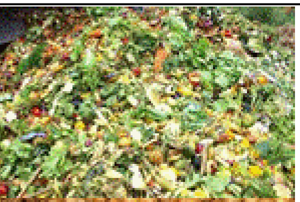

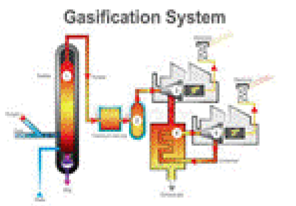

Thermochemical processes

Pyrolysis

Pyrolysis Products

Biochars and applications

Maria Bernardo

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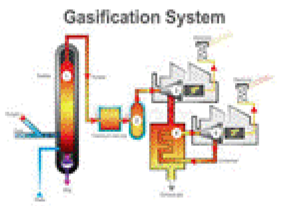


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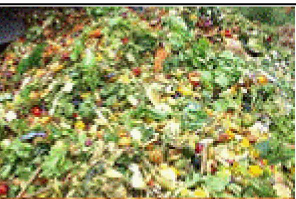
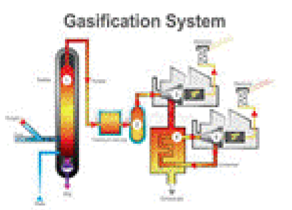
Departamento de Química
NOVA School of Science and Technology
Universidade NOVA de Lisboa




LAQV requimte | Laboratório Associado

Laboratório Associado para a Química Verde (LAQV)

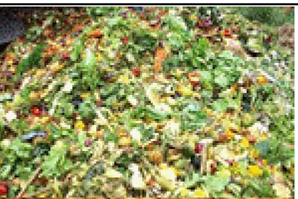
Associated Laboratory for Green Chemistry (LAQV)

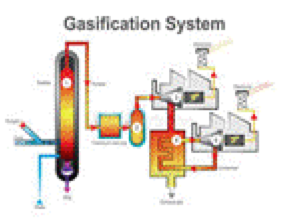
mac

Materials for Adsorption and Catalysis Group @ REQUIMTE

Materials for Adsorption and Catalysis Group

http://sites.fct.unl.pt/mac/




Materials for Adsorption and Catalysis Group

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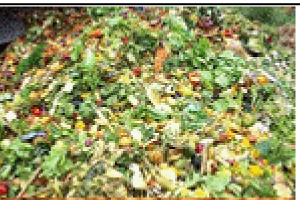
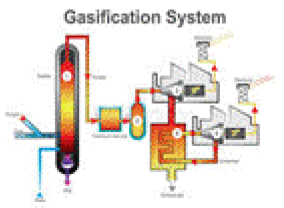
Synthesis of Materials

- Carbon materials: Biochars and Porous Carbons
- Mesoporous Silicas
- (Bio)Polymeric Materials
- Oxide Nanoparticles
- Catalysts

Applications

- Biofuels Production
- Waste Valorization
- Water/Gas Treatment
- Heterogeneous Catalysis
- Drug Delivery





Biomass/Biowastes

Organic matter from plants and animals (and fungus, bacteria,…)

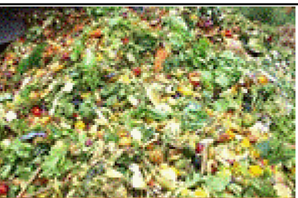
Renewable

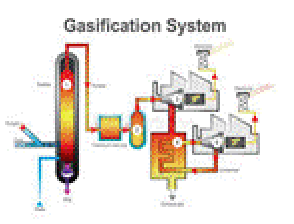
Used as chemical energy vector

Solid and liquid Biomass/Biowastes:

"biodegradable fraction of products, waste and residues from biological origin from agriculture, including vegetal and animal substances, from forestry and related industries, including fisheries and aquaculture, as well as the biodegradable fraction of waste, including industrial and municipal waste of biological origin"

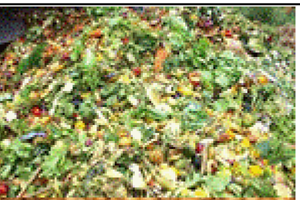
Directive EU 2018/2001 renewable energies

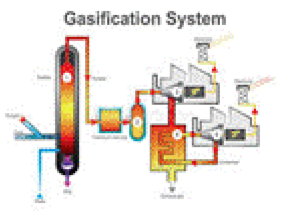




Solid Biomass/Biowastes

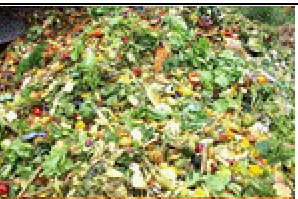
- Lignocellulosic materials
- Forestry
- Wood transformation Energetic Crops
- Agriculture
- Agrofood industry
- Pulp and paper industry
- Organic fraction of MSW
- Sewage sludge …
- …

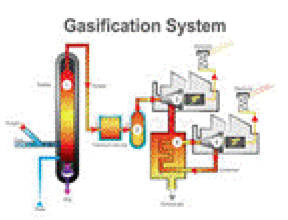


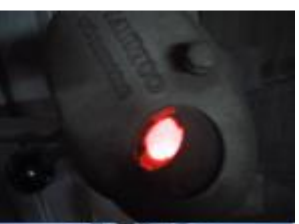




Liquid biomass/biowastes

- Agroindustry effluents: pig, poultry and dairy farms, etc.
- Agri-food industry effluents: breweries, dairy, vegetable oils, greases, etc.
- Pulp and paper industry effluents
- Sludges
- Other industrial wastewaters






BIOENERGY

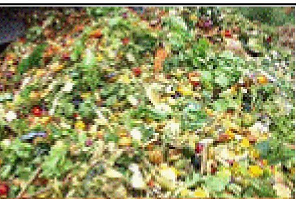
Energy from biomass (vegetal and animal organic matter)

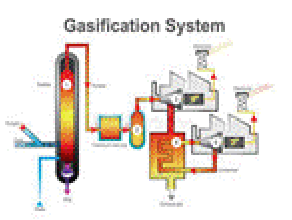
Conversion of the chemical energy contained on the biomass into another form of energy and products (Chemical – fuels, thermal – heat, electric – electricity)

Energetic vector with "neutral CO2 emissions"

The oldest way of renewable energy!

Direção Geral de Energia e Geologia

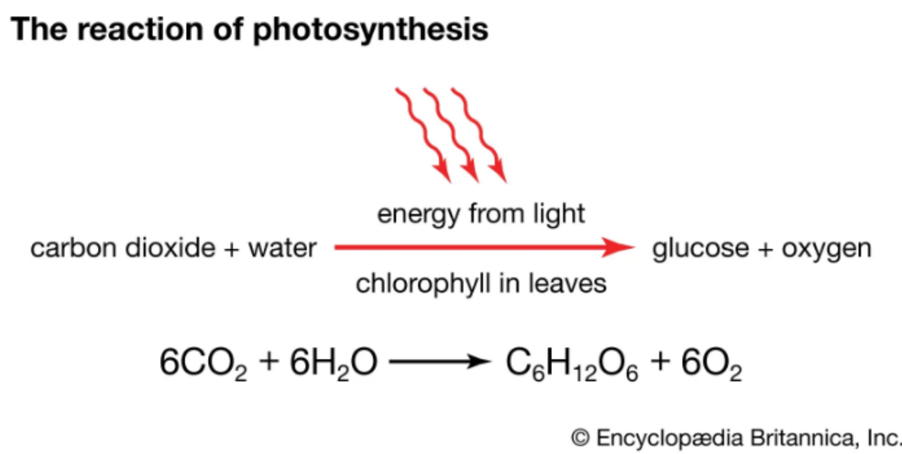


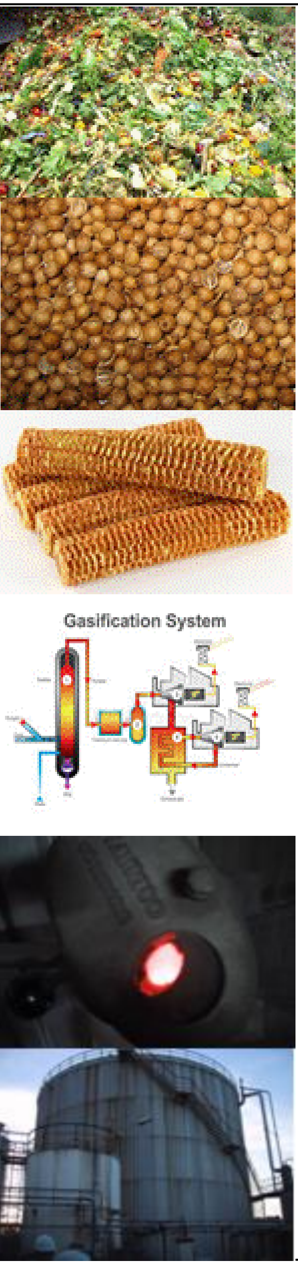

Where does it come from the chemical energy of biomass?

Photosynthesis !

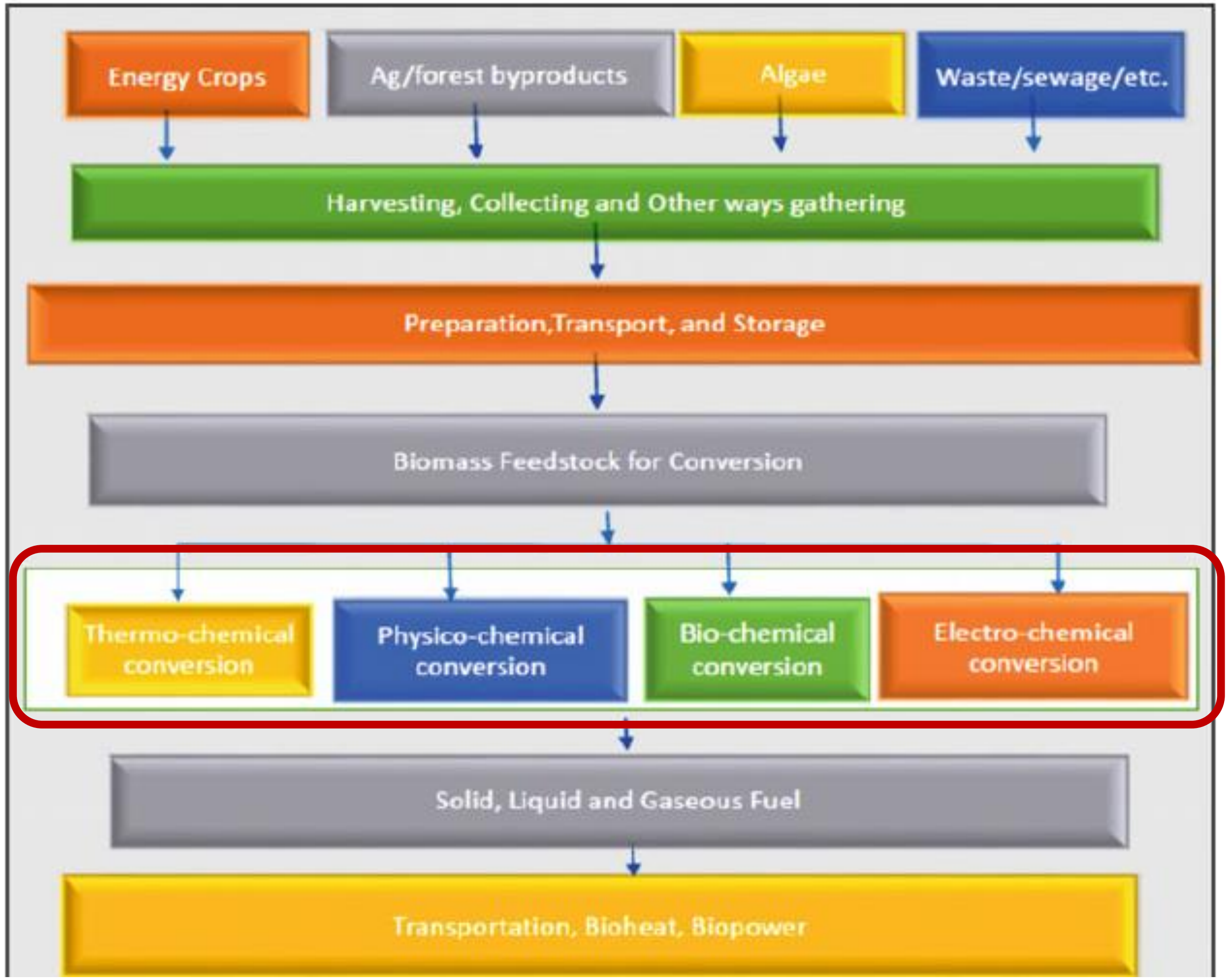
Biomass has its origin on solar energy



Chemical energy of the bonds C-C, C=C, C-H, C-O, H-H,

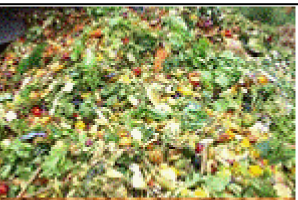


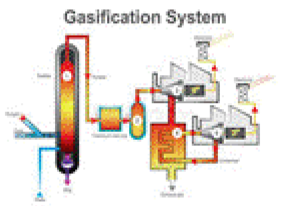
Biomass conversion



Practices and Perspectives in Sustainable Bioenergy, Mitra, Madhumi, Nagchaudhuri, Abhijit (Eds.), Springer India, 2020

