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Supplementary Materials

Techno-Economic and Environmental Analysis for Direct Catalytic Conversion of CO_2 to Methanol and Liquid/ High-Calorie-SNG Fuels

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1. Appendix A: Data for economic assessment

1.1. Methanol synthesis

Table S1. Equipment cost data.

Purchased equipment	Cost($)	Reference
Compressors	6,931,000	This work
Heat exchangers	932,000	This work
Reactor	5,640,000	This work
Decanter	243,000	This work
Flash separators	938,300	This work
Distillation column	2,427,882	[1]
Column condenser	139,000	This work
Total Equipment cost	**17,008,182**	

Equipment cost of distillation column was determined by the following equation [2], as can be seen in detail in Table S2:

$$\frac{A_1}{A_2} = \left(\frac{B_1}{B_2}\right)^d, \quad (1)$$

where A_1 is the calculated cost of a new capacity B_1, A_2 is the reference cost of the known capacity B_2, and d is the equipment specific scale factor.

Table S2. Equipment cost data from reference.

Process unit section	Reference cost (A_2) in M$	Design variable	Unit	Reference size (B_2)	Scaling factor (d)	New equipment size (B_1)	New equipment cost (A_1) in M$	Reference
Distillation column	0.623	Methanol production flowrate	kg/h	9,132	0.6	88,278	2.43	[1]

Table S3. Total capital investment estimation[3].

Cost elements	Ratio factor for fluid processing plant (of delivered equipment)	Costs ($)
	1. Direct cost	
Delivery	0.1	1,700,818
Subtotal: Purchased equipment (delivered)	1	18,709,000
Purchased equipment installation	0.47	8,793,230
Instrumentation & controls	0.36	6,735,240
Piping	0.68	4,579,963
Electrical systems	0.11	2,057,990
Buildings (including services)	0.18	3,367,620
Yard improvements	0.1	1,870,900
Service facilities	0.7	13,096,300
Total direct costs		59,210,244
	2. Indirect cost	
Engineering and supervision	0.33	6,173,970
Construction expenses	0.41	7,670,690
Legal expenses	0.04	748,360
Contractor's fee	0.22	4,115,980
Contingency	0.44	8,231,960
Total indirect costs	-	26,940,960
3. Working capital (WC)	0.89	16,651,010
Fixed capital investment (FCI)	Total direct cost + Total indirect cost	86,151,204
Total capital investment (TCI) = (WC) +(FCI)	**-**	**102,802,214**

Table S4. Total Operating cost estimation from the simulation result.

Cost parameters	Model cost ($/yr)
CO_2	26,617,127
H_2	368,896,364
Catalysts	1,645,873
Operating labor	1,550,185
Operating supervision	232,528
Cooling water	3,046,603
Electricity	386,603
Maintenance and repairs	2,660,000
Operating supplies	6,030,584
Laboratory charges	904,588
Insurance and taxes	1,723,024
Plant overhead costs	4,687,978
Administrative costs	1,171,994
Total Operating cost	**416,739,375**

Table S5. Total product cost and unit production cost estimation from the simulation result.

Cost parameters	Economic assumptions [4]	Cost($/yr)
Raw materials	-	398,805,236
Utilities	-	3,046,603
Maintenance and repairs	-	6,030,584
Operating supplies	15% of maintenance and repairs	904,588
Operating labor	-	1,550,185
Operating supervision	20% of operating labor	232,528
Laboratory charges	15% of operating labor	232,528
Insurance and taxes	2% of fixed capital investment	1,723,024
Plant overhead costs	60% of Total labor costs consisting of operating labor, operating supervision and maintenance labor	4,687,978
General expenses	2.5% of revenue	5,622,422
Total product cost	-	**422,835,675**
	Unit production	
Methanol capacity (kg/yr)	-	573,092,481
Total unit production cost($/kg)	-	**0.74**

Minimum selling price = Breakeven selling price = total unit production cost

Minimum selling price = 0.74$/kg

1.1. Fischer–Tropsch process model (liquid/high-calorie-SNG fuels synthesis)

Table S6. Equipment cost data.

