

## Supplementary Material

### A techno-economic and life cycle assessment for the production of green methanol from CO<sub>2</sub>: catalyst and process bottlenecks

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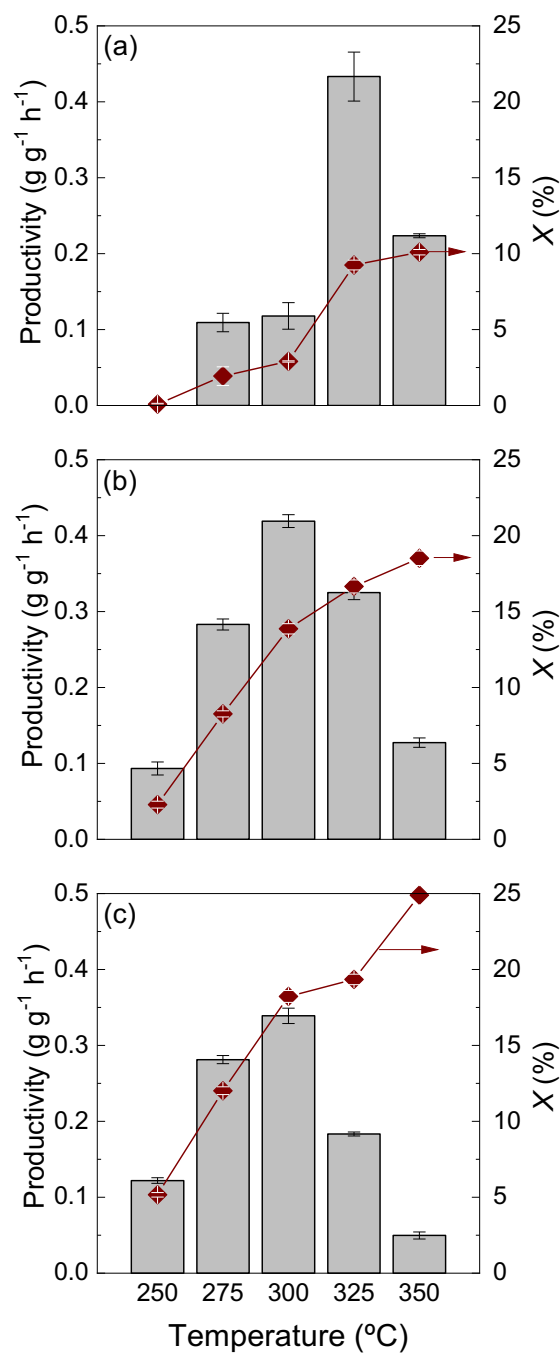
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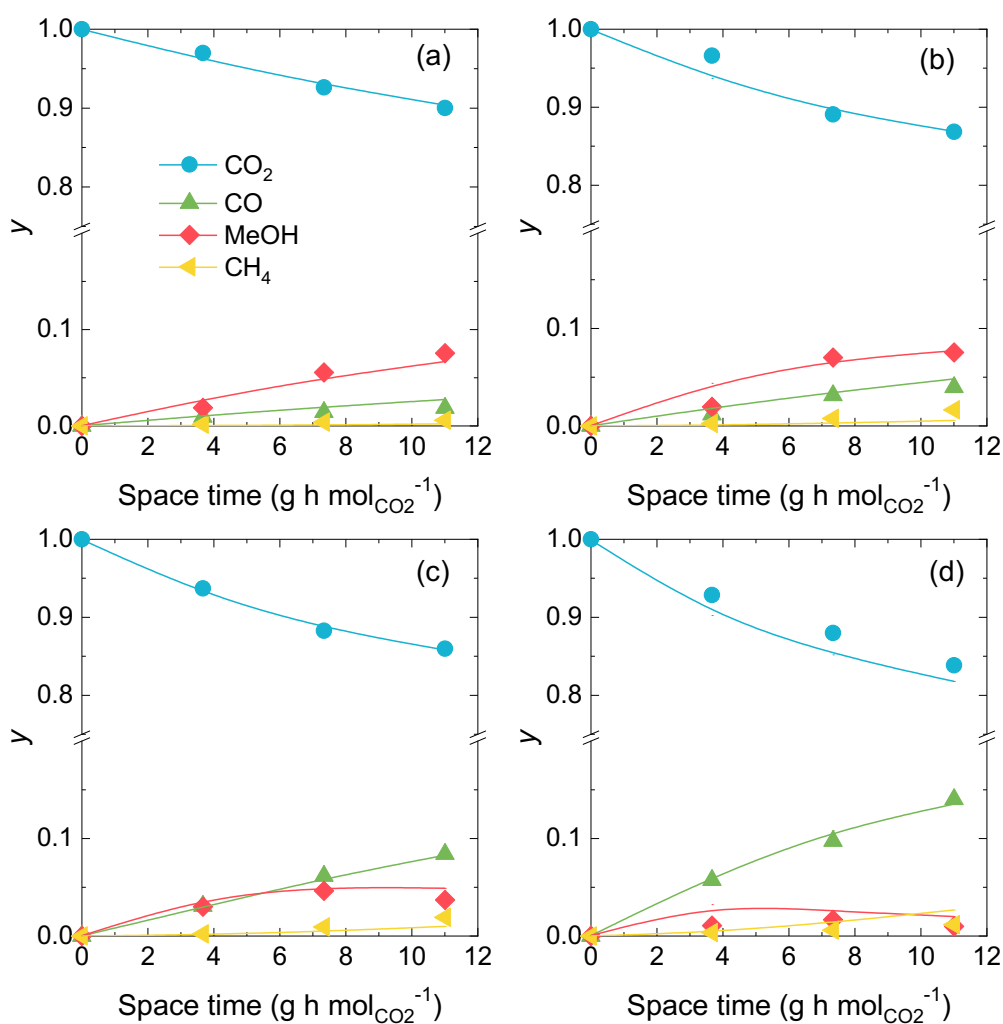
## S1. Experimental methanol activity tests



**Fig. S1.** Evolution with temperature of the methanol productivity and CO<sub>2</sub> conversion at 50 bar, H<sub>2</sub>/CO<sub>2</sub> molar ratio, 4 and using space time values of (a) 3.7, (b) 7.3 and (c) 11.0 g h mol<sub>CO2</sub><sup>-1</sup>.

