Chemical product centric sustainable process design: Targeted reverse process design & concept of process group based flowsheet synthesis

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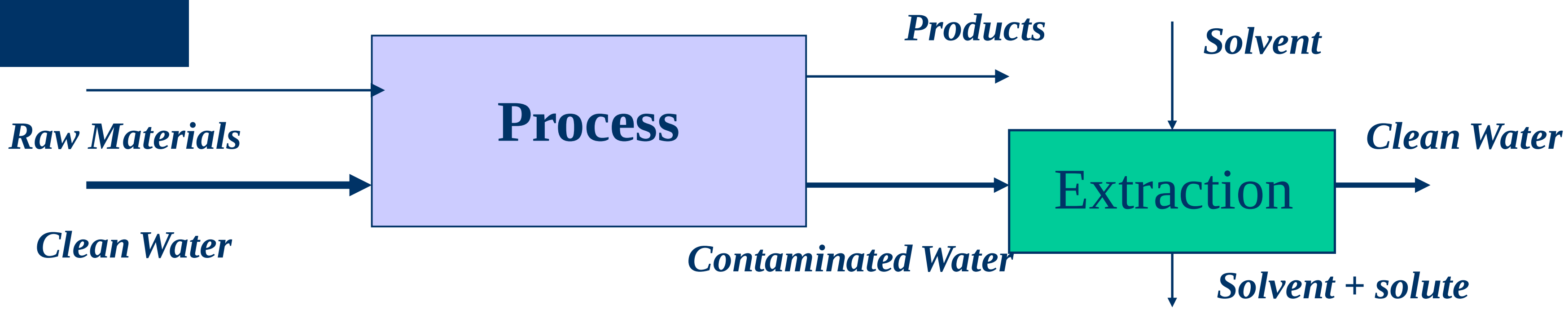
Targeted reverse process design & concept of process group based flowsheet synthesis:

- Solvent-based environmentally acceptable process design
- Driving force based separation process design
- Process group based flowsheet synthesis

Solvent substitution in process design

We have an aqueous mixture of phenol in a waste water stream. We need to remove the phenol. Benzene is known as a solvent but due to environmental reasons, we cannot use it. What should be a good replacement solvent for benzene?

Example of solvent-based separation



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**

→

Problem solution

*** $f_S = 100 (0.018 – 0.00)$**

Solubility, $S = 1.8/F_S$

- **Solvent ID provides S**
- **$F_S = S/1.8$**
- **Solvent ID decides extraction process; solvent-solute relations identify the process parameters**

Order different solutions according to cost of solvent & operation

Solvent substitution in process design

Define target (substitute benzene)

* Property specifications:

- Tb > 322 K
- Tm < 314 K
- 29 kJ/mol < Hvap < 34 kJ/mol
- logP > 1.5
- High solvent power
- High Phenol precipitation mole fraction at 298 K

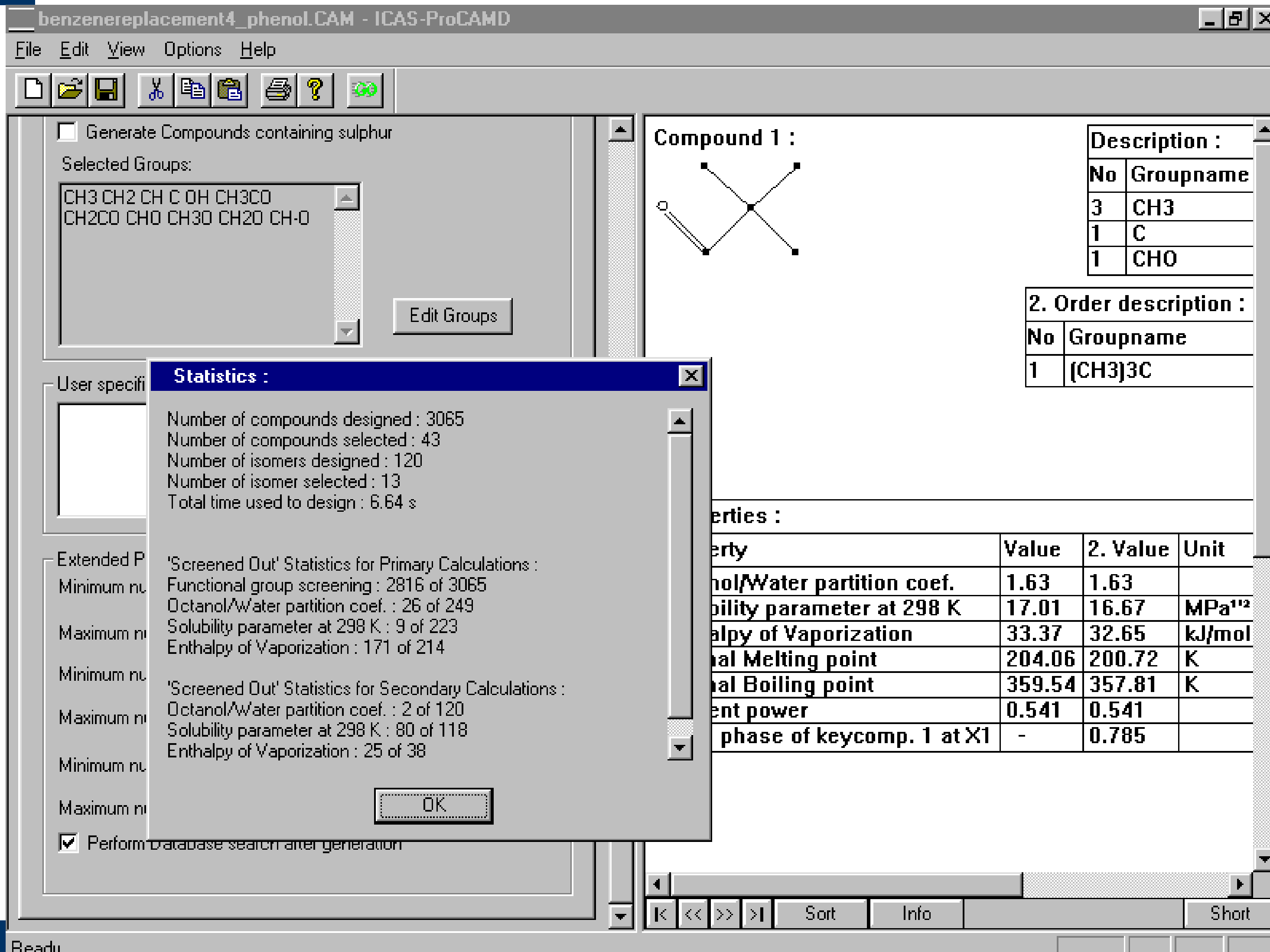
Solvent substitution in process design

Match target: Initial search (generate candidates)

* Property specifications (revised target):
  – Tb > 322 K
  – Tm < 314 K
  – δ_{SP}
* Use the above properties to search among non-aromatic compounds
* Design acyclic compounds: alcohols, ketones, aldehydes, ethers.

SPEED Solvent substitution in process design

Match target through CAMD – reverse design



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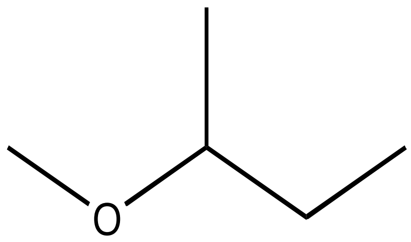
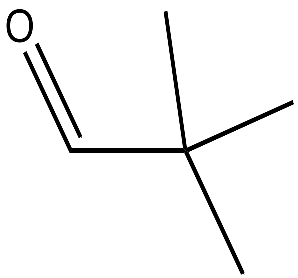
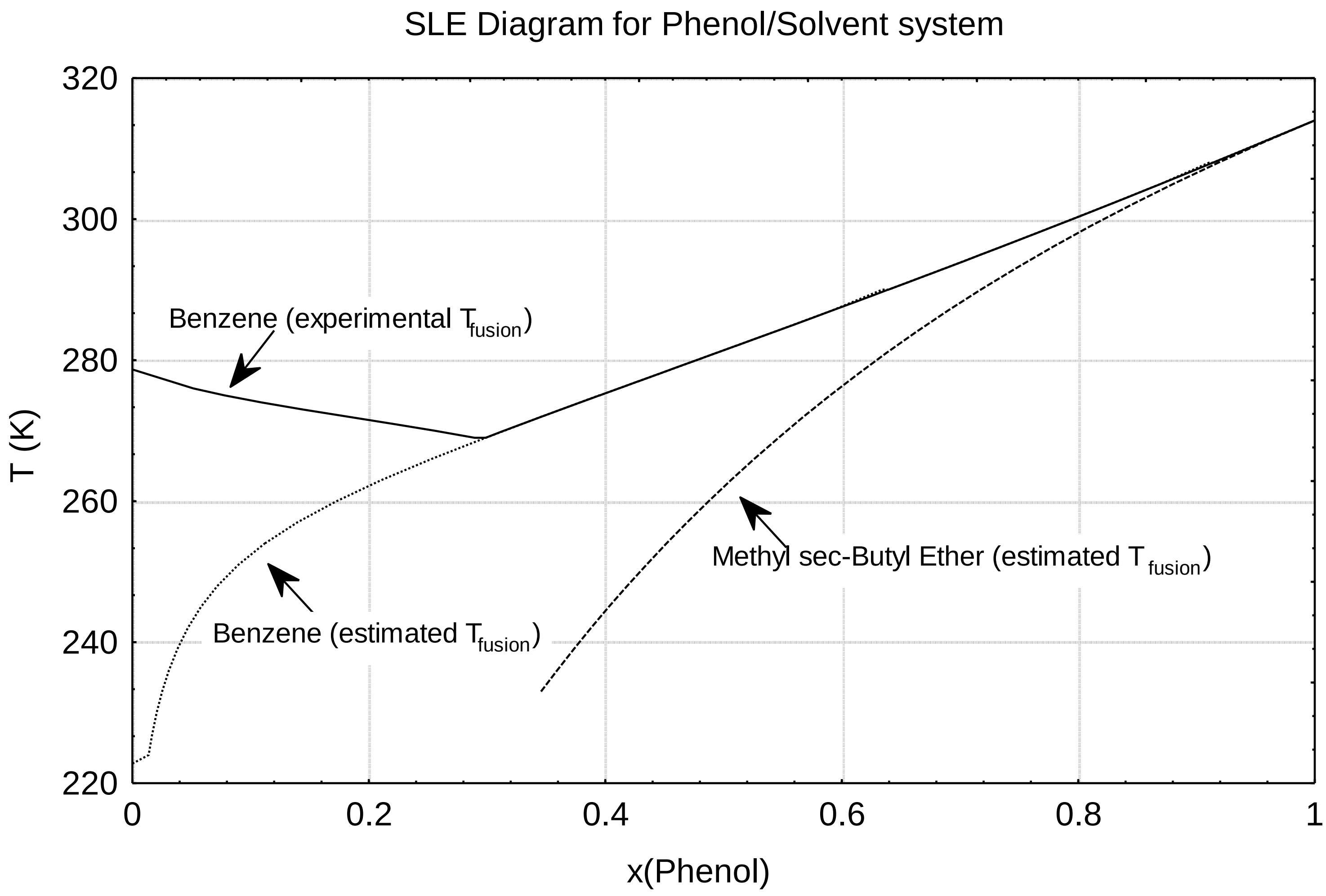
Solvent substitution in process design

- **Product-process evaluation**
  - **High precipitation mole fractions of phenol.**
  - **A CAS Registry number exists (availability & additional information)**

	
LogP = 1.56	LogP = 1.63
Phenol molefraction = 0.759	Phenol molefraction = 0.785
Methyl sec-Butyl Ether CASNO: 6795-87-5	2,2-Dimethyl-1-propanal CASNO: 630-19-3

Process evaluation



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Example:Separation of an azeotropic mixture

Problem: A process stream of 50 mole% Acetone and 50 mole% Chloroform at 300K, is to be separated.

