13. Drying

Drying

- **Drying**
  - Thermal removal of volatile substances to yield a solid
  - The last step in the separation process
  - For bioproducts, use drying methods that minimize or eliminate thermal product degradation
- **Common reason for drying**
  - Chemical and physical stability during storage
  - Convenience in the final use of the product
  - To remove undesirable volatile substances

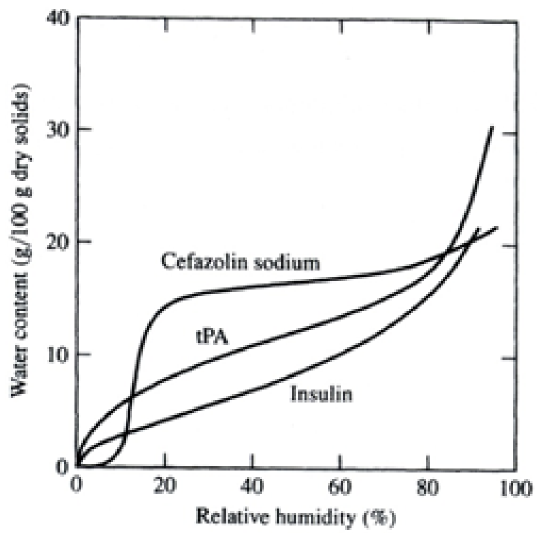
1. Drying Principles

Water in Biological Solids and in Gases

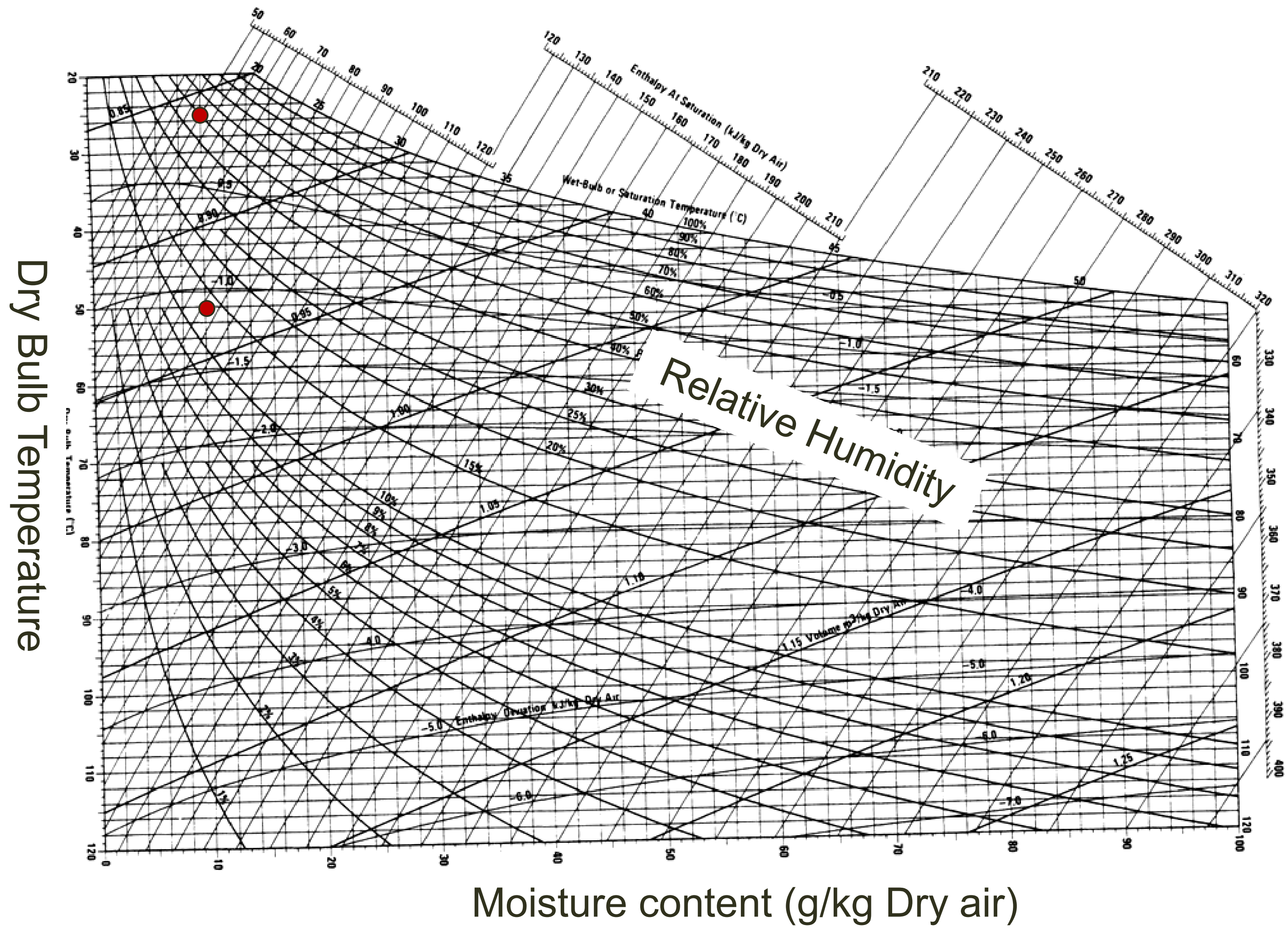
- **Water in biological solids**
  - Unbound (free) water
    - Free to be in equilibrium with water in the vapor phase
    - Mainly held in the voids of the solids
  - Bound water
    - Water in fine capillaries
    - Water containing a high level of dissolved solids
    - Water in physical or chemical combination with the biological solids
    - Hygroscopic : solids containing bound water