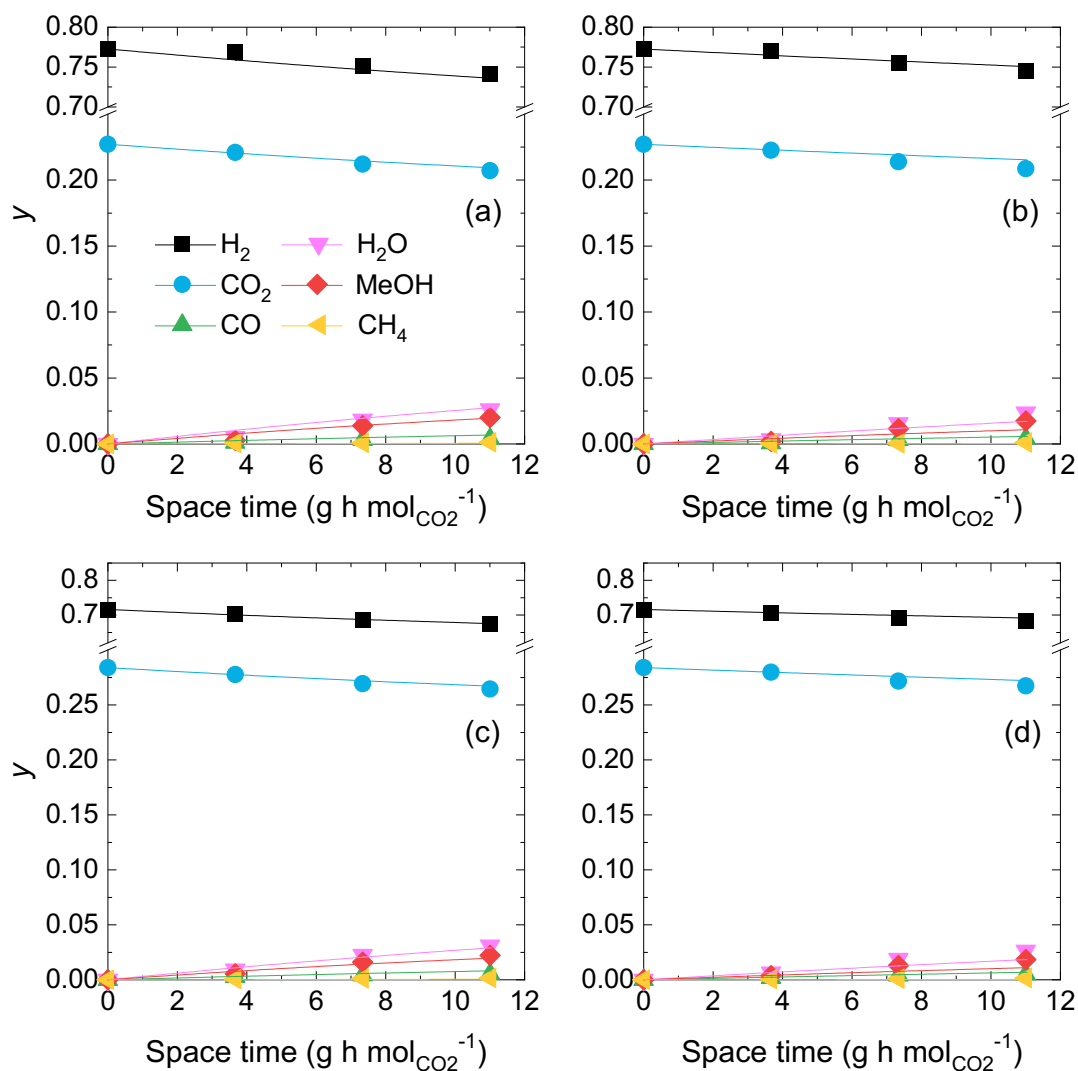
## S2. Experimental data fitting

The results in **Figs. 1d-g** correspond to the experimental data previously observed in **Figs. 1a-c**, collected at different temperatures, 50 bar and using a H<sub>2</sub>/CO<sub>2</sub> molar ratio of 4. Decreasing the H<sub>2</sub>/CO<sub>2</sub> molar ratio in the feed leads to a decrease in the CO<sub>2</sub> conversion. The experimental data fitting using a H<sub>2</sub>/CO<sub>2</sub> molar ratio of 3 at 275 and 300 °C is depicted in **Figs. S2a** and **S2b**, respectively. At both conditions, the concentration of methanol in the reaction medium is also lower than observed before. A similar tendency is observed using lower values of the reaction pressure. The fitting of the data collected at 40 bar is depicted in **Figs. S2c** and **S2d**. Now, CO<sub>2</sub> conversion is not only disfavored, but also the selectivity to methanol significantly decreases. The maximum concentrations of methanol at 325 and 350 °C are predicted to be lower and located at lower space time values. Despite the reaction conditions illustrated in this Figure are not optimal, the developed intrinsic kinetic model for the InCo catalysts is able to accurately predict the evolution of the reaction across a wide range of operating conditions. The fitting of the experimental data, including H<sub>2</sub> and water, at the above studied temperatures is depicted in **Figs. S3-S6**.

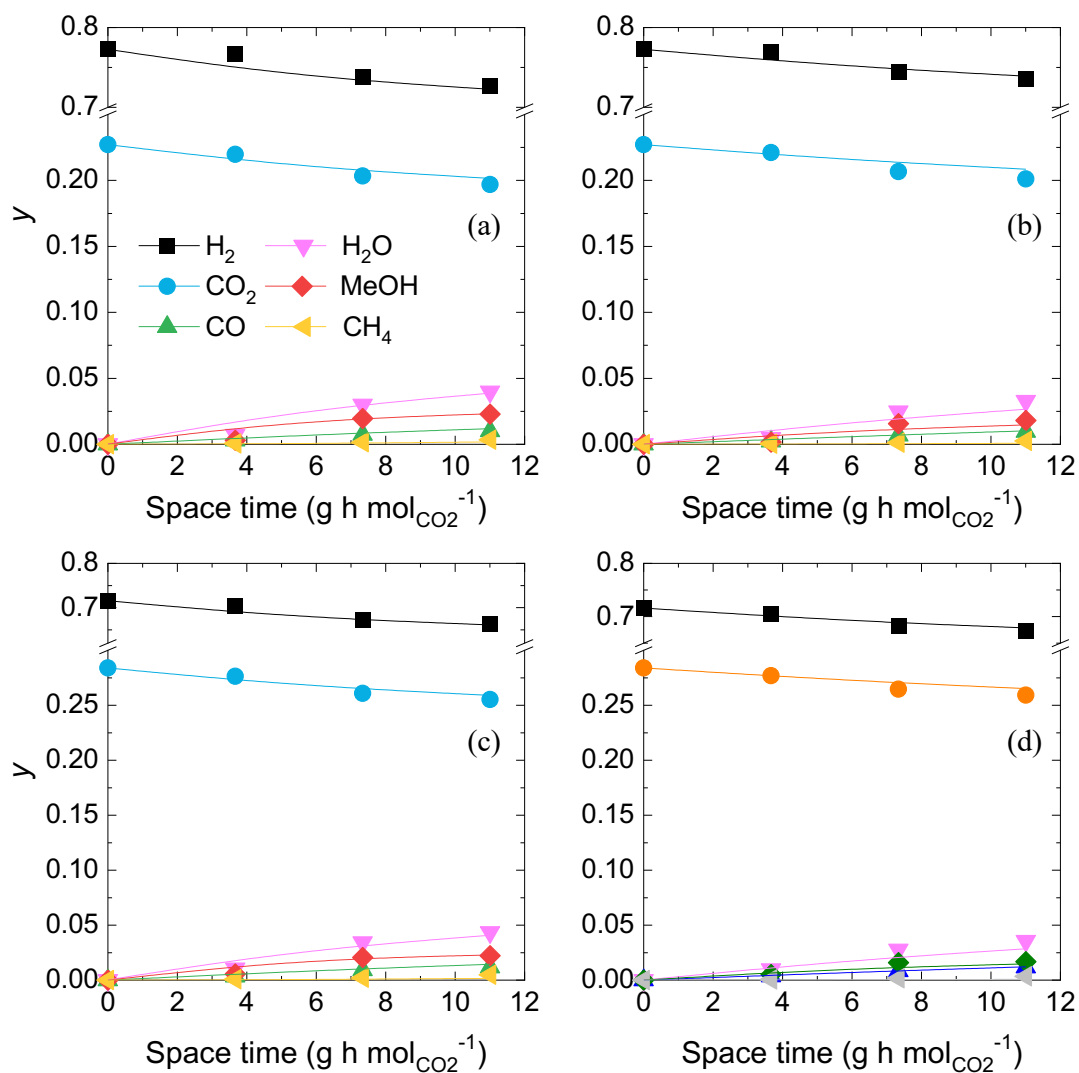


**Fig. S2.** Comparison of the experimental data (symbols) with those estimated by the model (line) for the evolution with space time of the molar fractions. (a) 275 °C, P = 50

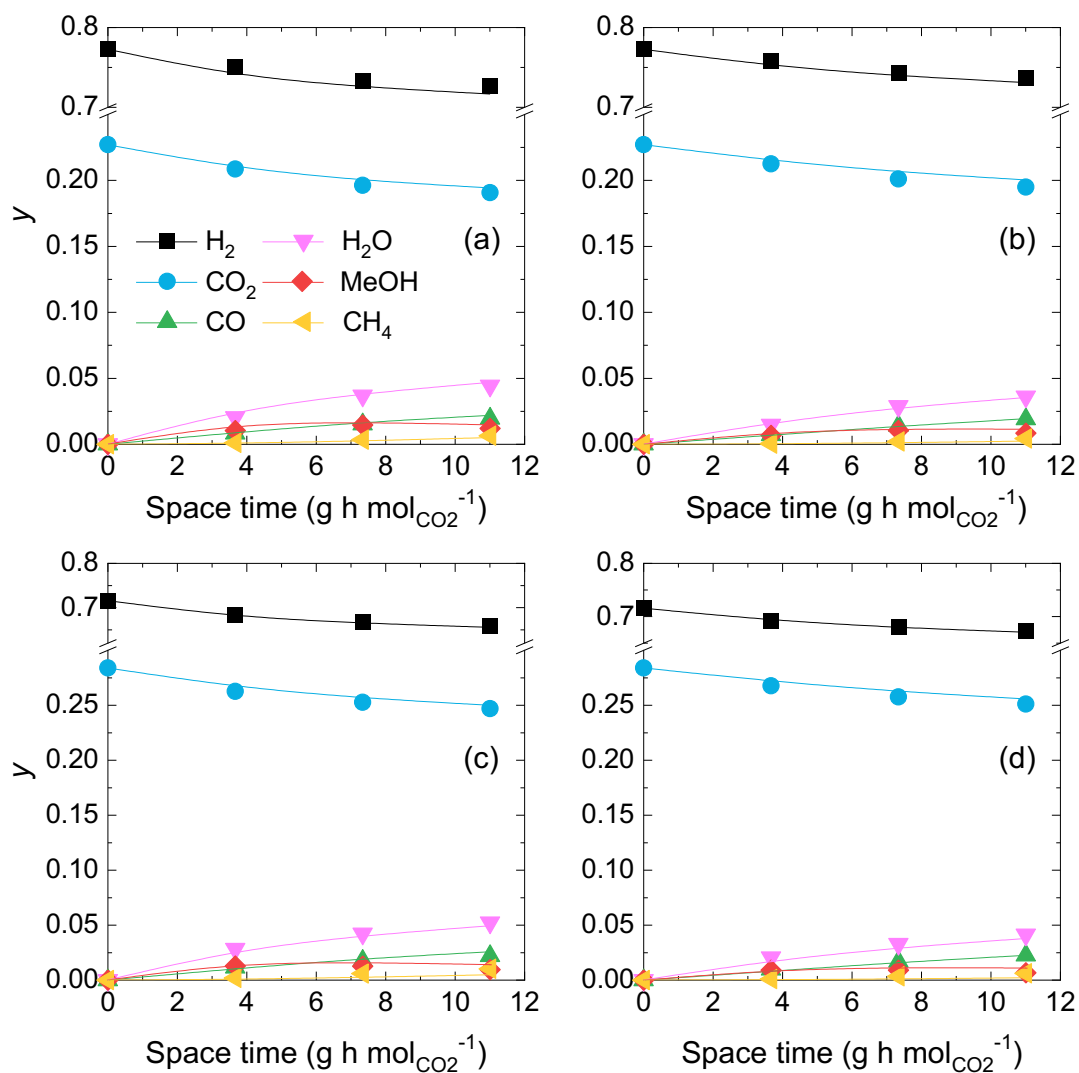
bar,  $H_2/CO_2 = 3$ ; (b) 300 °C,  $P = 50$  bar,  $H_2/CO_2 = 3$ ; (c) 325 °C,  $P = 40$  bar,  $H_2/CO_2 = 4$ ; and (d) 350 °C,  $P = 40$  bar,  $H_2/CO_2 = 4$ ;



