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~~METHANOL SYNTHESIS EXPERIMENTS ?~~

METHANOL SYNTHESIS – LIQUID PHASE REACTION DEVELOPMENT

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LENS CHEMICAL TECHNOLOGY

Block diagram – Power to X context

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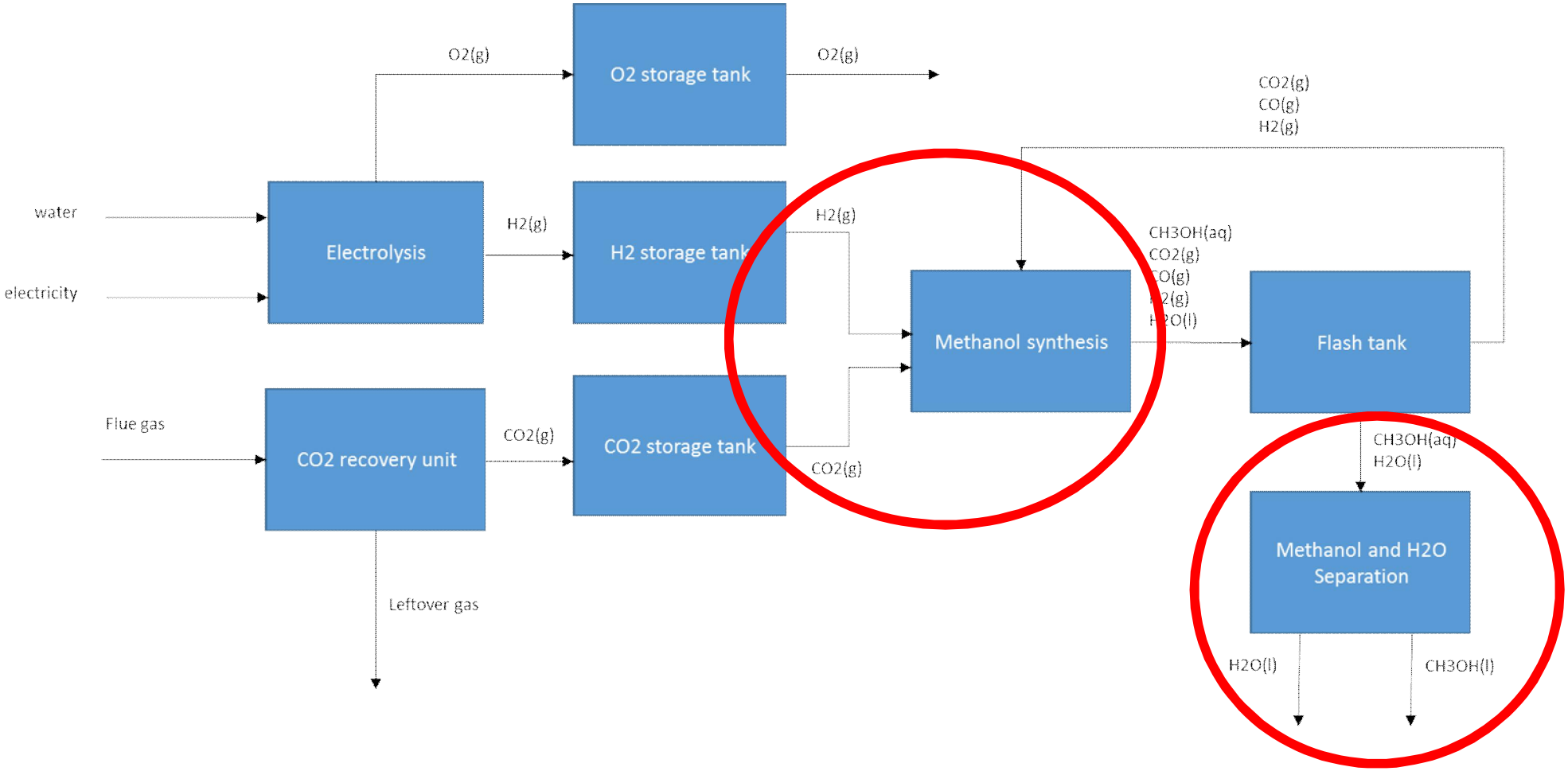

Motivation for Methanol synthesis study

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- Current gas phase synthesis routes:
  high pressure 30-100 bar
  high temperature 200-300 °C

- Milder conditions ? Lower investment costs ?

- Liquid phase reaction enabling to change equilibrium towards product side ?

