A detailed process and techno-economic analysis of the methanol synthesis from H_2 and CO_2 with intermediate condensation steps

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Supplementary Material

A. Mathematical derivation of the reactor equations

A global mole balance in the reactor gives:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \dot{n}_{in} - \dot{n}_{out} + r \cdot m_{cat} \tag{S1}$$

Where $\frac{\mathrm{d}n}{\mathrm{d}t}$ is the accumulation of material (mol·s^{-1}), $\dot{n}_{in}$ and $\dot{n}_{out}$ are the mole flows entering and leaving the reactor respectively (mol·s^{-1}), r is the total reaction rate (mol·kg$_{cat}$·s^{-1}) and m_{cat} is the total catalyst mass (kg) in the reactor.

There is no accumulation in steady-state operation: $\frac{\mathrm{d}n}{\mathrm{d}t} = 0$. With an infinitesimal control volume in the axial direction:

$$0 = \dot{n}_z - \dot{n}_{z+dz} + r \cdot dm_{cat} \tag{S2}$$

Here, dm_{cat} is the catalyst mass (kg) between position z and $(z + dz)$. Developing each term:

$$\mathrm{d}\dot{n} = \dot{n}_{z+dz} - \dot{n}_z \tag{S3}$$

$$r = \sum_{j=1}^{6}\sum_{k=1}^{2}\left(\nu_{jk} \cdot r_k\right) \tag{S4}$$

$$dm_{cat} = \frac{m_{cat}}{L} \cdot dz \tag{S5}$$

Where L is the reactor length (m), ν_{jk} is the stoichiometric coefficient of component j in reaction k, r_k is the rate of reaction k (mol·kg$_{cat}$·s^{-1}). Substituting Eqs. (S3-S5) in (S2) and isolating $\frac{\mathrm{d}\dot{n}}{\mathrm{d}z}$, the first differential equation is derived:

$$\frac{\mathrm{d}\dot{n}}{\mathrm{d}z} = \frac{m_{cat}}{L} \cdot \sum_{j=1}^{6}\sum_{k=1}^{2}\left(\nu_{jk} \cdot r_k\right) \tag{S6}$$

From the total mole balance (S6), a mole balance from each component is derived:

$$\frac{\mathrm{d}\dot{n}_j}{\mathrm{d}z} = \frac{m_{cat}}{L} \cdot \sum_{k=1}^{2} \left(\nu_{jk} \cdot r_k\right) \tag{S7}$$

The mole flow of component j ($\dot{n}_j$) and its derivative is rewritten as:

$$\dot{n}_j = \dot{n} \cdot y_j \tag{S8}$$

$$\frac{\mathrm{d}\dot{n}_j}{\mathrm{d}z} = \dot{n} \cdot \frac{dy_j}{dz} + y_j \cdot \frac{d\dot{n}_j}{dz} \tag{S9}$$

Substituting Eq. (S9) in Eq. (S7) and isolating $\frac{dy_j}{dz}$, the second differential equation is derived:

$$\dot{n} \cdot \frac{dy_j}{dz} + y_j \cdot \frac{d\dot{n}_j}{dz} = \frac{m_{cat}}{L} \cdot \sum_{k=1}^{2} \left(\nu_{jk} \cdot r_k\right) \tag{S10}$$

$$\frac{\mathrm{d}y_j}{\mathrm{d}z} = \frac{1}{\dot{n}} \cdot \left\{ \frac{m_{Cat}}{L} \cdot \sum_{k=1}^{2} \left(\nu_{jk} \cdot r_k\right) - y_j \cdot \frac{\mathrm{d}\dot{n}}{\mathrm{d}z} \right\} \tag{S11}$$

A global energy balance in the reactor is derived:

$$\frac{\mathrm{d}U_{int}}{\mathrm{d}t} = \dot{H}_{in} - \dot{H}_{out} + \dot{Q} \tag{S12}$$

Here, $\frac{\mathrm{d}U_{int}}{\mathrm{d}t}$ is the internal energy accumulation (W), $\dot{H}_{in}$ and $\dot{H}_{out}$ are the enthalpy flow entering and leaving the reactor respectively (W), and $\dot{Q}$ is the heat transfer between the reaction medium and the cooling fluid (W). $\dot{Q}$ is calculated as follows:

$$\dot{Q} = U \cdot A_i \cdot (T_w - T) \tag{S13}$$

Where U is the global heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$), A_i is the inner heat transfer area (m^2), T_w is the temperature of the cooling fluid (K), and T is the reactor temperature (K).

There is no accumulation in steady-state operation: $\frac{\mathrm{d}U_{int}}{\mathrm{d}t} = 0$. With an infinitesimal control volume in the axial direction:

$$0 = \dot{H}_z - \dot{H}_{z+dz} + U \cdot (T_w - T) \cdot dA_i \tag{S14}$$

$$0 = -d\dot{H} + U \cdot (T_w - T) \cdot \pi \cdot D_i \cdot dz \tag{S15}$$

The derivative of the enthalpy flow ($d\dot{H}$) is further developed:

$$d\dot{H} = d\left[\dot{n} \cdot \sum_{j=1}^{6} \left(y_j \cdot h_j\right)\right] \tag{S16}$$

$$d\dot{H} = \sum_{j=1}^{6} \left(\dot{n} \cdot y_j \cdot dh_j + \dot{n} \cdot h_j \cdot dy_j + y_j \cdot h_j \cdot d\dot{n}\right) \tag{S17}$$

Where h_j is the specific enthalpy of component j (J·mol^{-1}). The derivative of the specific enthalpy is developed considering only temperature dependency:

$$dh_j = \frac{dh_j}{dT} \cdot dT = C_{P,j} \cdot dT \tag{S18}$$

Here, $C_{P,j}$ is the specific heat capacity of component j (J·mol^{-1}·K^{-1}). The fluid specific enthalpy (h_f) and the fluid heat capacity ($C_{P,f}$) are defined as:

$$C_{P,f} = \sum_{j=1}^{6} C_{P,j} \cdot y_j \tag{S19}$$

$$h_f = \sum_{j=1}^{6} y_j \cdot h_j \tag{S20}$$

Substituting Eqs. (S17-S20) in Eq. (S15) and isolating $\frac{dT}{dz}$, the third differential equation is derived:

$$\frac{\mathrm{dT}}{\mathrm{d}z} = \frac{1}{\left(\dot{n} \cdot C_{P,f}\right)} \cdot \left[-\frac{\mathrm{d}\dot{n}}{\mathrm{d}z} \cdot h_f - \dot{n} \cdot \sum_{j=1}^{6} \left(h_j \cdot \frac{\mathrm{d}y_j}{\mathrm{d}z} \right) + U \cdot \pi \cdot D_i \cdot (T_w - T) \right] \tag{S21}$$

The specific heat capacity and the specific enthalpy were calculated by polinomial correlations. The parameters estimated by Goos et al. [1] are provided in Table S1.

$$C_{P,j}(T, 1\ bar) = R \cdot \left(a_{1,j} + a_{2,j} \cdot T + a_{3,j} \cdot T^2 + a_{4,j} \cdot T^3 + a_{5,j} \cdot T^4 \right) \tag{S22}$$

$$h_j(T, 1\ bar) = R \cdot \left(a_{1,j} \cdot T + \frac{a_{2,j}}{2} \cdot T^2 + \frac{a_{3,j}}{3} \cdot T^3 + \frac{a_{4,j}}{4} \cdot T^4 + \frac{a_{5,j}}{5} \cdot T^5 + a_{6,j} \right) \tag{S23}$$

Table S1. Parameters for the estimation of the specific heat capacity and specific enthalpy of selected components in the gas phase [1]. Reproduced with permission from [1].

Gas	a_1	$a_2 \cdot 10^3$	$a_3 \cdot 10^5$	$a_4 \cdot 10^8$	$a_5 \cdot 10^{11}$	$a_6 \cdot 10^{-4}$
H_2	2.3443311	7.9805208	-1.9478151	2.0157209	-0.7376118	-0.0917935
CO	3.5795335	-0.6103537	0.1016814	0.0907006	-0.0904424	-1.4344086
CO_2	2.3568130	8.9841299	-0.7122063	0.2457301	-0.0142885	-4.8371971
CH_3OH	5.6585105	-16.2983419	6.9193816	-7.5837293	2.8042755	-2.5611974
H_2O	4.1986352	-2.0364017	0.6520342	-0.5487927	0.1771968	-3.0293726
N_2	3.5310053	-0.1236610	-0.0502999	0.2435306	-0.1408812	-0.1046976

B. Calculation of the heat transfer coefficient in the reactor

In the methanol synthesis reactor, the global heat transfer coefficient between syngas and the cooling fluid (U) is calculated as a combination of four heat transfer resistances (R_{1-4}):

1. The heat transfer in the bulk of the two-phase system (catalyst and gas);
2. The heat transfer between the two-phase system and the tube inner wall;
3. The heat transfer through the reactor wall;
4. The heat transfer between the tube outer wall and the cooling fluid (boiling water).

This results from the use of a heat transfer coefficient model described in the VDI Heat Atlas (α_w – Model) [2], where the radial thermal conductivity of the two-phase system is constant over the radius of the reactor tube. According to Gruber,[3] the global heat transfer coefficient (U) can be calculated as follows:

$$U \cdot A_i = R_1 + R_2 + R_3 + R_4 \tag{S24}$$

$$U \cdot A_i = \left(\frac{D_i}{8 \cdot \Lambda_r \cdot A_i} + \frac{1}{\alpha_{w,i} \cdot A_i} + \frac{s_t}{\lambda_t \cdot A_m} + \frac{1}{\alpha_{w,o} \cdot A_o} \right)^{-1} \tag{S25}$$

Where Λ_r is the effective radial thermal conductivity of the two-phase system, A_i is the inner surface area of the reactor tube, $\alpha_{w,i}$ is the heat transfer coefficient between the reactive system and the inner wall, s_t is the thickness of the reactor tube, λ_t is the thermal conductivity of the reactor tube, A_m is the averaged surface area of the reactor tube, $\alpha_{w,o}$ is the heat transfer coefficient between the outer wall and the cooling fluid, and A_o is the outer surface area of the reactor tube.