Separation techniques considered:

- Adsorption (liquid, gas)
- Crystallization
- Desublimation
- Distillation – simple
- Distillation – extractive
- Distillation with decanter
- Liquid-liquid extraction
- Flash/evaporation
- Membrane (gas, liquid)
- Microfiltration
- Partial condensation

No external medium known; Binary ratios of properties identify the following alternatives:

Separation techniques:

- Distillation – simple
- Distillation – extractive
- Distillation – azeotropic
- Liquid extraction
- Pressure swing

Note: Acetone-chloroform forms a high boiling azeotrope that is slightly pressure sensitive

Solvent design sub-problem

- CAMD problem:
- 340 < T_{boil} < 420
- Selectivity > 3.5
- Solvent power > 2.0
- No azeotropes

Solution:
1-Hexanal
Methyl-n-pentyl ether
(Benzene)

- Number of compounds designed: 47792
  Number of compounds selected: 53
- Number of isomers designed: 528
  Number of isomer selected: 23
- Total time used to design: 57.01 s

Summary: CAMD-based solvent selection

- Solvent selection/design based on CAMD is very large but application is limited by availability of suitable property models (separation, reactions, formulated products, …)
- Extension to solvent mixture (blend) design is simple and easy
- Integration of process and product design is possible (requires methods & tools integration)
- Available software: ICAS-ProCAMD

Targeted reverse process design & concept of process group based flowsheet synthesis:

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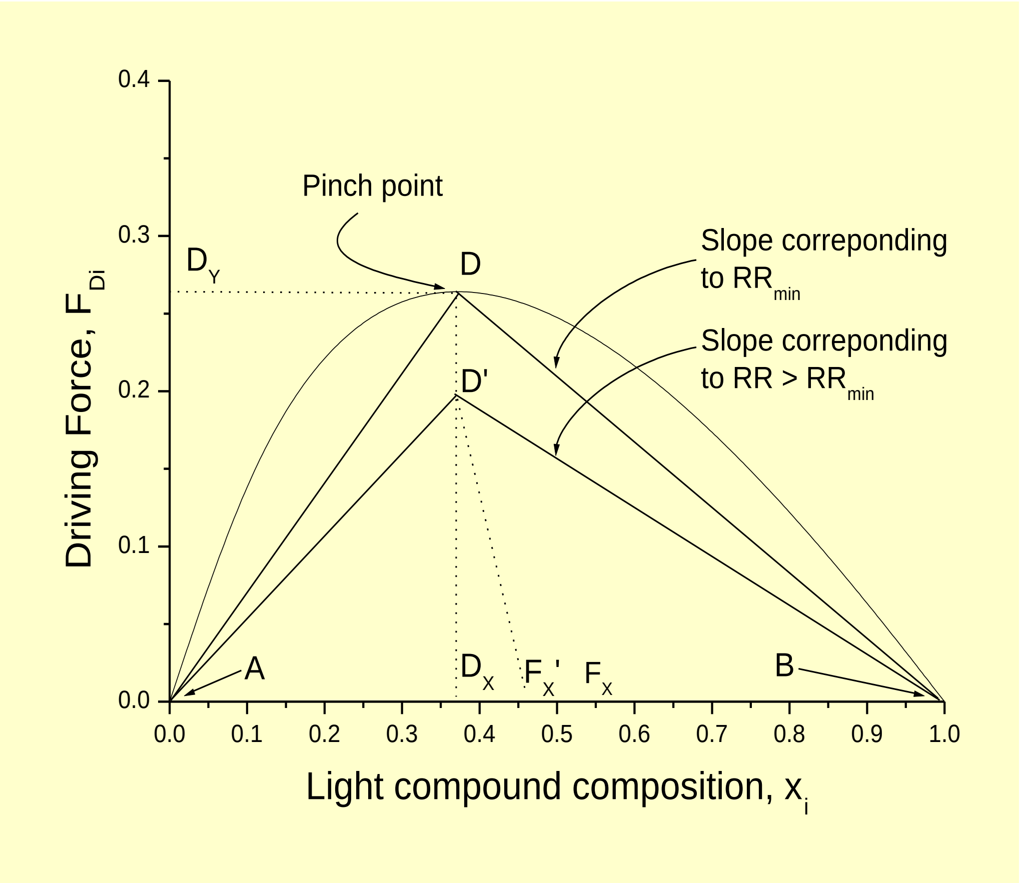
- Process group based flowsheet synthesis

Driving force based sustainable design

- **Sustainable process (design) alternatives can be generated by targetting designs that utilize the maximum available driving force**
- **Use of maximum driving force implies minimum corresponding energy, and therefore, improved sustainability**

Concept of targeted design

Definition of driving force



Separation of compound i from compound j

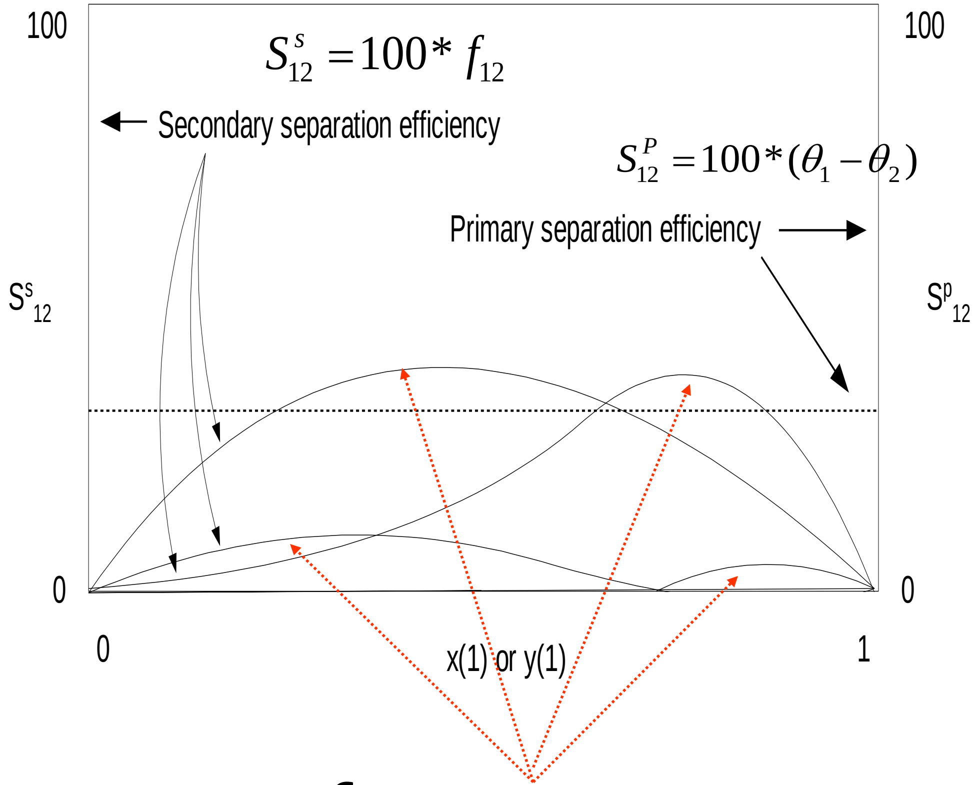
$$y_i = x_i \alpha_{ij} / (1 + x_i (\alpha_{ij} - 1))$$

$$F_{Di} = y_i - x_i$$
$$= x_i \beta_{ij} / (1 + x_i (\beta_{ij} - 1)) - x_i$$

$$\beta_{ij} = f(T, P, \underline{x}, \underline{y}, \underline{\phi})$$

Energy or work needed to perform an operation is inversely proportional to the driving force

Definition of Driving Force - D_{ij}



Separation of compound i from compound j

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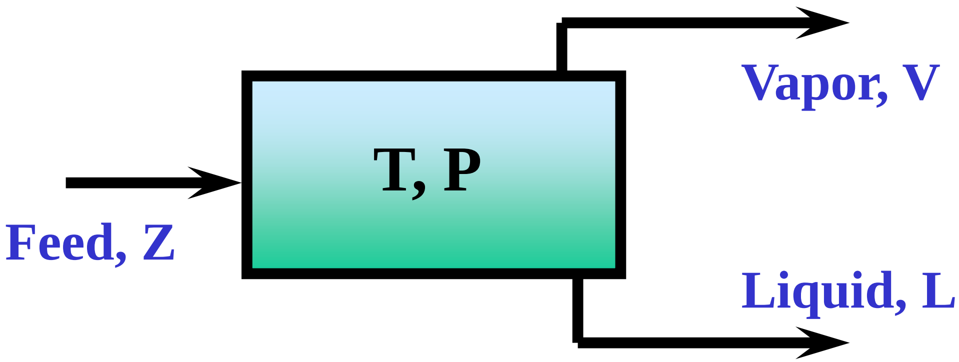
$$= x_i \beta_{ij} / (1 + x_i (\beta_{ij} - 1)) - x_i$$

$$\beta_{ij} = f(T, P, \underline{x}, \underline{y}, \underline{\phi})$$

D_{ij} for 4 types vapor-liquid separation range

Theory: D_{ij} is inversely proportional to energy consumption and directly proportional to separability

Example: VLE based separation using D_{ij}



Typical 2-Phase VLE-Model

Equilibrium condition $y_i = x_i \alpha_{ij}/[x_i (\alpha_{ij} - 1) + 1]$ w.r.t. relative volatility

