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LGC CHEMICAL ENGINEERING

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Process Design and Heat Integration for the Power-to-Methanol Route

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Outline

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3. Results
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1. Introduction

Background: <u>Renewable Energy Storage with Liquid Fuels</u>

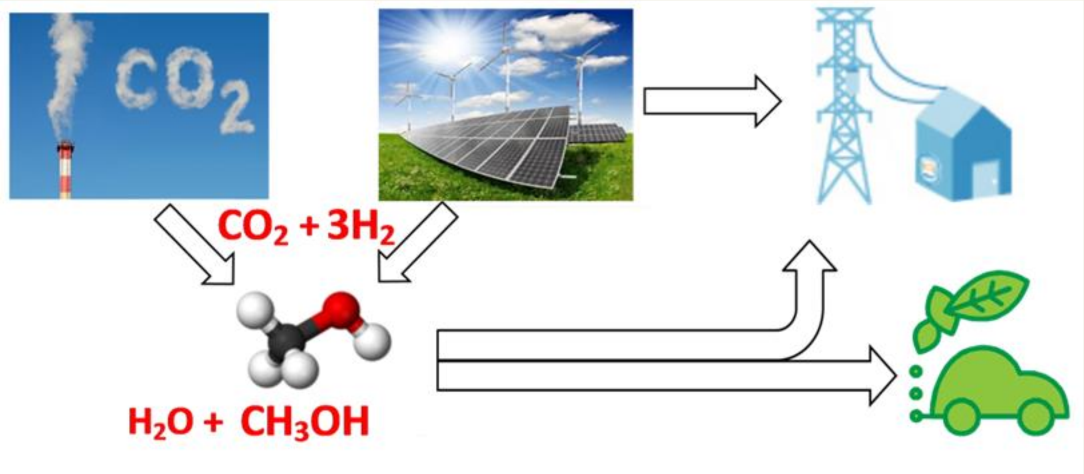
- European Commission goals to reduce greenhouse gas emissions by 80% below 1990 levels by 2050, 20% by 2020 (*Energy Roadmap 2050*).
- Varying nature of renewable sources causes time imbalance between production and consumption.
- Need for energy storage at different time-scales:
  - Second and minute scale for frequency regulation
  - Inter-seasonal scale: Power-to-gas, power-to-fuel

1. Introduction

Power-to-Methanol route

I. CO_2 Capture
II. H_2O/CO_2 Co-Electrolysis
III. Methanol Synthesis and Purification

Methanol as liquid energy carrier → - easy and cheap long term energy storage
(22.7 MJ/kg)
- converted to electricity or fuel use
- CO_2 neutral, if renewable sources are used



Léonard et al., 2015. Electricity storage with liquid fuels in a zone powered by 100% variable renewables, IEEE 978-1-4673-6692-2.

