Non-Equilibrium Thermodynamics: Foundations and Applications.

Lecture 11: Entropy production minimization. Examples

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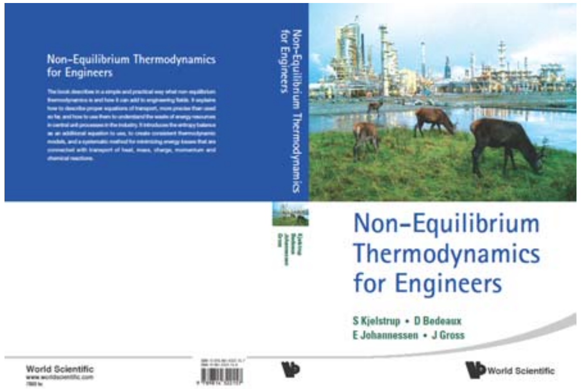
http://www.chem.ntnu.no/nonequilibrium-thermodynamics/

Non-Equilibrium Thermodynamics: Foundations and Applications

	Tuesday, Sept. 7	Wednesday, Sept. 8	Thursday, Sept.9	Friday, Sept.10
9:00-10:30	Why non-equilibrium thermodynamics?	Transport of heat and mass	Transport of heat and charge	Entropy production minimization theory
11:00-12:30	Entropy production for a homogeneous phase	Multi-component heat and mass diffusion	Transport of mass and charge	Entropy production minimization. Examples.
16:00-17:00	Flux equations and Onsager relations	Power from regular and thermal osmosis	Modeling the polymer electrolyte fuel cell	

11. Entropy production minimization
Examples of optimal units in chemical processes

Chapter 10



2. law optimisation: Which path gives minimum total entropy production?*

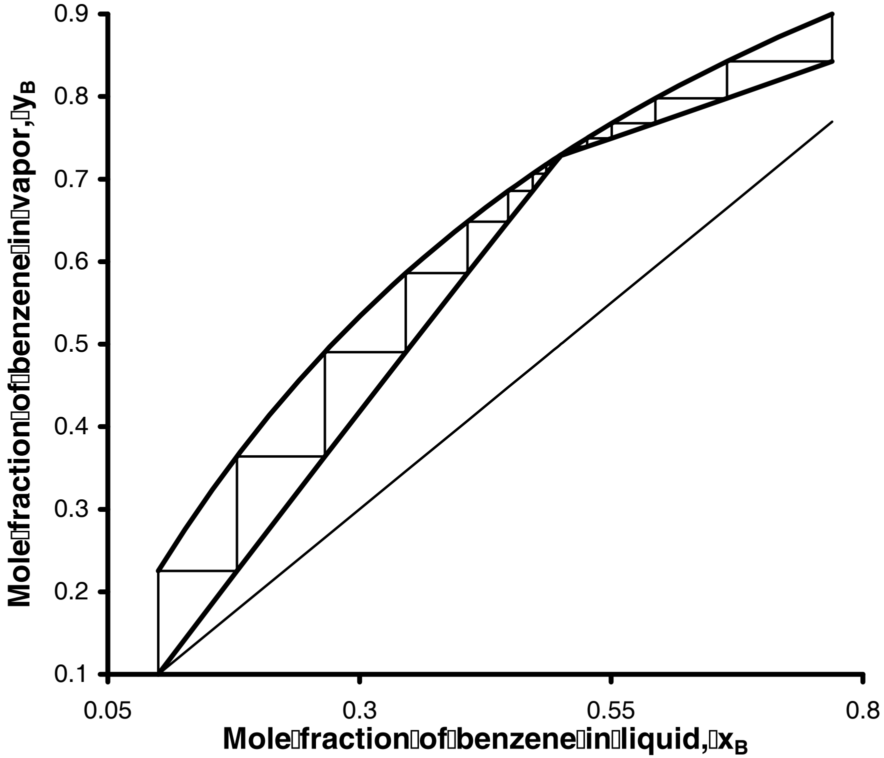
$$w_{lost} = T_0(dS_{irr} / dt) > 0$$

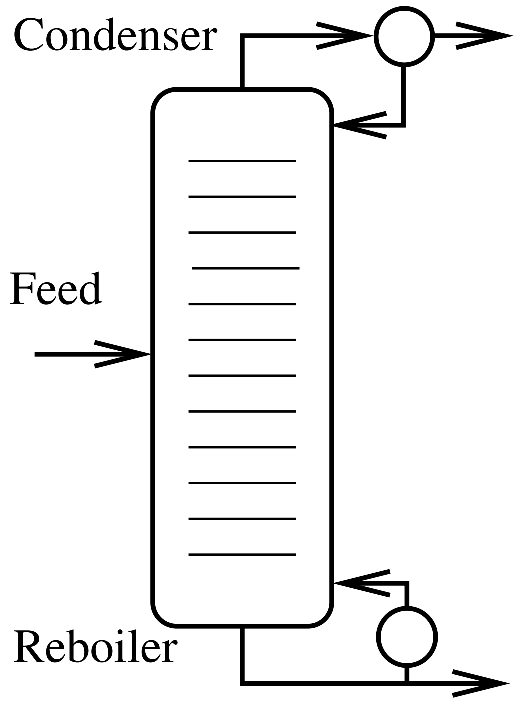
Two process unit examples

- The distillation column
- The chemical reactor

* Use control theory

The adiabatic distillation column





McCabe-Thiele diagram

Table 6.3: Governing equations for binary tray distillation.

