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Reactive distillation for selectivity improvement in the transesterification of dimethyl carbonate

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Introduction

Motivation

Process intensification with reactive distillation (RD)

Benefits
- Higher conversion of reactants
- In-situ heat integration
- Lower investment costs
- Avoidance of azeotropes
- Reduced formation of by-products
- Improved selectivity

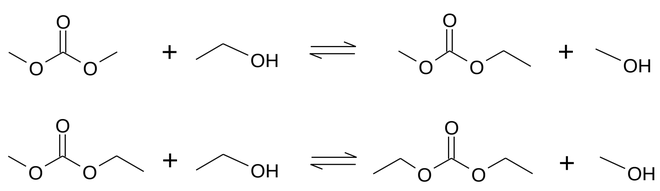
Drawbacks
- Volatility constraints
- Difficult scale-up
- Reduced degree of freedoms
- Higher design complexity

Most of the published papers about RD have been focused on chemical systems with **one main reaction**.

Is it possible to simultaneously improve yield and selectivity in **multiple main reaction** systems by reactive distillation?

Chemical system

The transesterification of dimethyl carbonate (DMC) with ethanol (EtOH) to produce ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) using RD offers an opportunity to enhance the selectivity of reaction:



- Only theoretical investigations published
- No suitable heterogeneous catalyst found yet
- In this work sodium ethoxide ($C_2H_5O^-Na^+$) was selected as a homogeneous catalyst

Tab. 1: Boiling points of pure components and azeotropes at p=1 atm

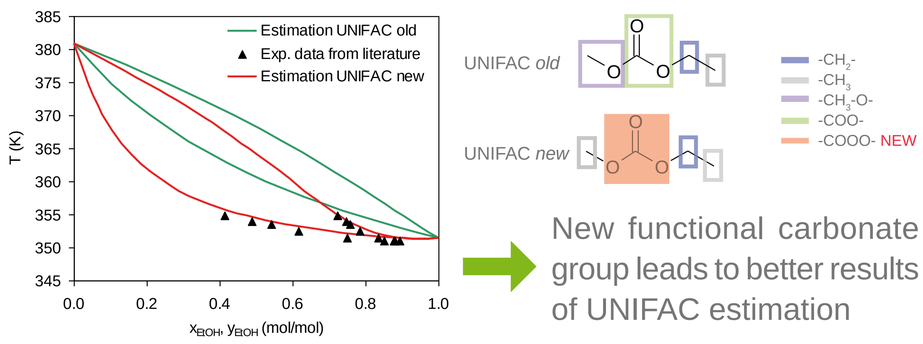
Comp.	T_b (°C)
MeOH-DMC	63.80
MeOH	64.70
EtOH-EMC	74.90
DMC-EtOH	77.80
EtOH	78.29
DMC	90.25
EMC	107.69
DEC	126.80

→ Theoretical and experimental investigation of homogeneously catalysed transesterification of DMC in a RD column

Modelling

Thermodynamic data

- Component EMC not available in the database of Aspen Properties Plus® and few experimental data published
  → Estimation of pure component data with different group contribution methods
- Calculation of activity coefficients with the UNIQUAC model
- Vapour-liquid equilibria of binaries including EMC estimated with the UNIFAC approach
  * New functional group -COOO- was used[1)]
  * Quality of estimation was checked for the system EtOH-EMC



→ New functional carbonate group leads to better results of UNIFAC estimation

Fig. 1: Comparison of estimated VLE data for EtOH-EMC (p=1 atm)

1) *Luo et al., Fluid Phase Equilibria, 175, 91–105, 2000.*

Kinetics

- Fast reaction: Chemical equilibrium is reached after a few minutes (e.g.: 6 min at T=70 °C, w_{Cat}=0.05 %)
- Equilibrium constants: K_{reac1}=1.7 and K_{reac2}=0.4

Residence time distribution (RTD)

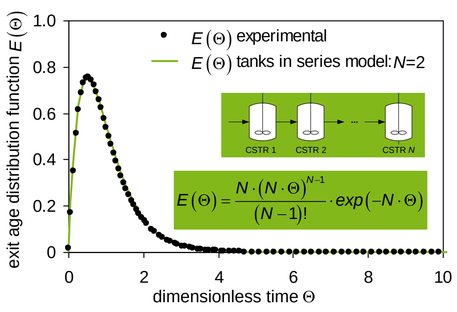


Fig. 2: RTD of distributor

- Reaction in liquid holdup of distributors
- Step experiment to evaluate RTD of distributors
- Tanks in series model: N=2

