Materials design & selection for Circular Economy

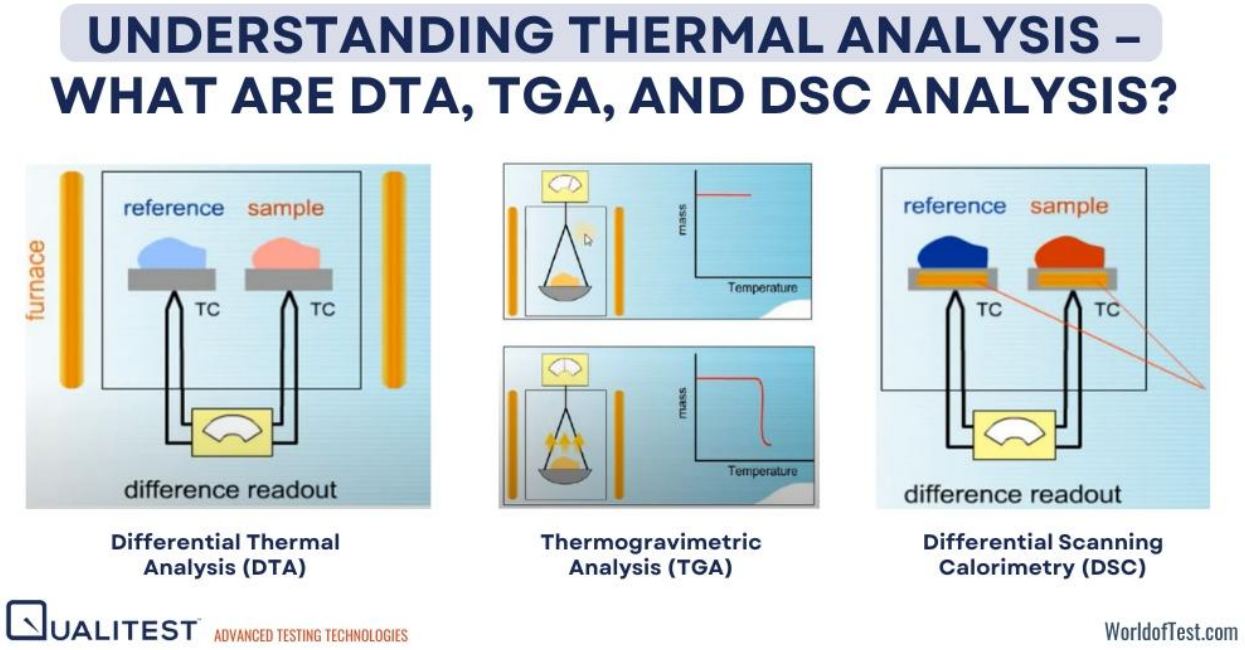
Module 3: Molecules and materials chemico-physical characterisation

Academic year 2026/2027

Lecturer: **Paolo Dolcet**

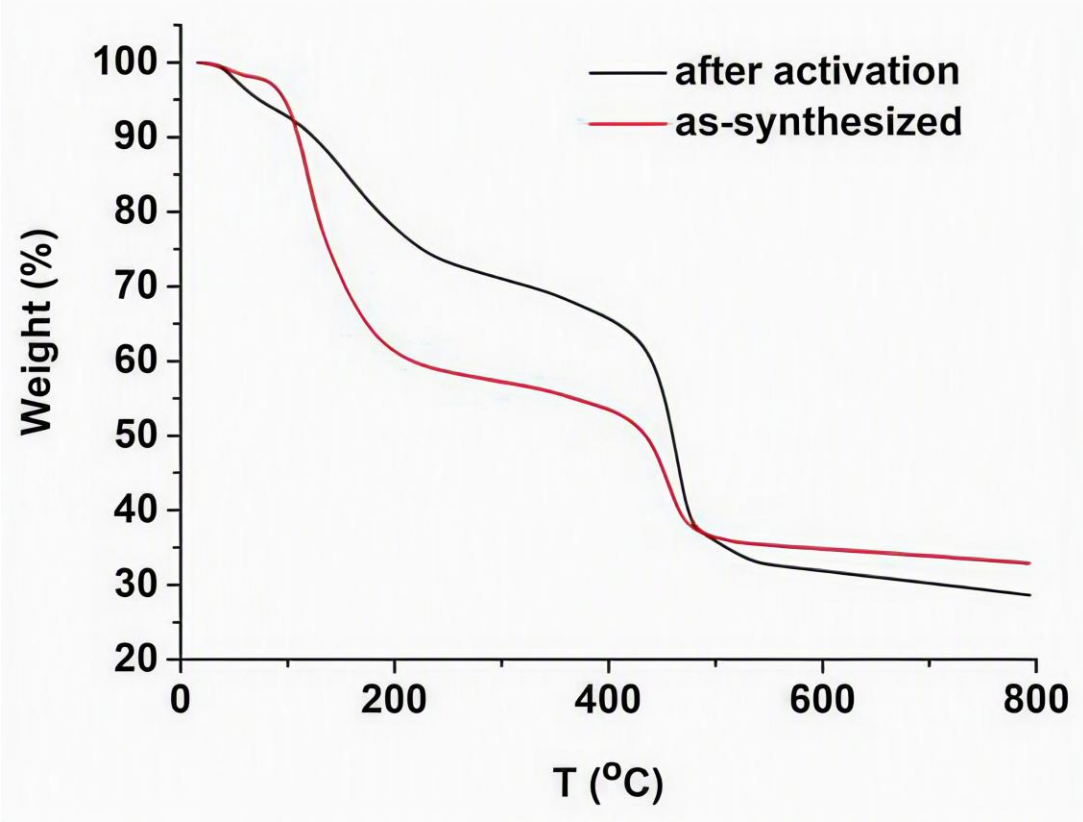
Thermogravimetric & calorimetric techniques

- Family of techniques that uses heat to extract chemical information about a substance or its reaction products
  - **Thermogravimetric analysis (TGA)**
  - **Differential thermal analysis (DTA)**
  - **Differential scanning calorimetry (DSC)**
  - **Microthermal analysis (MT)**



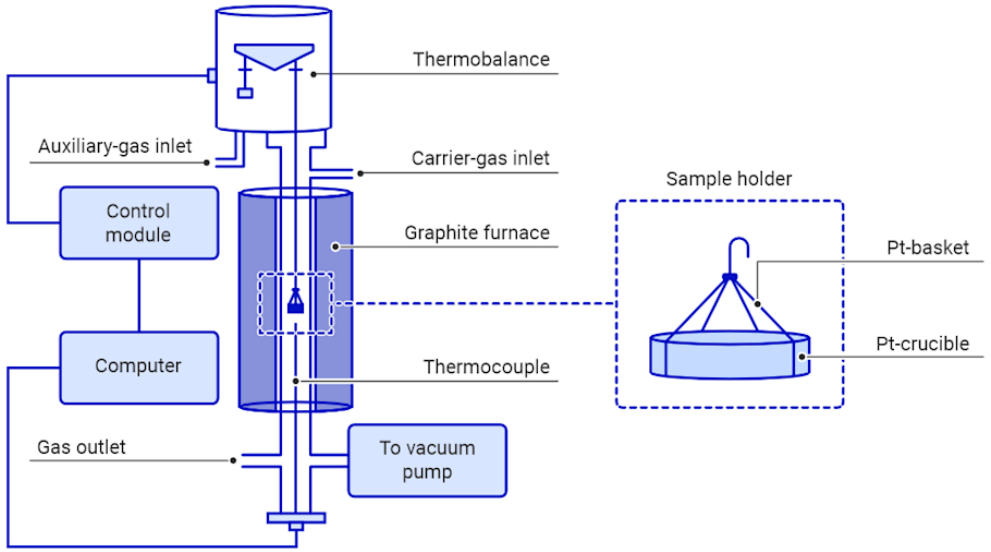
Thermogravimetric analysis (TGA)

