Summary septek
Sigurd's part

Equilibrium
Flash
Distillation
Absorption/stripping
Extraction
Process control

General approach separation

1. Overall material balance. What are the desired products?
2. Choose separation method
   – Gas mixture: Absorption (VLE: Henry's law), adsorption (SVE), membrane, …
   – Liquid mixture: Stripping (VLE), Flash/distillation (VLE), extraction (LLE), crystallization (SLE), …
3. Get equilibrium data for chosen method
4. Design equipment

S = solid, V = vapor, L=liquid
VLE = vapor-liquid equilibrium

Multistage processes

Equilibrium-stage models:

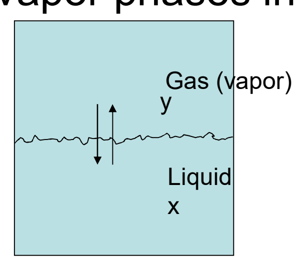
- Between stages: Material balance (“operating line”)
- On stages: Equilibrium
- Solution:
  - Graphical methods (assuming constant molar flows, but any equilibrium)
    - McCabe Thiele (distillation, absorption, extraction with two inerts)
    - Delta-method (extraction; may also be applied for 3-component distillation)
  - Analytical methods (constant molar flows + simple equilibrium)
    - Solve by hand (few stages, N=3 or less)
    - Kremser for constant K-value (absorption, distillation column ends, extraction)
    - Constant relative volatility for distillation
      - Nmin (Fenske), Lmin (King)
  - Simulations
    - Software: Hysys, Aspen, Chemsep (free)

Distillation/flash: Equilibrium stage concept

- Assume well mixed (turbulence!) and large contact area so that there are no diffusion limitations for mass transfer

Experiment: Menthos + diet coke

- Liquid and vapor phases in equilibrium!



Vapor/liquid-equilibrium (VLE)

Raoult's law (Ideal liquid): $\underbrace{p_A}_{y_A p} = x_A \, p_A^{\mathsf{sat}}(T)$

Nonideal liquid: $p_A = \gamma_A \, x_A \, p_A^{\mathsf{sat}}(T)$

Henry's law (dilute solution): $p_A = x_A H_A(T)$

- K-value. $K_i = y_i/x_i$

  K is generally a function of: T, p, x, y

  Raoult's law: $K_A = p_A^{\mathsf{sat}}(T)/p$

  Henry's law: $K_A = H_A(T)/p$

- Relative volatility, α (11.3B)

$$\alpha = \frac{K_A}{K_B} = \frac{y_A/x_A}{y_B/x_B}$$

Raoults law: $\alpha = \frac{p_A^{\mathsf{sat}}(T)}{p_B^{\mathsf{sat}}(T)}$

α can often be assumed constant (ideal mixture of simular components)!

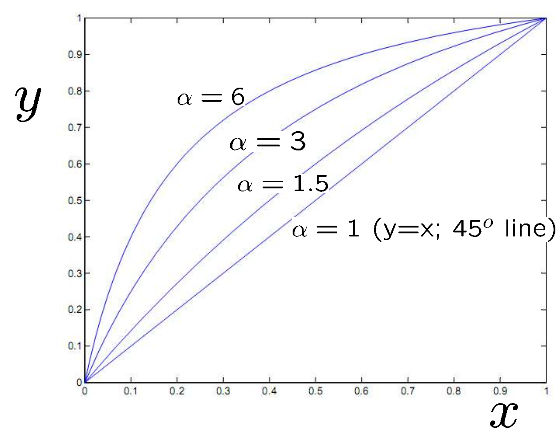
Binary mixture

Given pressure

Constant relative volatility

- Binary mixture: $\alpha = \frac{y_A/x_A}{y_B/x_B} = \frac{y/x}{(1-y)/(1-x)} \Rightarrow y = \frac{\alpha x}{1+(\alpha-1)x}$

xy-diagram



Vapor-liquid equilibrium. Flash

- Equilibrium condition:
  - $\Sigma_i x_i = 1$, $\Sigma_i y_i = 1$
  - Raoult's law:

$$p = p_A + p_B + \ldots = x_A\, p_A^{sat}(T) + x_B\, p_B^{sat}(T) + \ldots.$$

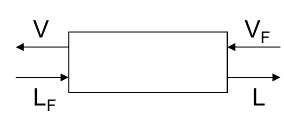
- Gibbs phase rule
  - Degrees of freedom among variables p, T and composition: $F = 2 + C - P - R$