Biomass conversion





Basically:

Thermochemical: heat (temperature), chemical energy conversion

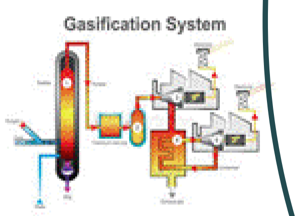
Physical: chipping, densification (pellets, briquets), extraction

Chemical: transesterification, hydrolysis

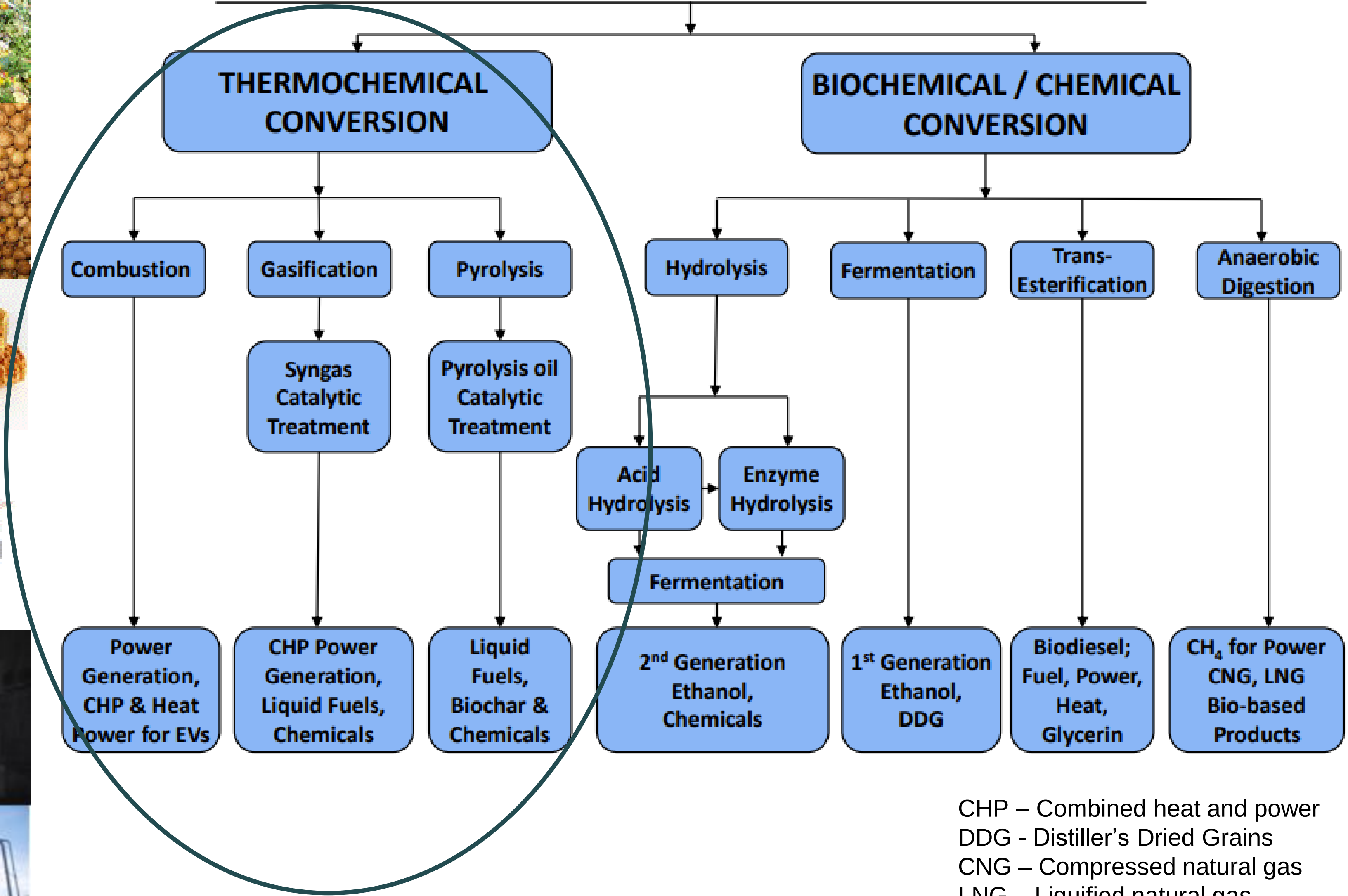
Biochemical: Biological and chemical processes, microorganisms (fermentation, digestion)

Electrochemical: oxidation/reduction reactions, electrochemical cells



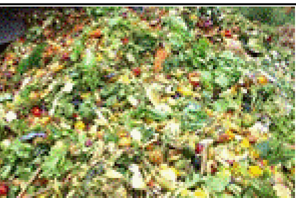



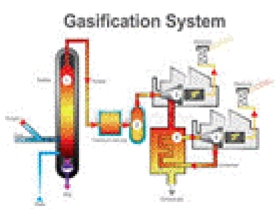

BIOMASS-to-BIOENERGY & BIOPRODUCTS CONVERSION PATHWAYS



CHP – Combined heat and power
DDG - Distiller's Dried Grains
CNG – Compressed natural gas
LNG – Liquified natural gas

Practices and Perspectives in Sustainable Bioenergy, Mitra, Madhumi, Nagchaudhuri, Abhijit (Eds.), Springer India, 2020



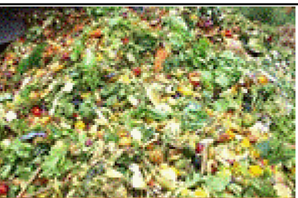

Biochemical conversion

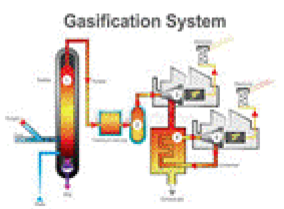
Biomass with C/N ratio < 30 and moisture > 30%

Example: wastewaters, organic fraction MSW, aquatic cultures, agroindustry effluents, etc.

Thermochemical conversion

Biomass with C/N ratio > 30 and moisture < 30%
Solid biomass, lignocellulosics.




Termochemical *vs* Biochemical

Feedstock flexibility

Complete conversion (high productivity)

High reaction rates

Short reaction times

Wastes reduction 70-80% mass and 80-90% volume

Use of microorganisms, enzymes and/or chemicals

Limited productivity

Only one product or few

Susceptible to climatic conditions

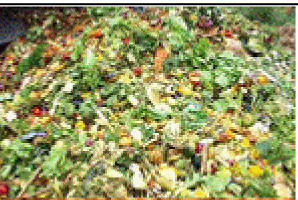
Low reaction rates

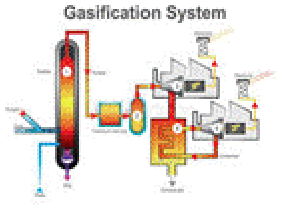
High reaction time

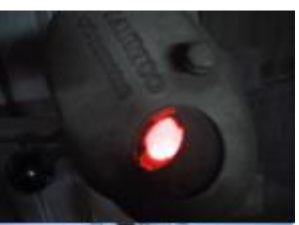
Sludges by-product

But…thermochemical processes have disadvantages

Energetic cost, pollutants emissions, biomass types *vs* technologies, among others.







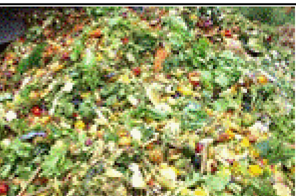
Thermochemical conversion of biomass

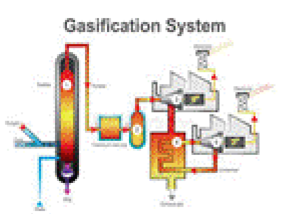
Chemical energy conversion into chemical, thermal and electrical energy and other bioproducts

Conversion of biomass components at high temperature in the presence or absence of oxygen, into solid, liquid or gaseous products

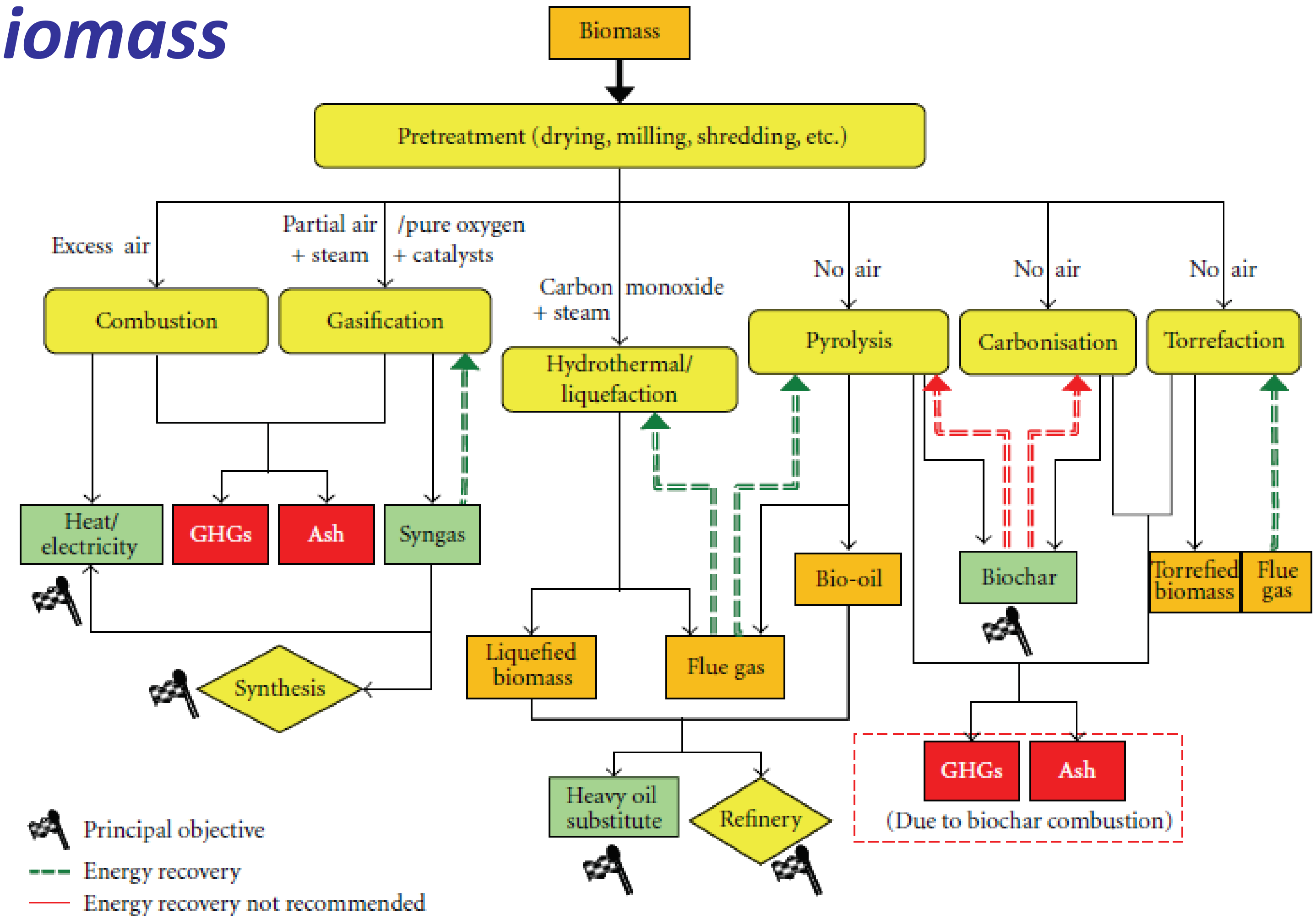
Biomass transformation into fuel products, energy (heat, electricity), chemicals, bioproducts

Degradation or decomposition (by means of chemical reactions) of the organic matter at high temperatures

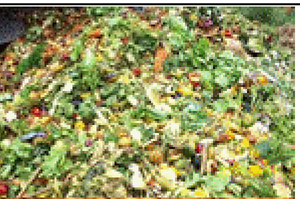


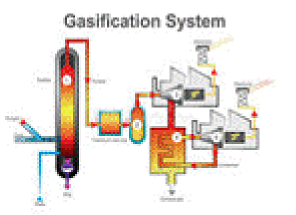


Thermochemical conversion of solid biomass



"Biofuels Production from Biomass by Thermochemical Conversion Technologies", International Journal of Chemical Engineering, 2012. https://doi.org/10.1155/2012/542426