- In TGA, the sample is heated and a curve of mass (or % mass) as a function of T or time is collected (**thermogram** or **thermal decomposition curve**)
- No direct chemical information, but it can be achieved via:
  - Comparison with the literature
  - Coupling with FTIR or mass spectrometry
- Derivative t.g. (DTG) profiles can be used for poorly resolved steps



Thermogravimetric analysis (TGA)

- **Main components**
  - Thermobalance
  - Furnace
  - Purge gas system
  - Computer for data acquisition and processing



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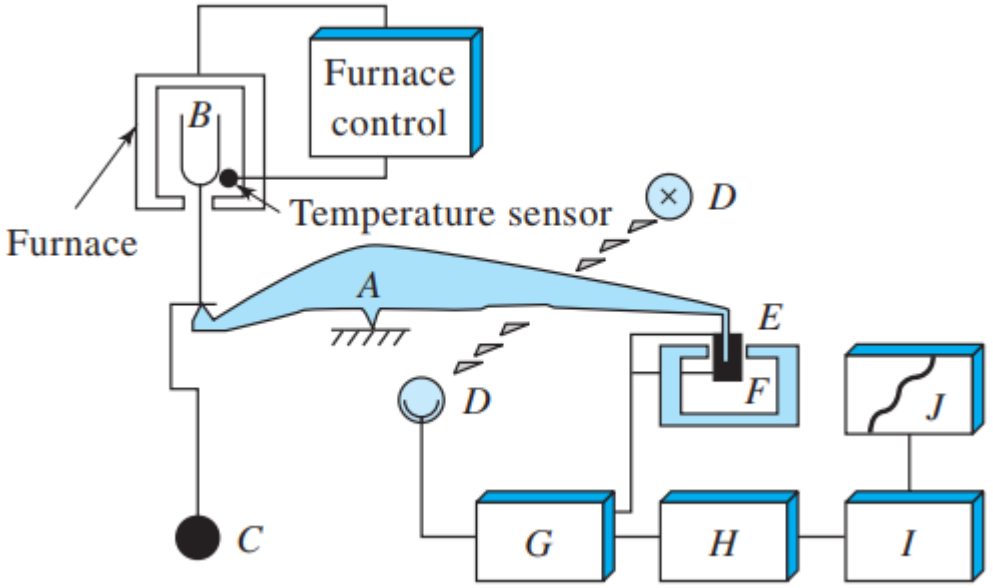
- **Thermobalance** is **very sensitive**
  - Can detect changes of **0.1 µg**
  - Must be thermally isolated
  - Changes in sample mass induce changes in the monitoring photodiode → deflection proportional to weight loss



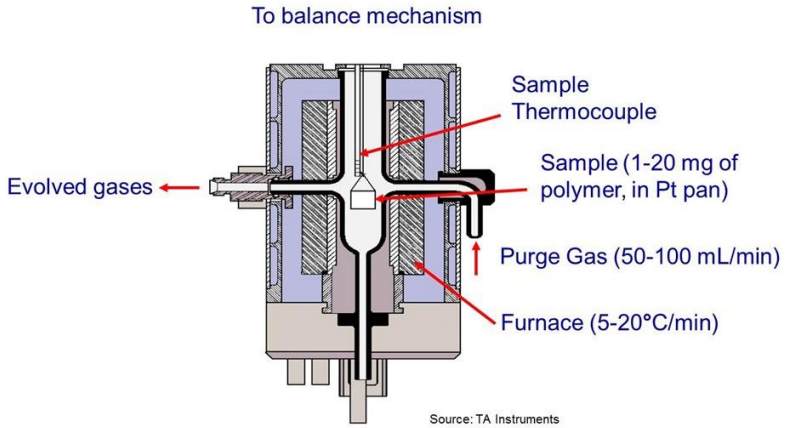
Thermobalance components: The balance beam is shown as *A*. The sample cup and holder are *B*; *C* is a counterweight. *D* is a lamp and photodiodes, *E* is a magnetic coil, and *F* is a permanent magnet. The computer data-acquisition, data-processing, and control systems are components *G*, *H*, and *I*.

Thermogravimetric analysis (TGA)

- **Sample holders**
  - Typically made of:
    - Pt: inert, easy to clean
    - Al: inexpensive, T max 600°C
    - Al_2O_3: best for low-density samples or samples that might react with Pt
  - V: 40 – 500 µL, typically 1-20 mg of sample
  - Typically autosamplers are used to load the samples



- **Furnace**
  - Can reach 1000°C (some also 1600°C)
  - Heating ramps 0.1 – 100°C/min
  - Has to be well isolated externally
  - In the furnace, N_2 or Ar are typically purged – O_2 also possible
  - Cooling: forced air (1000°C → 50 °C in < 15 min)



Chemical information from TGA

- For chemical information, coupling with Evolved Gas Analysis (EGA):
  - FT-IR spectrometer
  - Mass spectrometer
  - (Micro) Gas Chromatography



- **FT-IR**: when several gaseous products form
- **MS**: for small gaseous molecules
- **GC**: volatile molecule up to ca. 250 amu



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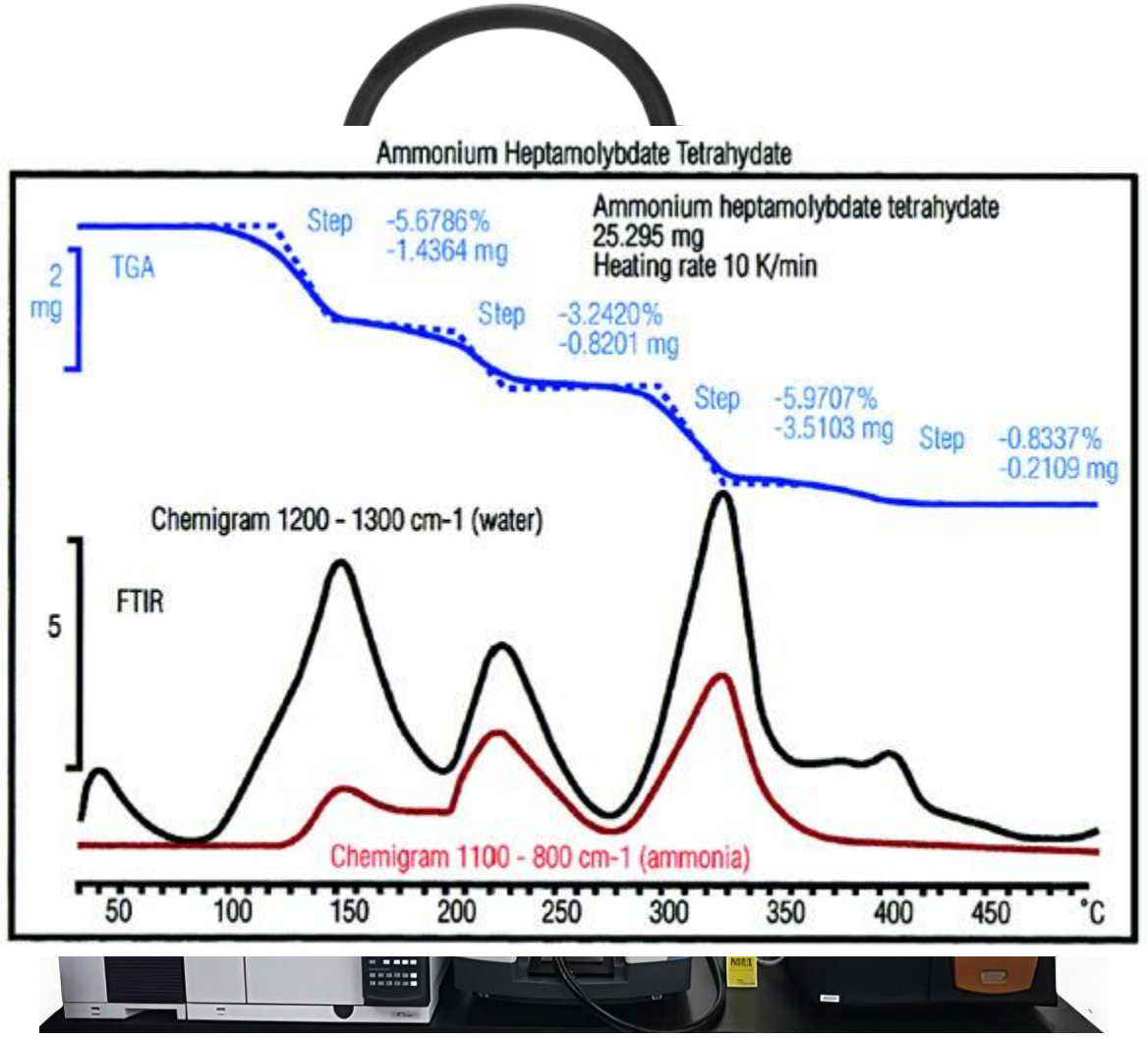