Total mole balance:

$$V_{n+1} - L_n = \begin{cases} D, & n \in [0, N_\mathrm{F} - 2] \\ D - (1-q)\,F, & n = N_\mathrm{F} - 1 \\ D - F, & n \in [N_\mathrm{F}, N+1] \end{cases}$$

Mole balance for the light component:

$$V_{n+1}\,y_{n+1} - L_n\,x_n = \begin{cases} D\,x_\mathrm{D}, & n \in [0, N_\mathrm{F} - 2] \\ D\,x_\mathrm{D} - (1-q)\,F z_\mathrm{F}, & n = N_\mathrm{F} - 1, \\ D\,x_\mathrm{D} - F\,z_\mathrm{F}, & n \in [N_\mathrm{F}, N+1]. \end{cases}$$

Balance equation for the internal energy:

$$Q_n = V_n\,H_n^\mathrm{V} + L_n\,H_n^\mathrm{L} - V_{n+1}\,H_{n+1}^\mathrm{V} - L_{n+1}\,H_{n+1}^\mathrm{L} - \kappa$$

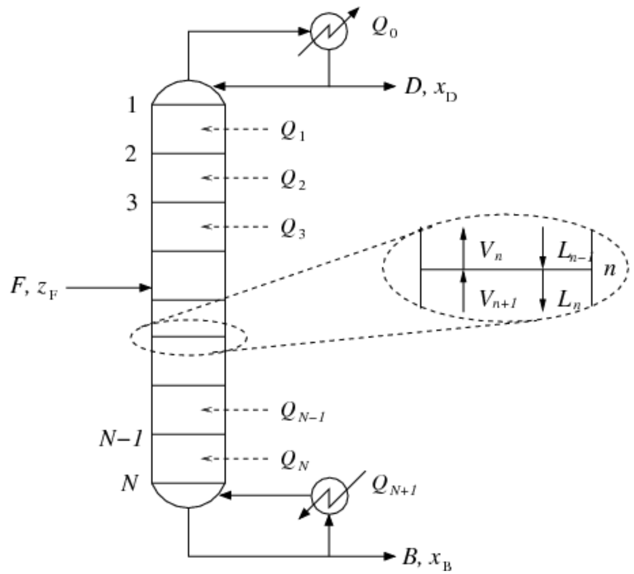
$$\text{where } \kappa = \begin{cases} (1-q)\,F\,H_\mathrm{F}^\mathrm{V}, & n = N_\mathrm{F} - 1, \\ q\,F\,H_\mathrm{F}^\mathrm{L}, & n = N_\mathrm{F}, \\ 0, & \text{otherwise.} \end{cases}$$

Average heat exchange force:

$$X_n = (\delta/\lambda_n\,T_n^2)\,(Q_n/A_n)$$

The total entropy production:

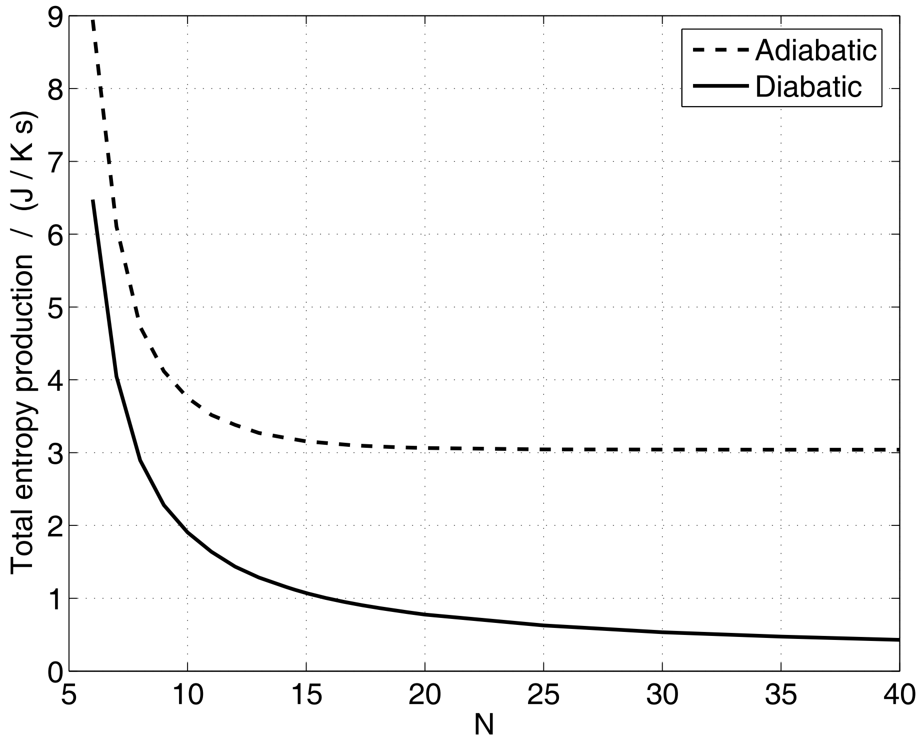
$$\frac{dS_\mathrm{irr}}{dt} = B\,S^\mathrm{B} + D\,S^\mathrm{D} - F\,S^\mathrm{F} + \sum_{n=0}^{N+1}\left(-\frac{Q_n}{T_n} + Q_n\,X_n\right)$$



Find the minimum total entropy production, given the product purity!