11.2 Single-stage equlibrium contact for vapor-liquid system

Flash

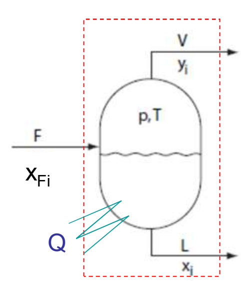
- **Flash: Products L and V in equlibrium**
  1. Important process in itself
     - Separators for mixtures with large relative volatility (Example: Offshore oil and gas)
  2. Building block for multistage processes

  Comment: *The book calls "flash" for "flash distillation" or "equlibrium distillation", but in the process industry the term "distillation" is used for multistage processes with reflux.*



- **Equations (steady-state operation)**
  - VLE:
    - $y_i = K_i\, x_i$ $(i=1,2,\ldots,N_c)$
    - K_i: given function of p,T,x_i,y_i
  - Component balanses (steady-state)
    - $Fx_{Fi} = Lx_i + Vy_i$ [mol/s] $(i=1,2,\ldots,N_c)$
  - 2 summation equations:
    - $\Sigma x_i = x_1 + x_2 + x_3 + \ldots. = 1$
    - $\Sigma y_i = y_1 + y_2 + y_3 + \ldots. = 1$

      (Also have total material balance $F = L + V$ but not independent from the others)
  - 1 energy balance*
    - $H_F + Q = H_L + H_V$
  - In total: $2N_c+3$ independent equations
- Unknowns with given feed (F, x_F):
  - $2N_c+5$ unknowns: x_i, y_i, V, L, p, T, Q
  - Need 2 more specifications



* Energy balance: Normally not needed in this course.
Often replaced ny "constant molar flows" assumption ($V = V_F$, $L=L_F$ for adiabatic flash, Q=0)

Single-stage flash

- pT flash.
- p V/F flash.
  - Graphical solution: Feed line
  - Analytical solution; Constant relative volatility
- Batch (Rayleigh) distillation

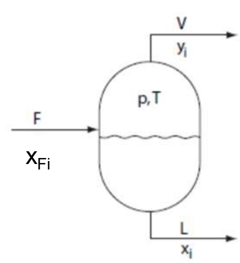
$$\int_{L_0}^{L_1} dl = \ln \frac{L_1}{L_0} = \int_{x_0}^{x_1} \frac{dx}{y-x}$$ (y=K(x) from VLE)