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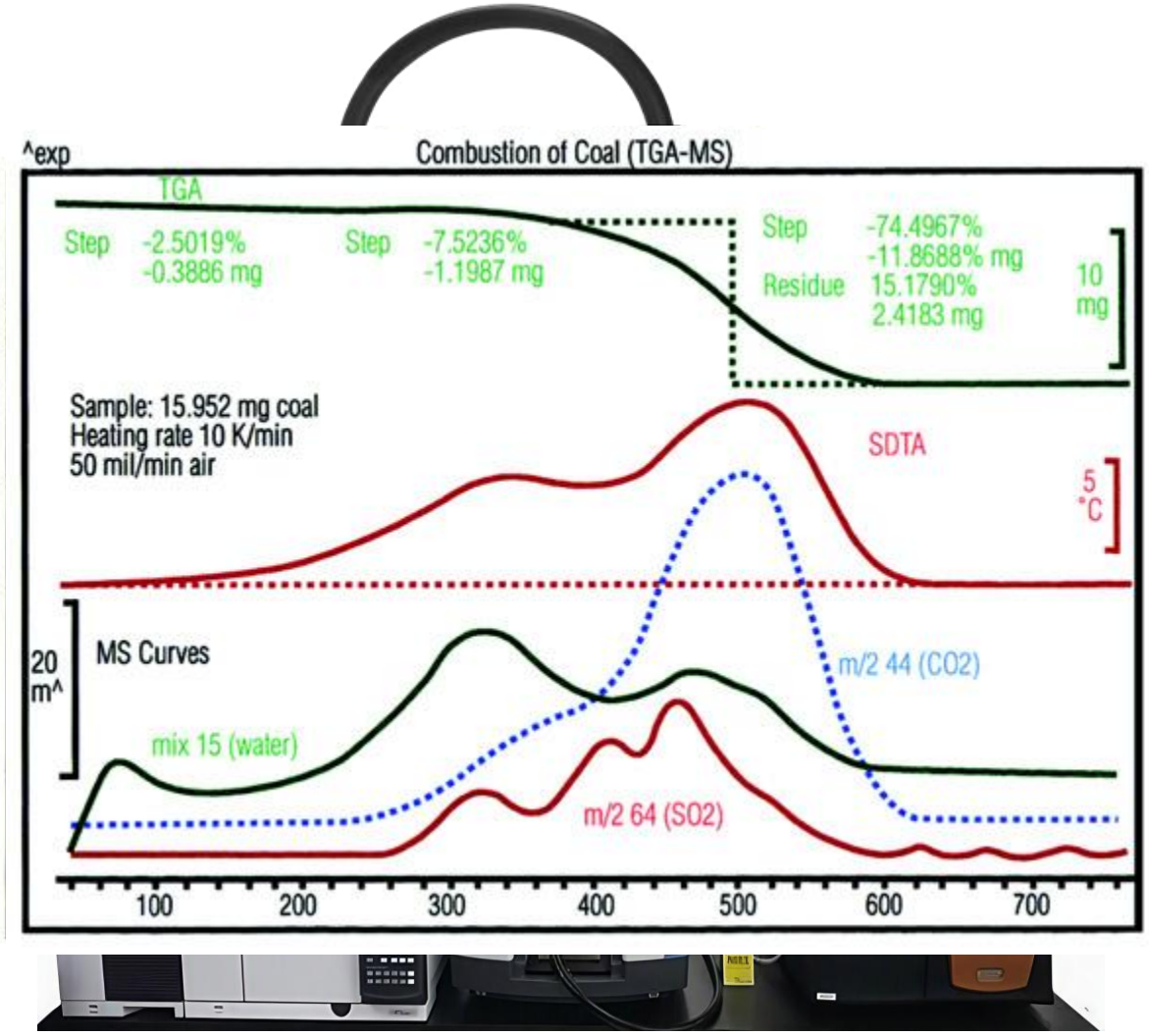
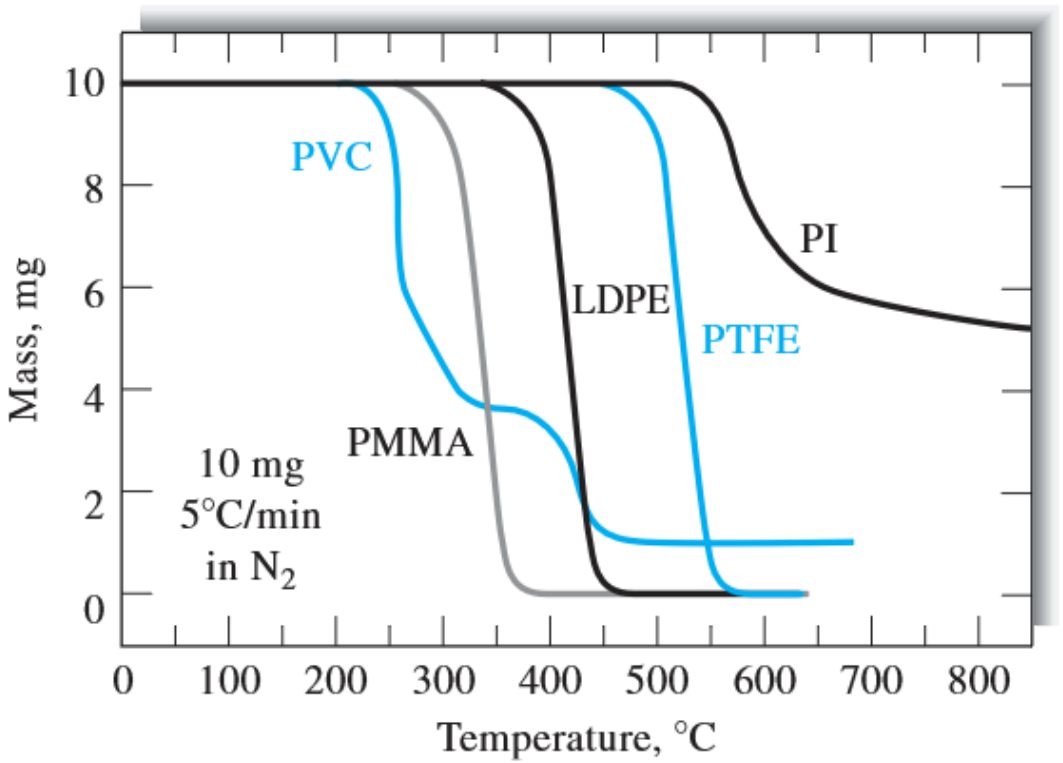
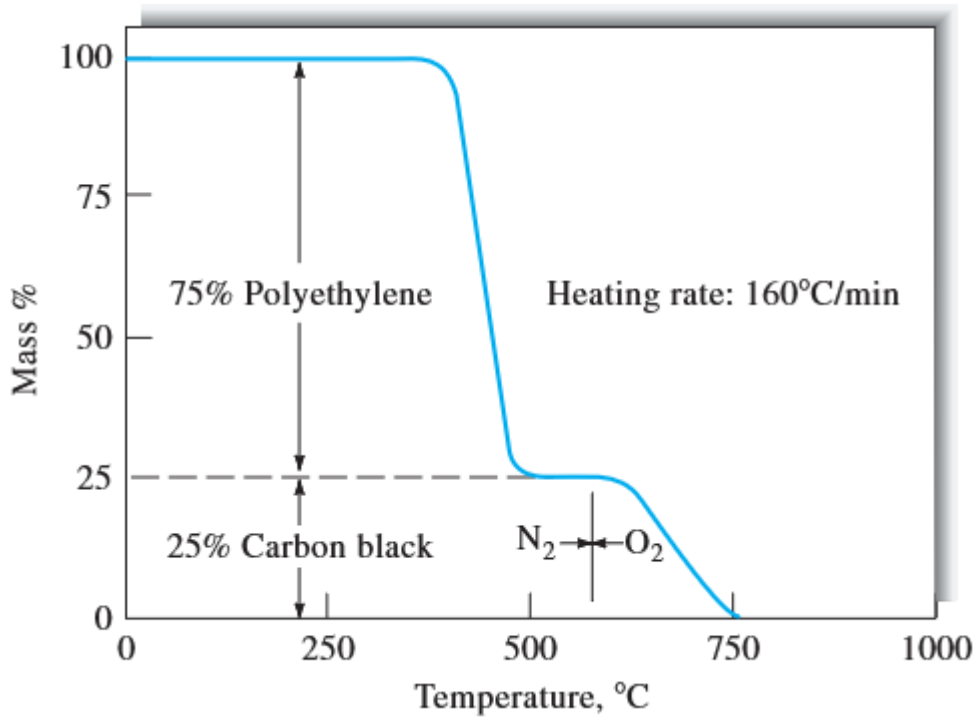


