FACULTY OF SCIENCE AND TECHNOLOGY
SUSTAINABLE PROCESS TECHNOLOGY

UNIVERSITY OF TWENTE.

DESIGN OF AZEOTROPIC AND EXTRACTIVE DIVIDING-WALL COLUMNS BY MINLP METHODS

WORKSHOP ON DIVIDED-WALL DISTILLATION IN TRONDHEIM, OCTOBER 5, 2023

IN THIS PRESENTATION:

MINLP OPTIMIZATION OF DWC COLUMNS

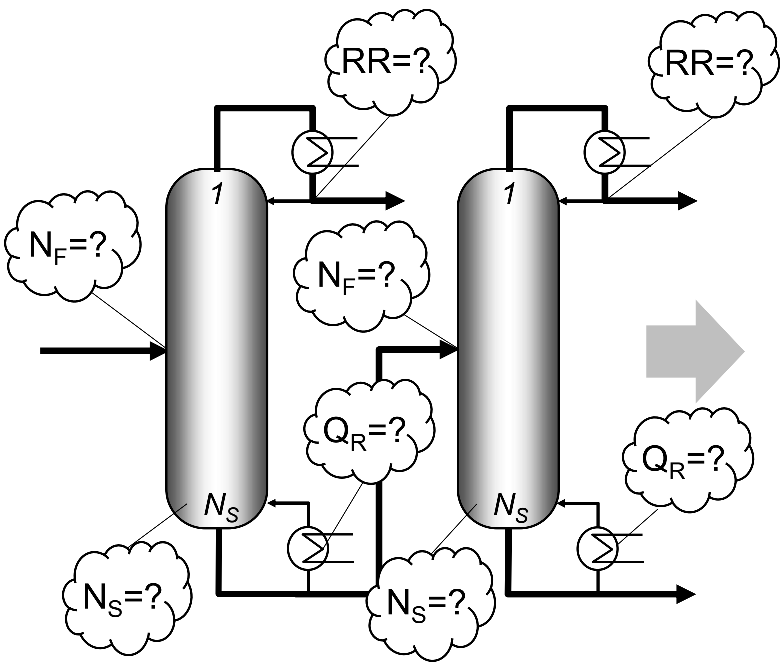
THERMODYNAMIC EFFICIENCY

EXTRACTIVE DIVIDING-WALL COLUMNS

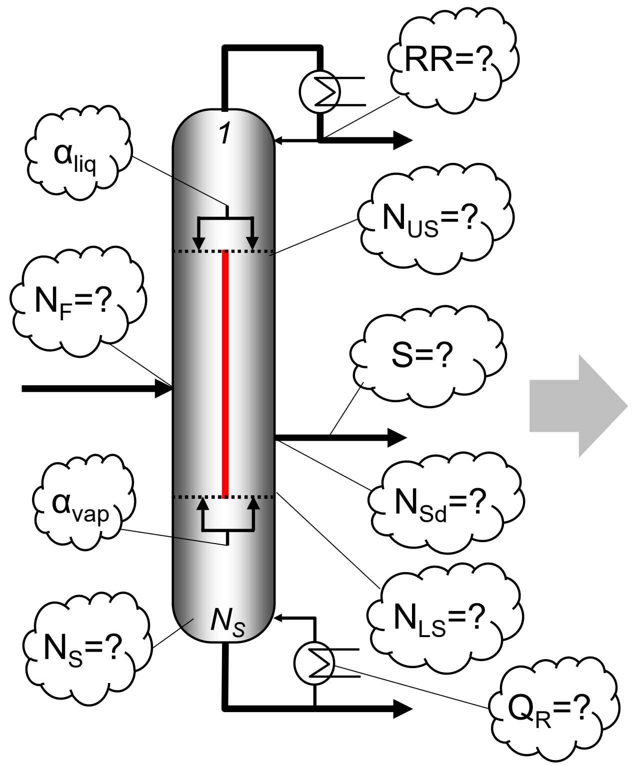
AZEOTROPIC DIVIDING-WALL COLUMNS

UNIVERSITY OF TWENTE.

For a DWC, many degrees of freedom must be fixed…



of Operational DOF: 4
of Design DOF: 4

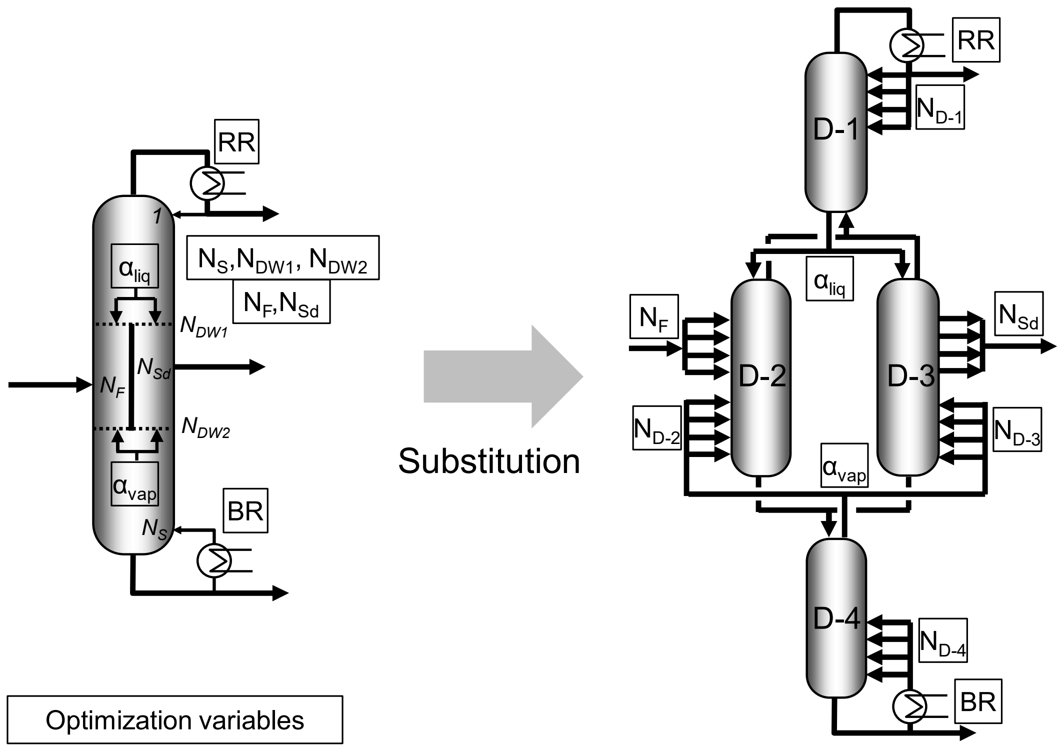


of Operational DOF: 5
of Design DOF: 5

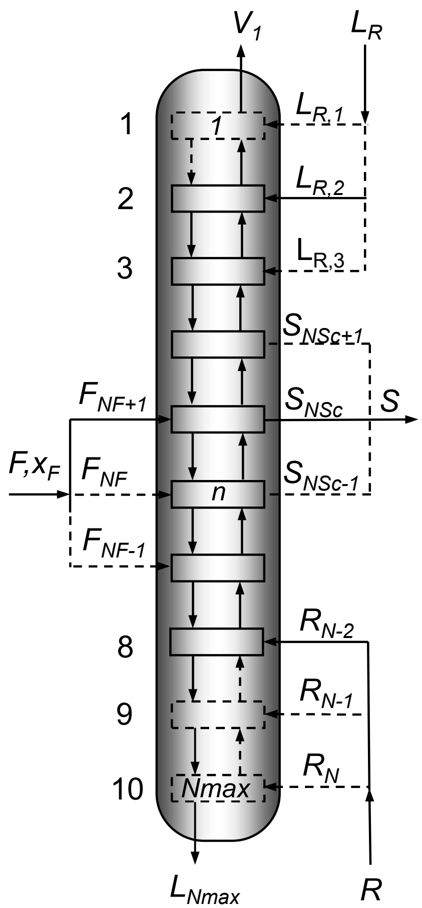
[Bayer MaterialScience: Neue TDI-Anlage in Dormagen eröffnet (plasticker.de)]

… a suitable model structure must be chosen …

- Thermodynamic equivalent representation of DWC by 4-section column model



… the model equations must be written …



- MESH equations for $n = 1 \ldots Nmax$ stages:

$$V_{n+1}x_{Vn+1} + L_{n-1}x_{Ln-1} + F_n x_{Fn} + L_{Rn}x_{LRn} + R_n x_{Rn} = V_n x_{Vn} + L_n x_{Ln} + S_n x_{Sn}$$

$$x_{Vn} = K_n x_{Ln}$$

$$\sum x_{Vn} = 1 \quad \text{and} \quad \sum x_{Ln} = 1$$

$$V_{n+1}h_{Vn+1} + L_{n-1}h_{Ln-1} + F_n h_{Fn} + L_{Rn}h_{LRn} + R_n h_{Rn} = V_n h_{Vn} + L_n h_{Ln} + S_n h_{Sn}$$

- Mixed-integer and pure integer constraints:

$$F_n \le F \cdot y_{F,n} \quad \text{and} \quad \sum y_{F,n} = 1$$

$$L_{R,n} \le L_R \cdot y_{R,n} \quad \text{and} \quad \sum y_{LR,n} = 1$$

$$R_n \le R \cdot y_{R,n} \quad \text{and} \quad \sum y_{R,n} = 1$$

$$S_n \le S \cdot y_{R,n} \quad \text{and} \quad \sum y_{S,n} = 1$$

- Auxiliary model equations:

$$N_S = \sum y_{R,n} \cdot n - \sum y_{LR,n} \cdot n + 1$$ + Pressure Drop Correlations