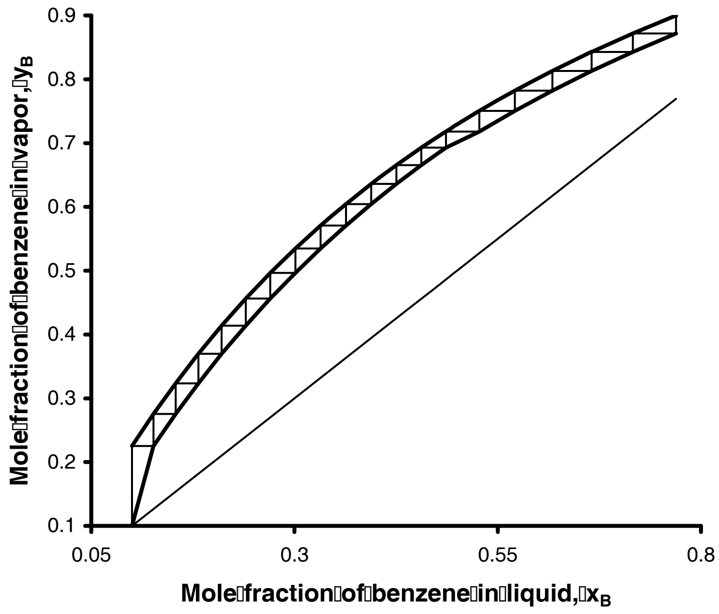
Optimal distillation is diabatic

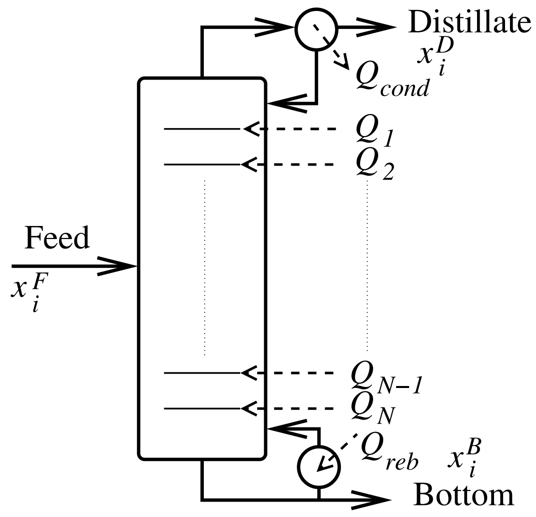
- The entropy production is smaller in a diabatic column!
- It is also reduced when the number of trays, N, increases



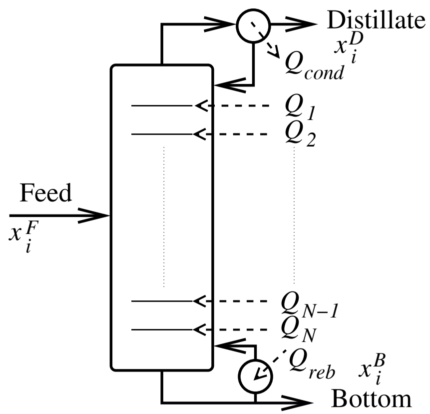
The area for heat transfer was not constrained in this optimisation