The effective radial thermal conductivity Λ_r is calculated as follows:

$$\frac{\Lambda_r}{\lambda_f} = \frac{\lambda_{bed}}{\lambda_f} + \frac{Pe_0}{K_r} \tag{S26}$$

Here, λ_f is the thermal conductivity of the fluid, Pe_0 is the Peclet number calculated with the superficial velocity, and K_r is the inverse of the inclination parameter.

The thermal conductivity of the two-phase system λ_{bed} is calculated from the ZBS-Model [2]. In this work, only the primary parameters (λ_f), the thermal conductivity of the catalyst particles (λ_p) and the porosity of the bed (ψ = 0.39) were included. λ_{bed} can then be calculated as

$$\frac{\lambda_{bed}}{\lambda_f} = 1 - \sqrt{1-\psi} + \sqrt{1-\psi} \cdot k_c \tag{S27}$$

Where k_c is the thermal conductivity of the core of the unit cell. The estimation of $\alpha_{w,i}$ is made through the Nusselt number (Nu_w):

$$Nu_w = \frac{\alpha_{w,i} \cdot d_p}{\lambda_f} \quad \text{(S28)}$$

Here, d_p is the particle diameter (d_p = 2 mm). A correlation for Nu_w is used:[2]

$$Nu_w = \left(1.3 + 5 \cdot \frac{d_p}{D_i}\right) \cdot \frac{\lambda_{bed}}{\lambda_f} + 0.19 \cdot Re_0^{0,75} \cdot Pr^{1/3} \quad \text{(S29)}$$

Where d is the particle diameter, Re_0 is the Reynolds number, and Pr is the Prandtl number. This function is valid for a Peclet number (Pe_0) between 1 and 10^4, and for D_i / d_p between 1.2 and 51.

Finally, a constant value of $\alpha_{w,o}$ = of 1000 W·m^{-2}·K^{-1} was considered for the heat transfer between the tube outer wall and boiling water [3].

C. Flash drums and distillation column – Assumptions for the Matlab simulations

Table S2. Liquid and gas fractions (% mol/mol) of the phase separation via flash drums and the separation via the distillation column in the one-step process. Values taken from Aspen Plus calculations and used for the Matlab simulations.

Equipment	Phase	H_2	CO	CO_2	CH_3OH	H_2O	N_2
Flash drums 1-2	Gas	100.00	99.92	99.12	28.32	6.41	99.93
	Liquid	0	0.08	0.88	71.68	93.59	0.07
Flash drum 3	Gas	99.87	97.93	77.16	1.09	0.21	98.08
	Liquid	0.13	2.07	22.84	98.91	99.79	1.92
Flash drum 4	Gas	99.97	99.58	94.69	6.42	1.37	99.61
	Liquid	0.03	0.42	5.32	93.59	98.63	0.39
Distillation Column	Gas Dist.	99.89	98.62	87.93	3.80	0.01	98.70
	Liquid Dist.	0.11	1.38	12.07	96.13	0.57	1.30
	Bottoms	0.00	0.00	0.00	0.06	99.42	0.00

Table S3. Liquid and gas fractions (% mol/mol) of the phase separation via flash drums and the separation via the distillation column in the three-step process. Values taken from Aspen Plus calculations and used for the Matlab simulations.

Equipment	Phase	H_2	CO	CO_2	CH_3OH	H_2O	N_2
Flash drums 1-2	Gas	100.00	99.94	99.32	34.02	8.29	99.94
	Liquid	0	0.06	0.68	65.98	91.71	0.06

Flash drum 3	Gas	99.91	98.86	88.92	4.39	0.98	98.93
	Liquid	0.09	1.14	11.08	95.61	99.02	1.07
Flash drum 4	Gas	99.92	98.77	86.22	2.37	0.50	98.86
	Liquid	0.08	1.23	13.78	97.63	99.50	1.14
Flash drum 5	Gas	99.69	95.56	61.86	0.60	0.12	95.85
	Liquid	0.31	4.44	38.14	99.40	99.88	4.15
Flash drum 6	Gas	99.95	99.29	91.34	3.90	0.82	99.34
	Liquid	0.05	0.71	8.66	96.10	99.18	0.66
Distillation Column	Gas Dist.	99.88	98.46	86.67	3.41	0.01	98.55
	Liquid Dist.	0.12	1.54	13.33	96.58	0.68	1.45
	Bottoms	0.00	0.00	0.00	0.01	99.31	0.00

D. Kinetic model implementation in Aspen Plus

In order to implement a kinetic model in Aspen Plus, parameters must be rearranged to fulfill specific format requirements. The kinetic model type of Langmuir-Hinshelwood-Hougen-Watson (LHHW) was chosen, with a reacting phase containing only vapor, a rate basis in catalyst weight, and the concentration basis (C_i) in fugacity (Pa). As the fugacities of Model-6p[4] are with the unit 'bar', the reference pressure (p_0 = 1 bar) were omitted. However, since Aspen Plus require fugacity in 'Pa', the reference pressure (p_0 = 10^5 Pa) must appear, and therefore is seen in corresponding expressions between Aspen and Model-6p.

The reaction rates of the LHHW kinetic model type (kmol·kg^{-1}·s^{-1}) follow this expression:

$$r = \frac{[kinetic\ factor] \cdot [Driving\ force\ expression]}{[Adsorption\ expression]} \tag{S30}$$

The kinetic factor is described as:

$$[kinetic\ factor] = k \cdot T^n \cdot exp\left(\frac{-E_A}{R \cdot T}\right) \tag{S31}$$

The corresponding expressions from Model-6p in relation to parameters k, n, E_A are detailed in Table S4.

The driving force expression has two terms, how are described as:

$$[Term\ 1] = exp\left[A + \frac{B}{T} + C \cdot ln(T) + D \cdot T\right] \cdot \prod_{j=1}^{N_g} \left(f_j^{\upsilon_j}\right) \tag{S32}$$

$$[Term\ 2] = exp\left[A + \frac{B}{T} + C \cdot ln(T) + D \cdot T\right] \cdot \prod_{j=1}^{N_g} \left(f_j^{\upsilon_j}\right) \tag{S33}$$

$$[Driving\ force\ expression] = [Term\ 1] - [Term\ 2] \quad \text{(S34)}$$

Table S4. Aspen kinetic factor and Model-6p corresponding expressions.

Parameter in Aspen	Corresponding expression from Model-6p [4]	Value		Unit
		CO_2 hyd.	rWGSR	
$\boldsymbol{k}$	$\phi_{Zn} \cdot exp(A_i) \cdot \frac{1\ kmol}{1000\ mol}$	181.211	$4.4771 \cdot 10^8$	$\frac{kmol}{kg_{cat} \cdot s}$
$\boldsymbol{n}$	0	0	0	–
$\boldsymbol{E}$	$E_{A,i}$	94.73	132.79	$\frac{kJ}{mol}$

In Table S5, the corresponding expressions from Model-6p in relation to the coefficients of the driving force constant (A, B, C, D) are detailed, while the concentration exponents υ_j are described in Table S6.

Table S5. Coefficients of the driving force constant and the corresponding expressions from Model-6p.

Term	Reaction	Parameter in Aspen	Corresponding expression in Model-6p	Value
1	CO_2 hydrog.	A	$ln({p_0}^{-2.5})$	- 28.7823
		B	0	0
		C	0	0
		D	0	0
	rWGSR	A	$ln({p_0}^{-2})$	- 23.0259
		A	0	0
		B	0	0
		C	0	0
2	CO_2 hydrog.	A	$ln({p_0}^{-0.5}) - A_{eq.const.CO_2hyd.}$	- 14.1255
		B	$-B_{eq.const.CO_2hyd.}$	- 4755.7
		C	$-C_{eq.const.CO_2hyd.}$	4.481
		D	0	0
	rWGSR	A	$ln({p_0}^{-2}) - A_{eq.const.rWGSR}$	- 35.5949
		B	$-B_{eq.const.rWGSR}$	5337.4
		C	$-C_{eq.const.rWGSR}$	1.097

	D	0	0

Table S6. Concentration exponents (v_j) of the driving force expression.

Gas component	Methanol synthesis		rWGSR	
	Term 1	**Term 2**	**Term 1**	**Term 2**
H_2	1.5	- 1.5	0	- 1
CO	–	–	0	1
CO_2	1	0	1	0
CH_3OH	0	- 1	–	–
H_2O	0	- 1	1	2

The adsorption expression is:

$$[Adsorption\ exp.] = \sum_{k=1}^{N_t} \left\{ exp\left[A_k + \frac{B_k}{T} + C_k \cdot ln(T) + D_k \cdot T\right] \cdot \prod_{j=1}^{N_g} \left(f_j^{v_{j,k}}\right) \right\}^n \quad \text{(S35)}$$

Where N_t is the number of terms. By looking at the expressions from Model-6p:

$$[Adsorption\ exp. Model - 6p] = (\theta_b \cdot \theta_c)^{-1} \quad \text{(S36)}$$

$$[Adsorption\ exp. Model - 6p] = \left(\overline{K_2} \cdot \frac{f_{H_2}^{0.5} \cdot f_{CO_2}}{p_0^{1.5}} + 1\right) \cdot \left(\overline{K_3} \cdot \frac{f_{H_2}^{-0.5} \cdot f_{H_2O}}{p_0^{0.5}} + 1\right) \quad \text{(S37)}$$

$$[Adsorption\ exp. Model - 6p] = 1 + \overline{K_2} \cdot \frac{f_{H_2}^{0.5} \cdot f_{CO_2}}{p_0^{1.5}} + \overline{K_3} \cdot \frac{f_{H_2}^{-0.5} \cdot f_{H_2O}}{p_0^{0.5}} + \overline{K_2} \cdot \overline{K_3} \cdot \frac{f_{CO_2} \cdot f_{H_2O}}{p_0^2} \quad \text{(S38)}$$

From Eq. (9), the adsorption expression exponent is $n = 1$. The correspondence with Model-6p is described in Table S7 (adsorption constants) and in Table S8 (concentration exponents).

