Supplementary Information

Thermally self-sufficient process for cleaner production of e-methanol by CO_2 hydrogenation

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This *Supplementary Information* file provides more details about the cash flow analysis, the equipment sizing and the main design parameters, the dividing wall column simulation model, as well as the greenhouse gas (GHG) emissions calculation.

1) Cash flow analysis:

The following equations have been used to obtain the cash flow analysis:

Year 0:

- Cash flow = Investment.
  - Investment = TIC + Circulating Capital + R&D Investment.

Rest of the years:

- Cash flow = Profit After Taxes + Depreciation.
  - Profit After Taxes = Profit Before Taxes - Taxes.
    - Profit Before Taxes = Profit – Depreciation
      - Profit = Revenue - OPEX.
        - Revenue = Methanol Production x Methanol Selling Price.

Table S1 shows the parameters considered for the economic evaluation:

Table S1. Economic analysis. Main factors.

Parameter	Value	Units
Circulating Capital	5	% TIC
R&D Investment	3	% TIC
Depreciation time	10	years
Taxes	25	% Yearly benefit

2) Equipment sizing and main design parameters

Table S2. Equipment sizing and main design parameters

Equipment & Parameters	Value	Units
CO_2 Compressor		
Inlet Pressure	1.1	bar
Outlet Pressure	65	bar
Number of Stages	4	stages
Pressure Ratio	2.77	bar/bar
Compressor Efficiency	72	%
Intercooling	-1,991	kW
Compressor Power	2,299	kW
H_2 Compressor		
Inlet Pressure	1.1	bar
Outlet Pressure	65	bar
Number of Stages	5	stages
Pressure Ratio	2.26	bar/bar
Compressor Efficiency	72	%
Intercooling	-4,447	kW
Compressor Power	5,685	kW
Recycle Compressor		
Inlet Pressure	63.5	bar
Outlet Pressure	65	bar
Number of Stages	1	stages
Compressor Efficiency	72	%
Pressure Ratio	1.024	bar/bar
Compressor Power	212	kW
Reactor		
Operating Pressure	65	bar
Operating Temperature	250	ºC
Number of Tubes	670	tubes
Tube Diameter	6	cm
Tube Length	12	m
Mass of Catalyst	865	kg
Duty	-3,924	kW
Dividing Wall Column		
Number of Trays	29	trays
Reflux Ratio	9.2	mol/mol
Boilup Ratio	0.93	mol/mol
Methanol Draw Tray	4	tray
FEHE		
Type	Shell and Tubes	-
Duty	6,454	kW
LMTD	72	K
Area	1,053	m^2

HEATER		
Type	Shell and Tubes	-
Duty	3,916	kW
LMTD	32	K
Area	821	m^2
VAPORIZER		
Type	Shell and Tubes	-
Duty	8,143	kW
LMTD	44	K
Area	735	m^2
COOLER		
Type	Air Cooler	-
Duty	-2,824	kW
LMTD	46	K
Area	1,364	m^2
REBOILER		
Type	Shell and Tubes	-
Duty	4,793	kW
LMTD	40	K
Area	805	m^2
CONDENSER		
Type	Shell and Tubes	-
Duty	-12,135	kW
LMTD	23	K
Area	703	m^2

3) Dividing wall column: simulation model

The DWC is simulated using four rigorous distillation RADFRAC columns located in a simulation subflowsheet (Figure S1). All the RADFRAC columns are simulated without reboiler or condenser since the DWC reboiler and condenser are located outside the subflowsheet (Figure S2).