Water Capacity of Solids

- **Water content of the solid vs. relative humidity of air**
  - Independent of temperature
  - Humidity: mass of water/mass of dry air
- **From ideal gas law**
  - $c_w = p_w/(RT)$
    $= \mathscr{H}(M_{air}/M_{water})/[1+\mathscr{H}(M_{air}/M_{water})] \bullet p/(RT)$
    $= \mathscr{H}(28.9/18)/[(1+\mathscr{H}(28.9/18))] \bullet p/(RT)$
    - c_w: water concentration (moles/volume)
    - $\mathscr{H}$: humidity
    - p: total pressure
    - p_w : partial pressure of water
    - M: molecular weight
  - Relative humidity R_m
    - $R_m = p_w/p_{ws}$ x100
      - p_{ws}: saturation vapor pressure (a function of temperature only)



Properties of Air and Water Vapor Mixture



Enthalpy of the Drying Gas

- **Total enthalpy H_y at T of a unit mass of gas plus water vapor**
  - $H_y = C_s(T-T_0) + \mathscr{H}\lambda_0$
    - C_s : specific heat (humid heat) of the gas and water vapor mixture
    - λ_0 : latent heat of the liquid at T_0
    - $C_s = C_{pg} + C_{pw}\mathscr{H}$
      - C_{pg} : specific heat of the gas
      - C_{pw}: specific heat of water vapor
    - For air and water vapor mixture

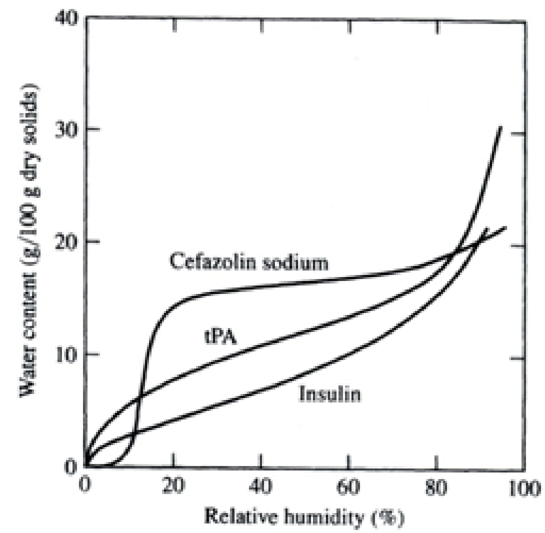
      C_s (kcal/kg dry air °C) = 0.24 + 0.46$\mathscr{H}$