Binary mixture

Given pressure

p+V/F-flash

Graphical solution

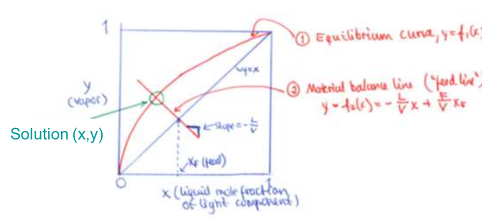


- **Book 11.2, example 11.2-1**

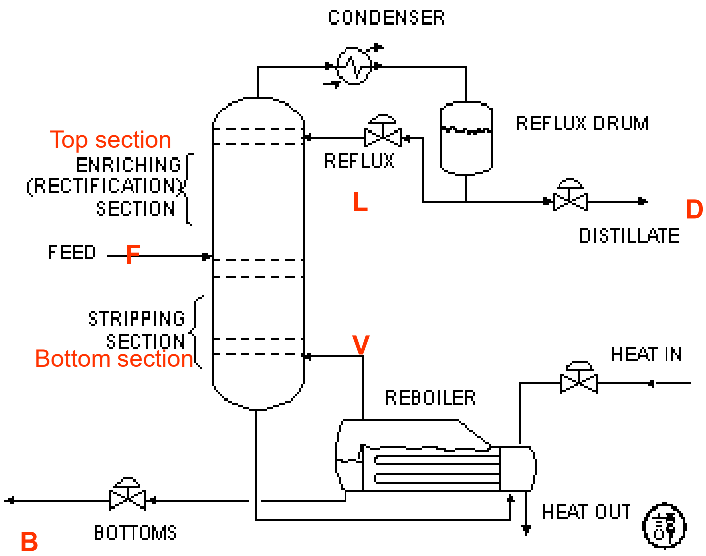
1. VLE: Equilibrium curve
   - $y = f_1(x)$
2. Component mass balance (”feed line”, ”q-line”)
   - $y = f_2(x) = -\frac{L}{V}x + \frac{F}{V}x_F = -\frac{q}{1-q}x + \frac{1}{1-q}x_F$

q = L/F = liquid fraction
1-q = V/F = vapor fraction

– Solution at intersection

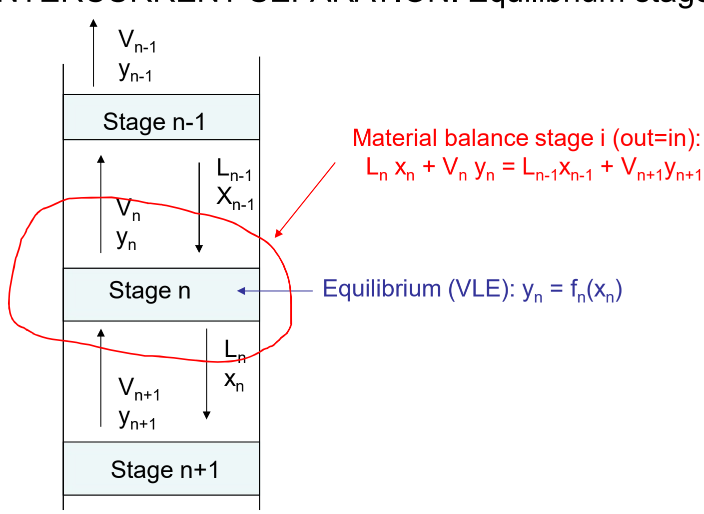


DISTILLATION



QB = V*dHvap

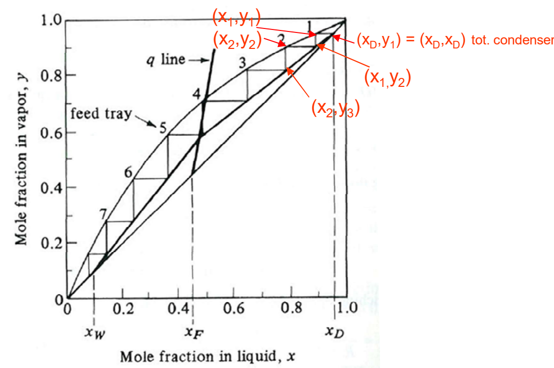
COUNTERCURRENT SEPARATION. Equilibrium stage concept



Note: Numbering is here from top (as in book); many use from bottom.

McCabe-Thiele graphical solution

1. Draw equilibrium curve: (x,y) on stages.
2. Draw upper operating line: (x,y) between stages. Starts in (x_D,x_D) and has slope $L_{top}/V_{top} = R/(R+1)$ where $R=L/D$
3. Draw feed lines (goes through (x_F,x_F)) and has slope $-q(1-q)$.
   - Feed sat. liquid (q=1): Vertical.
   - Feed sat. vapor (q=0): Horizontal
4. Draw lower operating line : (x,y) between stages. Starts in (x_B,x_B) and goes through crossing of feed line and upper operating line
5. Graphical solution to find number og stages: Switch between on stages (x_n,y_n) and between stages (x_n,y_{n+1}) by making staircase.
6. Optimal feed location (design): Switch between operating lines at feed line