Thermochemical processes

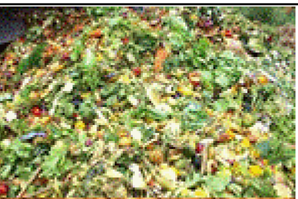
Solid biomass with low moisture content

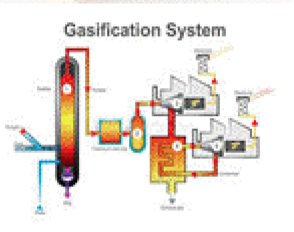
Classification according the involved oxygen

% air →

- Without oxygen ↓ **PYROLYSIS (without oxidation)**
- Limited oxygen ↓ **GASIFICATION (Partial oxidation)**
- Excess oxygen ↓ **COMBUSTION/Incineration (complete oxidation)**

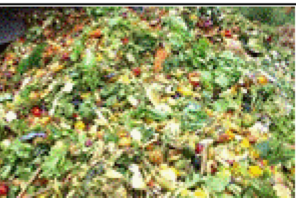
Oxygen supply in the stoichiometric quantity for complete combustion

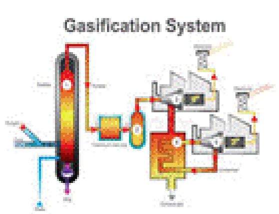




Thermochemical processes

	Combustion	Gasification	Pyrolysis
Main products	Heat, flue gas (CO_2, H_2O)	Flue gas (CO, H_2, CH_4), heat, ashes	Oils, gases (CO, H_2, CH_4), char
Source of heat	External (exothermic reactions)	External and internal (endothermic and exothermic reactions)	External (endothermic reactions)
Carbon conversion (%)	>99	80 - 95	≈ 75
Oxygen stoichiometry	> 1	0.2 – 0.4	0
Oxidants	air	Air, O_2, steam	-
Temperatures	850 - 1200	550 – 900 (with air) 1000 – 1600 (other oxidants)	500 - 800
Pressure	atmospheric	atmospheric	Atmospheric or above
By-products/ Pollutants	Particles, NOx, SO_2, Ashes, Dioxins, Furans	"Black ashes", tars, CO_2, N, Cl and S gases	Tars, N, Cl, S gases

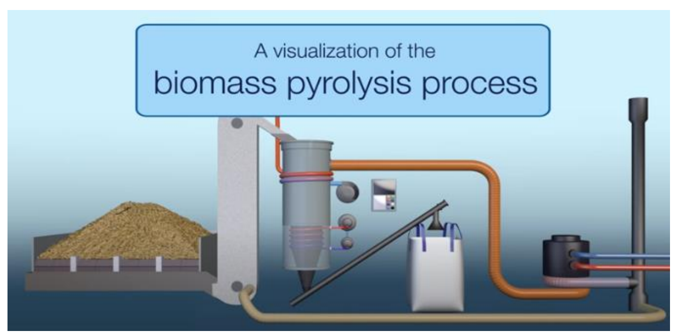


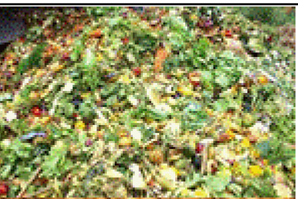

Pyrolysis

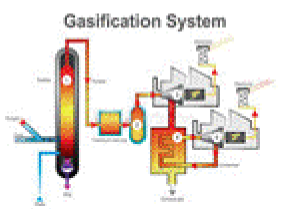
Thermochemical conversion** of organic substances (biomass and biowastes) into **liquids, gases and solids,** in the **absence of oxygen with heating

Endothermic degradation or thermolysis** (chemical bonds are broken) of organic substances in the **total absence of oxygen**, to obtain **oils, gases and chars



https://youtu.be/3K1zWAYDvMA





Pyrolysis

Biomass

Inert atmosphere (nitrogen, argon, vacuum)

Heat/Energy

Pyrolysis reactor

300 – 800ºC

No oxygen

Gas

Liquids oils

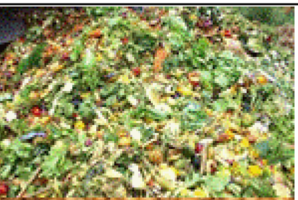
Solids Chars

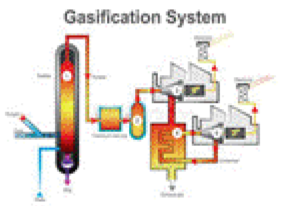
Endothermic Process

Chemical bonds cleavage and volatilization

External source of heat to maintain the pyrolytic reactor at the desired temperature

Source of heat might be the gas fraction



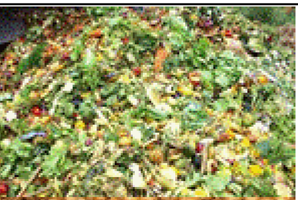

Pyrolysis - Products

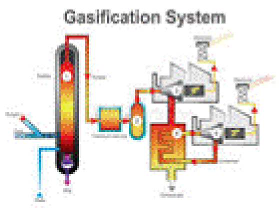
Liquid fraction – oils or bio-oils, tars (heavy oil)

Complex mixture of hydrocarbons (aromatics, oxygenated, olefins, aliphatic alkanes, cyclic alkanes, S, N - compounds) - “Crude oil”

Applications:

- Energy/heat production
- Fuels
- Fine Chemicals
- Feedstock for refining/reforming





Pyrolysis - Products

Gaseous fraction – Pyrolytic gas (≈ Syngas)

Composed by por H_2, CH_4, CO, CO_2, C_nH_m

Applications

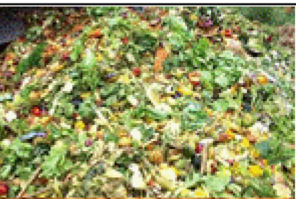
- Energy/heat production (10-40 MJ/m^3)
- Chemical synthesis

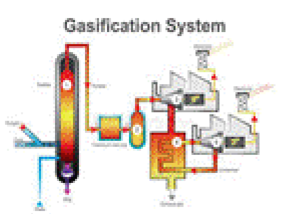
Solid fraction – Chars or biochars

Carbon material + mineral matter

Applications:

- Energy production (20-40 MJ/kg)
- Source of carbon/minerals for soils
- Activated carbon production



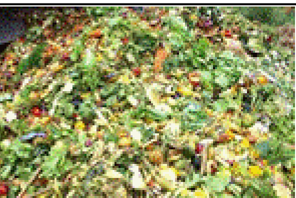

Pyrolysis types

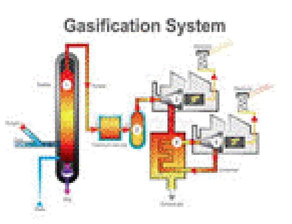
Type		Slow	Intermediate	Fast	Flash	Vacum
Temperature (°C)		300-700	500-650	500-1000	900-1200	400-600
Heating rate (°C/s)		0,1-2	1-10	10-200	> 1000	0,1-1
Residence time		min - hours	10-20 s	< 2 s	< 0,1 s	< 1 s
Pressure (MPa)		0,1	0,1	0,1	0,1	0,01-0,02
Particle size (mm)		5-50	1-5	<0.1	<0.1	< 1
Products (m/m %)	Liquids	30	50	75	> 75	60
	Gases	35	30	13	< 13	20
	Chars	35	20	12	<12	20

Low temperatures and long residence times – solids production (**carbonization**)

High temperatures and long residence times – gases production

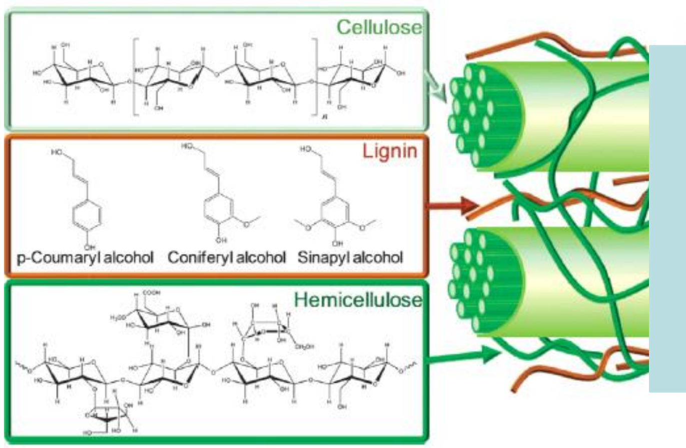
Moderate temperatures and short residence times – liquids production





Biowastes

Renewable, low cost, sustainable, abundant, easy-available

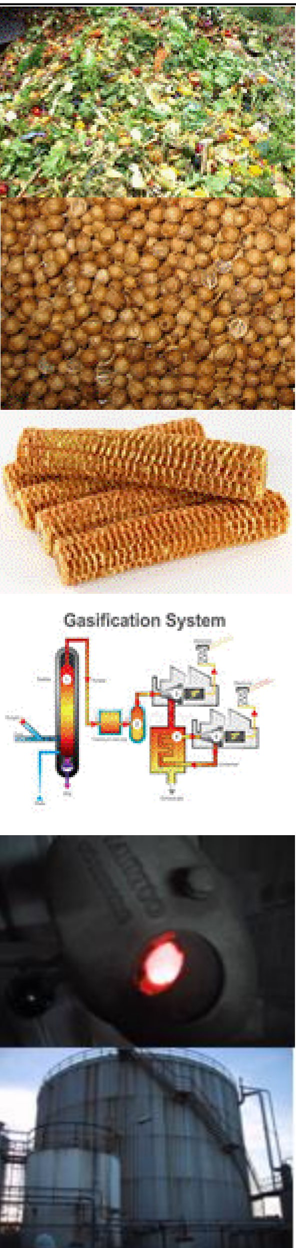


Lignocellulosic biomass

40–50% cellulose
20–30% hemicellulose
20–25% lignin
1–5% mineral matter

Soft, compressible, low density:
Shells/Peels/Straws: rice, peanut, fruits, vegetables,...

Hard, high density:
Wood, Stones nutshell herbaceous,…



Pyrolysis/
Carbonization

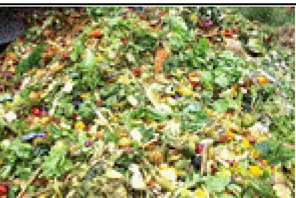
Biomass

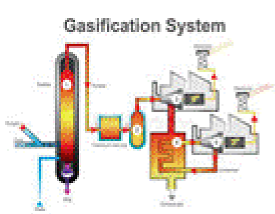
Cellulose — ≈ 10 %

Hemicellulose — 20-30 %

Lignin — 40-50 %

Biochar




Charcoal/Biochar - source

Fossil/Coal

Biomass

Non-renewable, mining, high-cost

Peat, lignite, bituminous, anthracite, graphite

Carbon content (C)