Methanol synthesis (net reactions)

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Hydrogenation of carbon dioxide into formic acid

$$CO_2 + H_2 \rightleftarrows HCOOH \quad (1)$$

Reactions of formic acid with alcohol producing formiate

$$HCOOH + R - OH \rightleftarrows HCOOR + \boldsymbol{H_2O} \quad (2)$$

Hydrogenation of formiate, forming methanol and alcohol

$$HCOOR + 2\,H_2 \rightleftarrows \boldsymbol{CH_3OH} + \boldsymbol{R - OH} \quad (3)$$

Equilibrium based reactions:

- Removal of water
- Removal of product (methanol)

could improve production

Methanol synthesis (net reactions)

Alcohols used as liquid phase:

- alcohol promoted reaction where alcohols can be e.g.

CH_3OH,
C_3H_7OH,

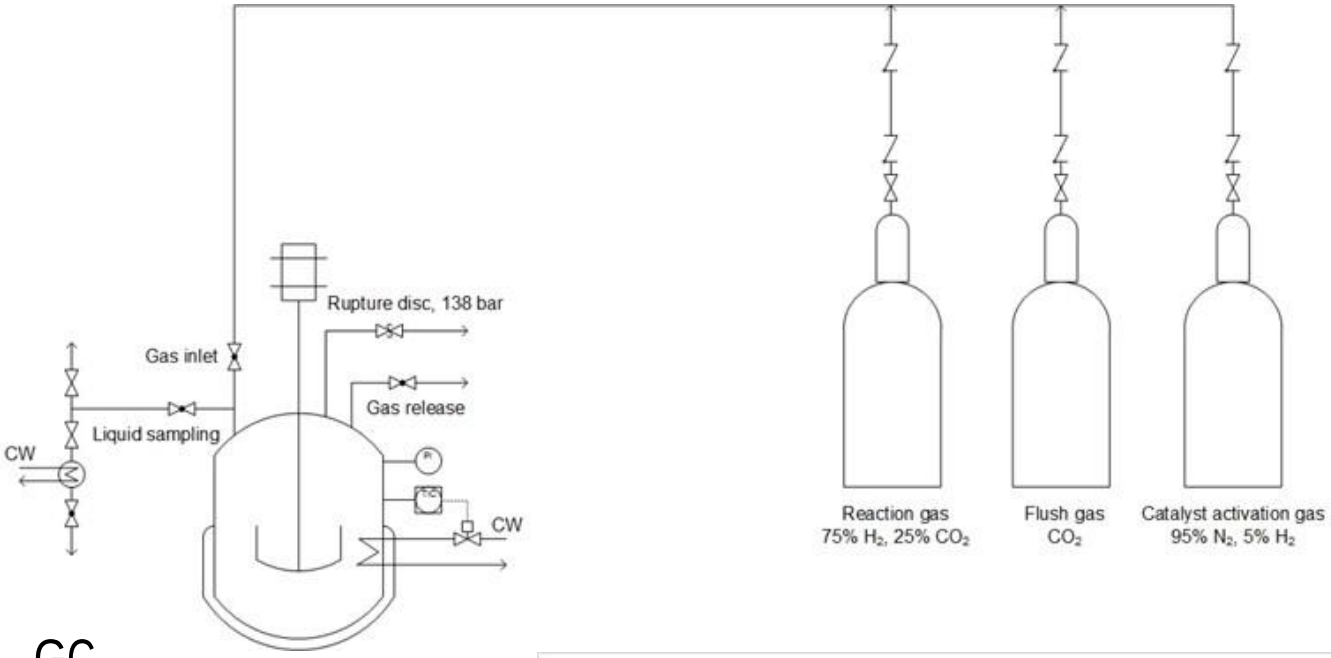
$\boldsymbol{C_2H_5OH}$/$\boldsymbol{C_4H_9OH}$(2-butanol) ***In this study***