Applications of TGA

TGA typically used for compositional analysis and decomposition profiles of multicomponent systems

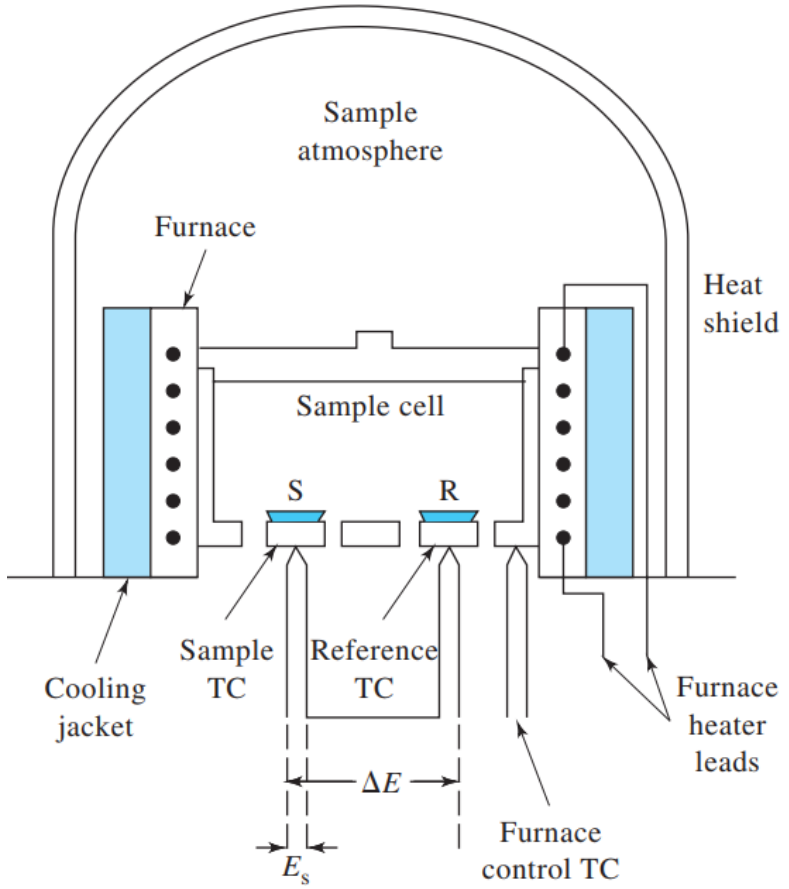




Carbon black added to inhibit photodegradation of PET

Differential thermal analysis (DTA)

- In DTA, the T of the sample is continuously compared to a reference material (inert: Al_2O_3, SiC, glass)
- Heat is provided so the **sample** warms with a **linear T ramp**
- Exp. curve shows the **ΔT between the sample** and **the reference**
- **Qualitative** technique

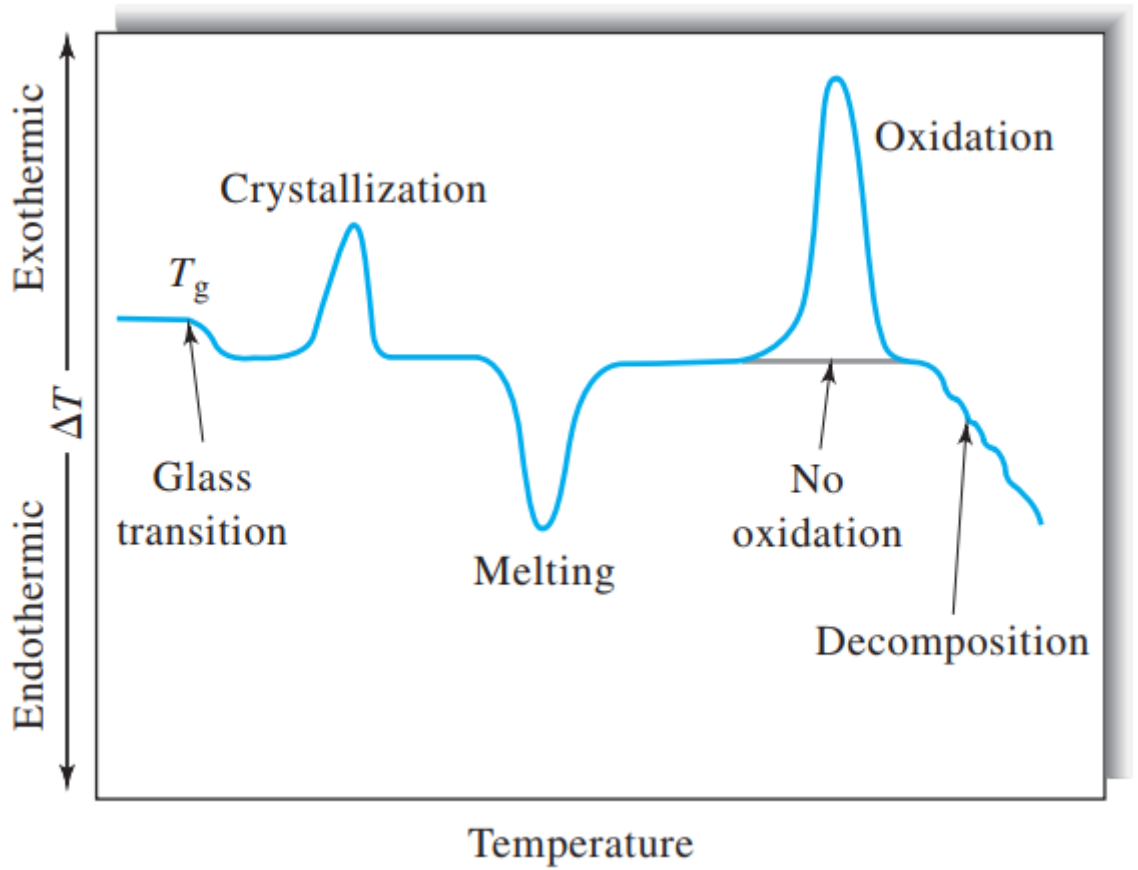


TC = thermocouple

Differential thermal analysis (DTA)

