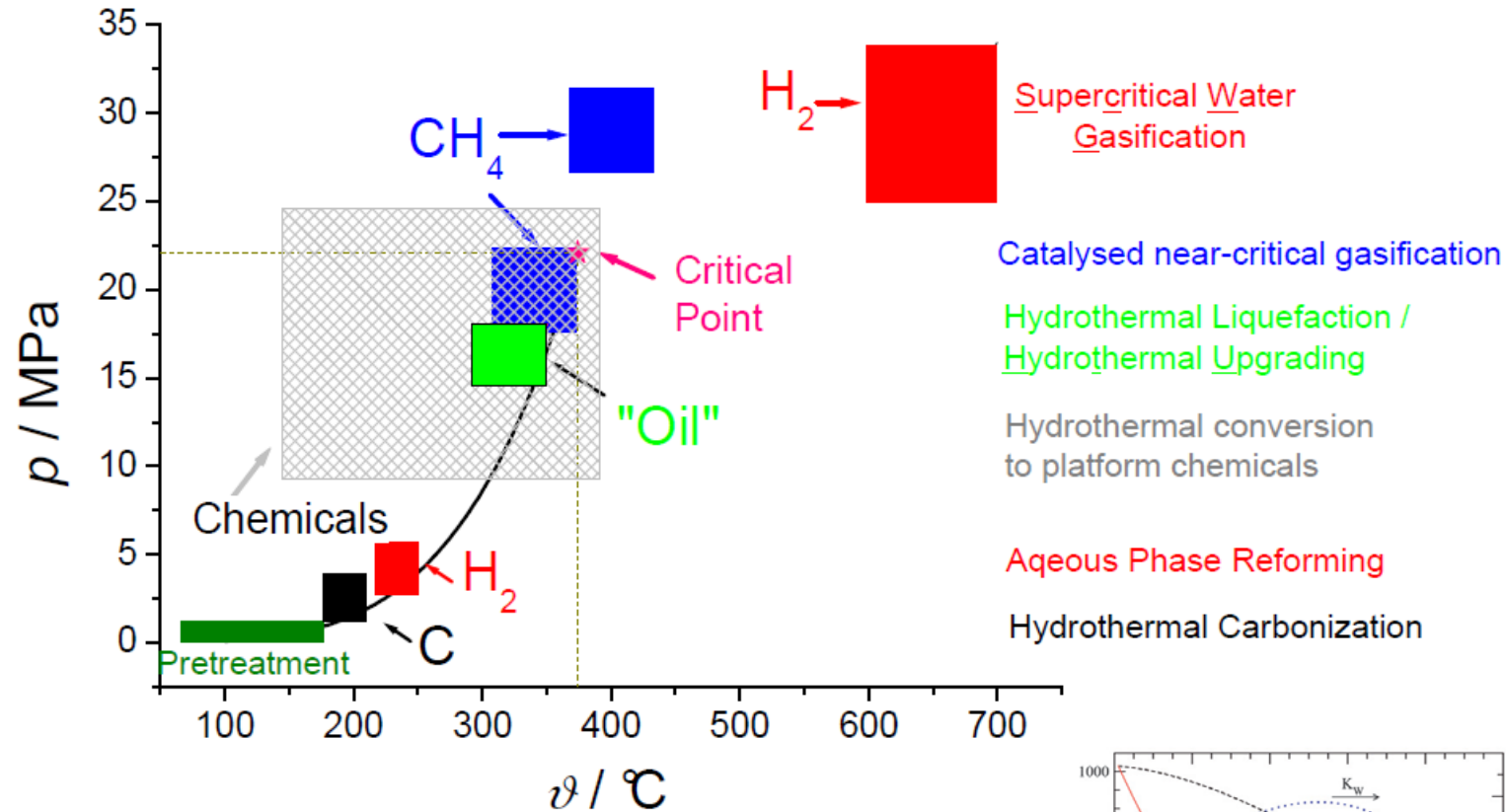
Gasificación integrada en ciclo combinado (IGCC)

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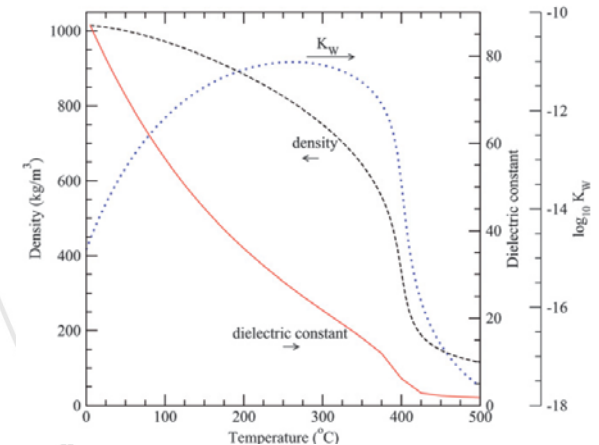


- + Más eficiencia que un combustor PFB con ciclo combinado
- + Menor volumen de emisiones de CO₂
- Mayor coste de instalación
- Problemas: alquitranes, H₂S y NH₃.

Procesado Hidrotermal (HTC/HTL/HTG)



A. Kruse. *J. Supercritical Fluids* **2009**, 47: 391



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rewind

HTC

HTC is an **exothermic process** that lowers both the oxygen and hydrogen content of the feed (described by the molar O:C and H:C ratio) by 5 main reaction mechanisms which include hydrolysis, dehydration, decarboxylation, polymerization and aromatization (Funke and Ziegler. *Biofuels Bioprod. Biorefin.* **2010**, 4, 4160-4177).