… the optimization problem must be set up

- Constraints:
  - Equality constraints (model equations) **h**
  - Inequality constraints (design specs) **g**
  - Mixed-integer constraints **x** - **My** <= **0**
  - Pure integer constraints **yE** = **e**
- Optimization variables:
  - Continuous variables **d**
  - Binary (integer) variables **y**
- Objective function ***f(x,y)***:
  - ***f(x,y)*** = *Total Annual Costs* (***TAC***)
  - ***TAC*** = C_{op} + 5 * C_{eqp} * 0.2

$$Z = \min_{\mathbf{d},\mathbf{y}} f(\mathbf{x},\mathbf{y})$$

subject to

$$\mathbf{h}(\mathbf{x},\mathbf{y}) = \mathbf{0}$$

$$\mathbf{g}(\mathbf{x},\mathbf{y}) \leq \mathbf{0}$$

$$\mathbf{x} - \mathbf{M}\mathbf{y} \leq \mathbf{0}$$

$$\mathbf{y}\mathbf{E} = \mathbf{e}$$

$$\mathbf{x} \in R^{nx}, \mathbf{y} \in \{0,1\}^{ny}$$

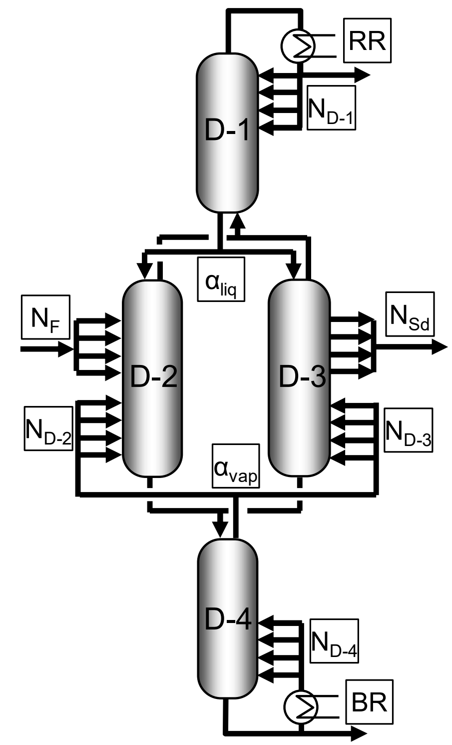
Remark:
d is the vector of optimization variables and a subset of all cont. **x**

… with special attention to DWC equipment costs …

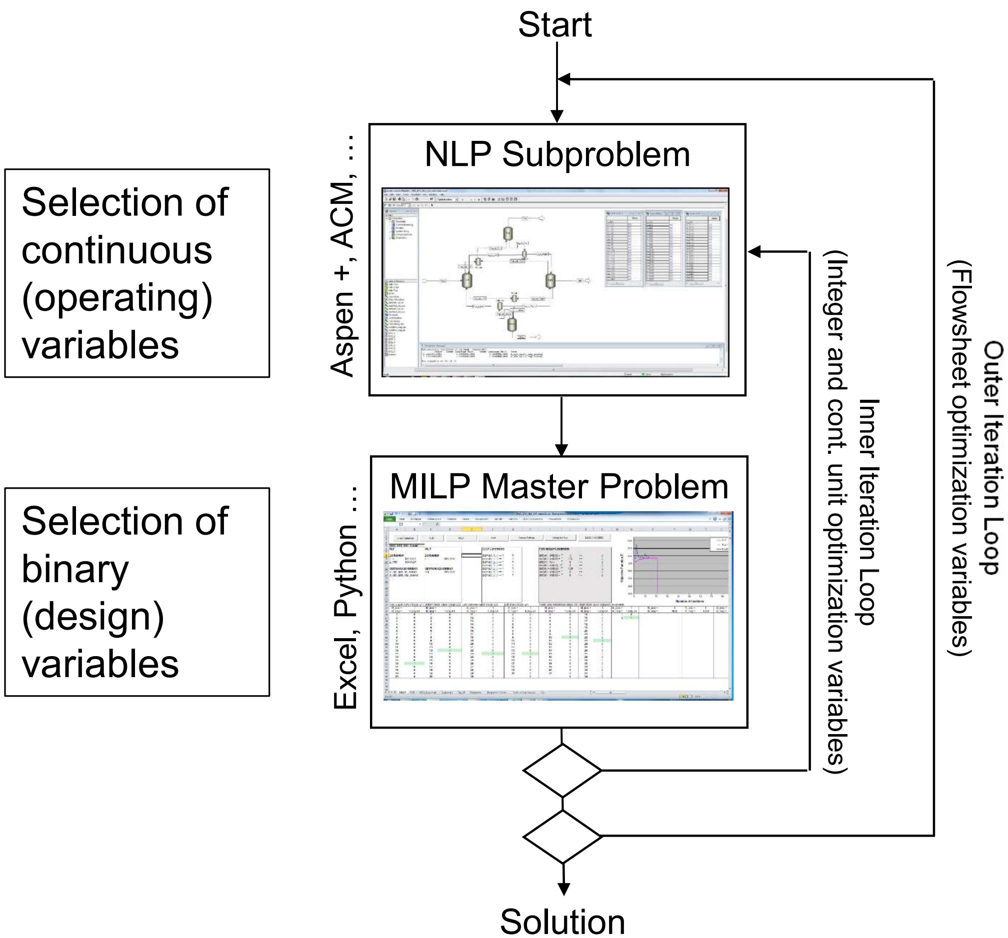
- Equipment costs of DWC consists of 4 pressure vessels with internals plus condenser and reboiler:

$$C_{eqp} = C_{eqp,D\text{-}1} + C_{eqp,D\text{-}2} + C_{eqp,D\text{-}3} + C_{eqp,D\text{-}4} + C_{eqp,Cond} + C_{eqp,Reb}$$

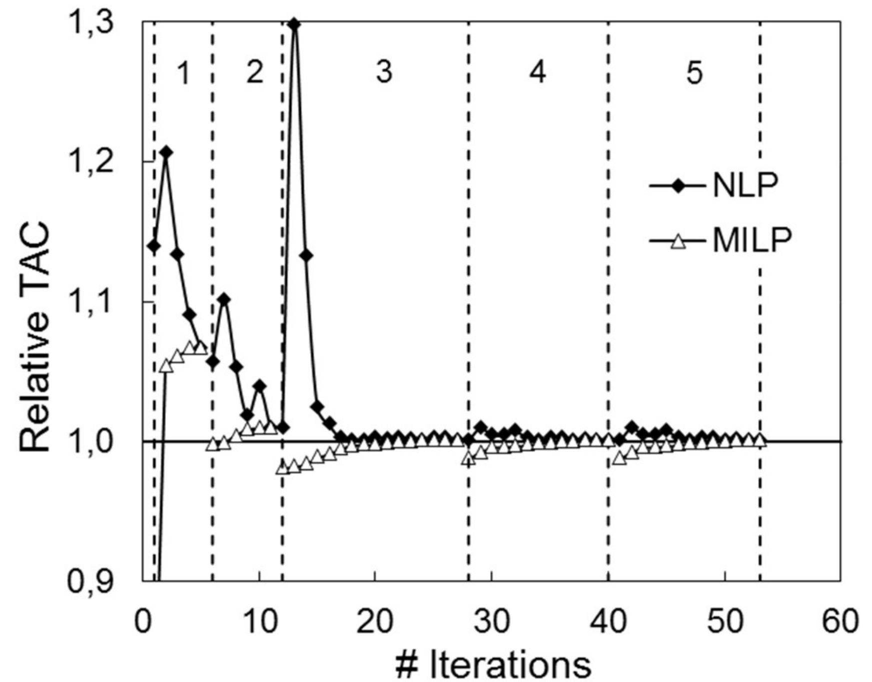
- Overestimation of DWC equipment costs, but consistent with model structure, easy to implement, and for comparative studies (probably) sufficient



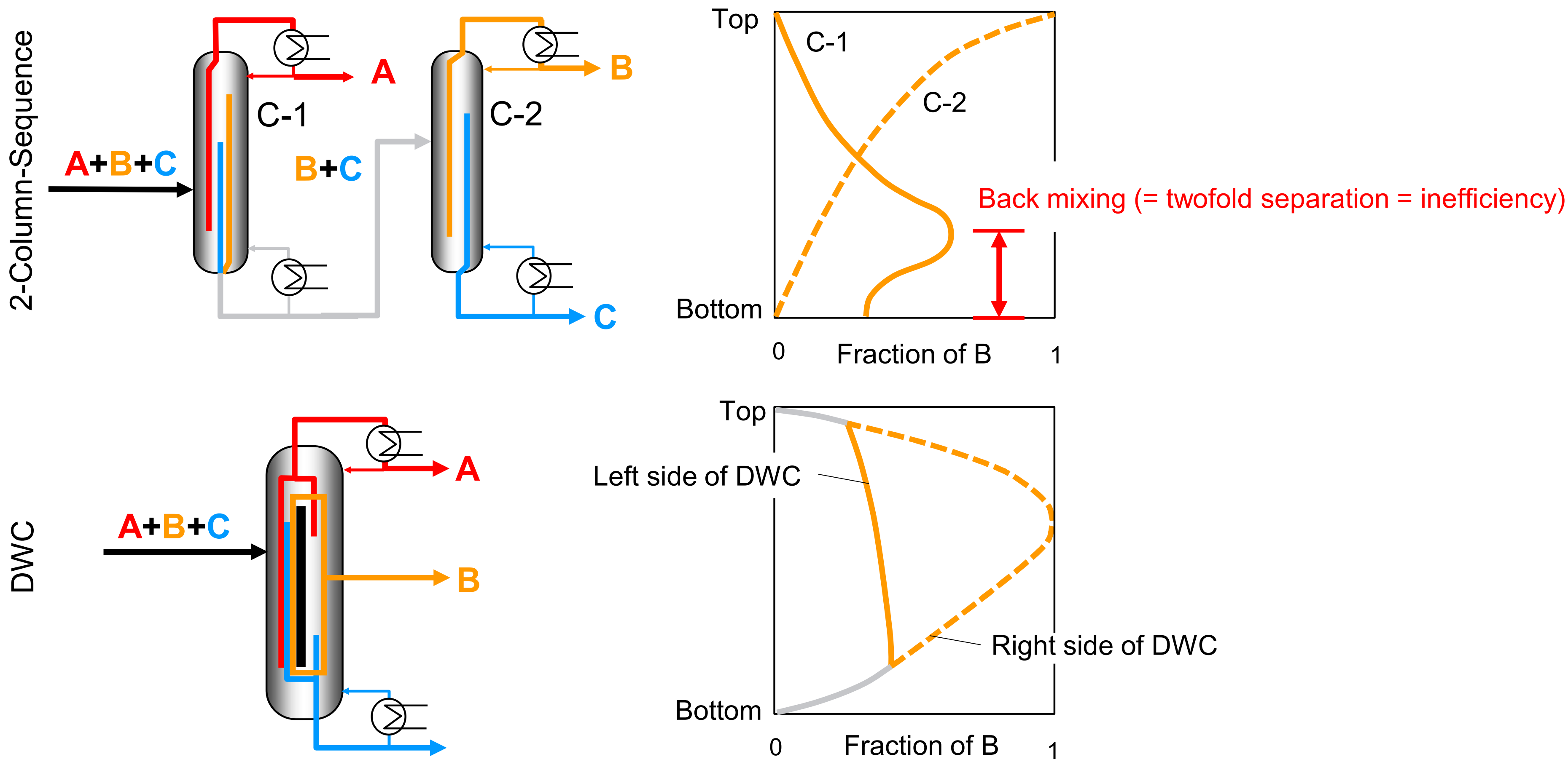
… and finally, the problem must be solved.



