Integrated Process for Producing Glycolic Acid from Carbon Dioxide Capture Coupling Green Hydrogen

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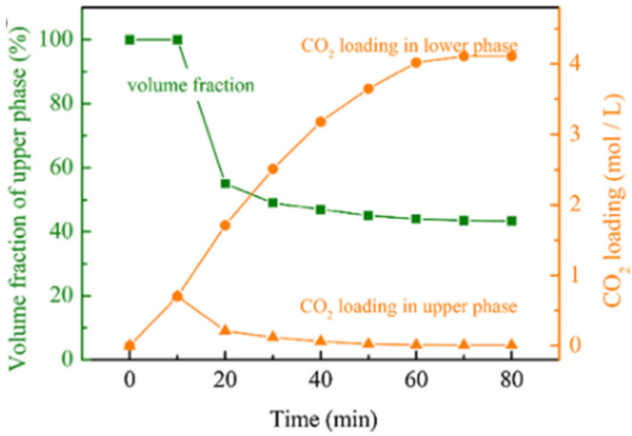

Figure S1. Volume fraction of the upper phase and CO_2 distribution in the 30 wt% MEA/40 wt% 1-propanol biphasic solvent [1]

Table S1. Comparison of the experimental density and the model density of MEA/1-propanol system with different CO_2 loading (at 293 K)

	Density (g/ml)	
CO2 loading (mol/L)	Experimental data	Simulation results
0	0.97685	0.98036
0.30	0.99049	0.99193
0.68	1.00722	1.00743
0.88	1.01694	1.01466
1.34	1.03781	1.03491
1.66	1.05227	1.04834
2.02	1.0688	1.06239
2.24	1.0781	1.0719

Table S2. The flow rate results of the unit of carbon capture

Stream	1	2	3	4	5	6
T (°C)	42	25	28	56	62.88	40
P (bar)	1	1	1	1	1	1
Mole flow rate (kmol/h)						
H_2O	1680	51060.1	45846.8	27946.2	22665.3	62.333
N_2	31160		0.21007			
O_2	1320		0.01731			
CO_2	5840	0.00115	4.41295	51.9507	5257.15	5256.74
MEA		10786.3	213.249	108.459	0.00102	
C_3H_8O		11481.6	7292.33	574.489	563.316	16.268
MEA^+		632.388	5854.56	5668.01		
$MEACOO^-$		617.039	5213.93	5155.13		
HCO_3^-		3.61343	602.693	509.451		
CO_3^{2-}		1.56348	18.9693	8.75931		

Table S3. Reaction kinetic parameter of k_1, k_2 and k_3

Term	Pre-exponential factor A_i ($kmol\cdot kgcat^{-1}\cdot s\cdot Pa^{-n}$)	Activation energy E_i ($KJ\cdot mol^{-1}$)
k_1	4.0638×10^{-6}	11.695
k_2	9.0421×10^{8}	11.286
k_3	1.5188×10^{-33}	266.01

$$\ln(K_{eq}) = A + \frac{B}{T} + C\times\ln T + D\times T + \frac{E(P-P_{ref})}{P_{ref}}$$

Table S4. Constants for driving force (adsorption data from [2]); and chemical equilibrium data from [3].

Term	A	B
K_1	-52.096	11840
K_2	5.639	-5285
K_3	-46.457	6555
K_{CO}	-23.20	14225
K_{CO2}	-22.48	9777

Table S5. K_i factors for adsorption term (terms 2, 3, 5 from [2]; rest is explicitly derived by calculation).

Term	Expression	a_i	b_i	$\Pi c_j^{v_i}$
1	1	$a_1=1$	$b_1=0$	$\sqrt{f_{H_2}}$
2	$\frac{K_{H_2O}}{\sqrt{K_H}}$	$a_2=4.3676\times10^{-12}$	$b_2=1.1508\times10^{5}$	f_{H_2O}
3	K_{CO}	$a_3=8.3965\times10^{-11}$	$b_3=1.1827\times10^{5}$	$f_{CO}\sqrt{f_{H_2}}$
4	$\frac{K_{CO}K_{H_2O}}{\sqrt{K_H}}$	$a_4=3.6673\times10^{-22}$	$b_4=2.3335\times10^{5}$	$f_{CO}f_{H_2O}$
5	K_{CO_2}	$a_5=1.7214\times10^{-10}$	$b_5=8.1287\times10^{4}$	$f_{CO_2}\sqrt{f_{H_2}}$
6	$\frac{K_{CO_2}K_{H_2O}}{\sqrt{K_H}}$	$a_6=7.5184\times10^{-22}$	$b_6=1.9727\times10^{5}$	$f_{CO_2}f_{H_2O}$
		$A_i=\ln(a_i)$	$B_i=b_i/R$	$\Pi c_j^{v_i}$
1	1	0	0	$\sqrt{f_{H_2}}$
2	$\frac{K_{H_2O}}{\sqrt{K_H}}$	-26.1568	13842	f_{H_2O}
3	K_{CO}	-23.2006	14225	$f_{CO}\sqrt{f_{H_2}}$
4	$\frac{K_{CO}K_{H_2O}}{\sqrt{K_H}}$	-49.3574	28067	$f_{CO}f_{H_2O}$
5	K_{CO_2}	-22.4827	9777	$f_{CO_2}\sqrt{f_{H_2}}$
6	$\frac{K_{CO_2}K_{H_2O}}{\sqrt{K_H}}$	-48.6395	23619	$f_{CO_2}f_{H_2O}$

