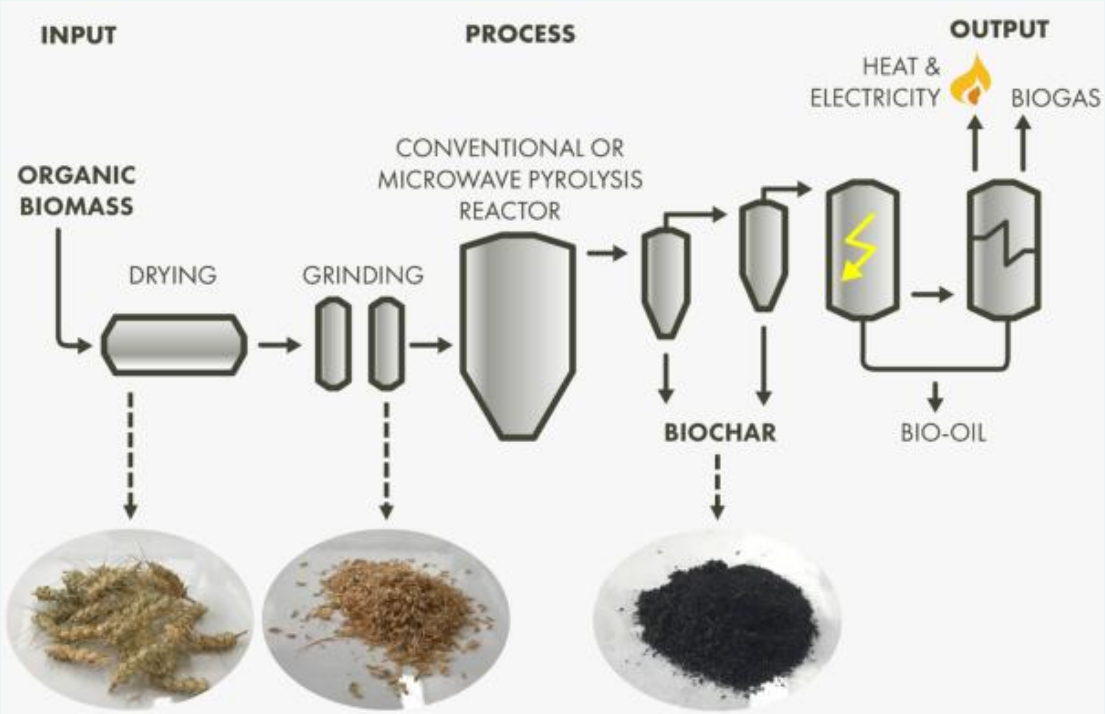
Biochar and Activated Carbons

M. Riccò a.a. 2026/27

Carbon Nanostructures

Organic Waste Derived Biochar



- ✓ **Bio-char** is a solid side-product generated during the **pyrolisis** or **pyrogassification of biomasses** (either of vegetal or animal origin), processes which are essentially designed for the production of **biofuel** (energy) in power-plants with **zero or negative CO_2 emission**
- ✓ Bio-char is a **very inexpensive** waste product, which has been generally used as **soil amendment**, so far