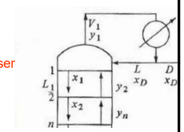


FIGURE 11.4-9. *McCabe–Thiele diagram for distillation of benzene–toluene for Example 11.4-1.*

Graphical Solution: McCabe-Thiele

- Assume: Equilibrium stages + constant molar flow
- (Any) equilibrium line: y=K(x)
- Operating lines: Mass balance each section,
  - $y = (L/V)\, x + \ldots$
- Number of theoretical stages: Staircase
  - Reboiler contributes 1 stage
  - Total condenser contributes 0 stage
  - Partial condenser contributes 1 stage
    - Example: Staircase gives 7.8 stages
    - With reboiler and partial condenser: Only 5.8 of these stages are inside column shell. (Usually LOT OF CONFUSION ON EXAM!)
- Optimal feed location: Switch operating lines at crossing of operating lines (=crossing with feed line)
  - If nonoptimal: Need more stages

Distillation

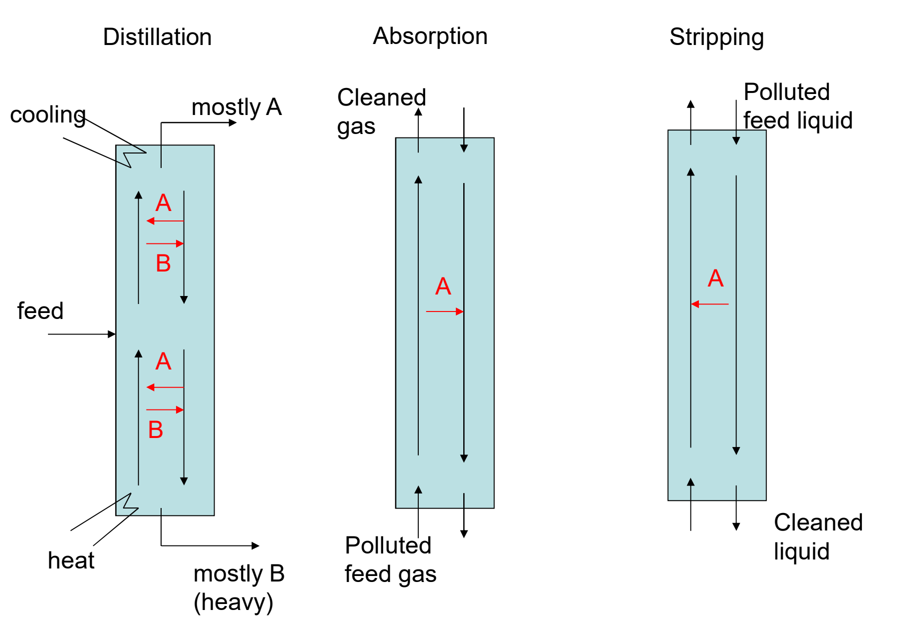
- Minimum stages and minimum flows
  - Graphical
    - Nmin (corresponding to infinite reflux): Operating line on diagonal
    - Lmin and Vmin (corresponding to infinite stages): Operating line pinch with equilibrium line (normally: at crossing eq.line & fine line)
  - Analytical (constant relative volatility).
    - Key components: L and H
    - Fenske: $N_{min} = \ln S / \ln \alpha$ where $S = (x_L/x_H)_D / (x_L/x_H)_B$
    - Minimum boilup (pure products). Kings formula
      - $L_{min} = F/(\alpha-1)$ (feed liquid)
      - $V_{min} = F/(\alpha-1) + q*D$ (q: frac.liquid in feed)
- Actual column
  - Recommended: N = 2.5 Nmin, Gives: V = 1.1 Vmin (or less)

Extension

- McCabe-Thiele can also be used for
  - simpler cases (no reboiler, no condenser, absorption, stripping)
  - more complex cases (side coolers, side reboilers, side streams, multiple feeds)
  - Approach:
    - Formulate mass balances for various sections to find "operating lines": $y_i = (L/V)x_{i+1} + \dots$ between stages
    - Use equilibrium line: $y_i = h(x_i)$ on stages
    - Use staircase to solve the equations graphically and determine number of stages

When use distillation?

