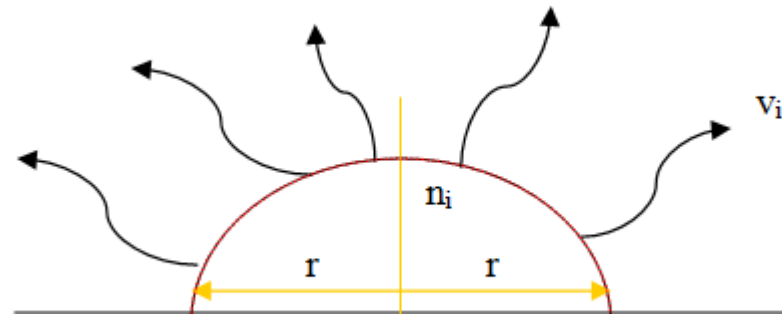# Case Studies
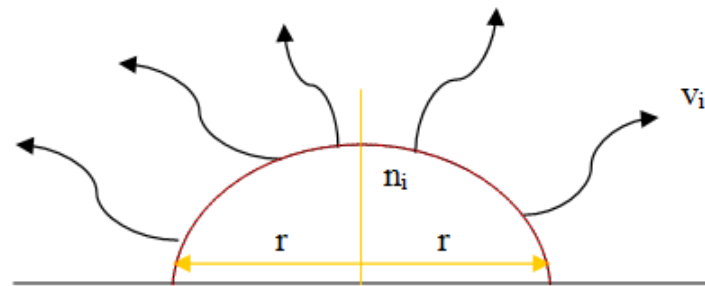
Lecture 10

Droplet Evaporation Model

1. **Problem definition**

    a) system description
        i)   Two-phase system (liquid and vapor)
        ii)   The liquid droplet is the mixture of water and methanol

    b) Goal
        i)   Generate the model which can calculate the vaporization of compound
        ii)   +/-10% accuracy

Droplet Evaporation Model

2. Assumption

a) Number of chemicals $= 2$ (water and methanol)
b) Equilibrium at the interface
c) Well-mixed droplet
d) Heat $= Q_R$ from environment
e) Uniformly decrease in volume (shape is the same)
f) Not steady state
g) Lump model
h) No accommodation of heat
i) Small amount of additive(methanol) in the droplet
j) Little change of temperature in the droplet

3. Volume balance

a) A single volume encapsulating the whole droplet.

Droplet Evaporation Model

Evaporator model (with Wilson's equations)

Number of equation:

Number of ODE equation = NC
Number of AE equation = 12NC+3

Dependent variable = n_j
Independent variable = t

Variable (not include

$V, H^{Vap}, Q_R, Cp, T, K_i$

$T_{ref}, \mu_{ij}, \upsilon_i, s_i, \Lambda_{ij}, R$

Number of variable (1
= 24NC+7

Therefore, degree of freedom = (24NC+7)-(11NC+4) = 13NC+3

Variable Classification

Fixed by Problem: $P, T_{ref\_i}, T_{ic} = 1+2NC$ variables

Fixed by system: $Q_R, \upsilon_i, Cp_i = 1+2NC$ variables

Fixed by model: $R = 1$ variable

Adjustable by parameter: $A_i^P, B_i^P, C_i^P, A_i^v, B_i^v, C_i^v, D_i^v, E_i^v, \mu_{ij} = 9$ NC variables

Total known variable = 13NC+3

SHORT PATH EVAPORATION
(MOLECULAR DISTILLATION)

M. Sales-Cruz and R. Gani, 2006.

Computer-Aided modelling of short-path evaporation for chemical product purification, analysis and design.

Chemical Engineering Research and Design, Part A. 84(A7): 583–594.

Short-Path Evaporation

❖ Conventional distillation is one of the oldest methods to separate liquid or molten substances

❖ However, it is not recommended for substances that can be degraded under distillation temperatures, such as:
  - vitamins
  - insecticides
  - drugs
  - flavours
  - fragrances

❖ Then, the *short-path distillation* or *molecular distillation* is used as an alternative

❖ It is a safe method suitable for separation and purification of substances that can be:
  - degraded
 - thermally unstable under distillation temperatures

Process Description
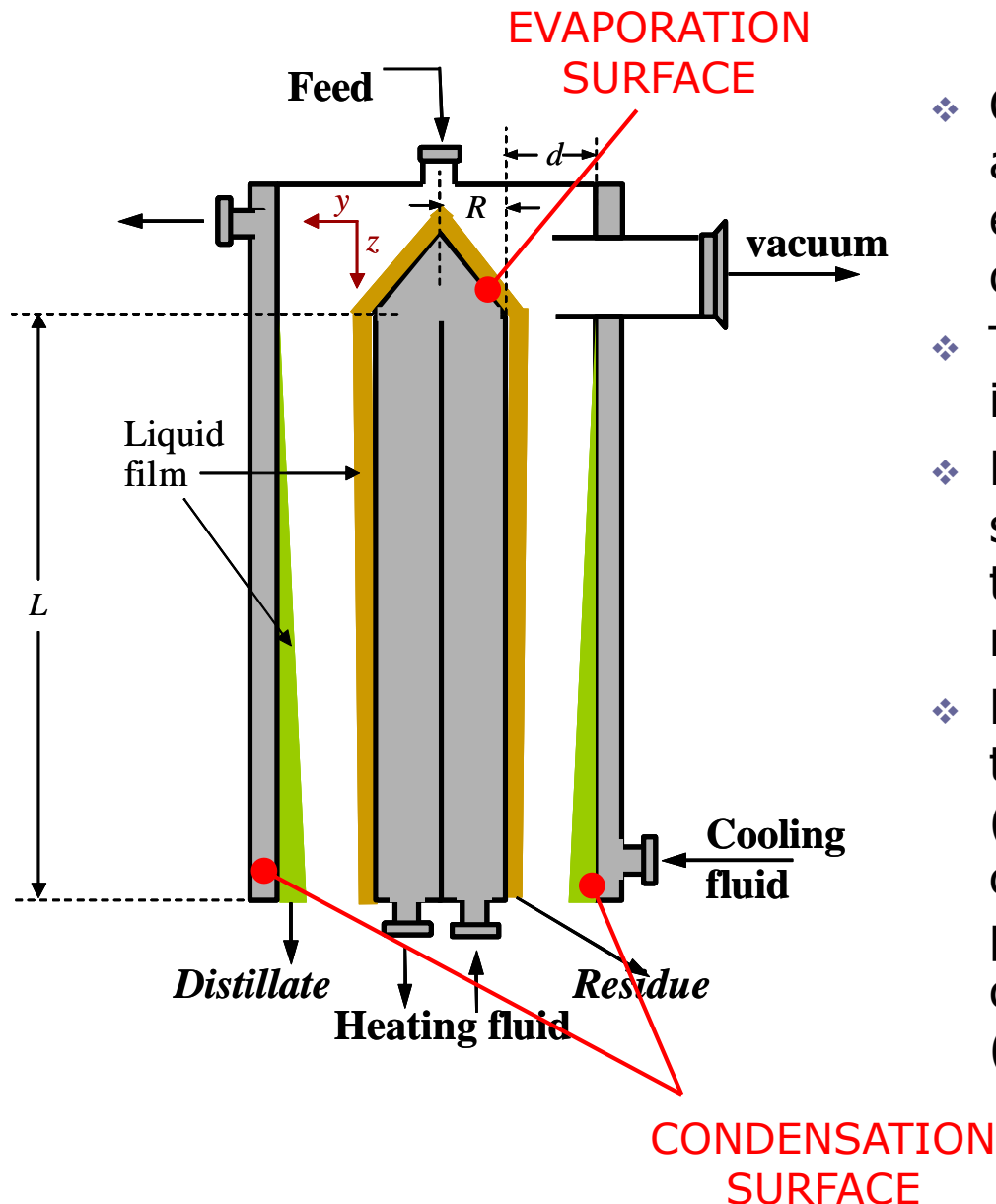
- ❖ Cylindrical body surrounded by a cylinder, one of them acts as evaporation surface and the other as condensation surface
- ❖ The liquid material to be distilled is fed in the evaporation wall.
- ❖ Evaporation and condensation surfaces are kept at constant temperatures *Tw1* and *Tw2*, respectively
- ❖ Due to the low pressure inside the separator, a falling film (without boiling) is formed and concentration/temperature profiles of the most volatile compounds decrease in the axial (z) and radial (y) directions

Temperature profiles

- ❖ The temperature is kept low by the high vacuum
- ❖ The short residence time is guaranteed by distributing the liquid in a thin film
- ❖ The distillation rate is increased by having small gap between condenser and evaporator
- ❖ Collisions between the vapor molecules (anisotropic properties) strongly affect separation