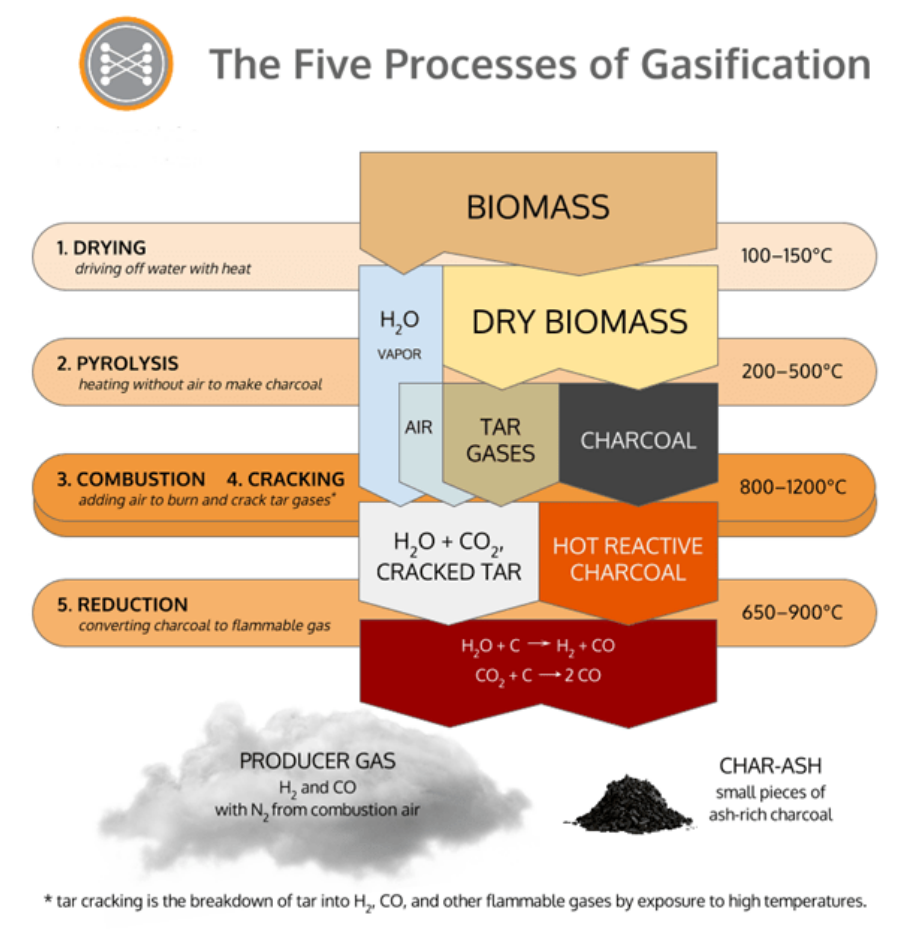
Pyrogassification

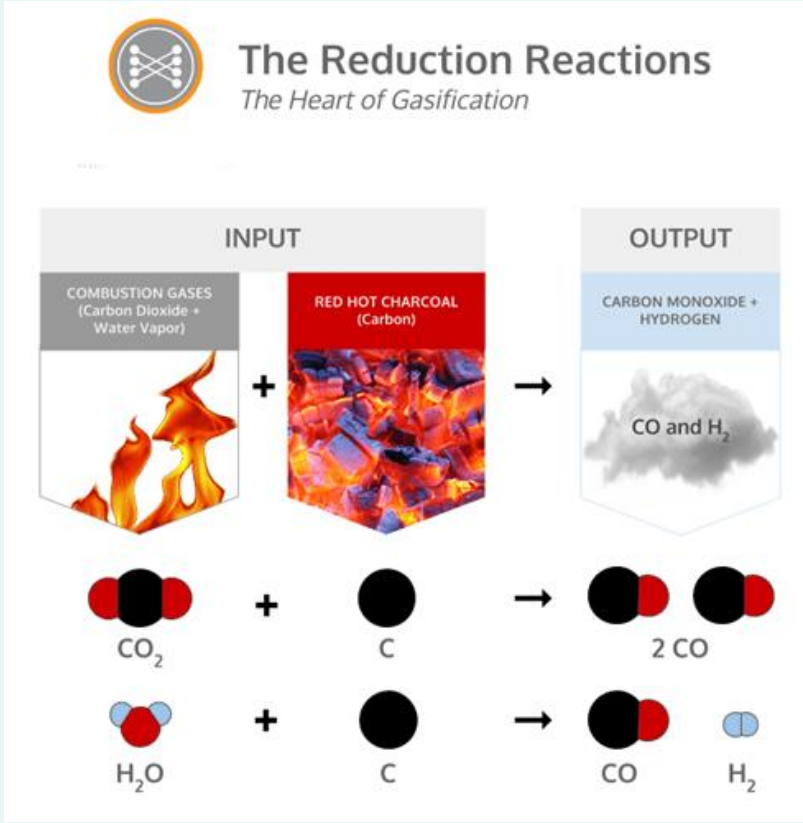




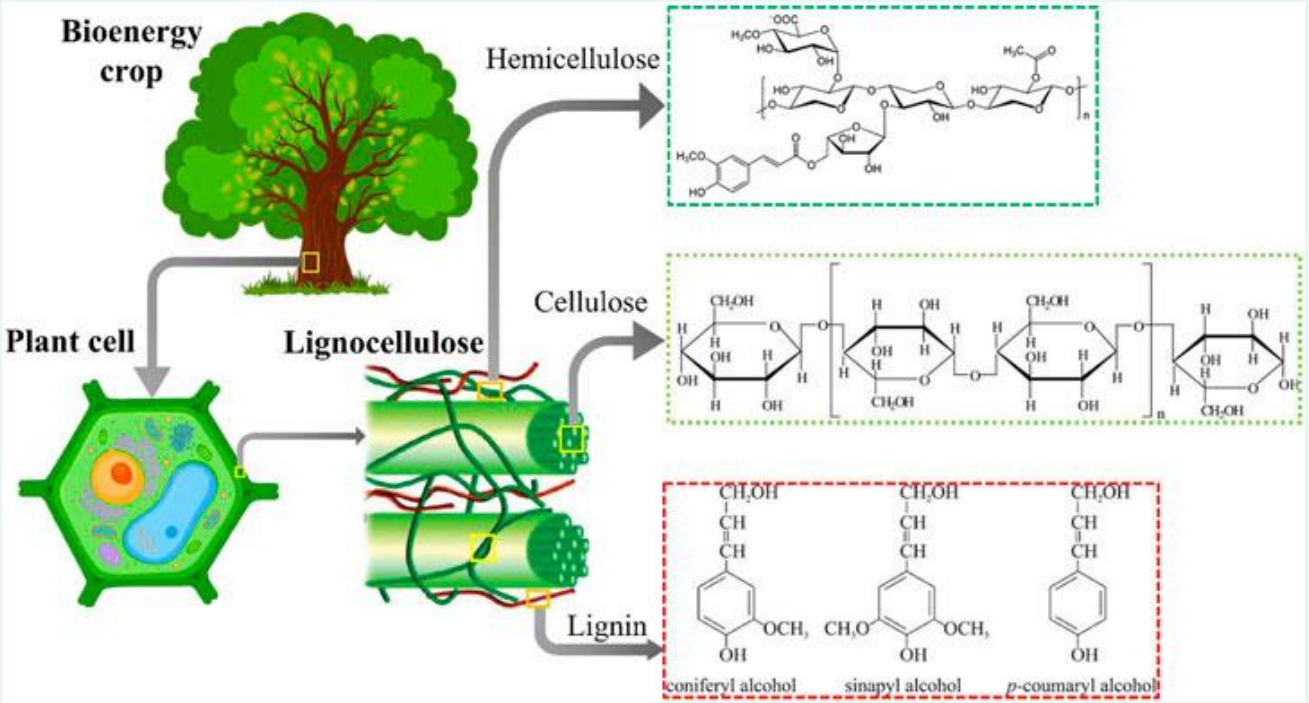
A. Pyrolysis (200ºC < T < 600ºC)The volatile components of the biomass (cellulose, hemicellulose) evaporate, generating what is known as pyrolysis gas, which is rich in hydrocarbons (tar); the remaining non-volatile components (lignin) stay in the solid phase, forming char.
B. Combustion (800ºC< T < 1,000ºC) A portion of the biomass is oxidized in a sub-stoichiometric air environment, generating the heat required for the gasification reactions to take place. The pyrolysis gas passes through the high-temperature combustion zone, where it undergoes thermal cracking: the hydrocarbons are broken down into elementary gas molecules.
C. Reduction (T drops to 600–700ºC)The char is consumed in the gasification reactions—fueled by the heat from combustion—producing H_2, CO, and CH_4.

Pyrogassification



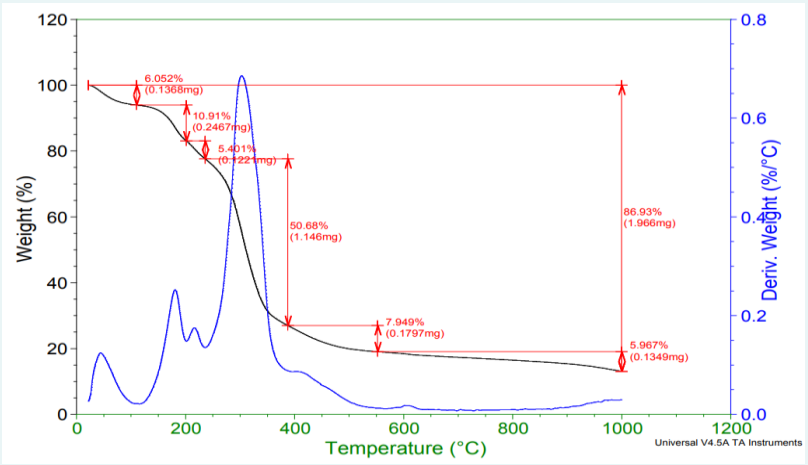


Biomasses characteristics



Degradation:
lignin from 160 °C
hemicellulose from 220 °C
cellulose around 315 °C

All over at 650 °C



How to produce lab-biochar?

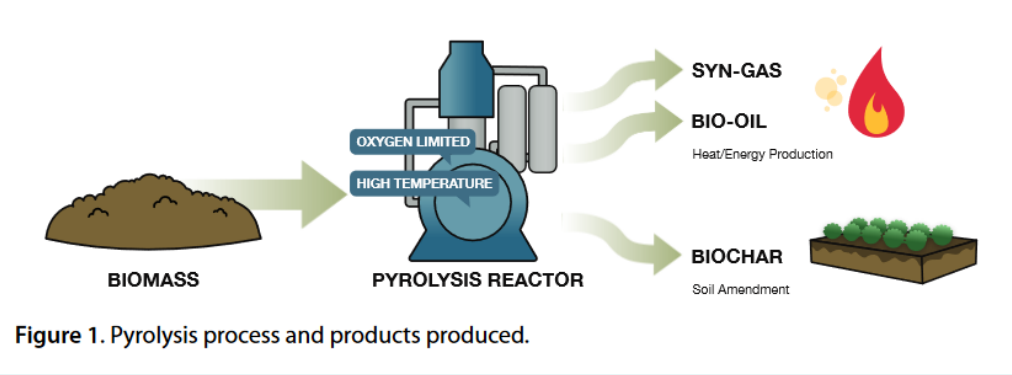


Figure 1. Pyrolysis process and products produced.