The liquid bottoms stream (DWC-10) of the upper RADFRAC column (DWC-TOP) is sent to a splitter (LIQ-SPLI) that models the liquid splitter and controls the liquid split ratio. The resulting liquid streams (DWC-1 & DWC-6) are sent to the first trays of the left and right RADFRAC columns (DWC-LEFT & DWC-RIGH) that represent the middle-divided section. While the vapor streams obtained at the top of the left (DWC-LEFT) and right (DWC-RIGH) RADFRAC columns are sent to the last tray of the upper RADFRAC column (DWC-TOP), the liquid streams obtained at the bottoms of these RADFRAC columns (DWC-4 & DWC-11) are sent to the first tray of the lower RADFRAC column (DWC-BOT). Finally, the lower RADFRAC column overhead vapor stream (DWC-9) is sent to a splitter (VAP-SPLI) that models the vapor split, and the resulting vapor streams (DWC-2 & DWC-7) are sent to the last trays of the left and right RADFRAC columns (DWC-LEFT & DWC-RIGH).

In the main flowsheet (Figure S2) a condensation temperature of 40ºC is fixed in the DWC condenser (CONDENSE), modeled as a cooler. After the condenser, the overhead accumulator (OVH-ACCU) separates the vapor product (CO2-REC,) recycled to the CO_2 compressor, from the reflux (REFLUX), recycled to the top tray of the upper RADFRAC column (DWC-TOP). On the other hand, the column reboiler is simulated using a heat exchanger (REBOILER) that uses as a heat source the reactor product stream (F4). The vapor fraction of the reboiler outlet cold stream (REB-2) is adjusted to meet the required bottom product (WATER) specification (99.99% mass). After the reboiler, a flash vessel (REB-FLAS) separated the vaporized fraction (REB-3), returned to the last tray of the lower RADFRAC column (DWC-BOT) from the DWC bottoms product (WATER).