Table S7. Adsorption constants and the corresponding expression of Model-6p.

Adsorption constants	**Corresponding expression in Model-6p**	**Value**
A – Term 1	$\ln(1)$	0
A – Term 2	$\ln(\overline{K_2} \cdot p_0^{-1.5})$	-18.237
A – Term 3	$\ln(\overline{K_3} \cdot p_0^{-0.5})$	-3.64262
A – Term 4	$\ln(\overline{K_2} \cdot \overline{K_3} \cdot p_0^{-2})$	-21.8796

Table S8. Concentration exponents and the corresponding values of Model-6p.

Gas components	**Term 1**	**Term 2**	**Term 3**	**Term 4**
CO_2	0	1	0	1
H_2	0	0.5	-0.5	0
H_2O	0	0	1	1

E. One-step process – Simulation in Aspen Plus and stream properties

In Figure S1, the Aspen flowsheet of the one-step process is presented. Feed CO_2 (1-CO2, 4824 kmol·h^{-1}) is mixed with a recycle stream (39-REC, 2786 kmol·h^{-1}) (MIXER1), which mainly consists of CO_2, but also contains methanol, water, nitrogen, hydrogen and traces of CO. The mixed gas is compressed from 1 to 70 bar in three stages with equal pressure ratio (CP1-CO2, CP2-CO2, CP3-CO2). Intermediate cooling is performed with cooling water (HE1) and with a pressurized recycle stream (35) (HE2). Condensed methanol and water are separated in intermediate flash units (FLASH1 at 30 °C and FLASH2 at 45 °C), preventing liquid to enter the compressors. Finally, compressed CO_2 (9) is used to partially heat pressurized water (51W) (HE3), the latter serving as cooling fluid in the reactor modules later on.

Hydrogen (11-H2, 14472 kmol·h^{-1}) is compressed in a single stage from 30 to 70 bar (CP-H2). CO_2 (10) and H_2 (12) are combined with a pressurized recycle stream (36-REC, 51504 kmol·h^{-1}) (MIXER2), which is mainly composed of H_2 (73% mol/mol), CO_2 (18% mol/mol), and N_2 (7% mol/mol), but also contains low concentrations of CO, methanol and water.

The mixed gas (13) is pre-heated (HE4) with the product stream to 237.5 °C. The reactor feed stream (14) is split into the six reactor modules, which work in parallel and have boiling water at 247.5 °C as cooling fluid (54W and 56W). Here, the number of tubes of both RPLUG units (REACTOR1 and REACTOR2) was set to 99000 tubes, so that the parallel operation of six reactor modules with 33000 tubes each are simulated (tube quantity is limited to 99999 in Aspen). Reactor setpoint temperature (247.5 °C) is rapidly achieved (z = 0.09 m), after which isothermal conditions are maintained ($\Delta T_{max} < 3\,°C$).

The reactor product streams (16 and 18) are combined (MIXER3) and cooled down to 30 °C in four stages: first by the reactor feed (13) (HE4), second by the column feed (28) (HE5), third by the feed of flash drum 4 (26) (HE6), and finally by cooling water (HE7). The first phase

separation occurs in a flash drum (FLASH3 at 30 °C and 69.25 bar), with the gas phase (33) rich in H_2, CO_2 and N_2, and the liquid phase (24) rich in methanol and water, but still containing a considerable amount of CO_2.

The gas stream (33) has a 2% purge (44-PURGE, 1051 kmol·h^{-1}). The remaining recycle stream (34) is recompressed to 70 bar (CP-REC), partially heated (HE2), and mixed with the reactor feed (MIXER1).

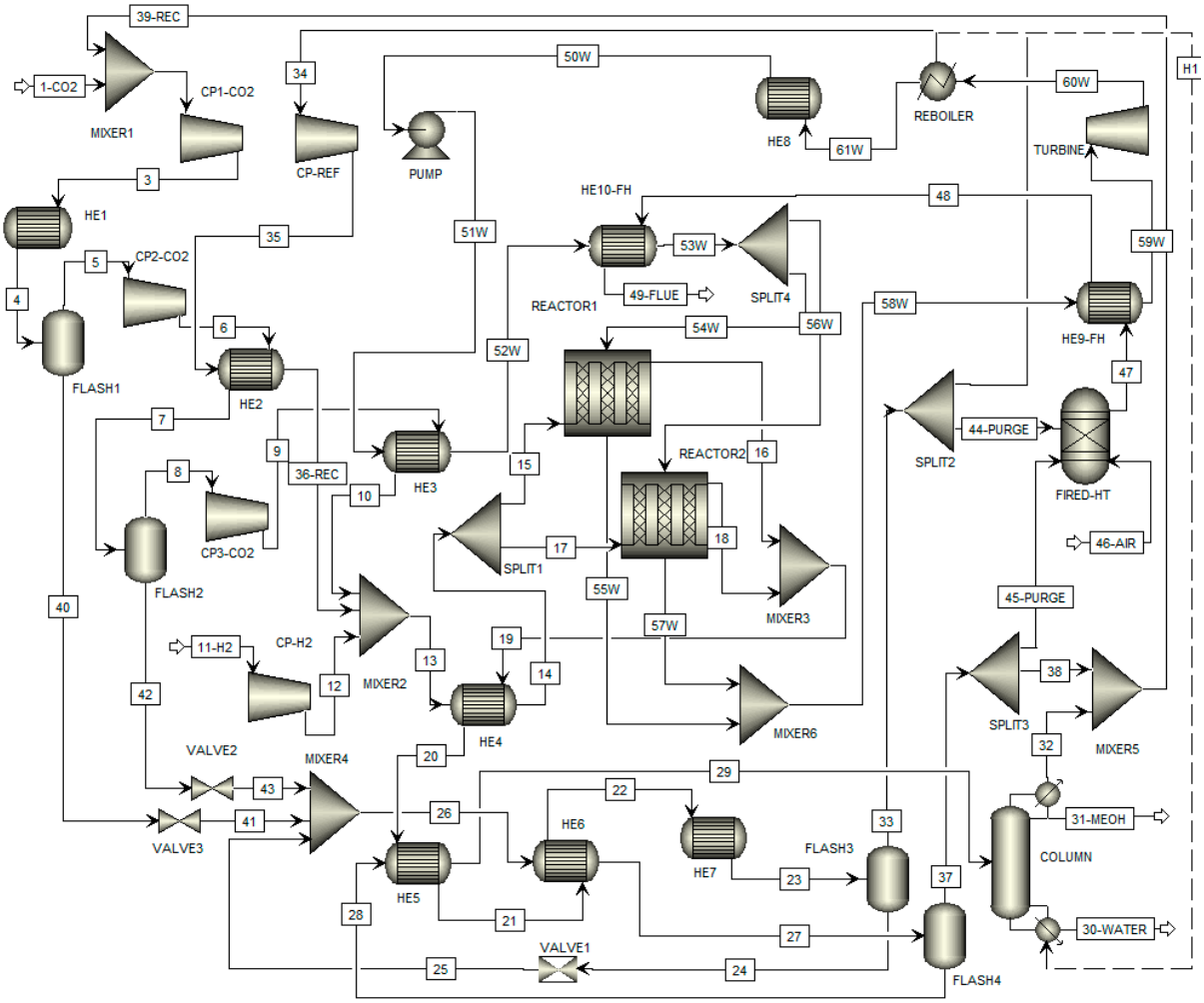

Figure S1. One-step process – Aspen Plus flowsheet.

The liquid stream (24) enters a choke valve (VALVE1), where its pressure is reduced to 1 bar, and afterwards is mixed (MIXER4) with the liquid fractions of FLASH1 and FLASH2 from the three-stage compression process. The mixed stream (26) is slightly heated to 30 °C (HE5), and enters another flash drum (FLASH4 at 30 °C and 1 bar), where more CO_2 is recovered in the gas phase (37). 2% of the gas stream (37) is purged from the system (45-PURGE, 51 kmol·h^{-1}), and the remaining stream (38) is mixed with the gas distillate (32) (MIXER5) and with feed CO_2 (1-CO2) (MIXER1).

The liquid phase (28) from FLASH4, which mainly consists of methanol and water, is pre-heated (HE5) and then enters a distillation column with a partial vapor-liquid condenser at 53 °C and a kettle reboiler at 99.6 °C. The column has 30 stages, a reflux ratio of 2, and the feed enters above the 24th stage. Water as bottom stream (30-WATER, 4581 kmol·h^{-1}) and methanol as liquid distillate (31-MEOH, 4542 kmol·h^{-1}) are obtained in a purity of 99.99% and 99.67% mol/mol, respectively, while the gas distillate (32) consists of a mixture between methanol (62.97% mol/mol) and CO_2 (36.91% mol/mol).

The purge streams (44-PURGE and 45-PURGE) are fed into a fired heater and burned with air (46-AIR, 2232 kmol·h^{-1}). Air excess is set to 15%, following the recommendation from the American Petroleum Institute [5]. The fired heater is composed of the burner (FIRED-HT) and two heat exchangers (HE9-FH and HE10-FH).