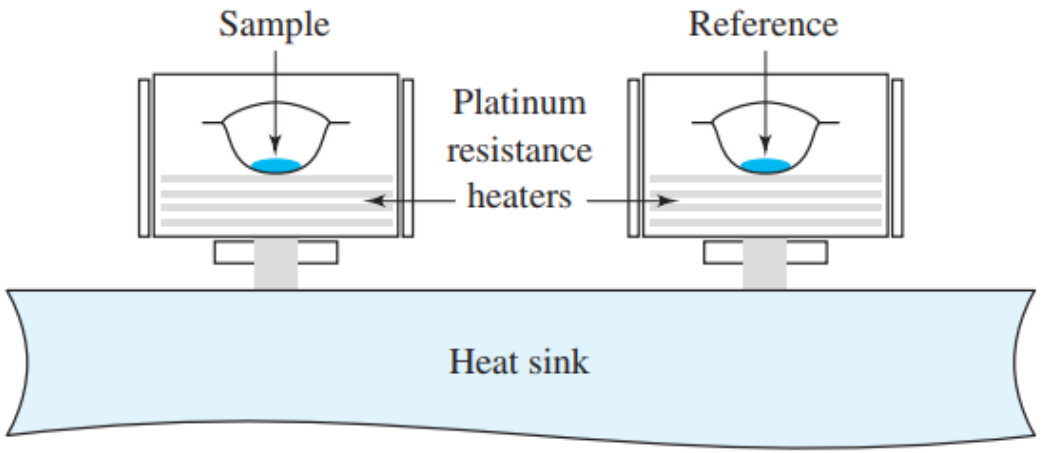
Glass temperature T_g: Characteristic T at which glassy **amorphous polymers become flexible** because of the onset of concerted motion of large segments of the polymer molecule (ΔH = 0).

Not a phase transition!



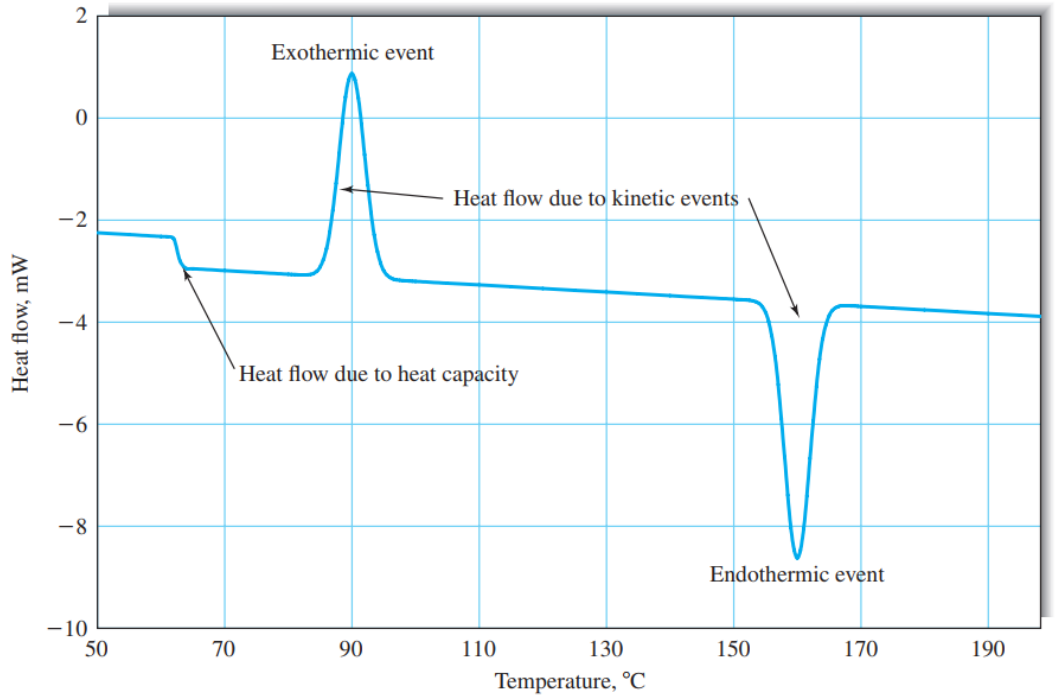
Differential Scanning Calorimetry (DSC)

- In DSC, the instrument measures the difference in the heat flow between sample and reference
- Most common thermal analysis method: fast, simple and easy to use
- Three main modes
  - Power-compensated
  - Heat-flux
  - Modulated DSC



! Important !
DTA: differences in T
DSC: differences in energy

Differential Scanning Calorimetry (DSC)



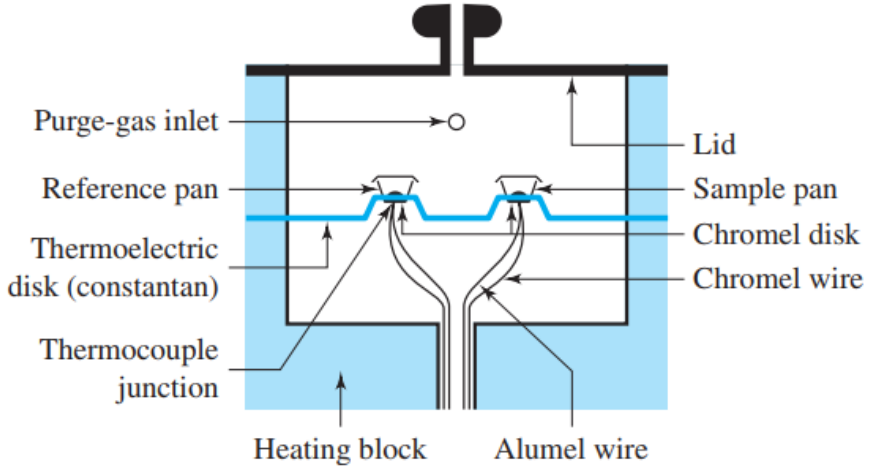
$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T,t)$$

Specific heat capacity (J K^{-1} mol^{-1})

Kinetic response (J mol^{-1})

Heat flux

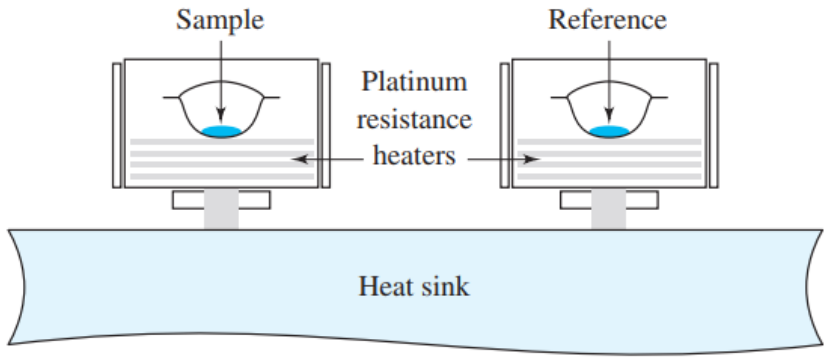
- Most common DSC method
- Sample & ref heated by the same unit
- Sample T is changed at constant rate, difference in heat flow is monitored



Differential Scanning Calorimetry (DSC)

Power-modulated

- T of sample and ref are kept = while T is linearly changed. Power needed is monitored
- Fast response, suited for kinetics studies