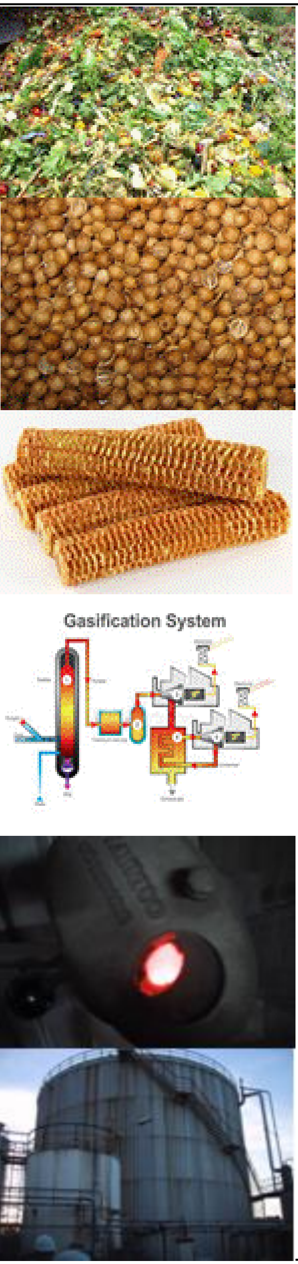


Renewable, low cost, abundant

Wood, Agro-forestry and food wastes,…

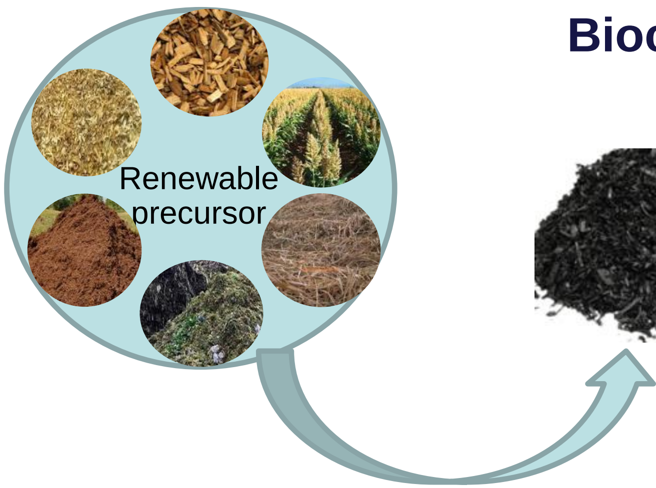


Precursors with high fixed carbon content



Char ≈ Biochar ≉ Charcoal ≈ Coal

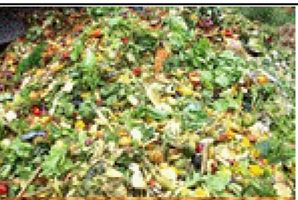
Biomass

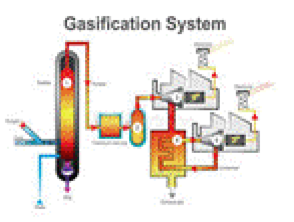


Pyrolysis/
Carbonization

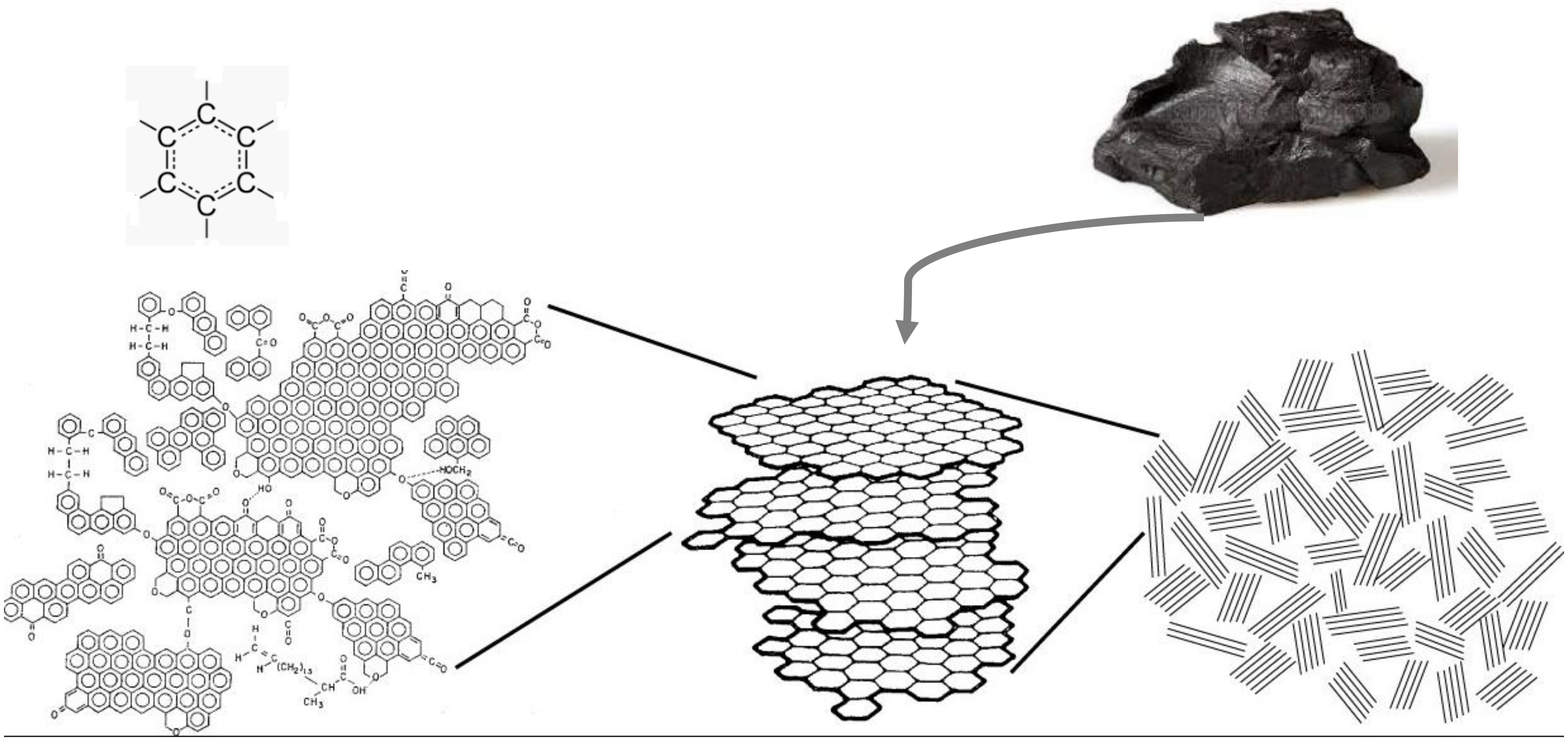
Biochar

Charcoal - fossil

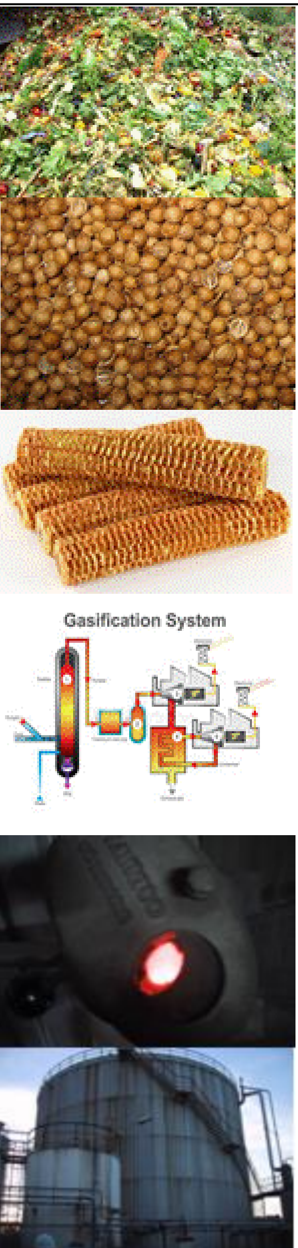



Biochar – Amorphous Carbon

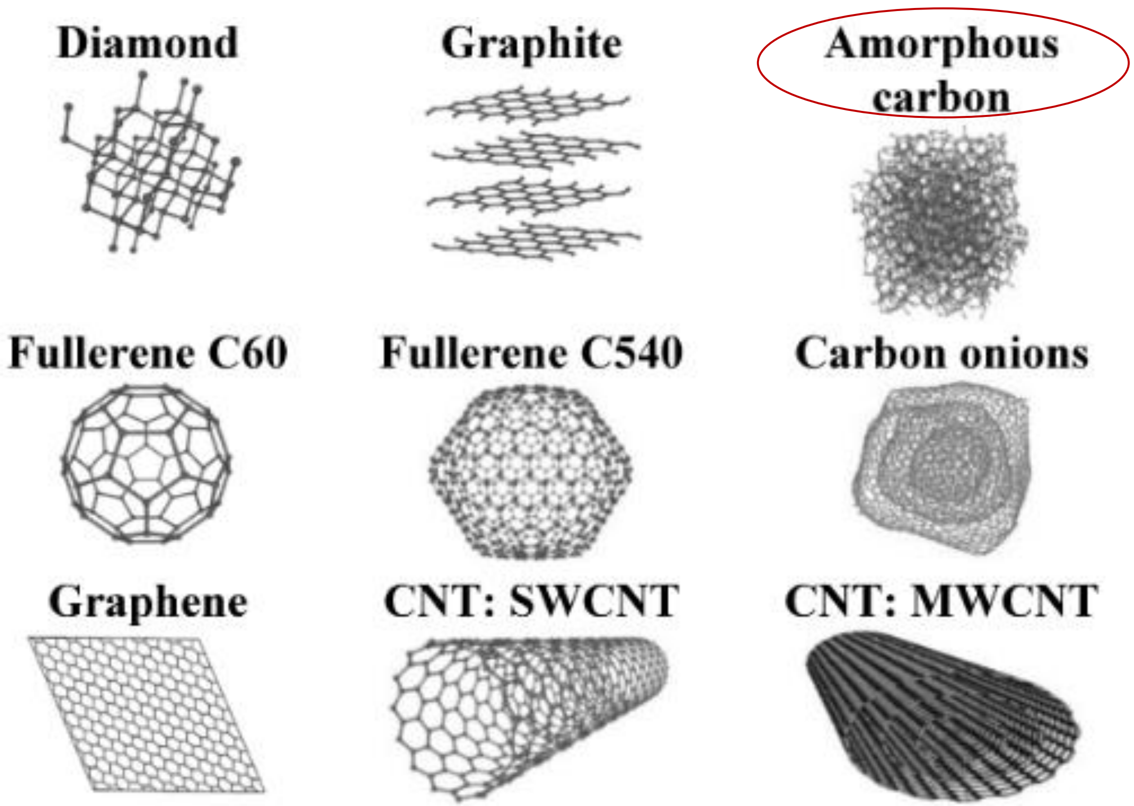


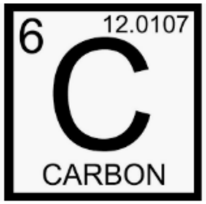
Solid product from the decomposition of organic matter
Composed mianly by carbon (C)
H, O, N, S, minerals,…

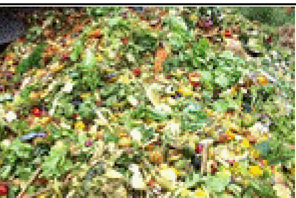


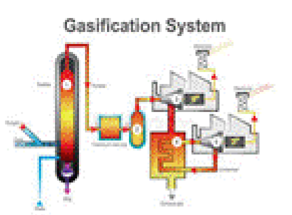
Carbon materials

Carbon allotropes









Biochars

- Biomass
- Operational conditions

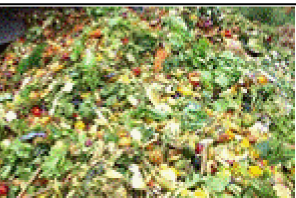
↓

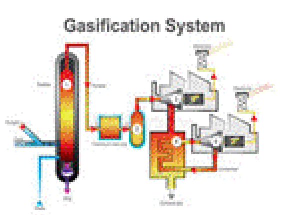
- Incipient porosity
- (Surface area: 5 – 300 m^2/g)
- Tars
- Metals
- Minerals

CO_3^{2-}, SiO_3^{2-}, PO_4^{3-}

Na, Ca, K, Mg,...

Zn, Pb, Ni, Cr,…



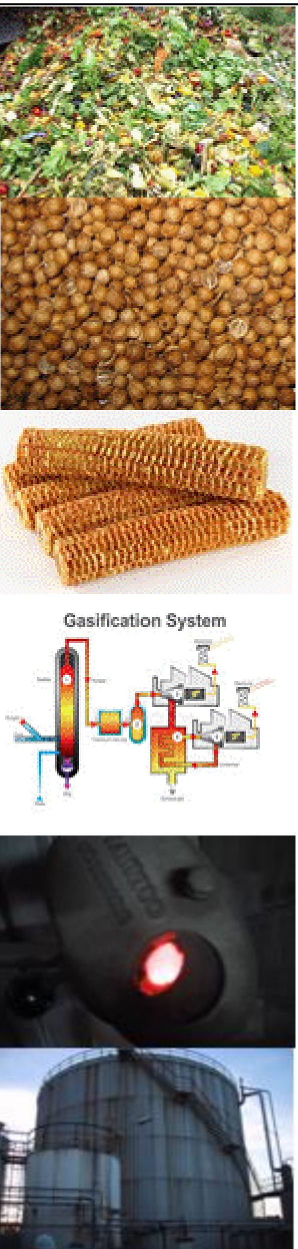




Biochars - *Applications*

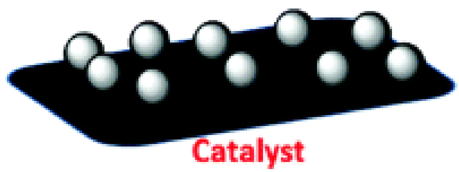
Fuel
Barbecue
(PCS: 15-32 MJ/kg)

Soil amendment
Water retention
Source of carbon/Carbon sequestration
Source of nutrients

Adsorbent
Water treatment (Pollutants removal)
Flue gas treatment (COx, NOx, SOx removal)