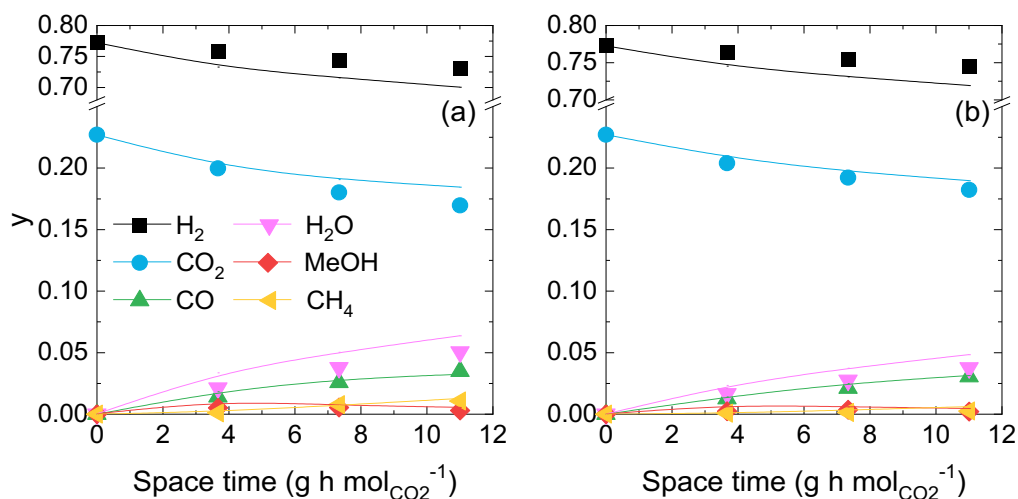
**Fig. S3.** Comparison of the experimental data (symbols) with those estimated by the model (line) for the evolution with space time of the molar fractions at 275 °C. (a)  $P = 50$  bar,  $H_2/CO_2 = 4$ ; (b)  $P = 40$  bar,  $H_2/CO_2 = 4$ ; (c)  $P = 50$  bar,  $H_2/CO_2 = 3$ ; (d)  $P = 40$  bar,  $H_2/CO_2 = 3$



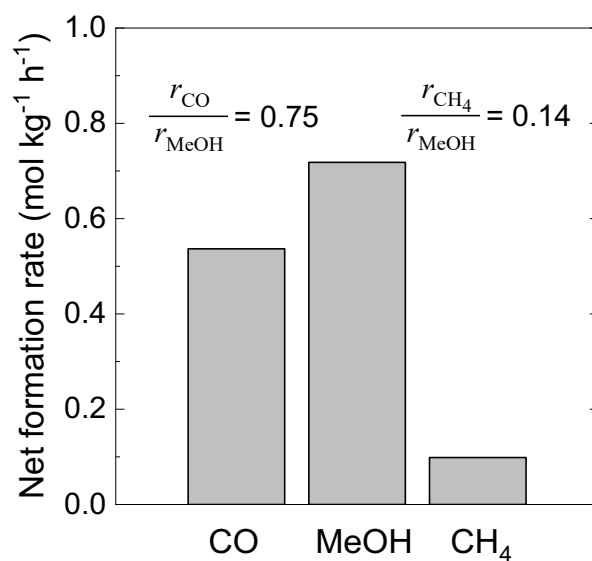
**Fig. S4.** Comparison of the experimental data (symbols) with those estimated by the model (line) for the evolution with space time of the molar fractions at 300 °C. (a)  $P = 50$  bar,  $\text{H}_2/\text{CO}_2 = 4$ ; (b)  $P = 40$  bar,  $\text{H}_2/\text{CO}_2 = 4$ ; (c)  $P = 50$  bar,  $\text{H}_2/\text{CO}_2 = 3$ ; (d)  $P = 40$  bar,  $\text{H}_2/\text{CO}_2 = 3$



**Fig. S5.** Comparison of the experimental data (symbols) with those estimated by the model (line) for the evolution with space time of the molar fractions at 325 °C. (a)  $P = 50$  bar,  $\text{H}_2/\text{CO}_2 = 4$ ; (b)  $P = 40$  bar,  $\text{H}_2/\text{CO}_2 = 4$ ; (c)  $P = 50$  bar,  $\text{H}_2/\text{CO}_2 = 3$ ; (d)  $P = 40$  bar,  $\text{H}_2/\text{CO}_2 = 3$



**Fig. S6.** Comparison of the experimental data (symbols) with those estimated by the model (line) for the evolution with space time of the molar fractions at 350 °C. (a) P = 50 bar, H<sub>2</sub>/CO<sub>2</sub> = 4; (b) P = 40 bar, H<sub>2</sub>/CO<sub>2</sub> = 4



**Fig S7.** Net formation rates of the three main reaction products at the optimal conditions. 300 °C, P = 50 bar, H<sub>2</sub>/CO<sub>2</sub> = 4, and space time of 7.3 g h mol<sub>CO2</sub><sup>-1</sup>



### S3. Kinetic parameters rearrangement for Aspen Plus® simulation

The used kinetics follows Langmuir–Hinshelwood equations. All reactions occur in the vapor phase and the reaction rate is based on catalyst weight. Since Aspen Plus® requires a specific input based on a kinetic factor, a driving force expression and an adsorption term with logarithmic/based constants (see **Eqs. (S1)** and **(S2)**), the developed kinetic equations had to be recalculated. Moreover, parameters must be given in SI units. By way of example, the reaction rate expression for the first step of the reaction network, the reverse water gas shift reaction, should be given as:

$$r_1 \left( \frac{\text{mol}}{\text{kg h}} \right) = \frac{k_1 P_{\text{CO}_2} P_{\text{H}_2} - k'_1 P_{\text{CO}} P_{\text{H}_2\text{O}}}{1 + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}}, \quad (\text{S1})$$

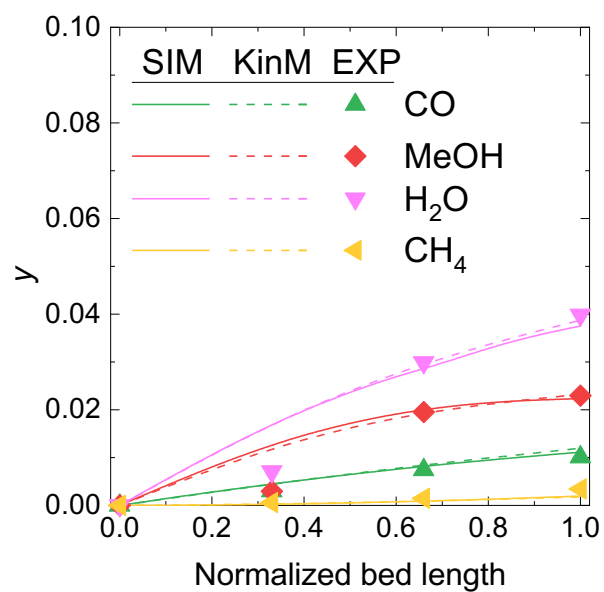
with all constants being expressed as regular Arrhenius-like equations (without the reparametrized form used for kinetic modeling):

$$\ln(k) = A + \frac{B}{T}. \quad (\text{S2})$$

Therefore, the values of A and B constant for all kinetic parameters are listed in **Table S1**.