$C_5H_{11}OH$

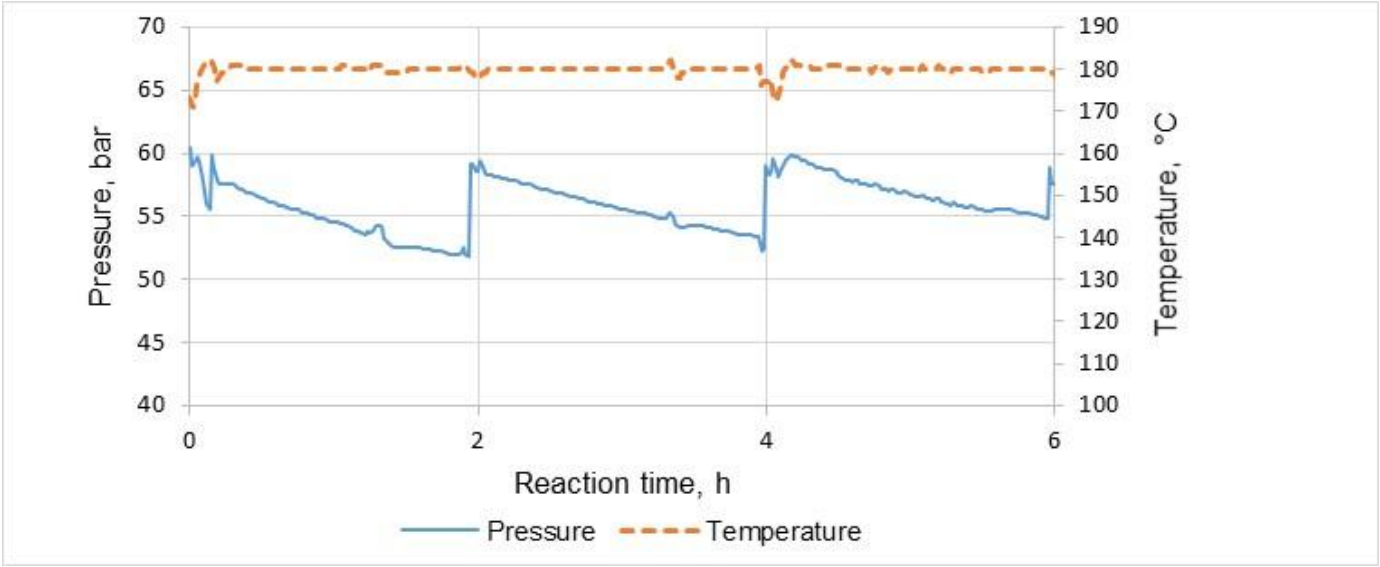
Catalyst: Commercial Cu/ZnO (63.5 % CuO, 24.7 % ZnO, 10.1 Al_2O_3,1.3 % MgO)

Side products: water (Reaction and RWGS)
ketone (acetaldehyde/butanone) from solvent decomposition
(no starting material consumption)

FED BATCH REACTION
Stoichiometric gas mixture in alcohol-catalyst liquid suspension

