



Limit Cycles in Homogeneous Azeotropic Distillation

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Scope

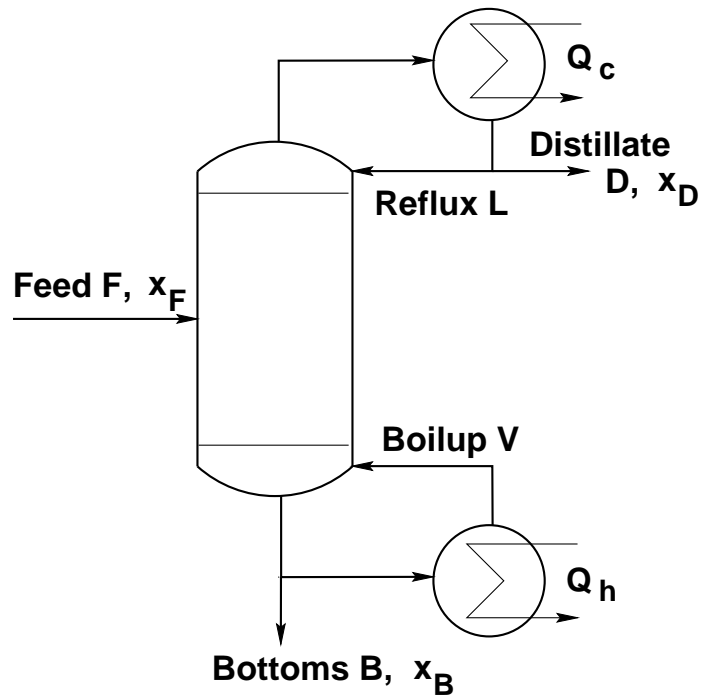
Preparation of the experimental validation of sustained oscillations

- Detailed, dynamic analysis
- Selection of a system for experimental investigation
- Definition of design guidelines for the experimental set-up

Outline

1. Oscillations in Distillation Columns - Background
2. Detailed Analysis of Dynamic Behaviour
3. Preparations of Experimental Set-Up
4. Conclusions and Outlook

Distillation Column



Given:

- Design
- Feed conditions:
 F, x_F , and quality

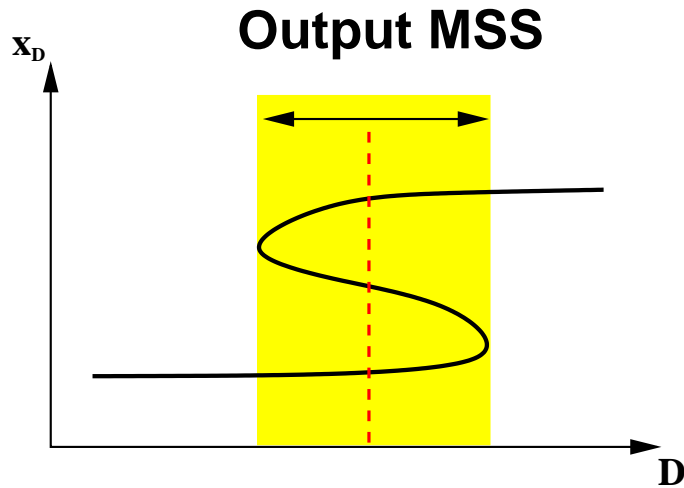
2 degrees of freedom:

- E.g. D and Q_h

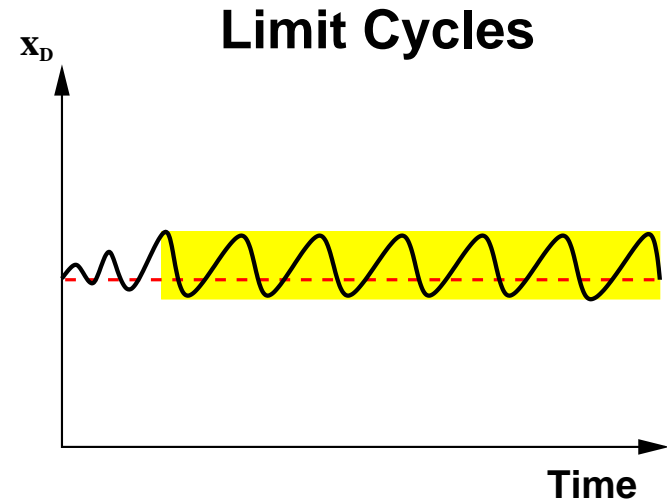
Outputs:

- Compositions: x_D, x_B
- Column profiles

Nonlinear Behavior of Distillation Columns



- Theoretically predicted
- Validated with simulations
- Validated experimentally

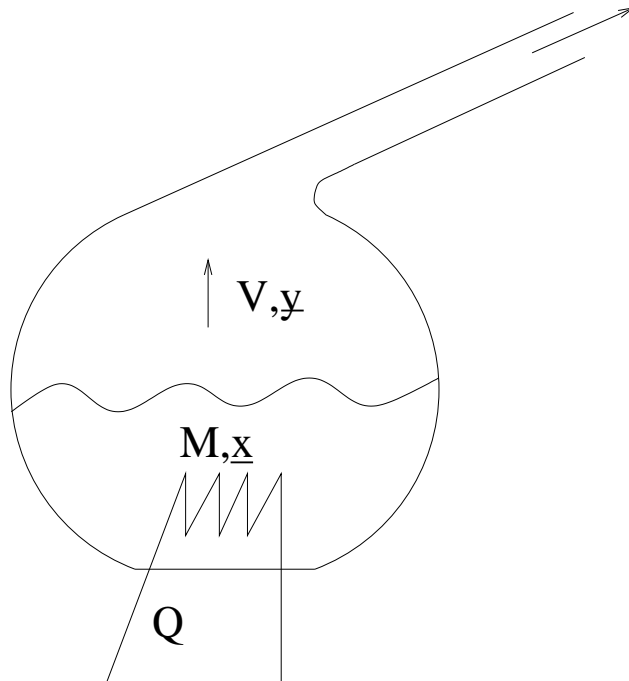


- Theoretically predicted
- Validated with simulations only

Experimental validation still missing

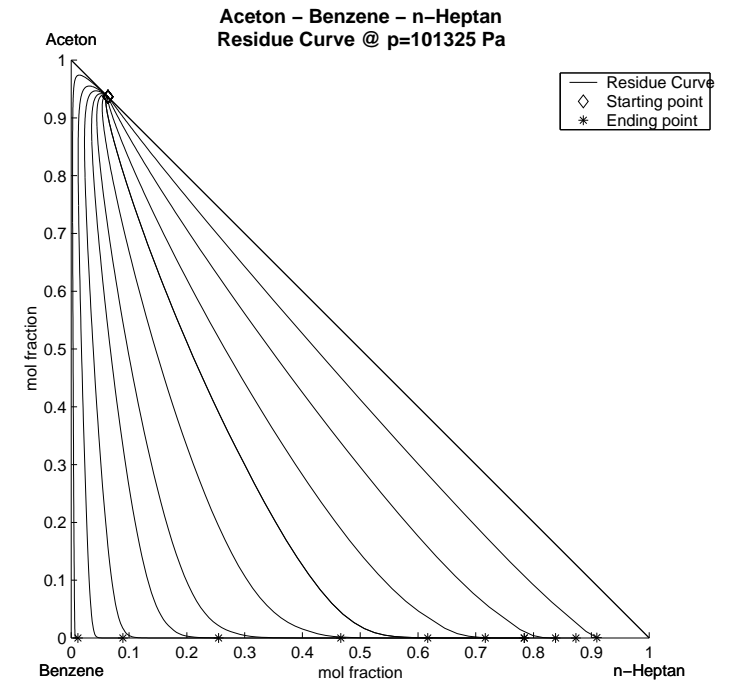
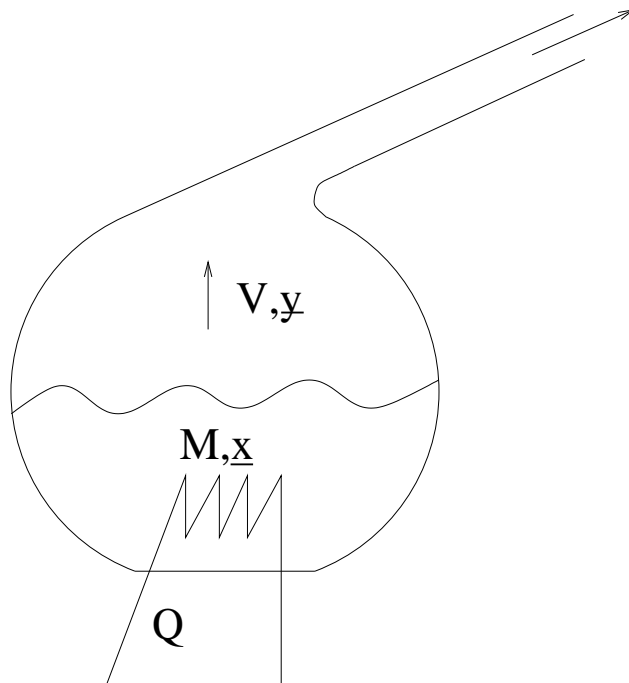
Residue Curve Maps