**Table S1.** Kinetic parameters values for the rearranged Aspen Plus kinetic model.

	<i>A</i>	<i>B</i> (K)
$k_1$	$-3.00 \cdot 10^1$	$-5.77 \cdot 10^3$
$k'_1$	$-3.30 \cdot 10^1$	
$k_2$	$-5.84 \cdot 10^1$	$-6.25 \cdot 10^3$
$k'_2$	$-5.71 \cdot 10^1$	
$k_3$	$-4.14 \cdot 10^1$	$-7.70 \cdot 10^3$
$k'_3$	$-3.72 \cdot 10^1$	
$k_4$	$-5.88 \cdot 10^1$	$-5.65 \cdot 10^3$
$K_{\text{CO}_2}$	$-1.29 \cdot 10^1$	$7.58 \cdot 10^2$
$K_{\text{H}_2\text{O}}$	$-1.94 \cdot 10^1$	$7.10 \cdot 10^2$



**Fig. S8.** Comparison of the experimental data and those predicted by the intrinsic kinetic model and the isolated reactor of the ASPEN process simulation.

#### S4. Stream properties for the MeOH production plant

**Table S2a.** Stream results for the MeOH process described in Fig. 1.

<b>Stream</b>	<b>CO<sub>2</sub></b>	<b>H<sub>2</sub></b>	<b>MEOH</b>	<b>PURGE1</b>	<b>PURGE2</b>	<b>RECYCLE</b>	<b>WATER</b>
H <sub>2</sub> (Mole Frac)	0.00	1.00	0.00	0.64	0.01	0.64	0.00
CO <sub>2</sub> (Mole Frac)	1.00	0.00	0.00	0.18	0.85	0.18	0.00
CH <sub>4</sub> (Mole Frac)	0.00	0.00	0.00	0.14	0.02	0.14	0.00
MeOH (Mole Frac)	0.00	0.00	0.99	0.00	0.09	0.00	0.01
CO (Mole Frac)	0.00	0.00	0.00	0.00	0.02	0.00	0.99
H <sub>2</sub> O (Mole Frac)	0.00	0.00	0.01	0.03	0.00	0.03	0.00
Total Flow (kmol/h)	1750	5500	1000	1949	31	76039	1666
Total Flow (ton/h)	77.0	11.1	32.1	24.5	1.3	953.7	30.4
Temperature (°C)	25.0	25.0	46.8	23.7	25.0	30.0	94.1
Pressure (bar)	1.0	1.0	0.9	1.0	0.9	50.0	0.9

**Table S2.b.** Stream results for the MeOH process described in Fig. 1.

<b>Stream</b>	<b>S1</b>	<b>S2</b>	<b>S3</b>	<b>S4</b>	<b>S5</b>	<b>S6</b>	<b>S7</b>	<b>S8</b>	<b>S9</b>	<b>S10</b>	<b>S11</b>	<b>S12</b>
H <sub>2</sub> (Mole Frac)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	1.00	1.00
CO <sub>2</sub> (Mole Frac)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00
CH <sub>4</sub> (Mole Frac)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MeOH (Mole Frac)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO (Mole Frac)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H <sub>2</sub> O (Mole Frac)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Flow(kmol/h)	1750	1750	1750	1750	1750	1750	1750	5500	5500	5500	5500	5500
Total Flow (ton/h)	77.0	77.0	77.0	77.0	77.0	77.0	77.0	11.1	11.1	11.1	11.1	11.1
Temperature (°C)	132.8	30.0	150.6	30.0	140.8	30.0	80.5	177.8	30.0	202.9	30.0	185.6
Pressure (bar)	3.0	3.0	10.0	10.0	30.0	30.0	50.0	3.0	3.0	10.0	10.0	30.0

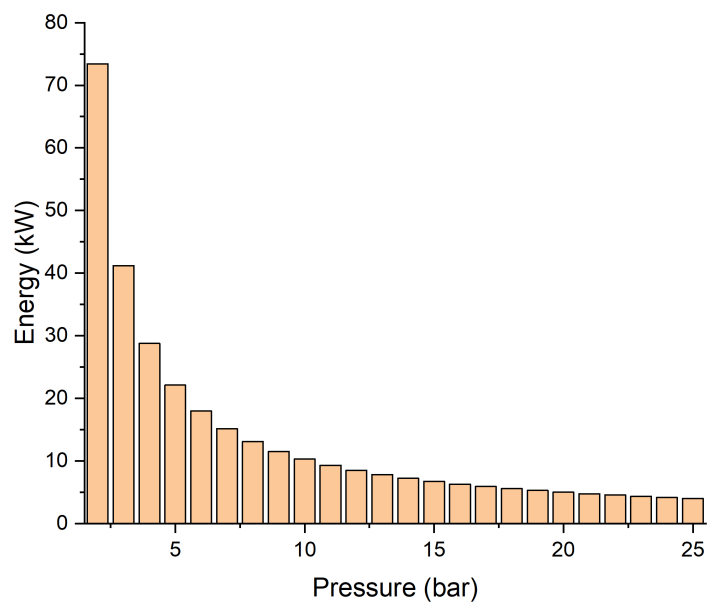
**Table S2.c.** Stream results for the MeOH process described in Fig. 1.

<b>Stream</b>	<b>S13</b>	<b>S14</b>	<b>S15</b>	<b>S16</b>	<b>S17</b>	<b>S18</b>	<b>S19</b>	<b>S20</b>	<b>S21</b>	<b>S22</b>	<b>S23</b>
H <sub>2</sub> (Mole Frac)	1.00	1.00	0.65	0.65	0.62	0.62	0.64	0.64	0.00	0.00	0.00
CO <sub>2</sub> (Mole Frac)	0.00	0.00	0.19	0.19	0.18	0.18	0.18	0.18	0.01	0.01	0.00
CH <sub>4</sub> (Mole Frac)	0.00	0.00	0.13	0.13	0.14	0.14	0.14	0.14	0.00	0.00	0.00
MeOH (Mole Frac)	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.38	0.38	0.38
CO (Mole Frac)	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.61	0.61	0.62
H <sub>2</sub> O (Mole Frac)	0.00	0.00	0.03	0.03	0.03	0.03	0.03	0.03	0.00	0.00	0.00
Total Flow(kmol/h)	5500	5500	83289	83289	80677	80677	77989	1949	2697	2697	2666
Total Flow (ton/h)	11.1	11.1	1041.8	1041.8	1041.8	1041.8	978.1	24.5	63.7	63.7	62.4
Temperature (°C)	30.0	96.8	34.5	225.0	300.0	30.0	30.0	30.0	30.0	30.1	25.0
Pressure (bar)	30.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	0.9	0.9

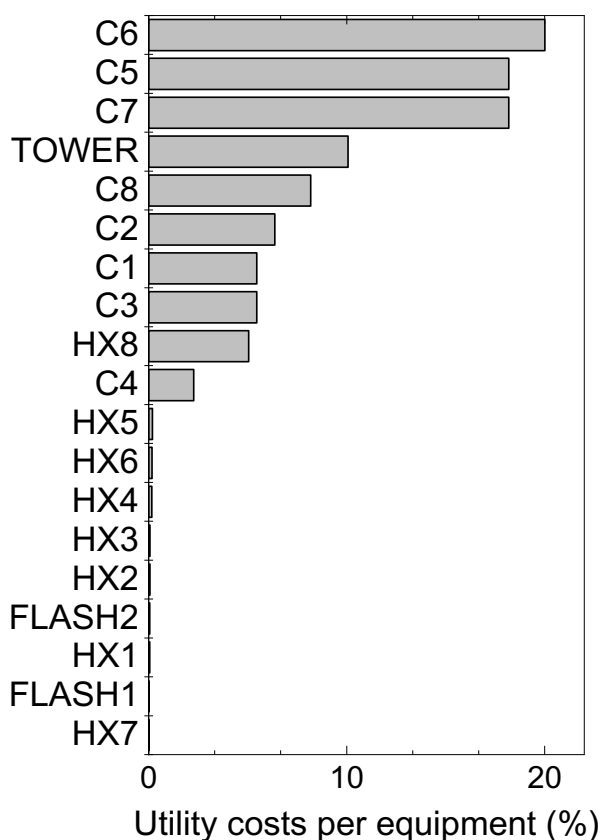
## S5. Additional Aspen Plus® simulations for the MeOH production plant

**Table S3.** Main equipment estimated costs with cost distribution for the MeOH process.

<b>Equipment ID</b>	<b>Individual cost (k\$)</b>	<b>% Total cost (%)</b>
<i>C5</i>	21 905.6	43.9
<i>C6</i>	9 244.6	18.5
<i>REACTOR</i>	3 550.0	7.1
<i>C7</i>	3 360.6	6.7
<i>C1</i>	2 812.1	5.6
<i>C8</i>	1 982.9	4.0
<i>C2</i>	1 480.5	3.0
<i>TOWER</i>	1 332.9	2.7
<i>HX8</i>	1 169.3	2.3
<i>C3</i>	1 162.1	2.3
<i>C4</i>	943.8	1.9
<i>HX7</i>	589.7	1.2
<i>FLASH1</i>	152.5	0.3
<i>FLASH2</i>	70.8	0.1
<i>HX6</i>	46.8	0.1
<i>HX5</i>	39.1	0.1
<i>HX4</i>	34.8	0.1
<i>HX3</i>	26.6	0.1
<i>HX2</i>	20.3	0.1
<i>HX1</i>	19.8	0.1



**Fig. S9.** Evolution of the energy consumption for pressurization of  $100 \text{ kmol h}^{-1}$  of  $\text{H}_2$  from one to 25 bar in one bar steps.

