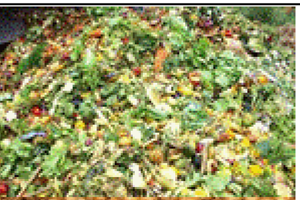
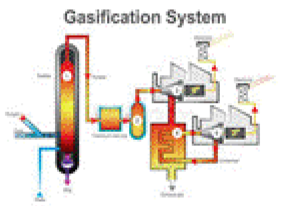




Thermochemical processes

Pyrolysis

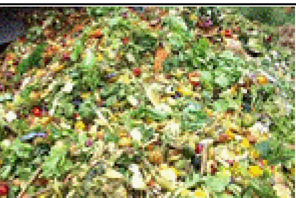
Pyrolysis Products

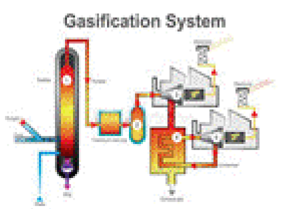
Biochars

Maria Bernardo

Investigadora FCT-NOVA

maria.b@fct.unl.pt

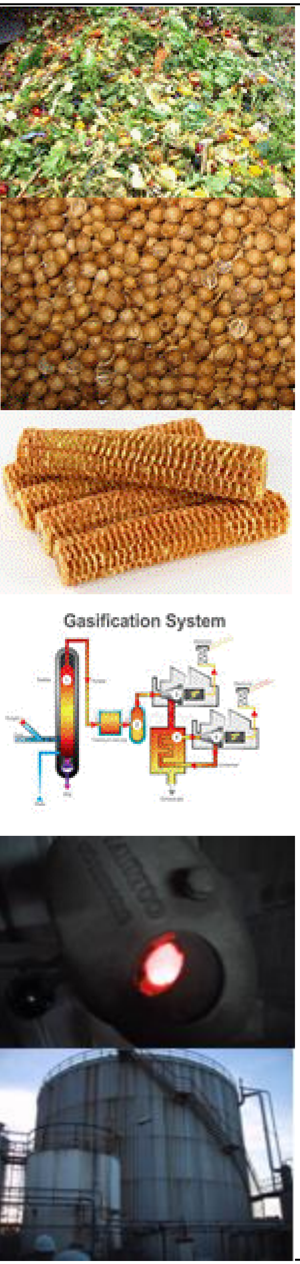



NOVA SCHOOL OF SCIENCE & TECHNOLOGY

UNIVERSIDADE NOVA DE LISBOA

Departamento de Química
NOVA School of Science and Technology
NOVA University Lisbon



Associated Laboratory for Green Chemistry (LAQV)

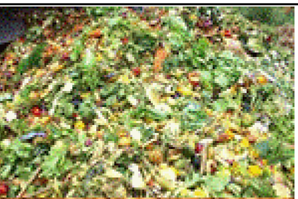
Network of Chemistry and Technology (REQUIMTE)

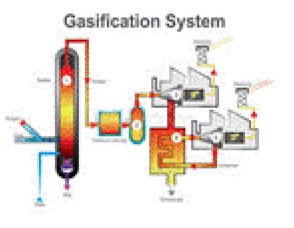
Portuguese Research Centre for Sustainable Chemistry

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

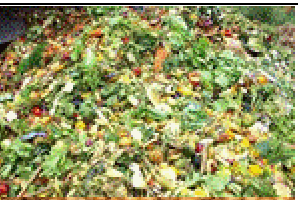
http://sites.fct.unl.pt/mac/

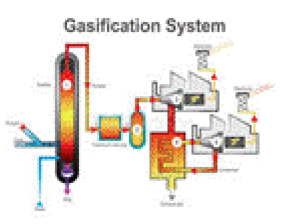
Synthesis of Materials

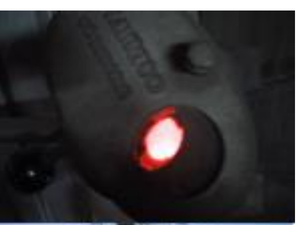
- Carbon materials: Biochars and Porous Carbons
- Mesoporous Silicas
- (Bio)Polymeric Materials
- Oxide Nanoparticles
- Catalysts

Applications

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







Thermochemical processes

Solid biomass with low moisture content

Classification according the involved oxygen

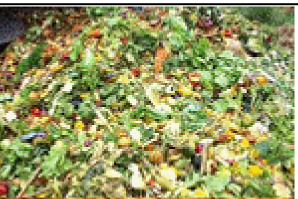
% air

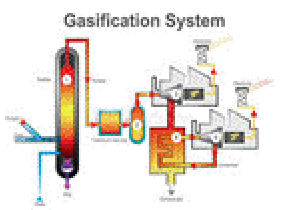
Without oxygen → **PYROLYSIS (without oxidation)**

Limited oxygen → **GASIFICATION (Partial oxidation)**

Oxygen supply in the stoichiometric quantity for complete combustion

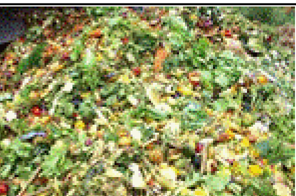
Excess oxygen → **Combustion/Incineration (complete oxidation)**

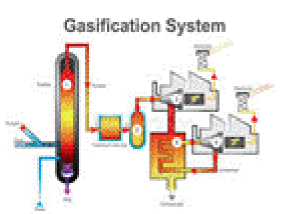




Thermochemical processes

	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

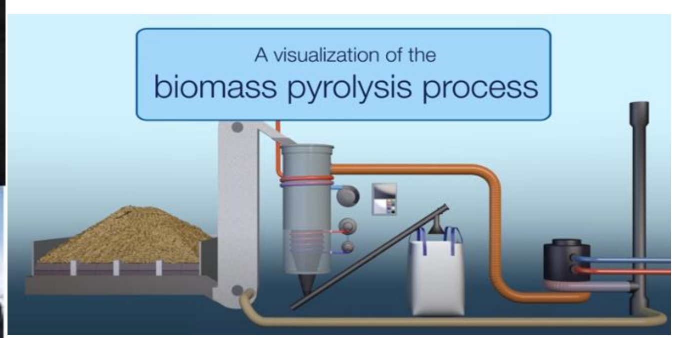



Pyrolysis

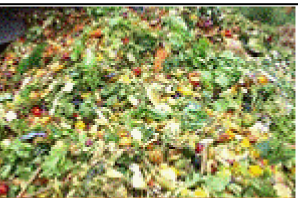
Thermochemical conversion *of organic substances (biomass and biowastes) into* ***liquids, gases and solids,*** *in the* ***absence of oxygen with heating***

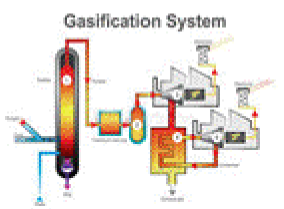
Endothermic degradation or thermolysis *(chemical bonds are broken) of organic substances in the* ***total absence of oxygen****, to obtain* ***oils, gases and chars***