In order to make use of the energy generated in the methanol synthesis, the reactor cooling fluid (water) flows in a Rankine cycle. The cycle starts with liquid water at 1 bar and 99.6 °C (50W, 8120 kmol·h^{-1}) being pumped to 38.07 bar, which is then heated until its boiling temperature (247.5 °C) in two steps: first by compressed CO_2 (9) (HE3), and then by the flue gas (48) in the fired heater (HE10-FH). The boiling water stream (53W) is split into the reactor modules and evaporates with the heat released by the methanol synthesis. The resulting streams of saturated vapor (55W and 57W) are merged (MIXER6), and then further heated in the fired heater (HE9-FH) up to 542 °C. The resulting superheated steam (59W) is expanded until 1.43 bar in a turbine coupled with an electric generator, and 30.3 MW of electricity is gained. Low pressure steam (59W) at 155 °C and a boiling temperature of 110 °C exits the turbine and is the heat source of the column reboiler. The hot side is simulated in Aspen Plus with a heater block named REBOILER, and a heat stream is sent to the column (dashed line, H1). After being partially condensed in the reboiler, the remaining steam (61W) (vapor fraction: 0.47) is completely condensed with cooling water (HE13), completing the water cycle.

Table S9. Properties of the streams from the one-step process.

Stream ID	Mole flow [kmol·h^{-1}]	Mass flow [t·h^{-1}]	Temp. [°C]	Pressure [bar]	Mole enthalpy [MJ·kmol^{-1}]	Mole entropy [kJ· kmol^{-1}·K^{-1}]	Total Exergy [MJ·kmol^{-1}]
1-CO2	4824	211.7	25.0	1.00	-392.75	3.02	0.0
2	7610	323.9	27.8	1.00	-373.65	-2.17	102.4
3	7610	323.9	155.3	4.12	-368.48	0.32	111.8
4	7610	323.9	30.0	4.12	-374.91	-17.99	109.7
5	7333	315.8	30.0	4.12	-379.32	-10.92	69.5
6	7333	315.8	158.6	16.98	-374.11	-8.44	78.6
7	7333	315.8	45.0	16.98	-379.57	-23.37	76.6
8	7138	309.3	45.0	16.98	-382.65	-18.86	47.1
9	7138	309.3	178.0	70.00	-377.20	-16.38	56.4
10	7138	309.3	111.0	70.00	-380.03	-23.16	54.8
11-H2	14472	31.1	25.0	30.00	0.00	-27.91	1176.9
12	14472	31.1	127.4	70.00	2.97	-26.38	1187.1
13	73113	948.6	81.4	70.00	-86.80	-22.14	4488.1
14	73113	948.6	237.5	70.00	-81.60	-10.00	4520.1
15	36557	474.3	237.5	70.00	-81.60	-10.00	2260.0
16	32021	474.3	247.9	69.25	-97.10	-17.44	2163.2
17	36557	474.3	237.5	70.00	-81.60	-10.00	2260.0
18	32021	474.3	247.9	69.25	-97.10	-17.44	2163.2
19	64042	948.5	247.9	69.25	-97.10	-17.44	4326.4
20	64042	948.5	133.2	69.25	-103.03	-30.71	4291.2
21	64042	948.5	62.0	69.25	-108.84	-46.20	4270.1
22	64042	948.5	56.9	69.25	-109.12	-47.04	4269.6
23	64042	948.5	30.0	69.25	-110.23	-50.19	4261.2
24	11488	328.0	30.0	69.25	-284.19	-162.33	950.1
25	11488	328.0	18.5	1.00	-284.19	-159.00	946.9
26	11960	342.6	18.9	1.00	-283.31	-160.44	1016.2
27	11960	342.6	30.0	1.00	-281.80	-155.45	1016.3
28	9412	238.8	30.0	1.00	-263.70	-195.62	949.2
29	9412	238.8	82.9	1.00	-224.18	-81.88	963.8
30-WATER	4581	82.5	99.6	1.00	-280.00	-145.98	1.0
31-MEOH	4542	145.7	53.0	1.00	-236.17	-231.08	912.6
32	289	10.5	53.0	1.00	-270.63	-71.02	36.8
33	52555	620.6	30.0	69.25	-72.20	-25.68	3311.1
34	51504	608.2	30.0	69.25	-72.20	-25.68	3244.9
35	51504	608.2	31.2	70.00	-72.16	-25.65	3245.3
36-REC	51504	608.2	56.7	70.00	-71.39	-23.19	3245.9
37	2548	103.8	30.0	1.00	-348.67	-7.11	67.2
38	2497	101.7	30.0	1.00	-348.67	-7.11	65.8
39-REC	2786	112.3	33.0	1.00	-340.58	-13.18	102.5
40	276	8.2	30.0	4.12	-258.07	-205.74	40.1
41	276	8.2	25.8	1.00	-258.07	-205.32	40.0
42	196	6.4	45.0	16.98	-267.32	-187.87	29.3
43	196	6.4	29.1	1.00	-267.32	-184.53	29.3
44-PURGE	1051	12.4	30.0	69.25	-72.20	-25.68	66.2
45-PURGE	51	2.1	30.0	1.00	-348.67	-7.11	1.3

46-AIR	2232	64.4	25.0	1.00	0.00	4.38	0.0
47	2944	78.9	1798.0	1.00	-31.81	65.74	38.9
48	2944	78.9	1095.9	1.00	-60.67	48.77	19.5

Table S9. *(continuation)*

Stream ID	Mole flow [kmol·h^{-1}]	Mass flow [t·h^{-1}]	Temp. [°C]	Pressure [bar]	Mole enthalpy [MJ·kmol^{-1}]	Mole entropy [kJ· kmol^{-1}·K^{-1}]	Total Exergy [MJ·kmol^{-1}]
49-FLUE	2944	78.9	162.5	1.00	-94.18	8.51	1.9
50W	8120	146.3	99.6	1.00	-280.01	-145.97	1.5
51W	8120	146.3	100.9	38.07	-279.90	-145.70	1.6
52W	8120	146.3	130.3	38.07	-277.42	-139.47	3.0
53W	8120	146.3	247.5	38.07	-265.27	-115.18	14.1
54W	4060	73.1	247.5	38.07	-265.27	-115.18	7.0
55W	4060	73.1	247.5	38.07	-234.21	-55.53	22.0
56W	4060	73.1	247.5	38.07	-265.27	-115.18	7.0
57W	4060	73.1	247.5	38.07	-234.21	-55.53	22.0
58W	8120	146.3	247.5	38.07	-234.21	-55.53	44.0
59W	8120	146.3	528.8	38.07	-223.74	-39.50	56.8
60W	8120	146.3	147.5	1.43	-237.66	-35.61	22.8
61W	8120	146.3	110.0	1.43	-261.46	-97.58	10.8

Table S10. Molar composition (% mol/mol) of the streams from the one-step process.

Stream ID	H_2	CO	CO_2	CH_3OH	H_2O	N_2	O_2
1-CO2	0.000	0.000	99.500	0.000	0.500	0.000	0.000
2	0.567	0.247	90.986	6.362	1.100	0.737	0.000
3	0.567	0.247	90.986	6.362	1.100	0.737	0.000
4	0.567	0.247	90.986	6.362	1.100	0.737	0.000
5	0.589	0.257	94.196	3.892	0.302	0.764	0.000
6	0.589	0.257	94.196	3.892	0.302	0.764	0.000
7	0.589	0.257	94.196	3.892	0.302	0.764	0.000
8	0.605	0.264	96.313	1.964	0.069	0.785	0.000
9	0.605	0.264	96.313	1.964	0.069	0.785	0.000
10	0.605	0.264	96.313	1.964	0.069	0.785	0.000
11-H2	99.500	0.000	0.000	0.000	0.000	0.500	0.000
12	99.500	0.000	0.000	0.000	0.000	0.500	0.000
13	71.346	1.515	21.874	0.292	0.026	4.946	0.000
14	71.346	1.515	21.874	0.292	0.026	4.946	0.000
15	71.346	1.515	21.874	0.292	0.026	4.946	0.000
16	60.170	1.765	17.855	7.415	7.147	5.647	0.000
17	71.346	1.515	21.874	0.292	0.026	4.946	0.000
18	60.170	1.765	17.855	7.415	7.147	5.647	0.000
19	60.170	1.765	17.855	7.415	7.147	5.647	0.000
20	60.170	1.765	17.855	7.415	7.147	5.647	0.000
21	60.170	1.765	17.855	7.415	7.147	5.647	0.000
22	60.170	1.765	17.855	7.415	7.147	5.647	0.000
23	60.170	1.765	17.855	7.415	7.147	5.647	0.000
24	0.383	0.167	18.545	40.688	39.718	0.498	0.000
25	0.383	0.167	18.545	40.688	39.718	0.498	0.000
26	0.368	0.161	18.226	41.958	38.809	0.478	0.000
27	0.368	0.161	18.226	41.958	38.809	0.478	0.000
28	0.000	0.001	1.285	50.041	48.671	0.002	0.000
29	0.000	0.001	1.285	50.041	48.671	0.002	0.000
30-WATER	0.000	0.000	0.000	0.015	99.985	0.000	0.000
31-MEOH	0.000	0.000	0.316	99.667	0.016	0.000	0.000
32	0.004	0.029	36.909	62.974	0.004	0.080	0.000
33	73.238	2.115	17.704	0.142	0.028	6.772	0.000
34	73.238	2.115	17.704	0.142	0.028	6.772	0.000
35	73.238	2.115	17.704	0.142	0.028	6.772	0.000
36-REC	73.238	2.115	17.704	0.142	0.028	6.772	0.000
37	1.728	0.751	80.793	12.107	2.386	2.235	0.000
38	1.728	0.751	80.793	12.107	2.386	2.235	0.000

39-REC	1.550	0.676	76.245	17.379	2.139	2.012	0.000
40	0.000	0.001	5.828	71.894	22.273	0.003	0.000
41	0.000	0.001	5.828	71.894	22.273	0.003	0.000

Table S10. *(continuation)*

Stream ID	H_2	CO	CO_2	CH_3OH	H_2O	N_2	O_2
42	0.001	0.004	16.991	74.209	8.783	0.012	0.000
43	0.001	0.004	16.991	74.209	8.783	0.012	0.000
44-PURGE	73.238	2.115	17.704	0.142	0.028	6.772	0.000
45-PURGE	1.728	0.751	80.793	12.107	2.386	2.235	0.000
46-AIR	0.000	0.000	0.000	0.000	0.000	79.000	21.000
47	0.088	0.136	8.612	0.000	26.662	62.336	2.166
48	0.088	0.136	8.612	0.000	26.662	62.336	2.166
49-FLUE	0.088	0.136	8.612	0.000	26.662	62.336	2.166
50W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
51W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
52W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
53W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
54W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
55W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
56W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
57W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
58W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
59W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
60W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
61W	0.000	0.000	0.000	0.000	100.000	0.000	0.000

F. Three-step process – Simulation in Aspen Plus and stream properties

In Figure S2, a detailed flowsheet of the three-step methanol synthesis plant implemented in Aspen Plus is presented. Feed CO_2 (1-CO2, 4655 kmol·h^{-1}) is mixed with a recycle stream (58-REC, 1927 kmol·h^{-1}) (MIXER1), which mainly consists of CO_2 (70% mol/mol), methanol (19% mol/mol), and nitrogen (6%), and has low amounts of other components. Similarly to the previous approach, CO_2 is compressed in a three-stage process from 1 to 70 bar (CP1-CO2, CP2-CO2, CP3-CO2), with intermediate cooling (HE1 and HE2) and intermediate phase separation (FLASH 1 at 30 °C and 4.12 bar, FLASH2 at 45 °C and 16.98 bar).