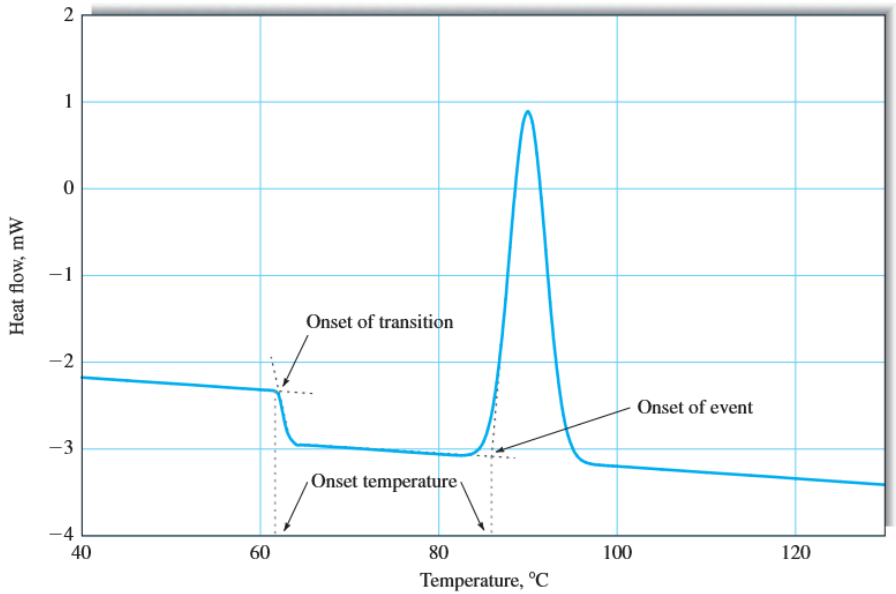
Modulated DSC (MDSC)

- Very similar to heat-flux DSC
- To heating profile of h-f DSC, a sinusoidal function is superimposed → micro heating/cooling cycles
- Via Fourier transform, signal deconvoluted in:
  - Reversing heat flow → heat capacity events
  - Nonreversing heat flow → kinetic processes

Standard DSC protocol

- Data calibration
  - When changing heat rates, T ranges or purge gases: **Baseline calibration** with no pans, using expected T profile
  - Periodically: **heat flow calibration**, by melting materia with know heat of fusion (e.g., indium)
  - For **heat capacity** determination, calibration is performed with sapphire as standard

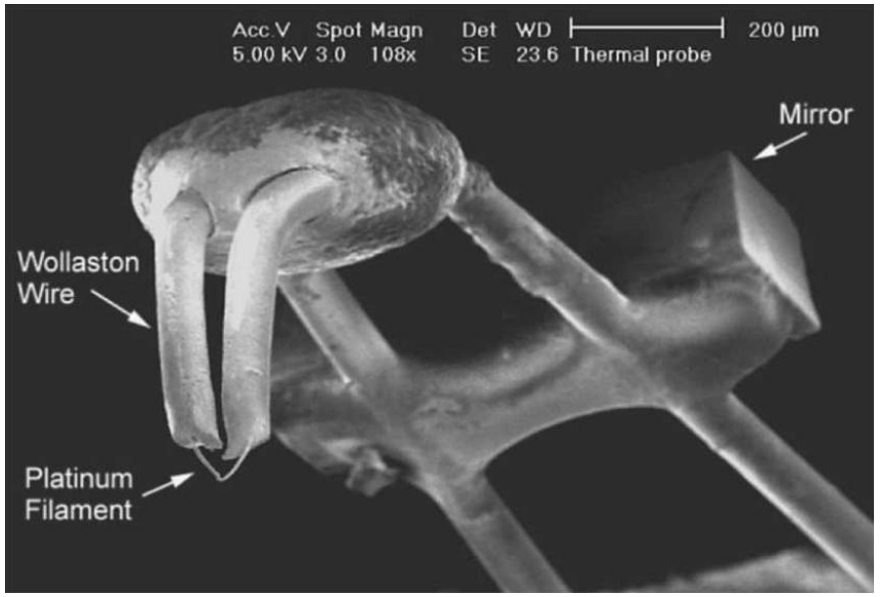
- Data analysis
  - Temperature as determined as onsets



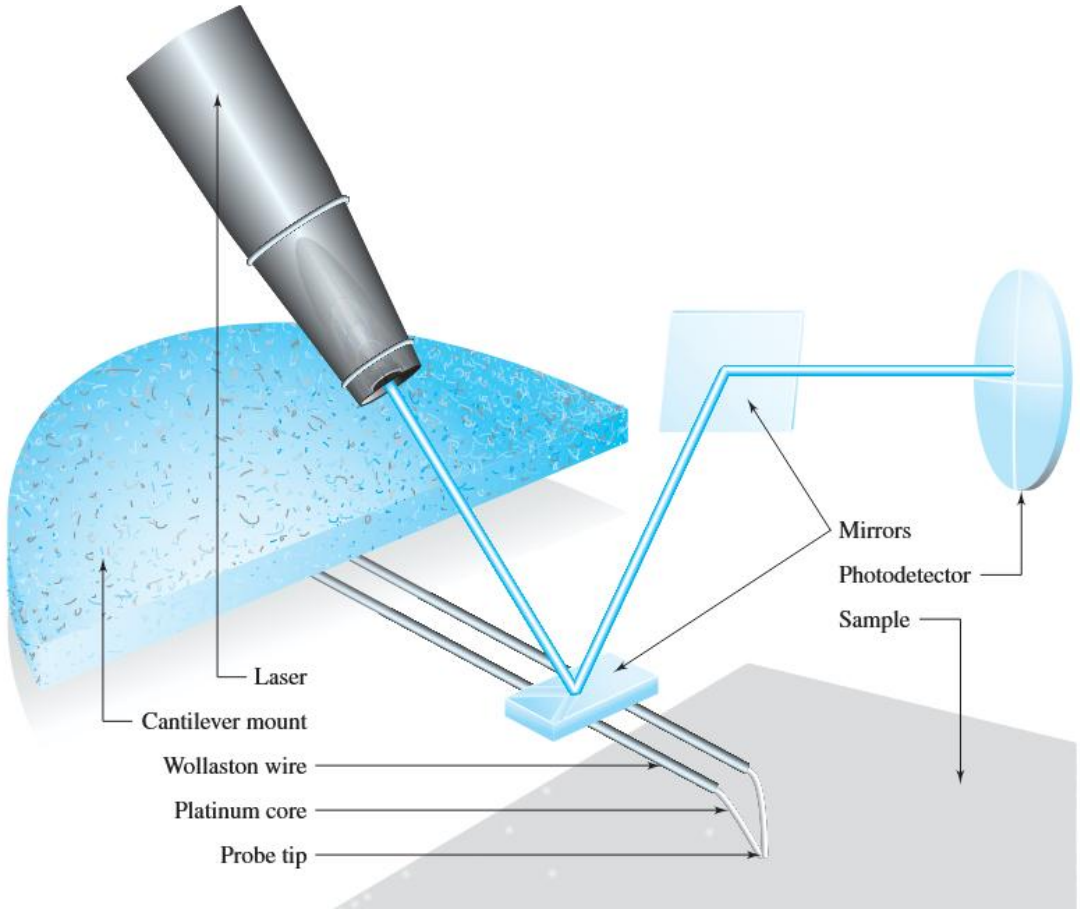
  - Can get info on:
    - Level of crystallinity, $(\Delta H_f)_{sample}/(\Delta H_f)_{crystal}$
    - Polymerization rate

Microthermal analysis

- MT combines thermal analysis with atomic force microscopy
- Information on thermal properties and surface topology