Evolution of liquid phase (residue) composition for a simple batch distillation



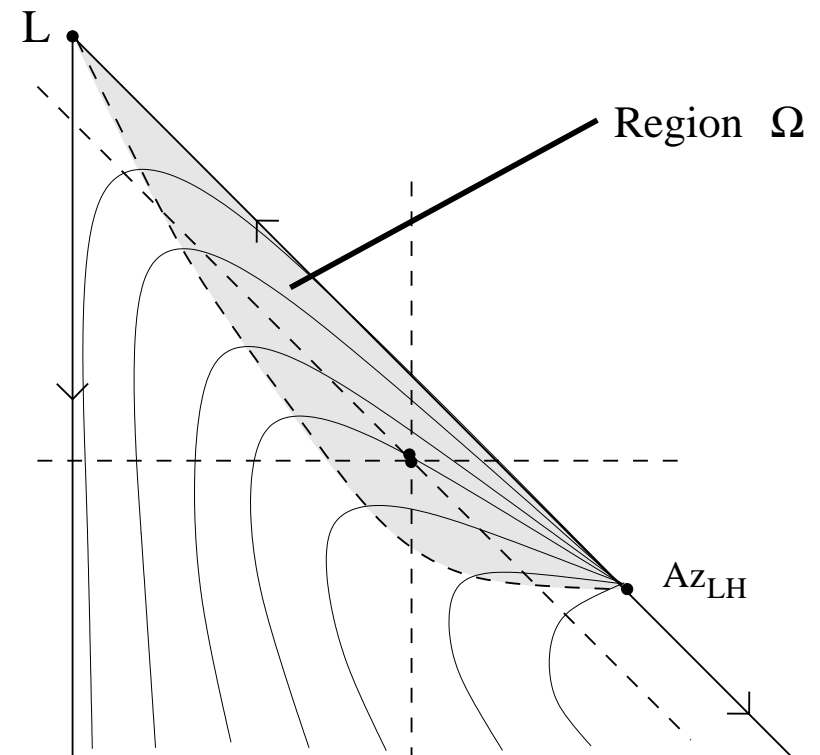
Residue Curve Maps

Evolution of liquid phase (residue) composition for a simple batch distillation



Prediction of Limit Cycles (Dorn 2000)

- 2 neighbouring saddles in residue curve diagram
- Non-monotonous in all three components
- Distillate composition must lie within Ω -region



Status Quo

Mixtures:

- Acetone - Benzene - Heptane
- Methanol - Methylbutyrate - Toluene
(→ Experimental Validation of Multiple Steady States)

Models used:

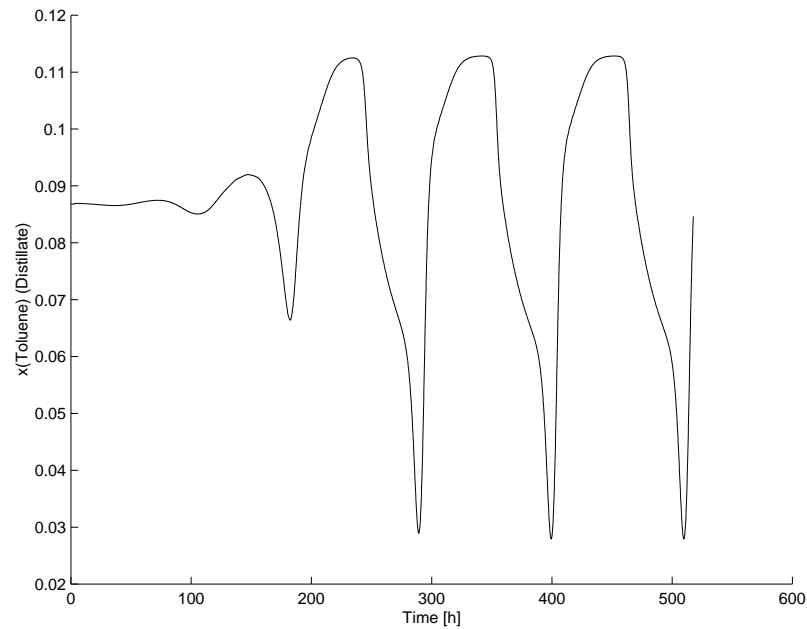
- Detailed investigations with CMO
- Validation with ASPEN Dynamics

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Oscillations

We want to measure oscillations:



Measurement of Oscillations

Measurement:

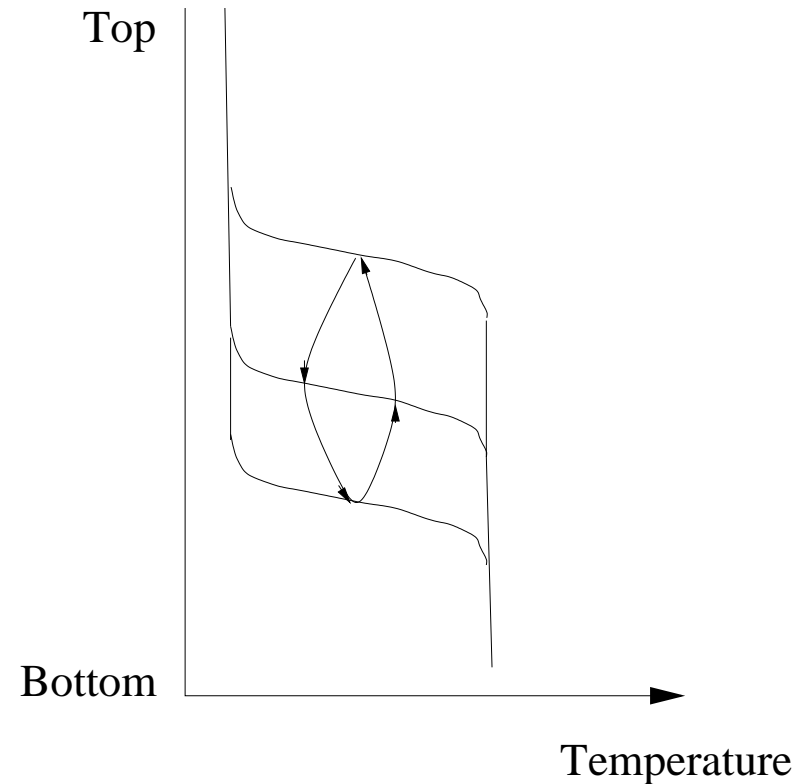
- Amplitude
- Period of oscillations

Measurement of Oscillations

Measurement:

- Amplitude
- Period of oscillations

Amplitude is not a problem:

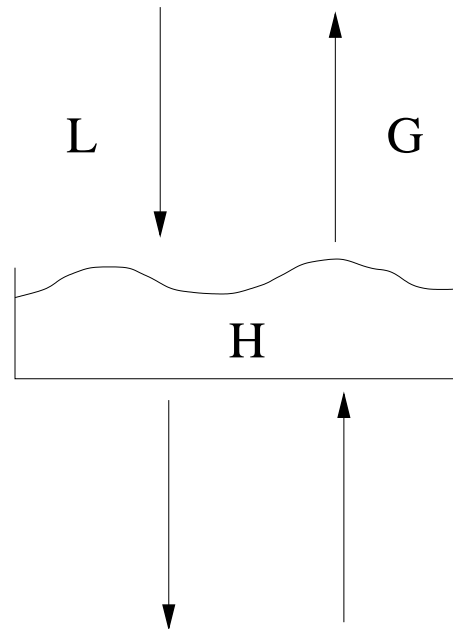


Characteristic Time of Plate Columns

$$\tau_{osc} = \mathcal{F} (\text{Design, Operating Parameter, Thermodynamics})$$