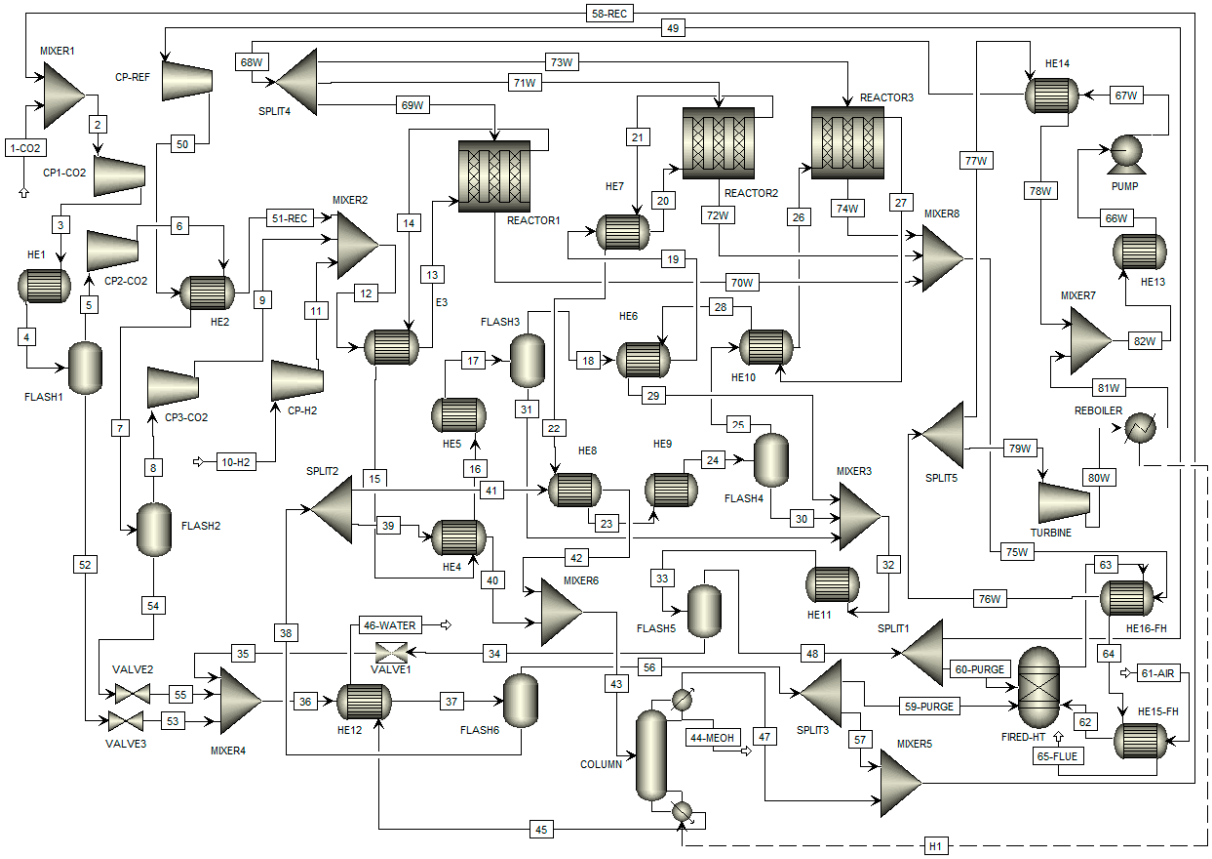

Figure S2. Three-step process – Aspen Plus flowsheet.

Hydrogen (10-H2, 13964 kmol·h^{-1}) is compressed in a single stage from 30 to 70 bar (CP-H2). Hydrogen (11) and CO_2 (9) are mixed (MIXER2) with a pressurized recycle stream (51-REC, 20654 kmol·h^{-1}), which is rich in H_2 (69% mol/mol), N_2 (16% mol/mol), and CO_2 (12% mol/mol).

The mixed stream (12) is pre-heated with the first product stream (14) up to 248.5 °C (HE3), and enters Reactor 1. The reactor cooling is performed with water at 248.5 °C and 45.75 bar

($T_{boiling}$ = 258.5 °C). Reactor setpoint temperature (258.5 °C) is rapidly achieved by both phases (z = 0.75 m), after which isothermal conditions are maintained ($\Delta T_{max} < 3\,°C$). Similar temperature profiles occur in Reactors 2 and 3.

The first product stream (14) is cooled down to 45 °C in three stages: first by the first feed stream (12) (HE3), second by a fraction of the column feed (39) (HE4), and finally by cooling water (HE5). A phase separation of the cooled stream (17) occurs in flash drum (FLASH3, 45 °C and 69.25 bar), where most water (98.8%) and methanol (94.7%), as well as some CO_2 (9.3%) remain in the liquid stream (31).

The remaining gas stream (18) is warmed back to 248.5 °C in two stages: first by the third product stream (28) (HE6), and then by the second product stream (21) (HE7). The warmed stream (20) enters Reactor 2, where similar cooling to the first reactor is applied. The product stream (21) is cooled down to 30 °C in three stages: first by the second reactor feed (19) (HE7), second by a fraction of the column feed (41) (HE8), and finally by cooling water (HE9). Then, a phase separation occurs (FLASH4, 30 °C and 68.5 bar), where most water (99.5%), methanol (97.5%), as well as some CO_2 (12.6%) remain in the liquid stream (30).

The gas stream (25) is heated to 248.5 °C by the third product stream (27) (HE10). The warmed stream (26) enters Reactor 3, with similar cooling to the other ones. The product stream (27) is cooled by the third reactor feed (25) (HE10), and then by the gas stream of flash drum 3 (18) (HE6). After that, the third product stream (29) is mixed with the liquid streams from the intermediate condensation steps (30 and 31) (MIXER3), and the mixture is cooled down to 30 °C with cooling water (HE11). A phase separation occurs (FLASH5, 30 °C and 67.75 bar), where most water (99.9%), methanol (99.3%), and a significant amount of CO_2 (34.5%) remain in the liquid stream (34).

The gas stream (48) has a 2% purge (60-PURGE, 422 kmol·h^{-1}). The remaining recycle stream (49) is recompressed to 70 bar (CP-REC), and pre-heated by feed CO_2 (6) (HE2). Then, the recycle stream (51-REC, 20654 kmol·h^{-1}) is mixed with the compressed feed streams (MIXER2).

The liquid stream from flash drum 5 (34) has a pressure reduction to 1 bar in a choke valve (VALVE1), and is mixed with the liquid fraction from the flash drums 1-2 (53 and 55) (MIXER4). The mixed stream (36) is slightly heated to 30 °C with boiling water from the column (45) (HE12), and then a phase separation occurs (FLASH6, 30 °C and 1 bar). Most of the water (99.1%) and the methanol (95.8%) from the feed stream are recovered in the liquid phase, as well as some CO_2 (8.1%).

The gas stream (56) has a 2% purge (59-PURGE, 34 $kmol \cdot h^{-1}$). The remaining recycle stream (57) is mixed with the gas distillate (47) (MIXER5), and the resulting stream (58-REC, 1927 $kmol \cdot h^{-1}$) is mixed with feed CO_2 (1) (MIXER1).

The liquid stream from flash drum 6 (38) is split into two parts (stream 39 with 65%, stream 41 with 35%), and these resulting streams are heated in parallel (HE4, HE8) with the first and the second product streams (15 and 22, respectively). The warmed streams (40 and 42) are mixed (MIXER6) and fed to the distillation column, which has a partial vapor-liquid condenser at 53 °C and a kettle reboiler at 99.6 °C. The column has 30 stages, a reflux ratio of 2, and the feed enters above the 24^{th} stage. Water as bottom stream (stream 45, 4563 $kmol \cdot h^{-1}$) and methanol as liquid distillate (44-MEOH, 4540 $kmol \cdot h^{-1}$) are obtained in a purity of 99.99% mol/mol and 99.67% mol/mol, respectively. The gas distillate is mainly composed of methanol (62.97% mol/mol) and CO_2 (36.68% mol/mol).

The purge streams (59-PURGE, 60-PURGE) are burned in a fired heater with air (61-AIR, 873 $kmol \cdot h^{-1}$) at 15% excess, the latter being pre-heated with the flue gas (64) (HE15-FH).