The result: Diabatic distillation

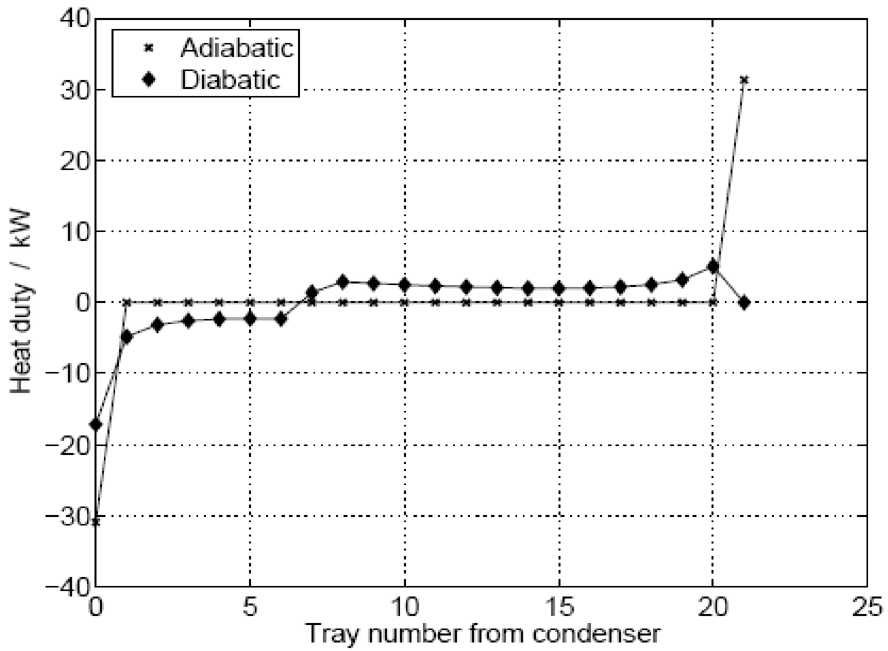




Optimal distillation is diabatic

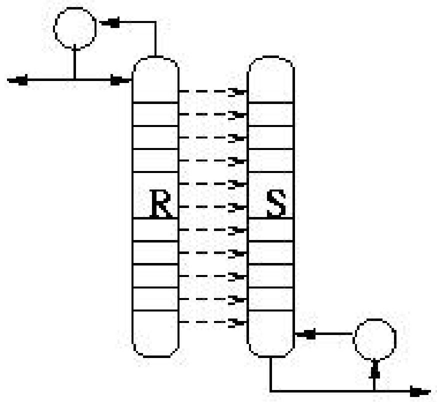


- The amount of heat added ("duty") in the stripping and rectifying section can be determined:

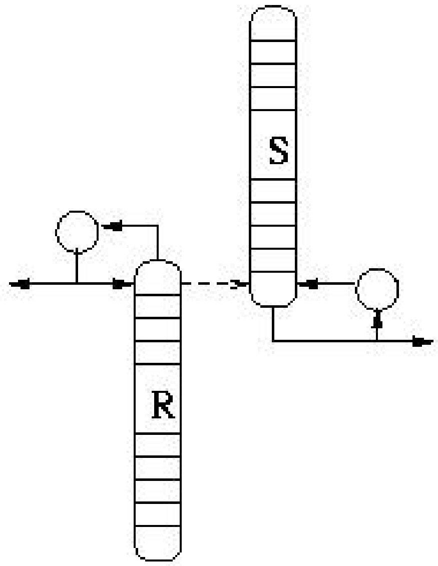


Distillation columns with high efficiency

- Left: Heat Integrated Distillation Column*
- Right: A good approxmiation. Solution from optimisation study of propane-propylene**



Nakaiwa (1986)