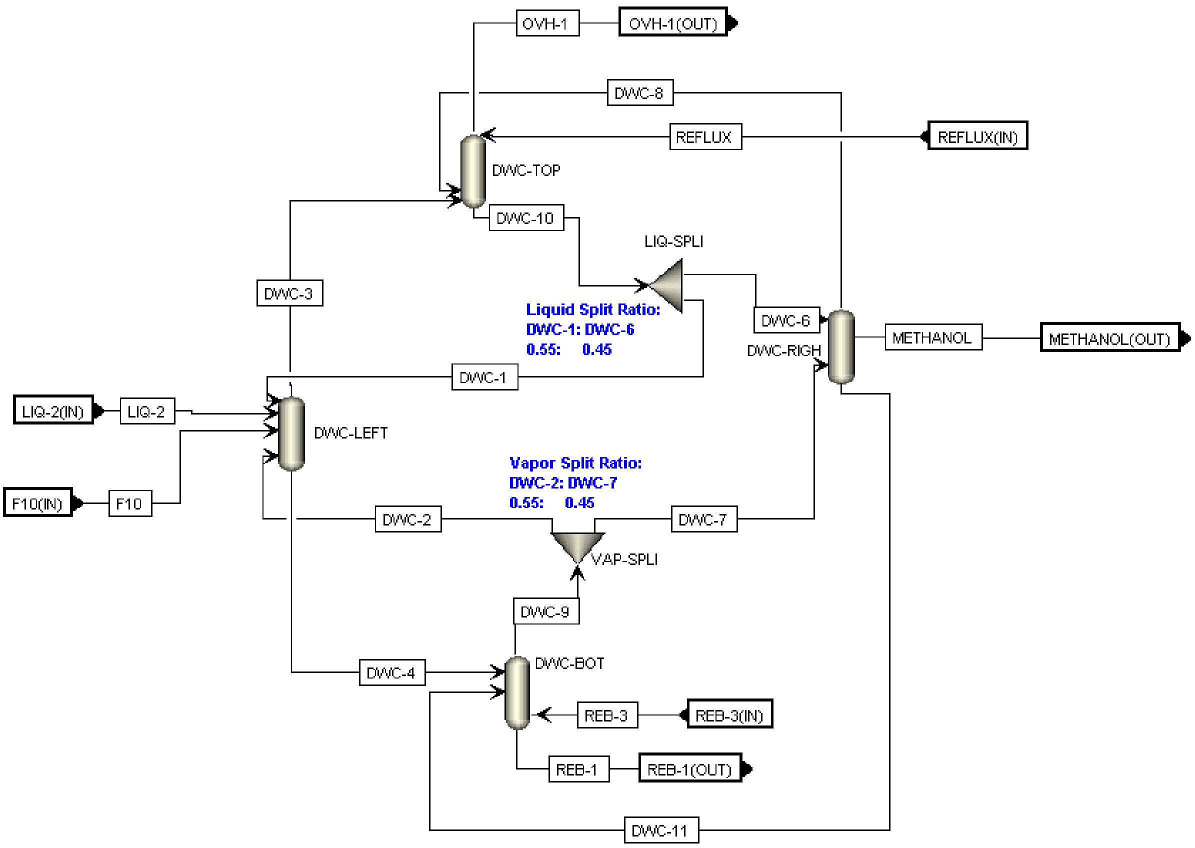

Figure S1. Dividing wall column: Aspen Plus simulation subflowsheet.

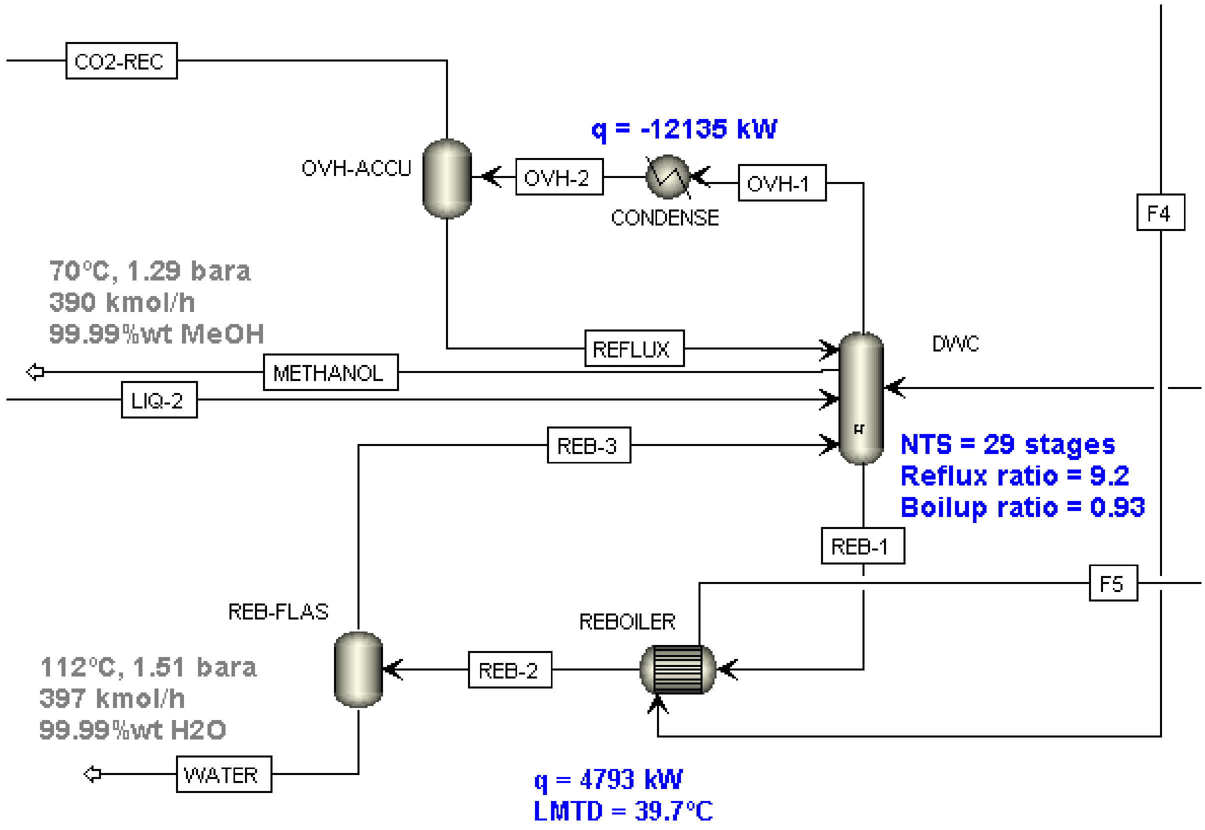

Figure S2. Dividing wall column: Aspen Plus simulation main flowsheet.