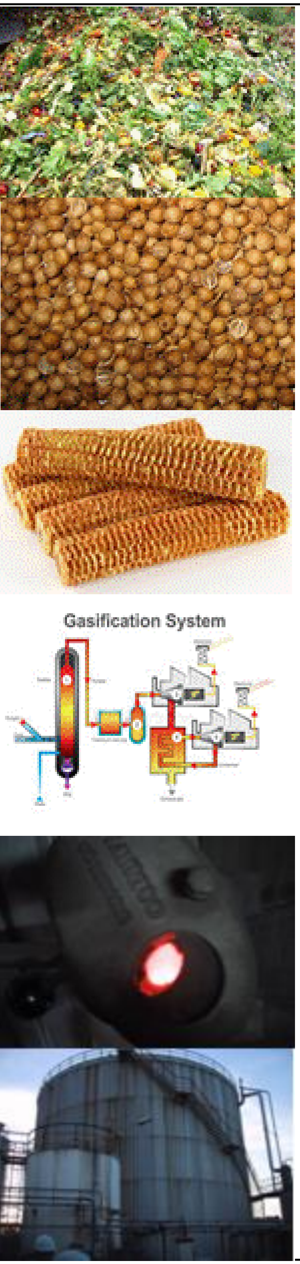


Biochars - *Applications*



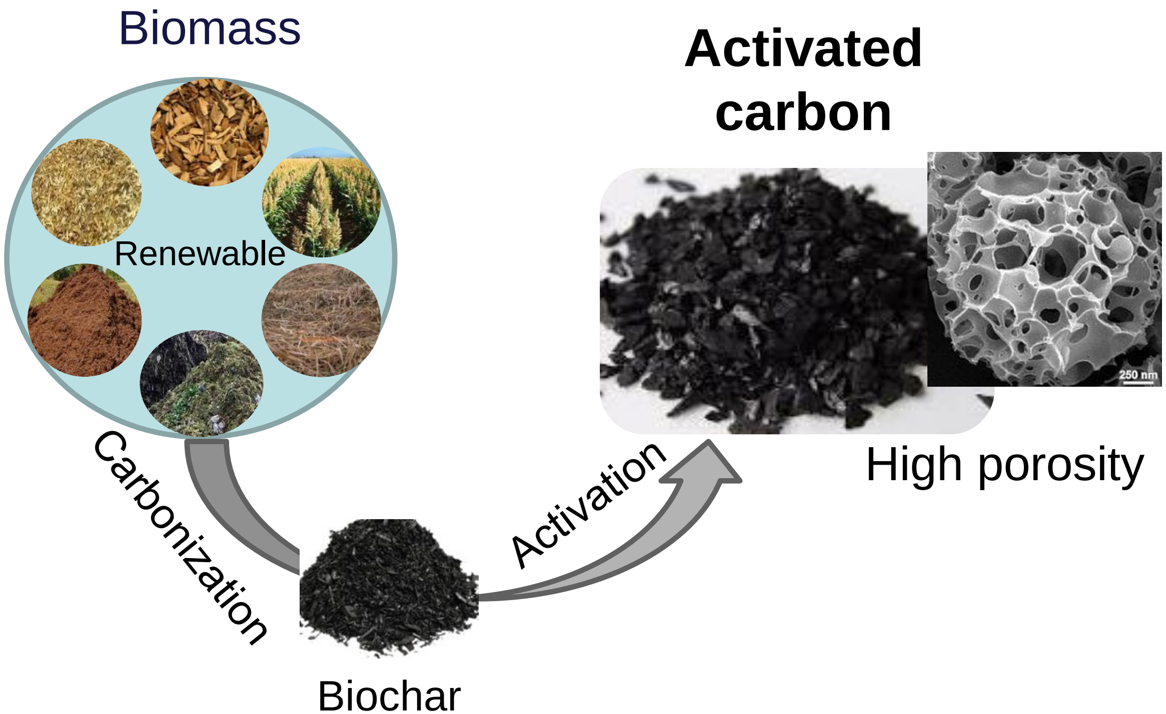
Catalyst
Tar cracking at gasification
Fuels production
NOx conversion

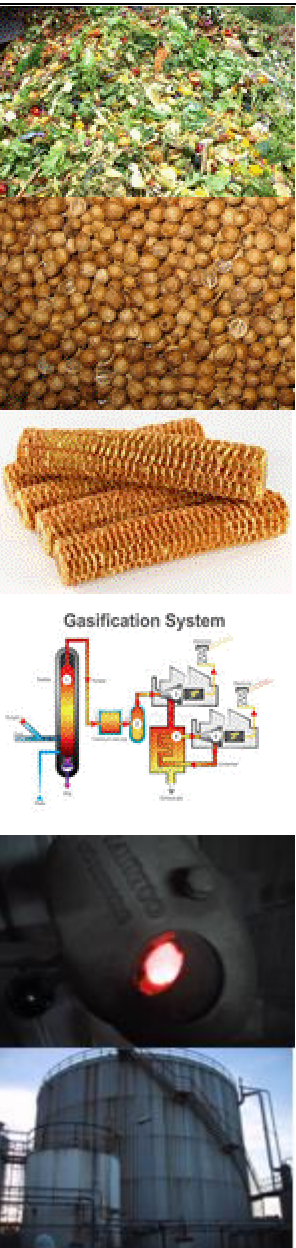
Energy Storage
Supercapacitor (Electrode)
Batteries (anode)



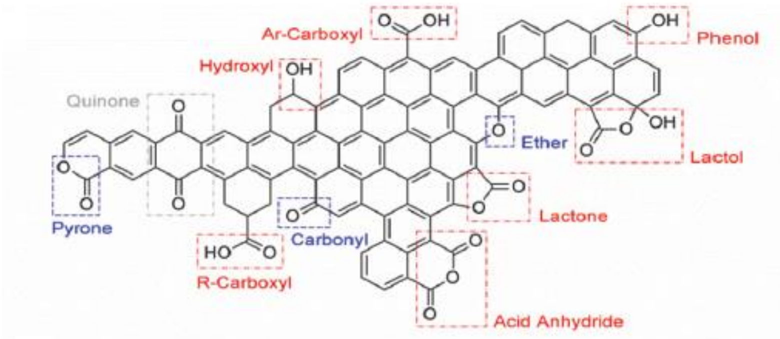
Biochar – *Applications*

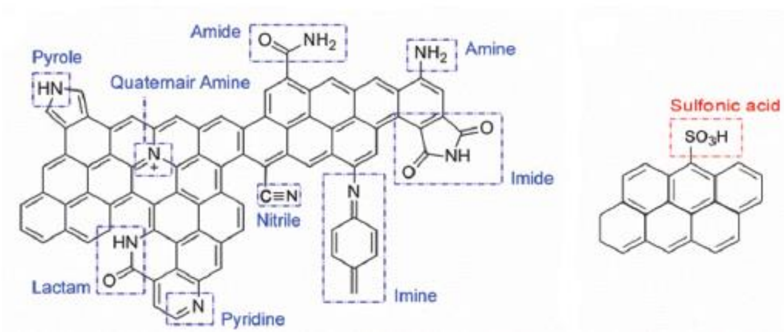
Precursor of Activated Carbon

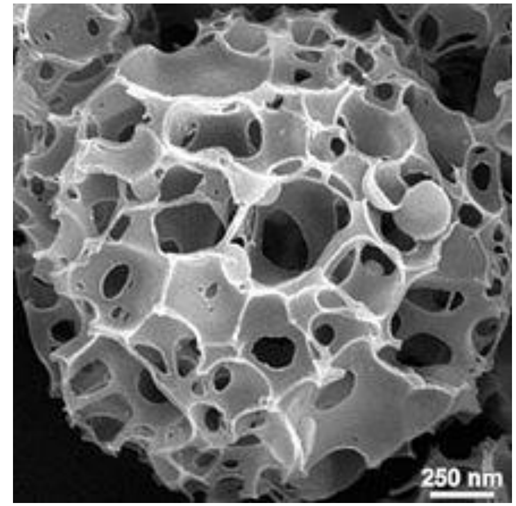


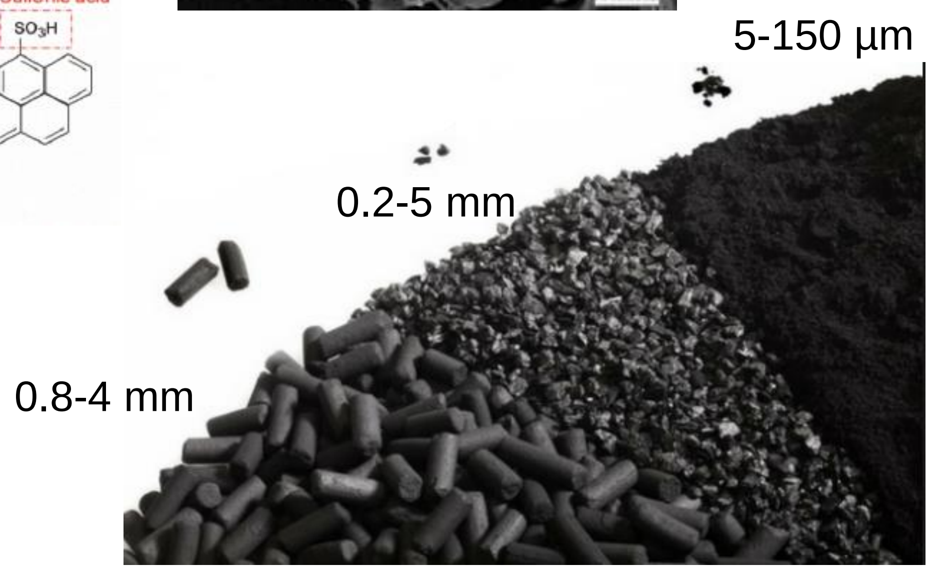


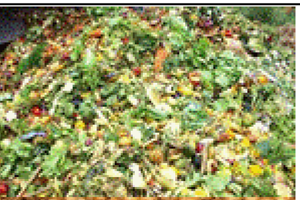
Activated carbon

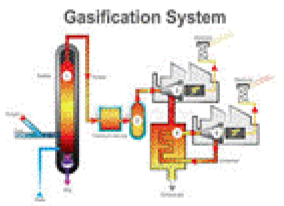




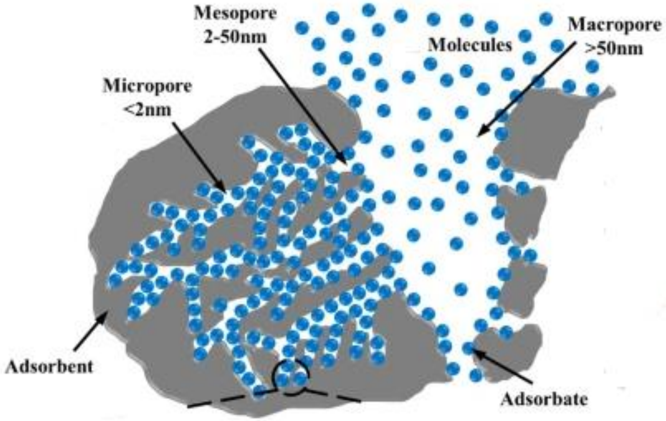


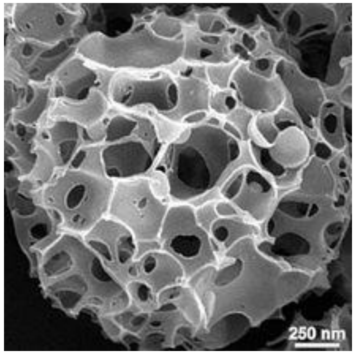


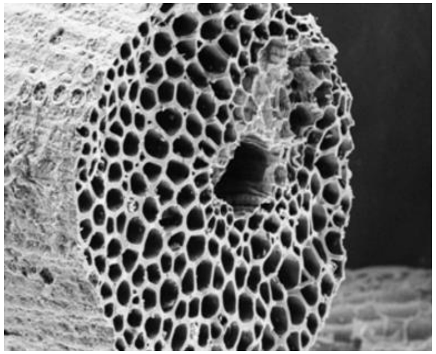



Activated carbon ≈ Activated charcoal





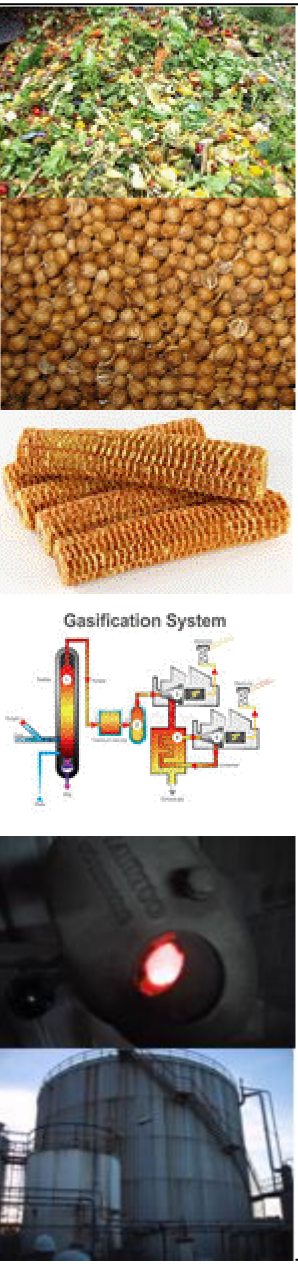


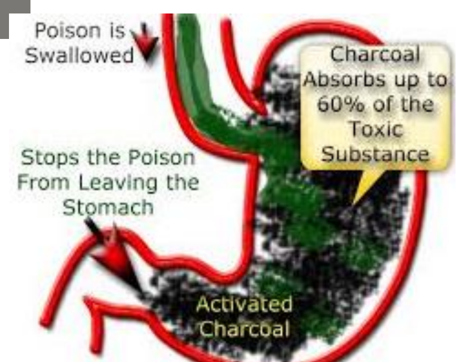
High porosity
Surface area ≈ 1000 - 3000 m²/g