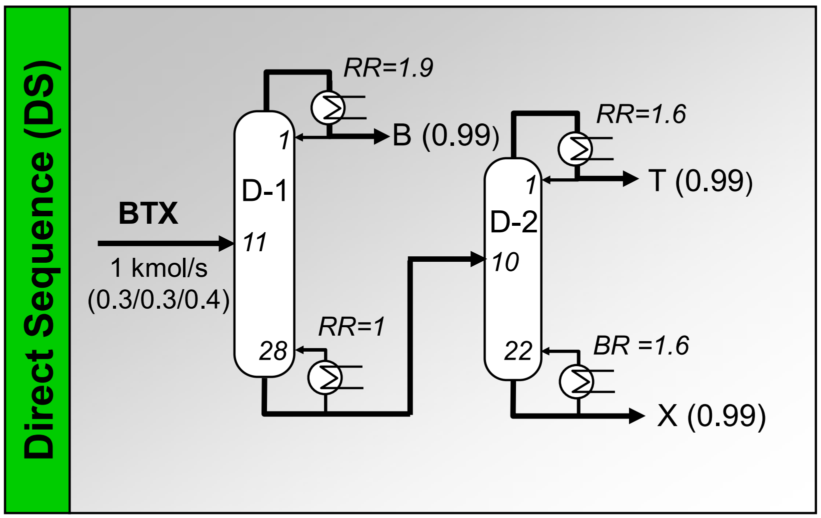
Franke. M.B. (2019), Comp. Chem. Eng.:
Modified Generalized Benders Decomposition (mGBD)

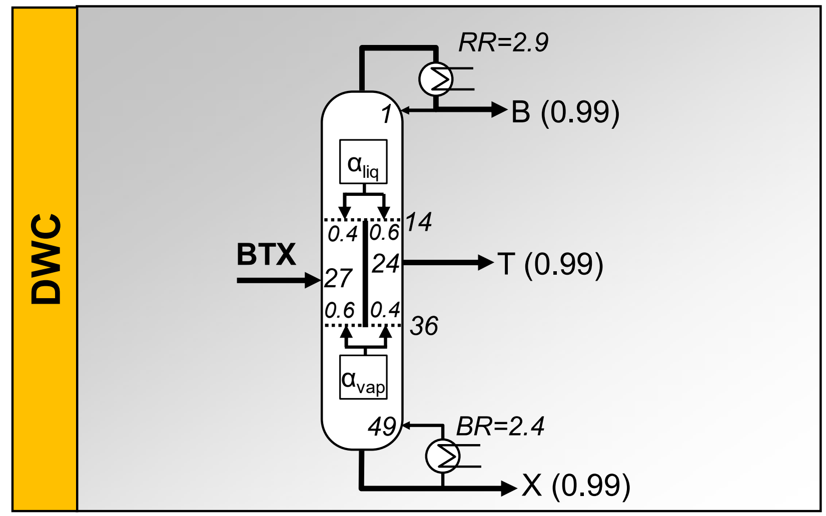


Thermodynamic Efficiency of DWC



MINLP Results for a Very Prominent Example



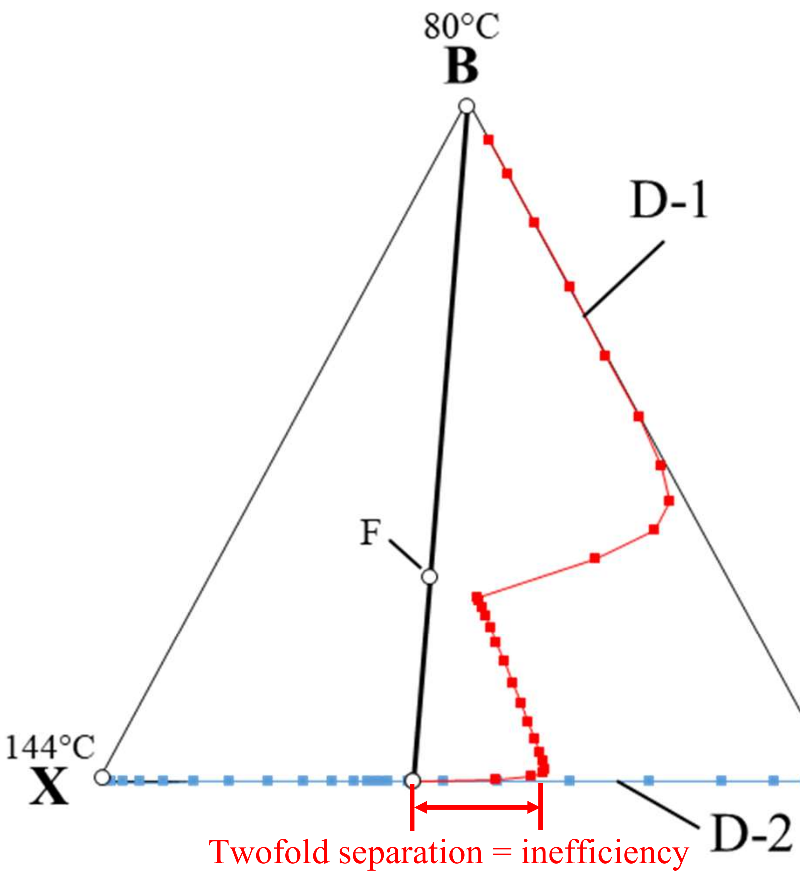


	D-1	D-2	DS	DWC	Sav.
Q / MW	24.9	24.6	49.5	35.6	28%
No. of stages	28	22	50	49	2%
Rel. OpEx	0.37	0.36	0.73	0.53	27%
Rel. CapEx	0.13	0.14	0.27	0.22	19%
Rel. TAC	0.5	0.5	1	0.75	25%

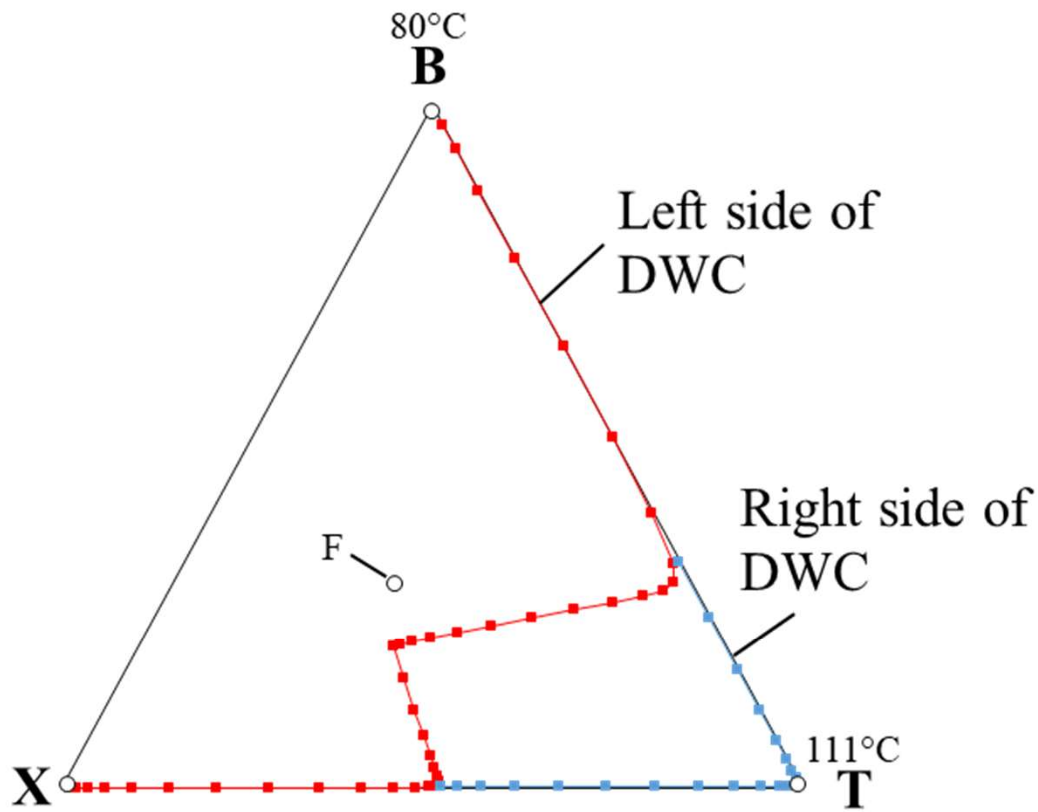
Ling, Luyben (2009), Ind. Eng. Chem. Res.
Franke (2017), Chem. Ing. Techn.

