Batch or continuous esterification?

Understanding key phenomena to improve industrial processes

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INTRODUCTION

General characteristics of esterifications:

- Generally slow reactions,
- Extent is limited by chemical equilibrium,
- Almost athermic reactions.

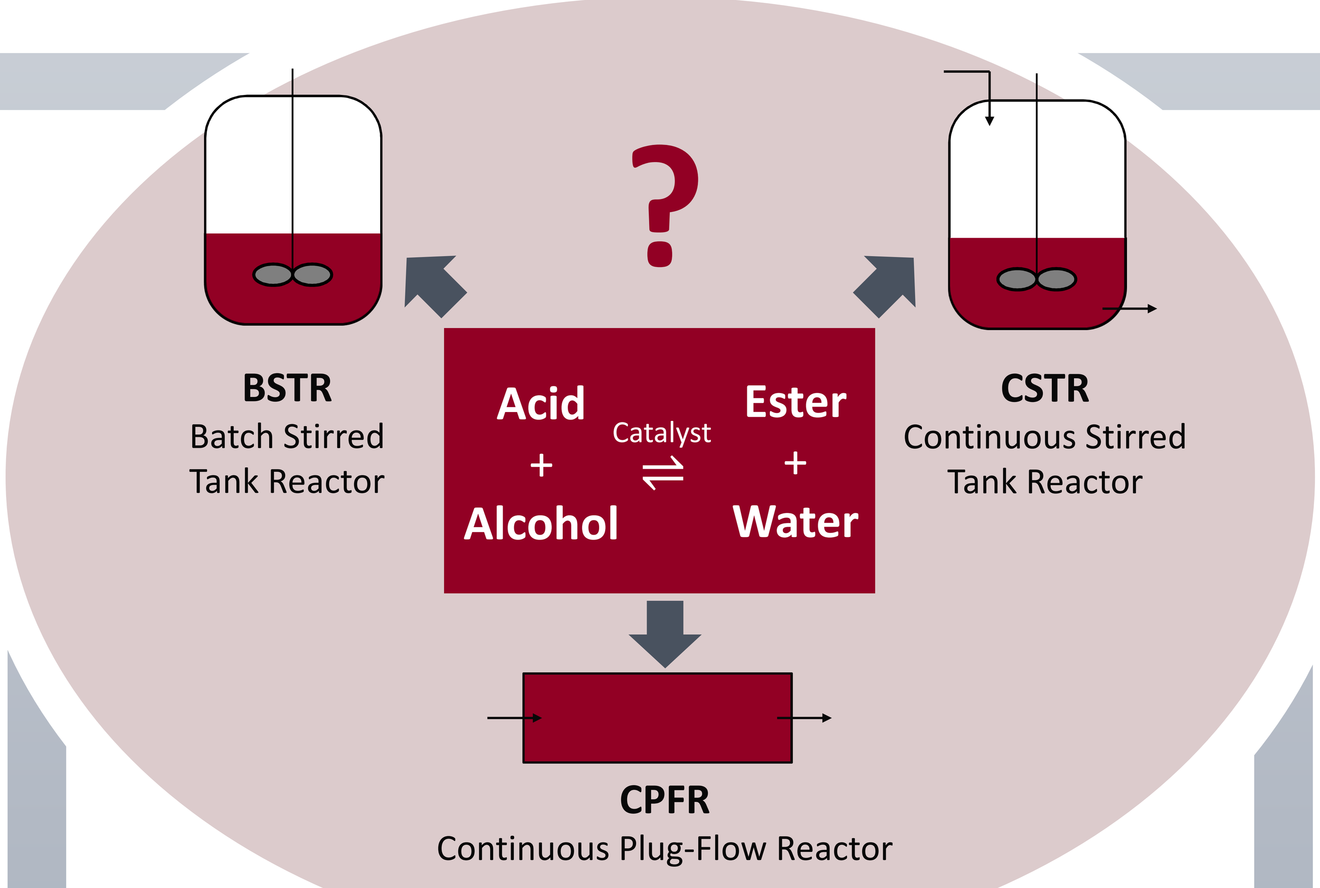
Consequences on process design

- Is there any benefit to expect by switching from batch to continuous?
- How to select the best process configuration?