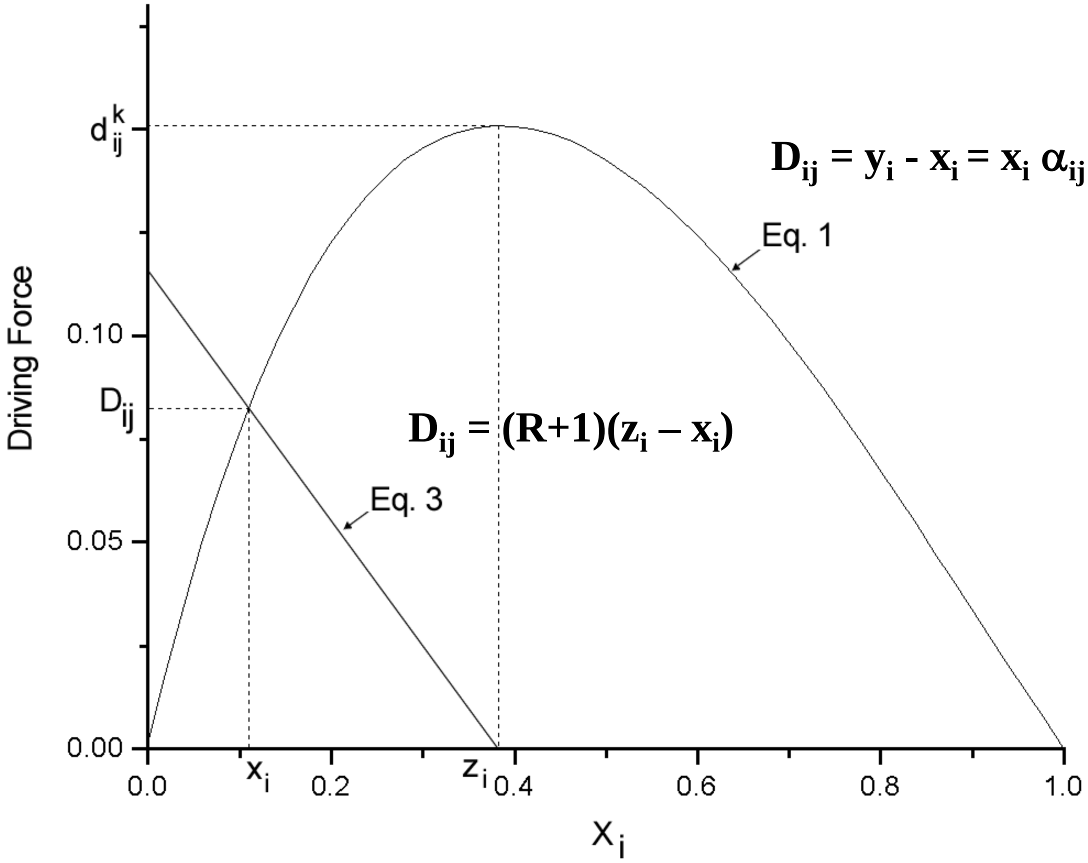
Equilibrium condition $D_{ij} = x_i \alpha_{ij} /[x_i (\alpha_{ij} - 1) + 1] - x_i$ w.r.t. driving force

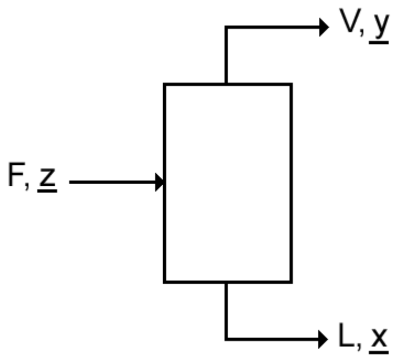
Mass Balance $Z z_i = V y_i + L x_i$ $i = 1,2,\ldots.c$

or $y_i = (R + 1) z_i – R x_i$ where $R = L/V$

or $D_{ij} = (R + 1) (z_i – x_i)$

Example: VLE based separation using D_{ij}



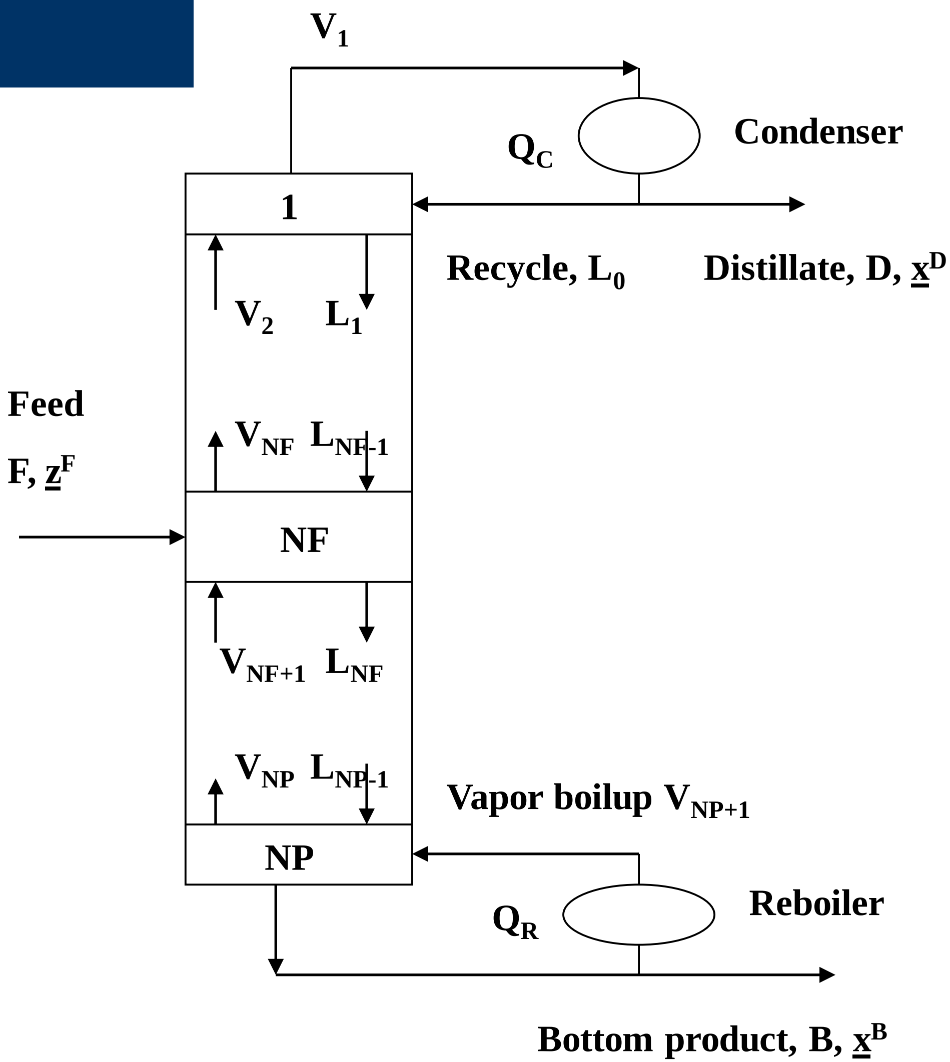


When $D_{ij} = 0$, there is no separation and $z_i = x_i$

When L = 0 or V= ∞, R= L/V= 0, $D_{ij} = z_i - x_i$

When $x_i = 0$, $D_{ij} = (R + 1)\, z_i$

Separation of Binary Mixtures by Distillation



Component Mass Balance

Overall

$$F\, z^F = D\, x^D + B\, x^B$$

Rectifying section

$$y_{n+1} = L_n / V_{n+1}\, x_n + D / V_{n+1} x^D$$

$$y = [R/(R+1)]\, x + [1/(R+1)] x^D$$

Stripping section

$$y_{m+1} = L_m / V_{m+1}\, x_m - B / V_{m+1} x^B$$

$$y = [(V_B+1)/V_B]\, x - 1/(V_B+1)] x^B$$

Equilibrium relation

$$y_i = x_i\, \alpha_{ij} / (1 + x_i\, (\alpha_{ij} - 1))$$

Separation of Binary Mixtures by Distillation

Equilibrium relation

$y_i = x_i \alpha_{ij} / (1 + x_i (\alpha_{ij} - 1))$

Component Mass Balance

Overall

$F z^F = D x^D + B x^B$

Rectifying section

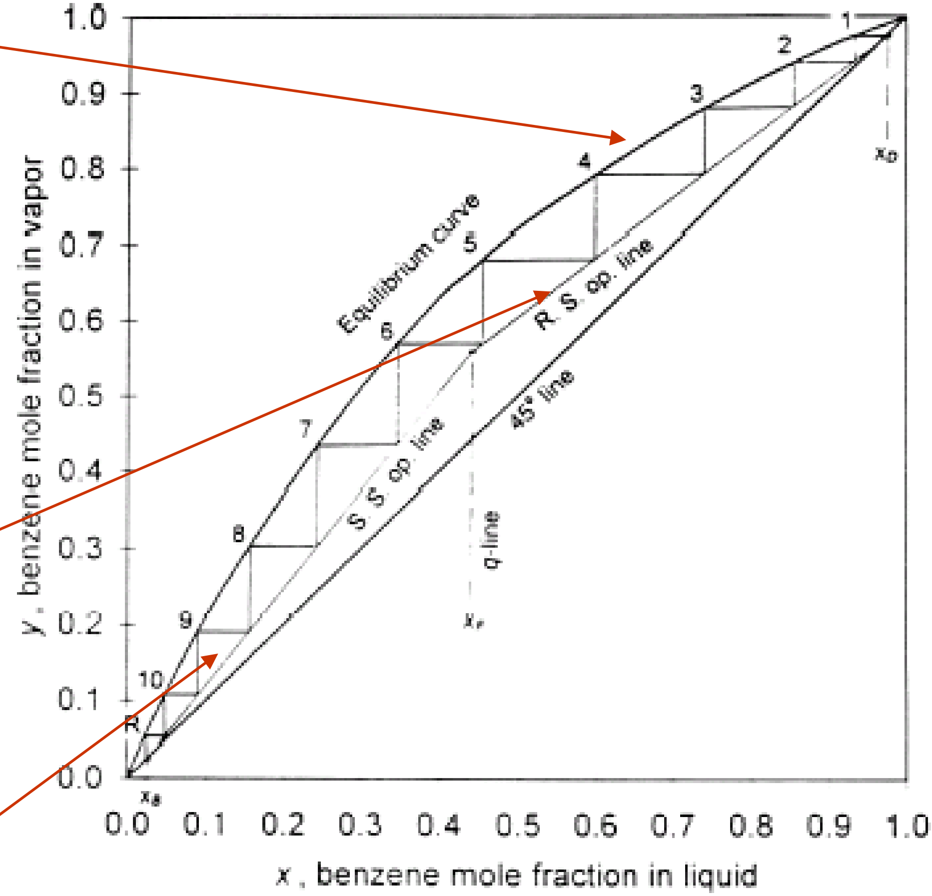
$y_{n+1} = L_n/V_{n+1} x_n + D/V_{n+1} x^D$