2. Model Description

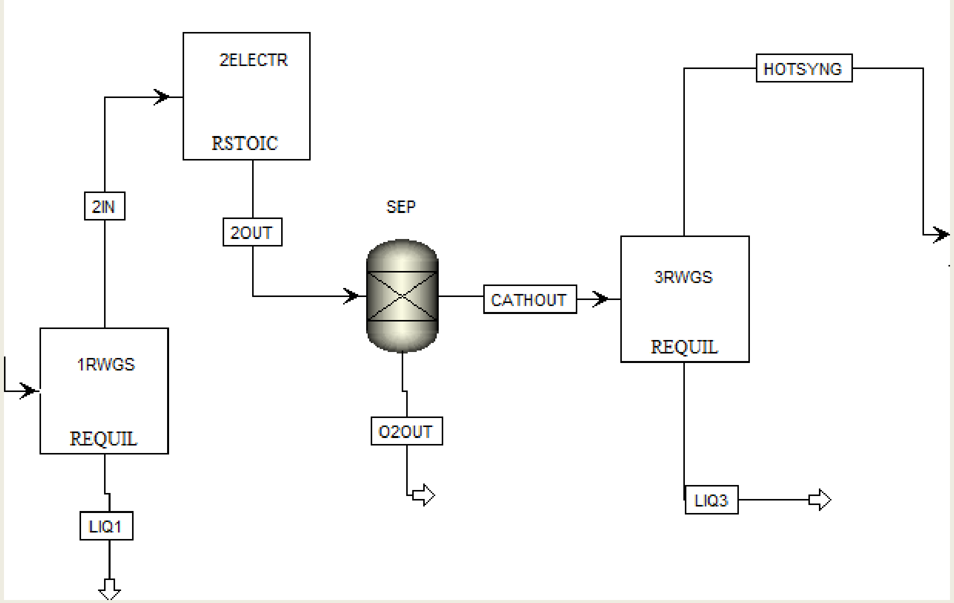
H_2O/CO_2 Co-Electrolysis model

1. $H_2 + CO_2 \rightarrow H_2O + CO$

2. $H_2O \rightarrow H_2 + \frac{1}{2} O_2$

   $CO_2 \rightarrow CO + \frac{1}{2} O_2$

3. $H_2 + CO_2 \rightarrow H_2O + CO$



Outlet Gas	Present Model	*Sun et al. (2012)*	Relative Error [%]
	Molar Fraction [%]	Molar Fraction [%]	
H_2O	15.2	15.0	1.33
H_2	39.7	40.0	0.75
CO	33.2	32.0	3.75
CO_2	11.7	12.0	2.50

- Redlich-Kwong-Soave equation of state
- Solid Oxide Electrolysis Cell at 850°C and 1.013 bar
- $H_2O/CO_2/H_2$ feed ratio: 100/45/10
- Operation at thermoneutral point
- H_2O and CO_2 utilization factor: 70%

2. Model Description

Methanol Synthesis model

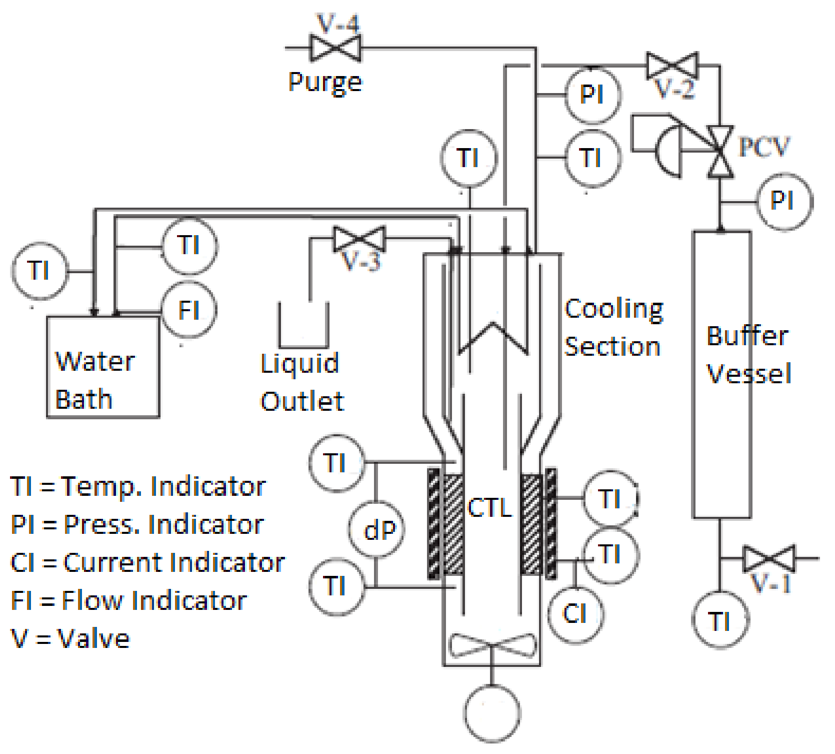
$$\begin{cases} CO_2 + 3\,H_2 \leftrightarrow CH_3OH + H_2O \\ CO_2 + H_2 \leftrightarrow CO + H_2O \end{cases}$$

Methanol Synthesis usually reaches low per-pass conversions:

- Strongly exothermic reaction (low temperature required)
- Need for high pressure (~50 bar)
- High recycle flow for industrial processes

Internal Condensation Reactor

- Internal liquid condensation and gas recirculation
- Leads to 100% conversion
- Small scale applications allow better heat management