      λ_0 = 597 kcal/kg water (at 0°C and 760 mmHg)

Drying Antibiotic Crystals

- **Drying conditions**
  - Air at 1 atm and 25 °C with a relative humidity of 50%

  → heated to 50 °C and used in drying wet crystals of the antibiotic cefazolin sodium
  - Wet crystals : 30g water /100g dry antibiotic
- **Determine the following**
  - The percentages of bound and unbound water in the wet crystals before drying
    - 100% humidity: 23g/100g dry weight
  - Moisture content of the crystals after drying
    - Relative humidity at 50 °C ? 13%
    - Water content ?
  - Water partial pressure at the drying temperature?
    - $p_w = \mathcal{H}(28.9/18)/[(1+ \mathcal{H}(28.9/18))]\bullet p$



2. Heat and Mass Transfer

Heat and Mass Transfer During Drying

- **Processes during drying**
  - Heat transfer
    - To evaporate liquid
  - Mass transfer
    - Transfer of liquid or vapor within the solid
    - Transfer of a vapor from the surface of the solid

Heat Transfer

- **Types**
  - Conduction
    - From a hot surface contacting the material
    - Vacuum-shelf dryers, batch vacuum rotary dryers, freeze dryers
  - Convection
    - From a gas that contacts the material
    - Spray drying
  - Radiation
    - From a hot gas or hot surface
  - Dielectric or microwave heating
    - In high frequency electric fields that generate heat within the wet material

Heat Transfer

- **Conductive drying**
  - Fourier's law of heat conduction
  - $q = -k\, dT/dy$
    - q : heat flux (heat flow rate per unit area)
    - k : thermal conductivity of the solid
    - y: measured in the direction of heat flow
- **Convective drying**
  - $Q = hA(T-T_s)$
    - h : heat transfer coefficient
    - Q: rate of heat flow into the solid
    - A: surface area through which heat flows
    - T : gas bulk phase temperature
    - T_s: temperature at the solid surface
  - $q = h(T-T_s)$
    - q : heat flux (heat transfer rate/unit area)

Heat Transfer

- ***U for conductive and convective drying***
  - $Q = UA\Delta T$
    - U: overall heat transfer coefficient
    - ΔT : average temperature difference
  - $Q = UaV\,\Delta T$
    - a: heat transfer area per unit dryer volume : unknown
    - Ua: volumetric heat transfer coefficient : calculated or measured
    - V: volume of the dryer

Mass Transfer

- **Convective drying**
  - Initial drying period
  - Constant drying rate period
    - Mass transfer is limited by a gas boundary layer at the surface of the solids
  - Falling drying rate period
    - At a critical moisture content X_c
    - Internal rate of water movement is not fast enough to keep the surface saturated
    - Drying rate approaches the equilibrium moisture content X_e