$y = [R/(R+1)] x + [1/(R+1)] x^D$

Stripping section

$y_{m+1} = L_m/V_{m+1} x_m - B/V_{m+1} x^B$

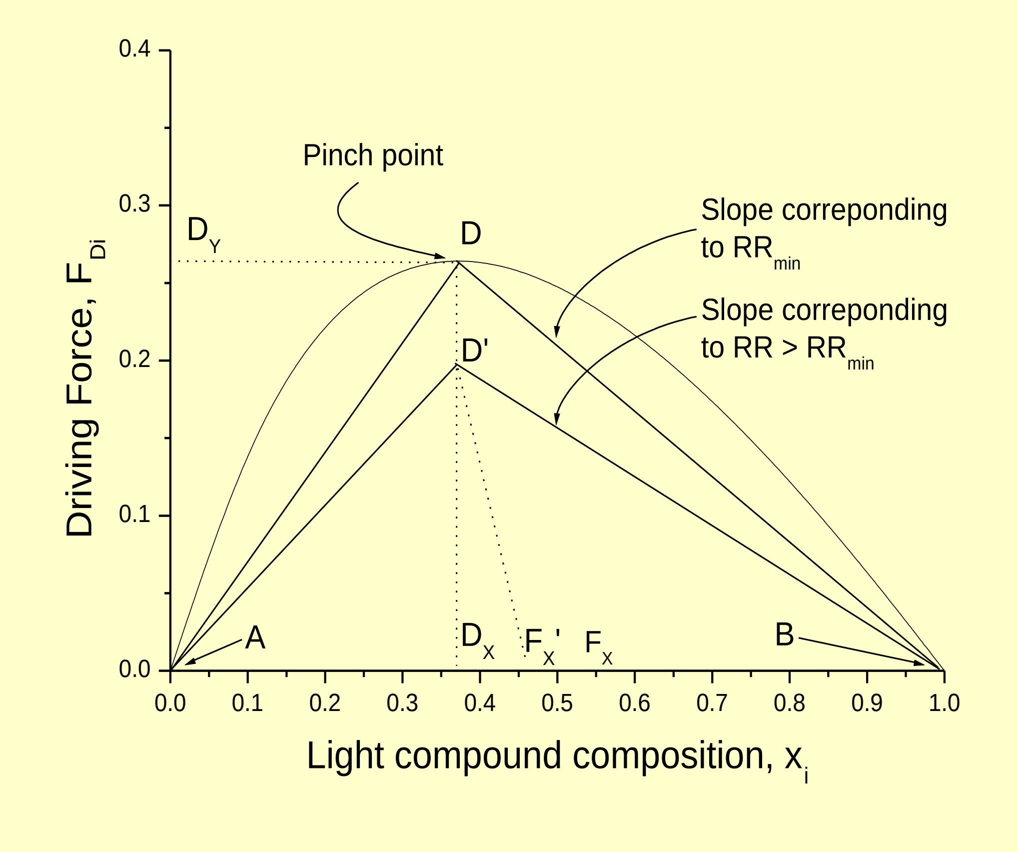
$y = [(V_B+1)/V_B] x - 1/(V_B+1)] x^B$

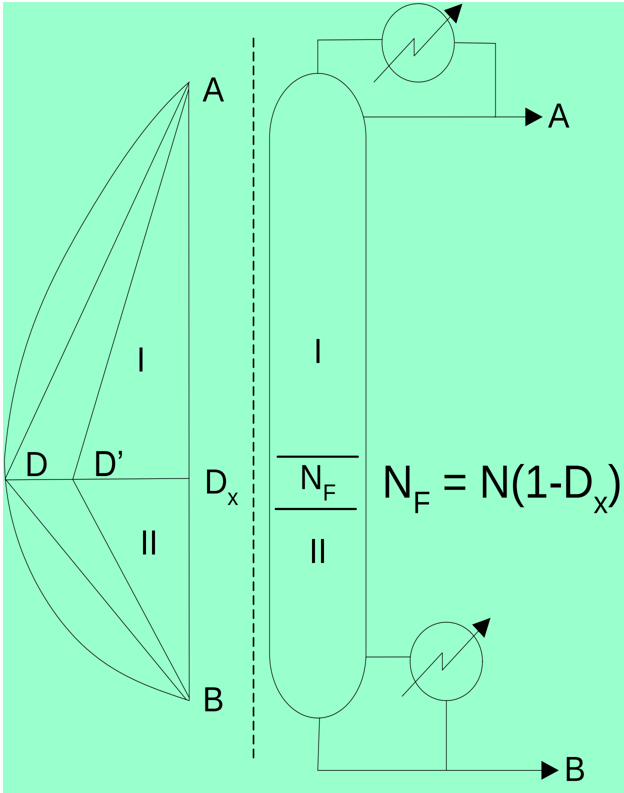


Concept of targeted design

Driving force versus reverse design

Given a mixture to be separated into two products in a distillation column with N trays. What is the optimal (w.r.t the costs of operation) feed plate location and the corresponding reflux ratio for different product purity specifications ?





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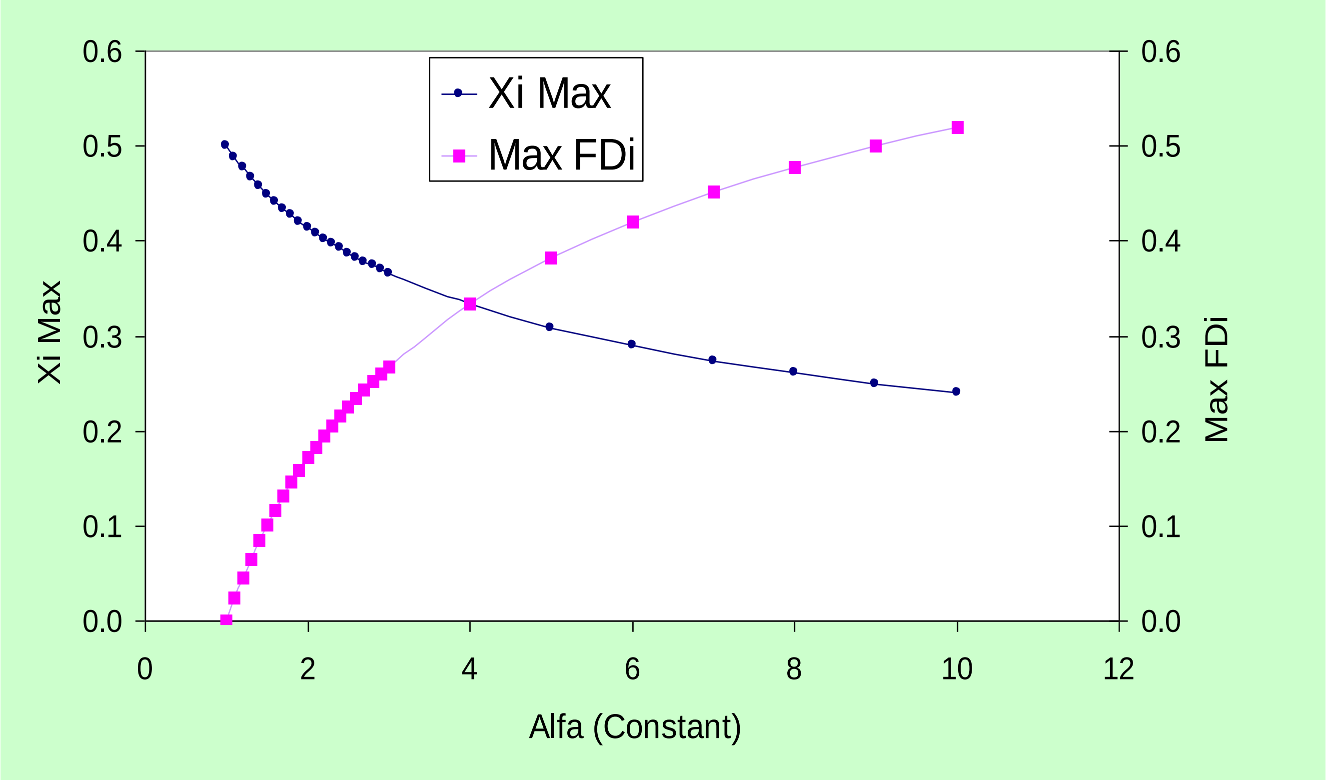
Relation between α_{ij}, D_{ij}(max), number of stages



$$\text{Max } FD_i \equiv d(D_{ij})/dx_i = 0 = d(x_i \, \alpha_{ij} / (1 + x_i (\alpha_{ij} - 1)))/dx_i - 1$$

Every α_{ij} has a corresponding D_{ij}(max) & x_i (max), which has a corresponding NP, NF, xD_i, xB_i

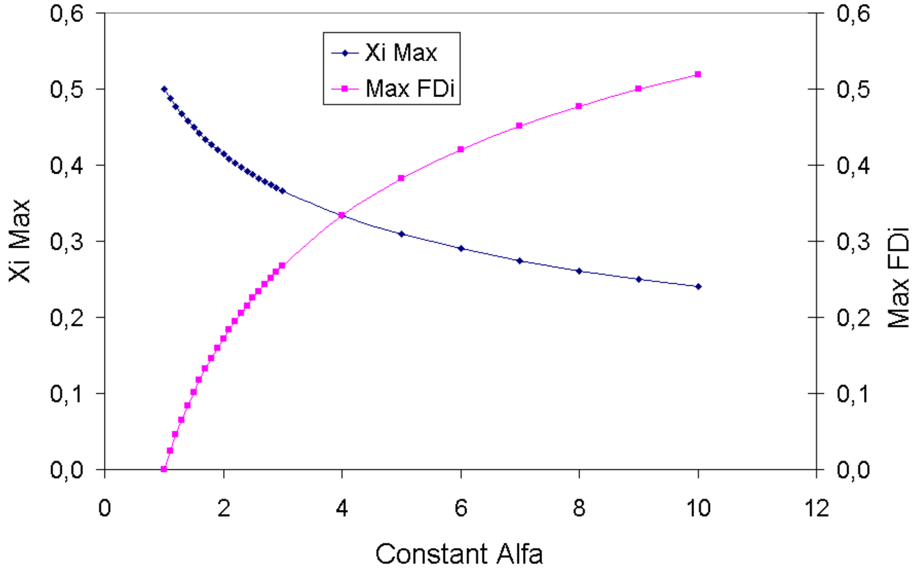
Identification of design targets

$FDi\|_{Max}$	$X_{i, Max}$	Limit X_{Feed}	$X_{LK,Dist}$	$X_{LK,Bot}$	RR_{Min}	C	RR_{Min}*C	N_{ideal}
			0.995	0.005	9.89	1.5	14.83	96
						1.5	14.36	71
						1.5	13.35	54
						1.5	12.33	41
						1.5	11.0	67
						1.5	10.65	50
						1.5	9.96	38
						1.5	8.58	29
						1.5	6.74	44
						1.5	6.52	33
						1.5	6.08	25
						1.5	5.33	19
						1.5	4.41	31
						1.5	4.26	23
						1.5	3.95	18
						1.5	3.44	14
						1.5	3.53	27
						1.5	3.40	20
						1.5	3.13	15

0.065	0.45	$0.2 < X_{F,LK} < 0.8$	0.995
			0.98
			0.95
			0.90
0.101	0.44	$0.2 < X_{F,LK} < 0.8$	0.995
			0.98
			0.95
			0.90
0.146	0.42	$0.2 < X_{F,LK} < 0.8$	0.995
			0.98
			0.95

0.195	0.005	7.33	1.5	11.0	67
	0.02	7.10	1.5	10.65	50
	0.05	6.64	1.5	9.96	38
0.225	0.10	5.72	1.5	8.58	29
	0.005	4.50	1.5	6.74	44
0.268	0.02	4.35	1.5	6.52	33
	0.05	4.05	1.5	6.08	25
0.382	0.10	3.56	1.5	5.33	19
	0.005	2.94	1.5	4.41	31
0.478	0.02	2.84	1.5	4.26	23
	0.05	2.63	1.5	3.95	18
	0.10	2.29	1.5	3.44	14

Simple and fast reverse design method



1. **Given a mixture to be separated by distillation**
2. **Select a pressure and calculate the D_{ij} for all pairs of binary mixtures (ordered w.r.t. boiling point)**
3. **Identify the αij and from it, D_{ij} (max), x_i (max) for specific products xD_i and xB_i**
4. **Use the table of α_{ij}, D_{ij} (max), x_i (max), NP, NF, …. To read out the remaining design variables**

Application example

Given:

Separation binary mixture of butane and i-butane;
P= 5 atm; NP = 60

Solution:

Calculate α_{ij} at 5 atm = 1.33

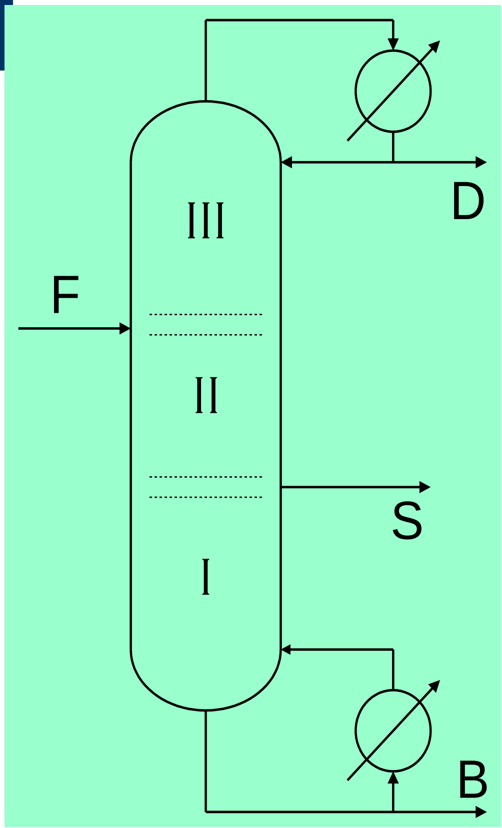
From Figure, obtain D_{ij} (max) = 0.074; x_i (max) = 0.45

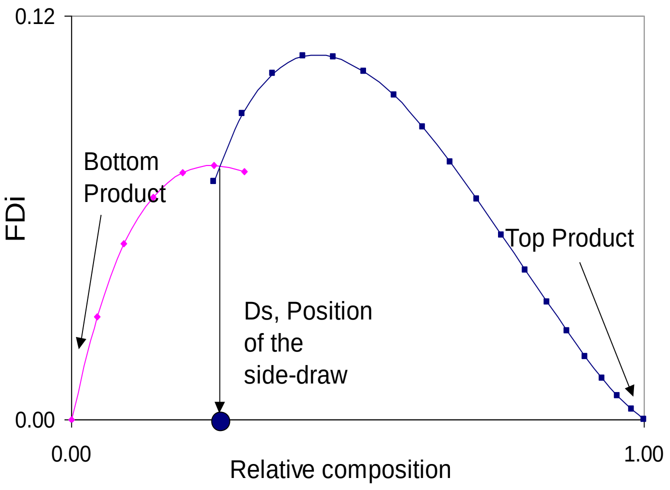
Select $X_{B,HK}$ = 0.995 & $X_{D,LK}$ = 0.995

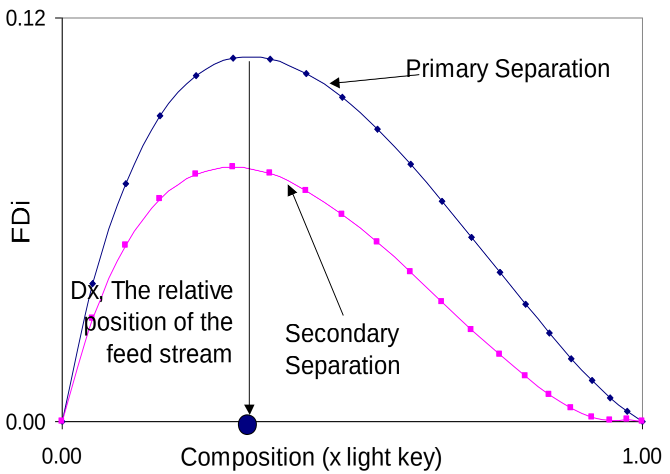
NF = 60 (1- 0.45) = 33

From Table, find RR_{min} = 6.4

Driving force based design – Complex columns

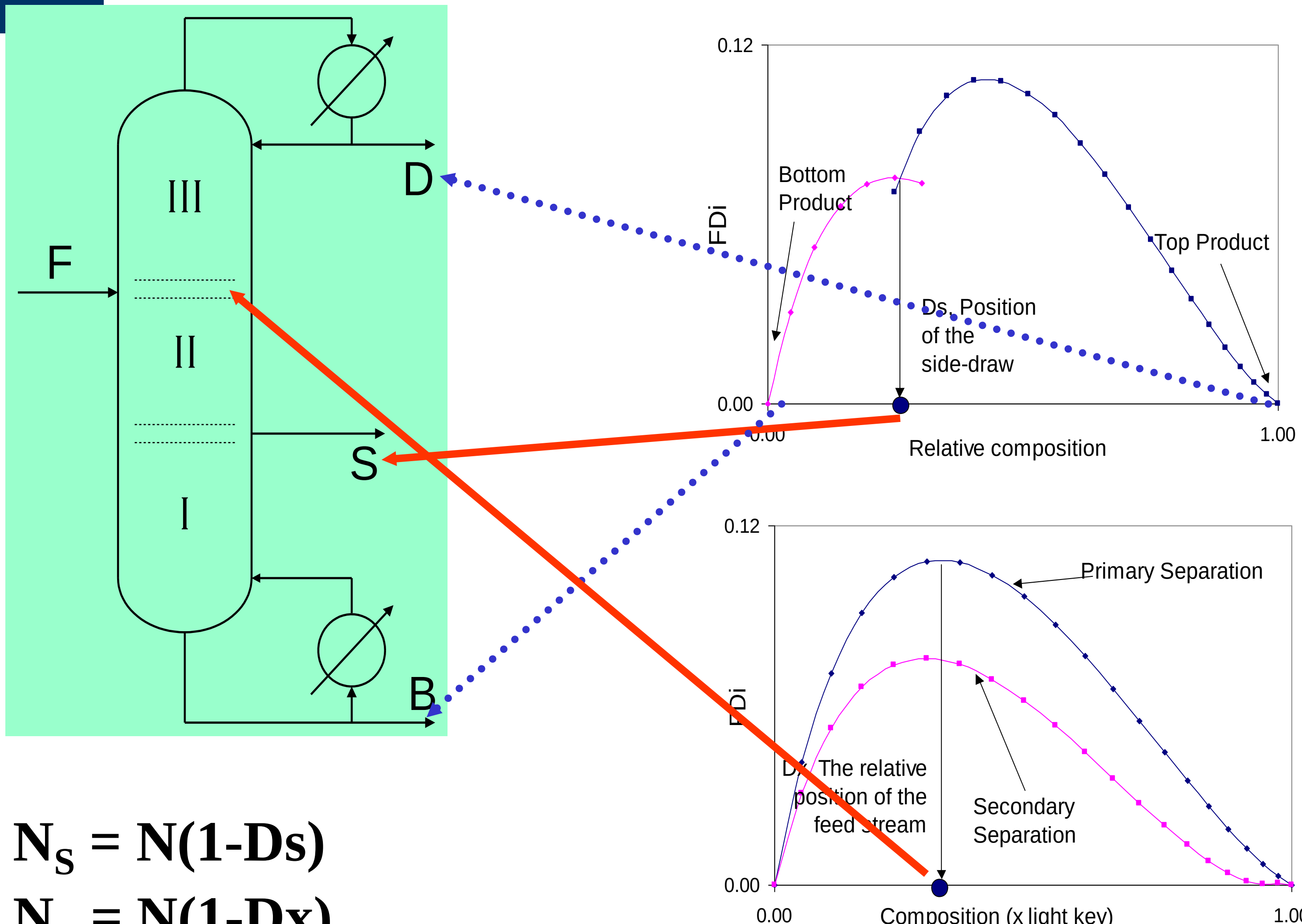






Specify: top and bottom compositions.
Determine: Dx (NF), Ds (NS) and RRmin.

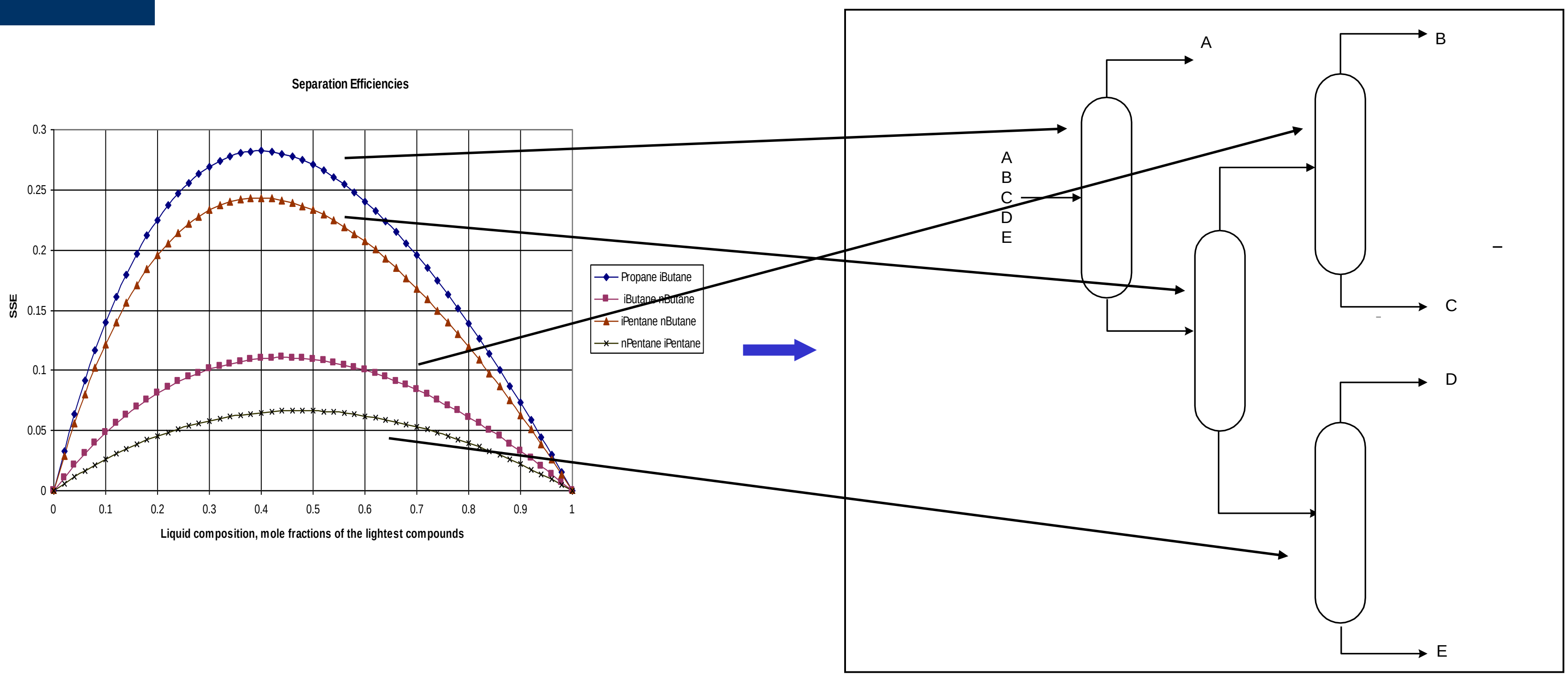
Driving force based design – Complex columns