Temperature Profile
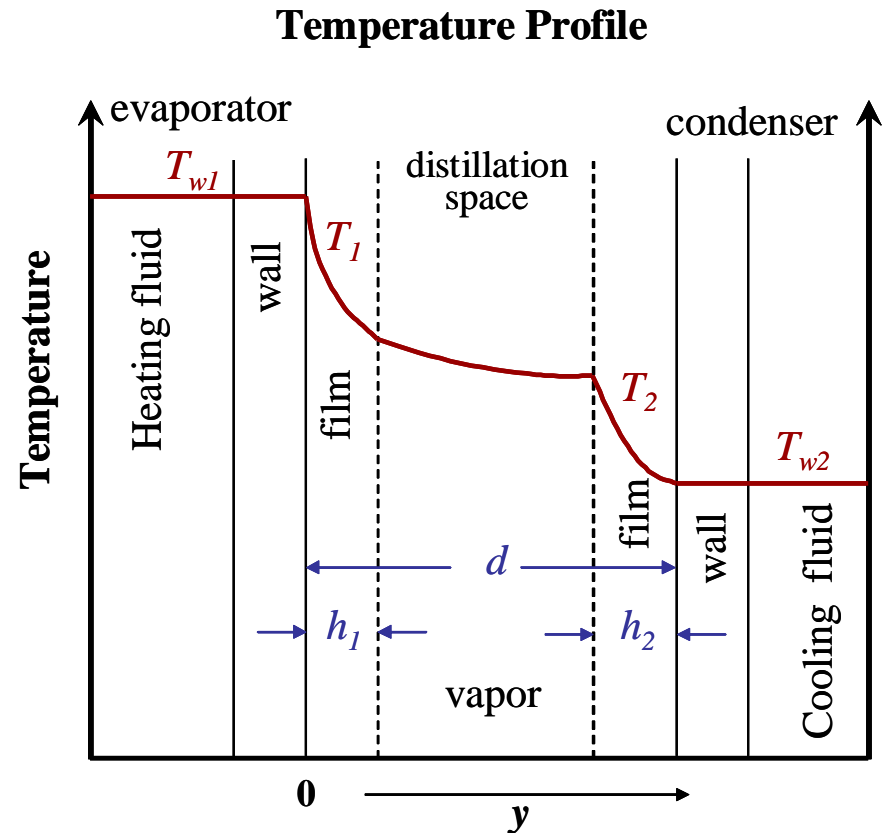
Information about the film surface temperature on the condensation surface is important to determine yield and purity of the distilled product, as well as to define the evaporator design (i.e., the feed position and the evaporator geometry)

Modelling Issues and Hypotesis

❖ **ISSUES:**
- Validity for multicomponent systems
- Consideration of anisotropic properties (collisions)
- Correction of evaporation rate with the vacuum effects
- Description of non-ideality of liquid phase (activity coefficient models)

❖ **HYPOTESIS:**
- Steady state
- Liquid films on the evaporation and condensation walls are much thinner than the corresponding cylinder diameters: rectangular coordinates (y, z) can be used instead of cylindrical
- Newtonian liquids
- Re-evaporation and splashing are neglected
- Evaporation happen far from extremities of evaporator: fully developed flow profile
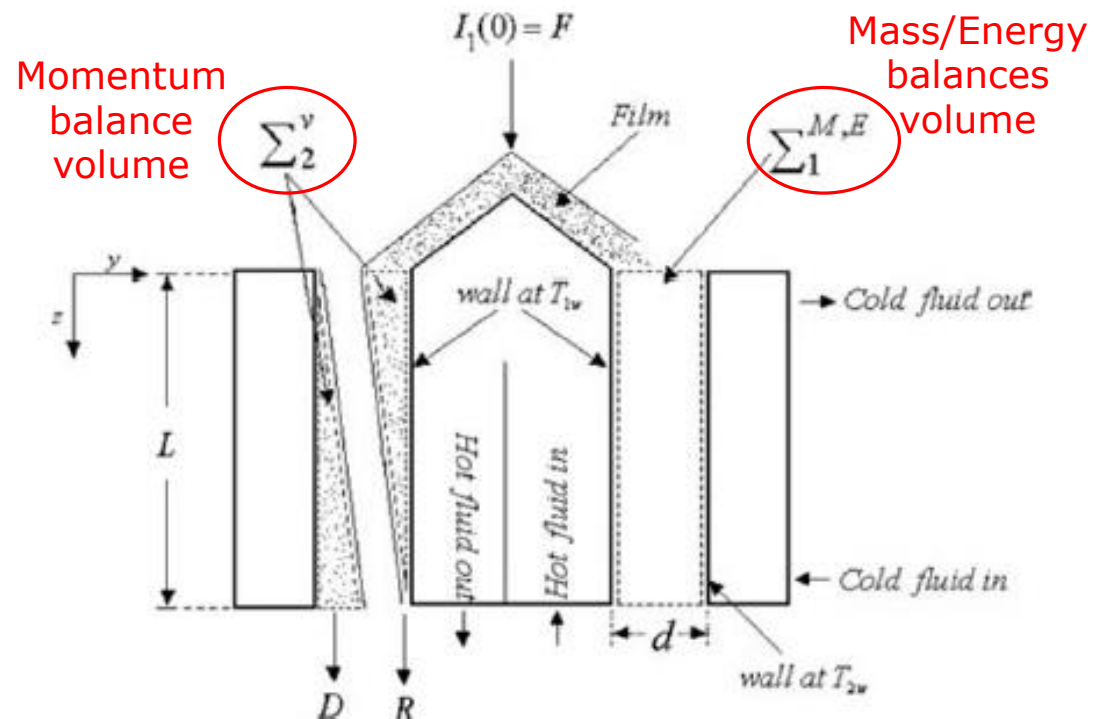- No diffusion in axial direction
- Radial flow is neglected

Error in your slides

radial

axial

Feed

vacuum

Liquid film

L

Cooling fluid

Distillate   Residue

Heating fluid
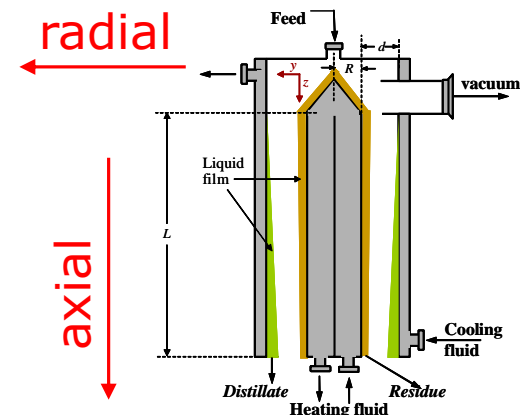
Mathematical model

❖ EQUATIONS:

- Momentum balance: velocity profiles

- Mass balances: concentration profiles

- Energy balance: temperatures profiles

- Rate of evaporation

- Film thickness

Momentum Balance

Evaporating liquid in short-path evaporation is highly viscous: Reynolds numbers are small, therefore there is laminar flow. The Navier-Stokes equation (at steady state) for laminar regimen describes the velocity (v) profile of falling film:

$$v(y,z)\frac{\partial^2 v(y,z)}{\partial y^2} = -g \qquad (1)$$

Boundary conditions:

$$v(0,z)=0, \qquad v(y,z)=v_{max} \qquad (2)$$

v = velocity
g = gravity constant
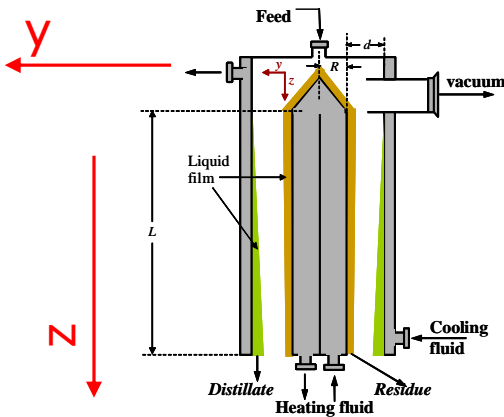y = radial coordinate
z = axial coordinate
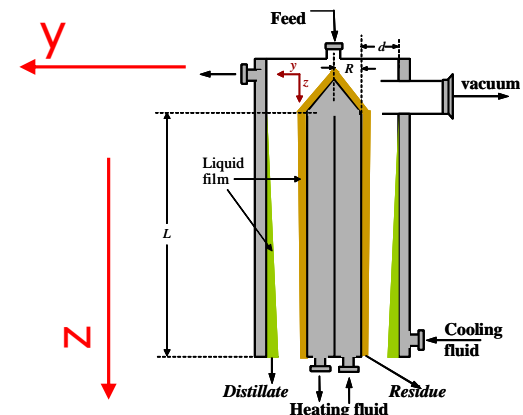
Mass Balance

The composition (C_i) profiles for each component are calculated from the diffusion equation:

$$v(y,z)\frac{\partial C_i(y,z)}{\partial z} = D_i\left[\frac{\partial^2 C_i(y,z)}{\partial y^2} + \frac{\partial^2 C_i(y,z)}{\partial z^2}\right], \qquad i = 1,\mathrm{K}, N \quad (3)$$