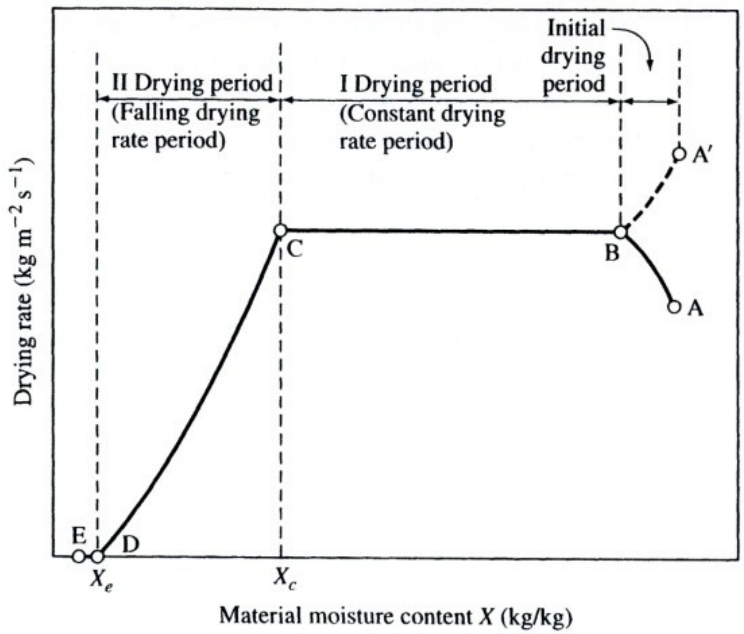
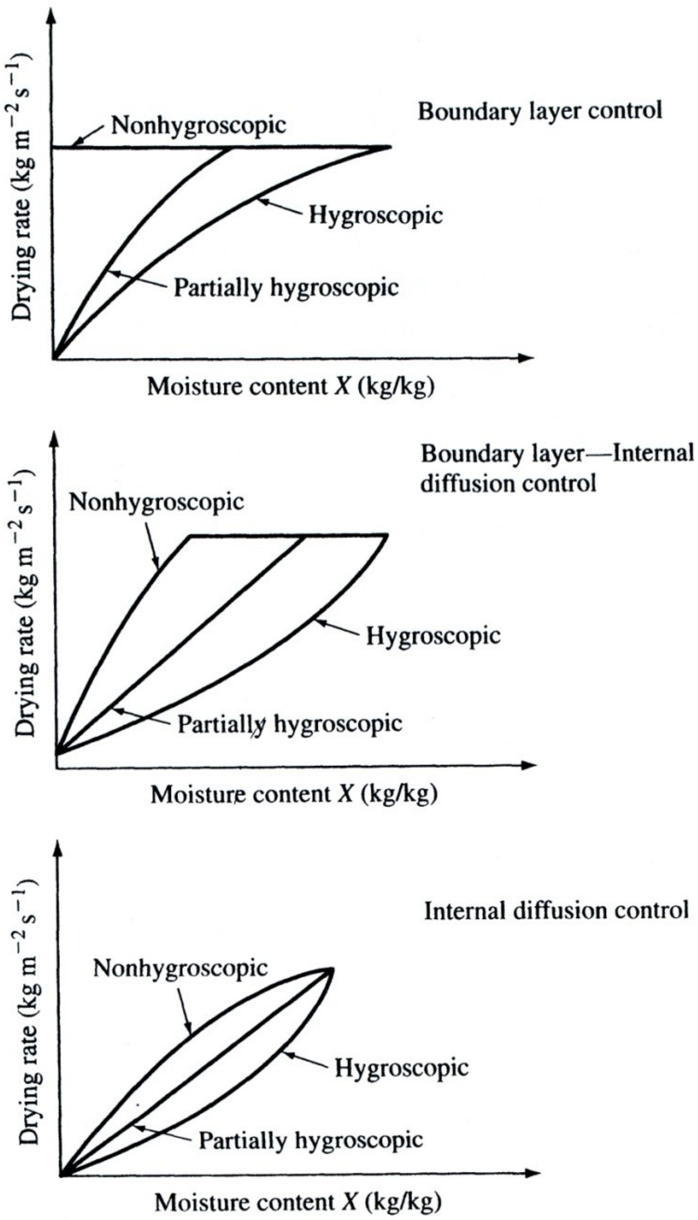


Figure 10.3 Drying rate curve, illustrating the periods of drying.

Drying Rate Curve



- Drying rate is influenced by
  - The type of material being dried
  - The type of mass transfer that is controlling

- No constant drying period
  - Hydroscopic biological solids
  - When mass transfer is controlled by internal diffusion

Mass Transfer

- $N_w = k_G \Delta p_w$
  - Mass transfer of water being evaporated at the solid surface by gas flowing past the surface
  - N_w : molar flux of water
  - k_G : mass transfer coefficient
  - Δp_w : difference in partial pressure of water between the surface and the bulk gas stream
- **During the constant drying rate period**
  - Steady state between heat and mass transfer
    - $q = \lambda N_w$
      - q: heat flux
      - λ : heat of vaporization of water
    - $N_w = h(T-T_s)/ \lambda$
      - h : 10 to 100 kcal m^{-2} h^{-1} $^oC^{-1}$ for forced convection of gases