Table S6. The flow rate results of the unit of CO_2 hydrogenation to methanol

Stream	1	2	3	4	5	6	7
T (°C)	83.78	30.41	40.45	220	80	63.57	103.73
P (bar)	50	50	50	50	1.2	1	1.2
Mole flow rate (kmol/h)							
CO_2	5256.53	8925.99	14182.52	9031.23	14.80	8.41	0.00
CO	31.89	828.72	860.61	837.13	0.00	0.00	0.00
H_2	16387.13	88544.00	104931.12	89430.31	0.00	0.00	0.00
CH_4O	0.00	261.90	261.90	5436.66	5172.12	5139.41	29.20
H_2O	0.00	47.90	47.90	5199.19	5150.81	7.44	5143.37

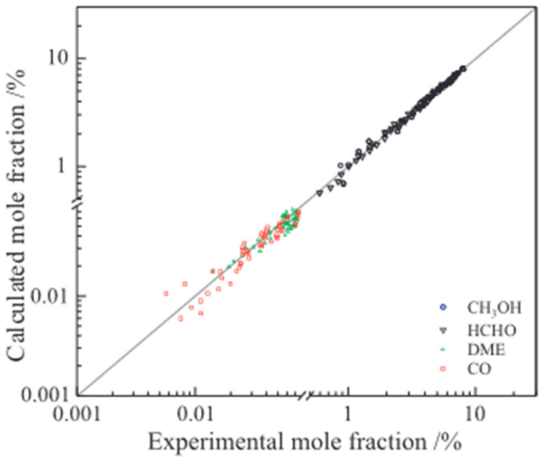

Figure S2. Experimental and calculated values for the fraction of each component [4]

Table S7. The flow rate results of the unit of methanol to formaldehyde

Stream	1	2	3	4	5	6	7	8
T (°C)	25	129.81	193.85	386.42	30	30	42.16	32.93
P (bar)	2.16	2.16	2.16	2.16	5	5	5	5
Mole flow rate (kmol/h)								
O_2	0.00	34514.00	34514.00	32035.30	0.00	32035.30	32035.00	0.30
CO	0.00	0.00	0.00	5.88	0.00	5.88	5.88	0.00
HCHO	0.00	0.00	0.00	4945.63	0.00	4945.63	0.00	4945.63
CH_3OH	5139.00	5139.00	5139.00	0.00	0.00	0.00	0.00	1.77
C_2H_6O	0.00	0.00	0.00	98.40	0.00	98.40	96.63	0.00
H_2O	7.44	7.44	7.44	5062.20	10000.00	5062.20	1896.81	13165.39
N_2	0.00	80532.70	80532.70	80532.70	0.00	80532.70	80532.31	0.39
O_2	0.00	34514.00	34514.00	32035.30	0.00	32035.30	32035.00	0.30
CO	0.00	0.00	0.00	5.88	0.00	5.88	5.88	0.00

Table S8. Solubility of glycolic acid in water

T/K	x_{exp} (mole)	x_{exp} (mass)
257.6	0.1931	0.28516
263.13	0.2151	0.313572
268.08	0.2257	0.327003
273.83	0.2471	0.353621
278.15	0.272	0.383784
283.05	0.2903	0.405416
288.72	0.3214	0.441182
293.74	0.3504	0.47345
295.46	0.3536	0.476949
298.77	0.3696	0.494262
303.76	0.4147	0.541507
308.84	0.4509	0.577848
313.51	0.4812	0.607245

Table S9. The flow rate results of the unit of formaldehyde carbonylation to glycolic acid

Stream	1	2	3	4	5	6
T (°C)	11.62	60	60	5	5	15
P (bar)	3	3	3	1	1	1
Mole flow rate (kmol/h)						
CO	4945.63	8389.33	3443.88	0.00	0.00	0.00
HCHO	4945.63	5038.36	126.68	0.00	0.00	0.00
WATER	13165.39	13421.1	8541.77	6002.87	6002.87	0.93
$OHCH_2COOH$	0.00	1.35	4819.01	6424.45	1607.97	0.25
Diglycolic acid	0.00	0.00	46.21	0.00	46.21	46.21
$C_2H_4O_3$(S)	0.00	0.00	0.00	0.00	4818.99	4818.99

Table S10. Temperature parameters for utilities.

Utilities	T_{in} [a]/°C	T_{out} [b]/°C
Refrigerant 1	-25.0	-24.0
Cooling water	20.0	25.0
LP steam	125.0	124.0
MP steam	175.0	174.0
HP steam	250.0	249.0

[a] T_{in} is the supply temperature.

[b] T_{out} is the target temperature.

Table S11. The parameters of indirect CO_2 emission

GHG emission	value	unit
Wind energy	22	kg/MWh$_e$
coal-fired power	832	g/KWh
CO_2 capture	0.2	kg CO_2/kgCO_2 caputred
Natural gas extraction	4	kg CO_2/GJ
Natural gas combustion	0.05	kg CO_2/MJ
Combustion efficiency	0.8	

Table S12. Input parameters and assumptions for techno-economic analyses.

Items	Values	Units	Items	Values	Units
H_2O	3.56	CNY/t	LP steam	9.23	10^{-6} \$/kJ
MEA	9000	CNY/t	MP steam	12.99	10^{-6} \$/kJ
C_3H_8O	6500	CNY/t	HP steam	16.55	10^{-6} \$/kJ
H_2	21.93	CNY/kg	Cooling water	1.81	10^{-6} \$/kJ
CO	300	CNY/t	Refrigerant 1	12.79	10^{-6} \$/kJ
AIR			Electricity	29.28	10^{-6} \$/kJ

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