Pyrolysis

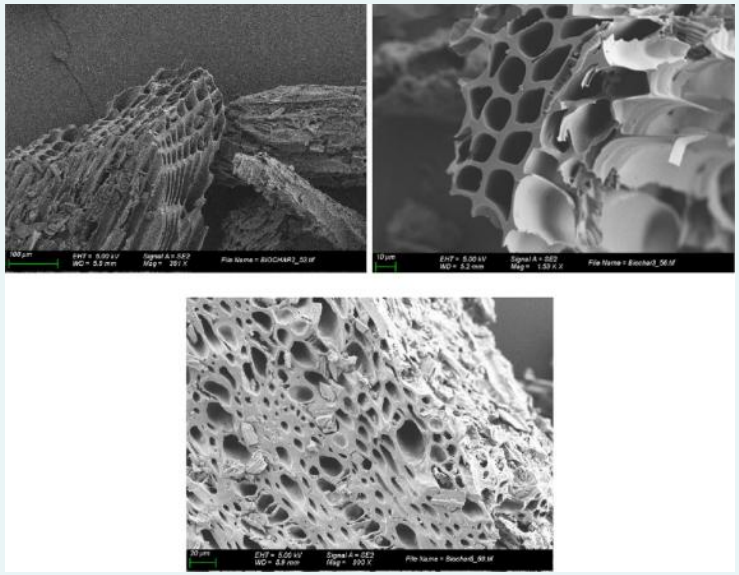
650°C 2h – 6h

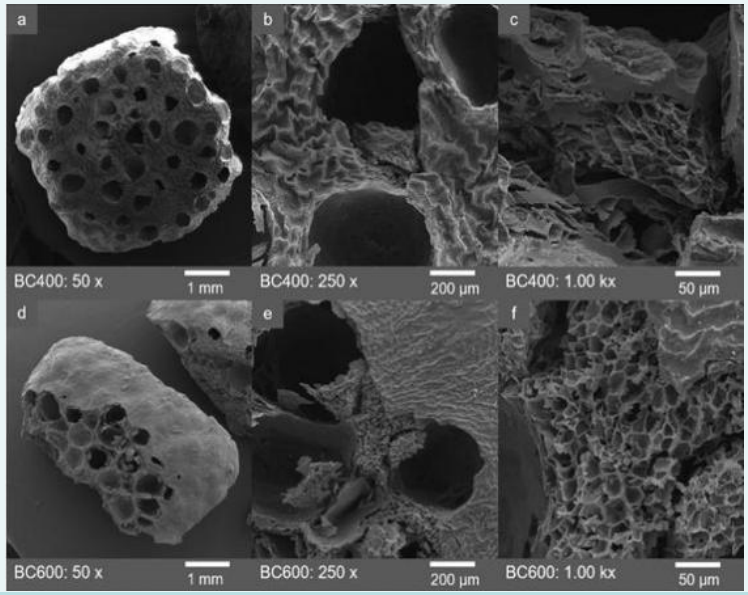
Biochar



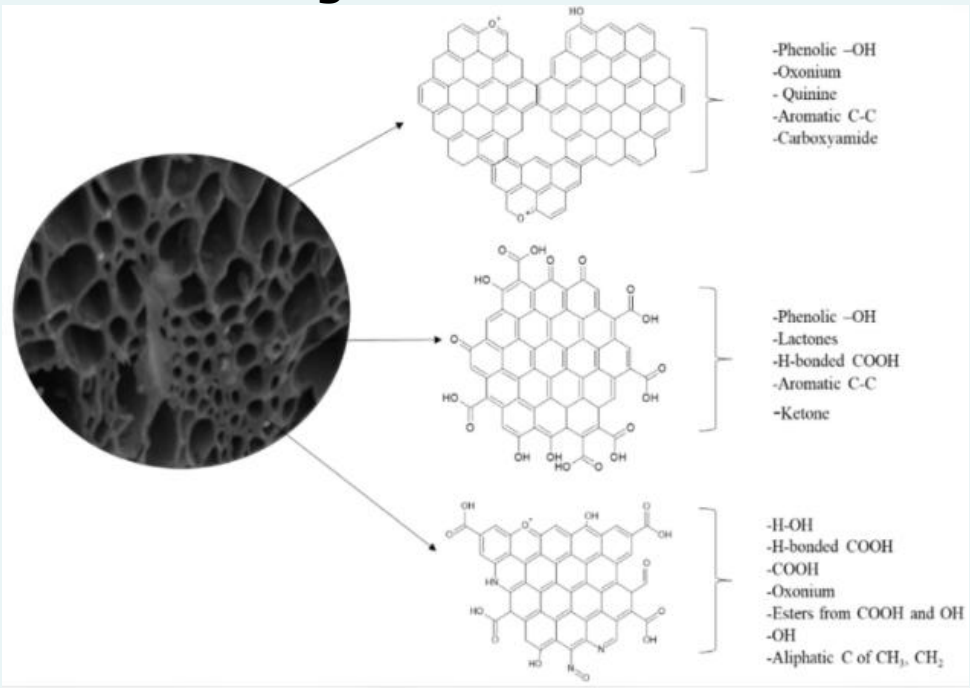


Structural and compositional analysis





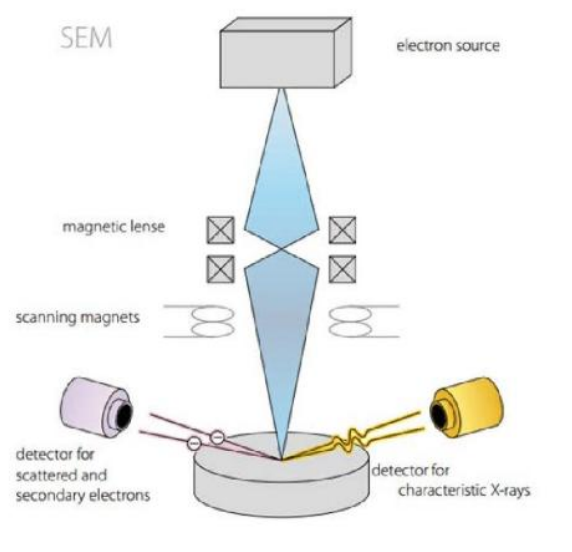
- **Carbonaceous matrix, primarily composed of disordered aromatic structures.**
- **Surface functional groups containing oxygen, hydrogen, and other heteroatoms.**
- **Mineral fraction, consisting of ash.**
- **Porous structure, partially inherited from the original biomass.**