3. Dryer Description and Operation

Heat Transfer by Conduction

- **Vacuum-shelf dryer**
  - Heat conduction
    - Shelves→ trays → wet solids
  - Vacuum
    - To speed up the drying
    - To allow drying at lower temperature
  - Usages
    - Up to square meters of shelf area are available
    - Extensively used for pharmaceutical products
- **Batch vacuum rotary dryers**
  - Tumbling of solids
  - Not suitable for particles forming larger balls or sticking to the metal surface in the drum

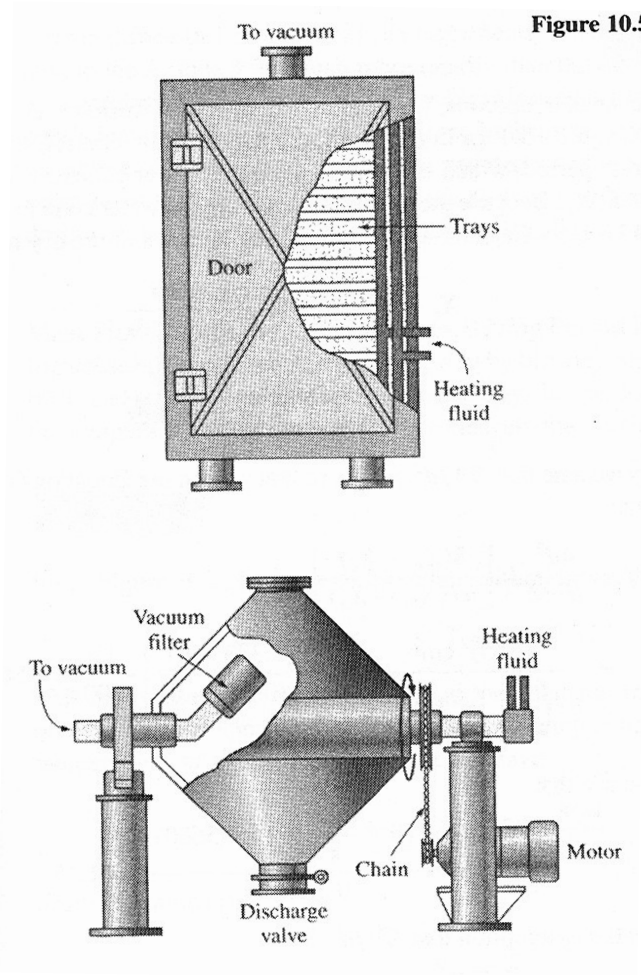
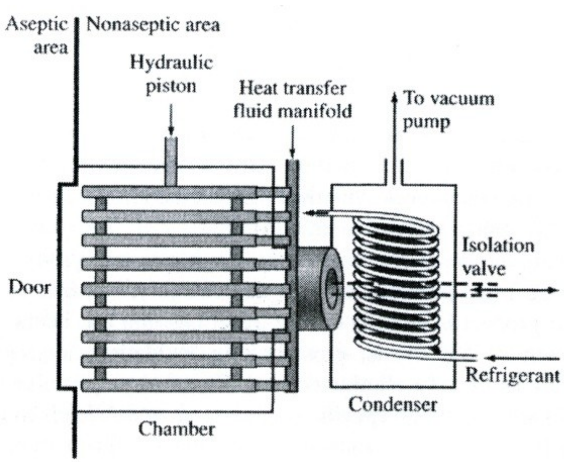


Figure 10.5

Freeze Dryers

- **Drying process**
  - Cooling to allow complete solidification
  - Drying by sublimation
    - Reduction of pressure to below the vapor pressure at the triple point (0.01 °C, 4.6 mmHg)of water
    - Increase in temperature to provide energy for sublimation
  - Primary drying
    - Removal of unbound water
  - Secondary drying
    - Removal of bound water