Thermodynamic Efficiency of DWC

Conventional Sequence

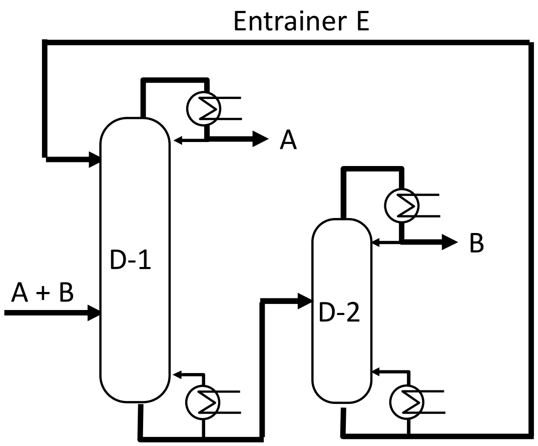


Dividing-Wall Column (DWC)

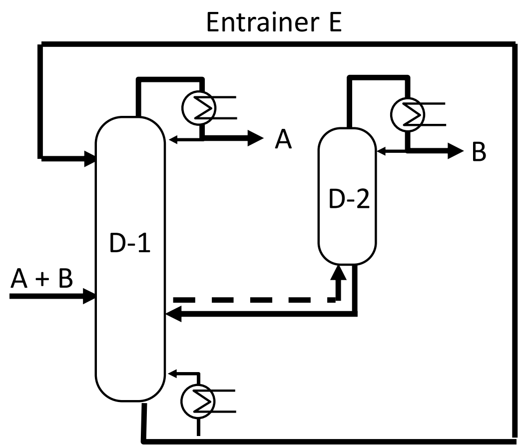


Derivation of Extractive Dividing-Wall Column

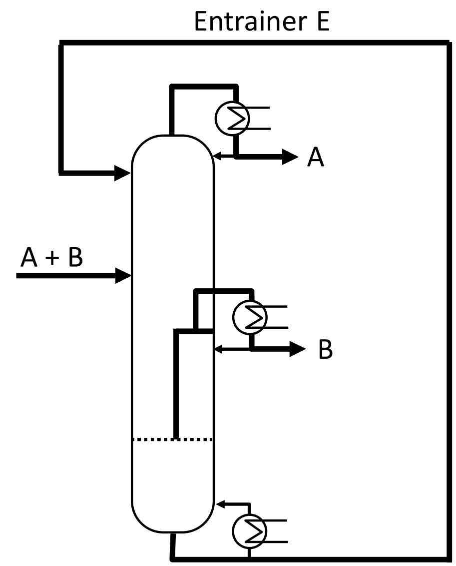
Extractive Distillation



Extractive Distillation w/ Side Rectifier

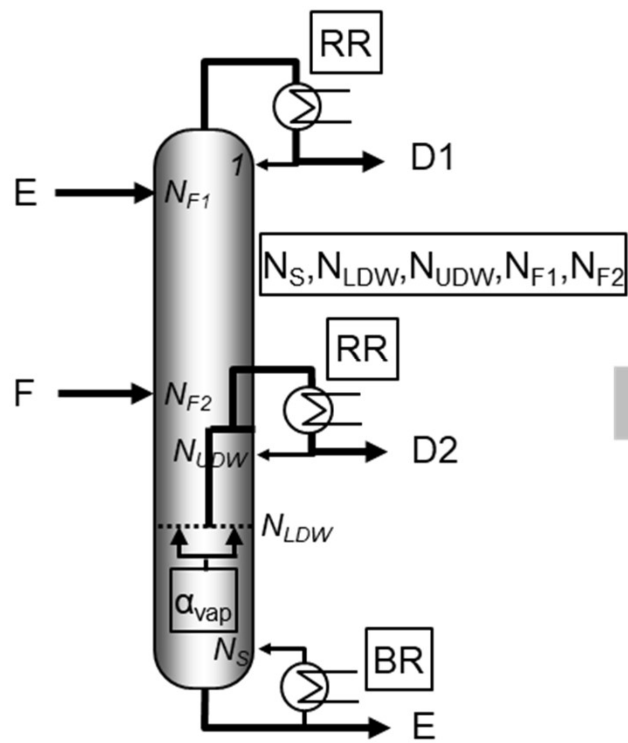


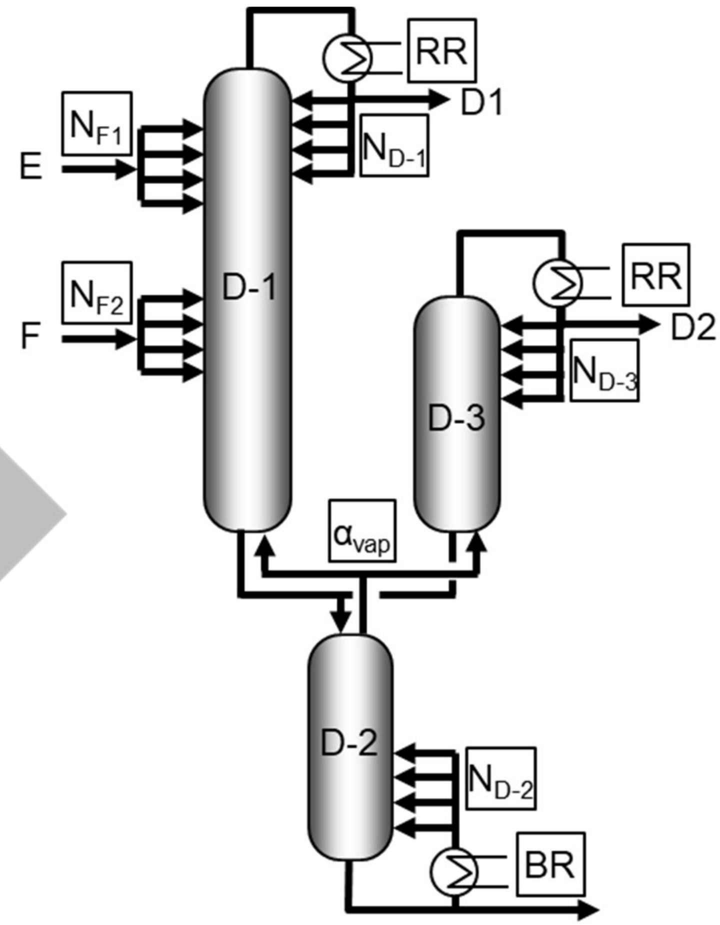
Extractive Dividing-Wall Column (Ledge Wall)



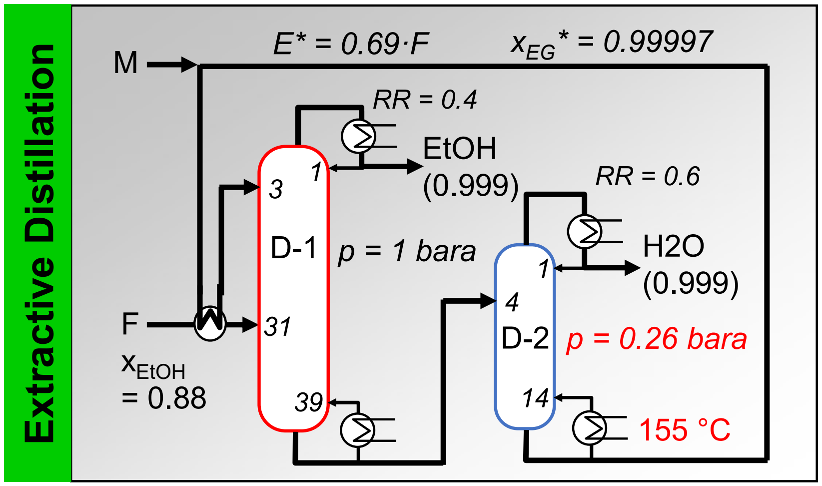
Kiss, Suszwala (2015): Enhanced bioethanol dehydration by extractive and azeotropic distillation in DWC
Czarnecki et al. (2023): Extractive Dividing Wall Column for Separating Azeotropic Systems: A Review

Extractive DWC: 3-Column Substitution Model



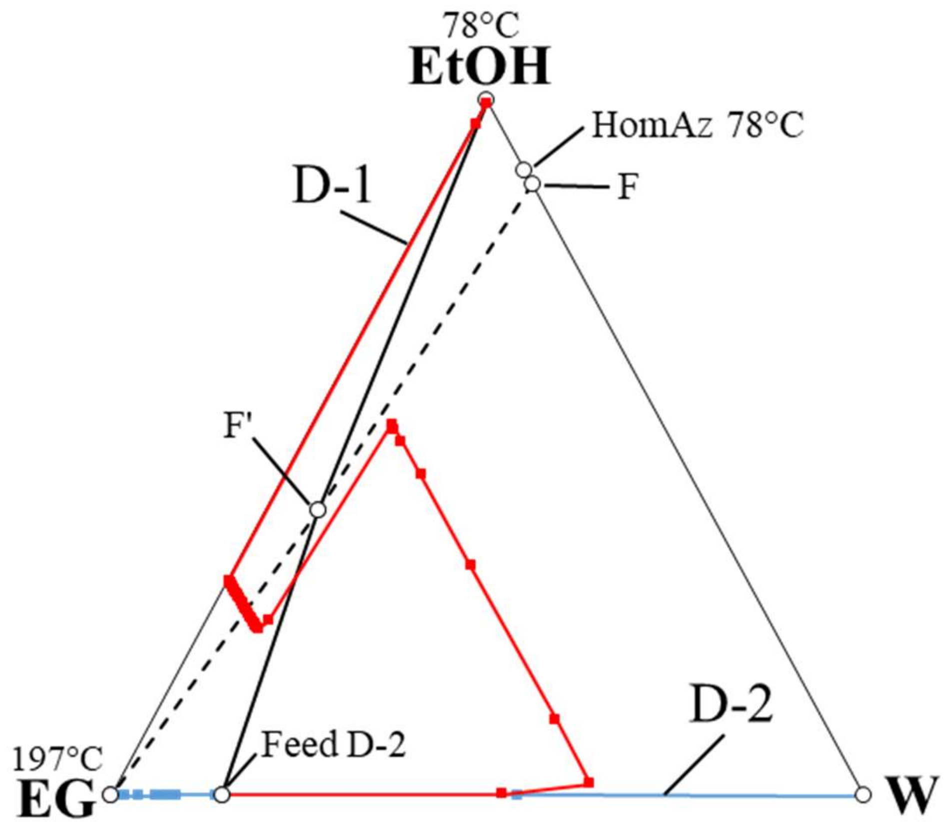


Extractive Distillation in a Dividing-Wall Column (EDWC)