METHODOLOGY

Chemical reactions → Reaction modelling → Simulation of reactors → Performance comparison

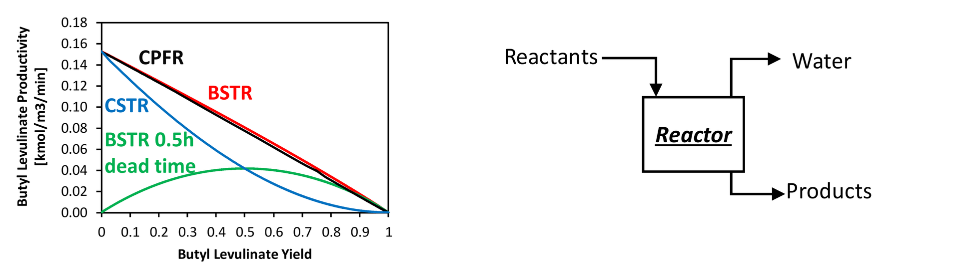
Performance indicator	Unit	Batch reactor	Continuous reactor
Productivity	$\frac{mol}{min\ m^3}$	$\frac{\text{Moles of ester produced}}{\text{Reactor Volume} \cdot (\text{Reaction Time} + \text{Dead Time})}$	$\frac{\text{Produced Ester Molar flow rate}}{\text{Reactor Volume}}$
Ester Yield	–	$\frac{\text{Moles of Ester produced}}{\text{Moles of starting Acid}}$	$\frac{\text{Produced Ester Molar flow rate}}{\text{Acid feed Molar flow rate}}$
Ester Selectivity	–	$\frac{\text{Moles of Ester produced}}{\text{Moles of reacted Acid}}$	$\frac{\text{Produced Ester Molar flow rate}}{\text{Reacted Acid Molar flow rate}}$
Acid Conversion	–	$\frac{\text{Moles of reacted Acid}}{\text{Moles of starting Acid}}$	$\frac{\text{Reacted Acid Molar flow rate}}{\text{Acid feed molar flow rate}}$



BYPASSING THE CHEMICAL EQUILIBRIUM

Goal: to maximize reactor productivity and ester yield

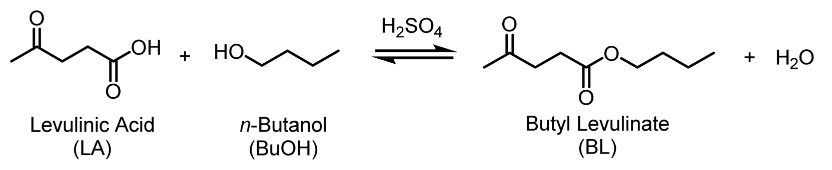
Water vaporization to bypass equilibrium



- No change in reactor performance ranking compared to chemical equilibrium limited case

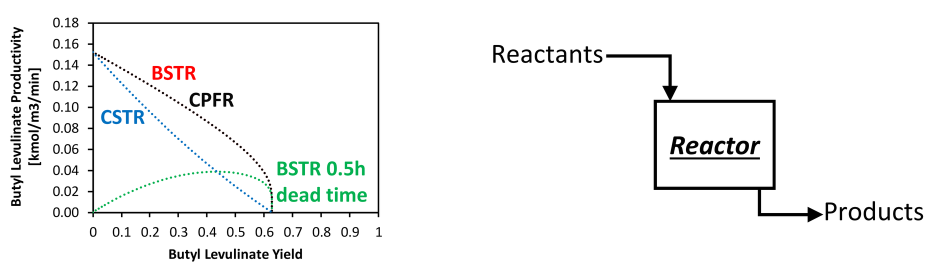
Chemical equilibrium limitation

Esterification of levulinic acid with *n*-butanol to butyl levulinate



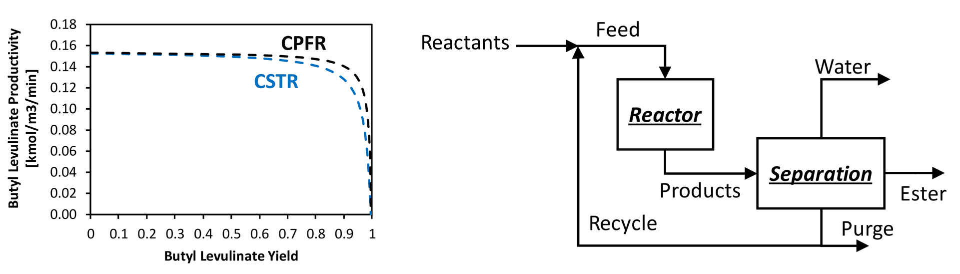
Nr	Reaction	$\ln(k_0\ [(m^3)^2\ kmol^{-2}\ s^{-2}])$	E_a [kJ mol^{-1}]
1	$LA + BuOH \rightarrow BL + H_2O$	12.564	54.275
2	$BL + H_2O \rightarrow LA + BuOH$	9.636	48.431

Data from: H. Bart, J. Reidetschläger, K. Schatka, A. Lehmann; *Ind. Eng. Chem. Res.* **1994**, *33*, 21. Calculations done by Ypso-Facto.