Similarly to the one-step process, a water Rankine cycle is also present in this approach. Condensed water at 99.6 °C and 1 bar (66W, 7680 $kmol \cdot h^{-1}$) is pumped to 45.75 bar. Compressed water (67W) is heated up to 248.5 °C with superheated vapor (77W) (HE14). The warmed water (68W, $T_{boiling}$ = 258.5 °C) is split into three fractions, and each one is fed to a reactor as cooling fluid. The split fraction are chosen according to the heat duty from each respective reactor, that is: 27.7% for Reactor 1, 38.4% for Reactor 2, and 33.9% for Reactor 3. The saturated steams (70W, 72W, 74W), which were vaporized with the reaction enthalpy, are mixed (MIXER8) and further heated in the fired heater up to 513 °C (HE16-FH). The supersaturated steam (76W) is split into two fractions. The first one (77W, 2077 $kmol \cdot h^{-1}$) is used to pre-heat the water that flows to the reactors (67W) (HE14), while the second one (79W, 5602 $kmol \cdot h^{-1}$) generates 20.94 MW of work in a turbine. Low pressure steam (80W) leaves the turbine at 123 °C and 1.43 bar and enters the reboiler of the distillation column as the hot fluid. This is simulated in Aspen Plus with a Heat unit and a heat stream (H1). Finally, a water stream (81W) at 110 °C, 1.43 bar and a vapor fraction of 0.105 is mixed with the water stream from heat exchanger 14 (78W) (MIXER7), and the mixed stream (82W) is fully condensed (HE13), completing the cycle.

Table S11. Properties of the streams from the three-step process.

Stream ID	Mole flow [kmol·h^{-1}]	Mass flow [t·h^{-1}]	Temp. [°C]	Pressure [bar]	Mole enthalpy [MJ·kmol^{-1}]	Mole entropy [kJ·kmol^{-1}·K^{-1}]	Total Exergy [MJ·kmol^{-1}]
1-CO2	4655	204.3	25.0	1.00	-392.75	3.02	0.0
2	6582	279.8	27.5	1.00	-370.74	-0.89	78.7
3	6582	279.8	155.6	4.12	-365.58	1.59	86.8
4	6582	279.8	30.0	4.12	-371.65	-15.58	85.1
5	6406	274.6	30.0	4.12	-374.75	-10.38	60.0
6	6406	274.6	159.1	16.98	-369.54	-7.90	68.0
7	6406	274.6	45.0	16.98	-374.99	-22.79	66.2
8	6239	269.1	45.0	16.98	-377.87	-18.39	41.3
9	6239	269.1	178.5	70.00	-372.42	-15.90	49.4
10-H2	13964	30.0	25.0	30.00	0.00	-27.91	1135.6
11	13964	30.0	127.4	70.00	2.97	-26.38	1145.4
12	40857	545.2	122.3	70.00	-80.39	-18.34	2439.9
13	40857	545.2	248.5	70.00	-76.20	-9.14	2456.3
14	37619	545.2	259.4	69.25	-84.52	-12.09	2387.1
15	37619	545.2	138.1	69.25	-89.08	-21.88	2370.1
16	37619	545.2	60.0	69.25	-94.99	-37.62	2357.3
17	37619	545.2	45.0	69.25	-95.54	-39.05	2353.8
18	33222	427.0	45.0	69.25	-71.44	-22.73	2012.5
19	33222	427.0	90.5	69.25	-70.03	-18.61	2014.1
20	33222	427.0	248.5	69.25	-65.02	-7.17	2028.9
21	30048	426.9	259.4	68.50	-74.94	-12.82	1962.2
22	30048	426.9	125.1	68.50	-80.48	-25.08	1946.4
23	30048	426.9	65.0	68.50	-85.02	-37.32	1939.0
24	30049	426.9	30.0	68.50	-86.55	-41.76	1935.1
25	26387	323.5	30.0	68.50	-60.12	-24.05	1602.1
26	26387	323.5	248.5	68.50	-53.34	-7.23	1615.1
27	23738	323.5	259.0	67.75	-62.71	-13.64	1559.4
28	23738	323.5	100.5	67.75	-70.26	-31.14	1544.1
29	23738	323.5	72.0	67.75	-72.22	-36.59	1541.8
30	3661	103.4	30.0	68.50	-276.99	-169.43	333.0
31	4397	118.3	45.0	69.25	-277.64	-162.34	341.3
32	31796	545.2	59.6	67.75	-124.21	-69.10	2217.0
33	31796	545.2	30.0	67.75	-125.88	-74.13	2212.6
34	10721	294.1	30.0	67.75	-274.41	-171.56	944.0
35	10721	294.1	21.5	1.00	-274.41	-169.30	942.0
36	11064	304.7	21.7	1.00	-274.05	-170.03	991.6
37	11064	304.7	30.0	1.00	-273.01	-166.60	991.7
38	9368	237.5	30.0	1.00	-263.55	-195.79	945.6
39	6089	154.4	30.0	1.00	-263.55	-195.79	614.6
40	6089	154.4	81.8	1.00	-227.00	-90.43	623.3
41	3279	83.1	30.0	1.00	-263.55	-195.79	331.0
42	3279	83.1	83.7	1.00	-221.93	-76.18	336.4
43	9368	237.5	82.5	1.00	-225.22	-85.43	959.7
44-MEOH	4540	145.6	53.0	1.00	-236.17	-231.08	912.2
45	4563	82.2	99.6	1.00	-280.00	-145.98	0.9
46-WATER	4563	82.2	67.8	1.00	-282.55	-153.01	0.4
47	265	9.6	53.0	1.00	-269.76	-70.90	33.7
48	21075	251.2	30.0	67.75	-50.33	-24.57	1268.6

Table S11. *(continuation)*

Stream ID	Mole flow [kmol·h^{-1}]	Mass flow [t·h^{-1}]	Temp. [°C]	Pressure [bar]	Mole enthalpy [MJ·kmol^{-1}]	Mole entropy [kJ·kmol^{-1}·K^{-1}]	Total Exergy [MJ·kmol^{-1}]
49	20654	246.1	30.0	67.75	-50.33	-24.57	1243.2
50	20654	246.1	33.5	70.00	-50.23	-24.50	1243.7
51-REC	20654	246.1	89.3	70.00	-48.54	-19.44	1244.8
52	176	5.2	30.0	4.12	-258.84	-204.42	24.9
53	176	5.2	25.9	1.00	-258.84	-204.01	24.9
54	167	5.5	45.0	16.98	-267.39	-187.51	24.8
55	167	5.5	29.3	1.00	-267.39	-184.22	24.7
56	1696	67.2	30.0	1.00	-325.19	-5.35	46.1
57	1662	65.9	30.0	1.00	-325.19	-5.35	45.2
58-REC	1927	75.5	34.0	1.00	-317.58	-13.64	78.8
59-PURGE	34	1.3	30.0	1.00	-325.19	-5.35	0.9
60-PURGE	422	5.0	30.0	67.75	-50.33	-24.57	25.4
61-AIR	873	25.2	25.0	1.00	0.00	4.38	0.0
62	873	25.2	258.5	1.00	6.90	21.44	0.4
63	1181	31.5	1879.5	1.00	-22.21	67.16	16.5
64	1181	31.5	283.5	1.00	-83.55	16.68	1.4
65-FLUE	1181	31.5	124.4	1.00	-88.65	5.91	0.7
66W	7680	138.4	99.6	1.00	-280.01	-145.97	1.4
67W	7680	138.4	101.2	45.75	-279.88	-145.65	1.5
68W	7680	138.4	248.5	45.75	-265.14	-114.97	13.4
69W	2129	38.4	248.5	45.75	-265.14	-114.97	3.7
70W	2129	38.4	258.5	45.75	-233.85	-56.37	11.9
71W	2951	53.2	248.5	45.75	-265.14	-114.97	5.2
72W	2951	53.2	258.5	45.75	-234.04	-56.73	16.4
73W	2600	46.8	248.5	45.75	-265.14	-114.97	4.6
74W	2600	46.8	258.5	45.75	-233.86	-56.40	14.5
75W	7680	138.4	258.5	45.75	-233.92	-56.52	42.8
76W	7680	138.4	509.3	45.75	-224.49	-41.98	53.7
77W	2077	37.4	509.3	45.75	-224.49	-41.98	14.5
78W	2077	37.4	111.8	45.75	-279.00	-143.37	0.5
79W	5602	100.9	509.3	45.75	-224.49	-41.98	39.2
80W	5602	100.9	120.4	1.43	-238.59	-37.90	15.4
81W	5602	100.9	110.0	1.43	-274.91	-132.69	2.8
82W	7680	138.4	110.0	1.43	-276.02	-135.58	3.3

Table S12. Molar composition (% mol/mol) of the streams from the three-step process.