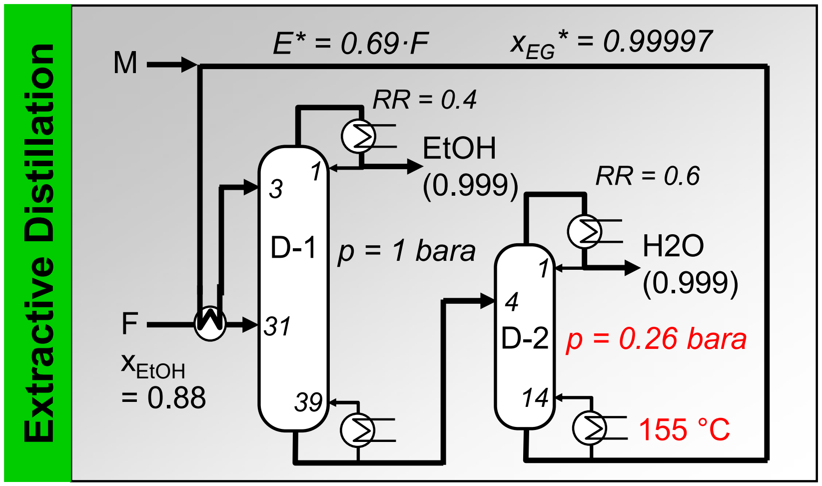


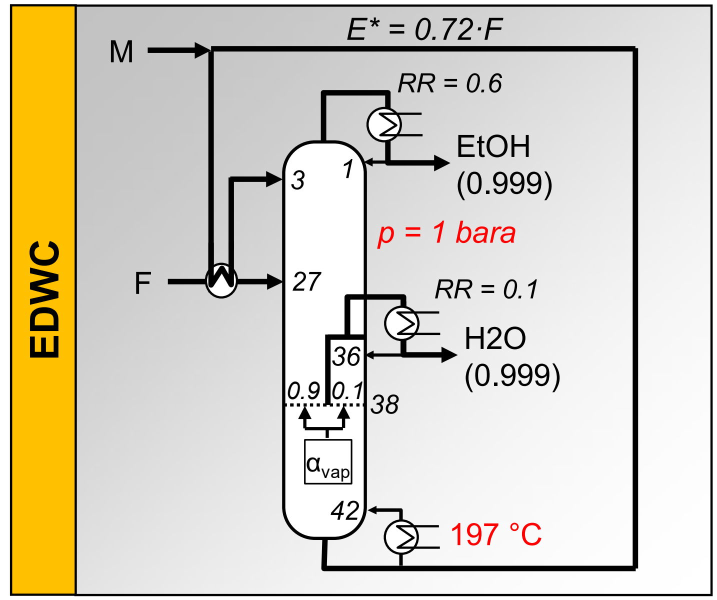
*Flowsheet optimization variables

	D-1	D-2	ED
Q / kJ/kg EtOH	1401	188	1589
No. of stages	39	14	53
Rel. OpEx	0.71	0.1	0.81
Rel. CapEx	0.16	0.03	0.19
Relative TAC	0.87	0.13	1



Extractive Distillation in a Dividing-Wall Column (EDWC)

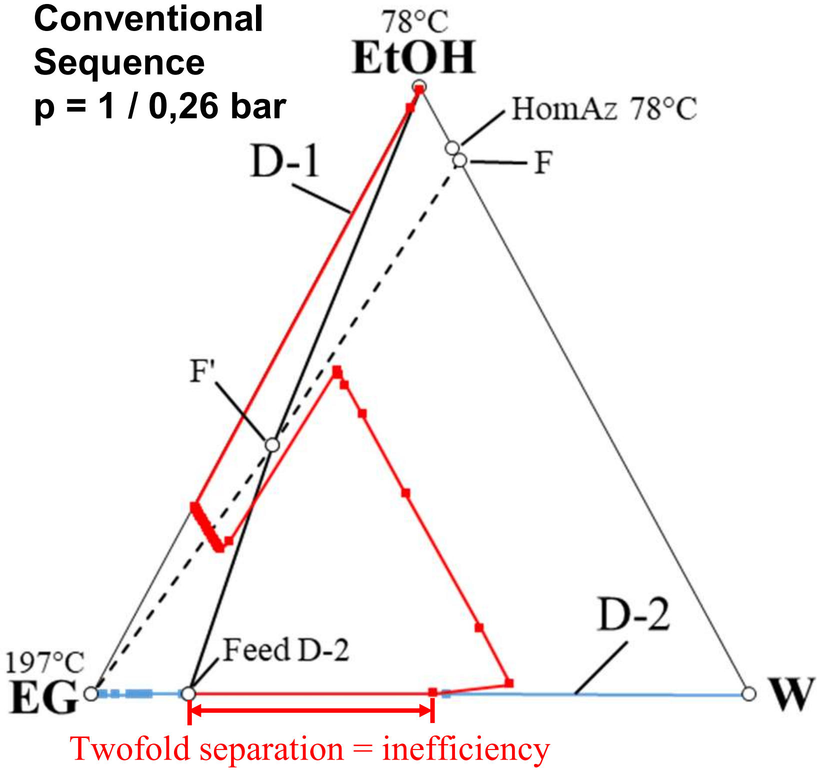




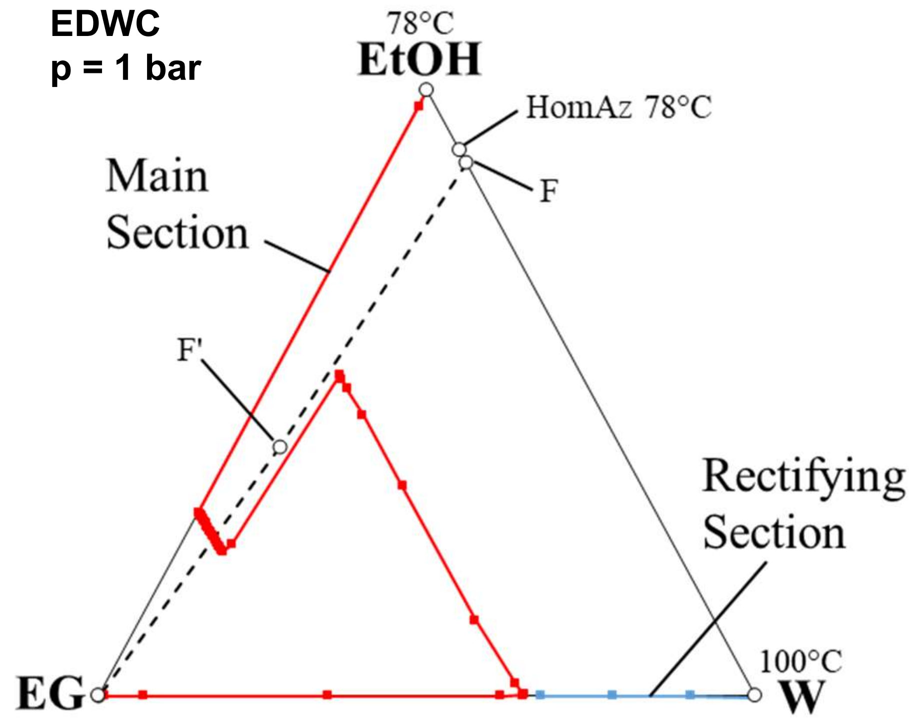
	D-1	D-2	ED	EDWC	Sav.
Q / kJ/kg EtOH	1401	188	1589	1664	-5%
No. of stages	39	14	53	42	21%
Rel. OpEx	0.71	0.1	0.81	0.94	-16%
Rel. CapEx	0.16	0.03	0.19	0.2	-5%
Relative TAC	0.87	0.13	1	1.14	-14%

Thermodynamic Efficiency of EDWC

Conventional Sequence
p = 1 / 0,26 bar



EDWC
p = 1 bar



Although double separation is avoided, the extractive dividing-wall column is **not** a viable option for separating near-azeotropic ethanol/water mixtures because the pressures cannot be selected independently.

Alternative: Side-stream Column

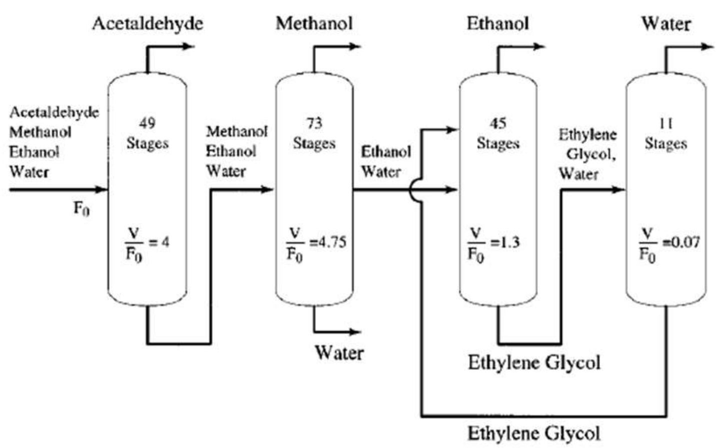


Figure 14. Second sequence to separate acetaldehyde, methanol, ethanol, and water. This sequence has a total of 4 columns, 8 heat exchangers, 178 stages, and a normalized vapor flow of 10.12.

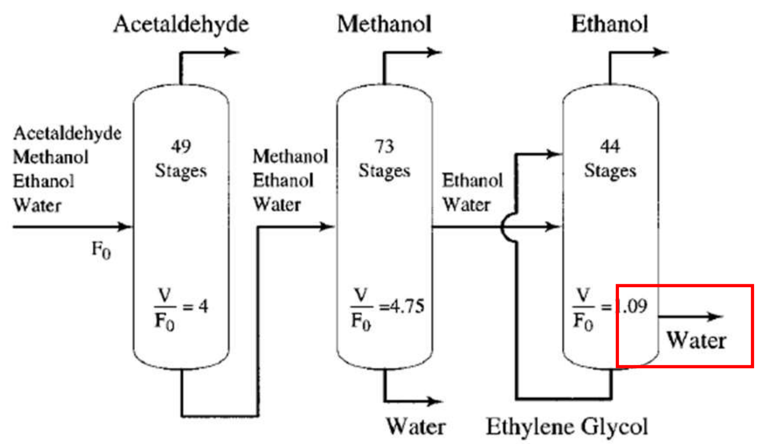


Figure 15. Third sequence to separate acetaldehyde, methanol, ethanol, and water. This sequence has a total of 3 columns, 6 heat exchangers, 166 stages, and a normalized vapor flow of 9.84.