Boundary conditions:

$$C_i(y,0) = C_{i,0} \qquad (4a)$$

$$\frac{\partial C_i(0,z)}{\partial y} = 0 \qquad (4b)$$

$$D_i\frac{\partial C_i(y,z)}{\partial y}\bigg|_{y=h_1} = I_i(z) \qquad (4c)$$

D_i = diffusion coefficient compound i

N = total number of compounds

I_i = evaporation rate of compound i

Energy balance

The temperature (T) profile in the falling film is given by:

$$v(y,z)\frac{\partial T(y,z)}{\partial z} = \frac{\lambda}{\rho Cp}\left[\frac{\partial^2 T(y,z)}{\partial y^2} + \frac{\partial^2 T(y,z)}{\partial z^2}\right] \tag{5}$$

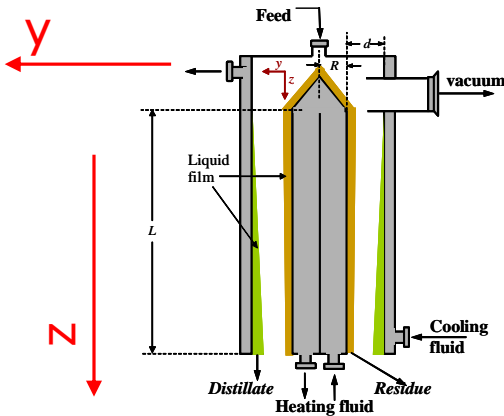Boundary conditions:

$$T(y,0) = T_F \tag{6a}$$

$$T(0,z) = T_{w1} \tag{6b}$$

$$\lambda\left.\frac{\partial T(y,z)}{\partial y}\right|_{y=h_1} = \Delta H^{vap} \cdot k \tag{6c}$$

$$k = \sum_{i=1}^{N}\left(\frac{C_i \cdot k_i}{\sum C_k}\right) \tag{6d}$$

λ = thermal conductivity
ρ = density
Cp = thermal capacity
ΔH^{vap} = heat of evaporation of the multi-component mixture
k_i = effective rate of evaporation of each component (in next slides)

Rate of evaporation

Evaporation flow rate (I_i) is described by continuity equation:

$$\frac{\partial I_i(z)}{\partial z} = -2\pi \cdot R \cdot k_i, \qquad i = 1, \text{K}, N \tag{7}$$

The effective rate of evaporation (k_i) is calculated through a modified Langmuir-Knudsen equation:

$$k_i = \frac{p_i^{vap} T_s(z)}{\sqrt{2\pi R_g M_i T_s(z)}} \left(\frac{P}{P_{ref}}\right) \left\{ 1 - (1-F)\left[1 - e^{h/(\kappa\beta)}\right]^n \right\}, \qquad i = 1, \text{K}, N \tag{8}$$

F is the surface ratio and κ is the anisotropy of the vapour phase given by:

$$F = \frac{A_k}{A_k + A_V}, \qquad log\kappa = 0.2F + 1.38(F + 0.1)^4 \tag{9}$$

p_i^{vap} = vapour pressure
M_i = molecular weight
P/P_{ref} = correction for vacuum pressure of operation
R = radius of the evaporator inside cylinder
T_s = surface temperature
A_k, A_v = condensation and evaporation areas
β = mean path of evaporation molecules

Film Thickness

The thickness film (h_1) along the evaporator height:

$$h_1(z) = \sqrt[3]{\frac{3\nu}{2\pi \cdot R \cdot g \cdot c} I(z)} \qquad (10)$$

$$I(z) = \sum_{i=1}^{N} I_i(z) \qquad (11)$$
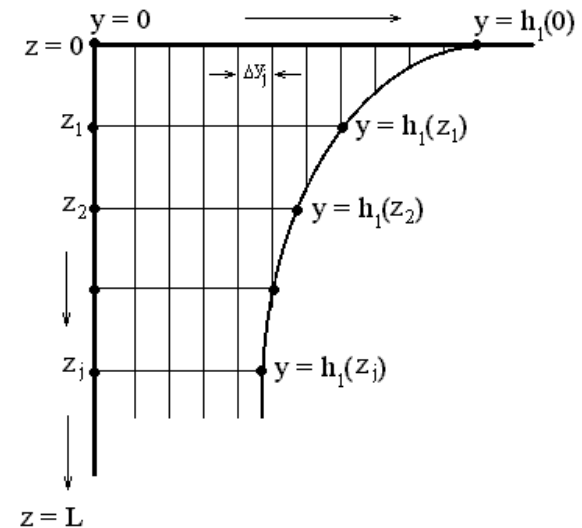
$$c = \sum_{i=1}^{N} C_i(z) \qquad (12)$$

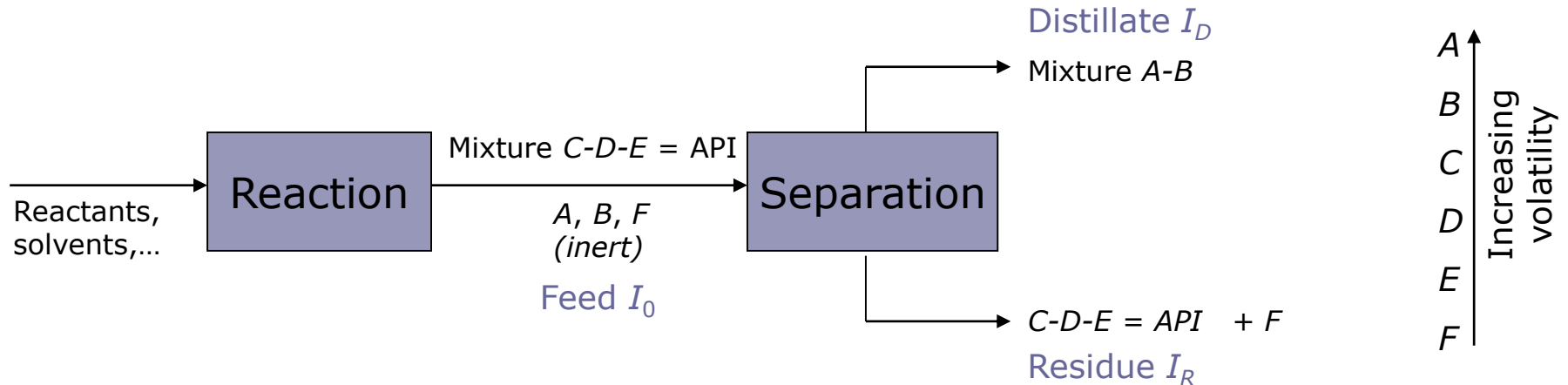$v = \mu/\rho$ = kinematic viscosity

I = total rate of evaporation

c = total concentration of the multicomponent mixture

Strategy of Solution

❖ Method of lines using centered finite difference is applied in order to solve the evaporator model that involves PDAEs

❖ An M-point discretization scheme for the radial coordinate "y" is considered. Good performances can be achieved with a minimum value of $M = 10$

❖ Afterwards, the resulting DAE system can be solved using for instance the BDF (Backward Difference Formula) method

Example: A pharmaceutical mixture

Distillate I_D
Mixture *A-B*

Mixture *C-D-E* = API

Reaction

Reactants, solvents,…

A, B, F (inert)

Feed I_0

Separation

C-D-E = API + *F*

Residue I_R

A
B
C
D
E
F

Increasing volatility

Pilot plant data

Compound	Pilot plant flows (mol s^{-1})		
	Feed I_0	Residue I_R	Distillate I_D
A	1.70E − 05	0.00E + 00	1.70E − 05
B	3.39E − 06	0.00E + 00	3.39E − 06
C	1.31E − 02	1.24E − 02	7.25E − 04
D	5.28E − 05	5.22E − 05	5.81E − 07
E	6.03E − 04	6.00E − 04	1.89E − 06
F	1.85E − 04	1.85E − 04	0.00E + 00

Objective:

Perform simulation and compare results with the pilot plant data → model validation

Solution procedure

The short-path evaporator model equations (Eqs. 1-12) are discretized as aforementioned, then a DAE system is obtained with the following number of equations and variables:

(a) 128 total equations:
- 17   ODEs
- 1   Implicit algebraic
- 110   Explicit AEs