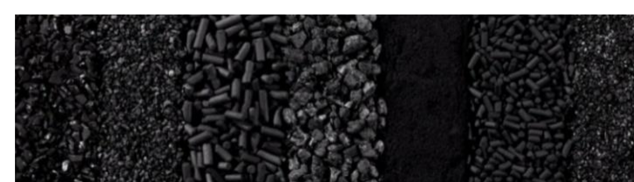
N_2 molecule - 0.162 nm²

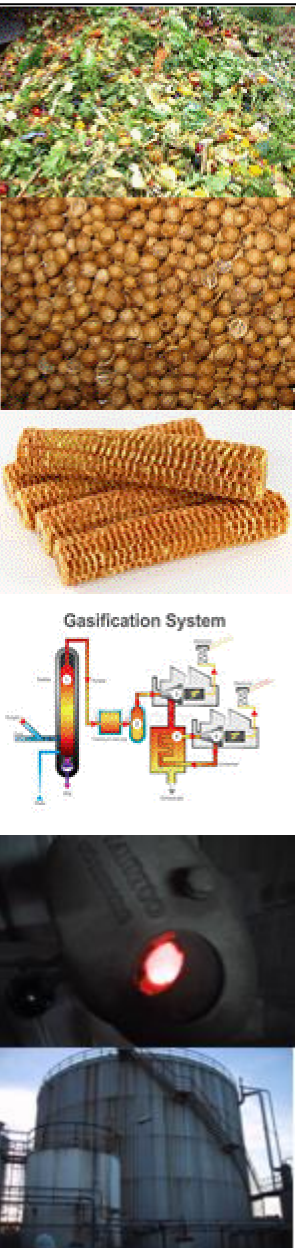
Micropores < 2 nm
Mesopores 2<Ø<50 nm
Macropores > 50 nm

Activated carbon – Commercial applications



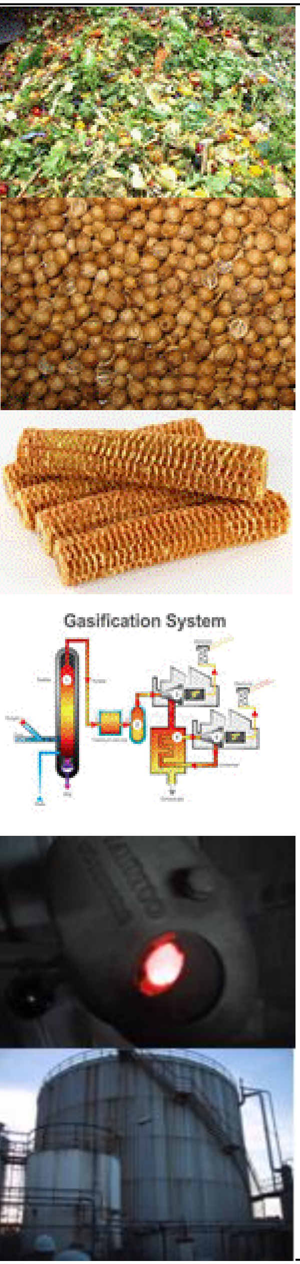






Activated carbon – Industrial applications

- **Adsorption; Energy storage; Chemical industry (catalysis)**



Activated carbon

Biochar

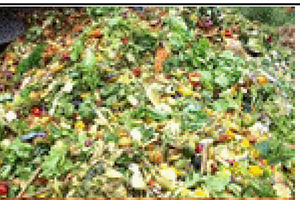
Chemical activation

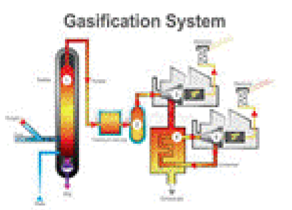
H_3PO_4, H_2SO_4, NaOH, KOH, $ZnCl_2$, K_2CO_3,…

Physical activation

Steam, Air, CO_2, ozone

Activated carbon





Chemical Activation

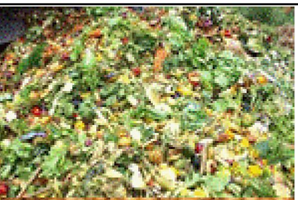
H_3PO_4, H_2SO_4, NaOH, KOH, $ZnCl_2$, K_2CO_3,…

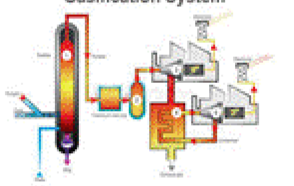
- Precursor impregnation
- Temperatures: 400-800 °C
- Advantage: Carbons with higher surface area, lower activation times
- Disadvantage: the removal of excess activation agent

Physical activation

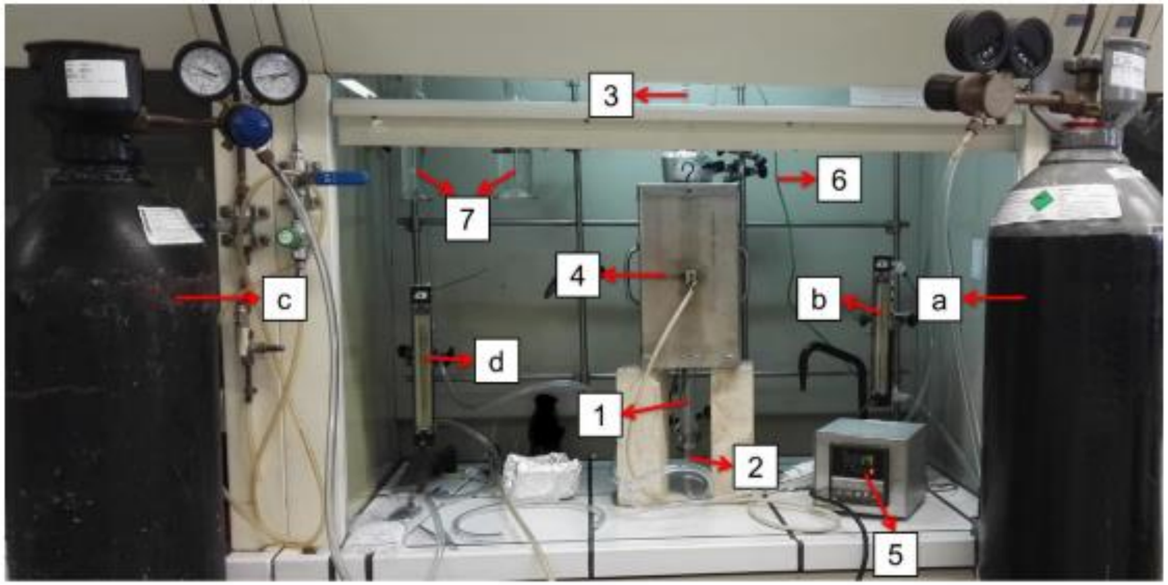
Steam, Air, CO_2, ozone

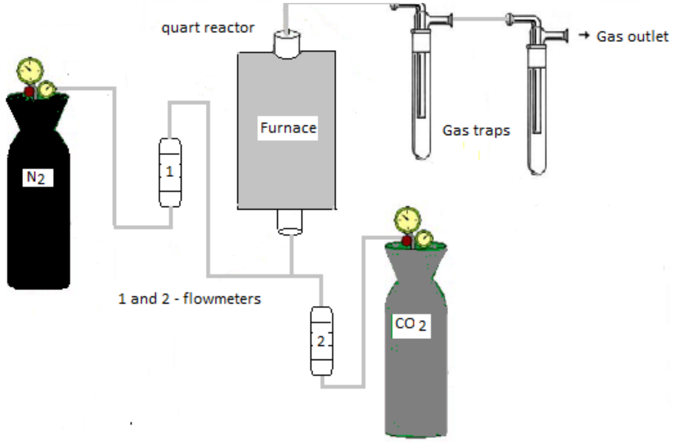
- 1^{st} carbonization step: 400-850 °C
- Activation with gases at 600-1000 °C
- Advantage: No need to wash the carbons
- Disadvantage: higher temperatures and longer activation times

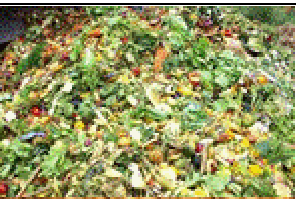


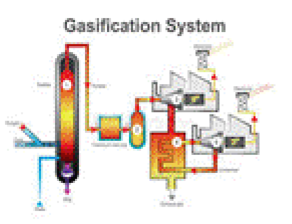


Experimental set-up - example





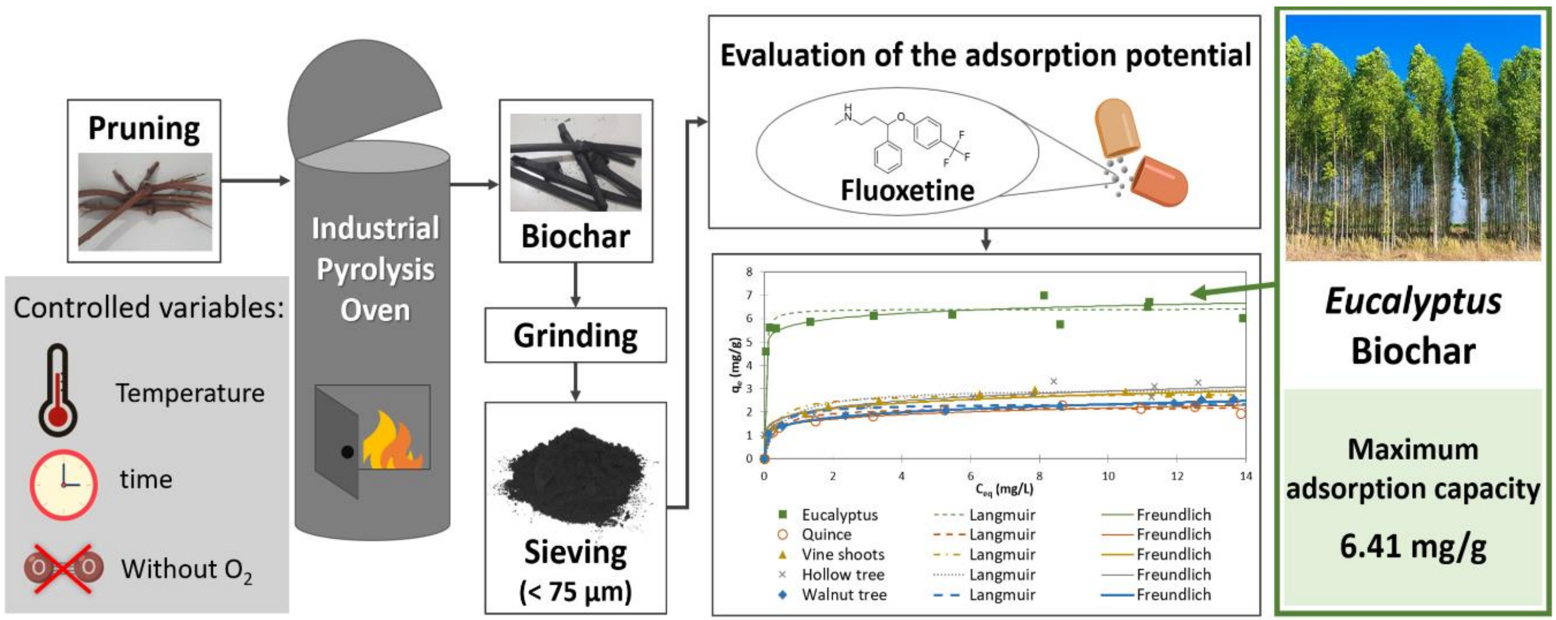


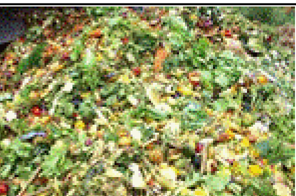

Biochars and Activated Carbons – applications

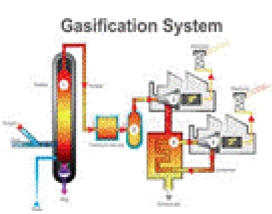
Evaluation of the adsorption potential of biochars prepared from forest and agri-food wastes for the removal of fluoxetine

Maria João Fernandes[a,b], Manuela M. Moreira[a,*], Paula Paíga[a], Diogo Dias[c], Maria Bernardo[c], Manuela Carvalho[a], Nuno Lapa[c], Isabel Fonseca[c], Simone Morais[a], Sónia Figueiredo[a], Cristina Delerue-Matos[a]