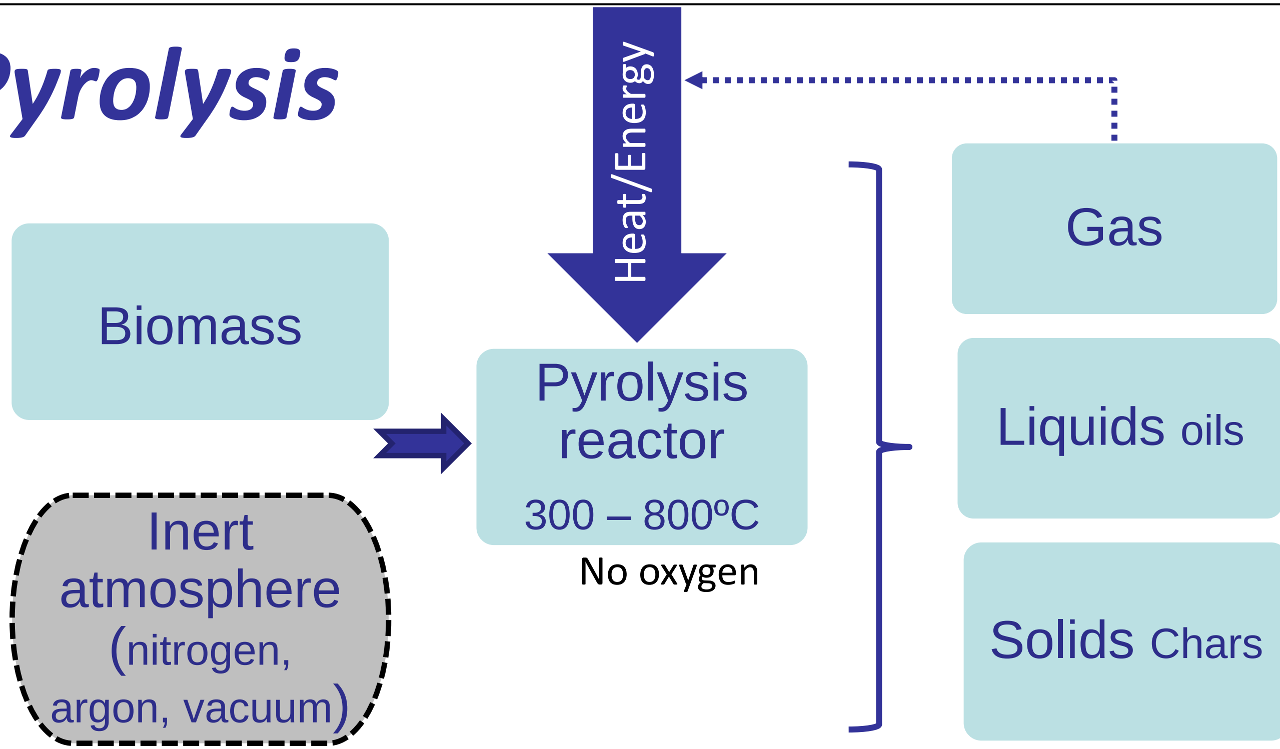
https://youtu.be/3K1zWAYDvMA

https://www.youtube.com/watch?v=mKTOdv0Yk4s





Pyrolysis

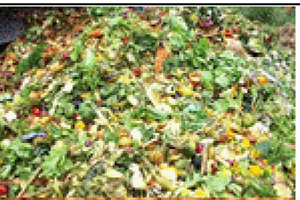


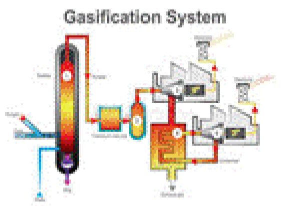
Endothermic Process

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



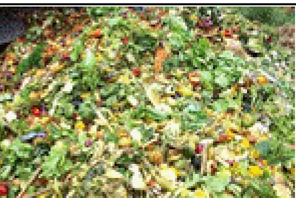

Pyrolysis - Products

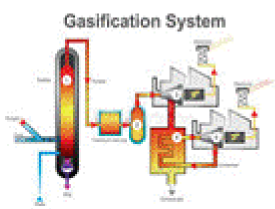
Liquid fraction – oils or bio-oils, tars (heavy oil)

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

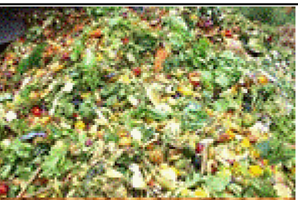
- Energy/heat production (10-40 MJ/m^3)
- Chemical synthesis

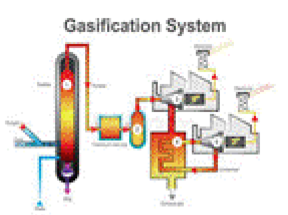
Solid fraction – Chars or biochars

Carbon material + mineral matter

Applications:

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



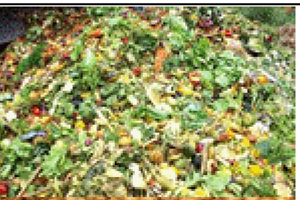

Pyrolysis types

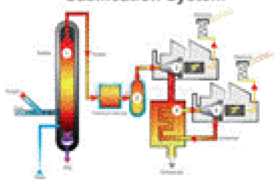
Type		Slow	Intermediate	Fast	Flash	Vacum
Temperature (°C)		300-700	500-650	500-1000	900-1200	400-600
Heating rate (°C/s)		0,1-2	1-10	10-200	> 1000	0,1-1
Residence time		min - hours	10-20 s	< 2 s	< 0,1 s	< 1 s
Pressure (MPa)		0,1	0,1	0,1	0,1	0,01-0,02
Particle size (mm)		5-50	1-5	<0.1	<0.1	< 1
Products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

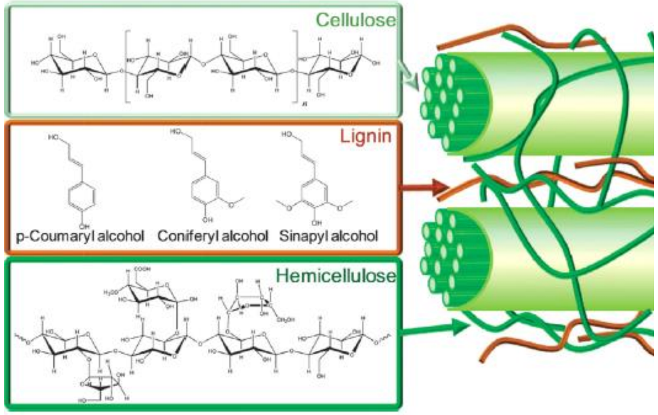
High temperatures and long residence times – gases production

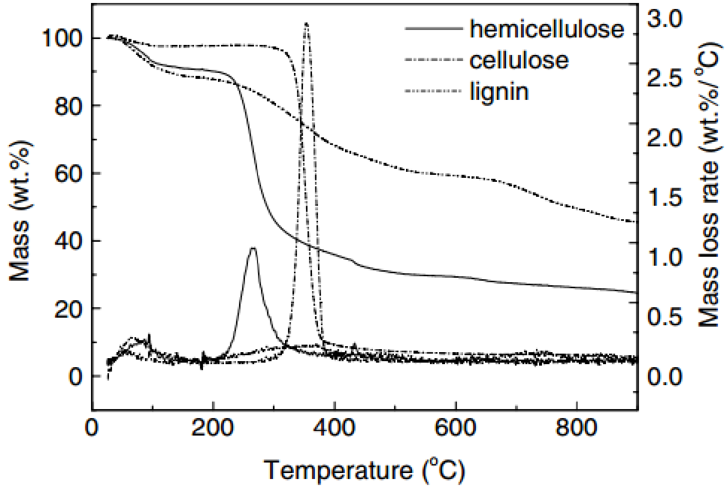
Moderate temperatures and short residence times – liquids production