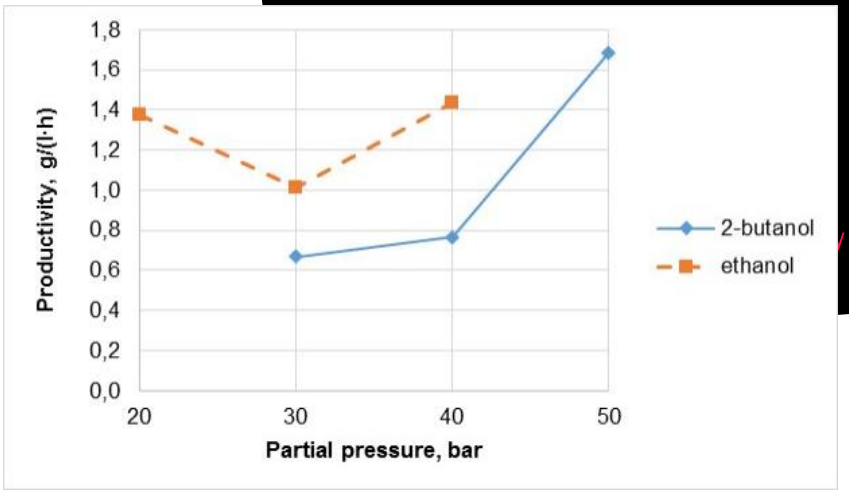


GC
-analysis

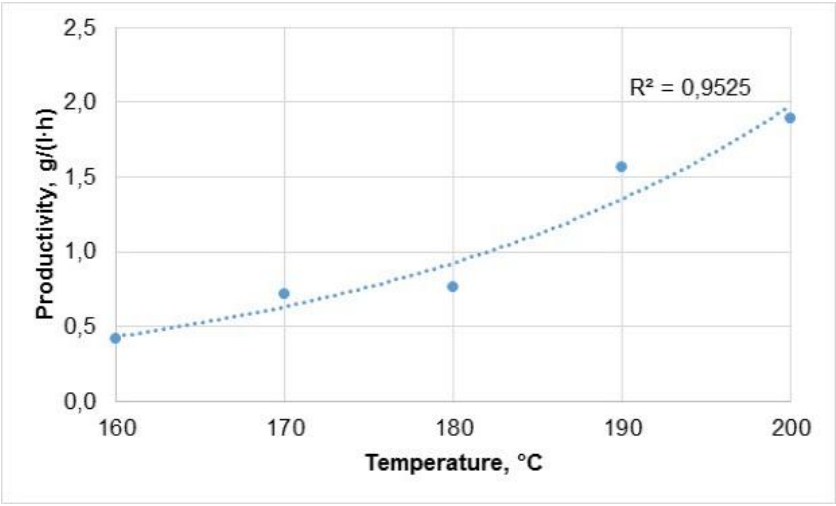


Methanol synthesis - Results

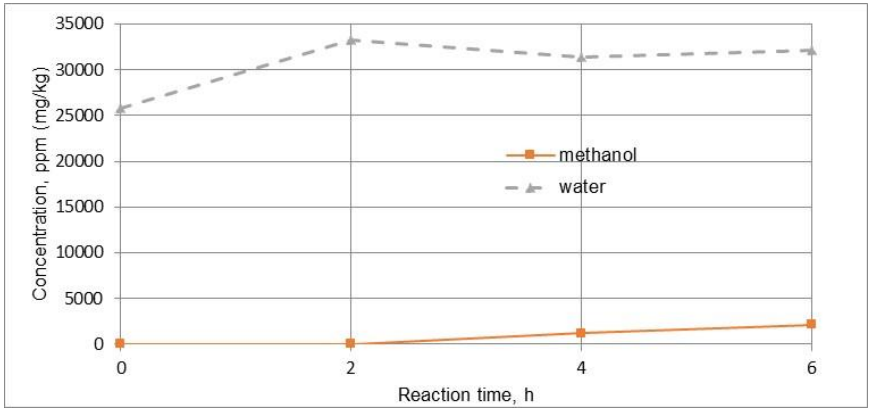
1) Effect of pressure: productivity increases

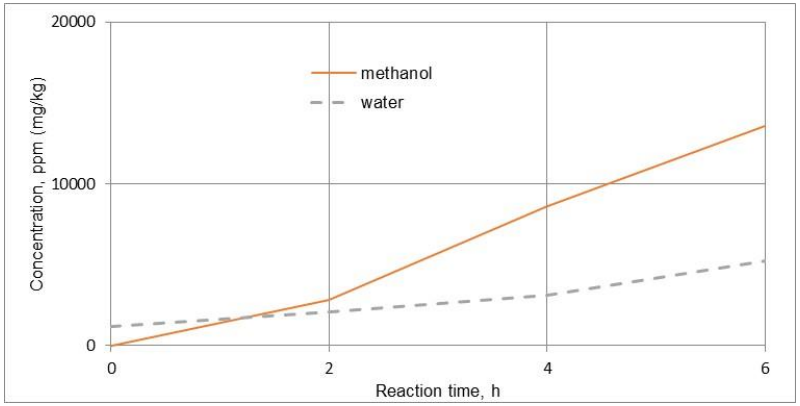


2) Effect of temperature: productivity increases, but water content also increases



3) Water: productivity decreases (water added/water removal) by **3Å molecular sieve**)