- Liquid mixtures (with difference in boiling point)
- Unbeatable for high-purity separations because
  - Essentially same energy usage independent of (im)purity!
    - » Pure products: $V_{min} = F/(\alpha-1) + qD$
    - » Going from 1% to 0.0001% (1 ppm) impurity in one product increases energy usage only by about 1%
  - Number of stages increases only as log of impurity!
    - » $N_{min} = \ln(x_L/x_H)_D/(x_L/x_H)_B / \ln \alpha$
    - » Going from 1% to 0.001% (1 ppm) impurity in one product increases required number of stages only by factor 2
- Well suited for scale-up
    - » Columns with diameters over 18 m
- Examples of unlikely uses of distillation:
    - » High-purity silicon for computers (via $SiCl_3$ distillation)
    - » Water – heavy-water separation (boiling point difference only 1.4C)



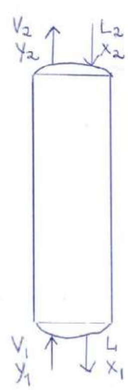
Absorption/Stripping

- Single section
- Notation varies…
- Dilute mixtures:
  - 1-x ¼1
  - Henry's law: $p_i = H x_i$
    - Using $p_i = y_i p$ gives
    - $y_i = (H/p) x_i = m x_i$
  - Constant molar flows: L = L' (inert)
- Modelling. Two approaches
  1. Equilibrium stage (as for distillation, but simpler)
     - Graphical: McCabe Thiele for nonideal VLE
     - Analytical for dilute mixtures: Kremser formulas. A = (L/V)/m
       - Absorption: A>1. Stripping: A<1
  2. Mass transfer (Non-equilibrium) models
     - Mass transfer: $N_A = K_y (y - y^*)$ [mol A/s, m2]
     - Mass balance over dz: $d(Vy) = N_A\, dA$, where $dA = aSdz$
     - Combine: $dz = V\, dy / K_y\, a\, S\, (y-y^*)$
       - Packing height (integrate): $z = \int_1^2 dz = \frac{V}{K_y a S} \int_{y_1}^{y_2} \frac{dy}{y-y^*}$
       - Integrate last part 1) numerically, 2) graphically or 3) analytically
         - » 3) Dilute mixtures: Analytic Log-mean approximation: $\int_{y_1}^{y_2} \frac{dy}{y-y^*} = \frac{y_2 - y_1}{(y-y^*)_{lm}}$

Equilibrium stage

Kremser equations

- Analytical solution for case with straight equilibrium line (y=mx) and L/V constant
- A = (L/V)/m – absorption factor



Sigurd's formulation:

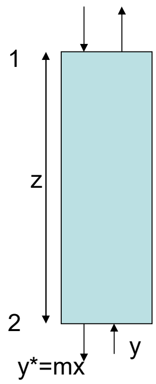
$$\frac{y_1 - y_1^*}{y_2 - y_2^*} = A^N \quad (1)$$

$$A = \frac{L/V}{m} \quad (2)$$

$$A = \frac{y_1 - y_2}{y_1^* - y_2^*} \quad (3)$$

Mass transfer (non-equilibrium stage)

Note: very useful log-mean formula (dilute mixtures)



Heat exchanger. Assume: constant heat capacities and constant UA

$$Q = UA\Delta T_{lm} \quad [J/s]$$

Countercurrent absorption.

Similar, but instead of $\Delta T = T_h - T_c$, driving force is $\Delta y = y - y^*(x)$ where $y^*(x)$ is in equilibrium with the liquid phase.

Assumptions: 1. Constant slopes for the equilibrium and operating lines (reasonable for dilute mixtures!) 2. Constant mass transfer coefficient $(K_y a)$ [mol A / m3].