(b) 306 total variables:
- 17   Dependent
- 1   Unknown
- 4   Known
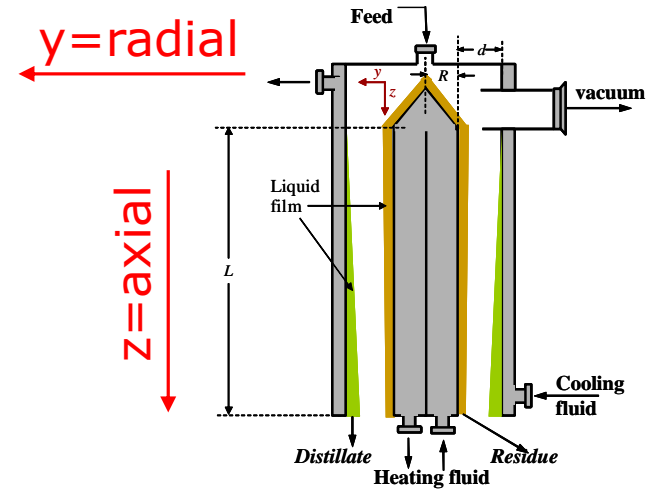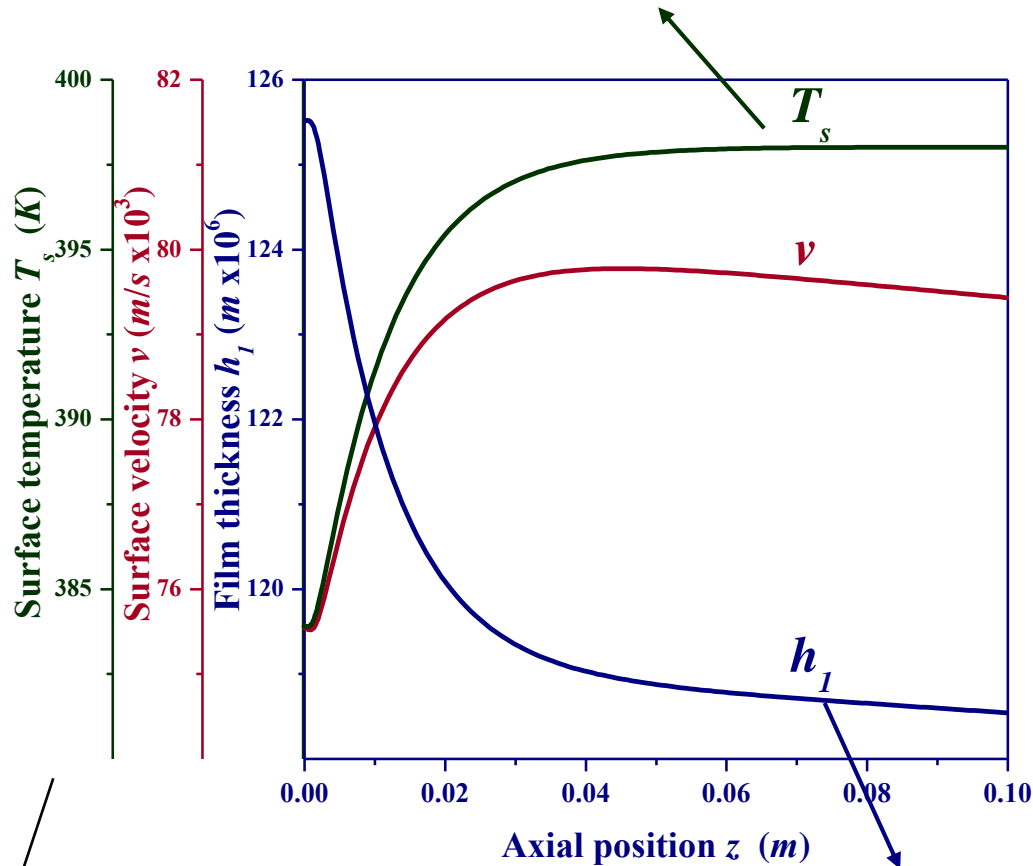- 174   Parameters
- 110   Explicit

> Note that the simulation results are completely predictive: not even one parameter has been regressed on the exp data!

Comparison Exp Data/ Simulation Results

	Pilot plant flows (mol s^{-1})		Calculated flows (mol s^{-1})	
Compound	Residue I_R	Distillate I_D	Residue I_R	Distillate I_D
A	0.00E + 00	1.70E − 05	0.000E + 00	1.70E − 05
B	0.00E + 00	3.39E − 06	7.593E − 07	2.63E − 06
C	1.24E − 02	7.25E − 04	1.294E − 02	1.71E − 04
D	5.22E − 05	5.81E − 07	5.269E − 05	8.36E − 08
E	6.00E − 04	1.89E − 06	6.007E − 04	2.11E − 06
F	1.85E − 04	0.00E + 00	1.851E − 04	0.00E + 00

Solution: profiles along the evaporator

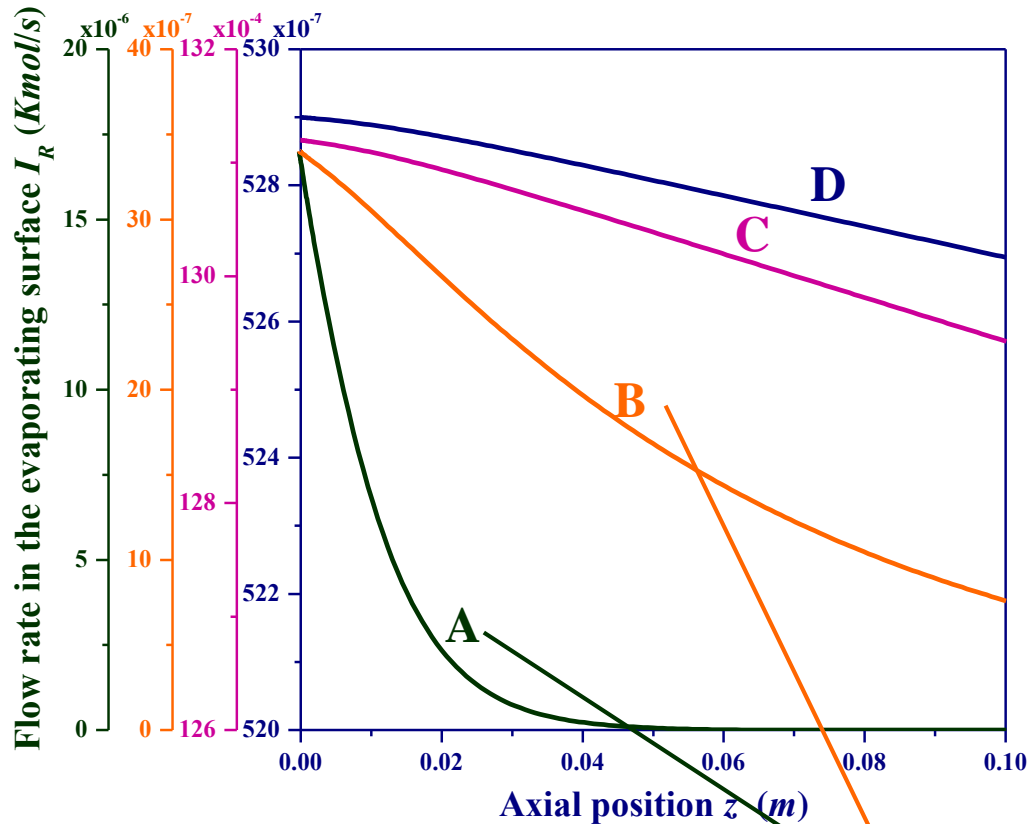Evaporation film temperature increases going down the evaporator since the flow rates of A and B increases too

y=radial

z=axial

Feed

vacuum

Liquid film

L

Cooling fluid

Distillate   Residue
Heating fluid

Remember:
A, B = distillate
C, D, E, F = residue

All these variables refer to the evaporating film, the one flowing down the evaporator (inside cilinder)
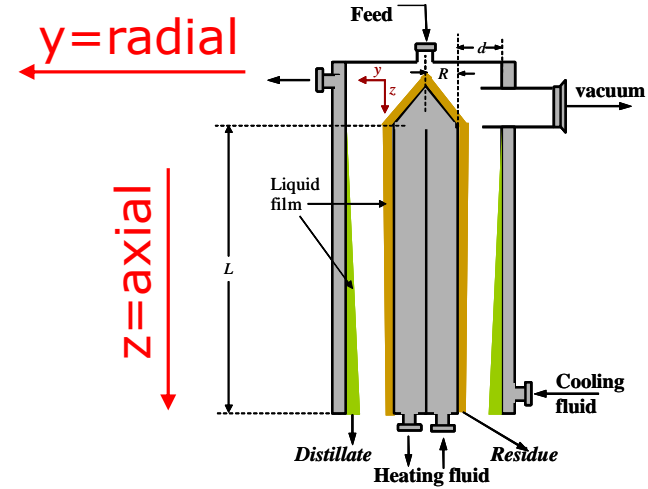
Film thickness on the evaporator diminishes going down the evaporator since compounds migrate to the film on the condenser

T_s

v

h_1

Surface temperature T_s (K)

Surface velocity v (m/s x10^3)

Film thickness h_1 (m x10^6)

Axial position z (m)

400

82   126

395   80   124

390   78   122

385   76   120

0.00   0.02   0.04   0.06   0.08   0.10

Solution: profiles along the evaporator

Flow rate in the evaporating surface I_R (Kmol/s)