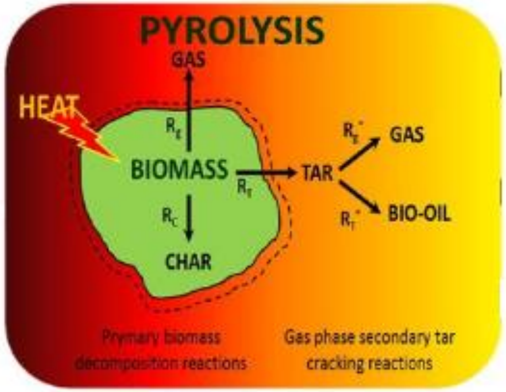


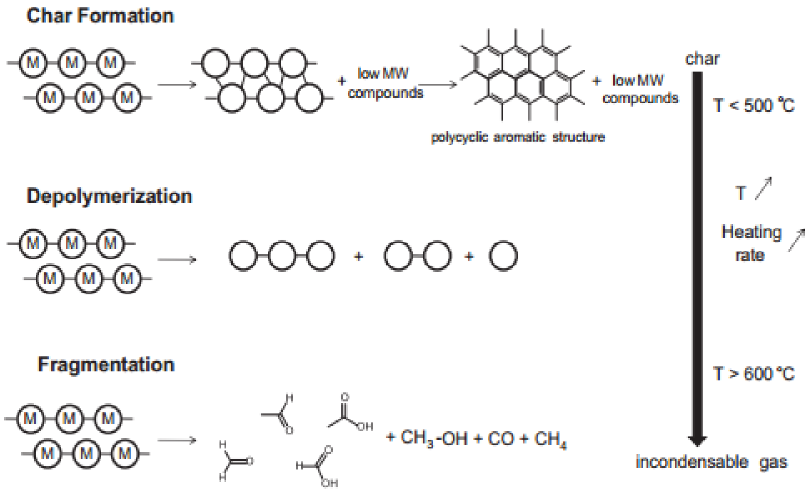



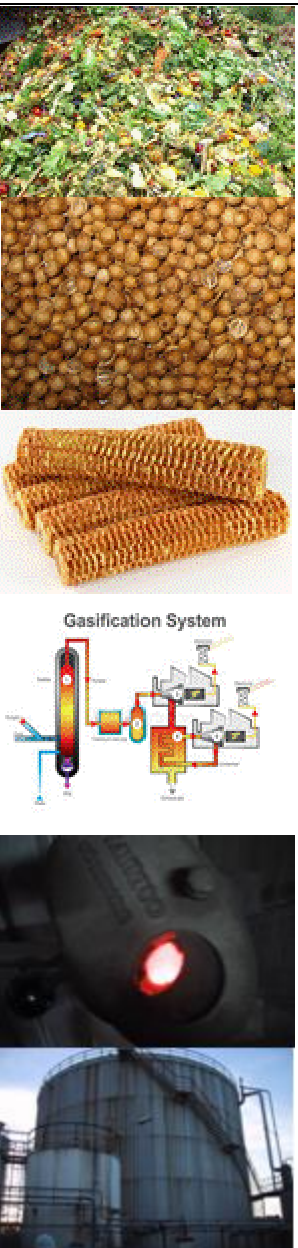

Pyrolysis – steps and reactions



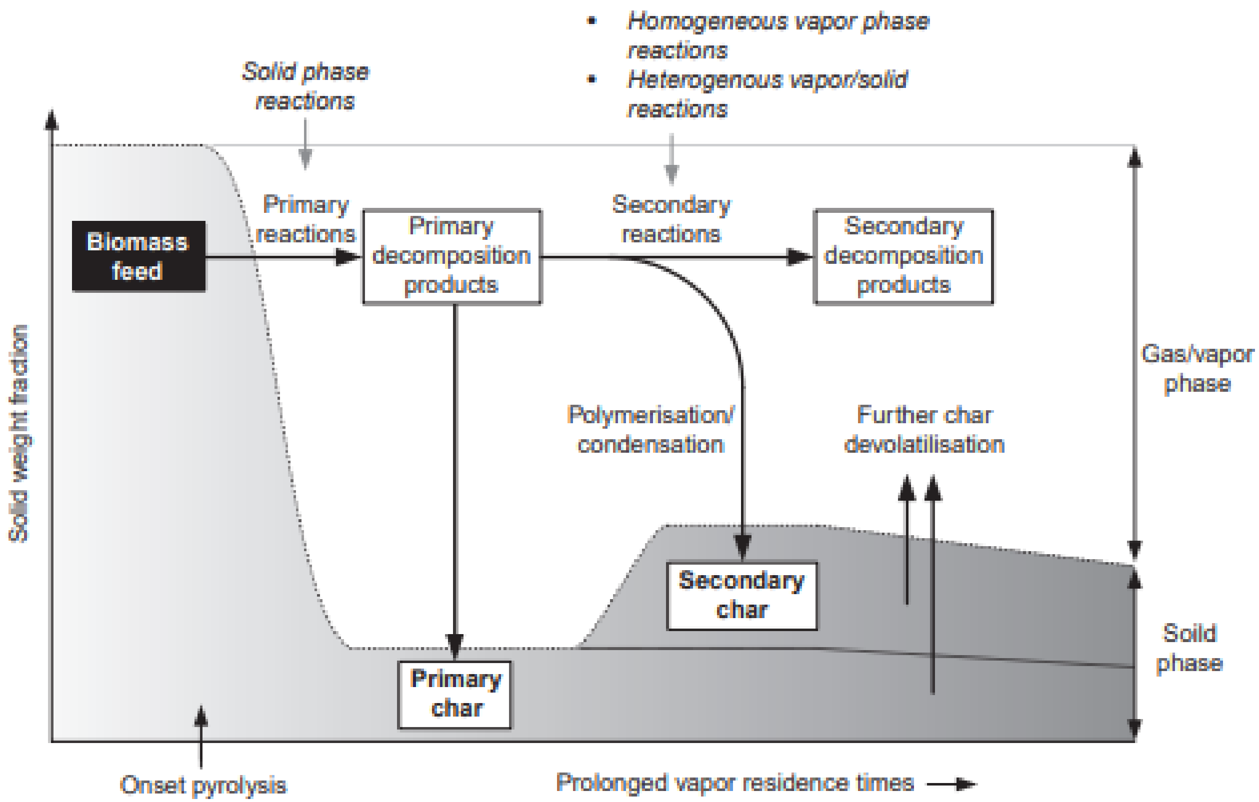




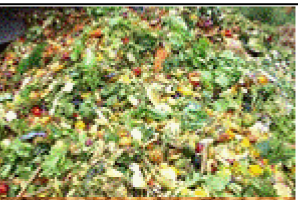


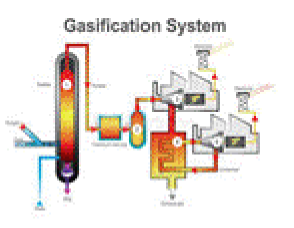


Pyrolysis - Products



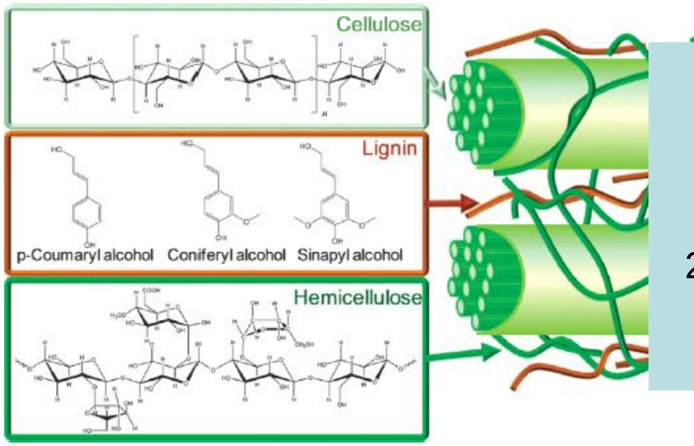
"Biochar Production", in Biochar - A Regional Supply Chain Approach in View of Climate Change Mitigation, Cambridge University Press, 2016. https://doi.org/10.1017/9781316337974.011