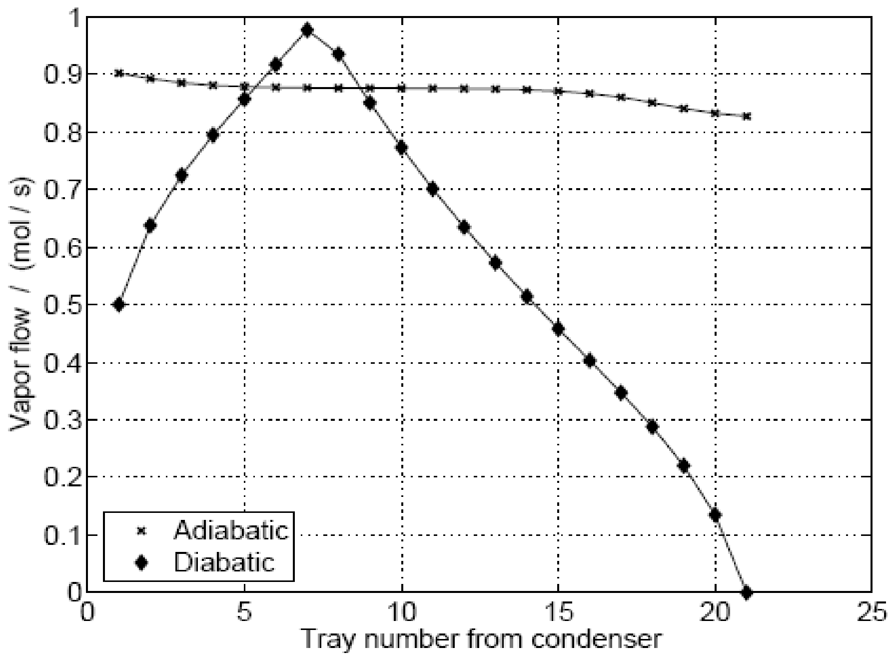
Linde technology

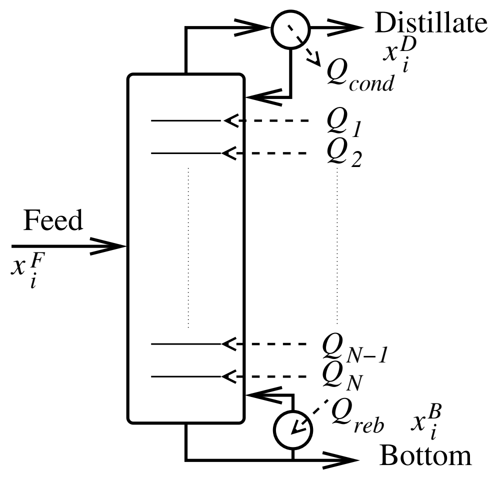
*Olujic et al., TU Delft

**PhD of Røsjorde, NTNU, 2005

Optimal distillation is diabatic

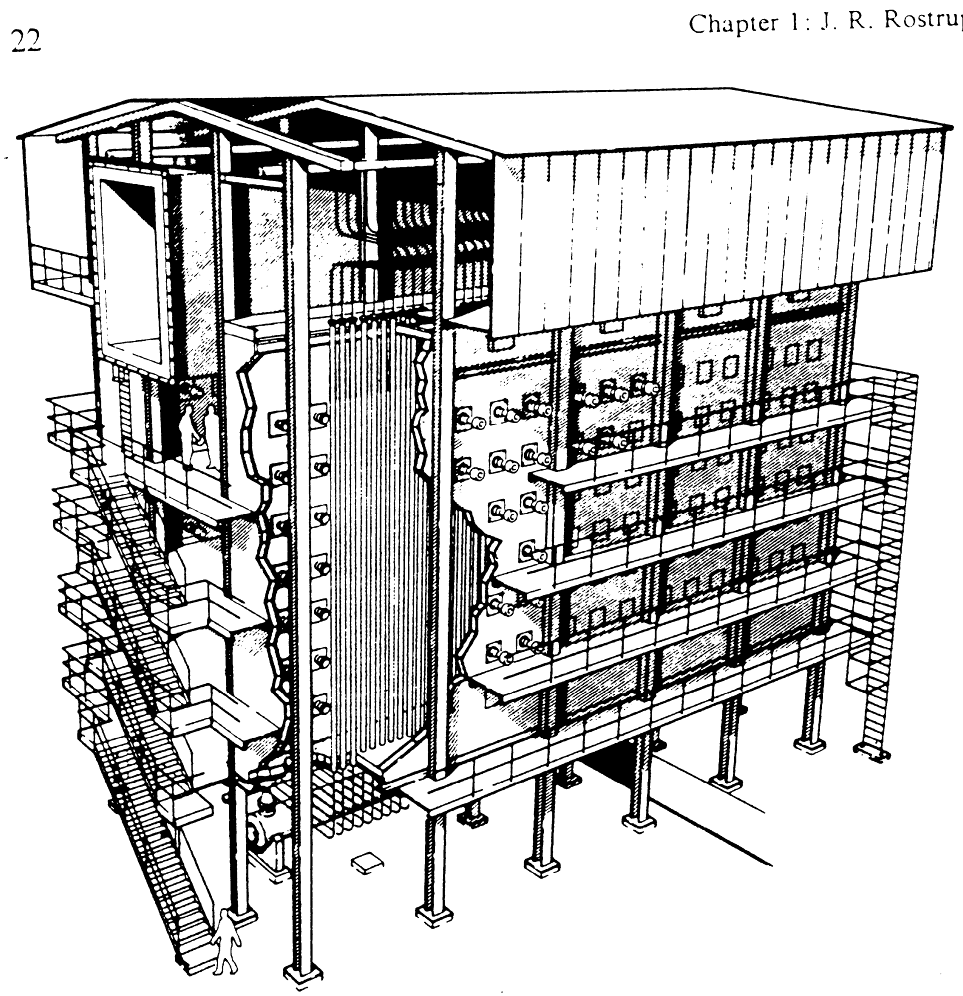
- The vapor and liquid flows are no longer constant