Axial position z (m)

y=radial

z=axial

Feed

vacuum

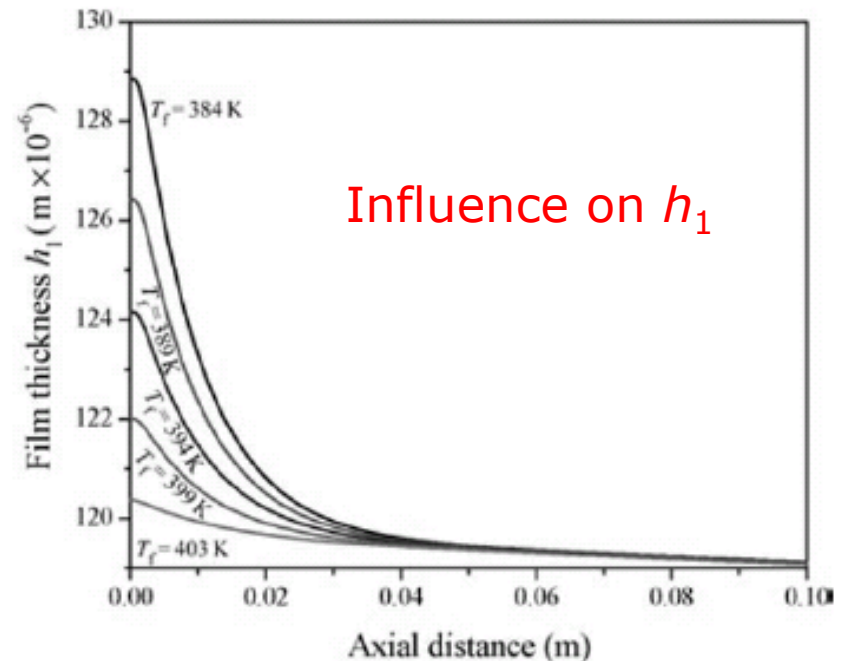Liquid film

Cooling fluid

Distillate   Residue

Heating fluid

Remember:
A, B = distillate
C, D, E, F = residue

A and B are the compounds involved in the evaporation since they constitute the distillate
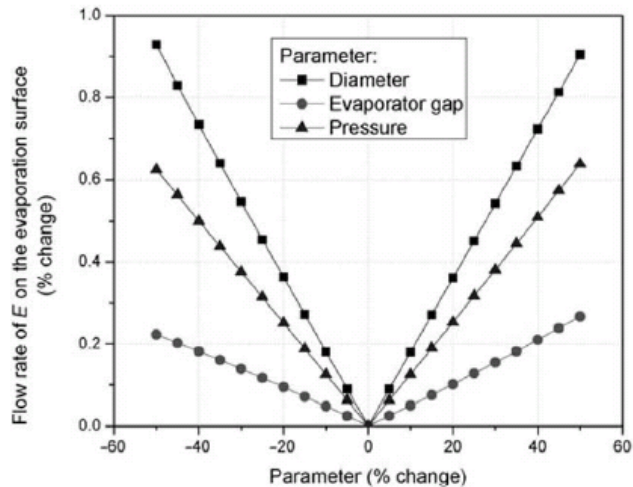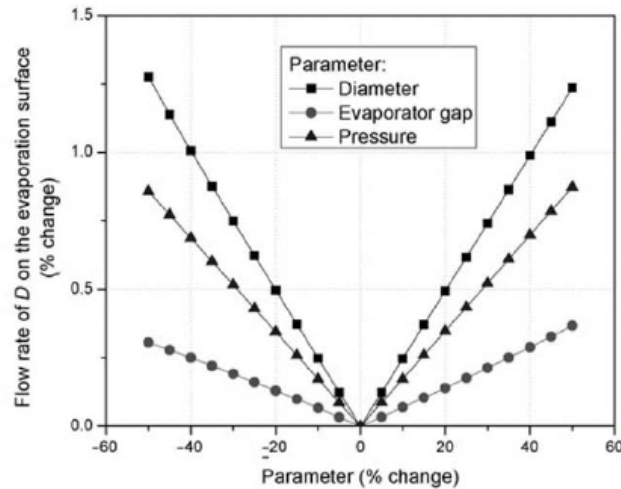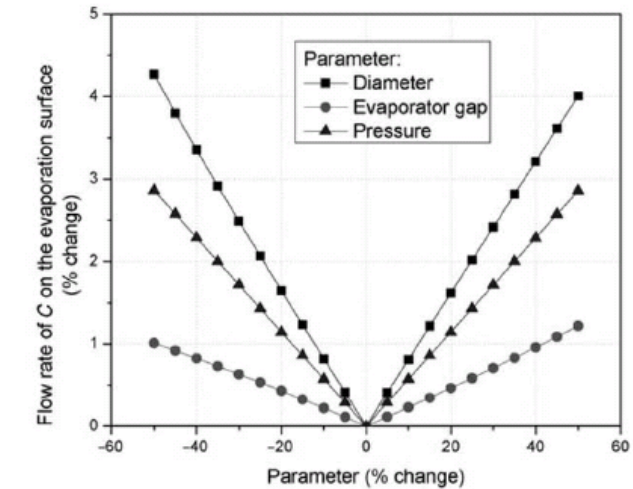
Solution: influence of feed temperature

Influence on T_s
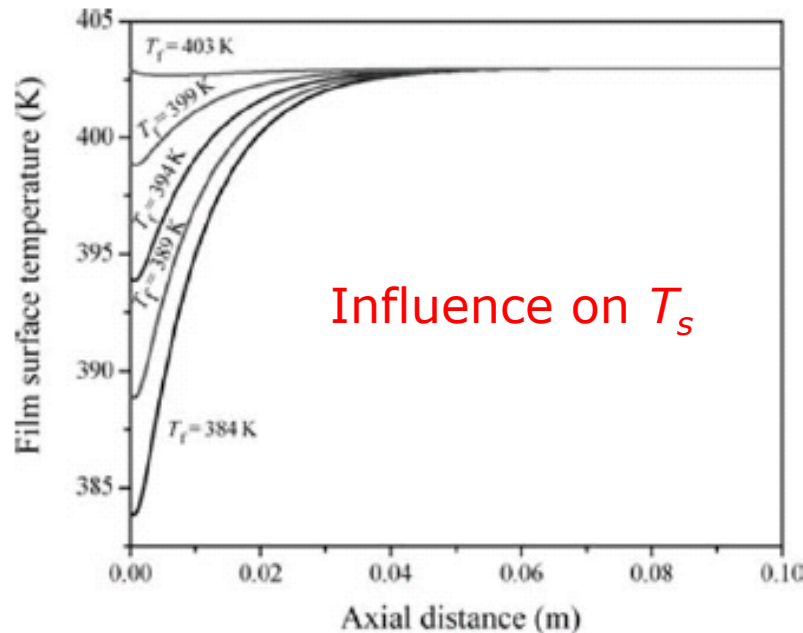
No matter the feed temperature value, the same asymptotic value is reached before the L/2

Influence on h_1

Solution: sensitivity analysis
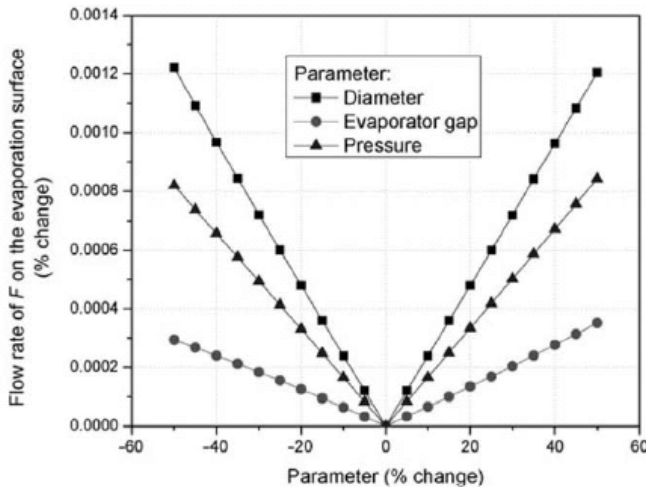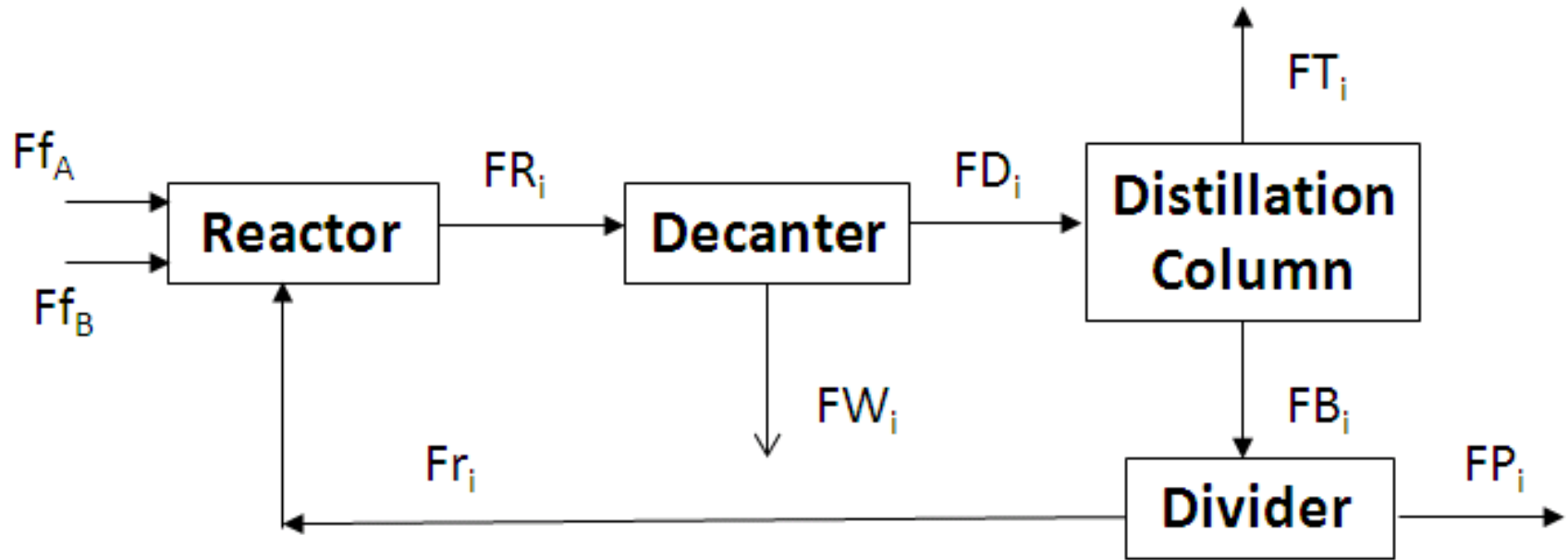