Purchased equipment	Cost($)	Reference
Compressors	9,159,000	This work
Heat exchangers	509,600	This work
Reactor	5,640,000	This work
Decanter	243,000	This work
Flash separator	420,000	This work
Pressure swing adsorption	28,141,443	[5]
CO_2 absorption	136,328	[6]
Total equipment cost	**44,249,372**	

Equipment cost of H_2 PSA and CO_2 adsorption were determined by the following equation [2], as can be seen in detail in Table S7:

$$\frac{A_1}{A_2} = \left(\frac{B_1}{B_2}\right)^d, \tag{2}$$

where A_1 is the calculated cost of a new capacity B_1, A_2 is the reference cost of the known capacity B_2, and d is the equipment specific scale factor.

Table S7. Equipment cost data from reference.

Process unit section	Reference cost (A_2) in M$	Design variable	Unit	Reference size (B_2)	Scaling factor (d)	New equipment size (B_1)	New equipment cost (A_1) in M$	Reference
Pressure swing adsorption	2.05	Feed flowrate (Hierarchy model with 4-adsorber column)	kmol/h	115.99	0.74	3995.2	28.1	[5]

CO_2 adsorption	0.05	Radfrac model with 4 stages, make-up: 142 kg/h	ton/h	29.5	0.6	168	0.136	[6]

Table S8. Total capital investment estimation [3].

Cost elements		Cost ($)
	1. Direct cost	
Delivery	0.1	4,424,937
Subtotal: Purchased equipment (delivered)	1	48,674,309
Purchased equipment installation	0.47	22,876,925
Instrumentation & Controls	0.36	17,522,751
Piping	0.68	11,915,470
Electrical systems	0.11	5,354,174
Buildings (including services)	0.18	8,761,375
Yard improvements	0.1	4,867,430
Service facilities	0.7	34,072,016
Total direct costs		**154,044,455**
	2. Indirect cost	
Engineering and supervision	0.33	16,062,522
Construction expenses	0.41	19,956,466
Legal expenses	0.04	1,946,972
Contractor's fee	0.22	10,708,348
Contingency	0.44	21,416,696
Total indirect costs	-	**70,091,005**
3. Working capital (WC)	0.89	43,320,135
Fixed capital investment (FCI)	Total direct cost + Total indirect cost	224,135,460
Total capital investment (TCI)= (WC) +(FCI)	-	**267,455,596**

Table S9. Total operating cost estimation from the simulation result.

Cost parameters	Model cost ($/yr)
CO_2	26,617,127
H_2	368,896,363
Catalysts	54,182
Operating labor	1,480,237
Operating supervision	222,035
Cooling water	184,730
Electricity	2,661,750
Maintenance and repairs	15,689,482
Operating supplies	2,353,422
Laboratory charges	684,720
Insurance and taxes	4,482,709
Plant overhead costs	10,435,053
Administrative costs	2,608,763
Total operating cost	**436,370,577**

Table S10. Total product cost and unit production cost estimation from the simulation result.

Cost parameters	Economic assumptions[4]	Cost ($/yr)
Raw materials	-	395,567,673
Utility	-	2,846,480
Maintenance and repairs	-	15,689,482
Operating Supplies	15% of maintenance and repairs	2,353,422
Operating labor	-	1,480,237
Operating supervision	20% of operating labor	222,035
Laboratory charges	15% of operating labor	684,720
Insurance and taxes	2% of fixed capital investment	4,482,709
Plant overhead costs	60% of Total labor costs consisting of operating labor, operating supervision and maintenance labor	10,435,053
General Expenses	2.5% of revenue	5,568,636
Total product cost	**-**	**439,276,268**
	Unit production	
Liquid fuel capacity(annual)	-	82,307,708
SNG capacity(annual)	-	175,582,374
Total capacity(annual)	-	257,890,083
Liquid fuel unit production	-	5.34
SNG unit production	-	2.50
Total unit production cost($/kg)	-	**1.70**