→ Distributors behave like an ideal CSTR

Non-equilibrium stage model

- Simulation environment: Aspen Custom Modeler®
- Multicomponent mass and heat transfer
- Hydrodynamics of packings considered

Experimental Model Validation

Experimental Setup

The transesterification of DMC was investigated in a pilot plant column DN50 (Fig. 3):
- Nominal diameter: 50 mm
- Packing height: 5.4 m
- Continuously operated
- Process control system SIMATIC PCS7
- Total feed rate: 4 kg/h

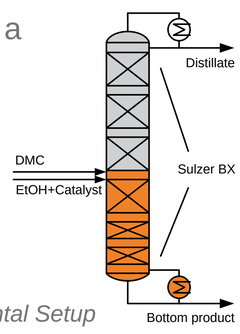


Fig. 3: Experimental Setup

Results I

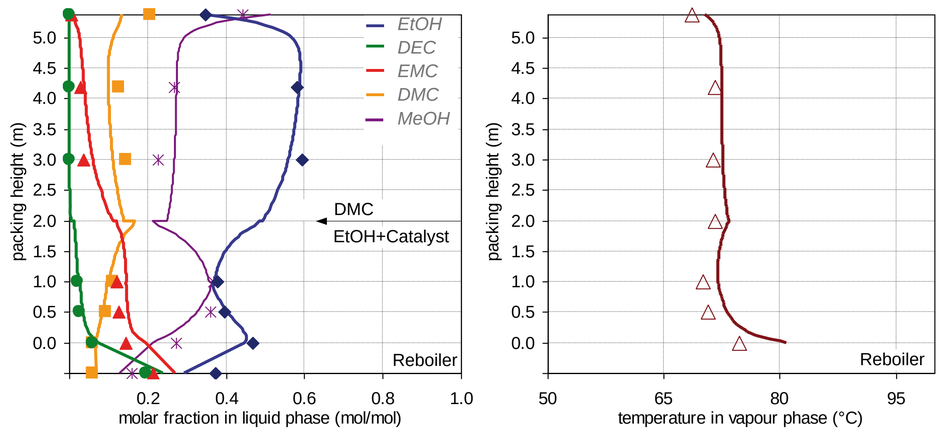


Fig. 4: Reflux ratio = 1, destillate to feed ratio = 0.40 kg/kg, n_{EtOH}/n_{DMC} = 1.95;

Results II

- No isolation between last packing section and reboiler
  → Higher content of low boilers in the reboiler
- Comparison of simulated and experimental selectivities

Selectivity	EXP	SIM
EMC	52.7	53.5
DEC	47.3	45.5

Satisfactory agreement

Future work

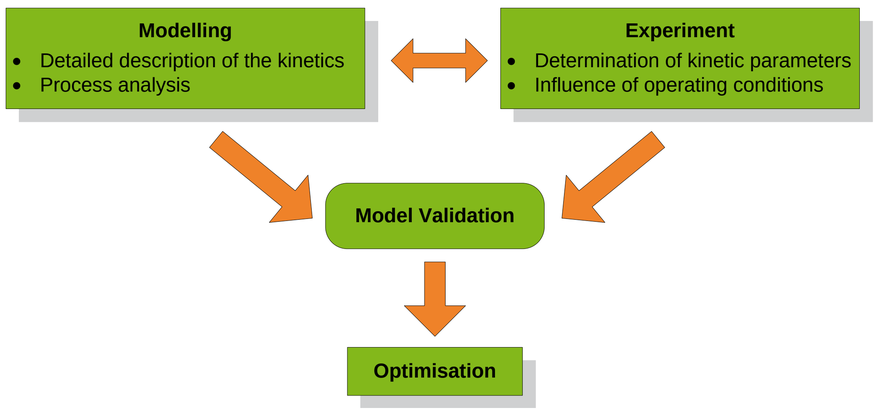


Fig. 5: RD column DN50

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