$$N_S = N(1\text{-}Ds)$$

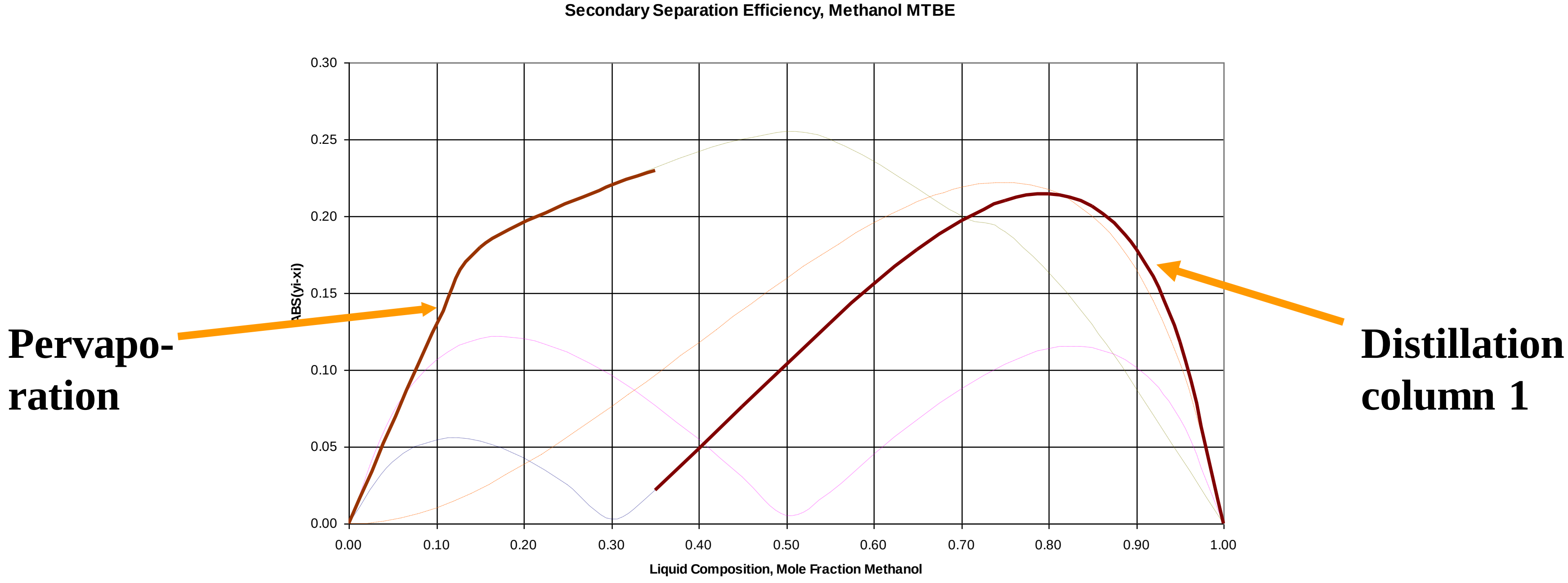
$$N_F = N(1\text{-}Dx)$$

Synthesis & Design of Distillation Trains



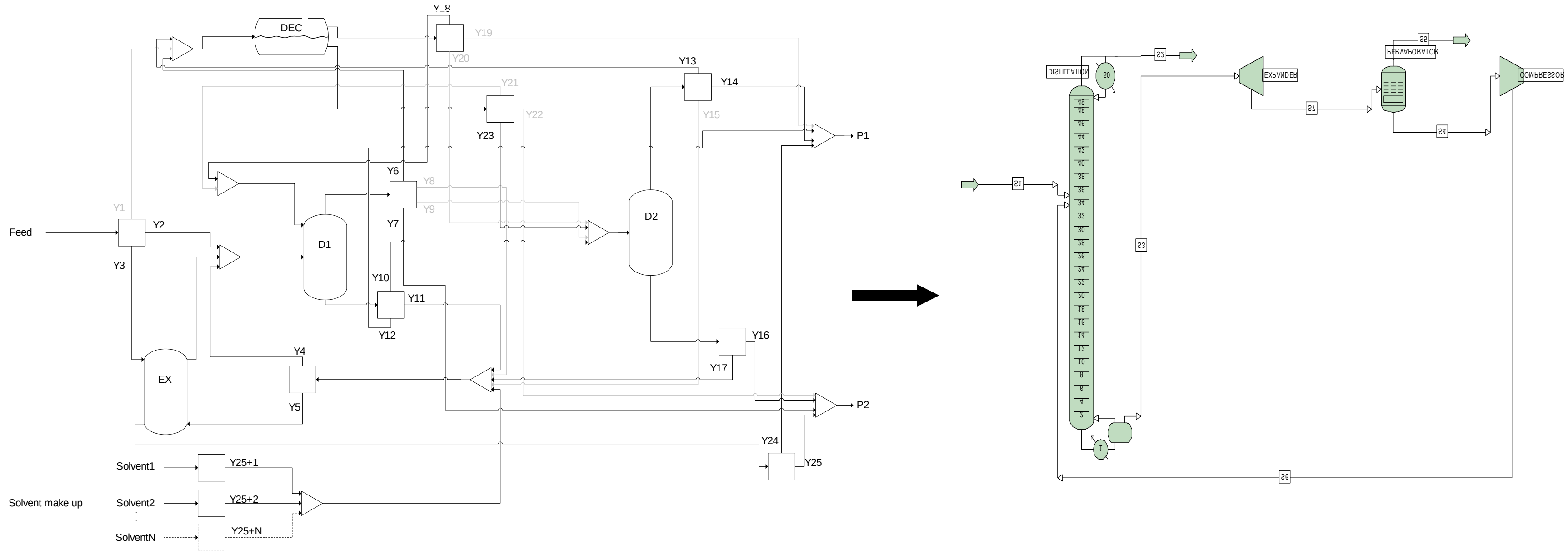
Order the driving force diagrams in terms of $f_{ij}|_{max}$; configure the distillation train in terms of $f_{ij}|_{max}$; design each distillation column in terms intersection on D_yD_x line.

Hybrid Separation: Driving force



Separation by single distillation operation not feasible; hybrid separation schemes (solvent based extraction or distillation plus pervaporation or pressure swing distillation) feasible

Hybrid Separation: Optimal design



Distillation plus pervaporation requires 34.5 % less energy if the product from the first distillation = 62% MTBE. Distillation columns in both schemes optimized in terms of intersection of operating lines

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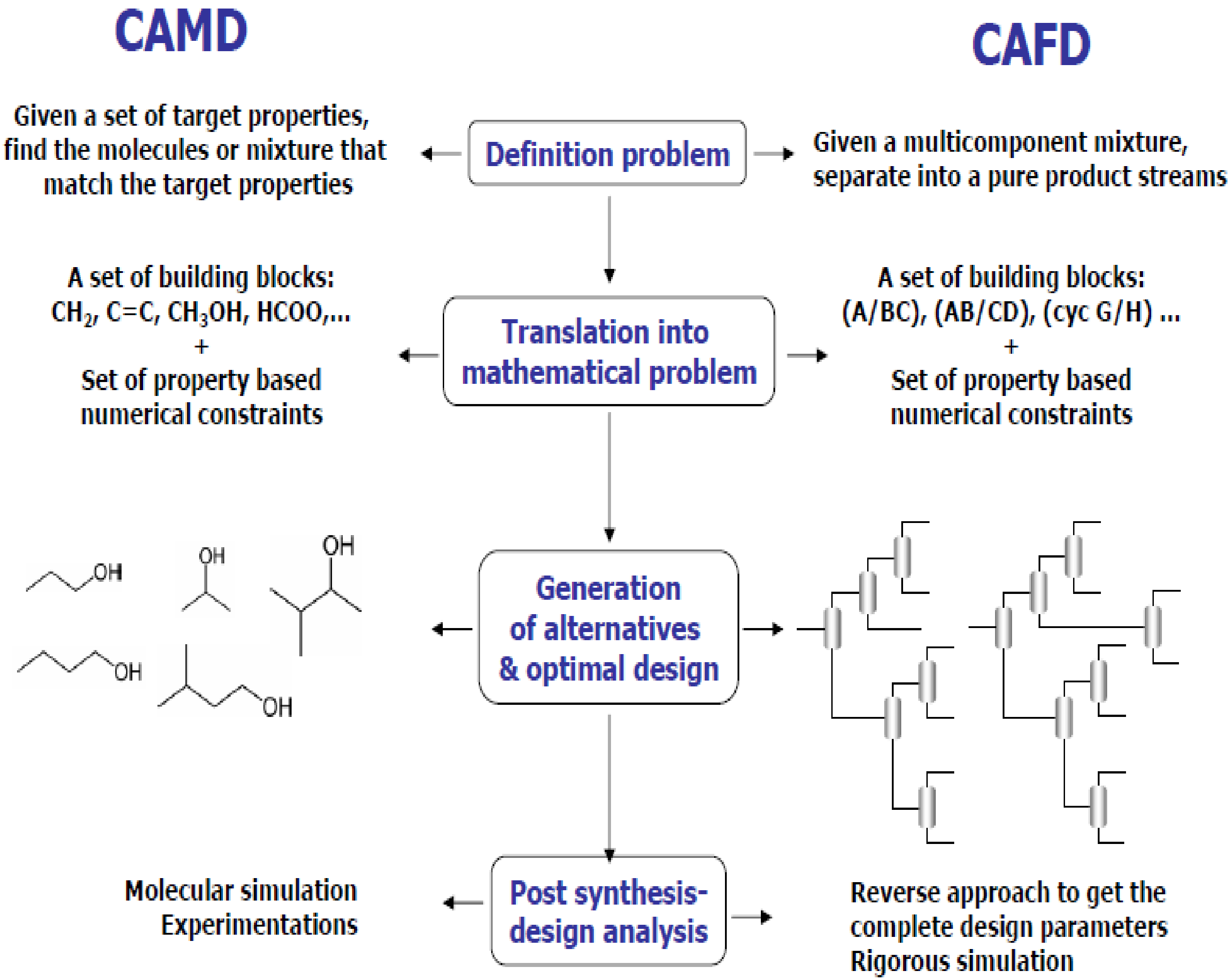
Process groups based flowsheet synthesis



Simultaneous product-process design

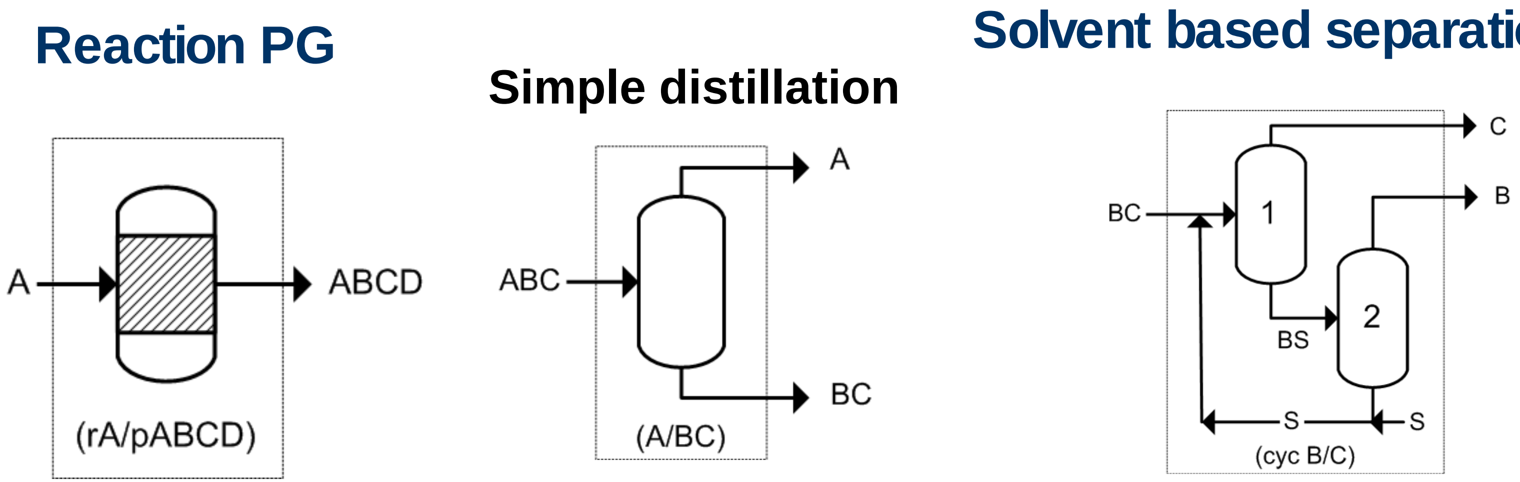
Group contribution approach for synthesis/design of molecules as well as process flowsheets