4) Greenhouse gas (GHG) emissions calculation:

The greenhouse gas (GHG) emissions are limited to those related to the production of electricity and hydrogen, and to the capture of CO_2.

GHG emissions related to power production

According to the United Nations Economic Commission for Europe (2022), the CO_2 equivalent emissions related to the production of power using natural gas and wind are equal to 430 gCO_2eq/kWh and 12 gCO_2eq/kWh respectively. In the process presented in this work, 9590 kWh of power is consumed to produce 12500 kg/h of methanol. Thus, the GHG emissions related to power production are equal to:

- $(kgCO_{2eq}/kgMeOH)_{power} = kgCO_{2eq}/kWh \cdot kW \cdot /(kgMeOH/h)$
    - 0.33 $kgCO_{2eq}$ / kg MeOH (natural gas).
    - 0.01 $kgCO_{2eq}$ / kg MeOH (wind).

GHG emissions related to hydrogen production

As reported by Bhandari et al. (2014), the GHG emissions related to the production of hydrogen are equal to 8.5 $kgCO_2eq/kgH_2$ and 2 $kgCO_2eq/kgH_2$ when hydrogen is produced by steam reforming of natural gas and by electrolysis power by wind electricity respectively.

Taking into account that 2650 kg/h of H_2 are consumed in the plant, the GHG emissions related to hydrogen production are equal to:

- $(kgCO_{2eq}/kgMeOH)_{H2} = kgCO_2eq/kgH_2 \cdot kgH_2/h/(kgMeOH/h)$
    - 1.802 $kgCO_{2eq}$ / kg MeOH (steam reforming).
    - 0.212 $kgCO_{2eq}$ / kg MeOH (electrolysis powered by wind).

GHG emissions related to CO_2 capture

As reported by Koorneef et al. (2008), the net GHG emissions related to CO_2 capture are equal to 0.015 $kgCO_2eq/kgCO_2$. Since 17164 kg/h of CO_2 are consumed in the plant, the GHG emissions related to hydrogen production are equal to:

- $(kgCO_{2eq}/kgMeOH)_{CO2} = kgCO_2eq/kgCO_2 \cdot kgCO_2/h/(kgMeOH/h)$
    - 0.02 $kgCO_{2eq}$ / kg MeOH.

Total GHG emissions

The total GHG emissions are equal to the sum of the emissions of the three previous sections:

- $(kgCO_{2eq}/kgMeOH)_{tot} = (kgCO_{2eq}/kgMeOH)_{power} + (kgCO_{2eq}/kgMeOH)_{H2} + (kgCO_{2eq}/kgMeOH)_{CO2}$
    - 2.15 $kgCO_{2eq}$ / kg MeOH (grey electricity).
    - 0.24 $kgCO_{2eq}$ / kg MeOH (green electricity).

Net GHG emissions

Considering that 17164 kg/h of CO_2 are consumed in the plant, the net GHG emissions are equal to:

- $(kgCO_{2eq}/kgMeOH)_{net} = (kgCO_{2eq}/kgMeOH)_{tot} - (kgCO_2/h/kgMeOH/h)$
    - 0.78 $kgCO_{2eq}$ / kg MeOH (grey electricity).
    - -1.13 $kgCO_{2eq}$ / kg MeOH (green electricity).

References

1) Bhandari, R., Trudewind, C. A., & Zapp, P. (2014). Life cycle assessment of hydrogen production via electrolysis - A review. In Journal of Cleaner Production (Vol. 85, pp. 151–163). Elsevier Ltd. https://doi.org/10.1016/j.jclepro.2013.07.048
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3) United Nations Economic Commission for Europe. (2022). Carbon Neutrality in the UNECE Region: Integrated Life-cycle Assessment of Electricity Sources. https://unece.org/sites/default/files/2022-04/LCA_3_FINAL%20March%202022.pdf