- BSTR without dead time or CPFR more performant than CSTR
- Dead time significantly decreases BSTR performance

Separation and recycle of unconverted reactants



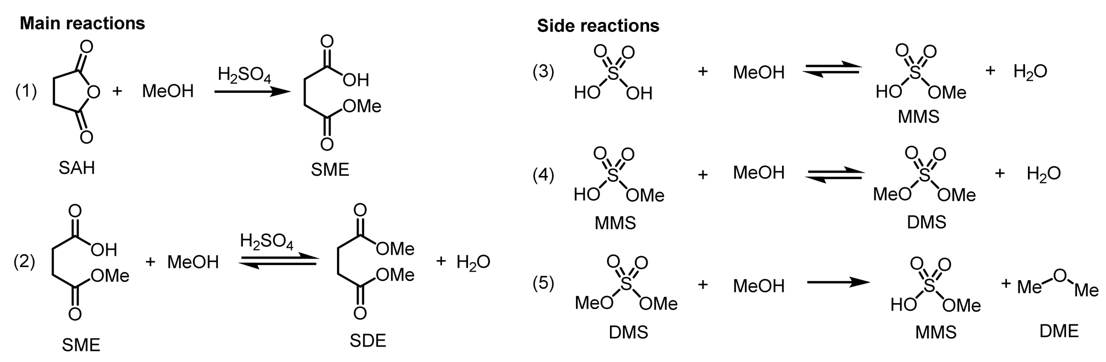
- Continuous process solutions can be more performant than BSTR with water vaporization thanks to recycle of unconverted reactants.

HANDLING SIDE REACTIONS

Goal: to minimize impurity formation

Esterification of phthalic anhydride and methanol to dimethyl succinate

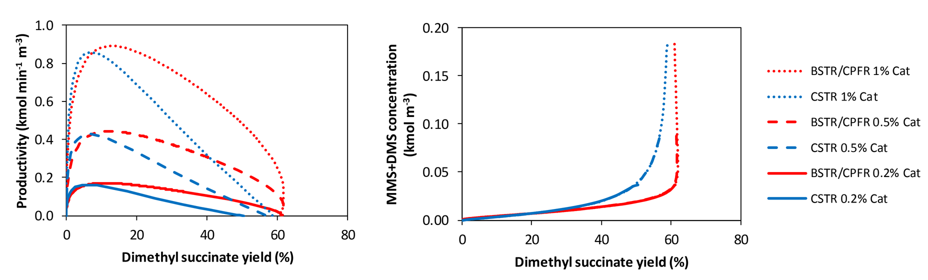
Possible side reactions leading to degradation of sulfuric acid catalyst into toxic byproducts



Nr	Reaction	Kinetic constant at 65 °C	Equilibrium constant at 65 °C
1	$SAH + MeOH \rightarrow SME$	$k_1 = 3.63\times10^{-2}\ L^2\ mol^{-2}\ s^{-1}$	–
2	$SME + MeOH \rightleftharpoons SDE + H_2O$	$k_2 = 2.97\times10^{-3}\ L^2\ mol^{-2}\ s^{-1}$	$K_{eq,2} = 2.73$
3	$H_2SO_4 + MeOH \rightleftharpoons MMS + H_2O$	$k_3 = 6.5\times10^{-5}\ L\ mol^{-1}\ s^{-1}$	$K_{eq,3} = 1000$
4	$MMS + MeOH \rightleftharpoons DMS + H_2O$	$k_4 = 4.9\times10^{-9}\ L\ mol^{-1}\ s^{-1}$	$K_{eq,4} = 3.77\times10^{-5}$
5	$DMS + MeOH \rightarrow MMS + DME$	$k_5 = 3.1\times10^{-5}\ L\ mol^{-1}\ s^{-1}$	–

Data from: H. J. Bart, J. Reidetschläger, K. Schatka, A. Lehmann; *Int. J. Chem. Kin.* **1994**, *26*, 1013. J. P. Guzowski, E. J. Delaney, M. J. Humora, E. Irdam, W. F. Kiesman, A. Kwok, A. D. Moran; *Org. Proc. Res. Dev.* **2012**, *16*, 232. Calculations done by Ypso-Facto.

BSTR or CPFR better than CSTR



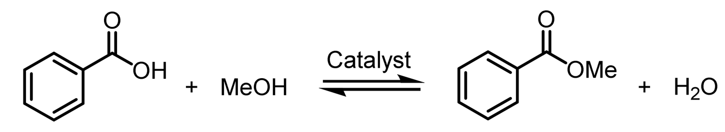
- At equal yields, the CSTR leads to higher impurity concentrations in the reaction mixture than BSTR or CPFR.

→ BSTR/CPFR should be preferred to reduce impurity formation.