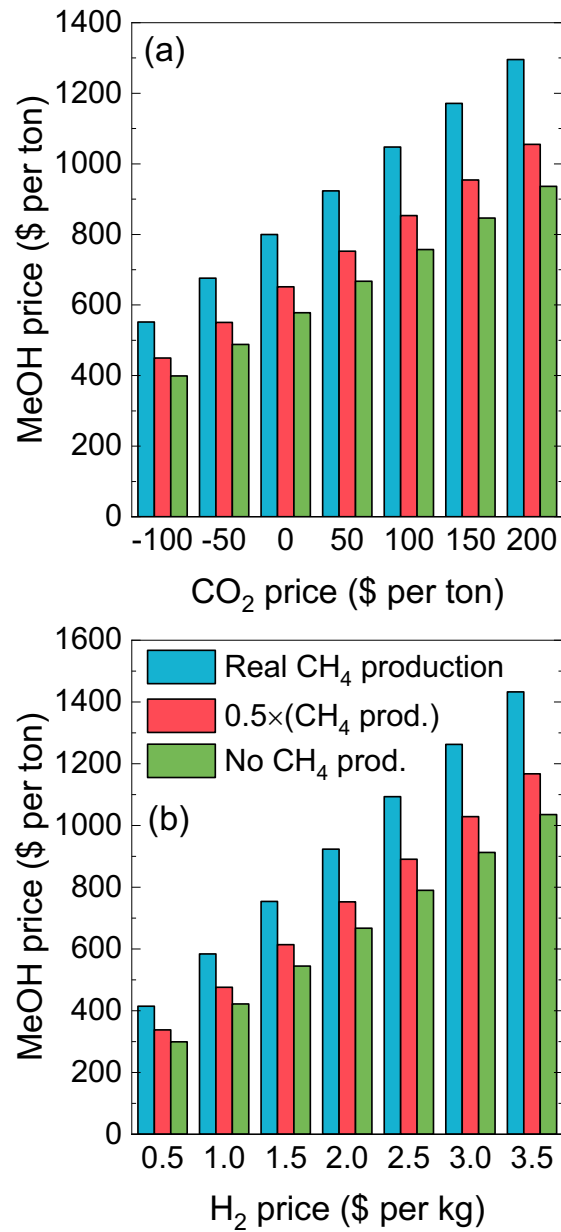


**Fig. S10.** Utilities estimated costs distribution as percentage for the different equipments in the MeOH process.

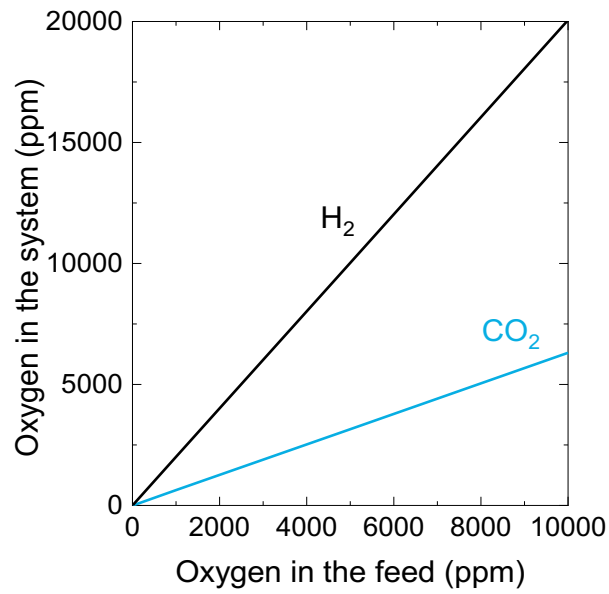
**Table S4.** Catalyst performance of the commercial Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst in the CO<sub>2</sub> hydrogenation to MeOH. CO<sub>2</sub>/H<sub>2</sub>=3, 50 bar.

Temp. (°C)	GHSV (ml/h/g)	Conv. (%)	Sel. CO (%)	Sel. CH <sub>4</sub> (%)	Sel. MeOH (%)
220	12000	14.93	36.84	0.07	63.10
220	6000	17.48	35.58	0.10	64.32
220	3000	16.66	21.85	0.19	77.96
240	12000	18.89	42.14	0.05	57.81
240	6000	19.67	37.15	0.09	62.76
240	3000	20.08	37.62	0.15	62.23
260	12000	17.22	51.77	0.06	48.17
260	6000	15.60	50.56	0.12	49.32
260	3000	10.21	56.53	0.35	43.12

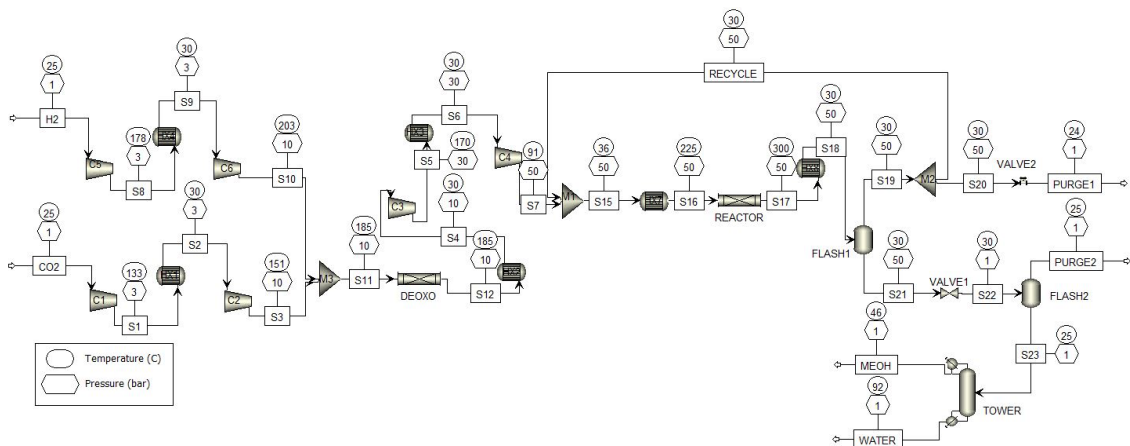




**Fig. S11.** Effect of CH<sub>4</sub> formation on final MeOH price to reach breakeven as function of (a) CO<sub>2</sub> and (b) H<sub>2</sub> prices. H<sub>2</sub> price was fixed to 2\$ per Kg in case (a) and CO<sub>2</sub> to 50\$ per ton in case (b).



**Fig. S12.** Comparison of the O<sub>2</sub> content in the system depending on the O<sub>2</sub> content in the H<sub>2</sub> or CO<sub>2</sub> feeds for a recycle set to 99%.



**Fig. S13.** Process flow diagram of the MeOH plant with the deoxo reactor after the first compression steps.

**Table S5.** Summary of the TEA estimates for the two scenarios evaluated. Case 1, renewable energy sources. Case 2, conventional energy sources.

	<b>Case1</b>	<b>Case2</b>
Capital Cost (M\$)	95	95
Renewable Power Grid Cost (M\$)	100	0
H <sub>2</sub> price (\$/kg) [1,2]	2.5-3.5	0.5-1.5
Total Raw Materials Cost (M\$/year)	300-350	150-200
Breakeven MeOH price (\$/ton)	550-700	250-400
CO <sub>2</sub> abated (ton per ton <sub>MeOH</sub> )	1.75	0.7

## S6. Life cycle assessment

The recommended Environmental indicators by The European Platform on Life Cycle Assessment are classified as proposed by Fazio et al. [3] according to their confidence level. Each of the indicators is defined below, and units and classification are listed in **Table S6**.