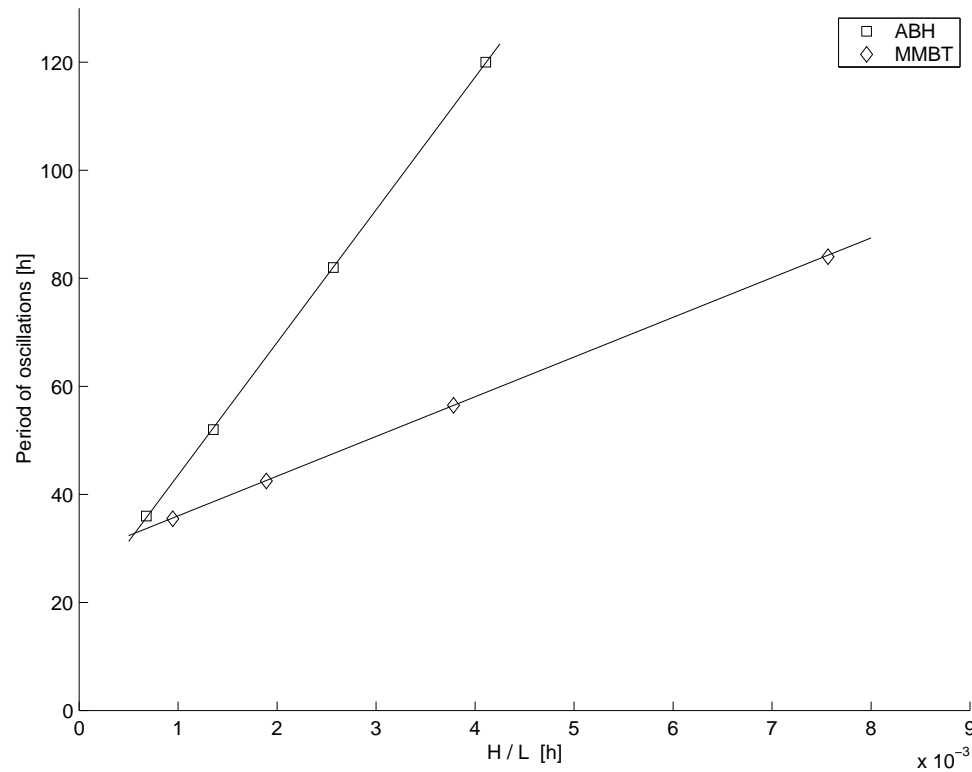
Characteristic Time of Plate Columns

$$\tau_{osc} = \mathcal{F} (\text{Design, Operating Parameter, Thermodynamics}) \\ = \mathcal{G} \cdot \frac{H}{L}$$



Characteristic Time of Plate Columns

Validation through simulation upon two systems



Holdup in Packed Columns

Holdup in a packed column:

$$\frac{H}{A} \sim u^{\frac{1}{3}} = \left(\frac{L}{\rho_L A} \right)^{\frac{1}{3}}$$

Therefore:

$$\tau_{osc} \sim \frac{H/A}{L/A} \sim \left(\frac{L}{A} \right)^{-\frac{2}{3}}$$

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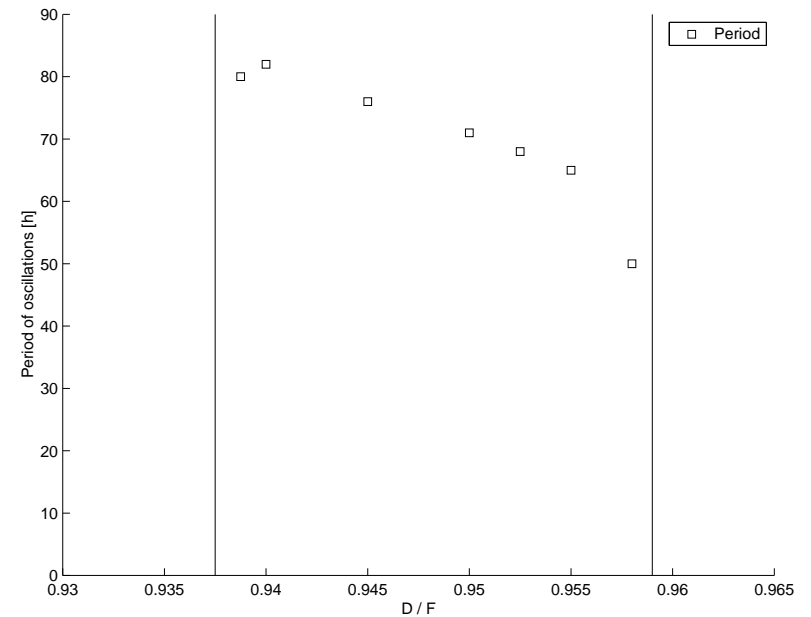
Conclusion:

- Operate at highest possible reflux.

Dependence on Distillate Flow Rate

Effects:

- Nonlinear
- Decreases at limits of oscillation
- Weak dependence in the middle



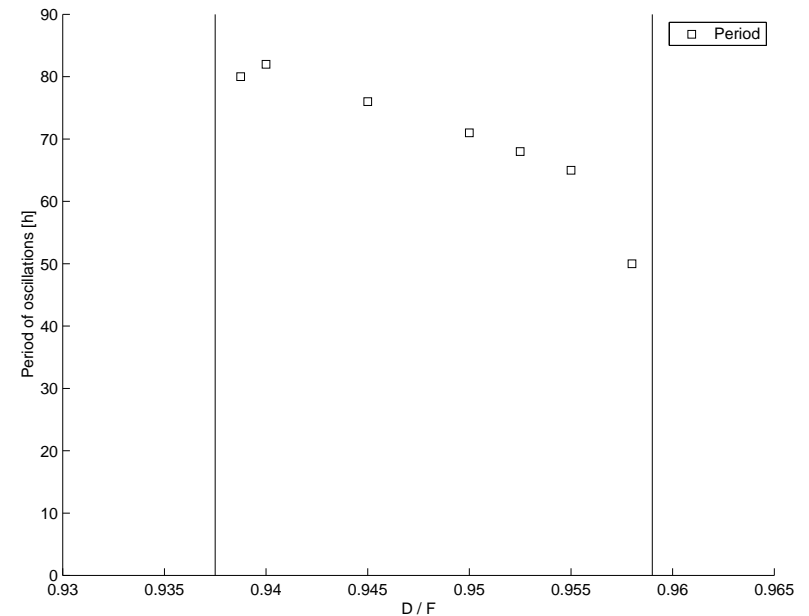
Dependence on Distillate Flow Rate

Effects:

- Nonlinear
- Decreases at limits of oscillation
- Weak dependence in the middle

Conclusion:

- Cannot be exploited to reduce time of oscillations.



Summary of Influences on τ_{osc}

Effects:

- Strong dependence on holdup/reflux
- Weak dependence on distillate flow rate
- No effect of feed tray position
- Weak dependence on feed composition

Conclusion:

- Period of oscillations is very high and cannot be reduced as desired for the given system.

Screening for a new System

Another system might have a smaller period of oscillation

Requirements:

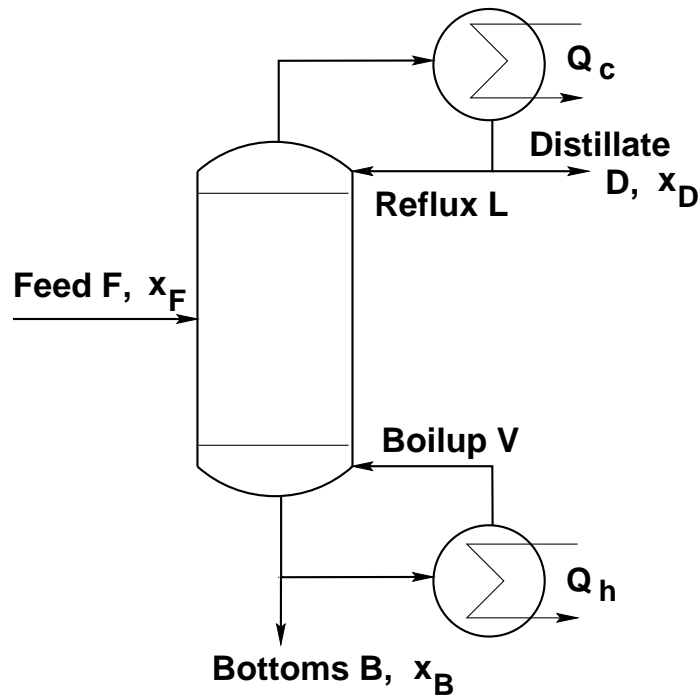
- No reactions between the components
- Harmless components (toxicity, acidity, flammability)
- Ease of separation
- Big Ω -region \rightarrow low sensitivity to operating conditions

Systematic screening of a database with about 50 components was not successful.