PhD of Gelein de Koeijer, NTNU, 2003
PhD of Aris de Rijke, TU Delft, 2007

Steam reforming



$$CH_4 + H_2O = CO + 3H_2$$

$$CH_4 + 2H_2O = CO_2 + 4H_2$$

$$CO + H_2O = CO_2 + 3H_2$$

Lost work in the reformer of an ammonia plant: 5.0 10^9 / 10^6 Tonnes

The energy efficiency of a reactor

Production of hydrogen by steam reforming, tubular reactors

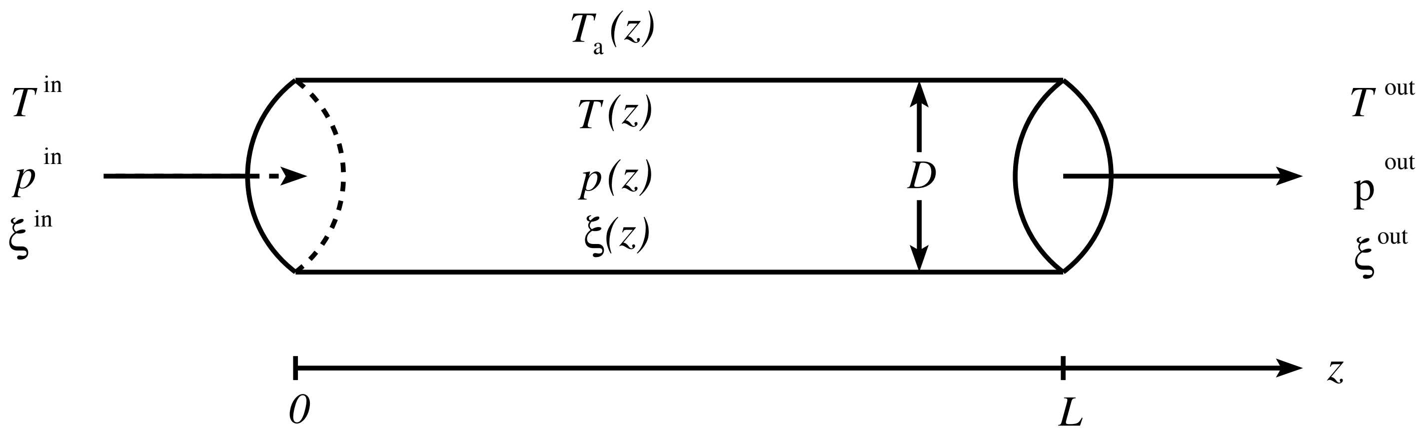
$$CH_4 + H_2O = CO + 3H_2$$

$$CH_4 + 2H_2O = CO_2 + 4H_2$$

$$CO + H_2O = CO_2 + H_2$$

Wilhelmsen, Johannessen, Kjelstrup, 2010, Int.J Hydrogen

The tubular reformer



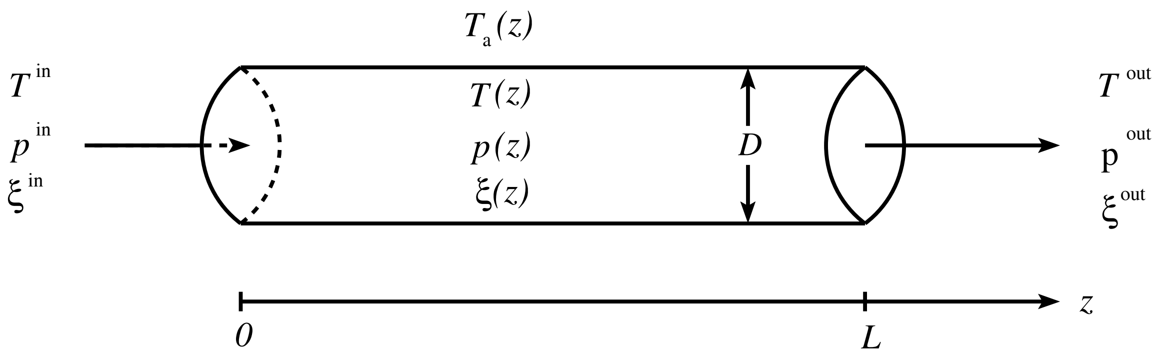
z

Problem definition:

- Given reactors that produce the same amount of hydrogen.
- What is the temperature $T_a(z)$ outside the reactor that gives minimum entropy production in the process?

Johannessen, Kjelstrup, Chem. Eng. Sci.2005

The plug flow reactor model



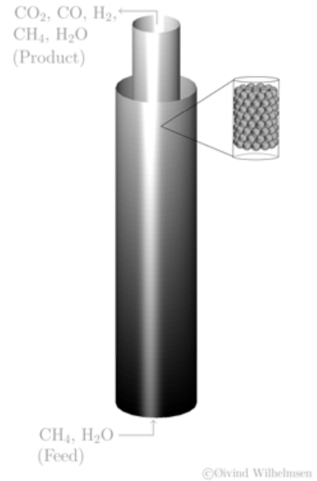
- No gradients in the radial direction
- The reference system to be optimized is given by Froment et al. -96, -89, Nielsen 1968.
- Rates are highly non-linear functions of the forces
- A constant overall heat transfer coefficient *U* is used

A stationary state plug flow reactor:

Balance equation for internal energy

A,B,C,D: geometry dependent constant

$$\frac{dT}{dz} = f_T = \frac{AJ_q' + B\sum_j r_j(-\Delta_r H_j)}{\sum_i F_i C_{p,i}}$$



Momentum balance

$$\frac{dp}{dz} = f_p = -Cv$$

Constraints

Mole balances

$$\frac{d\xi_j}{dz} = f_{\xi_j} = \frac{B}{F^0} r_j$$

Total entropy production

$$\frac{dS_{irr}}{dt} = S_{out} - S_{in} - A\int_0^L \frac{J_q'}{T_a} dz = \int_0^L D\sigma dz$$

$$= \int_0^L \left[B\sum_j r_j\left(-\frac{\Delta_r G_j}{T}\right) + AJ_q'\Delta\left(\frac{1}{T}\right) + Dv\left(-\frac{1}{T}\frac{dp}{dz}\right) \right] dz$$

Objective of the minimization

The optimal control problem

$$H = \sigma + \lambda_T f_T + \lambda_p f_p + \lambda_\xi f_\xi$$

$$H(\mathbf{y},\mathbf{u},\lambda) = \mathbf{x}(\mathbf{y},\mathbf{u})\Gamma \mathrm{J}(\mathbf{y},\mathbf{u},z) + \lambda^T \mathbf{A}(\mathbf{y})\Gamma \mathrm{J}(\mathbf{y},\mathbf{u},z)$$

State variable vector

Control variables

Flux vector

1. **When we can control all forces independently,** ***J(y, u, z)*** **=** ***J(y,z)*** **and the Spirkl-Ries quantity is constant*.**

$$H = -(\Gamma \mathrm{J}(\mathbf{y},z))^{\mathrm{T}} \left(\frac{\partial(\Gamma \mathrm{J}(\mathbf{y},\mathbf{u}))}{\partial z} \right)^{-1} (\Gamma \mathrm{J}(\mathbf{y},z))$$

2a. When also flux-force relations are linear, σ is constant.