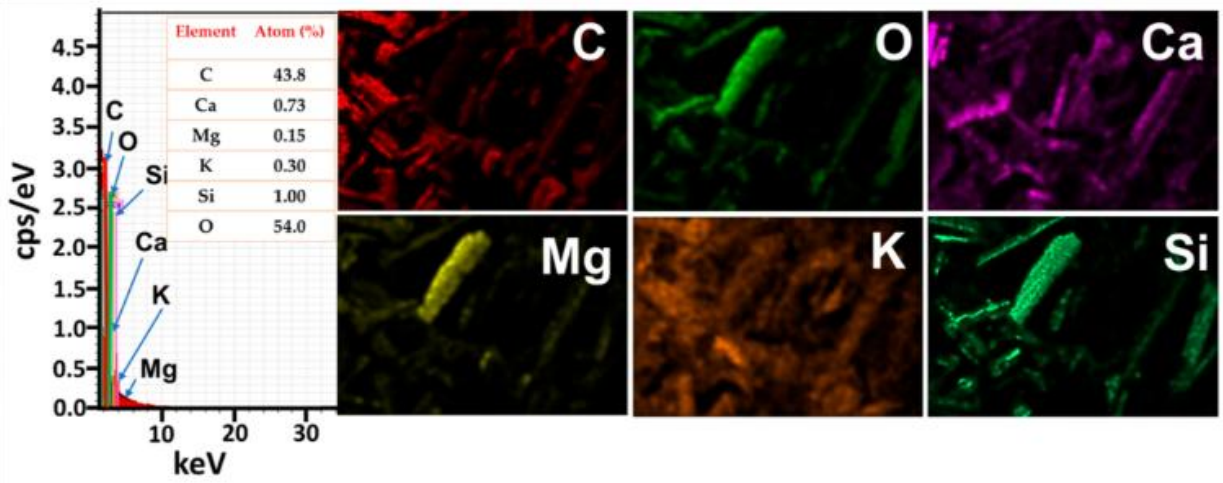


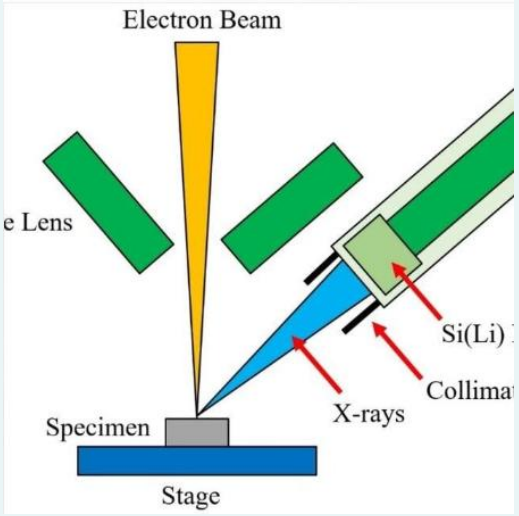
Structural and compositional analysis

SEM-EDX analysis

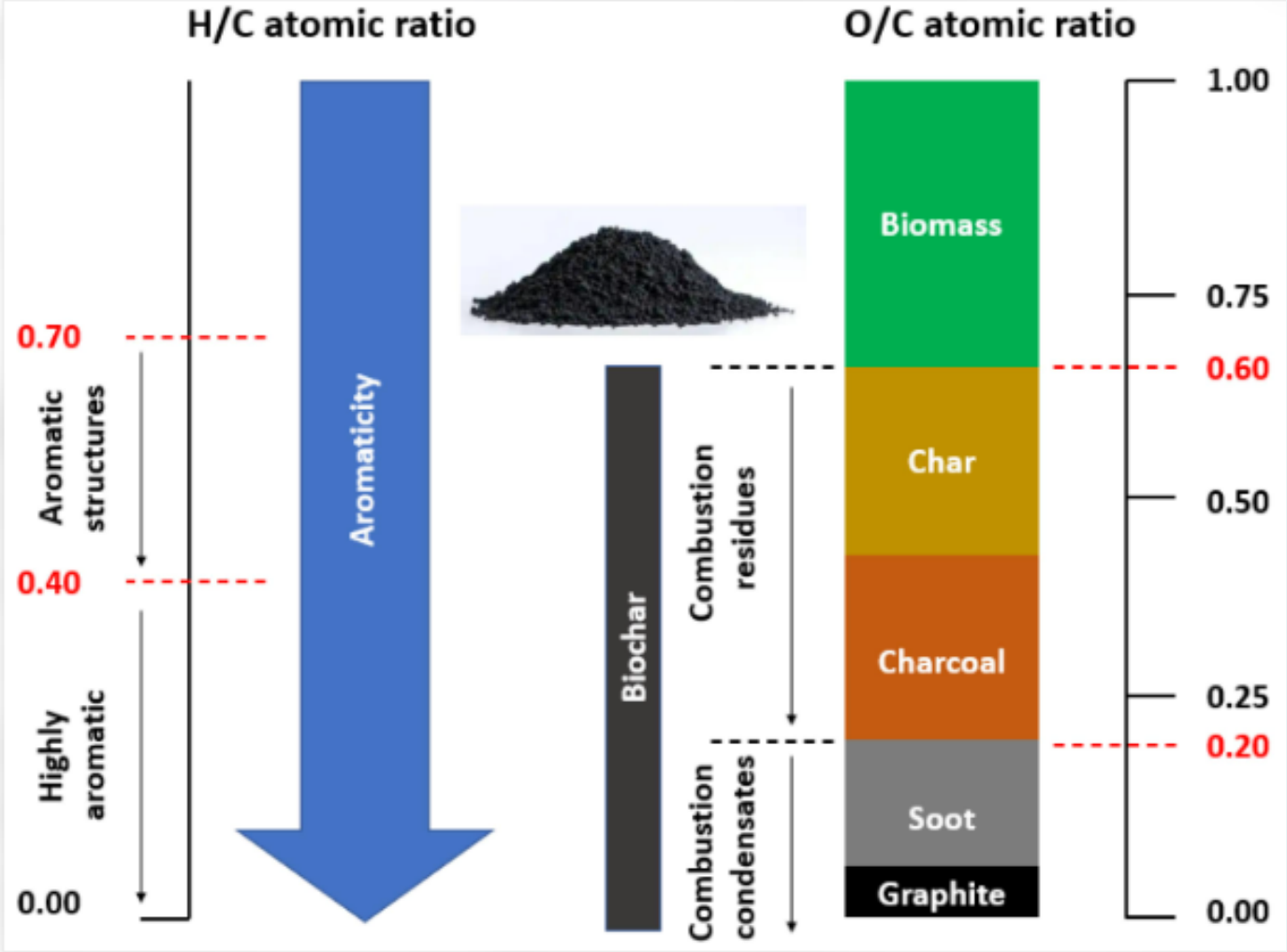








Structural and compositional analysis



Porosity

Origin: 1.Water evaporation: Moisture present in the biomass is removed.
2.Decomposition of the organic structure: Cellulose, hemicellulose, and lignin progressively undergo thermal degradation.
3.Release of volatile compounds: Gases and vapors are released, including CO_2, CO, H_2O, and various organic compounds.
4.Formation of the carbonaceous structure: The solid residue becomes enriched in carbon and develops cavities, cracks, and pores.
5.Partial preservation of the original plant structure: Particularly in woody biomass, the channels and cavities of the original plant cells remain recognizable.

Pore Type	Pore Size	Origin and Characteristics
Micropores	< 2 nm	Develop during carbonization and the release of volatile compounds.
Mesopores	2–50 nm	May originate from the decomposition of the organic matrix and the evolution of the carbonaceous structure.
Macropores	> 50 nm	Often originate from the original cellular structure of the biomass.

Surface area

Material	Typical BET Specific Surface Area
Non-activated biochar, low-temperature pyrolysis	< 10–30 m²/g
Non-activated biochar, intermediate-temperature pyrolysis	10–200 m²/g
Non-activated biochar, under conditions favorable for micropore development	Up to several hundred m²/g
Activated biochar	Often 500–2,000 m²/g, sometimes higher



BET porosimeter

Measuring an invisible surface with a gas: BET porosimetry

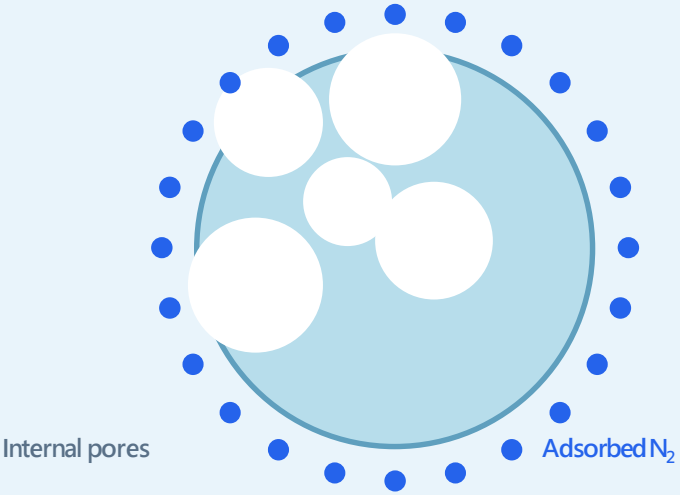
THE PRINCIPLE

The key question

How much surface area is accessible inside a powder?