**Table S6.** Environmental indicators, units and recommendation level

<b>Environmental Indicator</b>	<b>Unit</b>	<b>Classification</b>
Global Warming Potential (GWP)	Kg CO <sub>2</sub> Eq.	I
Ozone Depletion Potential (ODP)	Kg CFC-11 Eq.	I
Respiratory inorganics (IR)	Kg PM <sub>2,5</sub> Eq.	I
Ionizing radiation, human health effect model (IR)	Kg U235 Eq.	II
Photochemical ozone formation (POF)	Kg NMVOC Eq.	II
Acidification Potential (AC), accumulated exceedance.	Mole of H <sup>+</sup> Eq.	II
Terrestrial Eutrophication (EUT)	Mole f N Eq.	II
Freshwater Eutrophication (EUF)	Kg of P Eq.	II
Aquatic marine Eutrophication (EUM)	Kg of N Eq.	II
Human Toxicity Potential, Cancer effects (HTC)	Comparative Toxic Unit for Human Health (CTUh)	III
Human Toxicity Potential, Non-Cancer Effects (HTNC)	CTUh	III
Ecotoxicity freshwater (ECFW)	Comparative Toxic Unit for ecosystems (CTUe)	III
Land Use (LU)	Soil Quality Index (Pt)	III
Resource use mineral and metals (RDM)	Kg Sb Eq.	III
Water Use (WU)	m <sup>3</sup> Eq.	III
Resource use energy carriers (RU)	MJ Eq.	III

- **Global Warming Potential (GWP).** This indicator measures the global warming potential of the greenhouse gaseous emissions in kg of CO<sub>2</sub> equivalents. Another names of this indicator are carbon footprint and climate change potential.
- **Ozone Layer Depletion (ODP).** This indicator measures the potential of the gaseous emissions to affect to the ozone layer in kg of CFC-11 equivalents.

- **Respiratory Inorganics (RI).** Impact category that accounts for the adverse health effects on human health caused by emissions of particulate matter and its precursors (NO<sub>x</sub>, SO<sub>x</sub>, NH<sub>3</sub>). It is measured in kg of inorganic particles smaller than 2.5 µm equivalents.
- **Ionising radiation, human health effect model (IR).** This indicator covers the impacts arising from the release of radioactive substances as well as direct exposure to radiation. It is measured in kg of U235 equivalents.
- **Photochemical Ozone Formation (POF).** Tropospheric ozone, or ground level ozone, has been recognized as one of the most important environmental threats on the regional scale. At high concentrations it is hazardous to human health, but already at lower concentrations, it causes damage to vegetation. It is measured in kg equivalents of volatile organic compound different from methane.
- **Acidification Potential (AC).** This indicator provides a measure of the decrease in the pH-value of rainwater and fog, which has the effect of ecosystem damage due to, for example, nutrients being washed out of soils and increased solubility of metals into soils. It is measured in mole of H<sup>+</sup> equivalents.
- **Eutrophication Potential, Terrestrial, Freshwater, Aquatic Marine (EUT, EUF, EUM).** These indicators provide a measure of nutrient enrichment in aquatic or terrestrial environments, which leads to ecosystem damage to those locations from over enrichment and are measured in mol of nitrogen, kg of phosphorous, and mol of nitrogen equivalents, respectively.
- **Human Toxicity Potential, Cancer, Non-Cancer (HTC, HTNC).** In general terms, these indicators refer to the impact on humans, as a result of emissions of toxic substances to air, water and soil, and is expressed in terms of Comparative Toxic Unit for human (CTUh). This unit refers to the increase in morbidity in the total human population per unit mass of a chemical emitted (cases per kg).
- **Ecotoxicity Freshwater (ECFW).** It refers to effects of chemical outputs on nonhuman living organisms in freshwater. Expressed in comparative toxic units (CTUe) it provides an estimate of the potentially affected fraction of species integrated over time and volume per unit mass of a chemical emitted.
- **Land Use (LU).** This indicator provides a measure of the impact of different land use interventions on soil quality, hence higher values correspond to larger impacts.
- **Resource Use Mineral and Metal (RDM).** It provides an indication of the potential depletion (or scarcity) of non-energetic natural resources (or elements) in the earth's crust, such as iron ores, aluminium or precious metals, and it accounts for the ultimate

geological reserves (not the economically feasible reserves) and the anticipated depletion rates. It is measured in mass of antimony equivalents.

- **Resource Water Depletion (RDW).** It provides an indication of the total net input of water used throughout the life cycle of the product/system.
- **Resource use energy carrier (RU).** It provides an indication of the potential depletion of energetic natural resources in the earth's crust, such as natural gas, coal or oil, and it accounts for the ultimate geological reserves (not the economically feasible reserves) and the anticipated depletion rates. It is measured in MJ equivalents.

Three study cases are evaluated in this work, considering the energy requirements to be supplied by renewable and non-renewable sources. **Figs. 4a** and **4b** show the diagrams for each study case, respectively. In all cases, CO<sub>2</sub> is considered to be produced and captured in cement plant. Europe was considered as the location of the whole process. The impact of the cement production operation process is not taken into account on the LCA boundaries for the initial 2 cases (case 1, renewable energy sources, case 2, non-renewable energy sources). An efficiency of 90% is assumed for CO<sub>2</sub> emission capture. The solvent solution used in the chemical absorption of CO<sub>2</sub> was assumed to be composed of 30% monoethanolamine (MEA). The energy required in the CO<sub>2</sub> desorption process was calculated as 3.8 GJ/ton CO<sub>2</sub> captured and the needs for new amine solution as 0.35–2 kg solution/ton CO<sub>2</sub> captured [4]. Moreover, a ratio of 0.51 kg of CO<sub>2</sub> per kWh is reported for a natural gas plant with an efficiency of 58%; efficiencies of 48% in plants provided with amine-based CO<sub>2</sub> capture are reported (Gabi® database). Methanol synthesis is not included in GaBi® database and has been simulated using data from Chen et al. [5] The environmental impacts derived from the production of this electricity was subtracted as it is reintroduced in the electric grid. In the study case 1, H<sub>2</sub> is produced by water electrolysis, for which 50 kWh and 11.4 kg water are required per kg of H<sub>2</sub> produced [6]. Thermal energy is supplied by the combustion of this green H<sub>2</sub> assuming a thermal enthalpy of 120 MJ kg<sup>-1</sup>. The values of each indicator and the contribution of each process variable for the study cases 1 and 2 are detailed in **Tables S7** and **Table S8**, respectively.

**Table S7.** Indicator values for the study case 1, renewable energy sources.

	<b>CO<sub>2</sub> capture</b>	<b>Catalyst</b>	<b>Electricity</b>	<b>Thermal energy</b>	<b>Hydrogen</b>	<b>Total</b>
GWP [kg CO <sub>2</sub> eq]	-5.38 10 <sup>8</sup>	8.98 10 <sup>6</sup>	5.48 10 <sup>6</sup>	1.61 10 <sup>7</sup>	9.49 10 <sup>7</sup>	-4.13 10 <sup>8</sup>
ODP [kg CFC-11 eq]	5.58 10 <sup>-5</sup>	1.80 10 <sup>-8</sup>	1.32 10 <sup>-5</sup>	2.13 10 <sup>-5</sup>	2.25 10 <sup>-4</sup>	3.15 10 <sup>-4</sup>
RI [Deaths eq]	3.22 10 <sup>0</sup>	8.29 10 <sup>-1</sup>	2.29 10 <sup>-1</sup>	5.03 10 <sup>-1</sup>	3.94 10 <sup>0</sup>	8.72 10 <sup>0</sup>
IR [kg U235 eq]	9.94 10 <sup>6</sup>	2.09 10 <sup>5</sup>	4.05 10 <sup>5</sup>	3.79 10 <sup>6</sup>	7.30 10 <sup>6</sup>	2.16 10 <sup>7</sup>
POF [kg NMVOC eq]	8.06 10 <sup>4</sup>	2.37 10 <sup>4</sup>	1.29 10 <sup>4</sup>	3.05 10 <sup>4</sup>	2.22 10 <sup>5</sup>	3.70 10 <sup>5</sup>
AC [mol of N eq]	3.97 10 <sup>5</sup>	1.25 10 <sup>5</sup>	1.94 10 <sup>4</sup>	4.71 10 <sup>4</sup>	3.34 10 <sup>5</sup>	9.23 10 <sup>5</sup>
EUT [mol of N eq]	1.50 10 <sup>6</sup>	4.09 10 <sup>4</sup>	4.31 10 <sup>4</sup>	1.07 10 <sup>5</sup>	7.47 10 <sup>5</sup>	2.34 10 <sup>6</sup>
EUf [kg N eq.]	1.09 10 <sup>2</sup>	1.41 10 <sup>1</sup>	8.12 10 <sup>0</sup>	4.01 10 <sup>1</sup>	2.22 10 <sup>2</sup>	3.94 10 <sup>2</sup>
EUM [kg P eq.]	3.44 10 <sup>4</sup>	5.28 10 <sup>3</sup>	3.87 10 <sup>3</sup>	9.83 10 <sup>3</sup>	6.73 10 <sup>4</sup>	1.21 10 <sup>5</sup>
HTC [CTUh]	1.56 10 <sup>-1</sup>	2.66 10 <sup>-2</sup>	3.61 10 <sup>-2</sup>	5.94 10 <sup>-2</sup>	6.15 10 <sup>-1</sup>	8.92 10 <sup>-1</sup>
HTNC [CTUh]	1.47 10 <sup>0</sup>	8.67 10 <sup>-1</sup>	3.10 10 <sup>-1</sup>	5.56 10 <sup>-1</sup>	5.33 10 <sup>0</sup>	8.53 10 <sup>0</sup>
ECFW [CTU]	3.87 10 <sup>8</sup>	1.12 10 <sup>8</sup>	5.18 10 <sup>7</sup>	1.39 10 <sup>8</sup>	9.14 10 <sup>8</sup>	1.60 10 <sup>9</sup>
LU [Pt]	2.14 10 <sup>8</sup>	9.04 10 <sup>6</sup>	2.57 10 <sup>7</sup>	8.17 10 <sup>7</sup>	4.45 10 <sup>8</sup>	7.76 10 <sup>8</sup>
RDM [kg Sb eq.]	5.85 10 <sup>2</sup>	4.31 10 <sup>3</sup>	1.38 10 <sup>2</sup>	2.24 10 <sup>2</sup>	2.35 10 <sup>3</sup>	7.61 10 <sup>3</sup>
WU [m <sup>3</sup> world eq.]	6.75 10 <sup>8</sup>	4.02 10 <sup>8</sup>	1.57 10 <sup>8</sup>	2.58 10 <sup>8</sup>	2.72 10 <sup>9</sup>	4.21 10 <sup>9</sup>
RU [MJ]	6.16 10 <sup>8</sup>	2.02 10 <sup>8</sup>	6.30 10 <sup>7</sup>	2.28 10 <sup>8</sup>	1.10 10 <sup>9</sup>	2.21 10 <sup>9</sup>