Atomic-groups are used to design molecules while process-groups are used to design flowsheets

L. d'Anterroches, et al. 2005

Idea of GC Based Process Property Model

We need process groups (PG) to represent the process flowsheet

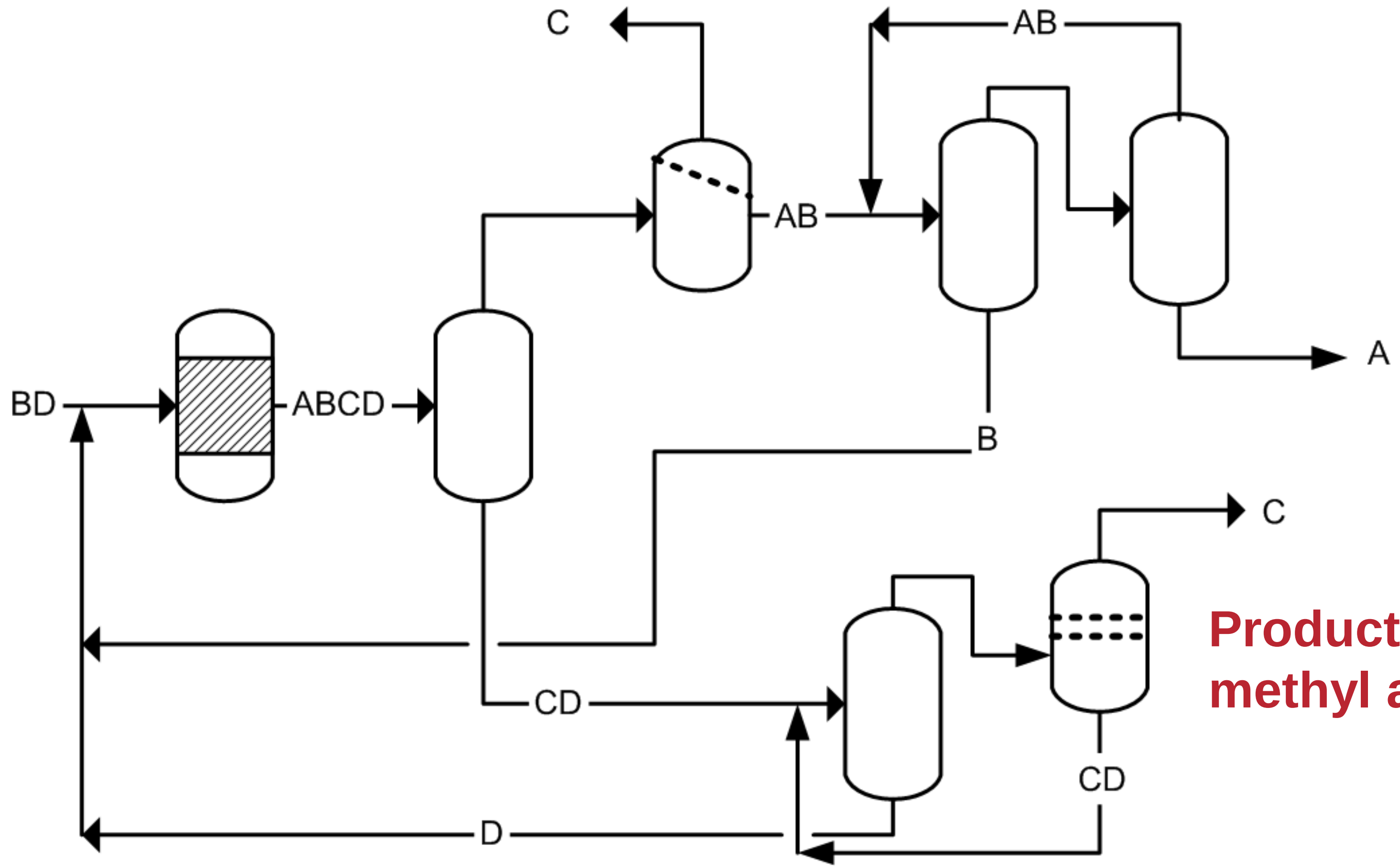


- A process-group ensures a satisfied mass-balance
- Connectivity is component, P and T dependent

L. d'Anterroches, PhD-Thesis, 2005

Idea of GC Based Process Property Model

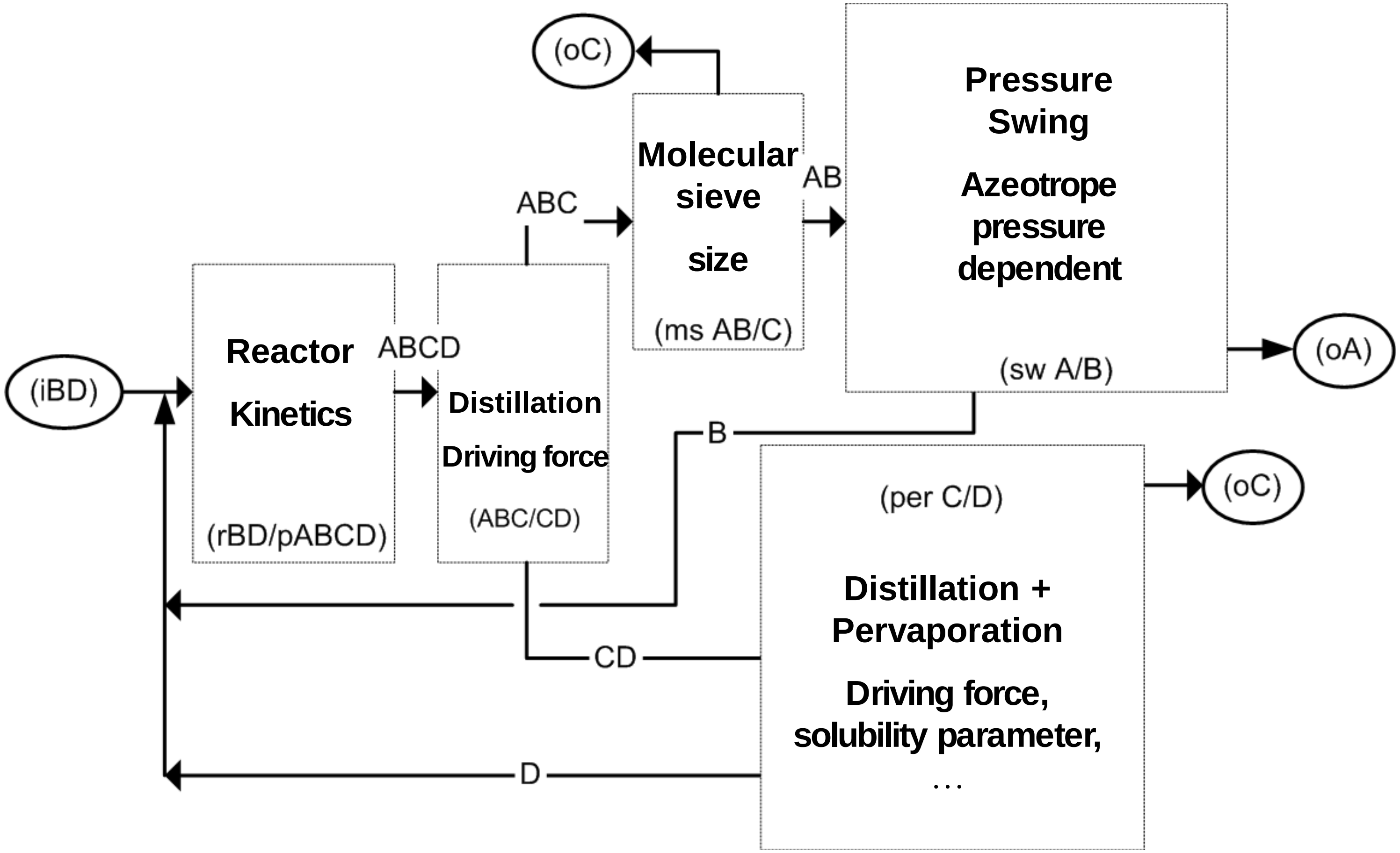
We need PGs to represent the process flowsheet



Production of methyl acetate

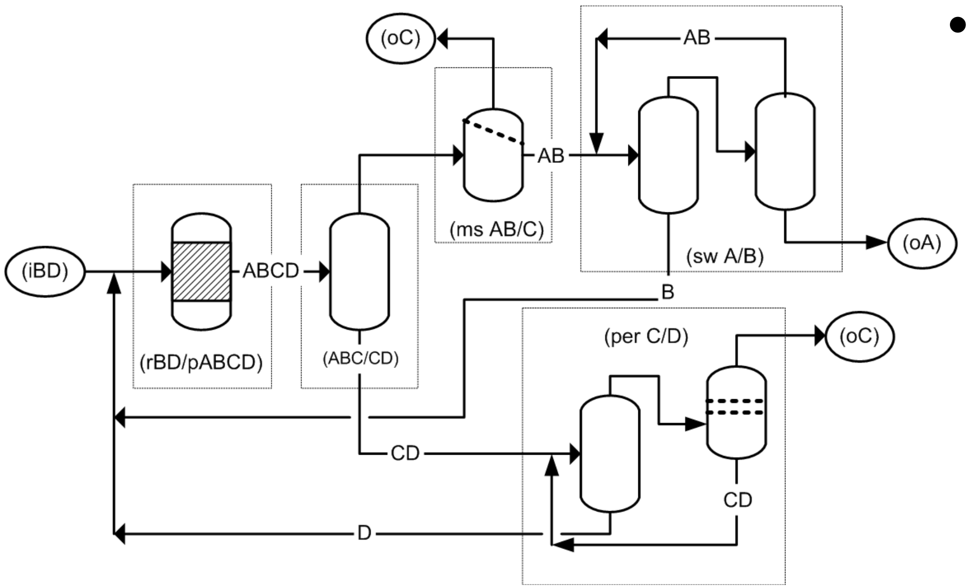
Idea of GC Based Process Property Model

We need PGs to represent the process flowsheet



Idea of GC Based Process Property Model

We need PG parameter tables & GC-based property model!