Minimum selling price = Breakeven selling price = total unit production cost
Minimum selling price = 1.70$/kg

The following equation was used to compute the payback time

$$\text{Payback time(years)} = \left(\frac{\text{Fixed capital investment + start up}}{\text{profit after taxes +Depreciation}}\right) \quad . \tag{3}$$

2. Appendix B: Data for environmental assessment

2.1. Methanol synthesis

Table S11. Environmental assessment data from the simulation results.

	GWP factor	Unit	Used amount (Unit/h)	$kgCO_2$ emitted ($kgCO_{2\text{-eq}}$/h)
CO_2	0.875	$kgCO_{2\text{-eq}}/kgCO_2$	95,061 $kgCO_2$	83,137
H_2	0.97	$kgCO_{2\text{-eq}}/kgH_2$	13,063 kgH_2	12,671
Electricity	0.492	$kgCO_{2\text{-eq}}$/kwh	18,724 kwh	9,211
CO_2(purged)	-	-	4,151	4,151
	Total CO_2 emission			109,170
	Methanol produced		65,377 kg	
GWP of methanol from model process = total CO_2 emission / total methanol produced			1.67 $kgCO_{2\text{-eq}}$/kgMeOH	

2.2. Fischer–Tropsch process model (liquid/high-calorie-SNG fuels synthesis)

Table S12. Environmental assessment data from the simulation results.

	GWP factor	Unit	Used amount (Unit/h)	$kgCO_2$ emitted ($kgCO_{2\text{-}eq}/h$)
CO_2	0.875	$kgCO_{2\text{-}eq}/kgCO_2$	95,061 $kgCO_2$	83,137
H_2	0.97	$kgCO_{2\text{-}eq}/kgH_2$	13,063 kgH_2	12,671
Electricity	0.492	$kgCO_{2\text{-}eq}/kwh$	30,836 kwh	15,169
CO_2(purged)	-	-	5,351	5,351
Total CO_2 emission				116,328
Synthetic fuel produced			29,419 kg	
GWP of Fischer–Tropsch from model process = total CO_2 emission / total synthetic fuel produced			3.95 $kgCO_{2\text{-}eq}/kg$ product	

3. Appendix C. Simulation related data

3.1. Methanol synthesis process model

Table S13. Mass flow data of main streams from methanol synthesis process simulation results.

Stream Name	Units	2	10	13	14	19	21	26	27	30	31
Temperature	C	25	155	210	210	30	30	40	100	1,520	260
Pressure	bar	1	80	80	80	75	75	1	1	1	1
Mass Flows	kg/h	95,061	13,063	403,782	403,782	295,658	297,144	65,377	36,751	46,645	46,645
CO_2	kg/h	95,061	0	279,905	190,071	184,844	185,773	642	0	4,151	4,151
H_2	kg/h	0	13,063	118,245	105,901	105,182	105,711	0	0	0	0
CO	kg/h	0	0	980	987	980	985	0	0	0	0
Methanol	kg/h	0	0	4,192	69,590	4,192	4,214	64,725	18	0	0
Water	kg/h	0	0	460	37234	460	463	10	36,732	6,786	6,786
N_2	kg/h	0	0	0	0	0	0	0	0	32,114	32,114
O_2	kg/h	0	0	0	0	0	0	0	0	3,595	3,595

3.1. Fischer–Tropsch process model (liquid/high-calorie-SNG fuels synthesis)

Table S14. Mass flow data of main streams from the Fischer–Tropsch process simulation results.