The ***BET (Brunauer, Emmett e Teller)*** method estimates specific surface area from the amount of gas adsorbed onto a sample.

Schematic of a porous particle



How the instrument works

MEASUREMENT WORKFLOW

01

DEGASSING

Heat + vacuum or inert gas to remove previously adsorbed species.

02

COOLING

The sample is cooled; N_2 is typically measured at 77 K (−196 °C).

03

N_2 DOSING

N_2 is introduced in controlled pressure increments.

04

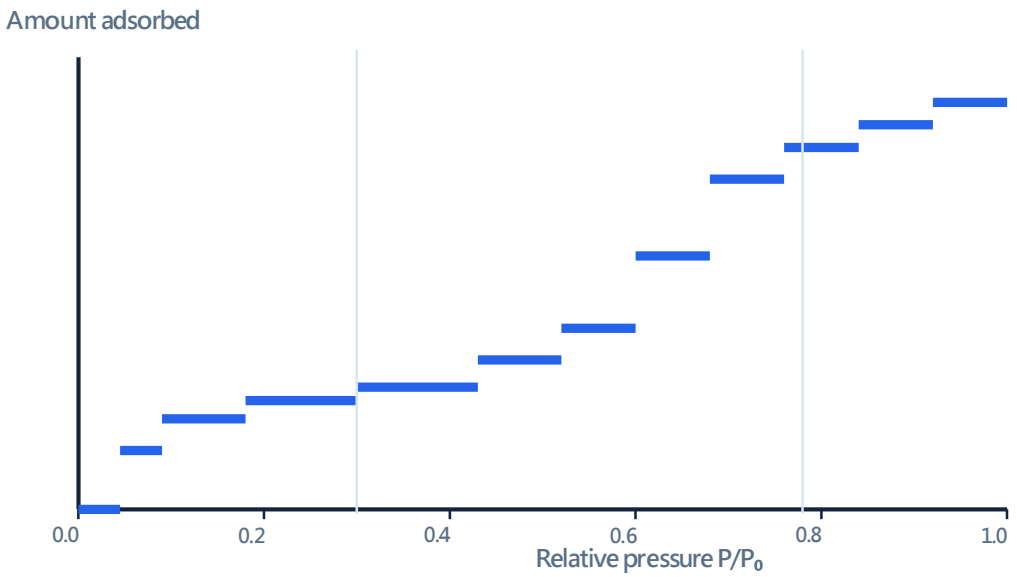
MEASUREMENT

Adsorbed amount is recorded at each equilibrium pressure.

OUTPUT → Isotherm: amount of N_2 adsorbed versus relative pressure P/P_0.

How to read an adsorption isotherm

THE KEY GRAPH



Three typical regions

A · Low P/P_0

Initial adsorption; possible data range for BET fitting.

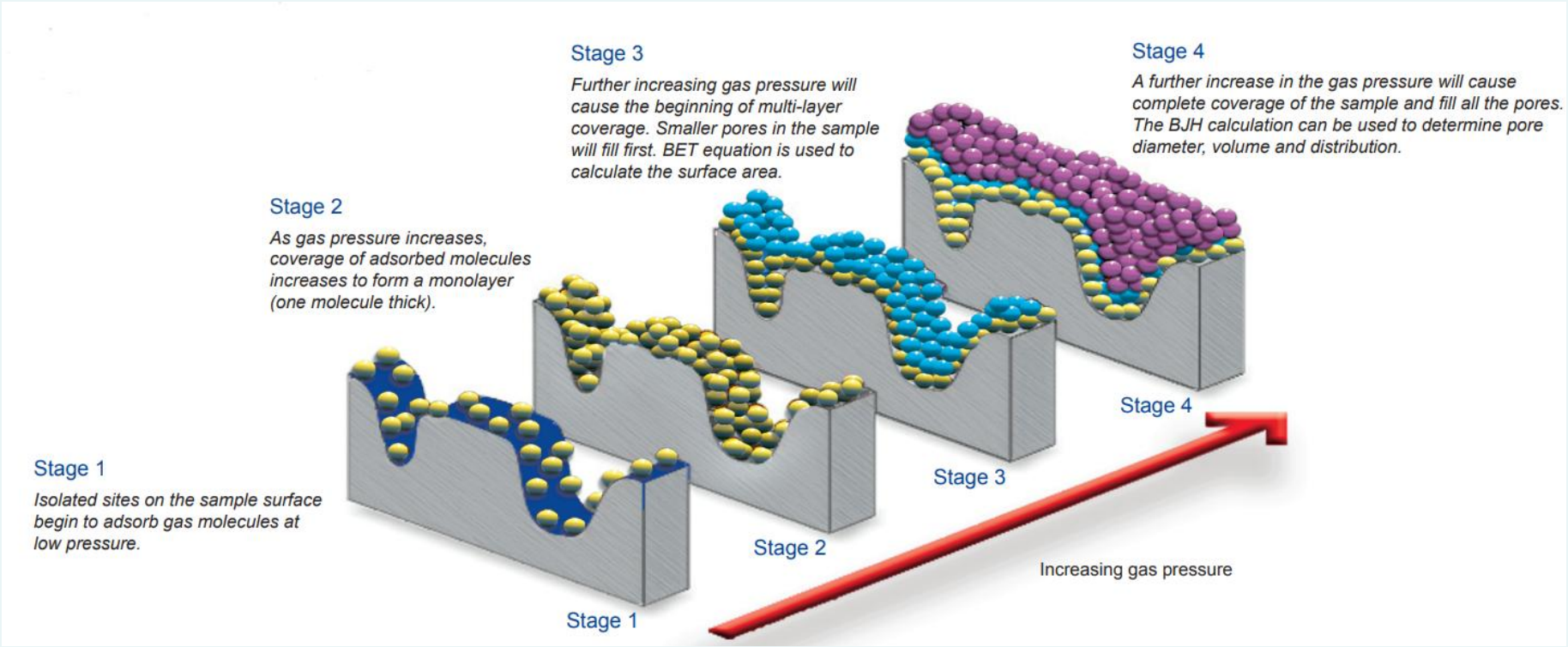
B · Mid-range P/P_0

Multilayer adsorption and capillary condensation in mesopores.

C · High P/P_0

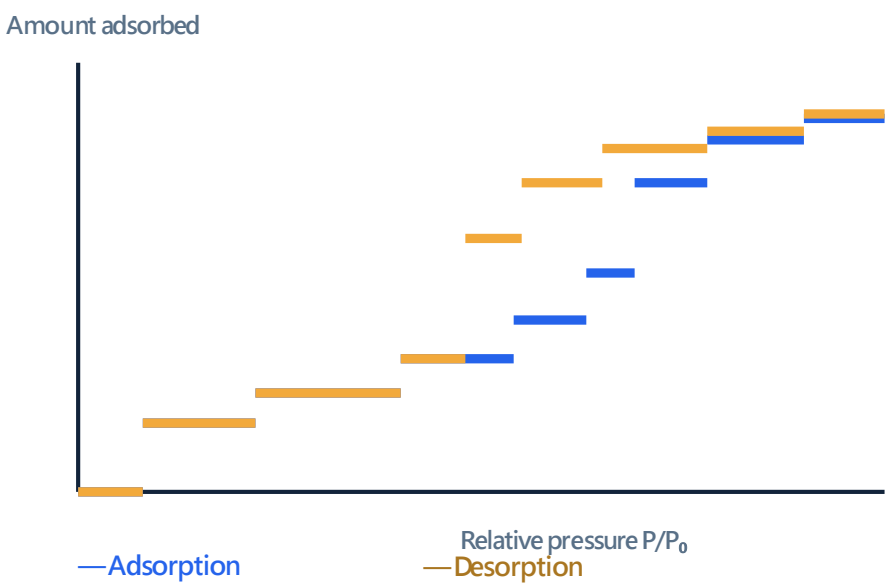
Filling accessible pores; estimating pore volume.