Methanol manufacturing: process development

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Kinetic model

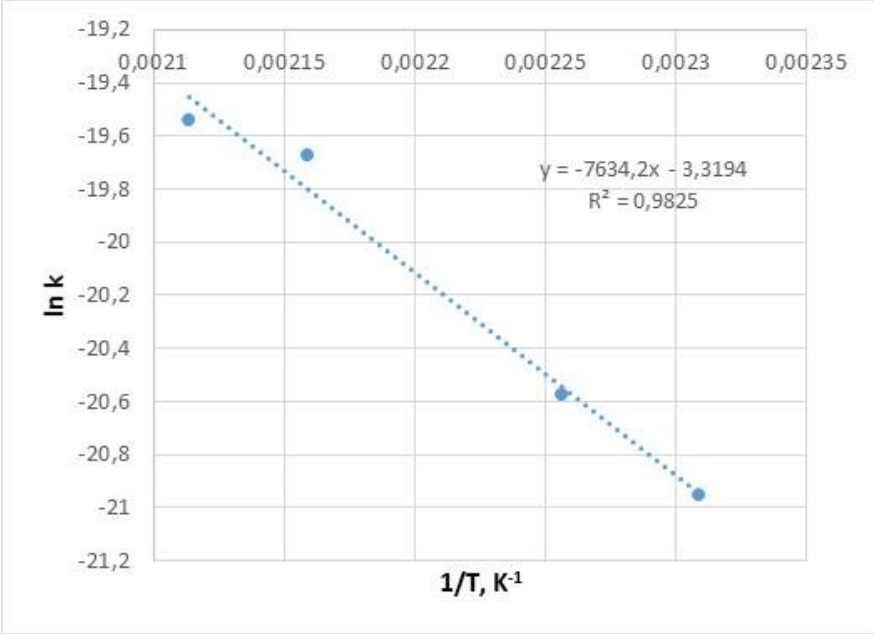
- Initial modeling to get idea of activation energies and reaction orders

- Determined from experimental data

$$r = \frac{-dc_{\mathrm{MeOH}}}{dt} = \frac{-dp_{\mathrm{CO_2+H_2}}}{dt} = k \cdot p^{m}_{\mathrm{CO_2+H_2}}$$

$$k = A \cdot e^{-E_a/RT}$$

=>



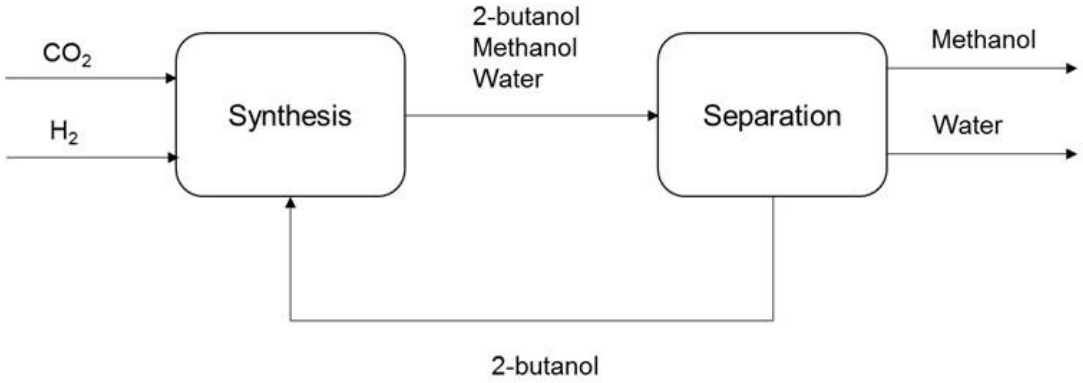
$$r = 1.82 \cdot 10^{-9} \cdot p^{1.89}_{\mathrm{CO_2+H_2}} \ \mathrm{mol/s}$$

$$A = 0.036\ bar^{1.89}$$

$$E_a = 63.5\ kJ/mol$$

Methanol manufacturing: process development

Process block diagram



- Separation step: Alcohol recycling and product recovery
- Initial design based on distillation: clear separation steps without azeotropes