Table 4. Summary of Design Results for the Four-Component Separation Sequences

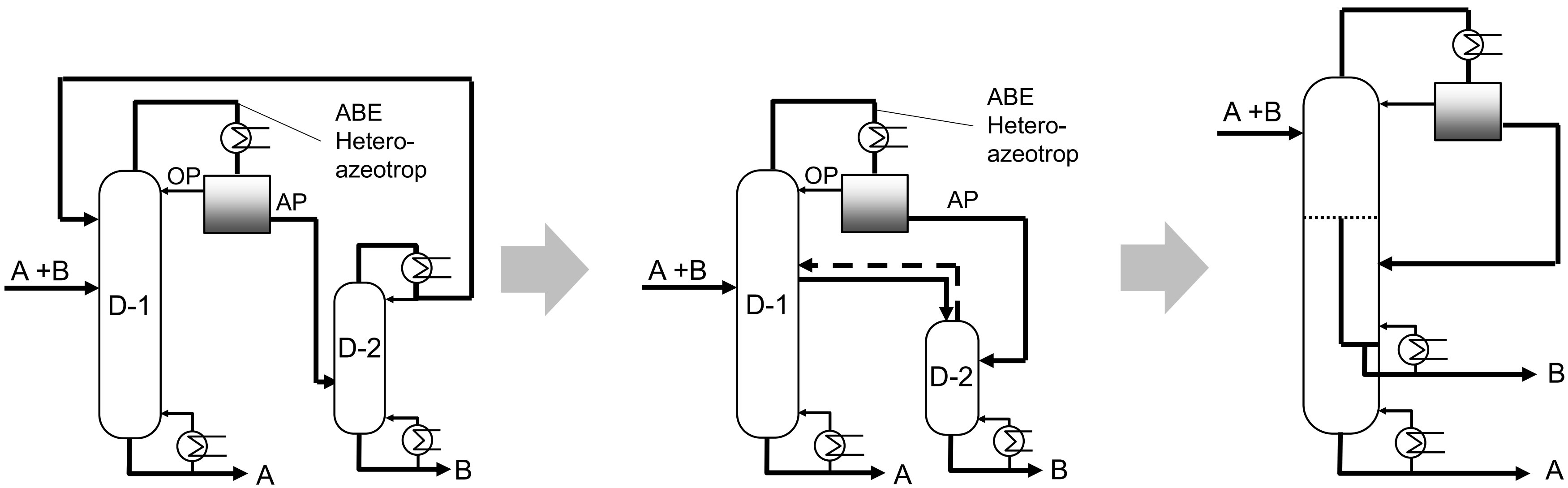
	sequence		
	first	second	third
stages	178	178	166
shells	5	4	3
heat exchangers	10	8	6
vapor flows $\sum V/F_0$	12.19	10.12	9.84

For low-purity specifications of water stream, side-stream columns can be a viable option.

Rooks, Malone, Doherty (1996): Ind. Eng. Chem. Res., 35, 3653-3664

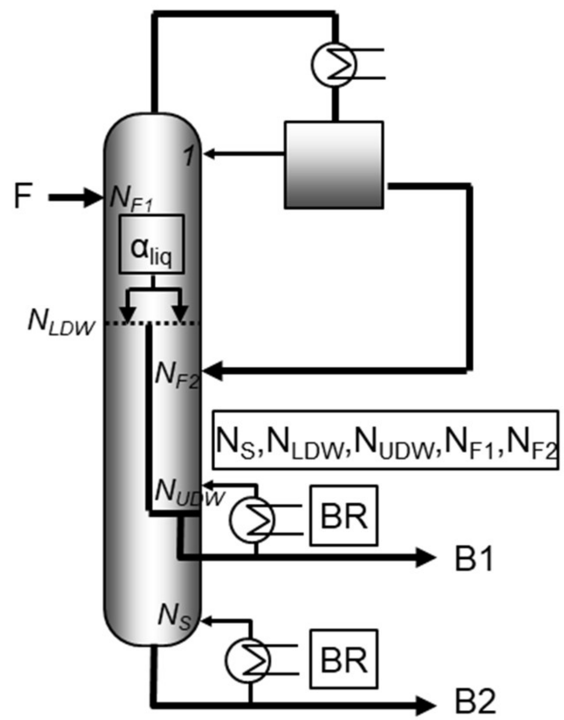
Derivation of Azeotropic Dividing-Wall Column

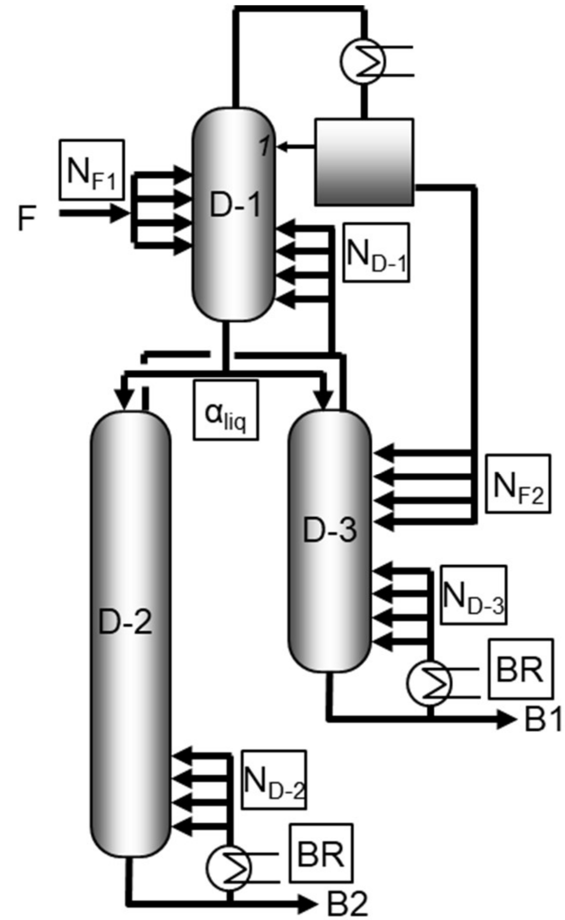
Heteroazeotropic Distillation | **Heteroazeotropic Distillation /w Side Stripper** | **Heteroazeotropic Dividing-Wall Column**



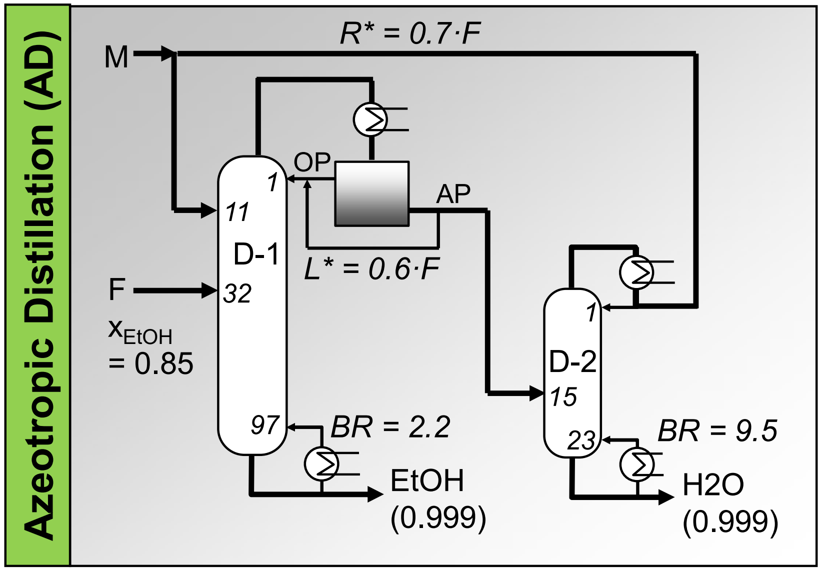
Examples:
Sun et al. (2011): Implementation of Ethanol Dehydration Using Dividing-Wall Heterogeneous Azeotropic Distillation Column
Le, Halvorsen, Pajalic, Skogestad (2015): Dividing wall columns for heterogeneous azeotropic distillation

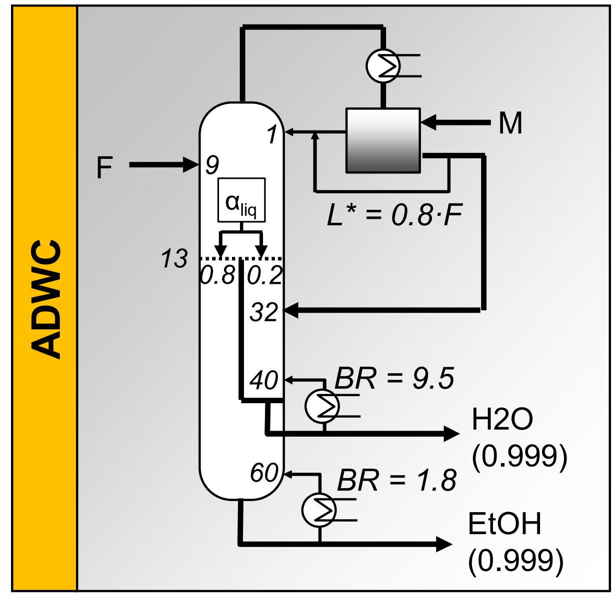
Azeotropic Distillation: 3-Column Substitution Model





Azeotropic Dividing-Wall Column (ADWC)





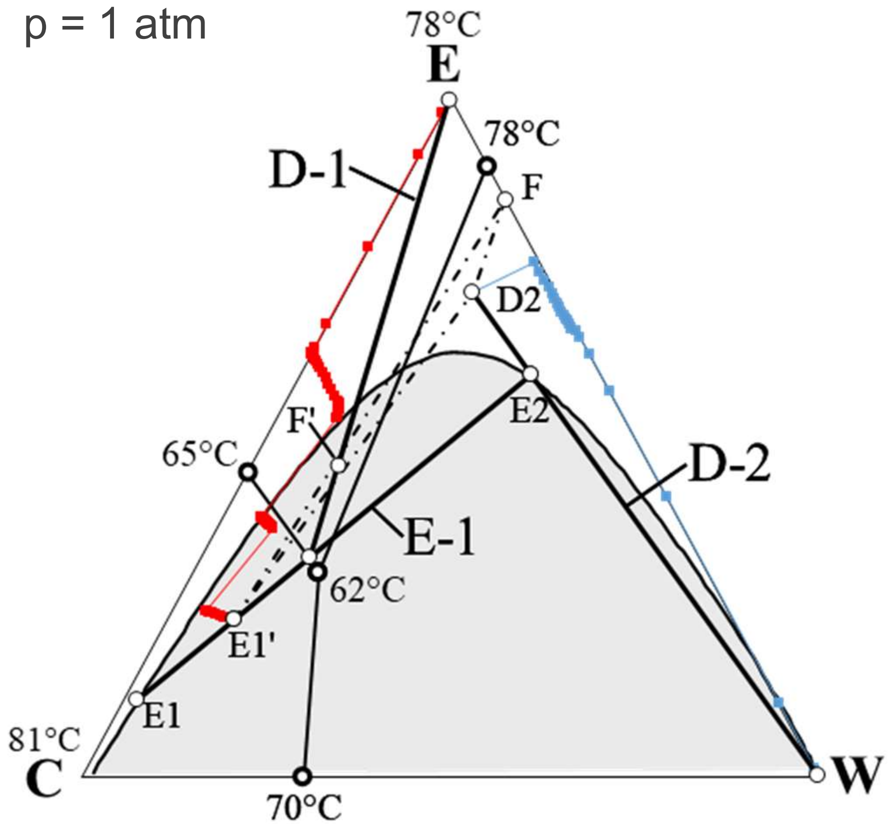
*Flowsheet Optimization Variables

	D-1	D-2	AD	ADWC	Sav.
Q / kJ/kg EtOH	2020	1483	3503	3197	9%
No. of stages	97	23	120	60	50%
Rel. OpEx	0.38	0.28	0.66	0.59	**11%**
Rel. CapEx	0.25	0.09	0.34	0.29	**15%**
Rel. TAC	0.63	0.37	1	0.88	**12%**