2b. Or, when ***J(y,z)*** **=** ***J(z)*** **and A(y) is constant, σ is constant.**

- **But: Numerical evidence for constant σ has been obtained for several <u>non-linear</u> processes (chemical reactions, radiative heat transfer) !**

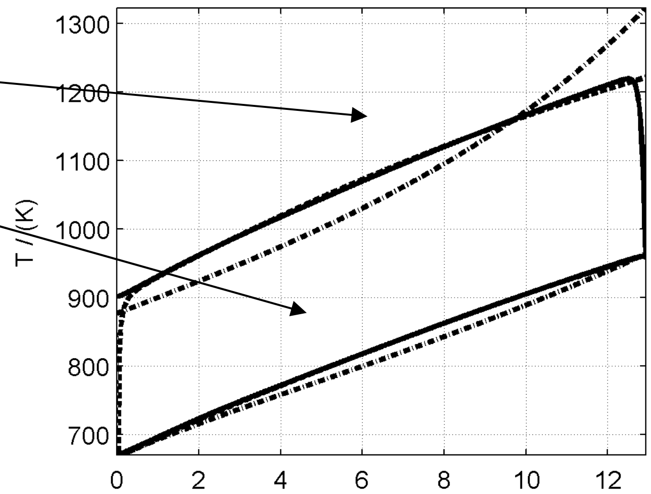
1. Spirkl and Ries, Phys. Rev. E, 1995, De Vos and Desoete, J. Non-Equilib. Thermodyn. 2000

2. Johannessen and Kjelstrup, Chem. Eng. Sci., 2005, J. Non-Equilibr. Thermodyn. 2005

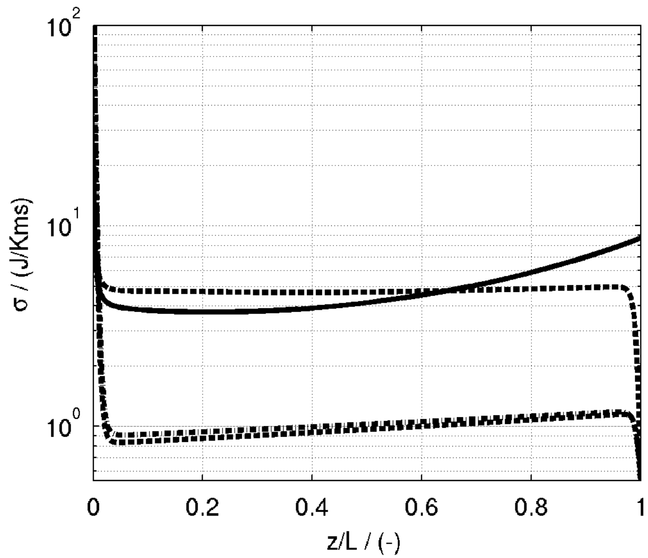
The entropy production of an optimal reformer

Heating temperature
Reactor temperature

--- State-of-the art reactor
— Reactor w/ min. entropy prod.

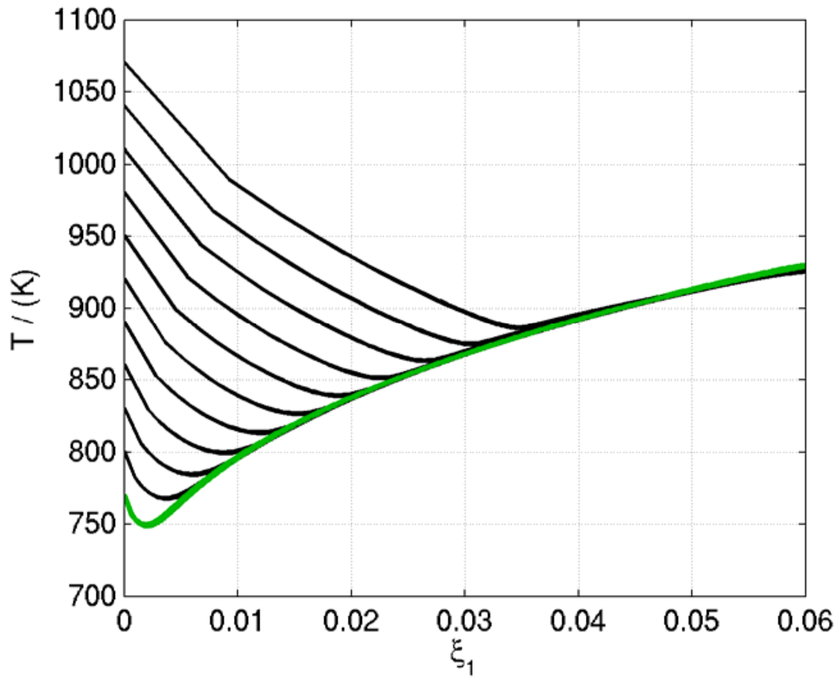


- The entropy production becomes approximately constant in parts of the reactor's state space in the optimal state!



States of minimum entropy production end up on a ”highway” in state space

- The highway: A preferred path for energy efficient travel!