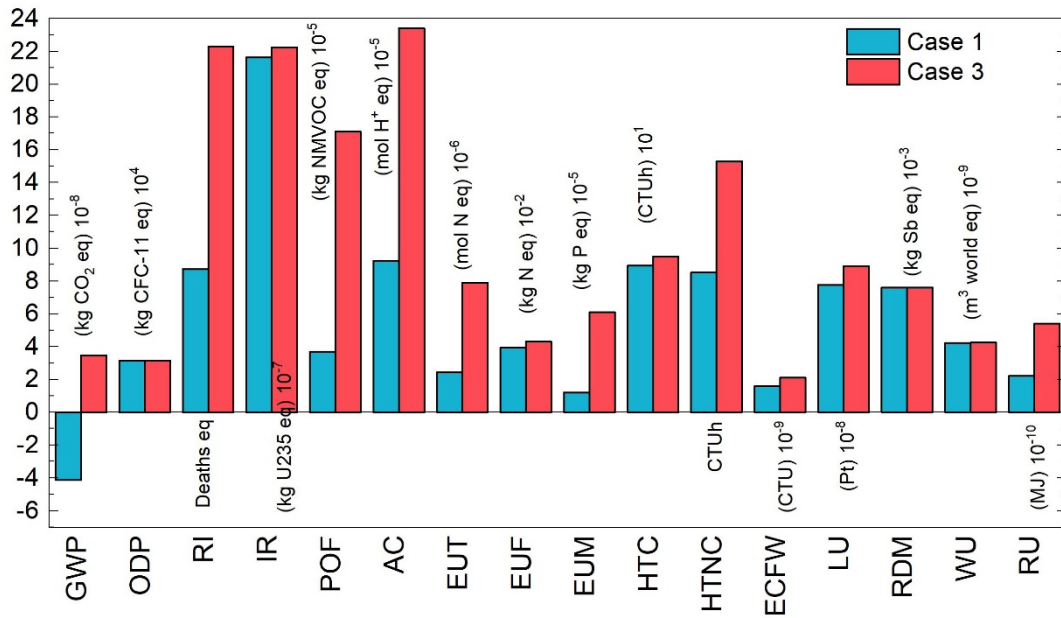
**Table S8.** Indicator values for the study case 2, non-renewable energy sources.

	<b>CO<sub>2</sub> capture</b>	<b>Catalyst</b>	<b>Electricity</b>	<b>Thermal energy</b>	<b>Hydrogen</b>	<b>TOTAL</b>
GWP [kg CO <sub>2</sub> eq]	-3.78 10 <sup>8</sup>	8.98 10 <sup>6</sup>	9.65 10 <sup>7</sup>	7.73 10 <sup>7</sup>	3.73 10 <sup>8</sup>	1.77 10 <sup>8</sup>
ODP [kg CFC-11 eq]	7.53 10 <sup>-9</sup>	1.80 10 <sup>-8</sup>	1.72 10 <sup>-6</sup>	7.45 10 <sup>-9</sup>	2.70 10 <sup>-7</sup>	2.03 10 <sup>-6</sup>
RI [Deaths eq]	2.51 10 <sup>0</sup>	8.29 10 <sup>-1</sup>	2.13 10 <sup>0</sup>	1.57 10 <sup>0</sup>	5.43 10 <sup>0</sup>	1.25 10 <sup>1</sup>
IR [kg U235 eq]	5.49 10 <sup>4</sup>	2.09 10 <sup>5</sup>	2.35 10 <sup>7</sup>	8.78 10 <sup>4</sup>	4.92 10 <sup>6</sup>	2.87 10 <sup>7</sup>
POF [kg NMVOC eq]	7.00 10 <sup>4</sup>	2.37 10 <sup>4</sup>	1.67 10 <sup>5</sup>	1.81 10 <sup>5</sup>	8.51 10 <sup>5</sup>	1.29 10 <sup>6</sup>
AC [mol of N eq]	3.38 10 <sup>5</sup>	1.25 10 <sup>5</sup>	2.60 10 <sup>5</sup>	1.66 10 <sup>5</sup>	8.23 10 <sup>5</sup>	1.71 10 <sup>6</sup>
EUT [mol of N eq]	1.45 10 <sup>6</sup>	4.09 10 <sup>4</sup>	6.15 10 <sup>5</sup>	5.89 10 <sup>5</sup>	2.18 10 <sup>6</sup>	4.87 10 <sup>6</sup>
EUf [kg N eq.]	6.13 10 <sup>0</sup>	1.41 10 <sup>1</sup>	1.14 10 <sup>2</sup>	3.93 10 <sup>0</sup>	3.58 10 <sup>2</sup>	4.97 10 <sup>2</sup>
EUM [kg P eq.]	2.90 10 <sup>4</sup>	5.28 10 <sup>3</sup>	5.72 10 <sup>4</sup>	5.32 10 <sup>4</sup>	2.04 10 <sup>5</sup>	3.48 10 <sup>5</sup>
HTC [CTUh]	6.49 10 <sup>-3</sup>	2.66 10 <sup>-2</sup>	2.62 10 <sup>-2</sup>	1.64 10 <sup>-2</sup>	1.86 10 <sup>-1</sup>	2.62 10 <sup>-1</sup>
HTNC [CTUh]	1.08 10 <sup>-1</sup>	8.67 10 <sup>-1</sup>	5.73 10 <sup>-1</sup>	2.46 10 <sup>-1</sup>	7.76 10 <sup>0</sup>	9.55 10 <sup>0</sup>
ECFW [CTU]	3.43 10 <sup>7</sup>	1.12 10 <sup>8</sup>	6.03 10 <sup>8</sup>	3.26 10 <sup>7</sup>	8.52 10 <sup>9</sup>	9.30 10 <sup>9</sup>
LU [Pt]	2.35 10 <sup>6</sup>	9.04 10 <sup>6</sup>	3.73 10 <sup>8</sup>	3.53 10 <sup>6</sup>	7.96 10 <sup>7</sup>	4.68 10 <sup>8</sup>
RDM [kg Sb eq.]	1.87 10 <sup>0</sup>	4.31 10 <sup>3</sup>	2.87 10 <sup>1</sup>	4.63 10 <sup>0</sup>	3.98 10 <sup>1</sup>	4.38 10 <sup>3</sup>
WU [m <sup>3</sup> world eq.]	2.58 10 <sup>5</sup>	4.02 10 <sup>8</sup>	1.32 10 <sup>8</sup>	4.75 10 <sup>5</sup>	7.00 10 <sup>7</sup>	6.04 10 <sup>8</sup>
RU [MJ]	1.20 10 <sup>9</sup>	2.02 10 <sup>8</sup>	1.79 10 <sup>9</sup>	3.09 10 <sup>9</sup>	1.59 10 <sup>10</sup>	2.22 10 <sup>10</sup>