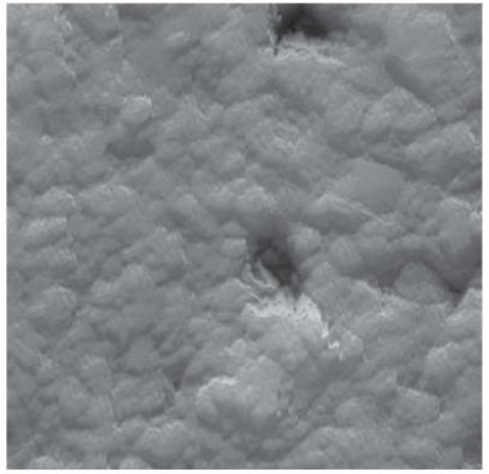


Pt wire coated by a thick Ag layer

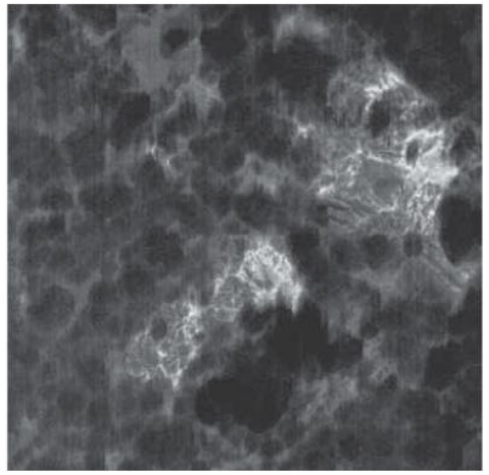


Microthermal analysis

- In the MT probe, the electrical resistance is located at the tip → only the tip becomes hot when an electrical current is applied
- Two operational modes
  - Constant T: most commonly used, simple. Power needed to keep T constant is monitored, depending on heat flow
  - Constant i: the electrical potential is monitored, depending on the resistance



Conventional AFM topography of paracetamol

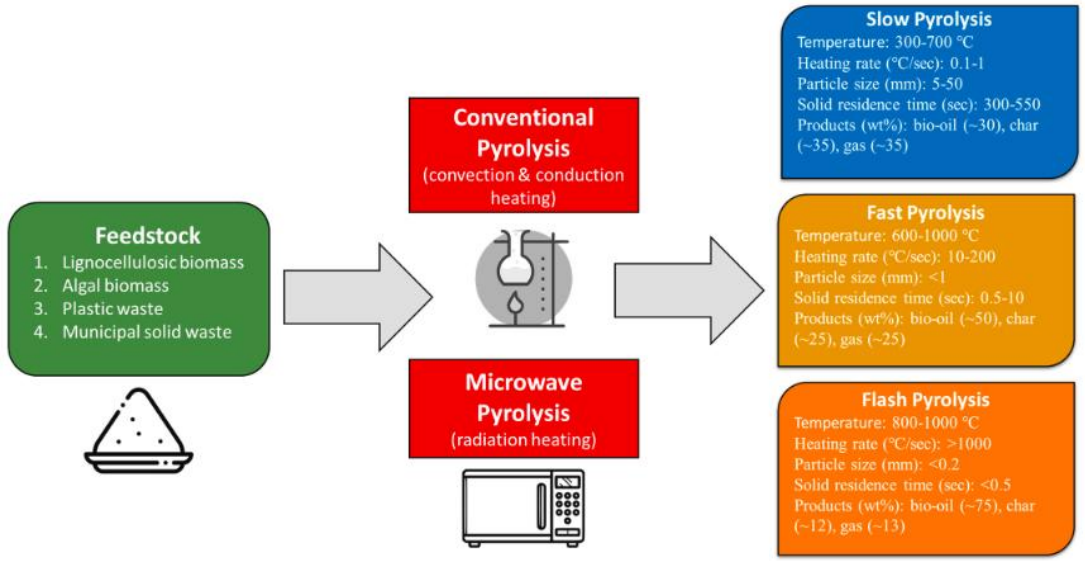


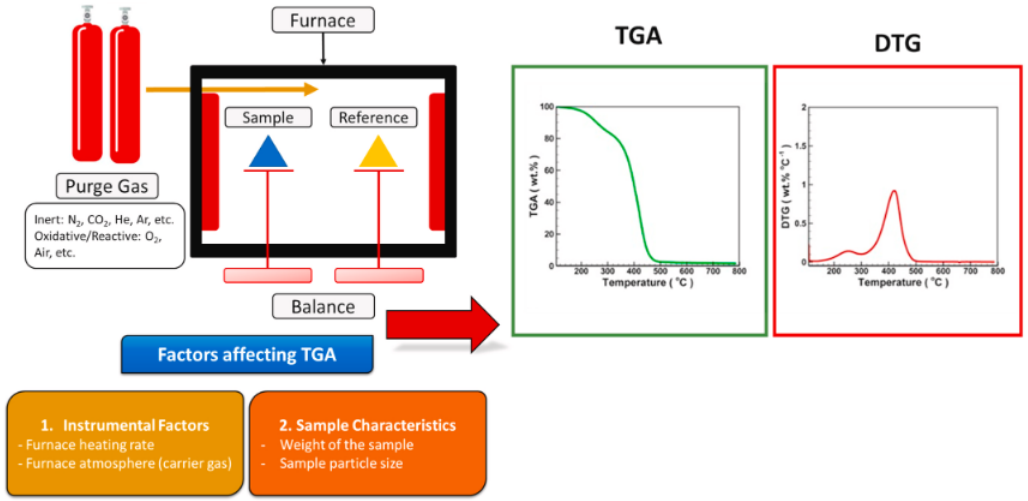
AFM topography + thermal image of paracetamol