Stream ID	H_2	CO	CO_2	CH_3OH	H_2O	N_2	O_2
1-CO2	0.000	0.000	99.500	0.000	0.500	0.000	0.000
2	0.575	0.310	90.708	5.592	0.957	1.858	0.000
3	0.575	0.310	90.708	5.592	0.957	1.858	0.000
4	0.575	0.310	90.708	5.592	0.957	1.858	0.000
5	0.590	0.318	93.045	3.814	0.322	1.909	0.000
6	0.590	0.318	93.045	3.814	0.322	1.909	0.000
7	0.590	0.318	93.045	3.814	0.322	1.909	0.000
8	0.606	0.327	95.083	1.950	0.075	1.960	0.000
9	0.606	0.327	95.083	1.950	0.075	1.960	0.000
10-H2	99.500	0.000	0.000	0.000	0.000	0.500	0.000
11	99.500	0.000	0.000	0.000	0.000	0.500	0.000
12	69.148	1.301	20.603	0.376	0.027	8.545	0.000
13	69.148	1.301	20.603	0.376	0.027	8.545	0.000
14	60.953	2.651	16.835	4.711	5.570	9.279	0.000
15	60.953	2.651	16.835	4.711	5.570	9.279	0.000
16	60.953	2.651	16.835	4.711	5.570	9.279	0.000
17	60.953	2.651	16.835	4.711	5.570	9.279	0.000
18	68.971	2.974	17.283	0.283	0.074	10.415	0.000
19	68.971	2.974	17.283	0.283	0.074	10.415	0.000
20	68.971	2.974	17.283	0.283	0.074	10.415	0.000
21	61.037	2.664	14.451	5.594	4.739	11.515	0.000
22	61.037	2.664	14.451	5.594	4.739	11.515	0.000
23	61.037	2.664	14.451	5.594	4.739	11.515	0.000
24	61.037	2.664	14.451	5.594	4.739	11.515	0.000
25	69.456	3.001	14.377	0.157	0.028	12.982	0.000
26	69.456	3.001	14.377	0.157	0.028	12.982	0.000
27	61.594	2.209	11.528	5.754	4.484	14.431	0.000
28	61.594	2.209	11.528	5.754	4.484	14.431	0.000
29	61.594	2.209	11.528	5.754	4.484	14.431	0.000
30	0.362	0.236	14.984	44.780	38.689	0.949	0.000
31	0.370	0.213	13.448	38.169	47.100	0.699	0.000
32	46.077	1.706	12.192	14.731	14.316	10.979	0.000
33	46.077	1.706	12.192	14.731	14.316	10.979	0.000
34	0.360	0.194	12.500	43.384	42.399	1.164	0.000
35	0.360	0.194	12.500	43.384	42.399	1.164	0.000
36	0.349	0.188	12.458	44.266	41.612	1.128	0.000
37	0.349	0.188	12.458	44.266	41.612	1.128	0.000
38	0.000	0.001	1.188	50.087	48.715	0.008	0.000
39	0.000	0.001	1.188	50.087	48.715	0.008	0.000
40	0.000	0.001	1.188	50.087	48.715	0.008	0.000
41	0.000	0.001	1.188	50.087	48.715	0.008	0.000
42	0.000	0.001	1.188	50.087	48.715	0.008	0.000
43	0.000	0.001	1.188	50.087	48.715	0.008	0.000
44-MEOH	0.000	0.000	0.314	99.668	0.017	0.000	0.000
45	0.000	0.000	0.000	0.010	99.990	0.000	0.000
46-WATER	0.000	0.000	0.000	0.010	99.990	0.000	0.000
47	0.006	0.051	36.679	62.974	0.004	0.285	0.000
48	69.332	2.474	12.035	0.155	0.030	15.973	0.000

Table S12. *(continuation)*

Stream ID	H_2	CO	CO_2	CH_3OH	H_2O	N_2	O_2
49	69.332	2.474	12.035	0.155	0.030	15.973	0.000
50	69.332	2.474	12.035	0.155	0.030	15.973	0.000
51-REC	69.332	2.474	12.035	0.155	0.030	15.973	0.000
52	0.000	0.001	5.785	70.187	24.018	0.008	0.000
53	0.000	0.001	5.785	70.187	24.018	0.008	0.000
54	0.001	0.005	16.820	73.579	9.565	0.030	0.000
55	0.001	0.005	16.820	73.579	9.565	0.030	0.000
56	2.274	1.218	74.689	12.118	2.388	7.313	0.000
57	2.274	1.218	74.689	12.118	2.388	7.313	0.000
58-REC	1.963	1.058	69.470	19.100	2.061	6.348	0.000
59-PURGE	2.274	1.218	74.689	12.118	2.388	7.313	0.000
60-PURGE	69.332	2.474	12.035	0.155	0.030	15.973	0.000
61-AIR	0.000	0.000	0.000	0.000	0.000	79.000	21.000
62	0.000	0.000	0.000	0.000	0.000	79.000	21.000
63	0.145	0.216	7.548	0.000	25.558	64.303	2.230
64	0.145	0.216	7.548	0.000	25.558	64.303	2.230
65-FLUE	0.145	0.216	7.548	0.000	25.558	64.303	2.230
66W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
67W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
68W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
69W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
70W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
71W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
72W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
73W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
74W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
75W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
76W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
77W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
78W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
79W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
80W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
81W	0.000	0.000	0.000	0.000	100.000	0.000	0.000
82W	0.000	0.000	0.000	0.000	100.000	0.000	0.000

G. Equipment dimensioning

G.1 Flash drum

According to Towler & Sinnott,[6] the diameter (D) of a flash drum with a demister pad can be estimated by following equation:

$$D = \sqrt{\frac{4 \cdot \dot{V}_g}{\pi \cdot u_t}} \tag{S39}$$

Where $\dot{V}_g$ is the gas volumetric flow rate ($m^3 \cdot s^{-1}$) and u_t is the settling velocity of the liquid droplets, which is estimated as follows:

$$u_t = 0.07 \cdot \sqrt{\frac{\rho_L - \rho_g}{\rho_g}} \tag{S40}$$

Here, ρ_L and ρ_g are the liquid the gas densities ($kg \cdot m^{-3}$).

According to Towler & Sinnott,[6] the adequate height (H, in m) of the flash drum is estimated as follows:

$$H = 1.5 \cdot D + 0.5 + \frac{\dot{V}_L}{A_c} \cdot t_h \tag{S41}$$

Where $\dot{V}_L$ is the liquid volumetric flow rate ($m^3 \cdot s^{-1}$), A_c is the cross section area (m^2), and t_h is the liquid hold up time (s), which is typically 10 minutes for low viscous fluids.

The estimated dimensions of the flash drums are summarized in Table S13.

Table S13. Dimension of the flash drums of the one-step and the three-step processes.

Process	Equipment	Diameter (m)	Height (m)	Volume (m^3)
One-step	Flash 1	4.59	7.48	123.5
	Flash 2	3.25	5.54	46.0
	Flash 3	4.33	11.18	164.8
	Flash 4	3.77	10.37	115.6
Three-step	Flash 1	4.28	6.99	100.6
	Flash 2	3.04	5.21	37.7
	Flash 3	3.59	8.14	82.6
	Flash 4	3.13	7.77	59.8
	Flash 5	2.78	13.94	84.9
	Flash 6	3.05	11.47	84.0

G.2 Distillation column

Since methanol production is fixed for both processes, and the inlet feed of the distillation column mainly consists in methanol and water at 50/50% mol/mol, the operating conditions of this equipment is similar in both processes, and, therefore, the same dimensions applies for both cases.

In a packed distillation column, the capacity is associated with the column cross-section area (i.e. its diameter), while the separation efficiency is associated with the column height (i.e. the number of theoretical stages). Towler and Sinnott[6] recommend a packing size between 50 and 76 mm if the column diameter is larger than 0.9 m. We chose then carbon steel pall rings with 76 mm packing size, which correspond to a packing factor (F_P) of 52 m^{-1}.

In order to estimate the required cross-section area, first a stress factor (F_{LV}) is calculated:

$$F_{LV} = \frac{\dot{m}_L}{\dot{m}_g} \cdot \sqrt{\frac{\rho_g}{\rho_L}} \tag{S42}$$

Here, $\dot{m}_L$ and $\dot{m}_g$ are the liquid and gas mass flow rates ($kg \cdot s^{-1}$), ρ_L and ρ_g are the liquid and gas densities ($kg \cdot m^{-3}$).

Towler and Sinnot recommend a pressure drop in packed distillation columns to be between 40 and 80 (mm H_2O)·(m of packed height)$^{-1}$. Considering a pressure drop around 80 (mm H_2O)·(m of packed height)$^{-1}$, and a calculated stress factor of 0.059, a constant K_4 of 2.1 is obtained from a generalized pressure drop correlation.[6] The required cross-section area (m^2) of the column is 39.1 m^2, which is calculated with following equation: [6]

$$A_c = \dot{m}_g \cdot \sqrt{\frac{13.1 \cdot F_P}{K_4 \cdot \rho_g \cdot (\rho_L - \rho_g)} \cdot \left(\frac{\mu_L}{\rho_L}\right)^{0.1}} \tag{S43}$$

In order to provide the required cross-section area, two columns are proposed, each with a diameter of D = 5 m (combined A_c = 39.27 m^2). The height the packed columns is estimated by multiplying the number of stages (30) to a height equivalent to a theoretical plate (HETP). A typical value for large packing size of HETP = 1 m is assumed,[6] corresponding to a total column height of 30 m.

G.3 Heat exchanger

The estimation of the required surface area of a heat exchanger (A_S) is made considering a global heat transfer coefficient (U) and logarithmic mean temperature difference (ΔT_{LM}), as follows:

$$A_S = \frac{\dot{Q}}{U \cdot \Delta T_{LM}} \tag{S44}$$

$$\Delta T_{LM} = \frac{(\Delta T_{hot} - \Delta T_{cold})}{\ln\left(\frac{\Delta T_{hot}}{\Delta T_{cold}}\right)} \tag{S45}$$

Where ΔT_{hot} and ΔT_{cold} are the inlet/outlet temperature difference of the hot fluid and the cold fluid, respectively, and $\dot{Q}$ is the heat transfer duty.

The heat transfer coefficient of each heat exchanger (U), including the condenser and reboiler of the distillation columns, is selected from the typical values presented in the VDI Atlas,[2] which depend on the conditions of both fluids. In Table S14, the considered coefficients, the heat duties and the surface areas of the heat exchangers are summarized.

Table S14. Global heat transfer coefficients, heat transfer duty, and estimated surface area of the heat exchangers of the one-step and the three-step process.

Process	Equipment	$\dot{Q}$ (MW)	U (W·m^{-2}·K^{-1})	A_S (m²)
One-step	HE1	13.6	50	5800
	HE2	11.1	70	3610
	HE3	5.6	200	1160
	HE4	105.5	150	27270
	HE5	103.3	300	8520
	HE6	5.0	600	240
	HE7	24.2	300	4280
	HE8	41.8	1500	340
	Col. Condenser	143.6	1000	2360
	Col. Reboiler	53.7	1000	2580
Three-step	HE1	11.1	50	4730
	HE2	9.7	70	4280
	HE3	47.6	150	24060
	HE4	61.8	300	4940
	HE5	7.7	300	870
	HE6	13.0	150	5050
	HE7	46.3	150	15050
	HE8	14.3	300	2210
	HE9	37.9	300	3320
	HE10	49.7	150	10530
	HE11	14.8	300	2490
	HE12	3.2	300	190
	HE13	8.5	1500	70
	HE14	31.5	1000	410
	Col. Condenser	143.0	1000	2350
	Col. Reboiler	56.5	1000	2690

H. Techno-economic analysis

Table S15. Calculation of the Capital Expenses (CAPEX) depending on the total equipment costs (EC).