Biowastes

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

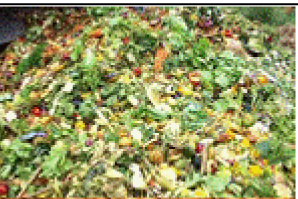


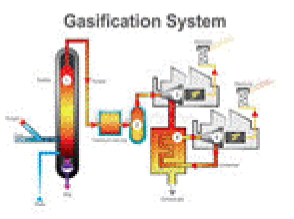
Lignocellulosic biomass

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

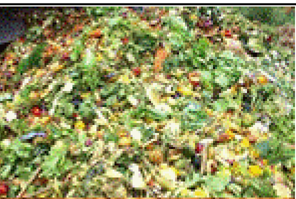
Biomass

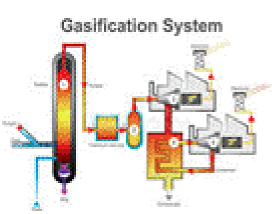
Cellulose — ≈ 10 %

Hemicellulose — 20-30 %

Lignin — 40-50 %

Biochar




Charcoal/Biochar - source

Fossil/Coal

Non-renewable, mining, high-cost

Peat, lignite, bituminous, anthracite, graphite

Carbon content (C)



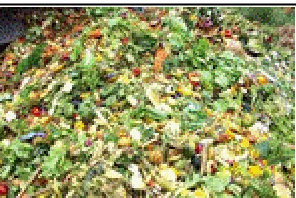
Biomass

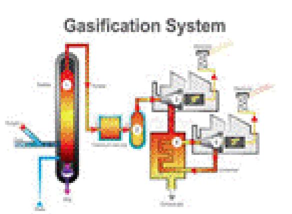
Renewable, low cost, abundant

Wood, Agro-forestry and food wastes,…



Precursors with high fixed carbon content





Biochars

Biomass
Operational conditions

Incipient porosity
(Surface area: 5 – 300 m^2/g)

Tars

Metals

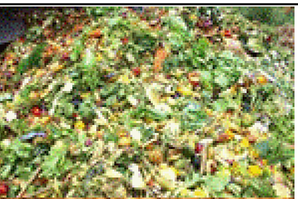
Minerals

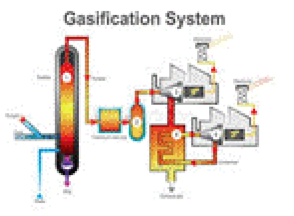
CO_3^{2-}, SiO_3^{2-}, PO_4^{3-}

Na, Ca, K, Mg,...

Zn, Pb, Ni, Cr,…

Potential release of PAH and Heavy Metals…



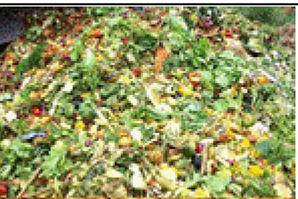

Biochars - *Applications*

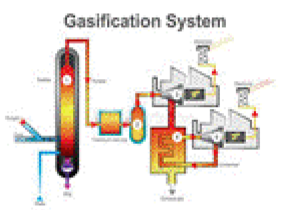
Fuel
Barbecue
(PCS: 15-32 MJ/kg)

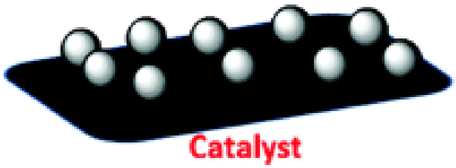
Soil amendment
Water retention
Source of carbon/Carbon sequestration
Source of nutrients

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

Biochars - *Applications*

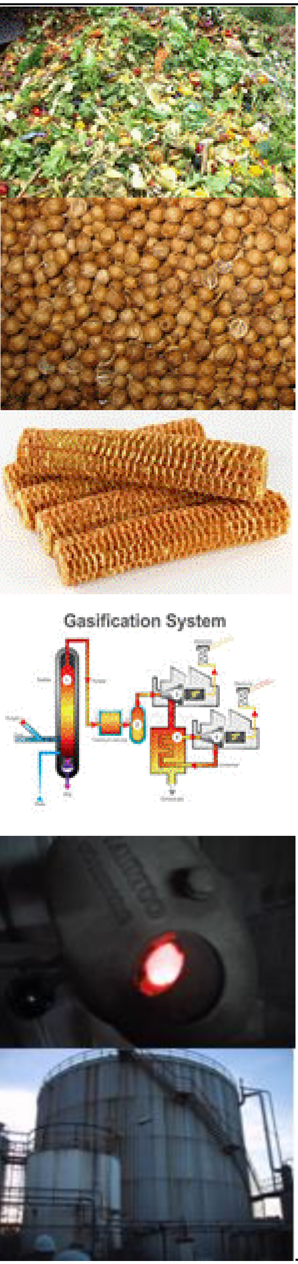


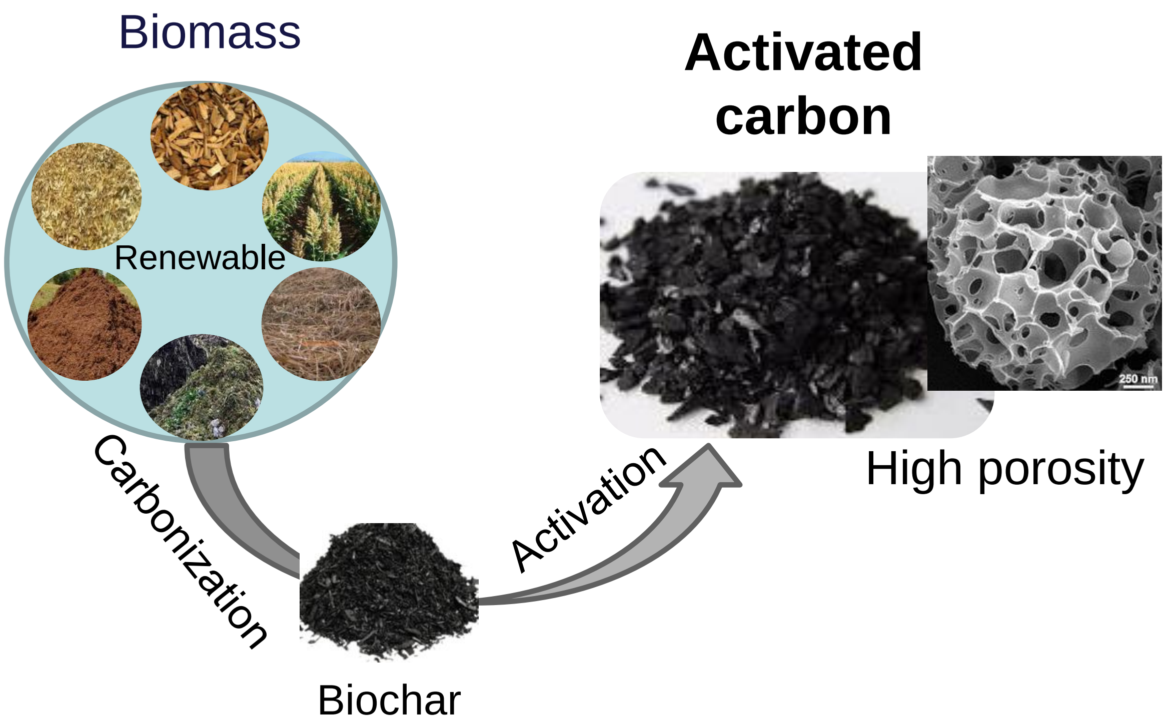
Catalyst
Tar cracking at gasification
Fuels production
NOx conversion