Pores filling



Adsorption ≠ desorption

HYSTERESIS



Why do the curves differ?

In mesopores, capillary condensation and evaporation may occur at different pressures.

Hysteresis suggests mesoporosity, but it does not, by itself, identify the shape of the pores.

Three key metrics

FROM ISOTHERM TO RESULTS

BET SURFACE AREA

120 m^2/g

Accessible area per unit mass, derived from monolayer capacity.

PORE VOLUME

0.40 cm^3/g

Accessible pore volume estimated from adsorbed / condensed gas.

CHARACTERISTIC PORE SIZE

12 nm

Representative pore size calculated using BJH or DFT models.

Illustrative values for a mesoporous material; not experimental results.

What to check before interpreting

INTERPRETATION CHECKLIST

Quick interpretation

- Isotherm type and presence of hysteresis
- Relative-pressure range used for BET fitting
- Specific surface area: m^2/g
- Pore volume and size distribution: method used
- Degassing quality and sample mass

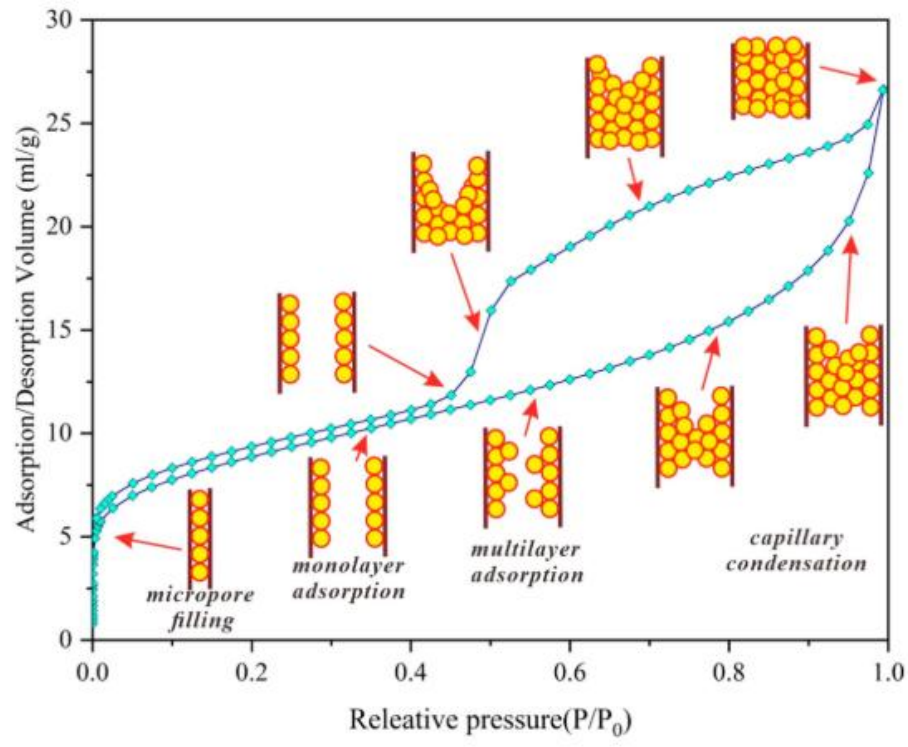
Remember

BET = specific surface area

Pore analysis requires additional models (BJH, DFT, NLDFT…).

The isotherm reveals structure, not just a number.

How to read an adsorption isotherm



Three typical regions

A · Low P/P_0

Initial adsorption; possible data range for BET fitting.

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Multilayer adsorption and capillary condensation in mesopores.

C · High P/P_0

Filling accessible pores; estimating pore volume.