The process is:

• not so much sensitive to the evaporation gap (distance evaporator-condenser)
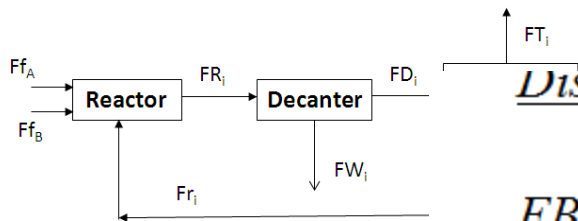
• very sensitive to the evaporometer diameter

• very sensitive to the pressure

Important design parameters

Williams Otto Plant

Williams Otto Plant

Distillation Column (component splitter) – 2*NC equations:

$$FB_i = \xi_{iS2} *FD_i \qquad\qquad i=A,\ B,\ C,\ E,\ G$$

$$FB_P = \xi_{PS2} *FD_E$$

$$FT_i = (1- \xi_{iS2}) *FD_i \qquad\qquad i=A,\ B,\ C,\ E,\ G$$

$$FT_P = FD_P - \xi_{PS2} *FD_E$$

Flow splitter (stream divider) – 2*NC equations:

$$FP_i = \beta *FB_i \qquad\qquad i=A,\ B,\ C,\ E,\ P,\ G$$

$$Fr_i = (1-\beta) *FB_i \qquad\qquad i=A,\ B,\ C,\ E,\ P,\ G$$

$\underline{Definiti}$

$$FR_A=$$

$$X_i = FR_i/$$

$$FR_B=$$

$\underline{Constit}$

$$FR_C=$$

$$k_i = k_{0i} *e$$

$$FR_E=$$

$\underline{Decante}$

$$FR_P=$$

$$FD_i = \xi$$

$$FR_G=$$

$$FW_i = (.$$

Final optimal design: solvent + process

Maximize, Profit

= Earnings – Solvent cost

– Energy costs

Subject to

Acetone purity > 0.99

Chloroform purity > 0.98

Results:

Solvent	Solvent flow rate	Reflux Reb. 1	Reflux Reb. 2	Objective function
1-hexanal	0.082 kmol/hr	0.45	0.65	2860.51 $/hr

Process

Extraction

Raw Materials

Clean Water

Products

Solvent

Clean Water

Contaminated Water
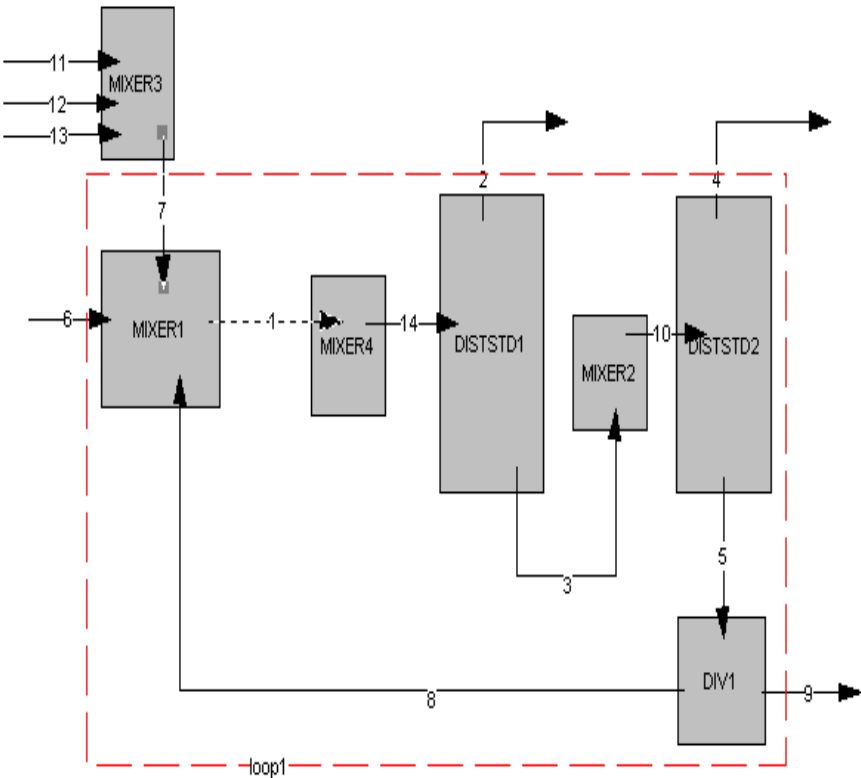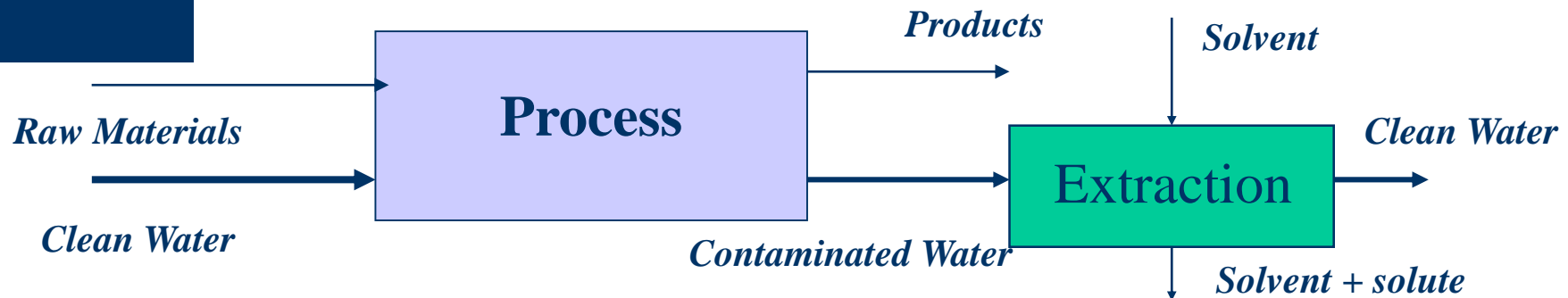
Solvent + solute