**Table S9.** Indicator values for the study case 3 which considers the impact of the cement plant operation for case 1.

	<b>CO<sub>2</sub> capture</b>	<b>Catalyst</b>	<b>Electricity</b>	<b>Thermal energy</b>	<b>Hydrogen</b>	<b>Cement Plant</b>	<b>TOTAL</b>
GWP [kg CO <sub>2</sub> eq]	-3.78 10 <sup>8</sup>	8.98 10 <sup>6</sup>	9.65 10 <sup>7</sup>	7.73 10 <sup>7</sup>	3.73 10 <sup>8</sup>	7.60 10 <sup>8</sup>	3.47 10 <sup>8</sup>
ODP [kg CFC-11 10q]	7.53 10 <sup>-9</sup>	1.80 10 <sup>-8</sup>	1.72 10 <sup>-6</sup>	7.45 10 <sup>-9</sup>	2.70 10 <sup>-7</sup>	3.38 10 <sup>-7</sup>	3.15 10 <sup>-4</sup>
RI [D 10aths 10q]	2.51 10 <sup>0</sup>	8.29 10 <sup>-1</sup>	2.13 10 <sup>0</sup>	1.57 10 <sup>0</sup>	5.43 10 <sup>0</sup>	1.84 10 <sup>1</sup>	2.22 10 <sup>1</sup>
IR [kg U235 10q]	5.49 10 <sup>4</sup>	2.09 10 <sup>5</sup>	2.35 10 <sup>7</sup>	8.78 10 <sup>4</sup>	4.92 10 <sup>6</sup>	1.00 10 <sup>6</sup>	2.26 10 <sup>7</sup>
POF [kg NMVOC 10q]	7.00 10 <sup>4</sup>	2.37 10 <sup>4</sup>	1.67 10 <sup>5</sup>	1.81 10 <sup>5</sup>	8.51 10 <sup>5</sup>	1.40 10 <sup>6</sup>	1.77 10 <sup>6</sup>
AC [mol of N 10q]	3.38 10 <sup>5</sup>	1.25 10 <sup>5</sup>	2.60 10 <sup>5</sup>	1.66 10 <sup>5</sup>	8.23 10 <sup>5</sup>	1.58 10 <sup>6</sup>	2.40 10 <sup>6</sup>
10UT [mol of N 10q]	1.45 10 <sup>6</sup>	4.09 10 <sup>4</sup>	6.15 10 <sup>5</sup>	5.89 10 <sup>5</sup>	2.18 10 <sup>6</sup>	5.45 10 <sup>6</sup>	7.89 10 <sup>6</sup>
10UF [kg N 10q.]	6.13 10 <sup>0</sup>	1.41 10 <sup>1</sup>	1.14 10 <sup>2</sup>	3.93 10 <sup>0</sup>	3.58 10 <sup>2</sup>	3.68 10 <sup>1</sup>	4.31 10 <sup>2</sup>
10UM [kg P 10q.]	2.90 10 <sup>4</sup>	5.28 10 <sup>3</sup>	5.72 10 <sup>4</sup>	5.32 10 <sup>4</sup>	2.04 10 <sup>5</sup>	4.98 10 <sup>5</sup>	6.19 10 <sup>5</sup>
HTC [CTUh]	6.49 10 <sup>-3</sup>	2.66 10 <sup>-2</sup>	2.62 10 <sup>-2</sup>	1.64 10 <sup>-2</sup>	1.86 10 <sup>-1</sup>	6.13 10 <sup>-2</sup>	9.54 10 <sup>-1</sup>
HTNC [CTUh]	1.08 10 <sup>-1</sup>	8.67 10 <sup>-1</sup>	5.73 10 <sup>-1</sup>	2.46 10 <sup>-1</sup>	7.76 10 <sup>0</sup>	6.80	1.53 10 <sup>1</sup>
10CFW [CTU]	3.43 10 <sup>7</sup>	1.12 10 <sup>8</sup>	6.03 10 <sup>8</sup>	3.26 10 <sup>7</sup>	8.52 10 <sup>9</sup>	5.14 10 <sup>8</sup>	2.12 10 <sup>9</sup>
LU [Pt]	2.35 10 <sup>6</sup>	9.04 10 <sup>6</sup>	3.73 10 <sup>8</sup>	3.53 10 <sup>6</sup>	7.96 10 <sup>7</sup>	1.15 10 <sup>8</sup>	8.91 10 <sup>8</sup>
RDM [kg Sb 10q.]	1.87 10 <sup>0</sup>	4.31 10 <sup>3</sup>	2.87 10 <sup>1</sup>	4.63 10 <sup>0</sup>	3.98 10 <sup>1</sup>	7.51	7.61 10 <sup>3</sup>
WU [m <sup>3</sup> world 10q.]	2.58 10 <sup>5</sup>	4.02 10 <sup>8</sup>	1.32 10 <sup>8</sup>	4.75 10 <sup>5</sup>	7.00 10 <sup>7</sup>	3.12 10 <sup>7</sup>	4.25 10 <sup>9</sup>
RU [MJ]	1.20 10 <sup>9</sup>	2.02 10 <sup>8</sup>	1.79 10 <sup>9</sup>	3.09 10 <sup>9</sup>	1.59 10 <sup>10</sup>	3.23 10 <sup>9</sup>	5.44 10 <sup>9</sup>



**Fig. S14.** Comparison of the total main environmental indicators for cases 1 (renewable energy sources) and 3 (renewable energy sources plus cement plant normal operation impact).

## S7. Techno economic assessment of a conventional Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> plant

The techno economic assessment of a plant using the conventional Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> methanol catalyst was also simulated as a comparison. The plant proposed by Szima et. al. [7] was scaled in order to match our target of 275000 tons of MeOH per year. The plant is composed by:

- A compressing unit that compress the inlet CO<sub>2</sub> from atmospheric pressure and the H<sub>2</sub> from 30MPa to 80MPa
- A multi-tubular reactor operating at 220°C and 8MPa. The reactor has 810 16m long tubes of 0.084m in diameter and it is cooled with boiling water.
- Two flash units operating at high and low pressure for the separation of the gas phase from the liquid phase of the stream exiting the reactor
- A distillation unit for the separation of the methanol from the water.
- A gas turbine driven by the combustion of the purge gases.
- A steam generator and a steam turbine for the recovery of the heat of the gases exiting the gas turbine and the heat of the steam produced in the reactor.
- An organic Rankine cycle for the recovery of the heat of the medium temperature flue gases exiting the steam generator.

The plant is supposed to run for 8000h/year with a total lifespan of 25 years. The inlet and outlet flows of the plant and are listed in **Table S10**. The energy requirements are listed in **Table S11**. The CO<sub>2</sub> abatement and emissions are listed in **Table S12**. The installed costs of the equipment are listed in **Table S13**. The raw material costs are kept the same as in our initial base techno economic assessment: 3,5\$/kg<sub>H2</sub> and 50\$/t<sub>CO2</sub>. The operating costs are listed in **Table S14**.

The total CAPEX is 134478 k\$ and the total OPEX is 229063 k\$/year, the annual income due to the sale of the methanol are 151250 k\$/year. At these conditions, the plant is not able to generate a positive net income due to the high operational costs. The plant is able to reach breakeven at the end of its lifespan only if the cost of hydrogen is lowered to 1.94 \$/kg<sub>H2</sub> or if the taxation of CO<sub>2</sub> is raised to 209 \$/t<sub>CO2</sub>.

**Table S10.** Inlet and outlet flows of the Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> plant.

<b>Inlet flows</b>				
CO <sub>2</sub> in	48.5	t/h	1.41	t/t <sub>MeOH</sub>
H <sub>2</sub> in	6.67	t/h	0.194	t/t <sub>MeOH</sub>
<b>Outlet flows</b>				
MeOH out	34.4	t/h		
H <sub>2</sub> O out	19.5	t/h	0.566	t/t <sub>MeOH</sub>

**Table S11.** Energy requirements of the Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> plant.

<b>Energy requirement (kW)</b>	
Gas compression	7865
Other equipment	1760

**Table S12.** CO<sub>2</sub> abatement and emissions of the Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> plant.

CO <sub>2</sub> in (t/h)	48.5
CO <sub>2</sub> direct emissions (t/h)	1.38
CO <sub>2</sub> indirect emissions (t/h)	0
total CO <sub>2</sub> abated (t/h)	47.1
specific CO <sub>2</sub> abated (t/t <sub>M<sub>e</sub>OH</sub> )	1.37

**Table S13.** Equipment installed costs of the Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> plant.

Compressing trains (k\$)	38 999
Heat exchanger network (k\$)	52 447
Separation unit (k\$)	1 345
Recycling unit (k\$)	12 103
Distillation unit (k\$)	6 724
Gas turbine (k\$)	10 758
Reactor unit (k\$)	10 758
Organic Rankine cycles (k\$)	1 345
<b>Total CAPEX</b>	<b>134 478</b>

**Table S14.** Operating costs of the Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> plant.

<b>Fixed</b>	
Direct labor cost (k\$/y)	10 418
Administrative, support & overhead (k\$/y)	2 029
Annual maintenance cost (k\$/y)	10 823
<b>Variable</b>	
Catalyst (k\$/y)	10 846
Make up water (k\$/y)	2 169
Other utilities (k\$/y)	4 339
CO <sub>2</sub> cost (k\$/y)	1 941
H <sub>2</sub> cost (k\$/y)	186 725
Electrical energy (k\$/y)	228
<b>Total OPEX (k\$/y)</b>	<b>229 063</b>

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