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Distillation Column



Design:

- Tray or packed column
- Number of Stages (N_S)
- Reboiler and condenser

Influence of Holdup

Phenomenon:

- Oscillations disappear if holdup in reboiler or condenser becomes much higher than on stages

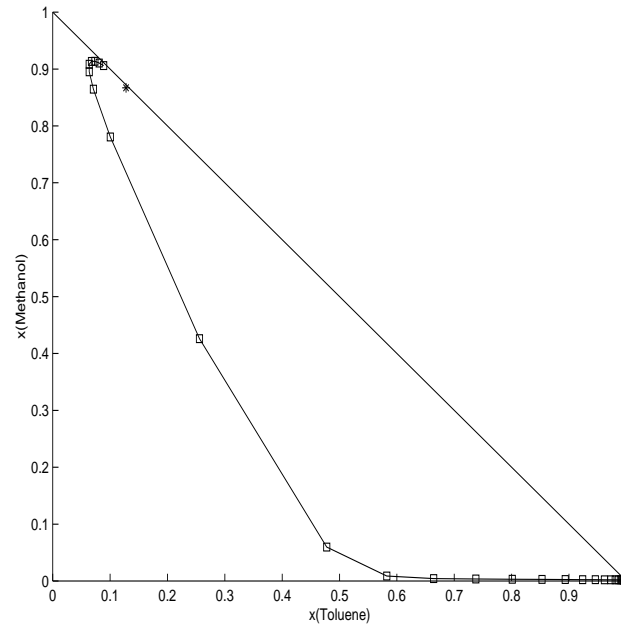
Ratio of Interest:

- $\frac{H_{Cond}}{H_S}$ and $\frac{H_{Reb}}{H_S}$

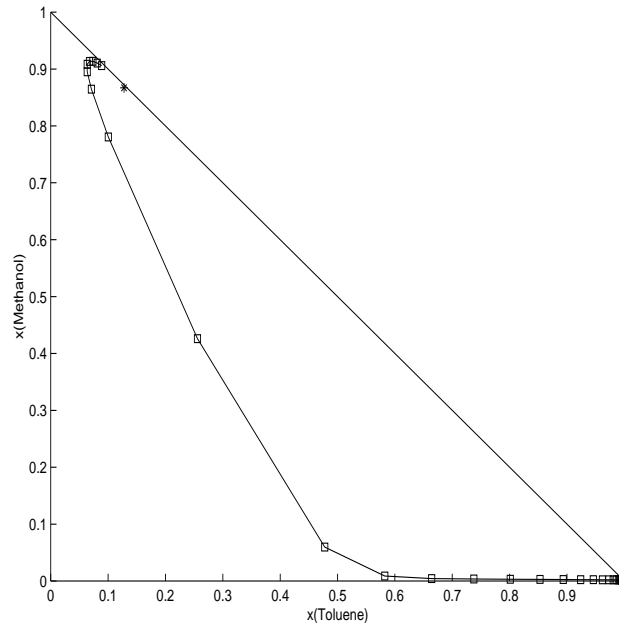
Critical Values:

- $H_{Cond}^c = 10 H_S$ (ASPEN) to $50 H_S$ (CMO)
- $H_{Reb}^c = f(N_S) \geq H_{Cond}^c$