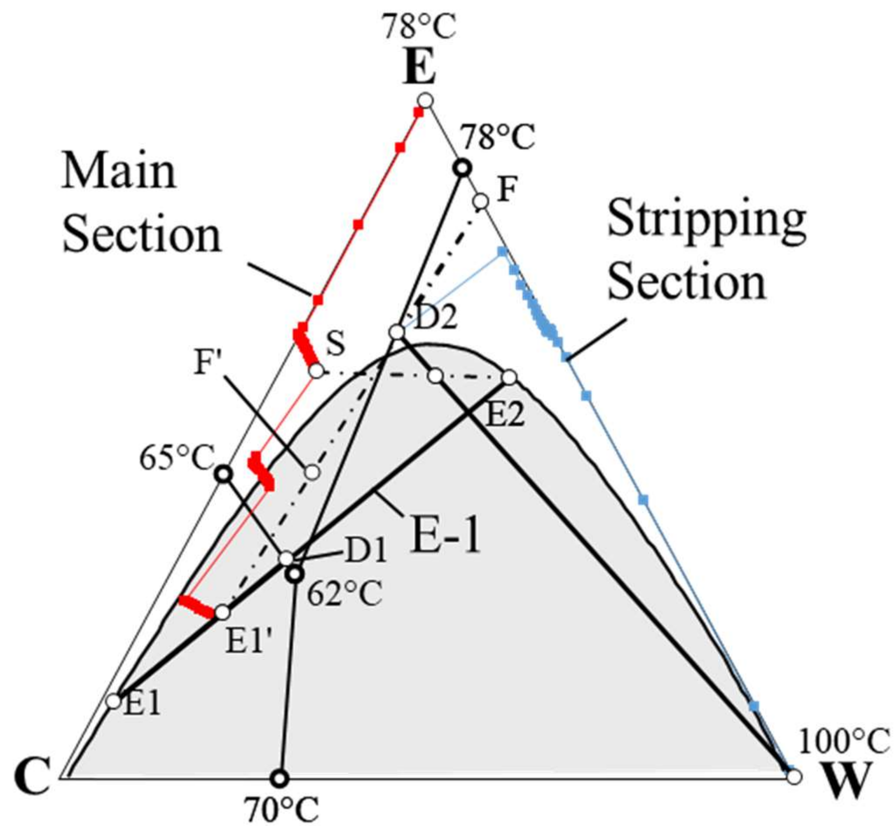
The ADWC is an economically attractive option for separating near-azeotropic ethanol/water mixtures.

Conventional Sequence vs. Dividing-Wall Column

p = 1 atm

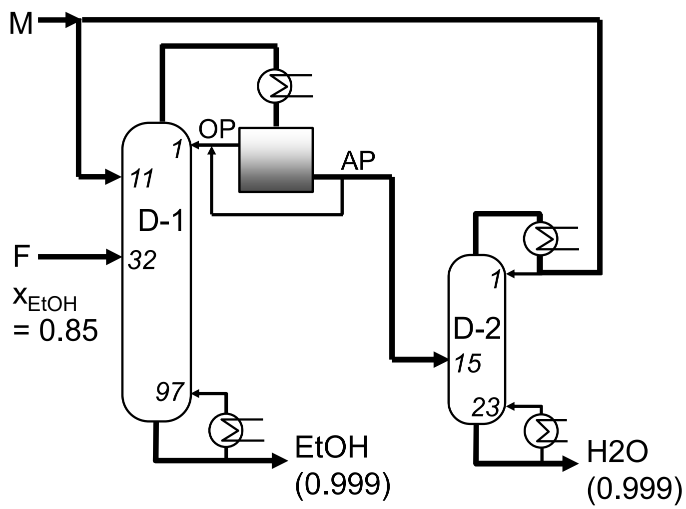


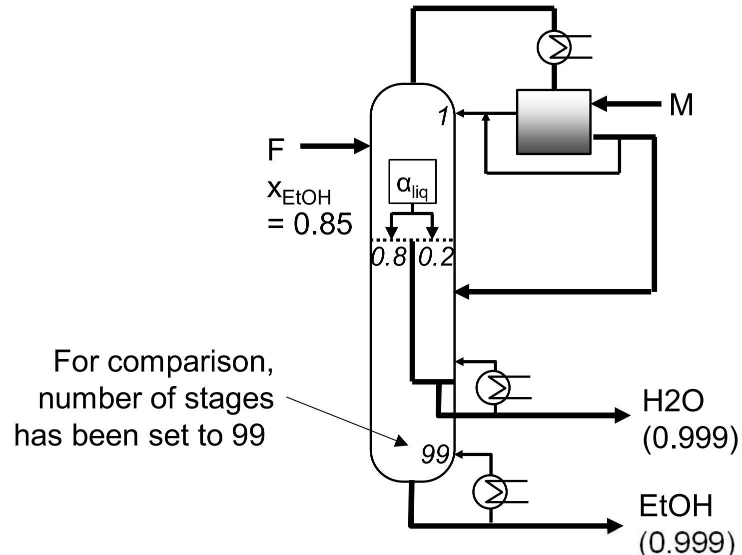
Conventional Sequence

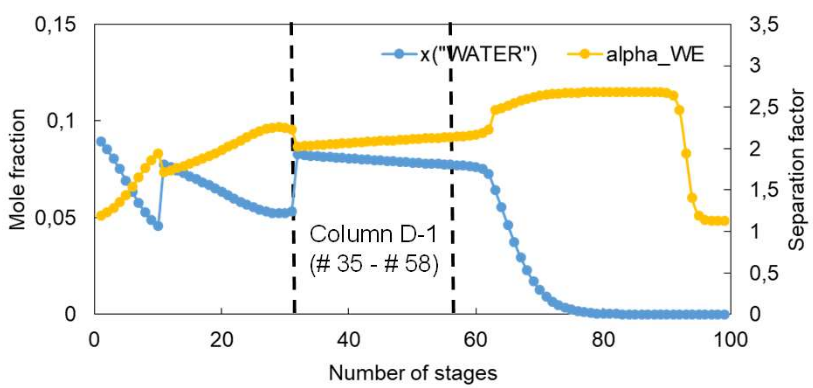


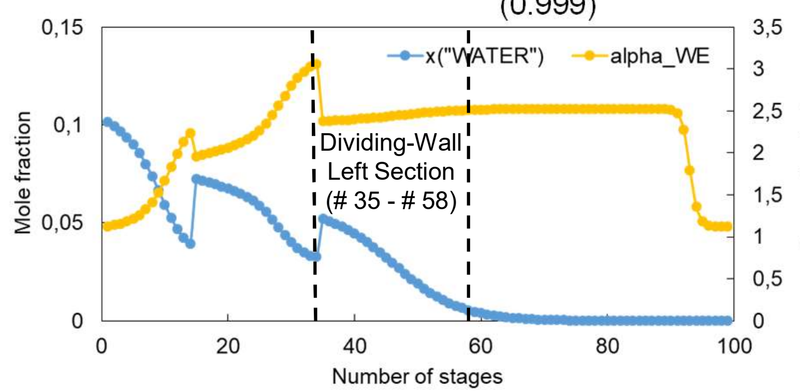
Dividing-Wall Column

Why does the ADWC perform better?