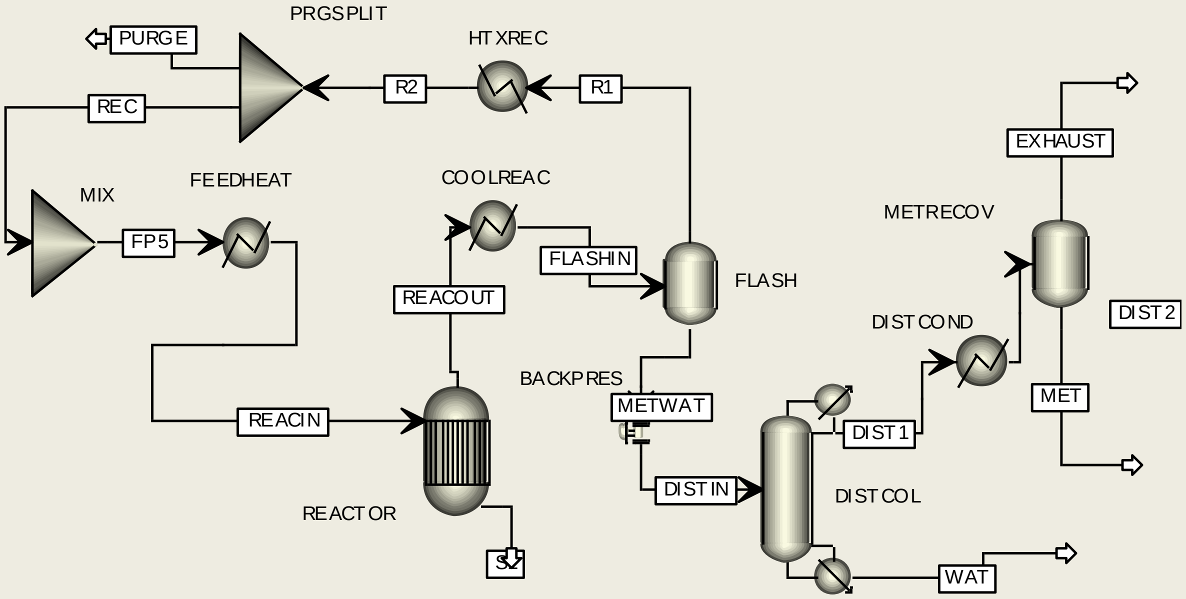
Bos and Brilman, 2014. DOI:*10.1016/j.cej.2014.10.059*

2. Model Description

Methanol Synthesis model

1. **Methanol Synthesis**

- Redlich-Kwong-Soave equation of state
- Simplified Reactor (equilibrium is achieved): 250°C; 50 bar
- Side reactions neglected
- Condenser: 25°C; 50 bar
- Recycle (2% purge)