Determine target for solvent

$* f_S = F_W (X_{in,s} - X_{out,s})$

Solubility, $S = f_S/F_S$

$*$ **Find solvent to match target S – use data & models**

Order different solutions according to cost of solvent & operation

→

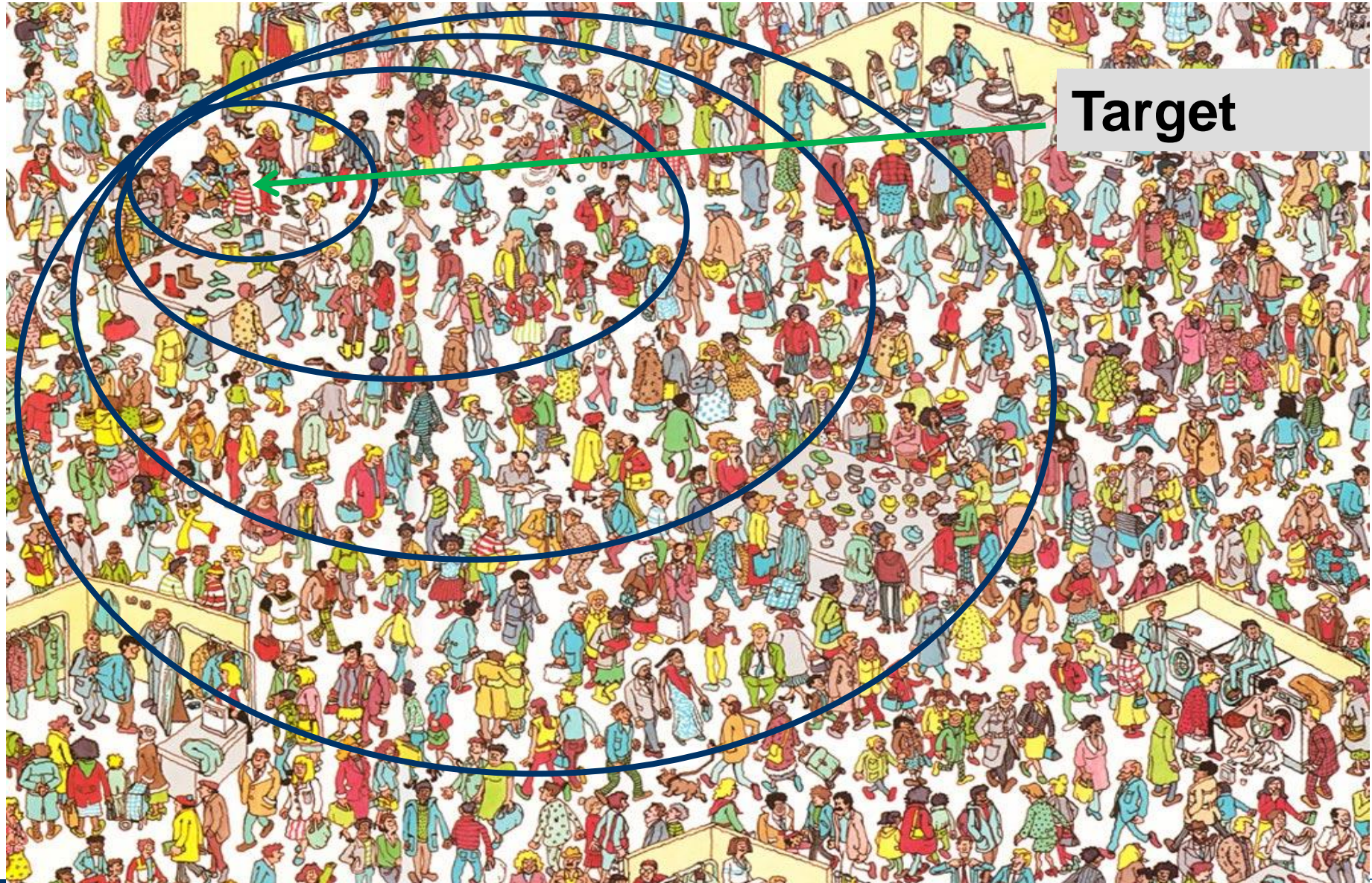**Problem solution**

$* f_S = 100 (0.018 - 0.00)$

Solubility, $S = 1.8/F_S$

• Solvent ID provides **S**

• $F_S = 1.8/S$

• Solvent ID decides **extraction process**; solvent-solute relations identify the **process parameters**

DTU

Target

Model Reduction - Derivation (1)

* **Verify if constitutive variables can be estimated independent of compositions using the operators**

$$a = \sum x_i \, \alpha_i \qquad ; \qquad b = \sum x_i \, \beta_i \qquad ; \, ...$$

* **Multiply balance equations with the pure component parameters α_i , sum for all components & replace summation term with operator a. Repeat for all operators**

* **Using only the operators a & b, NS(NC+2) equations is replaced by NS(2+2) equations independent of the number of components in the system**

Michelsen (1986), Gani & O'Connell (2001)

Model Reduction - Derivation (2a)

Example: One-stage Equilibrium Model

$Fz_i - Vy_i - Lx_i = 0$ **component mass balance**

$F\alpha_i z_i - V\,\alpha_i y_i - L\,\alpha_i x_i = 0$ **multiply with α_i**

$\sum\alpha_i z_i - V/F \sum V\alpha_i y_i - (F-V)/F \sum\alpha_i x_i = 0$ **Sum & divide by F**

$a_Z - \beta\,a_y - (1-\beta)\,a_x = 0$ **where, $a_k = (\sum\alpha_i k_i)^{1/2}$ & $\beta = V/F$**

Repeating for $b_k = \sum b_i k_i$, gives

$b_Z - \beta\,b_y - (1-\beta)\,b_x = 0$

Using the equilibrium definition,

$a_y = \sum (K_i\alpha_i z_i) / (1 + \beta\,(K_i - 1))$; $b_y = \sum (K_i b_i z_i) / (1 + \beta\,(K_i - 1))$

where, $K_i = \varphi^L/\varphi^V = f_L(a, b, \alpha_i, b_i, T, P)/ f_V(a, b, \alpha_i, b_i, T, P)$

Model Reduction - Derivation (2c)

Example: One-stage Equilibrium Model

$Fz_i - Vy_i - Lx_i = 0 \qquad i=1, NC$

$a_Z - \beta a_y - (1-\beta) a_x = 0 \quad (1)$

$b_Z - \beta b_y - (1-\beta) b_x = 0 \quad (2)$

Known: a_z, $\underline{z}$, T, P, $\underline{\alpha}$, $\underline{b}$

Solve Eqs 1-3 for

a_x, b_x & β

Using the equilibrium definition,

$a_y = \sum (K_i \alpha_i z_i) / (1 + \beta (K_i - 1)) ; b_y = \sum (K_i b_i z_i) / (1 + \beta (K_i - 1))$

where, $K_i = \varphi^L/\varphi^V = f_L(a, b, \alpha_i, b_i, T, P) / f_V(a, b, \alpha_i, b_i, T, P)$
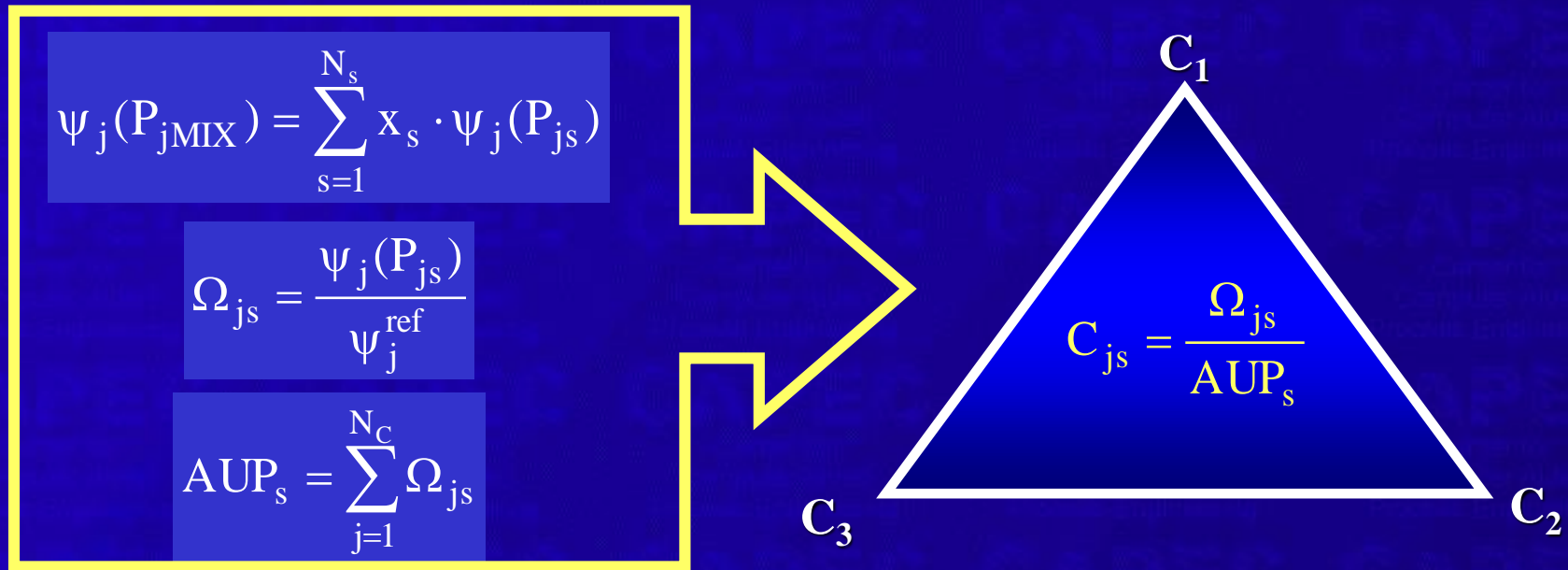
$\sum (K_i - 1) z_i / (1 + \beta (K_i - 1)) = 0 \quad (3)$ **Constraint Equation**

NC+1 Equations reduced to 2+1 (energy balance not counted)

Repeat for NS stages!