Item	Costs
Direct costs (D)	
Equipment costs (*EC*)	$\sum \mathrm{EC}_j$
Installation	$0.47 \cdot \sum EC_j$
Instrumentation controls	$0.36 \cdot \sum EC_j$
Piping	$0.68 \cdot \sum EC_j$
Electrical systems	$0.11 \cdot \sum EC_j$
Buildings	$0.18 \cdot \sum EC_j$
Yard improvement	$0.10 \cdot \sum EC_j$
Service facilities	$0.55 \cdot \sum EC_j$
Indirect costs (I)	
Engineering & supervision	$0.33 \cdot \sum EC_j$
Construction expenses	$0.41 \cdot \sum EC_j$
Legal expenses	$0.4 \cdot \sum EC_j$
Contractors	$0.05 \cdot (D + I) = 0.2115 \cdot \sum EC_j$
Contingency	$0.10 \cdot (D + I) = 0.4230 \cdot \sum EC_j$
Fixed capital investment (FCI)	$4.8645 \cdot \sum EC_j$
Working capital (WC)	$0.10\ of\ CAPEX = 0.5405 \cdot \sum EC_j$
Capital expenses (CAPEX)	$FCI + WC = 5.4050 \cdot \sum EC_j$

Table S16. Estimation of indirect operating expenses ($OPEX_{ind}$).

Item	Costs
Operating labor (***OL***)	OL
Operating supervision (***OS***)	$0.15 \cdot OL$
Maintenance labor (***ML***)	$0.02 \cdot FCI$
Maintenance material (***MM***)	$0.02 \cdot FCI$
Operating supplies	$0.15 \cdot (ML + MM) = 0.006 \cdot FCI$
Laboratory charges	$0.20 \cdot OL$
Insurance and taxes	$0.02 \cdot FCI$
Plant overhead (***PO***)	$0.60 \cdot (OL + OS + ML) = 0.69 \cdot OL + 0.012 \cdot FCI$
Administrative costs	$0.25 \cdot PO = 0.1725 \cdot OL + 0.003 \cdot FCI$
Distribution & Marketing costs	$0.06 \cdot NPC$
Research & Development	$0.04 \cdot NPC$
Total $\boldsymbol{OPEX_{ind}}$	$2.2125 \cdot OL + 0.081 \cdot FCI + 0.10 \cdot NPC$

Table S17. Equipment characteristic dimensions and equipment costs (EC) of the one-step approach. All equipment is built with carbon steel. All equipment reference price is taken from Peters et al. [7], except for the power generator, whose ref. price is taken from Henning and Haase. [8]

Equipment ID	Scaling factor	Characteristic capacity	Total cost in 2020 (M€)
Centrifugal compressors and pumps			
CP1-CO2	0.69	Power = 11.50 MW	9.15
CP2-CO2	0.69	Power = 11.16 MW	8.89
CP3-CO2	0.69	Power = 11.37 MW	9.06
CP-H2	0.69	Power = 12.58 MW	10.02
CP-REC	0.69	Power = 0.57 MW	0.52
Pump	0.33	Volumetric flow rate = 0.044 $m^3 \cdot s^{-1}$, Discharge pressure = 38.07 bar	0.11
Flash drums			
FLASH1	0.57	Volume = 124 m^3	0.05
FLASH2	0.57	Volume = 46 m^3	0.03
FLASH3	0.57	Volume = 165 m^3	0.05
FLASH4	0.57	Volume = 116 m^3	0.05
Fixed-tubed heat exchangers and reactor modules			
HE1	0.44	Heat transfer area = 5800 m^2	0.52
HE2	0.44	Heat transfer area = 3610 m^2	0.40
HE3	0.44	Heat transfer area = 1160 m^2	0.13
HE4	0.44	Heat transfer area = 27270 m^2	3.01
HE5	0.44	Heat transfer area = 8520 m^2	0.94
HE6	0.44	Heat transfer area = 240 m^2	0.04
HE7	0.44	Heat transfer area = 4280 m^2	0.48
HE8	0.44	Heat transfer area = 340 m^2	0.04
Reactor (6 units)	0.44	Heat transfer area = 48600 m^2	32.18

Table S17. *(continuation)*

Equipment ID	Scaling factor	Characteristic capacity	Total cost in 2020 (M€)
Distillation column (2 units of each equipment)			
Condenser	0.44	Heat transfer area = 2360 m²	0.43
Reboiler	0.60	Heat transfer area = 2580 m²	0.50
Packed Column	0.86	Diameter = 5 m, Height = 30 m	2.06
Fired heater and air blower			
Fired heater	0.60	Heat duty = 51.00 MW	3.54
Blower	0.616	Air flow = 15.36 $m^3 \cdot s^{-1}$	0.56
Steam turbine and power generator			
Steam Turbine	0.44	Power = 29.82 MW	1.04
Generator	1	Power = 29.82 MW	1.71

Table S18. Equipment characteristic dimensions and equipment costs (EC) of the three-step approach. All equipment is built with carbon steel, and the costs include 10% delivery costs. All equipment reference price is taken from Peters et al. [7], except for the power generator, whose ref. price is taken from Henning and Haase. [8]

Equipment ID	Scaling factor	Characteristic capacity	Total cost in 2020 (M€)
Centrifugal compressors and pumps			
CP1-CO2	0.69	Power = 9.94 MW	7.92
CP2-CO2	0.69	Power = 9.75 MW	7.77
CP3-CO2	0.69	Power = 9.95 MW	7.93
CP-H2	0.69	Power = 12.14 MW	9.97
CP-REC	0.69	Power = 0.63 MW	0.57
Pump	0.33	Volumetric flow rate = 0.042 $m^3 \cdot s^{-1}$, Discharge pressure = 45.76 bar	0.13
Flash drums			
FLASH1	0.57	Volume = 101 m^3	0.05
FLASH2	0.57	Volume = 38 m^3	0.03
FLASH3	0.57	Volume = 83 m^3	0.05
FLASH4	0.57	Volume = 60 m^3	0.04
FLASH5	0.57	Volume = 85 m^3	0.05
FLASH6	0.57	Volume = 84 m^3	0.05
Fixed-tubed heat exchangers and reactor modules			
HE1	0.44	Heat transfer area = 4730 m^2	0.42
HE2	0.44	Heat transfer area = 4280 m^2	0.48
HE3	0.44	Heat transfer area = 24060 m^2	2.66
HE4	0.44	Heat transfer area = 4940 m^2	0.55
HE5	0.44	Heat transfer area = 870 m^2	0.10
HE6	0.44	Heat transfer area = 5050 m^2	0.56
HE7	0.44	Heat transfer area = 15050 m^2	1.66
HE8	0.44	Heat transfer area = 2210 m^2	0.25
HE9	0.44	Heat transfer area = 3320 m^2	0.37

HE10	0.44	Heat transfer area = 10530 m²	1.17

Table S18. *(continuation)*

Equipment ID	Scaling factor	Characteristic capacity	Total cost in 2020 (M€)
Fixed-tubed heat exchangers and reactor modules			
HE11	0.44	Heat transfer area = 2490 m²	0.28
HE12	0.44	Heat transfer area = 190 m²	0.03
HE13	0.44	Heat transfer area = 70 m²	0.01
HE14	0.44	Heat transfer area = 410 m²	0.05
Reactor (3 units)	0.44	Heat transfer area = 48600 m²	16.09
Distillation column (2 units of each equipment)			
Fixed-tubed Condenser	0.44	Heat transfer area = 2350 m²	0.43
U-tubed Reboiler	0.60	Heat transfer area = 2690 m²	0.52
Packed Column	0.86	Diameter = 5 m, Height = 30 m	2.06
Fired heater and air blower			
Fired Heater	0.60	Heat duty = 21.80 MW	1.70
Blower	0.616	Air flow = 6.01 $m^3 \cdot s^{-1}$	0.22
Steam turbine and power generator			
Steam Turbine	0.44	Power = 20.84 MW	0.74
Generator	1	Power = 20.84 MW	1.19

Table S19. Detailed operating expenditures (OPEX) of the one-step and the three-step approach.

Item	Process Requirements		Costs (M€·a^{-1})	
	One-Step	**Three-Step**	**One-Step**	**Three-Step**
Direct OPEX			**874.94**	**839.6**
Hydrogen	31.1 ton·h^{-1}	30.0 ton·h^{-1}	769.50	742.51
Carbon dioxide	211.7 ton·h^{-1}	204.3 ton·h^{-1}	74.93	72.30
Cooling water	38490 ton·h^{-1}	34645 ton·h^{-1}	0.38	0.35
Clean water	1.46 ton·h^{-1}	1.38 ton·h^{-1}	0.02	0.02
Total organic carbon (TOC) abatement of process water	7.75 kg·h^{-1}	5.72 kg·h^{-1}	0.12	0.09
Electricity	17.6 MW	21.83 MW	12.66	15.72
Catalyst (Cu/ZnO/Al_2O_3)	956.2 ton·a^{-1}	478.1 ton·a^{-1}	17.31	8.65
Indirect OPEX			**142.08**	**128.6**
Operating labor (OL)	16 operators	16 operators	1.15	1.15
Operating supervision (OS)			0.17	0.17
Maintenance labor (ML)			8.06	6.23
Maintenance material (MM)			8.06	6.23
Operating supplies			2.42	1.87
Laboratory charges			0.23	0.23
Insurances and taxes			8.06	6.23
Plant overhead (PO)			5.63	4.53
Administrative Costs			1.41	1.13
Distribution & Marketing Costs			64.13	60.50
Research & Development			42.75	40.33

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