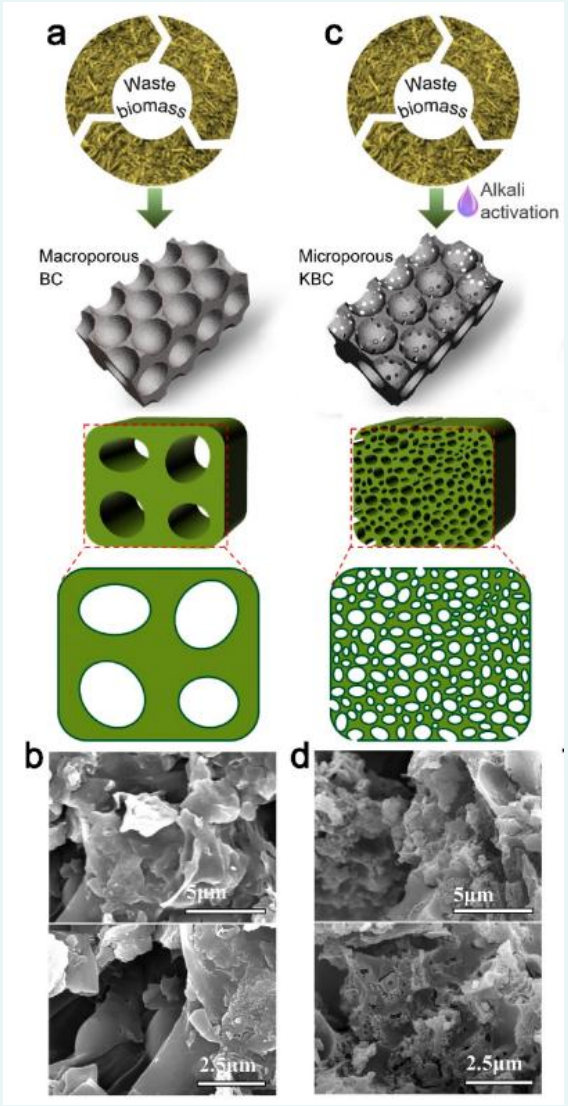
Surface area

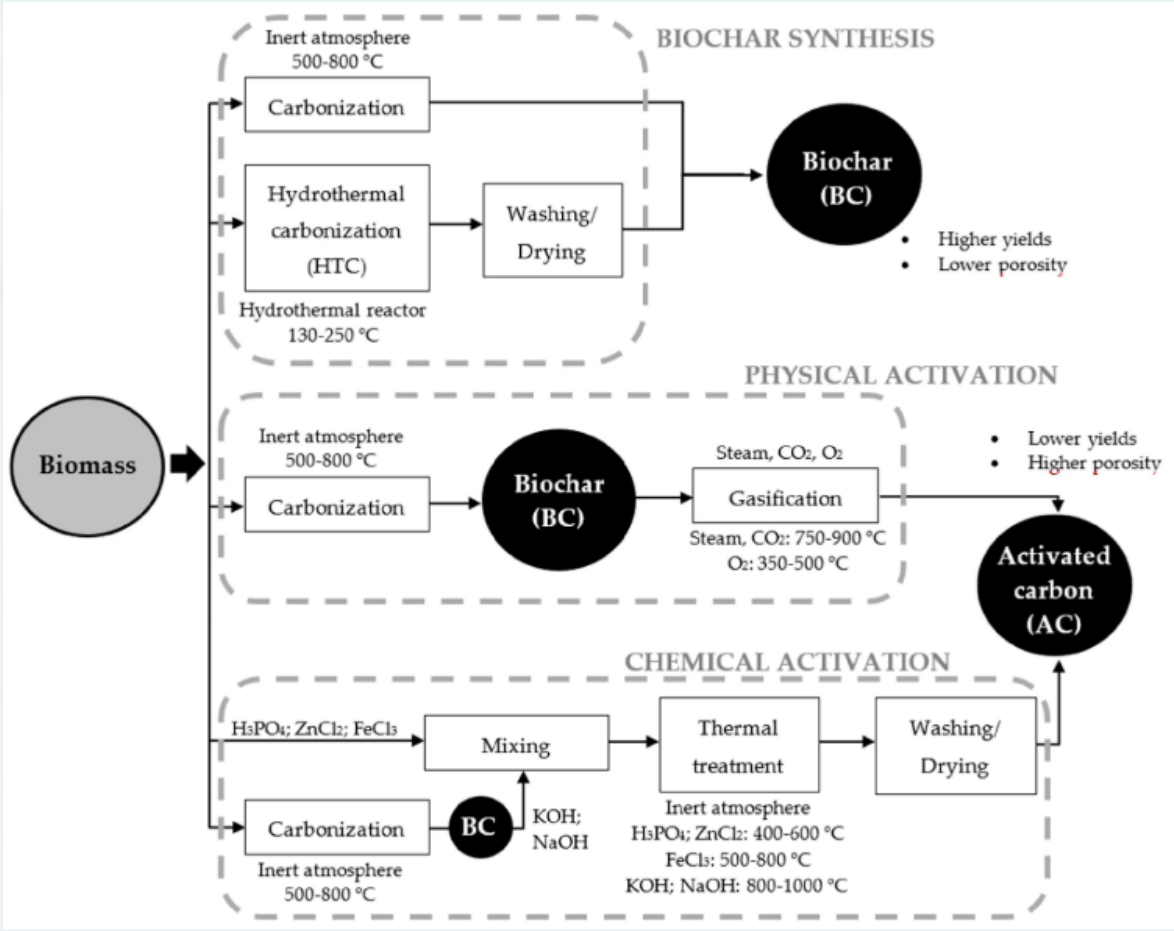
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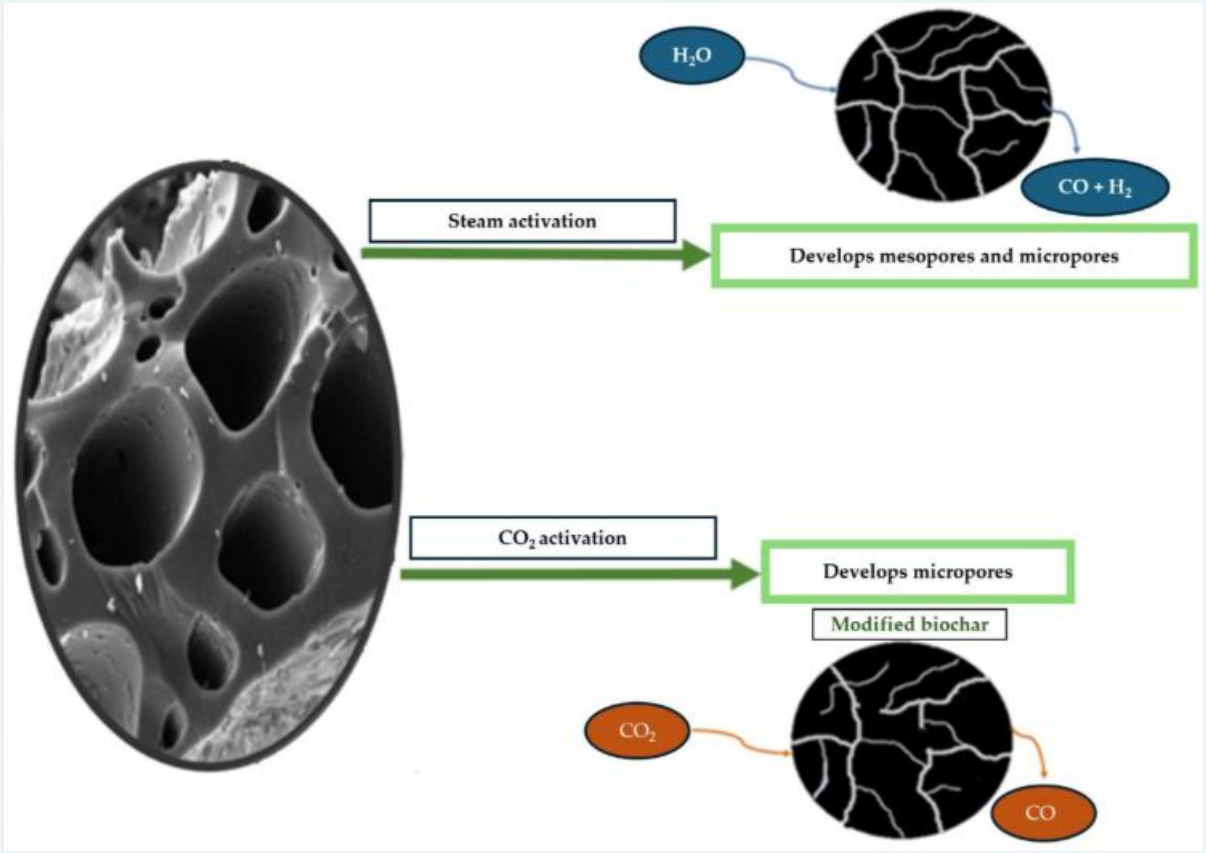
BET porosimeter

Activation


a
Waste biomass
Macroporous BC
b
5μm
2.5μm
c
Waste biomass
Alkali activation
Microporous KBC
d
5μm
2.5μm


BIOCHAR SYNTHESIS
Inert atmosphere
500-800 °C
Carbonization
Hydrothermal carbonization (HTC)
Hydrothermal reactor
130-250 °C
Washing/ Drying
Biochar (BC)
Higher yields
Lower porosity
PHYSICAL ACTIVATION
Biomass
Inert atmosphere
500-800 °C
Carbonization
Biochar (BC)
Steam, CO2, O2
Gasification
Steam, CO2: 750-900 °C
O2: 350-500 °C
Lower yields
Higher porosity
Activated carbon (AC)
CHEMICAL ACTIVATION
H3PO4; ZnCl2; FeCl3
Mixing
Thermal treatment
Washing/ Drying
Carbonization
Inert atmosphere
500-800 °C
BC
KOH; NaOH
Inert atmosphere
H3PO4; ZnCl2: 400-600 °C
FeCl3: 500-800 °C
KOH; NaOH: 800-1000 °C