Methanol manufacturing: process development

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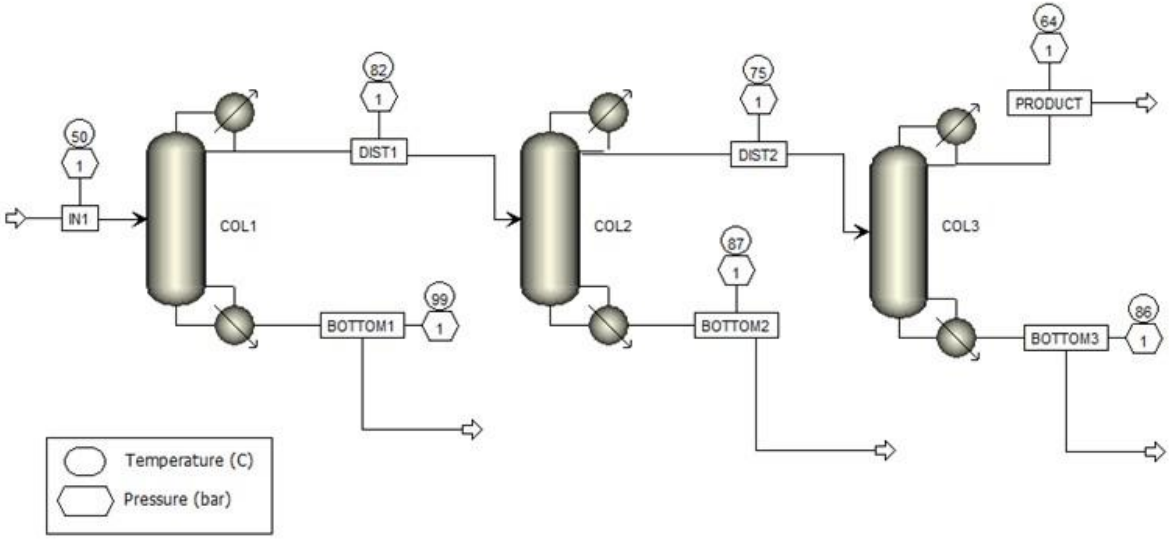
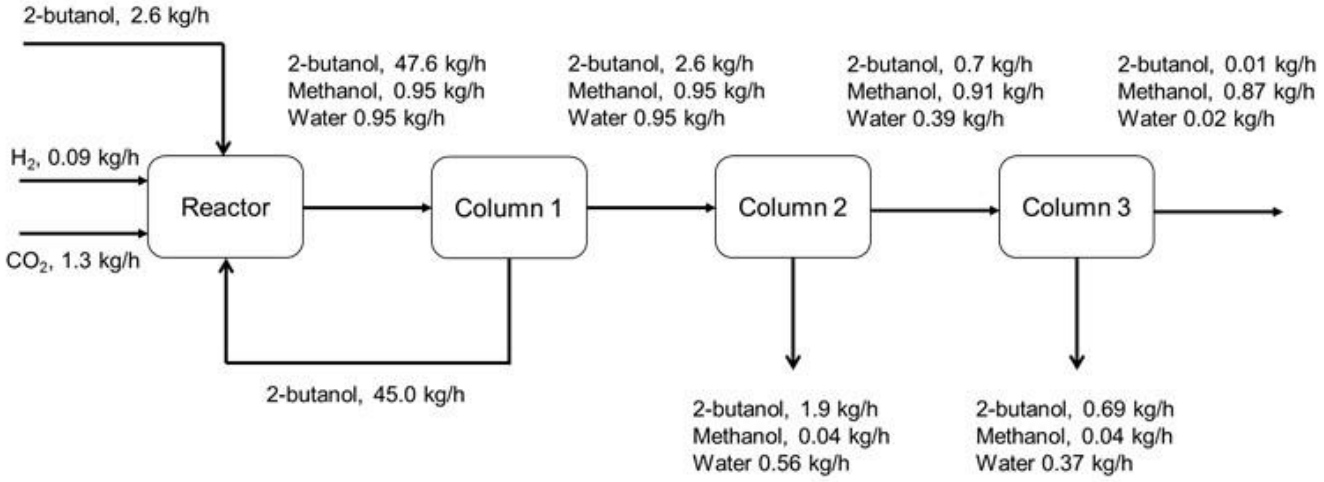
ASPEN+: Separation block

Design basis 1nm^3/h H_2





Three 1.5 m distillation columns, cooling duty 11 kW, product 97 w-%

SUMMARY

- LIQUID PHASE METHANOL REACTION CAN BE RUN IN RELATIVELY LOW CONDITIONS: T=180 °C, p = 40-50 bar, PRODUCTIVITY FOR CURRENT SET-UP QUITE LOW (2 g/Lh)

- MAY BE SUITABLE FOR SMALL SCALE PRODUCTION: FOR EACH 1 normal-m^3/h HYDROGEN PRODUCTION 21 kg/day (97 w-% purity)

- BETTER RESULTS WITH 2-BUTANOL COMPARED TO ETHANOL

- SOLVENT EXCHANGE MAY IMPROVE PROCESS (pressure+separation):
  2-BUTANOL (boiling point 100 °C, solubility in water 125 g/L 20 °C) vs.
  1-BUTANOL (boiling point 117 °C, solubility in water 0.07 g/L 20 °C)

- 1-BUTANOL: Low vapour pressure allows higher concentrations for CO_2 and H_2 (Better yields), easy separation due to low water solubility.

- **YIELD INCREASE AND CONTINUOUS PROCESS:** BY SIMULTANEOUS WATER REMOVAL AND SIMULTANEOUS METHANOL DISTILLATION DURING REACTION