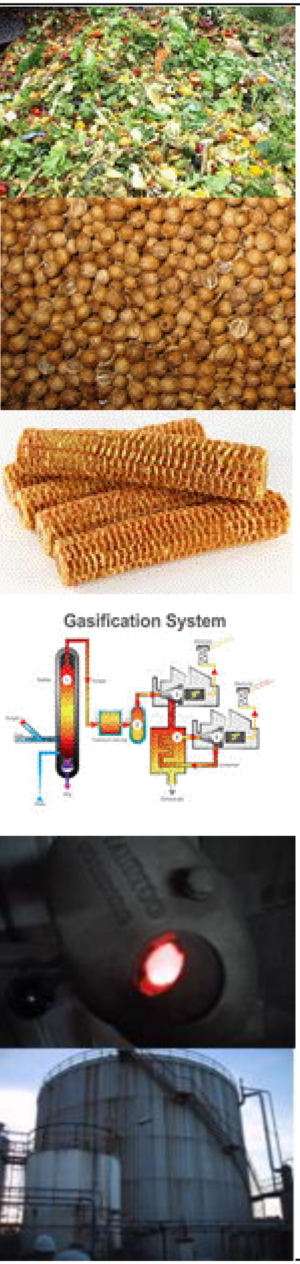
Energy Storage
Supercapacitor (Electrode)
Batteries (anode)



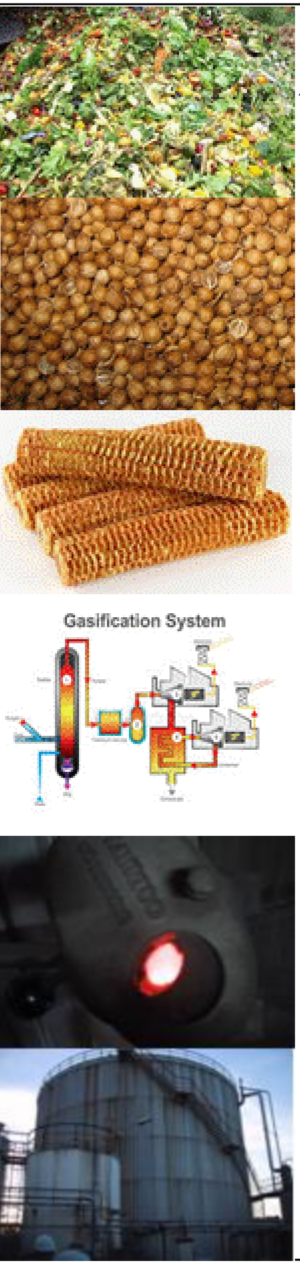
Biochar – *Applications*

Precursor of Activated Carbon



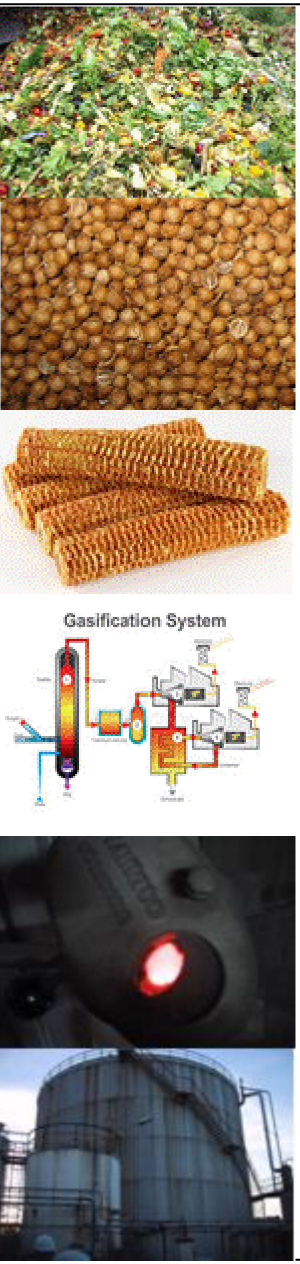


Activated carbon – Commercial applications

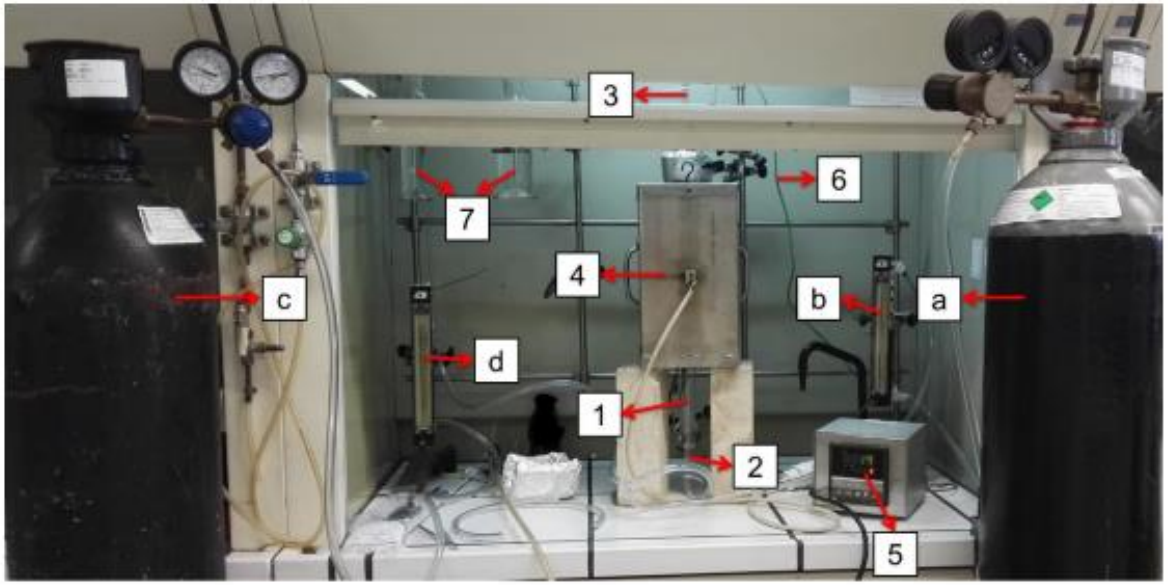


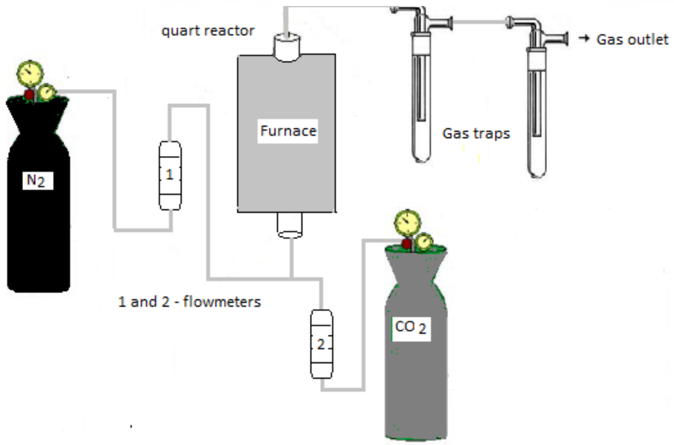
Activated carbon – Industrial applications

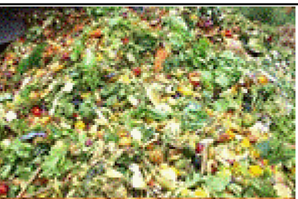
- **Adsorption; Energy storage; Chemical industry (catalysis)**