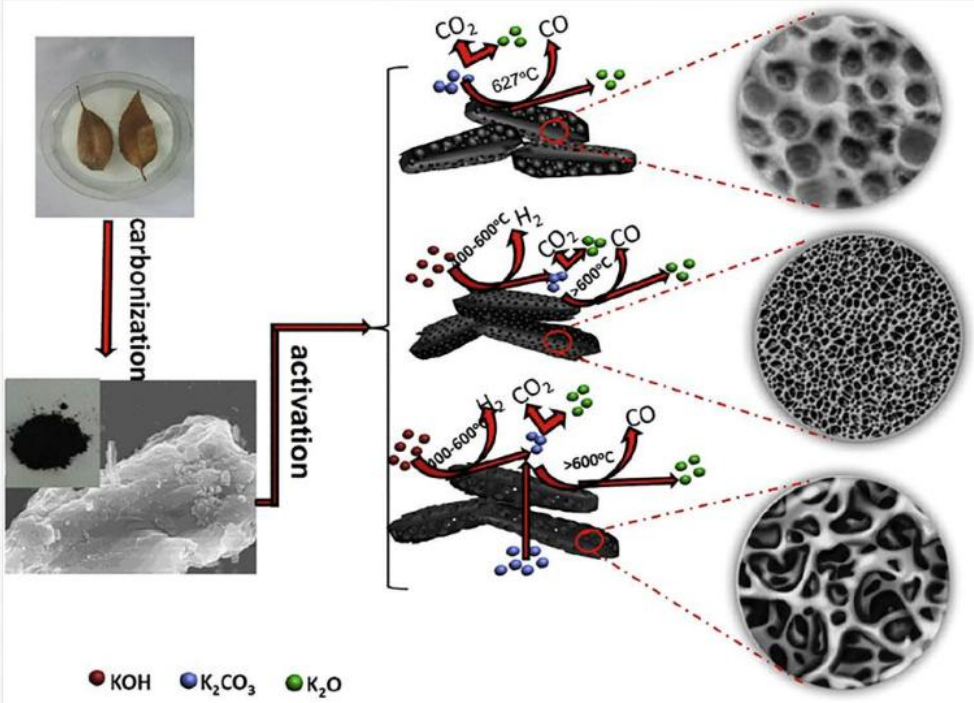
Physical Activation



$$C + H_2O \rightarrow CO + H_2$$

$$C + CO_2 \rightarrow 2CO$$

Chemical activation



$$6KOH + 2C \rightarrow 2K + 2K_2CO_3 + 3H_2$$

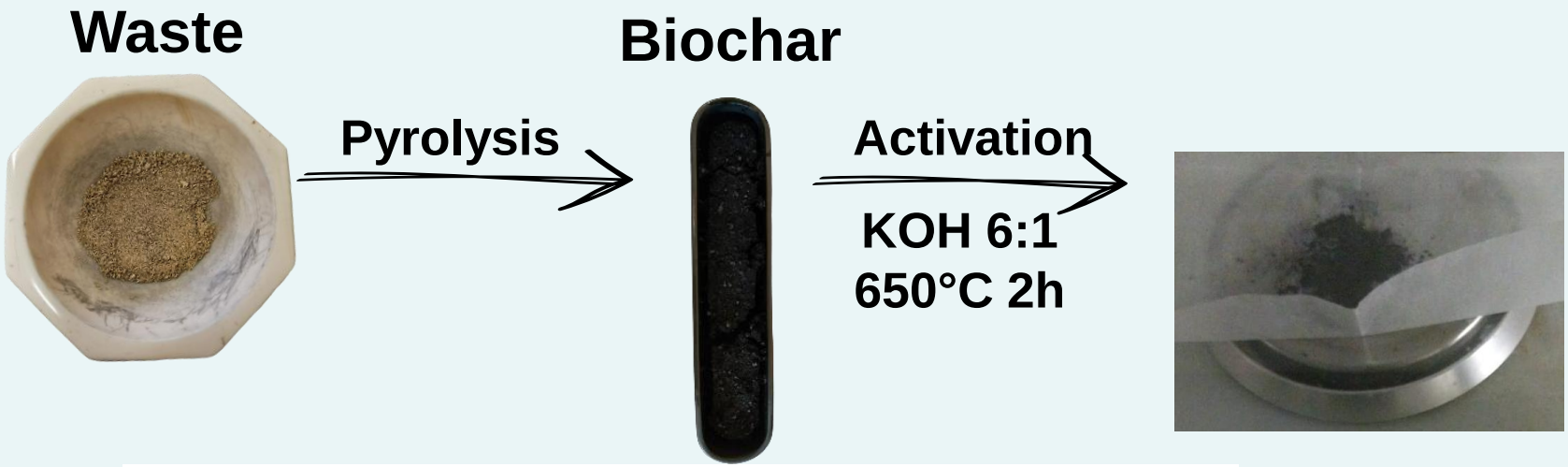
$$K_2CO_3 \rightarrow K_2O + CO_2$$

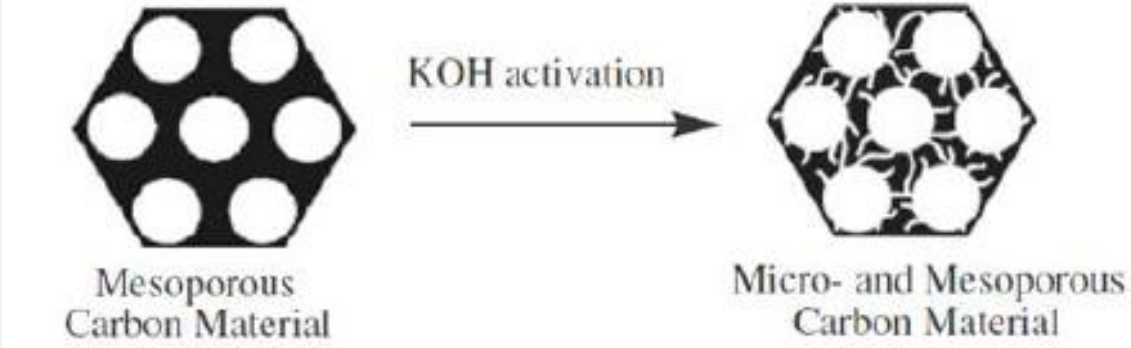
$$C + CO_2 \rightarrow 2CO$$

$$K_2O + C \rightarrow 2K + CO$$

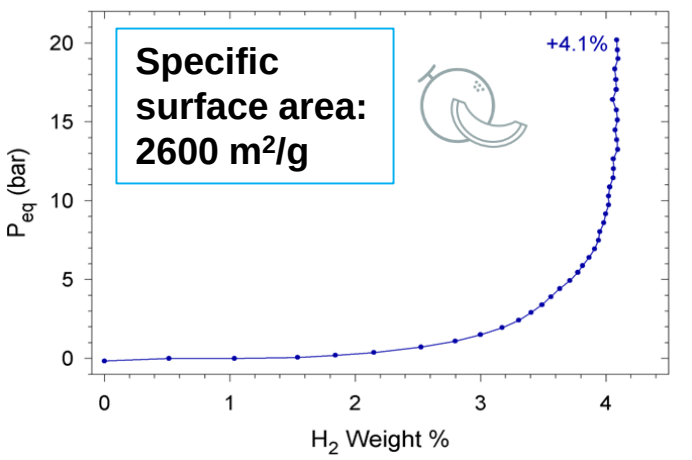
- **The consumption of the carbonaceous matrix contributes to the formation of cavities, while the reaction products can facilitate further structural transformations.**
- **Furthermore, metallic potassium can penetrate between disordered carbon domains, contributing to their separation.**
- **The reaction is a global representation; the actual mechanism involves numerous intermediate reactions.**

How to produce lab activated carbon?





Storage of hydrogen



T=77K
650°C 6h pyrolysis
6:1 KOH:AC