Then total mass transfer of A from the gas to liquid stream is

$$n_A = V(y_2 - y_1) = K_y(aSz)(y - y^*)_{lm} \quad [mol\ A/s]$$

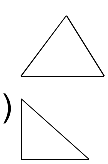
(aSV) [m^2] - total mass transfer area inside the column and

$$(y - y^*)_{lm} = \frac{(y - y^*)_1 - (y - y^*)_2}{\ln((y - y^*)_1/(y - y^*)_2)}$$

1=one end of column, 2=other end

Liquid-liquid equilibrium

- Triangular diagrams for 3 components
  - Two versions (both are common):
    - Triangular coordinates (Fig. 12.5-1/2)
    - Rectangular coordinates (Fig. 12.5-3/4)



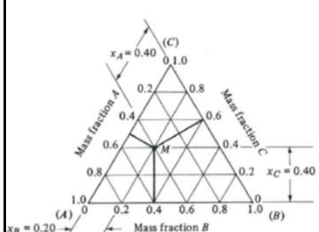


FIGURE 12.5-1. Coordinates for a triangular diagram.

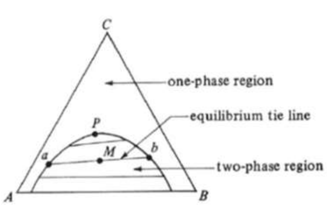


FIGURE 12.5-2. Liquid–liquid phase diagram where components A and B are partially miscible.

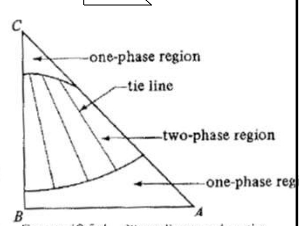


FIGURE 12.5-4. Phase diagram where the solvent pairs B–C and A–C are partially miscible.

Extraction

- Triangular diagrams
- Single-stage: Find M and then split
- Multistage:
  - Feeds L_0 and V_{N+1}
  - General case: Use Δ-operating point
    - $\Delta = L_0 – V_1 = L_1 - V_2 = \ldots$
    - -> "L_0 is a mixture of Δ and V1"
  - Immiscible liquids: Same as abs/stripping!
    - Can use McCabe-Thiele and even Kremser in some cases

Multistage separation with given products:
Minimum flows (Lmin, Vmin)

- Distillation: Minimum energy/reflux
- Absorption/stripping/extraction: minimum solvent or stripping gas

- Obtained with infinite no. of stages
- Occurs when we have "pinch" somewhere

  No change in composition between stages

  = Crossing of equilibrium and operating line

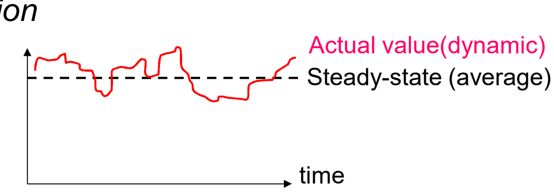
  = Compositions between stages in equilibrium
    - Distillation: usually occurs at feed
    - Absorption/stripping/extraction: usually occurs at column end (-> one product is in equilibrium with its feed)

Minimum number of stages

- There is no “minimum number of stages” in absorption/stripping/extraction
  – Get N -> 0 with very large flow (of solvent or stripping gas).
  – Note: Purities of incoming streams (column ends) are fixed, and this limits product purities, independent of the number of stages.
- Distillation is different: Here we “recycle” at the column ends and can achieve any product purity by increasing the number of stages.
  – Fenske: N_{min} = lnS/ln®

Why control?

- Until now: *Design* of process. Assume steady-state
- Now: *Operation*



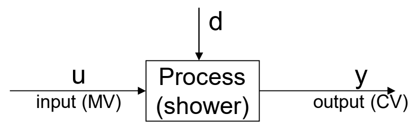
In practice never steady-state:

- Feed changes
- Startup
- Operator changes
- Failures
- …..