Influence of Holdup



Influence of Holdup



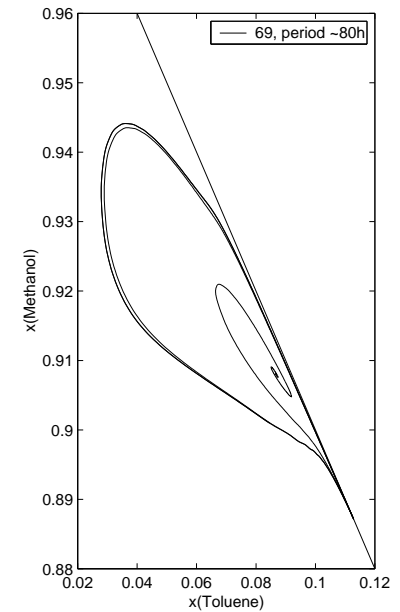
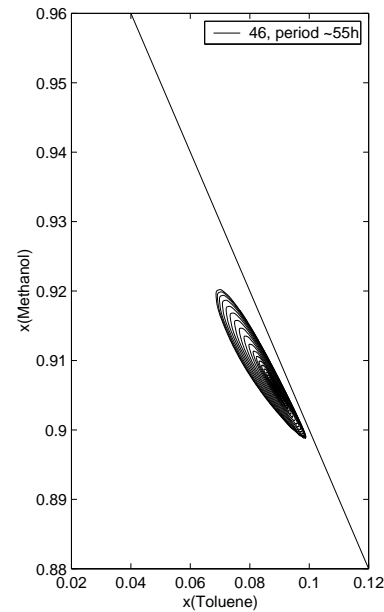
Conclusion:

- Reflux drum as small as possible
- Additional stages favourable
- Keep reboiler holdup small

Influence of N_S

When increasing N_S :

- τ_{osc} longer
- Limit cycle behaviour reached quicker



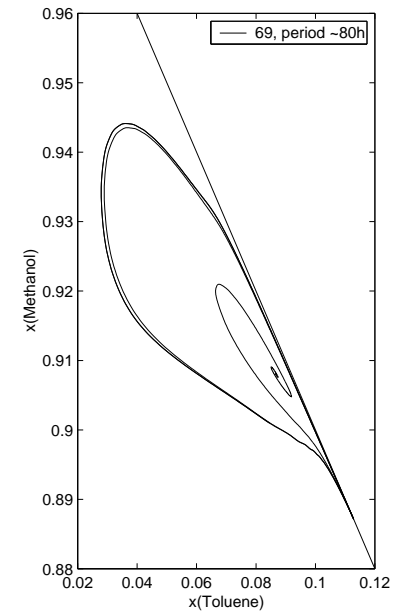
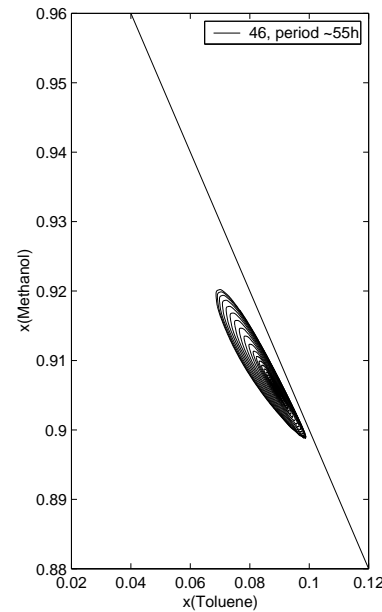
Influence of N_S

When increasing N_S :

- τ_{osc} longer
- Limit cycle behaviour reached quicker

Conclusion:

- Optimum must be found



A Rate based Approach

Change to a rate based model, RateFrac:

- Heat transfer
- Mass transfer

Motivation:

- Validation of our column design
- Retrieve efficiencies which can be used in dynamic simulations with a simpler model

RateFrac / Results

Results:

- Practically sensible Size around 3m
- Height of a theoretical stage $\sim 8\text{cm}$
- $\frac{H}{L} < 10^{-3}\text{h}$ for MMBT, thus $\tau_{osc} \sim 30\text{h}$

Disadvantages:

- No validation with dynamic simulation possible

Suggested Experimental Setup

- Mixture MMBT: $x_{Meth} = 0.8671$, $x_{Tol} = 0.1279$
- Feed flow rate 1 kg/h
- Packing: Sulzer DX, height 3.5m, diameter 0.1m
- Condenser as small as possible
- $\frac{L}{F} = 20$
- $\frac{D}{F} \sim 95.5$
- Temperature measurements 0.25 -1.75m from top
- Expected period of oscillation: 30h

Conclusions

- Experimental validation rather hard
 - Very high τ_{osc}
- More checks are necessary before the experimental validation