DEALING WITH PHYSICAL PHENOMENA

Goal: to improve process robustness

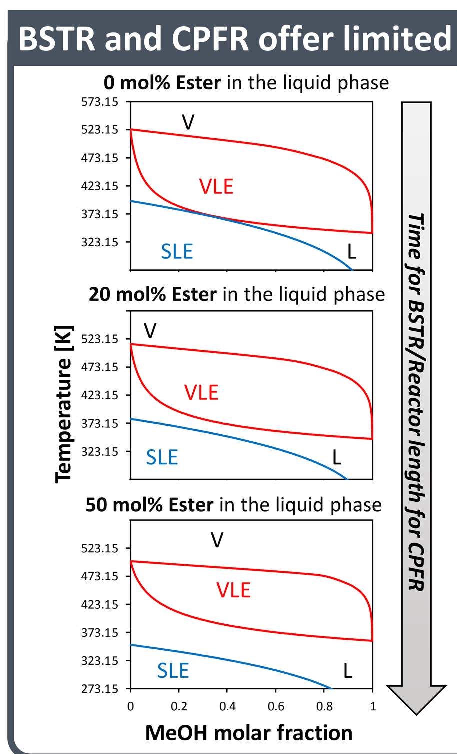
Esterification of benzoic acid with methanol to methyl benzoate



When carboxylic acids have high melting points, their solubility in the reaction mixture can be limited at some compositions. Their dissolution can impact the reaction performance.

→ How to run the reaction in fully **homogeneous conditions** to improve the performances without adding a solvent?

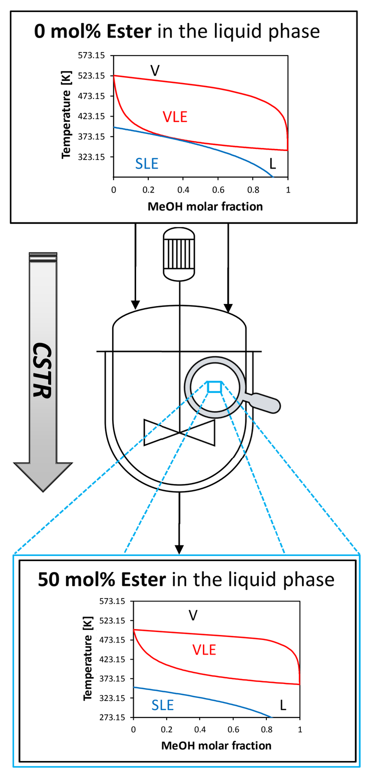
BSTR and CPFR offer limited options



- Composition and temperature evolve over time in a BSTR and reactor length in a CPFR.
- To obtain homogenous liquid phase conditions, excess alcohol must be added or the reaction performed in the ester as "solvent".
- A good operating window to keep the system away from heterogeneous regions can be difficult to realize.

Benefit of using a CSTR

- Concentrations and temperature in a CSTR are the same inside all the reacting volume.
- Conditions inside the reactor are identical to the ones at the reactor outlet.
- So, even if the CSTR feed is a solid-liquid mixture, fully homogeneous liquid conditions are reached instantaneously in the reactor.



Data obtained from: NIST Chemistry Webbook (http://webbook.nist.gov/chemistry/). Calculations done by Ypso-Facto assuming ideal behavior of the mixture.

INDUSTRIAL CASE STUDIES

Direct esterification

- Manufacturing of an ester used as chemical intermediate and ingredient in pharma, cosmetics and flavors
- Established process with more than 40 years of continuous improvements
- Customer wanted to switch production from batch to continuous

Benefits from going continuous

CSTR overcomes solubility issues and provides fully homogeneous operating conditions

- >35% reduction of alcohol and steam consumption
- 25% reduction of wastes

More literature on the switch from batch to continuous processes in the context of the fine chemical, pharma and biopharma industries: R.-M. Nicoud, *Chemistry Today* **2016**, *34(4)*, 38 and R.-M. Nicoud, *Chemistry Today* **2016**, *34(5)*, 33.

Transesterification

- Manufacturing of two esters used in cosmetics and flavors
- The processes are carried out in fully homogeneous liquid phase
- Customer wanted to switch production from batch to continuous

No benefits from going continuous

There was no intrinsic advantage of going to continuous processes, as the continuous process would reach essentially the same performances as the existing batch processes.

CONCLUSION

- In most situations, for a given ester yield the productivity of a CSTR is lower than the one of a BSTR without dead time and a CPFR.
- As the productivity of a real BSTR depends heavily on its dead time, one of the continuous reactors may be the most performant solution.
- Considering impurity formation, BSTR without dead time and CPFR remain generally more performant than a CSTR.
- A CSTR can be advantageous to assure fully homogeneous conditions that are difficult to achieve in BSTR and CPFR.

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