“Disturbances” (d’s)

- Control is needed to reduce the effect of disturbances
- 30% of investment costs are typically for instrumentation and control

Classification of variables



Independent variables ("the cause"):

(a) Inputs (MV, u): Variables we can adjust (valves)

(b) Disturbances (DV, d): Variables outside our control

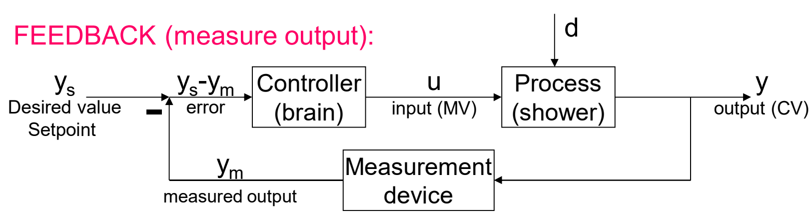
Dependent (output) variables ("the effect or result"):

(a) Primary outputs (CVs, y): Variables we want to keep at a given setpoint

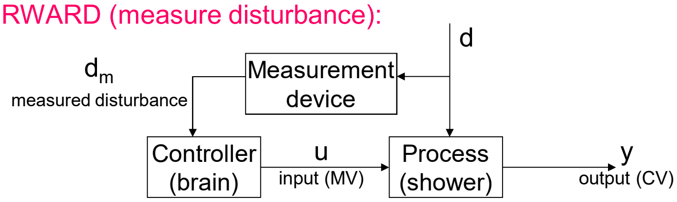
(b) Secondary outputs (y'): Extra measurements that we may use to improve control

BLOCK DIAGRAMS

FEEDBACK (measure output):



FEEDFORWARD (measure disturbance):



- All lines: Signals (information)
- Blocks: controllers and process
- Do not confuse block diagram (lines are signals) with flowsheet (lines are flows); see below

Procedure for design of control system

1. Define control objective (why control?)
2. Classify variables
   - MVs (u)
   - Disturbances (d)
   - CVs (y)
   - \+ measurements
3. Process description
   - Flow sheet
   - Process matrix
     - qualitative with 0, +, -, (+), (-)
     - Quantitative transfer matrix (see later courses)
4. Control structure
   - Feedforward / feedback
   - Pairing of variables (avoid pairing on 0!)
   - Cascade loops (MV from one controller is setpoint for another)
   - Put on process & instrumentation diagram (P&ID)
5. Control algorithm
   - On/off
   - PID (proportional-integral-derivative)
   - Model based (MPC)
6. Implementation
   - Today: Normally computer + connect measurements and valves (actuators)

Process matrix

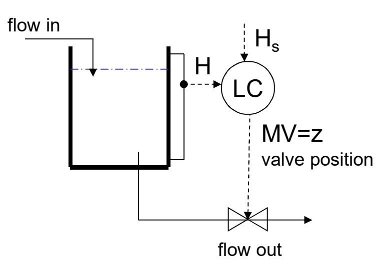
	Input 1	input2
Output 1	+	-
Output 2	0	+

Chemical engineer (YOU):
- Responsible for items 1- 4
- The most important is process understanding

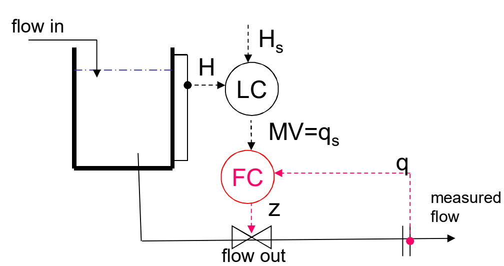
Cascade control

- Idea: Use “local control” based on extra measurements (y’) to improve control of primary output (y)
- Without cascade: “Master” controller directly adjusts input (MV=u)
- With cascade: “Master” controller adjusts setpoint to “local” controller (MV= y'_s) and “local” controller adjust original input (u) to keep y’ at this setpoint.