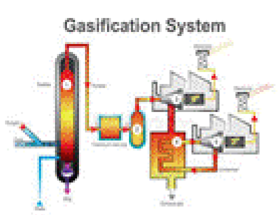


Experimental set-up - example





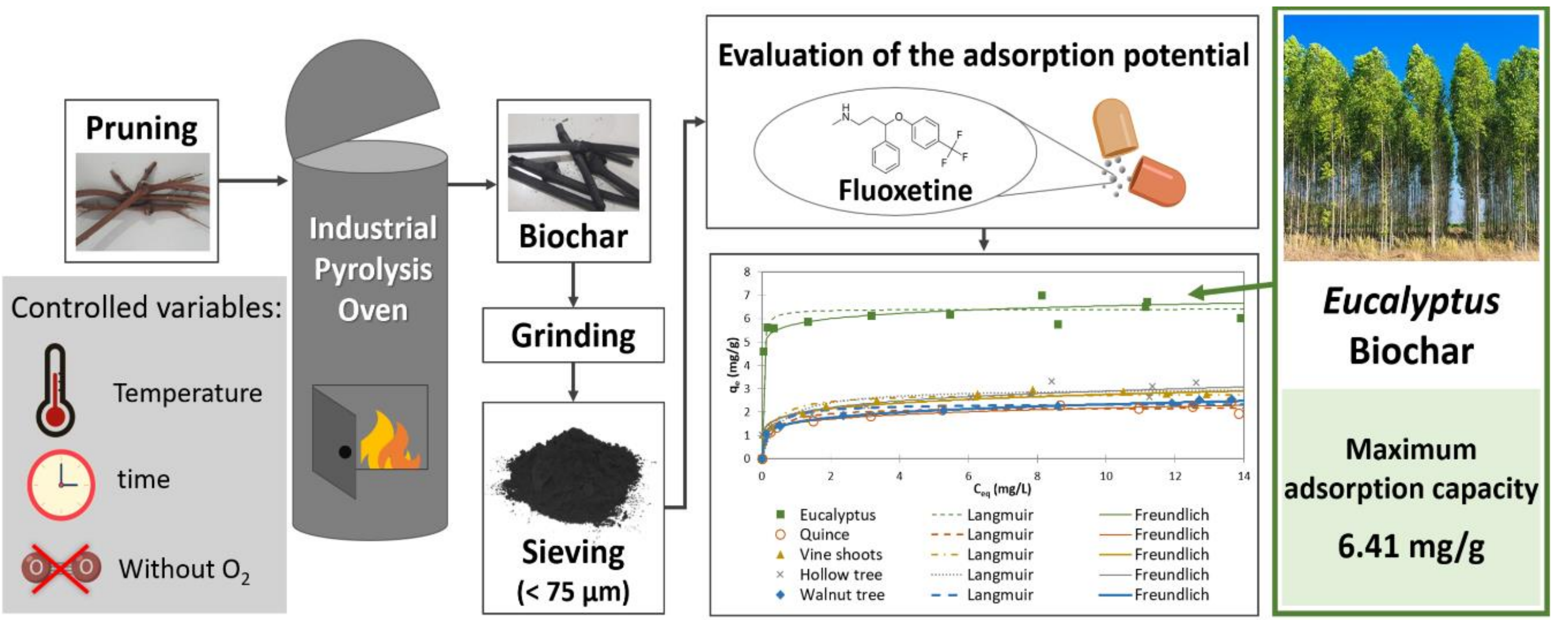




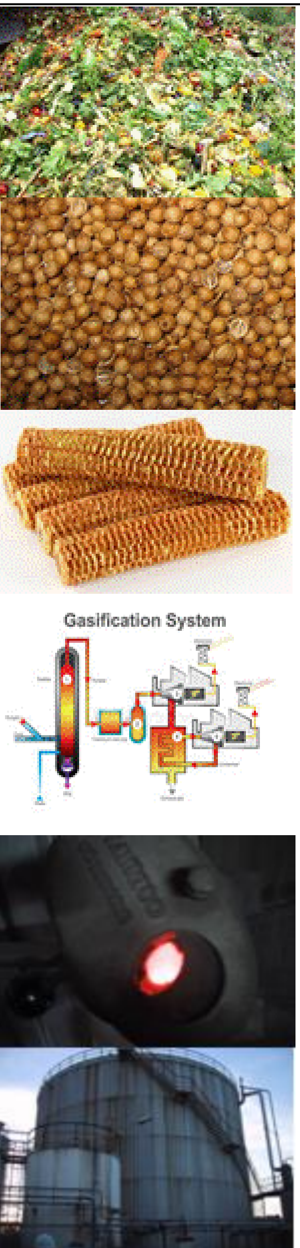
Biochars – applications

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]



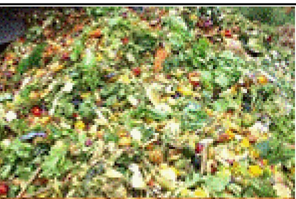
https://doi.org/10.1016/j.biortech.2019.121973

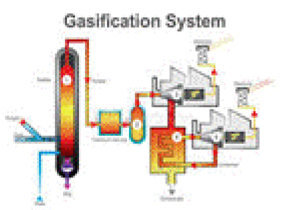


Recovery of Cr(III) by using chars from the co-gasification of agriculture and forestry wastes

Delfina Godinho[1] · Miguel Nogueira[2] · Maria Bernardo[2] · Diogo Dias[1] · Nuno Lapa[1] · Isabel Fonseca[2] · Filomena Pinto[3]

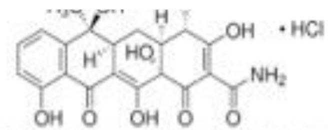
https://doi.org/10.1007/s11356-019-05609-w



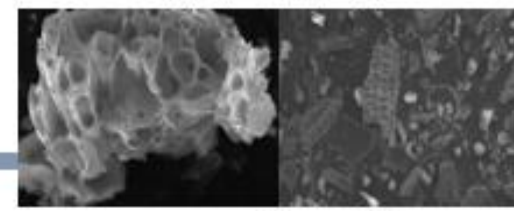




Study of the removal mechanism of aquatic emergent pollutants by new bio-based chars

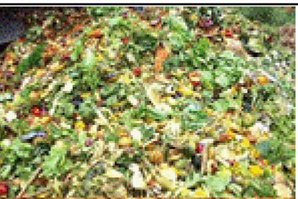
Maria Manuel Serrano Bernardo[1] · Catarina Alexandra Catanas Madeira[1] · Nuno Carlos Lapa dos Santos Nunes[2] · Diogo André Costa Messias Dias[2] · Delfina Maria Barbosa Godinho[1] · Maria Filomena de Jesus Pinto[3] · Inês Alexandra Morgado do Nascimento Matos[1] · Ana Paula Batista Carvalho[4] · Isabel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