Composition-free design (reverse simulation)

- Definition of Property-based Clusters

$$\psi_j(P_{jMIX}) = \sum_{s=1}^{N_s} x_s \cdot \psi_j(P_{js})$$

$$\Omega_{js} = \frac{\psi_j(P_{js})}{\psi_j^{ref}}$$

$$AUP_s = \sum_{j=1}^{N_C} \Omega_{js}$$

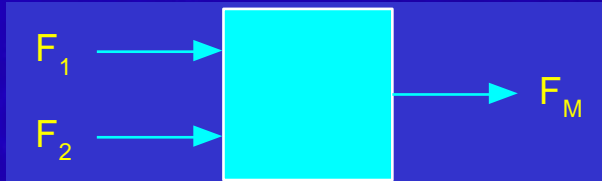$$C_{js} = \frac{\Omega_{js}}{AUP_s}$$

C_1

C_3 C_2

Linear Expression for Mixing 2 Ternary C

$$C_{jMIX} = \sum_{s=1}^{N_s} \beta_s \, C_{js} \quad , j = 1,2,3$$

Cluster "composition"

Composition Free Models – Mixer

$$F_1 \cdot y_{i1} + F_2 \cdot y_{i2} = F_M \cdot y_{iM}$$

$$\frac{F_1}{F_M} \cdot y_{i1} + \frac{F_2}{F_M} \cdot y_{i2} = y_{iM} \qquad , \beta_1 = \frac{F_1}{F_M}, \quad \beta_2 = \frac{F_2}{F_M}$$

$$y_{iM} = \beta_1 \cdot y_{i1} + \beta_2 \cdot y_{i2}$$

Multiplication by pure component property operator values and summation:

$$\Omega_{ji}^* \cdot y_{iM} = \Omega_{ji}^* \cdot \beta_1 \cdot y_{i1} + \Omega_{ji}^* \cdot \beta_2 \cdot y_{i2}$$

$$\sum_{i=1}^{NC} \Omega_{ji}^* \cdot y_{iM} = \beta_1 \cdot \sum_{i=1}^{NC} \Omega_{ji}^* \cdot y_{i1} + \beta_2 \cdot \sum_{i=1}^{NC} \Omega_{ji}^* \cdot y_{i2}$$

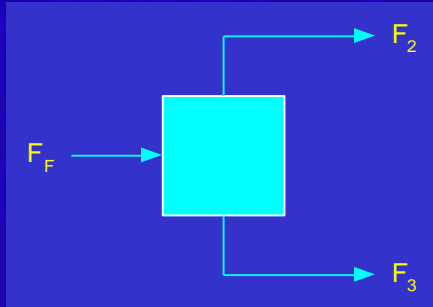$$\Omega_{jM} = \beta_1 \cdot \Omega_{j1} + \beta_2 \cdot \Omega_{j2}$$

$$AUP_M = \sum_j \Omega_{jM}$$

$$C_{jM} = \frac{\Omega_{jM}}{AUP_M}$$

Revised Composition Free Mixer Model

$$C_{jMIX} = \beta_1 \cdot C_{j1} + \beta_2 \cdot C_{j2} \quad , j = 1, NP$$

Composition Free Models – Splitter

$$F_F \cdot y_{iF} = F_2 \cdot y_{i2} + F_3 \cdot y_{i3} \qquad , \beta_2 = \frac{F_2}{F_F}, \quad \beta_3 = \frac{F_3}{F_F}$$

$$y_{iF} = \beta_2 \cdot y_{i2} + \beta_3 \cdot y_{i3} \quad , \quad S_i = \frac{F_2 \cdot y_{i2}}{F_F \cdot y_{iF}} \iff S_i \cdot y_{iF} = \beta_2 \cdot y_{i2}$$

$$y_{iF} = S_i \cdot y_{iF} + \beta_3 \cdot y_{i3}$$

Multiplication by pure component property operator values and summation:

$$\Omega_{ji}^* \cdot y_{iF} = \Omega_{ji}^* \cdot S_i \cdot y_{iF} + \Omega_{ji}^* \cdot \beta_3 \cdot y_{i3}$$

$$\sum_{i=1}^{NC} \Omega_{ji}^* \cdot y_{iF} = \sum_{i=1}^{NC} \Omega_{ji}^* \cdot S_i \cdot y_{iF} + \beta_3 \cdot \sum_{i=1}^{NC} \Omega_{ji}^* \cdot y_{i3}$$

$$\Omega_{jF} = \Omega_{jFSplit} + \beta_3 \cdot \Omega_{j3} \qquad , \Omega_{jFSplit} = \sum_{i=1}^{NC} \Omega_{ji}^* \cdot S_i \cdot y_{iF}$$

Function of initial data and split factors

$$AUP_M = \sum_j \Omega_{jM}$$

$$C_{jM} = \frac{\Omega_{jM}}{AUP_M}$$

Revised Composition Free Splitter Model

$$C_{j2} = \frac{\Omega_{jFSplit}}{\sum_j \Omega_{jFSplit}} \quad , \quad C_{j3} = \frac{\Omega_{jF} - \Omega_{jFSplit}}{\sum_j (\Omega_{jF} - \Omega_{jFSplit})} \quad , j = 1, NP$$
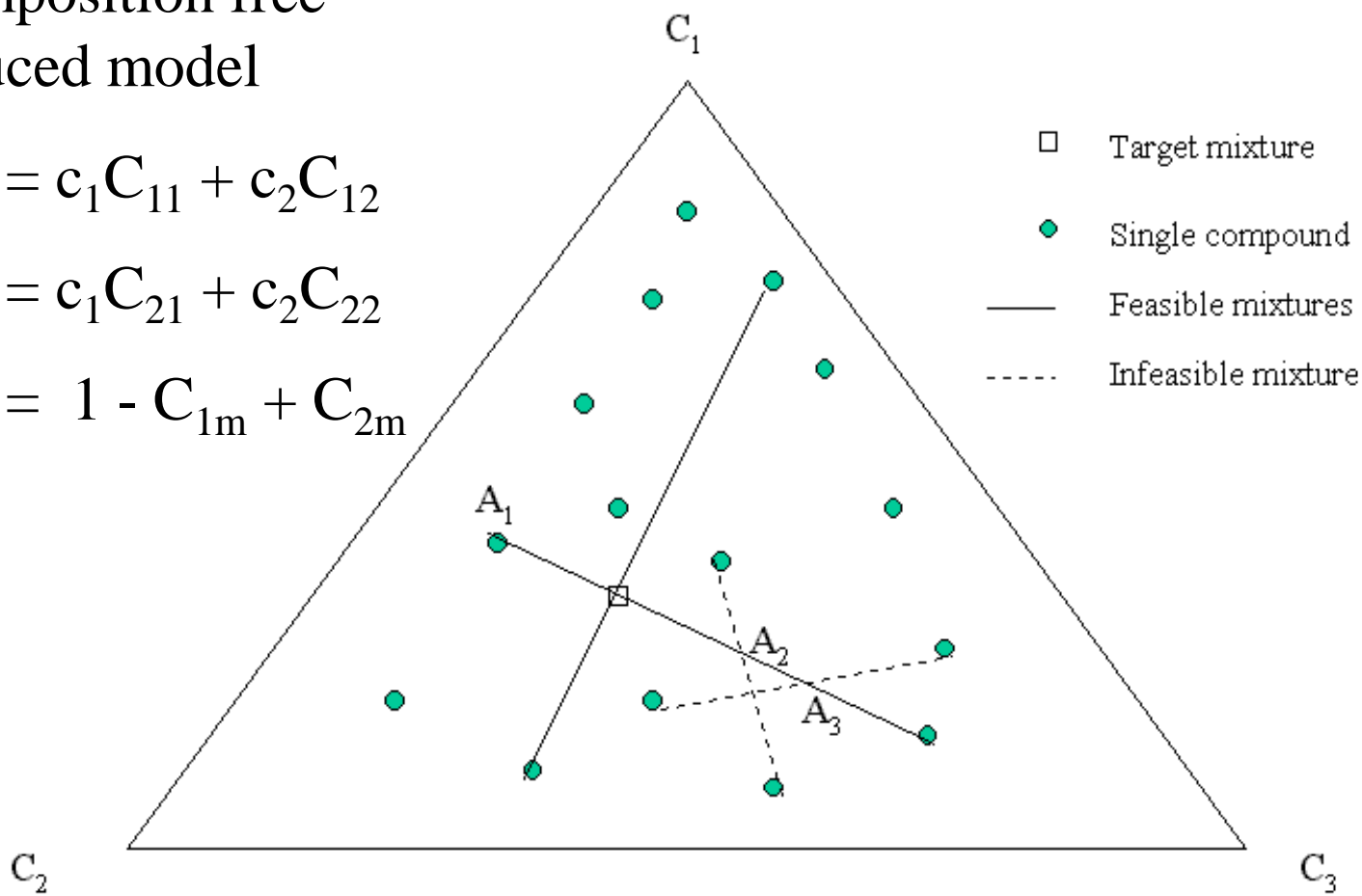
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Extension to other (formulation) Problems

Composition free
reduced model

$$C_{1m} = c_1 C_{11} + c_2 C_{12}$$

$$C_{2m} = c_1 C_{21} + c_2 C_{22}$$

$$C_{3m} = 1 - C_{1m} + C_{2m}$$

□   Target mixture

●   Single compound

──   Feasible mixtures

----   Infeasible mixture

Extension to other (formulation) Problems

Composition free
mixture design

$$C_{1m} = p_1C_{11} + p_2C_{12}$$

$$C_{2m} = p_1C_{21} + p_2C_{22}$$

$$C_{3m} = 1 - C_{1m} + C_{2m}$$

Feasible mixture

Infeasible mixture

C_1

C_2

C_3

A_1, A_2, A_3, A_4, A_j

p_1, p_2

C_{3j}, C_{1j}