- **Example: Flow controller on valve (very common!)**
  - y = level H in tank (or could be temperature etc.)
  - u = valve position (z)
  - y’ = flowrate q through valve

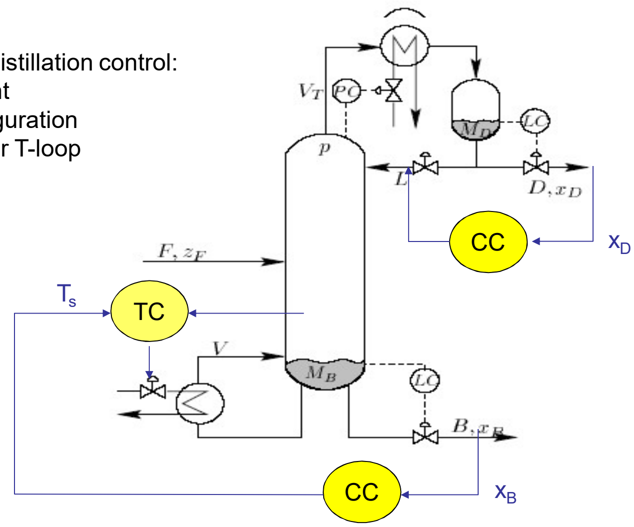


WITHOUT CASCADE



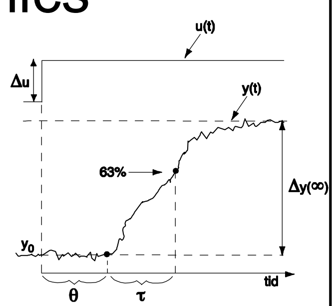
WITH CASCADE

Typical distillation control:
Two-point
LV-configuration
with inner T-loop



Process dynamics

- "Things take time"
- Step response (step in u):
  - k = Δy(∞)/ Δu – process gain
  - τ - process time constant (63%)
  - θ - process time delay

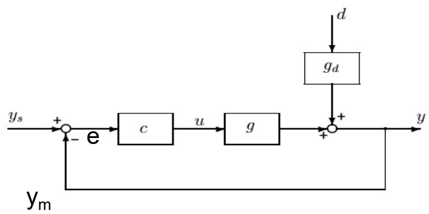


- Time constant τ: Often equal to residence time = V[m3]/q[m3/s] (but not always!)
- Can find τ (and k) from balance equations:

$$\frac{d}{dt}\,\text{Inventory} = \text{In - Out} \qquad [\text{mol/s; J/s, kg/s}]$$

  - Rearrange to match standard form of 1st order linear differential equation: $\tau \frac{dy}{dt} = -y + ku$

FEEDBACK CONTROL: TUNING OF PID-CONTROLLER



Block diagram of negative feedback control

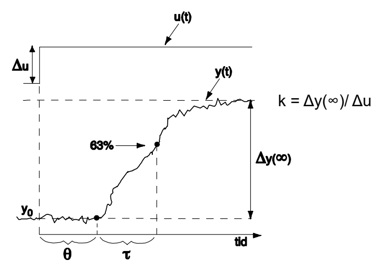
y = controlled variable (CV)
y_m = measured CV
y_s = setpoint (SP)
$e = y_s - y_m$ = control error
u = manipulated variable (MV)

PID-controller:

$$u(t) = u_0 + K_c[e(t) + \frac{1}{\tau_I}\int_0^t e(t)dt + \tau_D \frac{de(t)}{dt}]$$

3 tuning parameters:

1. (Proportional) Controller Gain: K_c
2. Integral time: τ_I [s]
3. Derivative time: τ_D [s]



SIMC tuning rule:

$$K_c = \frac{1}{k}\frac{\tau}{\tau_c + \theta}$$

$$\tau_I = \min(\tau, 4(\tau_c + \theta))$$

τ_c = desired response time with control (tuning parameter!).

Spørretime 2015. Control

- Q: Jeg har et spørsmål angående reguleringsdelen på eksamen 2014 i TKP4105.

  Hvorfor er det tau * (dy/dt)= -y+ k*d ?

  Skal det ikke være tau*(dy/dt)=-y +k*u? hvor u er input og ikke disturbance (d)

  Det er i hvert fall det som står i mine notater og på det ene dokumentet som du la ut fra prosessteknikk boken.

- SVAR: Det er det samme. Dvs. både d og u er uavhengige variable («inputs»), men d er utenfor vår kontroll.

  Det mest generelle ville være å skrive det som
  tau * (dy/dt)= -y+ k1*d + k2*u