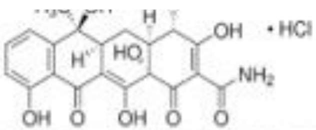
https://doi.org/10.1016/j.biortech.2019.121973



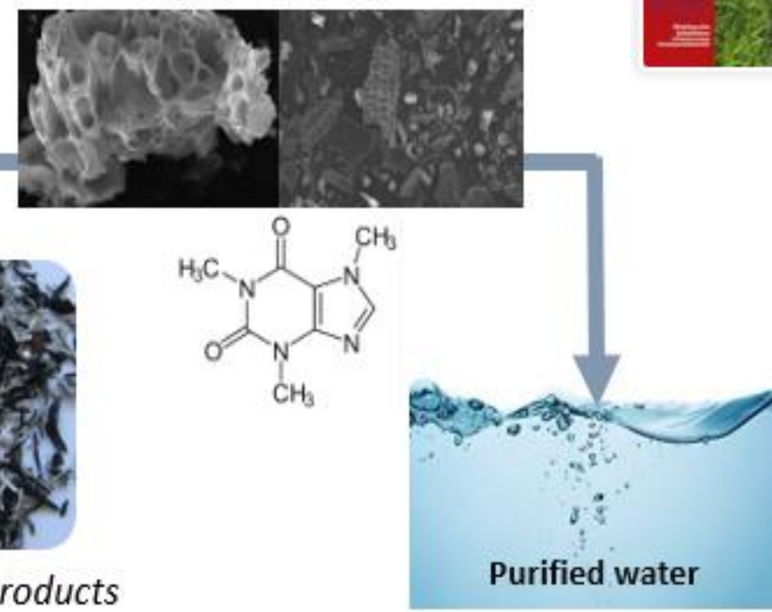



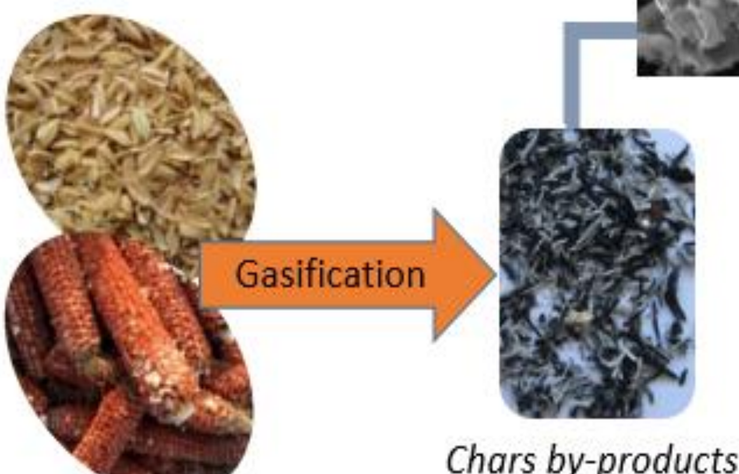

Study of the removal mechanism of aquatic emergent pollutants by new bio-based chars

Maria Manuel Serrano Bernardo[1] · Catarina Alexandra Catanas Madeira[1] · Nuno Carlos Lapa dos Santos Nunes[2] · Diogo André Costa Messias Dias[2] · Delfina Maria Barbosa Godinho[1] · Maria Filomena de Jesus Pinto[3] · Inês Alexandra Morgado do Nascimento Matos[1] · Ana Paula Batista Carvalho[4] · Isabel Maria de Figueiredo Ligeiro Fonseca[1]

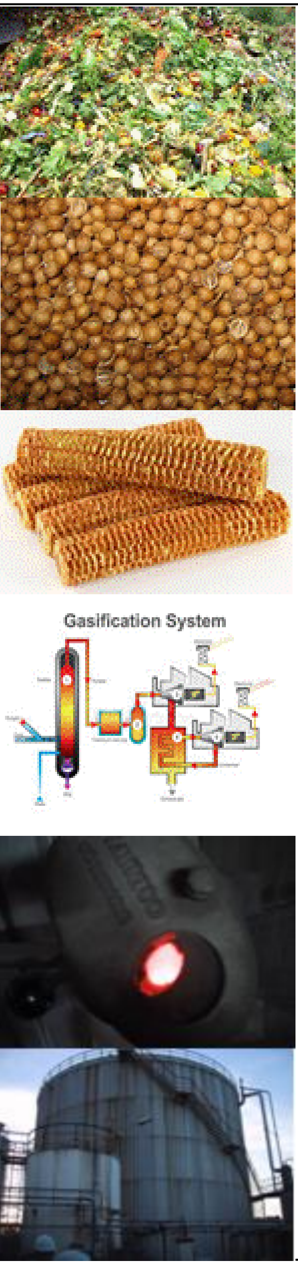


Removal of caffeine and tetracycline



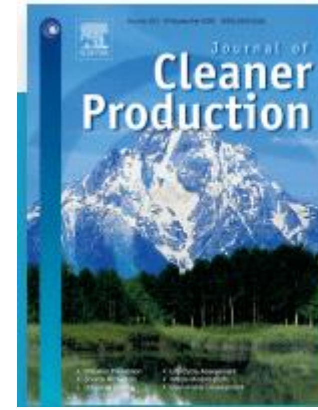


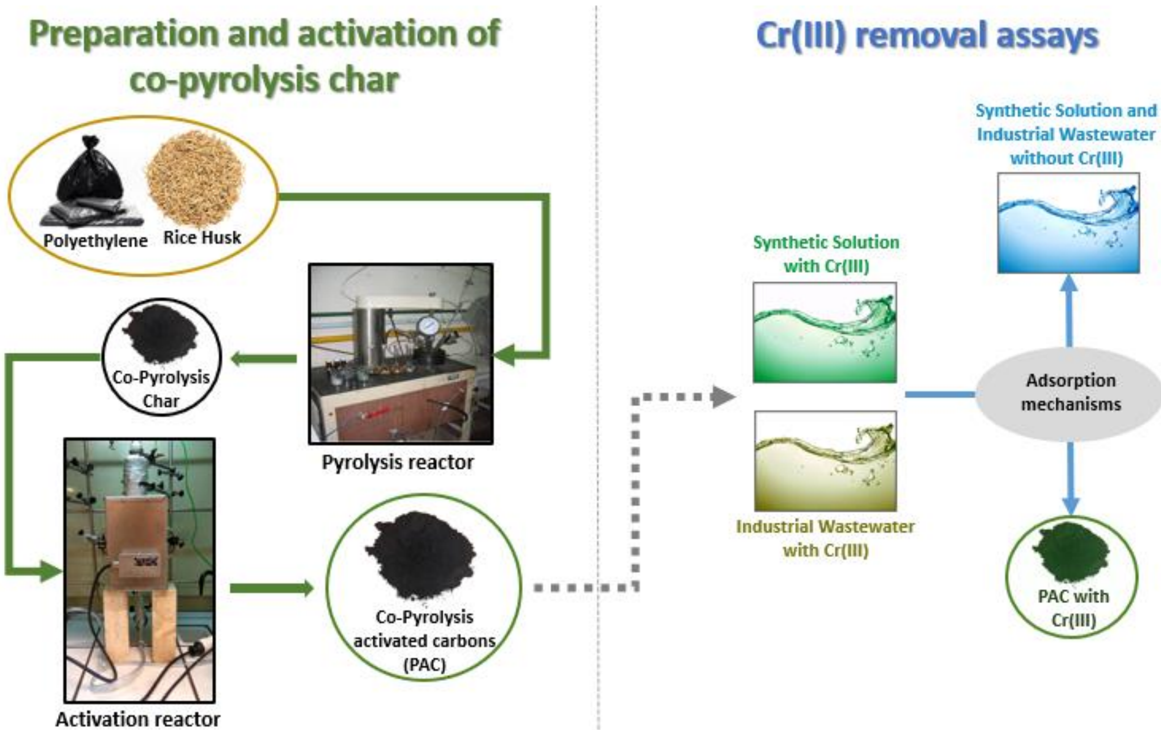
https://doi.org/10.1007/s11356-017-9938-9



Activation of co-pyrolysis chars from rice wastes to improve the removal of Cr^{3+} from simulated and real industrial wastewaters

Diogo Dias [a], Maria Bernardo [b], Inês Matos [b], Isabel Fonseca [b], Filomena Pinto [c], Nuno Lapa [a, *]





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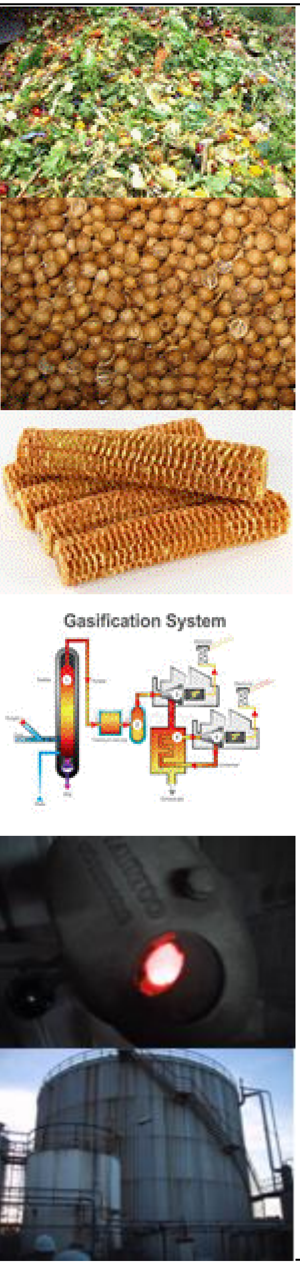
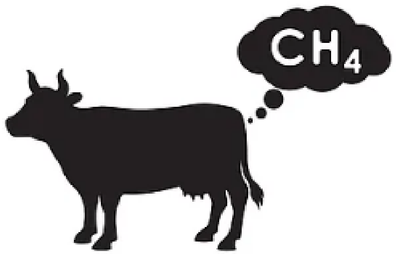
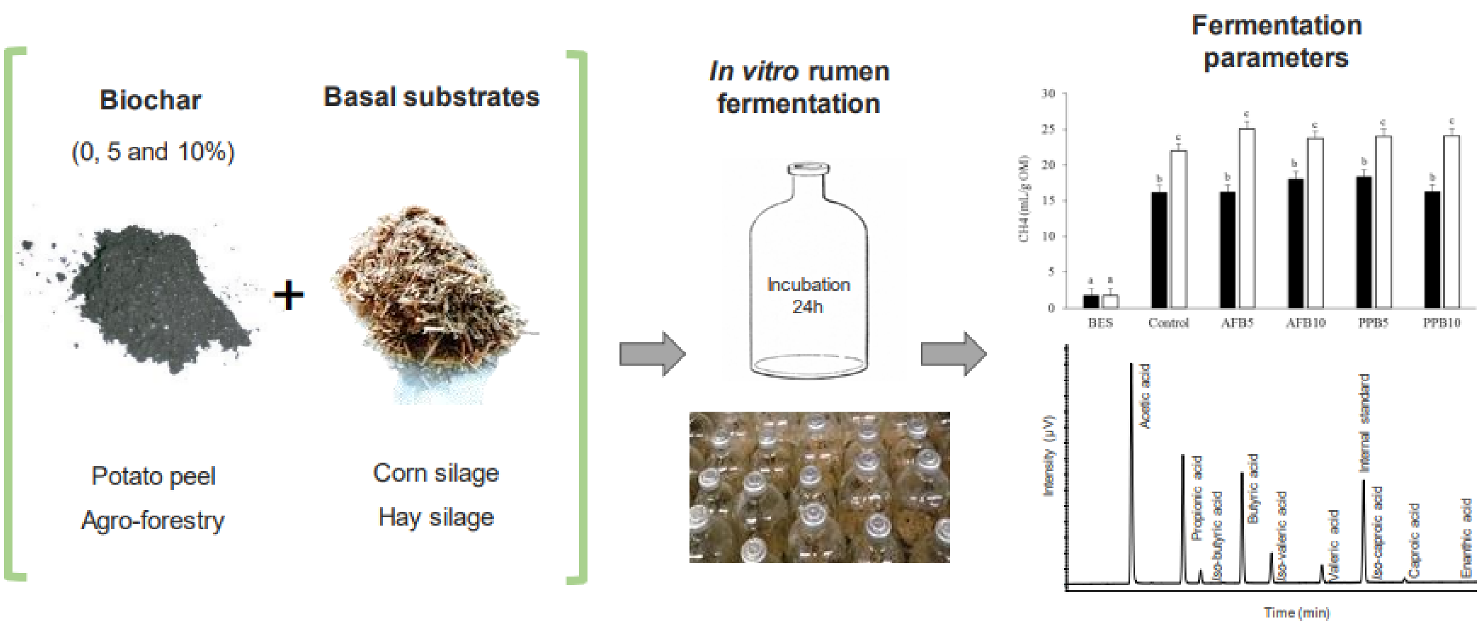