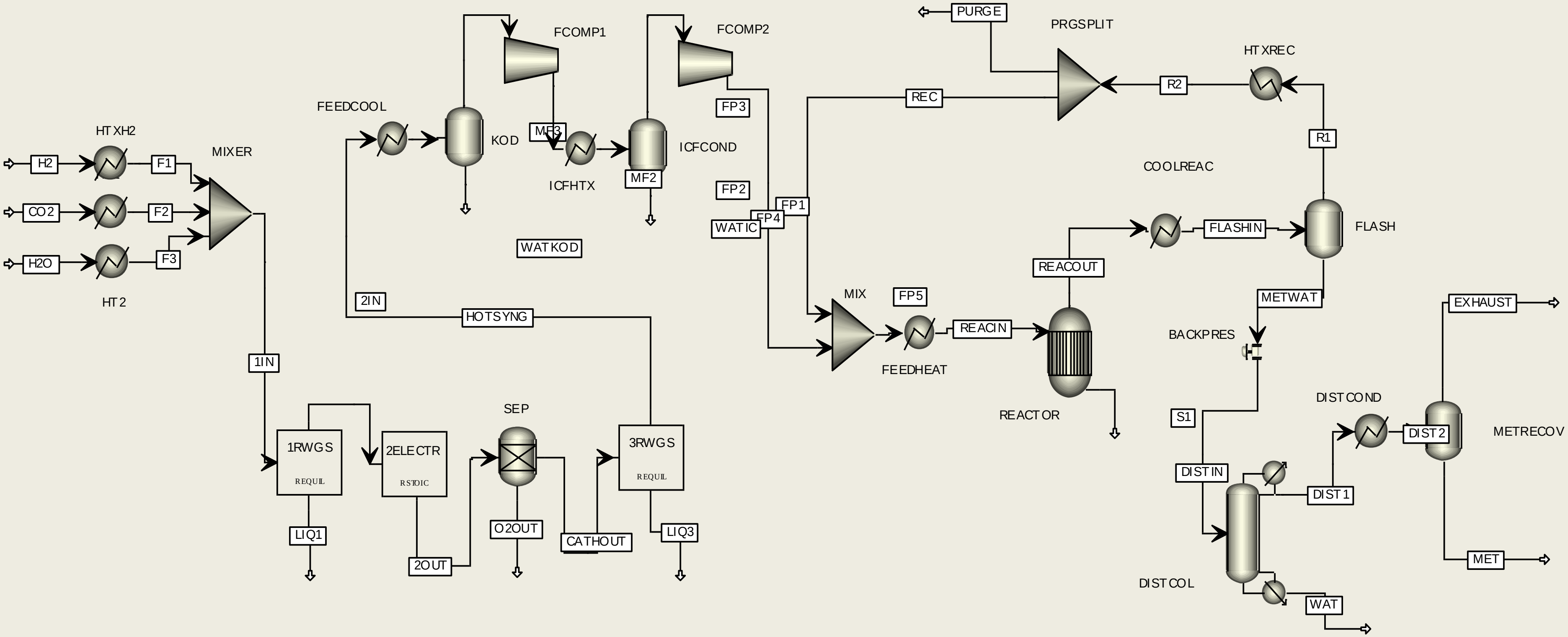


2. **Methanol Purification**

- NRTL model
- Distillation column
  with 11 stages
- 1.013 bar

2. Model Description

Global Model



Sub-processes linked through 2 stages-compression with intermediate cooling.

Models of the two parts are validated separately, according to experimental data available.

3. Results

- The H/C ratio achieved in the produced syngas is equal to 2.4.

  The electrical energy consumed by the electrolyser 5584 kW, almost 53% of the sub-process total energy demand.

- Results are validated with a relative error of 3.75%.

- Methanol synthesis reactor reaches per-pass conversion of hydrogen up to 22.4% and overall conversion of 99.8%.

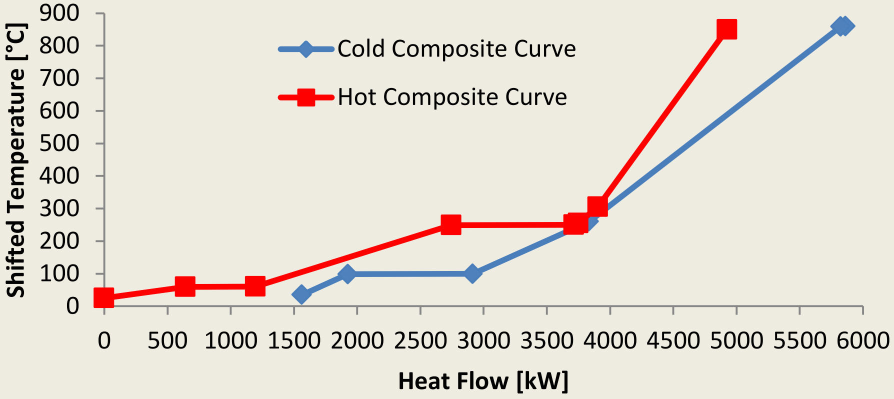
- Methanol productivity is 34.2 kmol/hr (about 1 ton/hr), with 97.7% purity.