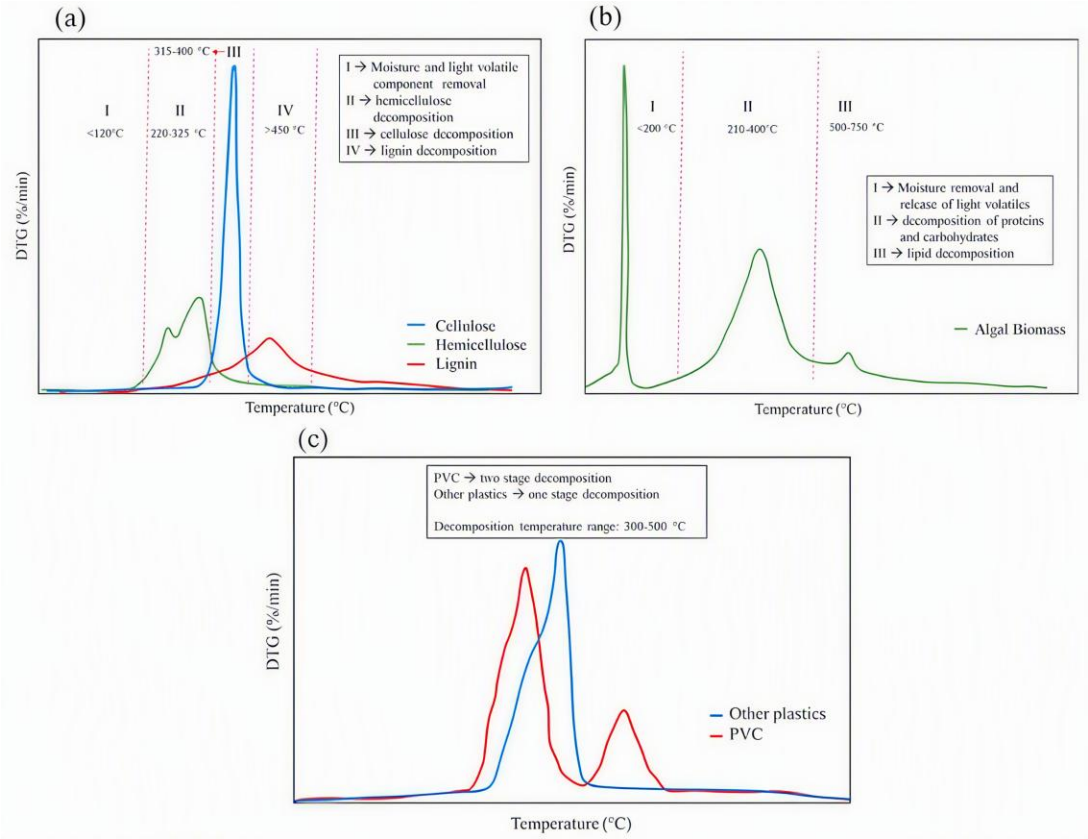
Summarizing

Property	TGA (Thermogravimetric Analysis)	DTA (Differential Thermal Analysis)	DSC (Differential Scanning Calorimetry)	Micro-TA (Microthermal Analysis)
Principle	Measures mass change vs. temperature/time	Measures temperature difference (ΔT) between sample and inert reference during heating	Measures heat flow difference between sample and reference (heat-flux or power-compensation)	AFM-based; a thermal probe scans the surface and measures local thermal conductivity/diffusivity and local thermal transitions
Complexity	Low–moderate (routine, simple data interpretation)	Moderate (mostly qualitative; baseline interpretation can be tricky)	Moderate (quantitative, but needs careful calibration and thermal-history control)	High (specialized instrument, probe calibration, surface preparation, data interpretation)
Sample types	Solids, powders, polymers, films, composites, minerals, some liquids	Solids and powders: inorganics, ceramics, minerals, metals, polymers	Polymers, pharmaceuticals, foods, organics, metals, some liquids/gels	Solids with flat, smooth surfaces: polymer blends, multilayers, composites, thin films, coatings
Typical amount	5–20 mg (up to ~100 mg for low-density or inhomogeneous samples)	5–50 mg (larger than DSC)	1–10 mg (typically 2–5 mg for polymers)	Bulk sample with a smooth area (µm2 scale); no real 'mass', probed volume ~µm3
Information gained	Thermal stability and decomposition temperature, composition (moisture, volatiles, filler, ash content), degradation kinetics, oxidation	Transition temperatures (melting, crystallization, glass transition, phase changes, decomposition); mostly qualitative (exo/endothermic)	T_g, T_m, T_c, enthalpies (ΔH), heat capacity, crystallinity, curing degree, purity, polymorphism, thermal history	Spatially resolved thermal conductivity, local T_g and T_m, phase distribution and miscibility in blends, surface/subsurface morphology and thermal mapping
Output	Mass (%) vs. T or t (and DTG, its derivative)	ΔT vs. T	Heat flow (mW) vs. T or t	Thermal conductivity map, local thermal transition curves (probe displacement vs. T)
Quantitative?	Yes (mass)	Mostly semi-quantitative	Yes (enthalpy, C_p)	Semi-quantitative (relative contrast; local T_g values)
Typical temp. range	RT to ~1000–1600 °C	RT to ~1500 °C (or higher)	−150 to ~700 °C	RT to ~300–400 °C (probe-limited)

Pyrolysis of biomass for biofuel production







https://doi.org/10.1016/j.rser.2022.112914

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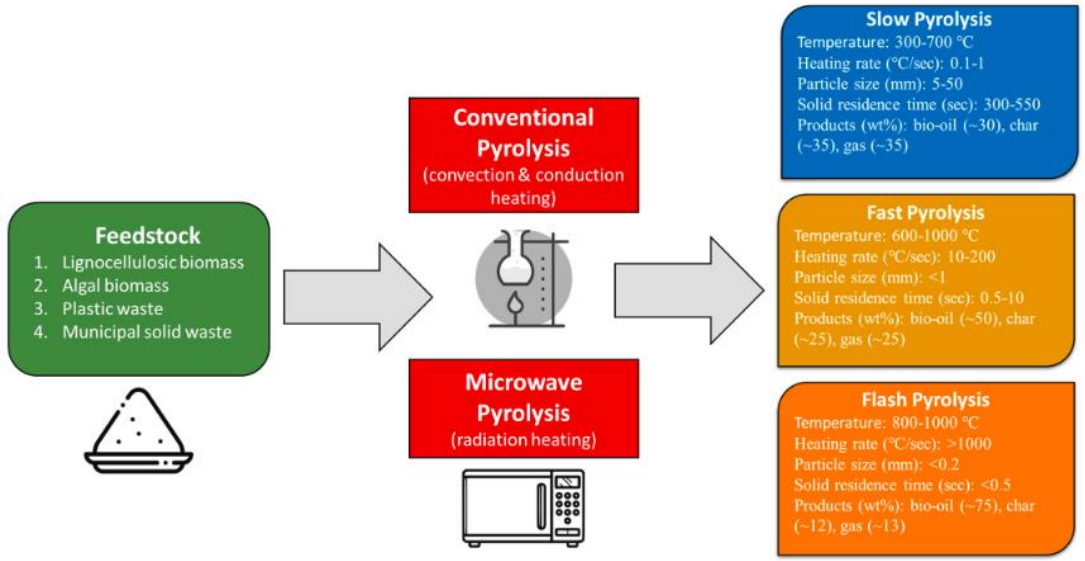

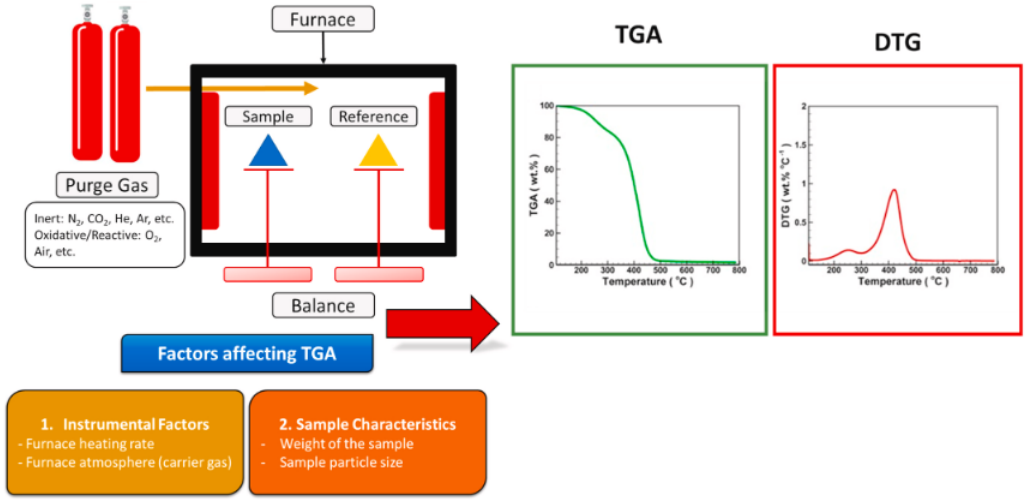

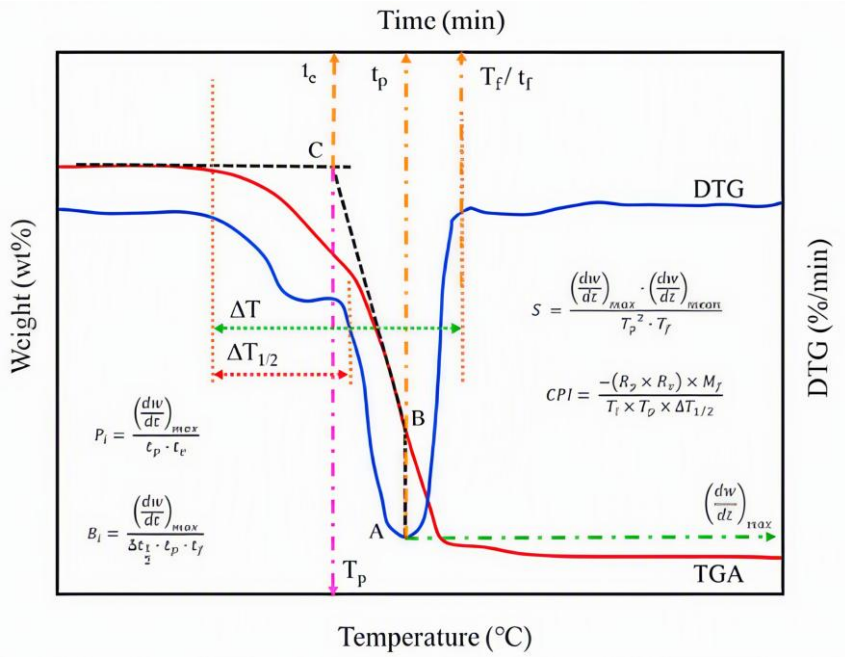

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