Assessment of potato peel and agro-forestry biochars supplementation on in vitro ruminal fermentation

Ana R.F. Rodrigues[1], Margarida R.G. Maia[1], Ana R.J. Cabrita[1], Hugo M. Oliveira[2], Maria Bernardo[3], Nuno Lapa[3], Isabel Fonseca[3], Henrique Trindade[4], José L. Pereira[4,5] and António J.M. Fonseca[1]

PeerJ





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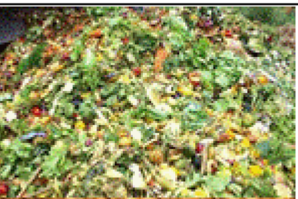
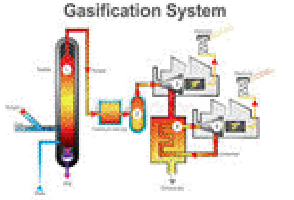
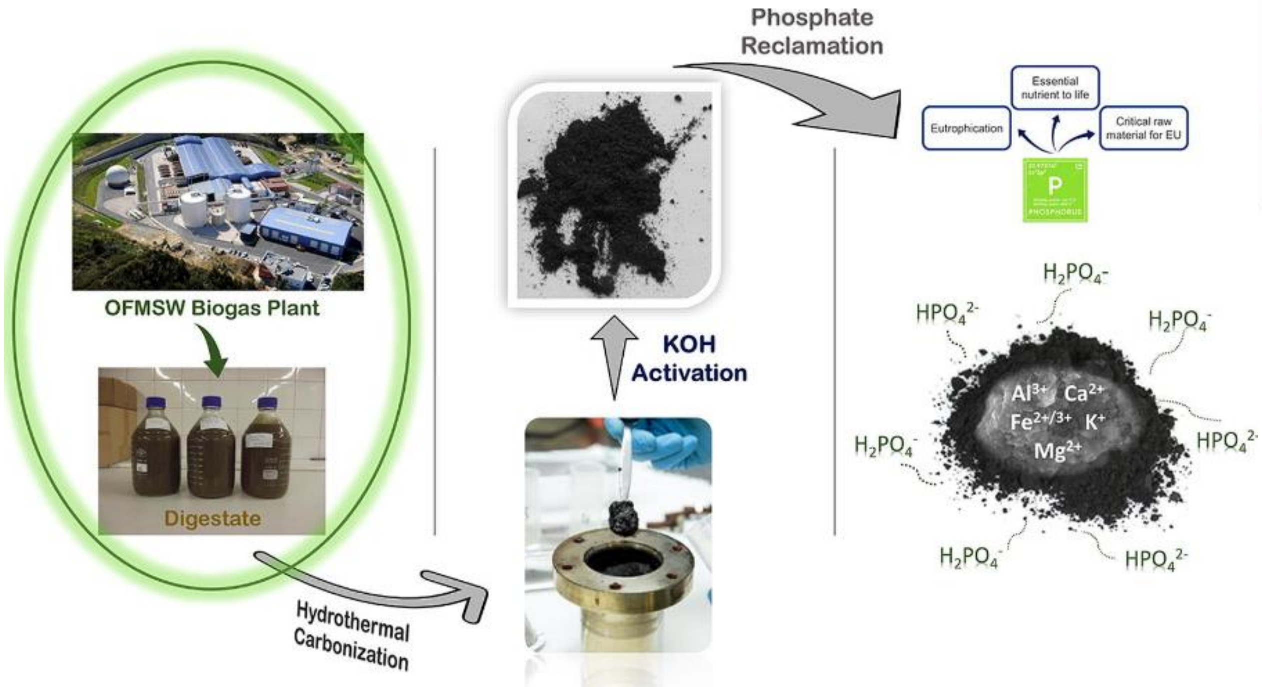



Porous carbons derived from hydrothermally treated biogas digestate

Maria Bernardo [a,*], Catalina Rodriguez Correa [b], Yvonne Ringelspacher [b], Gero C. Becker [b], Nuno Lapa [a], Isabel Fonseca [a], Isabel A.A.C. Esteves [a,*], Andrea Kruse [b,*]



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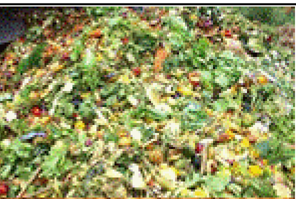
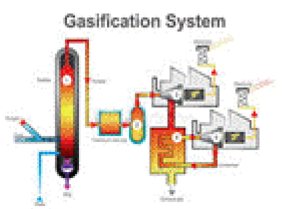
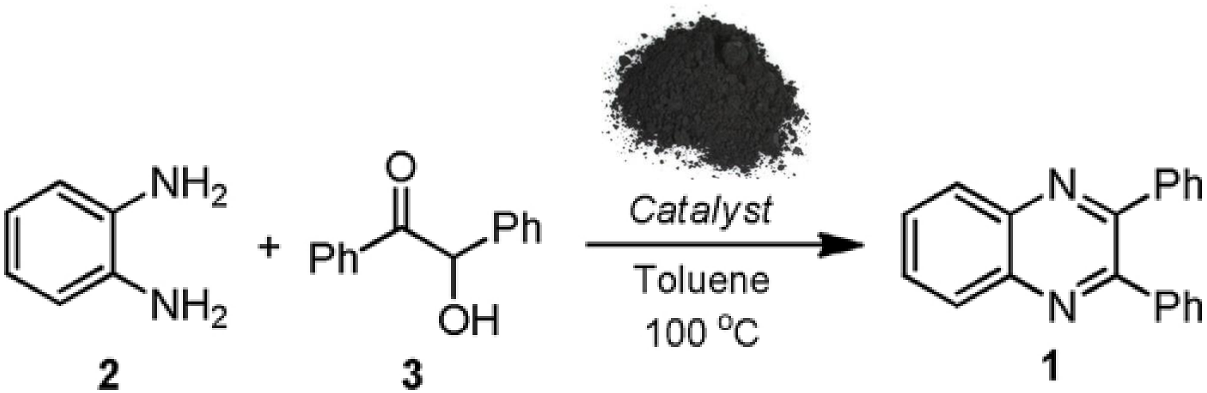




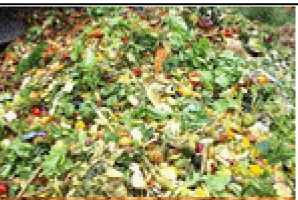
Porous carbons-derived from vegetal biomass in the synthesis of quinoxalines. Mechanistic insights

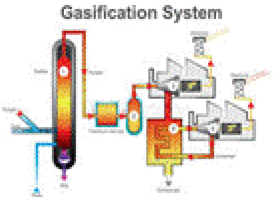
M. Godino-Ojer[a,b], R. Blazquez-García[a], I. Matos[c,*], M. Bernardo[c], I.M. Fonseca[c], E. Pérez Mayoral[a,*]

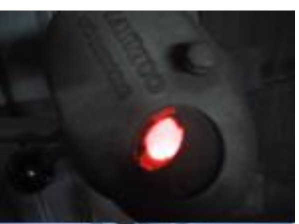
hedychium gardnerianum - Conteira



https://doi.org/10.1016/j.cattod.2019.06.043

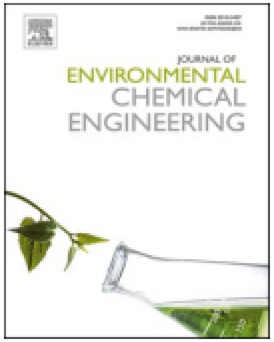


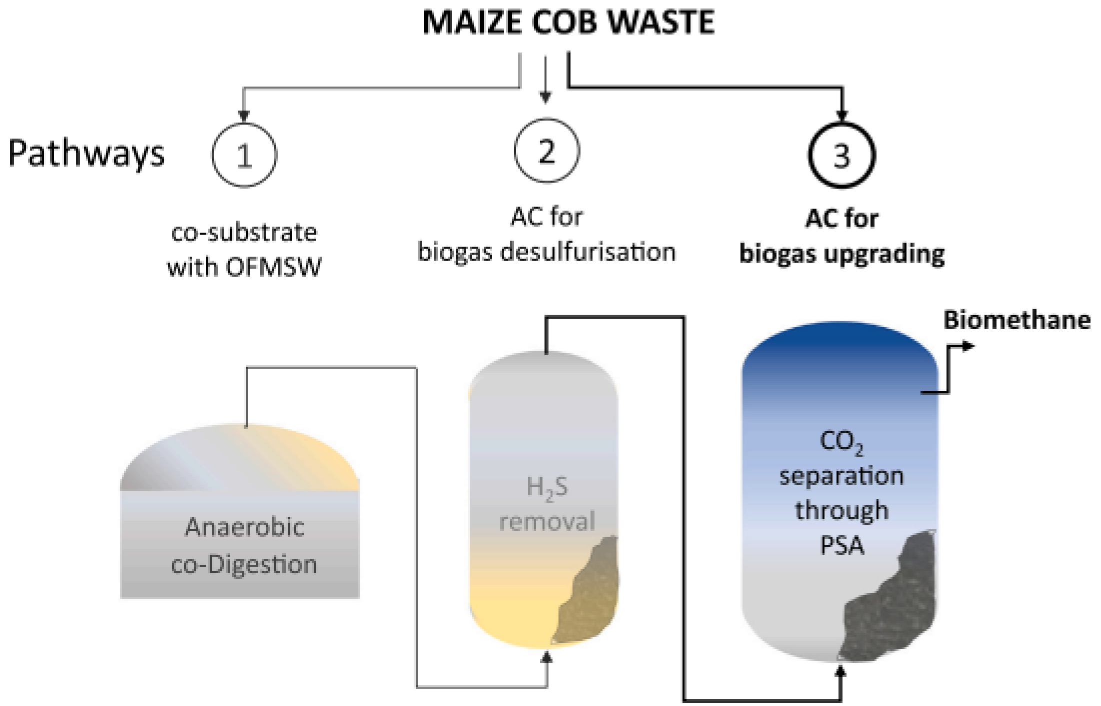





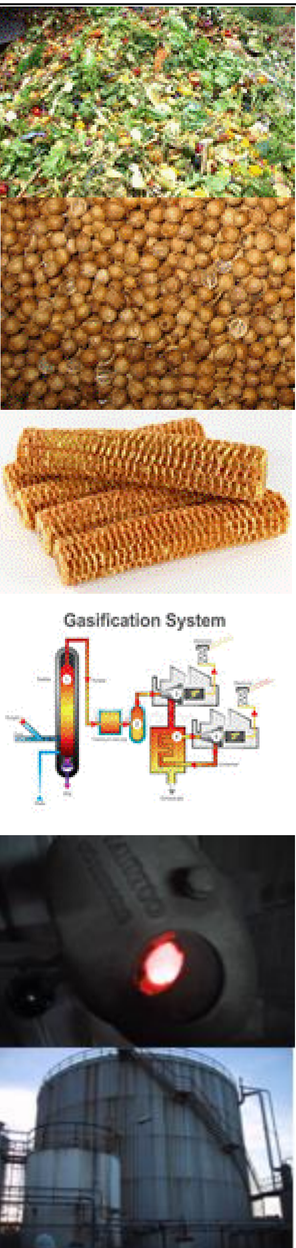

Evaluation of activated carbons produced from Maize Cob Waste for adsorption-based CO_2 separation and biogas upgrading

Elena Surra [a,c,**], Rui P.P.L. Ribeiro [b], Tiago Santos [b], Maria Bernardo [b], José P.B. Mota [b], Nuno Lapa [a], Isabel A.A.C. Esteves [b,*]





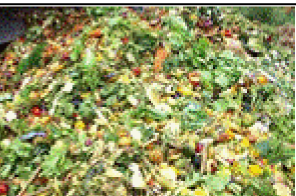
https://doi.org/10.1016/j.jece.2021.107065

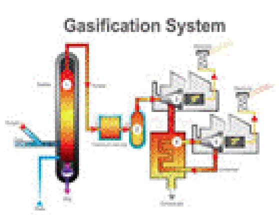


Effect of biochar addition in the anaerobic digestion of OFMSW

Biochar from forestry wastes

- Lower lag-phase (22%)
- Higher biogas production (31.3%)
- Higher daily rate production of CH_4 (5%)
- Higher substrate biodegradability

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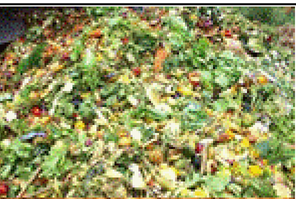

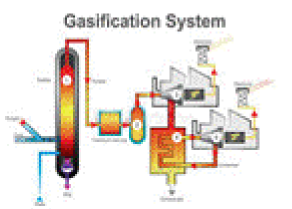

Brainstorming...
Discussion...

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