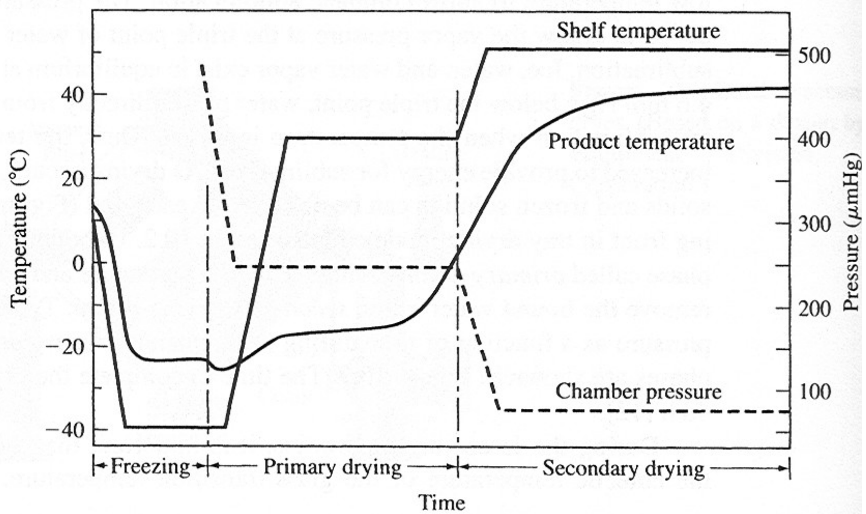
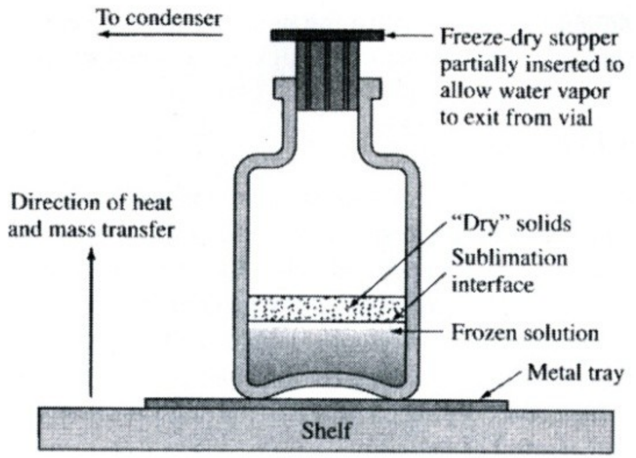


Figure 10.9 Process variables during the freeze-drying cycle.

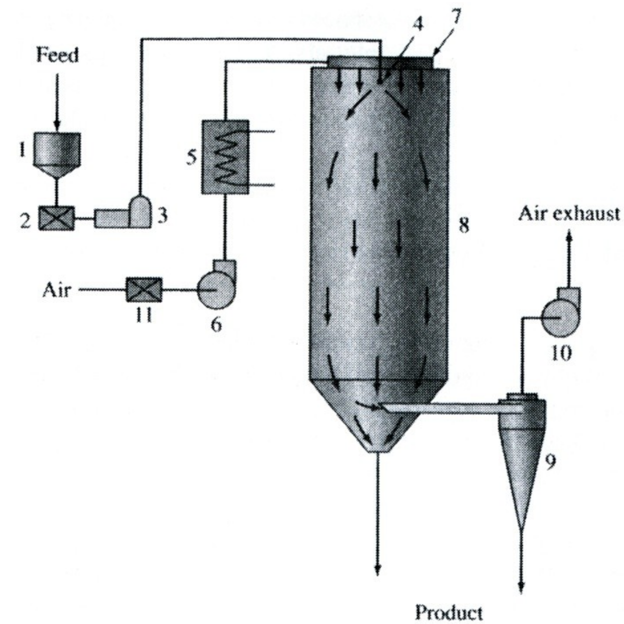
Freeze Dryers

- **Advantages**
  - For biological products with a high sensitivity to heat :most proteins
  - No liquid phase : prevent reactions such as hydrolysis, oxidation, aggregation etc.
  - The dry product has a high specific surface area : rapid redissolution



Spray Dryers

- **Process**
  - Spraying the liquid into a hot gas (air) → transformation of a feed in the liquid state into a dried particulate form
- **Basic units**
  - Liquid atomization
    - Pressure nozzle single-fluid atomizer
      - Larger particles (120-250 um)
    - Rotary wheel atomizers
      - Smaller particles (30-120 um)
  - Gas-droplet mixing
  - Drying from liquid droplets



Spray dryer with a pressure nozzle atomizer