The highway is preferred unless it is too far away from start!
EoEP is a good approximation for the highway

Johannessen and Kjelstrup, Chem.Eng.Sci, 2005
Wilhelmsen et al, 2010, submitted

The hypothesis of the state of minimum entropy production

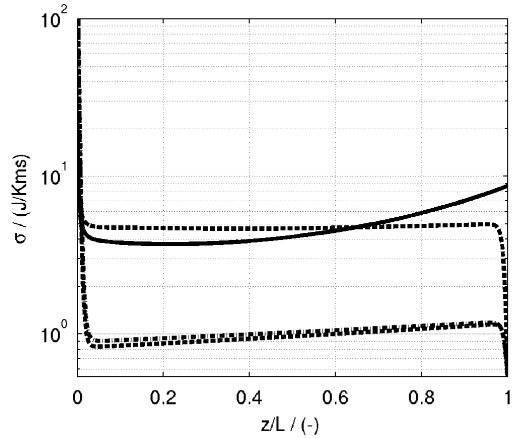
Equipartition of entropy production, EoEP, but also equipartition of forces, EoF, are good approximations to the state of minimum entropy production in parts of an optimally controlled system that have sufficient freedom

Comments:

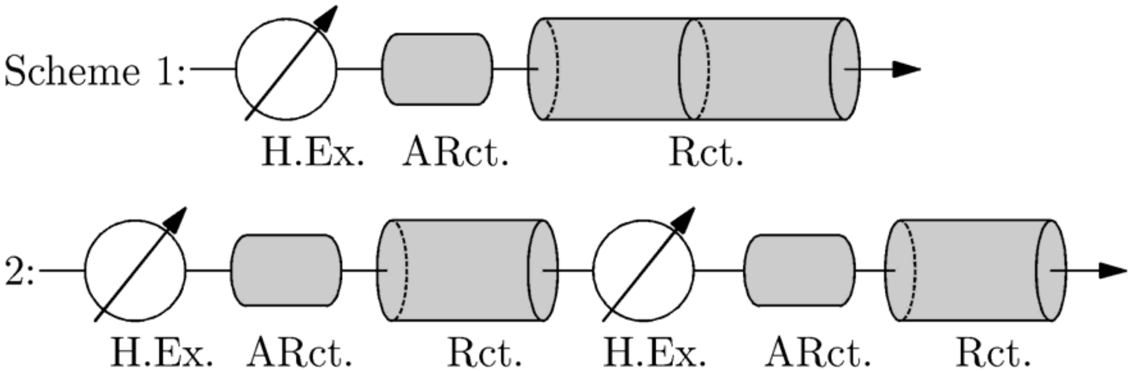
- **EoEP better than EoF. EoF more practical**
- **Sufficient freedom: Sufficient control variables**

*Johannessen and Kjelstrup, Chem. Eng. Sci., 2005

How can we do an efficient optimisation, knowing this?

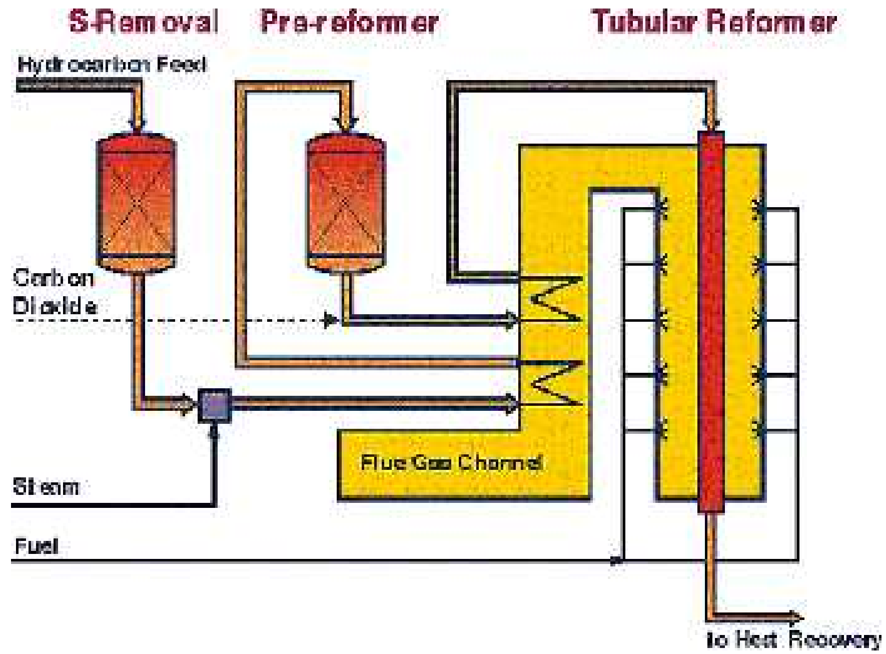


The variation in the entropy production indicate that combinations of three process units are central:



Reformer technologies*

- Prereformer: adiabatic
- Tubular reformer: with heat transfer



•From Haldor Topsoe ASA
http://www.topsoe.com/site.nsf/all/BBNN-5PFHXR?OpenDocument

Summary:

Energy efficient design means that

- Optimal distillation columns must allow for heat exchange along the column, and a distribution of available heat transfer area
- Optimal chemical reactors have a reaction mode and a heat exchange mode, plus an optimal length.
- Equipartition of entropy production in the heat exchange modes of operation is an aim.

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Course Completed!

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Thank you for the attendance!

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