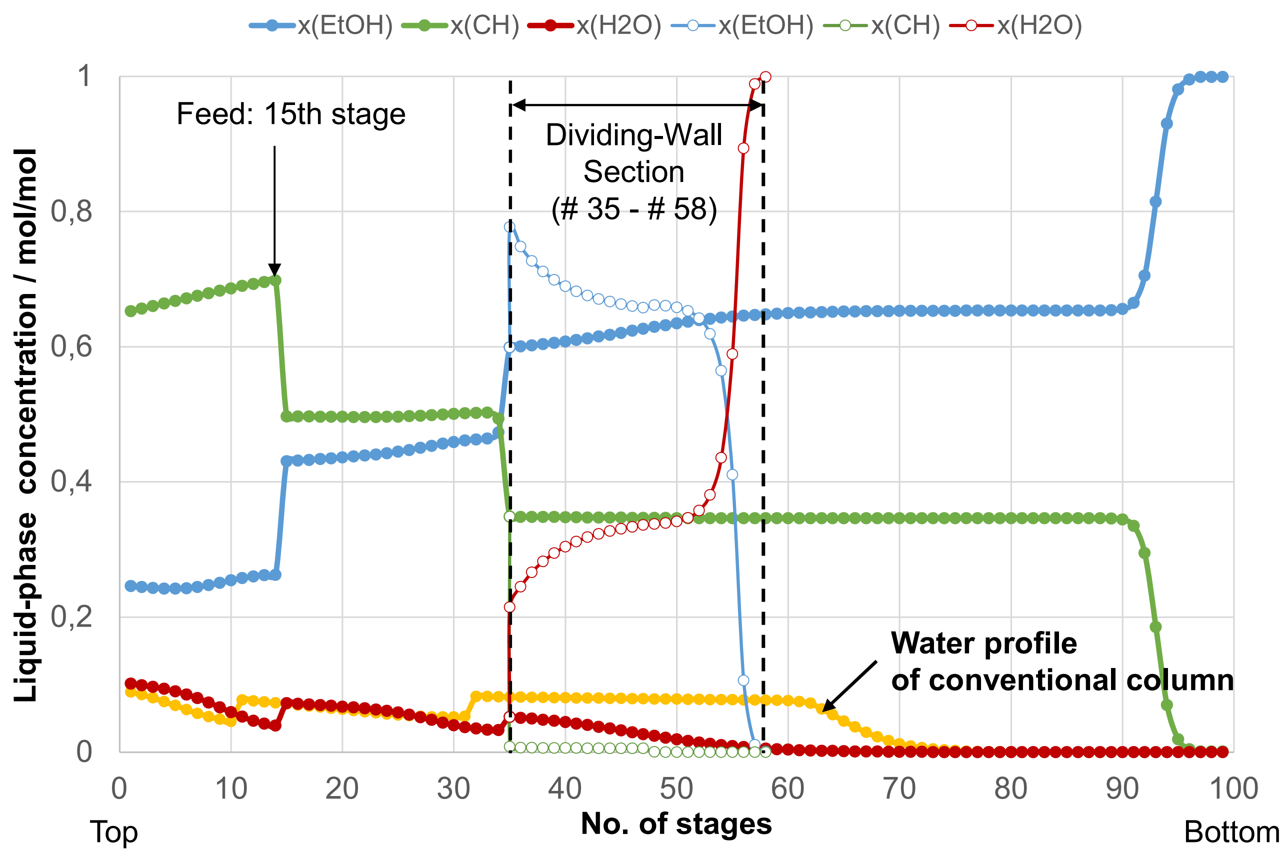




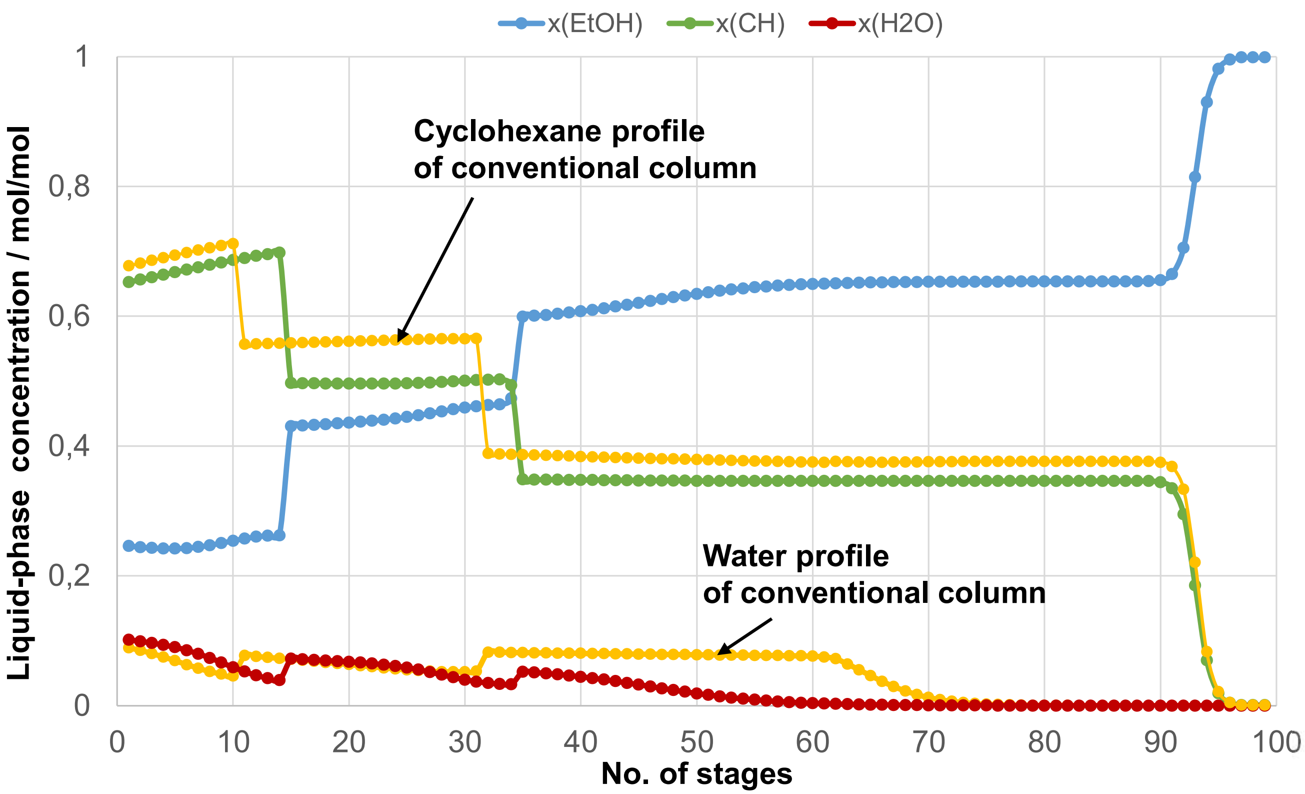


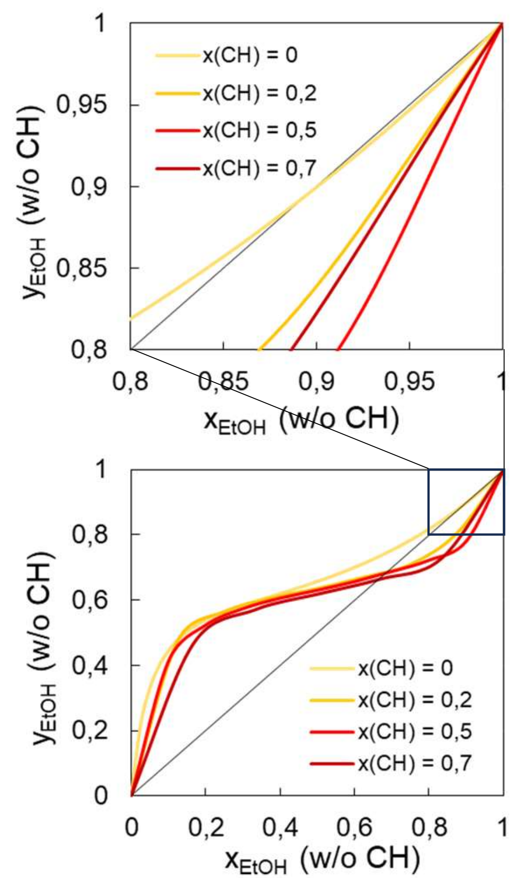


Why does the ADWC perform better? – cont'd

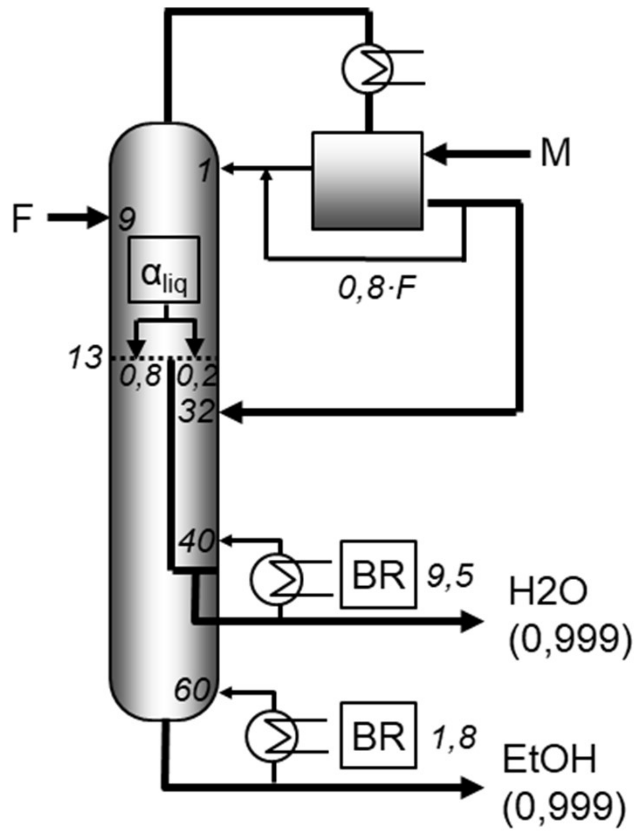


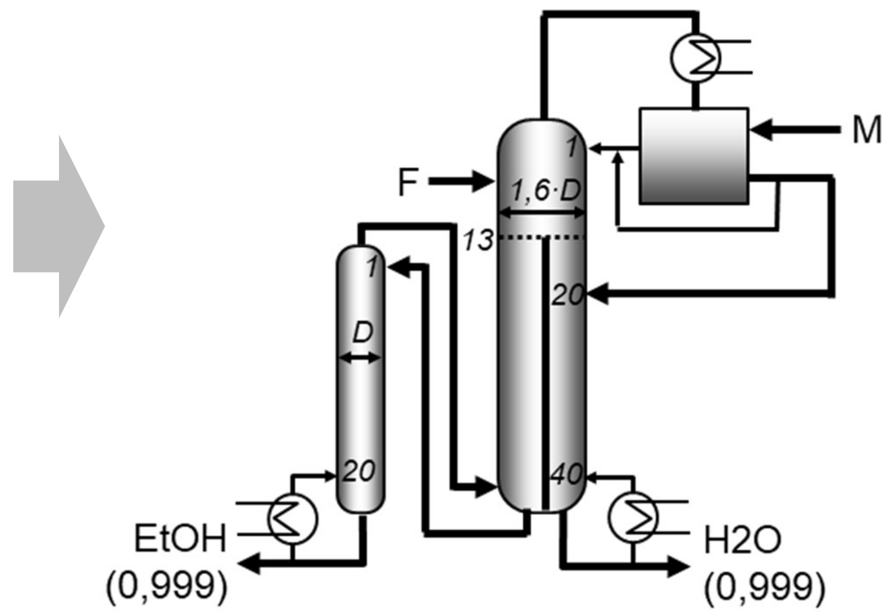
Why does the ADWC perform better? – cont'd





DWC Gives Rise to Alternative Designs





Conclusions

- DWC is not always the best choice
- Fair (optimization-based) comparison needed
- Visual inspection of concentration profiles not sufficient
- Pressure is an important (but often neglected) optimization variable (degree of freedom)