- **Energy index for distillation column process-group**

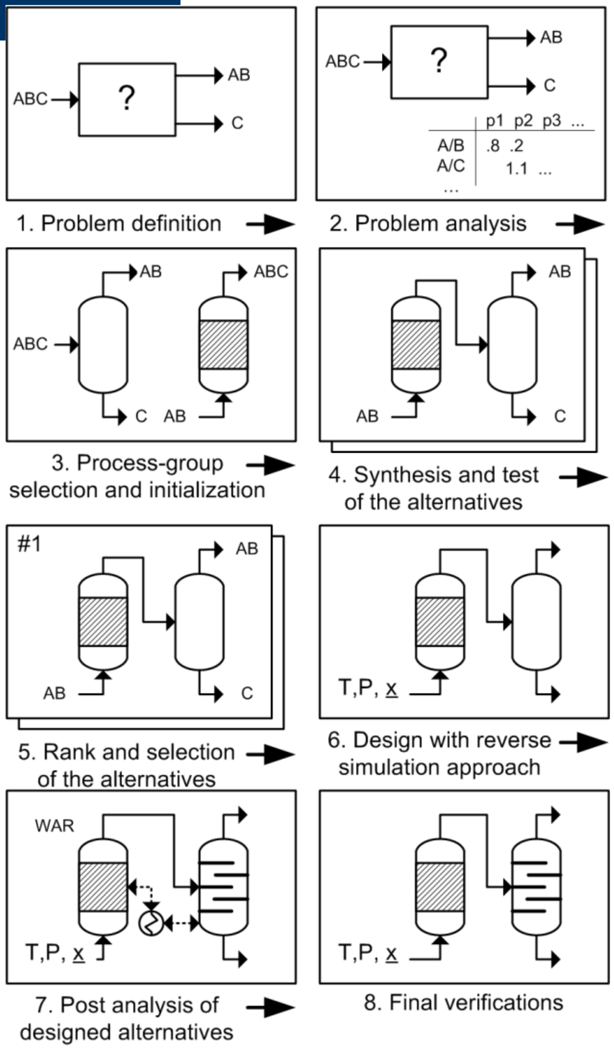
$$E_x = \sum_{k=1}^{n=NG} Q_k = \sum_{k=1}^{n=NG} \left(\frac{1+p_k}{d_{ij}^{k}} \times a_k + A \right)$$

  - p_k : Topology factor
  - a_k : Regressed contribution of PG k
  - d_{ij}^{k} : Driving force between the 2 key components
  - A : Regressed constant

Also, similar models for reactors; solvent-based extraction; membrane-based separation has been developed

L. d'Anterroches, PhD-Thesis, 2005

Simultaneous product-process design



Groups to represent operations

Table 1: List of currently available process-groups (PG)

Operation	Examples of Process-Groups
Distillation column	(A/BC), (ABC/DE)
Solvent based azeotropic distillation	(cycA/B)
Flash separation	(fABC/BCD)
Kinetic-model based reactor	(rABC/nE/pABCD)
Fixed conversion reactor	(rABC/nE/pABCD)
Pressure swing distillation	(swA/B)
Polar molecular sieve based separation	(pmsABC/D)
Molecular sieve based separation	(msABC/D)
Liquid membrane based separation	(lmemABC/D)
Gas membrane based separation	(gmemABC/D)
Crystallization	(crsABC/D)
Adsorption	(abEAB/eF/EABF/EF)

Method to represent flowsheets

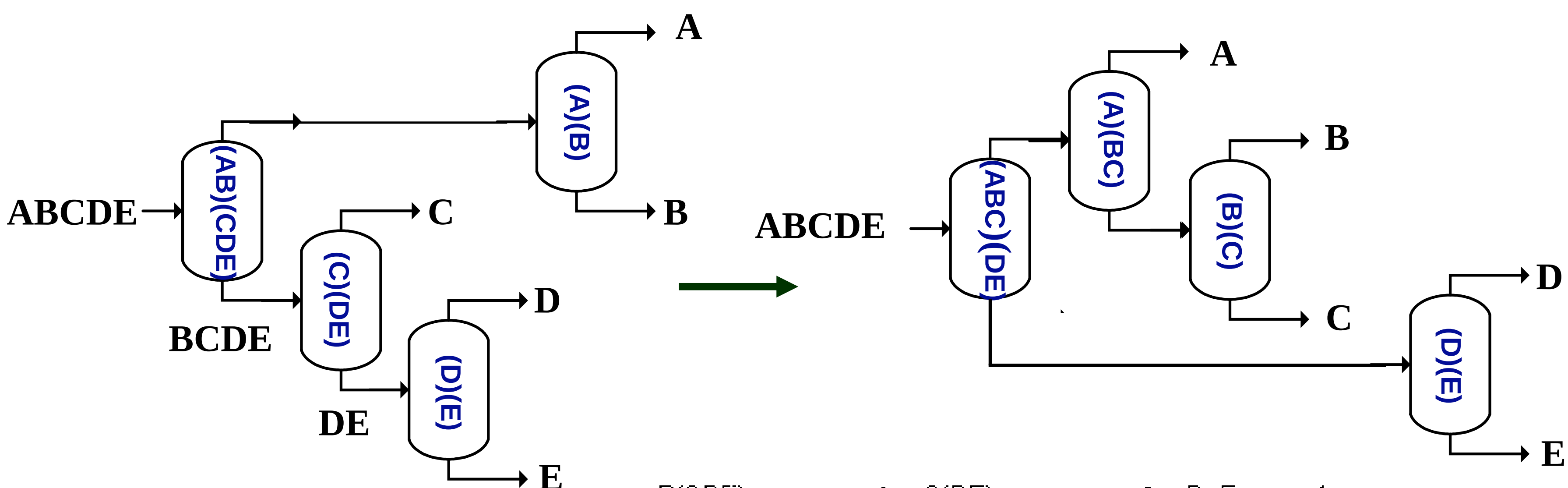
Algorithm for flowsheet structures generation

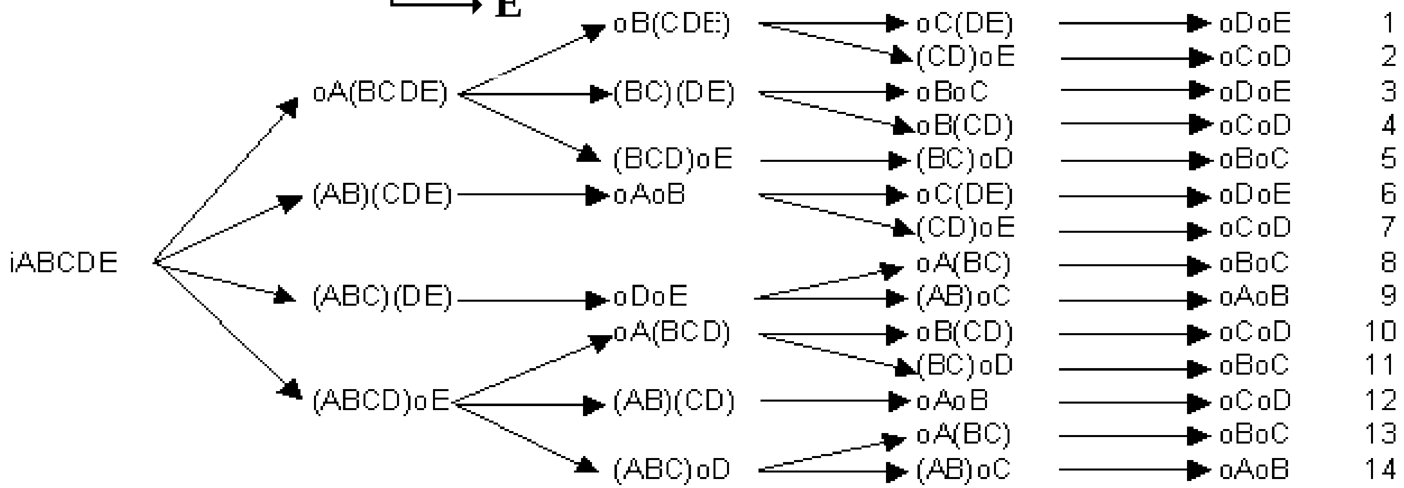
Evaluation of flowsheets: Property model

L. d'Anterroches, PhD-Thesis, 2005

Case Study: Distillation Sequence

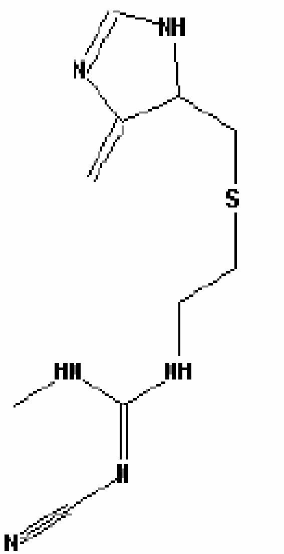
An example from literature



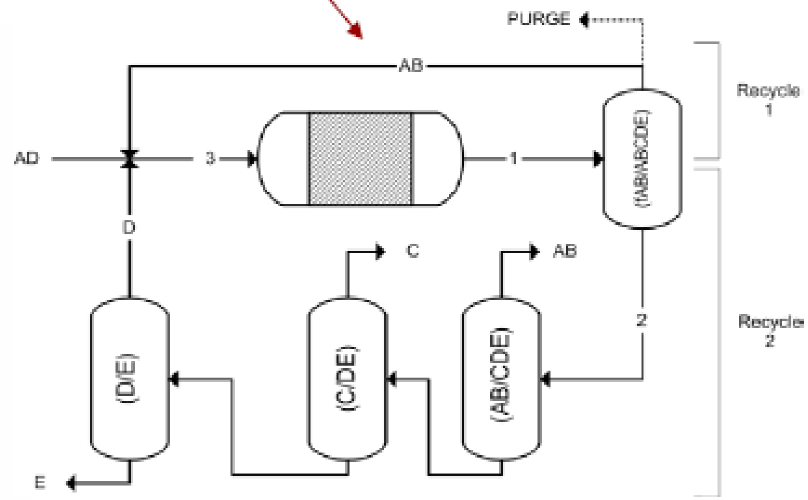


General notation system

Representation of molecule, process flowsheet or operations & reaction networks with SMILES & SFILES



$$
\begin{array}{ll}
(1) & H_2 + l \rightleftharpoons H_2l \\
(2) & H_2l + l \rightleftharpoons Hl + Hl \\
(3) & N_2 + l \rightleftharpoons N_2l \\
(4) & N_2l + l \rightleftharpoons Nl + Nl \\
(5) & N_2l + H_2l \rightleftharpoons N_2H_2l + l \\
(6) & N_2H_2l + l \rightleftharpoons NHl + NHl \\
(7) & Nl + Hl \rightleftharpoons NH_2l + l \\
(8) & NHl + Hl \rightleftharpoons H_2l \\
(9) & NHl + H2l \rightleftharpoons NH_3l + l \\
(10) & NH_2l + Hl \rightleftharpoons NH_3l + l \\
(11) & NH_3l \rightleftharpoons NH_3 + l
\end{array}
$$



N#CN=C(NC)NCCSCC1NC=NC1=C

SMILES & SFILES

(H2)(1)<1(H2l)2(5)4<3(1)>1<6<5[(3)[(N2l)3]<(n2)](6)[NH1)(9)5<2(NH3l)(11)6(NH3)]<(N2H2l)<4

(iAD)(rAD/pABCDE)<1<2(fAB/ABCDE)1[(AB/CDE)(oAB)](C/DE)[oC)](D/E)2(oE)

Summary: Targeted Process Design

- A systematic methodology for targeted process design matching the needs of specific products has been presented together with examples.
- Use of the concept for design of processes using solvents, processes using the maximum available driving force, & for generating and evaluating process flowsheets (CAFD) has been highlighted.