4. Heat Integration

Pinch Point Analysis

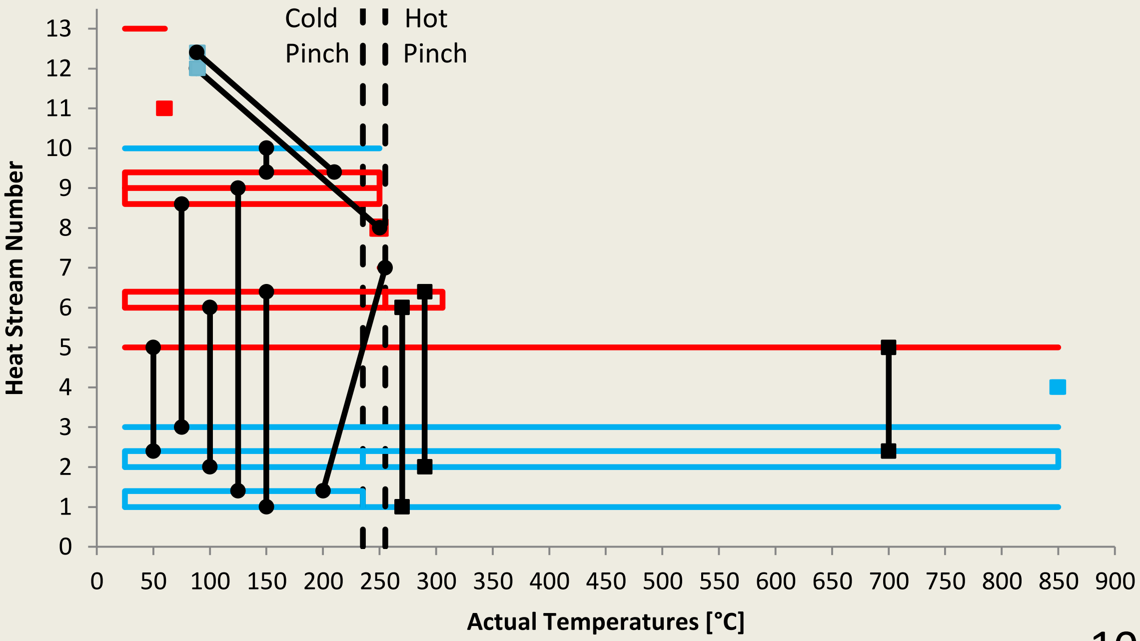
- Problem targeting:
  6 cold streams – 7 hot streams
- Minimum approach ΔT: 20°C
- Pinch point: 245.2°C
- Minimum utility requirements

  Hot: 935.6 kW
  Cold: 1563.3 kW



Heat Exchanger Network

- Maximum energy recovery design saves 73% of energy required.
- Above the pinch:
  3 HE and 5 hot utilities
- Below the pinch:
  9 HE and 6 cold utilities



4. Heat Integration

Economic Evaluation

- Overall Heat Transfer Coefficient (U) preliminary estimation for each exchanger.
- Total Heat Transfer Area (A) estimation: 2657 m^2.
- Bare module cost (C_{BM}) estimation using method described by *Turton et al. (2013)*, updated with CEPC Index (April 2015): 6,292,835 €.

$$Q = U \cdot A \cdot \Delta T_{LMTD} \cdot f$$

$$A_{tot} = \Sigma_i [Q_i / (\Delta T_{LMTD,i} \cdot U_i)]$$

$$C_{BM} = C_0 \cdot (B_1 + B_2 f_m f_p)$$

Efficiency Assessment

- Process efficiency without HEN: 51.4%.
- Process efficiency with HEN: 70.8%.

$$\eta = \frac{HHV_{out\_Met} - HHV_{in\_H2}}{Q_{in} + P_{el} + P_{comp}}$$

Inlet H_2 HHV (HHV_{in_H2})	**Outlet Methanol HHV (HHV_{out_Met})**	**Electrical Power Input (P_{el})**
0.795	7.053	7.316
Hot Utilities without HEN (Q_{in})	**Hot Utilities with HEN (Q_{in})**	**Compression Power Input (P_{comp})**
4.265	0.936	0.590 MW

5. Conclusions and Further Work

- An efficient process for CO_2-neutral methanol production is proposed as long-term energy storage.
- Production rate of 1 ton$_{CH3OH}$/hr, corresponding to typical decentralized energy storage.
- Benefits from a heat exchangers network design, but high capital cost needed.
- Solid Oxide cells allow both electrolysis and fuel cell mode.
- A preliminary model is proposed, some further improvements are required:
  - Use of recycled H_2 for the electrolyser
  - Pressurized electrolyser
  - Build a detailed reactor to implement methanol synthesis kinetics
- Integration of carbon capture (*Léonard, 2014)* in the efficiency assessment.

Thank you for your attention!

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