Stream Name	Units	1	2	11	12	13	14	15	16	17	18	19	20
Temperature	C	25	25	320	320	30	25	20	20	34	34	34	34
Pressure	bar	1	30	30	30	9	1	1	1	9	9	9	9
Mass Flows	kg/h	95,061	13,063	283,576	283,576	283,576	82,743	9,389	73,354	200,833	168,151	32,682	20,030
CO_2	kg/h	95,061	0	237,831	148,121	148,121	0	0	0	148,121	148,121	0	0
H_2	kg/h	0	13,063	45,745	32,682	32,682	0	0	0	32,682	0	32,682	0
CH_4	kg/h	0	0	0	3,988	3,988	0	0	0	3,988	3,988	0	3,988
CO	kg/h	0	0	0	0	0	0	0	0	0	0	0	0
C_3H_8	kg/h	0	0	0	2,216	2,216	0	0	0	2,216	2,216	0	2,216
C_3H_6	kg/h	0	0	0	13,743	13,743	0	0	0	13,742	13,743	0	13,742
H_2O	kg/h	0	0	0	73,445	73,445	73,372	18	73,354	73	73	0	73
$C_{10}H_{22}$	kg/h	0	0	0	9,381	9,381	9,371	9,371	0	9	9	0	9

Representative reactions selected in the Fischer–Tropsch synthesis reactor model based on the experimental data given in [7].

1. Olefins (C_2-C_4) yield
   $3CO_2 + 9H_2 \Leftrightarrow C_3H_6 + 6H_2O$
2. Lower paraffin's (C_1-C_4)
   $3CO_2 + 10H_2 \Leftrightarrow C_3H_6 + 6H_2O$
3. Higher paraffin's (C_{5+})
   $3CO_2 + 10H_2 \Leftrightarrow C_3H_6 + 6H_2O$
4. Methane:
   $CO_2 + 4H_2 \Leftrightarrow CH_4 + 6H_2O$

References

[1] S. Alsayegh, J. R. Johnson, B. Ohs, and M. Wessling, “Methanol production via direct carbon dioxide hydrogenation using hydrogen from photocatalytic water splitting: Process development and techno-economic analysis,” *J. Clean. Prod.*, vol. 208, pp. 1446–1458, 2019, doi: 10.1016/j.jclepro.2018.10.132.

[2] F. G. Albrecht, D. H. König, N. Baucks, and R. U. Dietrich, “A standardized methodology for the techno-economic evaluation of alternative fuels – A case study,” *Fuel*, vol. 194, pp. 511–526, 2017, doi: 10.1016/j.fuel.2016.12.003.

[3] M. S. Peters, K. D. Timmerhaus, and R. E. West, *Plant Design and Economics for Chemical Engineers*, vol. 35. McGraw-Hill Companies, Inc., 1221 Avenue of the Americas, New York, NY 10020, 2003.

[4] L. Tock, M. Gassner, and F. Maréchal, “Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis,” *Biomass and Bioenergy*, vol. 34, no. 12, pp. 1838–1854, 2010, doi: 10.1016/j.biombioe.2010.07.018.

[5] A. Mivechian and M. Pakizeh, “Hydrogen recovery from Tehran refinery off-gas using pressure swing adsorption, gas absorption and membrane separation technologies: Simulation and economic evaluation,” *Korean J. Chem. Eng.*, vol. 30, no. 4, pp. 937–948, 2013, doi: 10.1007/s11814-012-0221-y.

[6] T. N. Do and J. Kim, “Green C2-C4 hydrocarbon production through direct CO2 hydrogenation with renewable hydrogen: Process development and techno-economic analysis,” *Energy Convers. Manag.*, vol. 214, no. May, p. 112866, 2020, doi: 10.1016/j.enconman.2020.112866.

[7] T. Numpilai *et al.*, “Structure–activity relationships of Fe-Co/K-Al2O3 catalysts calcined at different temperatures for CO2 hydrogenation to light olefins,” *Appl. Catal. A Gen.*, vol. 547, no. May, pp. 219–229, 2017, doi: 10.1016/j.apcata.2017.09.006.