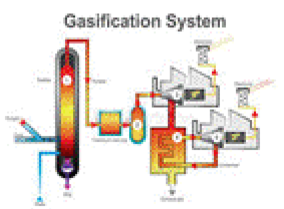


Removal of caffeine and tetracycline



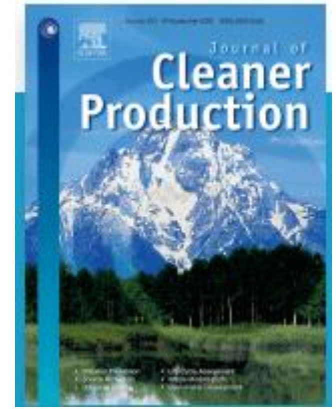

https://doi.org/10.1007/s11356-017-9938-9

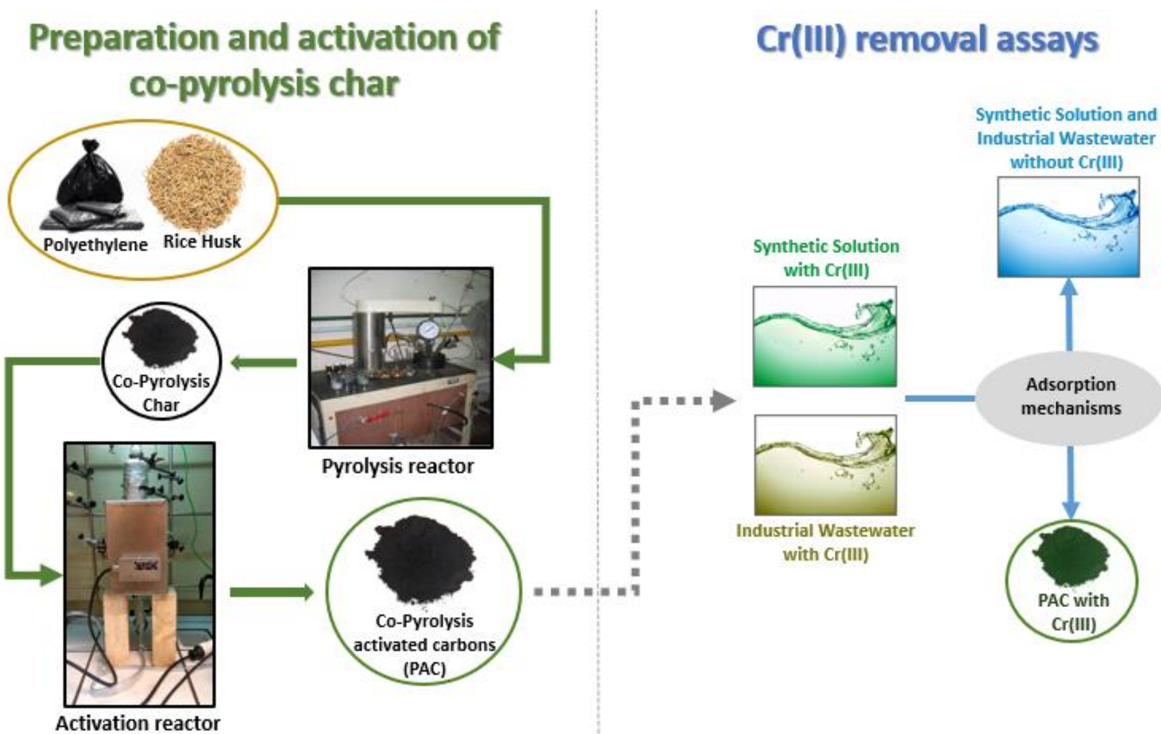




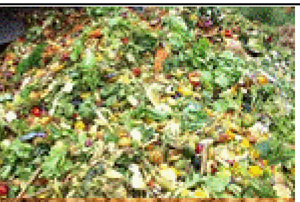
Activation of co-pyrolysis chars from rice wastes to improve the removal of Cr^{3+} from simulated and real industrial wastewaters

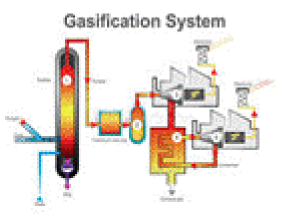
Diogo Dias [a], Maria Bernardo [b], Inês Matos [b], Isabel Fonseca [b], Filomena Pinto [c], Nuno Lapa [a, *]

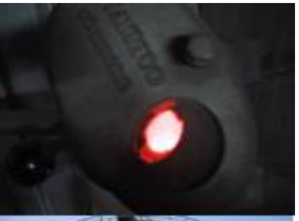




https://doi.org/10.1016/j.jclepro.2020.121993

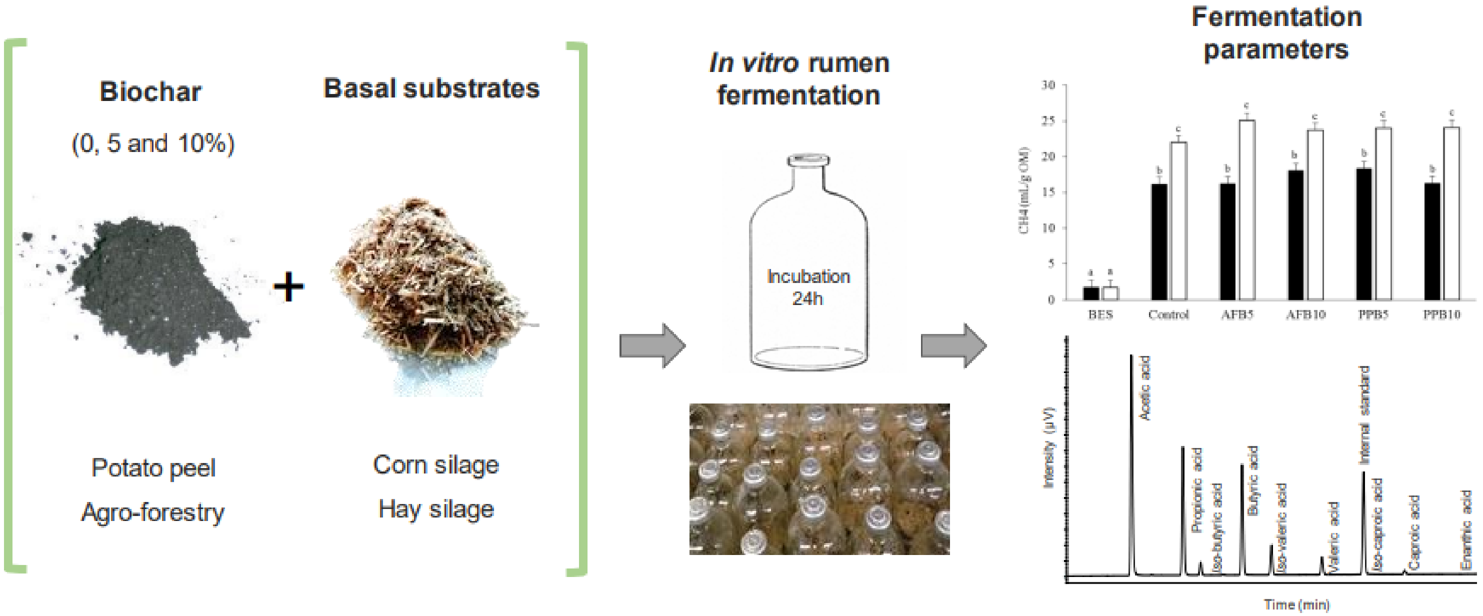




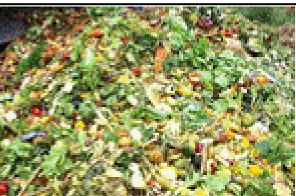


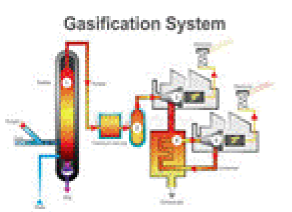
Assessment of potato peel and agro-forestry biochars supplementation on in vitro ruminal fermentation

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]



http://doi.org/10.7717/peerj.9488

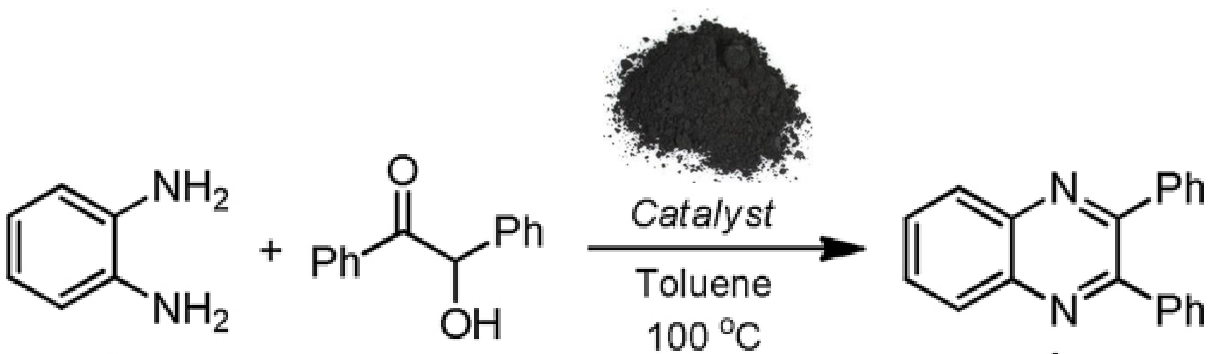




Porous carbons-derived from vegetal biomass in the synthesis of quinoxalines. Mechanistic insights

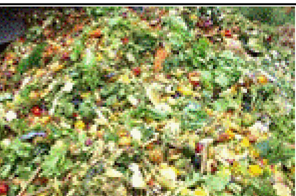
M. Godino-Ojer[a,b], R. Blazquez-García[a], I. Matos[c,*], M. Bernardo[c], I.M. Fonseca[c], E. Pérez Mayoral[a,*]

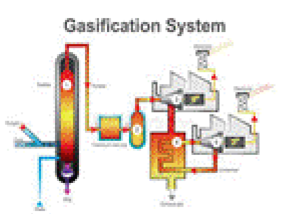
hedychium gardnerianum - Conteira



2 3 1

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

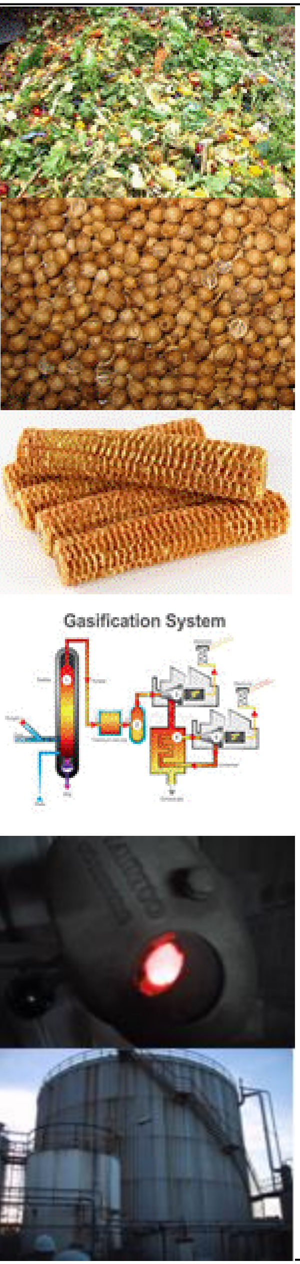




Effect of biochar addition in the anaerobic digestion of OFMSW

Biochar from forestry wastes

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



Biochar LCA

Carbon footprint CO_2eq?

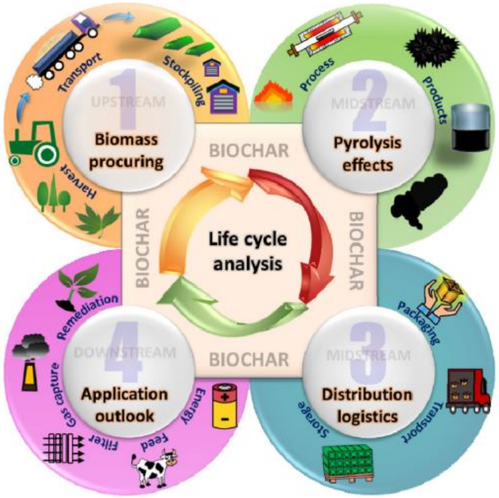
Energy needs
Coal – 0.069 kg
Natural gas – 0.0084 m^3;
Crude: 0.046 kg

Energy

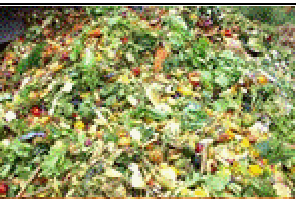
Wood → Pyrolysis/ Carbonization → Biochar

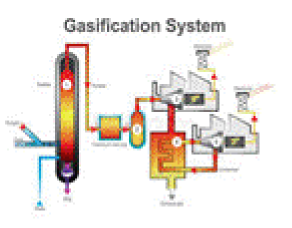
Inputs
0.0044m^3 wood
density = 560 kg/m^3
50% m/m C

Outputs
1 kg biochar
31 MJ/kg
80% m/m C



Ecoinvent Life Cycle Inventory (LCI) database




Bibliography

Maria Bernardo, Inês Matos, Marcia Ventura, Rubia Risso, Joaquim Vital, Nuno Lapa and Isabel Fonseca, Pyrolysis of Waste Materials, in: "Waste-to-Energy (WtE)" book. Editor: E. Jacob-Lopes. Publisher: Nova Science Publishers, Inc., New York, USA, 2019. ISBN: 978-1-53614-432-1. https://novapublishers.com/shop/waste-to-energy-wte/

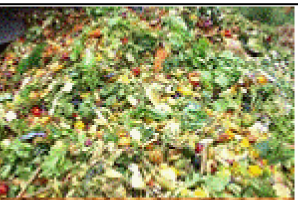
Frederik Ronsse, Biochar Production, in "Biochar - A Regional Supply Chain Approach in View of Climate Change Mitigation" edited by Viktor J. Bruckman, Esin Apaydın Varol, Başak B. Uzun, Jay Liu, Cambridge University Press, 2016. https://doi.org/10.1017/9781316337974.011

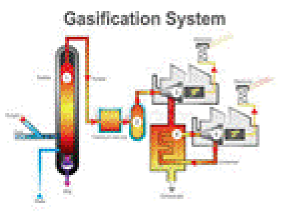
Rongge Zou, Moriko Qian, Chenxi Wang, Wendy Mateo, Yunpu Wang, Leilei Dai, Xiaona Lin, Yunfeng Zhao, Erguang Huo, Lu Wang, Xuesong Zhang, Xiao Kong, Roger Ruan, Hanwu Lei, "Biochar: From by-products of agro-industrial lignocellulosic waste to tailored carbon-based catalysts for biomass thermochemical conversions", Chemical Engineering Journal, 441, 2022, 135972. https://doi.org/10.1016/j.cej.2022.135972

Xiao-fei Tan, Shao-bo Liu, Yun-guo Liu, Yan-ling Gu, Guang-ming Zeng, Xin-jiang Hua, Xin Wang, Shao-heng Liu, Lu-hua Jiang, "Biochar as potential sustainable precursors for activated carbon production: Multiple applications in environmental protection and energy storage", Bioresource Technology 227 (2017) 359–372. http://dx.doi.org/10.1016/j.biortech.2016.12.083

Ling Xiang, Shaoheng Liu, Shujing Ye, Hailan Yang, Biao Song, Fanzhi Qin, Maocai Shen, Chang Tan, Guangming Zeng, Xiaofei Tan, Potential hazards of biochar: The negative environmental impacts of biochar applications, Journal of Hazardous Materials, 420, 2021, 126611. https://doi.org/10.1016/j.jhazmat.2021.126611

Naveed Ahmed Qambrani, Md. Mukhlesur Rahman, Seunggun Won, Soomin Shim, Changsix Ra, "Biochar properties and eco-friendly applications for climate change mitigation, waste management, and wastewater treatment: A review", Renewable and Sustainable Energy Reviews 79 (2017) 255–273. http://dx.doi.org/10.1016/j.rser.2017.05.057




Brainstorming…
Discussion…

maria.b@fct.unl.pt