Supplementary Information for

Direct dimethyl carbonate synthesis from CO_2 and methanol catalyzed by CeO_2 and assisted by 2-cyanopyridine: a cradle-to-gate greenhouse gases emission study

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S1 Chemical property estimation with group contribution methods (GCMs)

ASPEN Plus has a database for chemical and physical properties of many chemicals. However, some properties of not so common chemicals such as 2-cyanopyridine (2-CP) and 2-picolinamide (2-PA) in this study are missing. The missing parameters can be estimated by GCMs in ASPEN Plus. In this study, the most crucial missing parameter is the standard Gibbs free energy of formation (ΔG_f°) for 2-CP and 2-PA to simulate the equilibrium reaction of 2-PA => 2-CP + H_2O. ΔG_f° can be estimated by Joback[1], Benson[2], and Gani[3] group contribution methods (Table S1). Gani's GCM could not be utilized to estimate ΔG_f° of 2-CP due to the lack of appropriate functional group to be assigned for 2-CP in the definition of Gani's GCM. As shown in Table S1, ΔG_f° of 2-PA was highly varied with GCMs, while that of 2-CP was estimated in small difference. Due to this variation, the equilibrium of the 2-CP regeneration reaction (i.e., dehydration of 2-PA) differs associated with the choice of GCM as organized in Table S2. When Joback's GCM was applied to both 2-CP and 2-PA (the base case in the main manuscript), the change of Gibbs free energy in the reaction (ΔG_r°) became negative because the ΔG_f° of 2-PA in Joback's GCM was quite high compared to other GCMs. In this case, the reaction could be regarded as a spontaneous reaction although it does not match with the reality. Looking at the standard enthalpy of formation (ΔH_f°), the values estimated by GCMs were also varied. The estimated ΔH_f° of 2-CP was not that far from the value originally included in the database. On the other hand, the range of difference in ΔH_f° of 2-PA was relatively larger. Due to the huge difference between Joback's ΔH_f° and the originally included value, Joback's

GCM may be inappropriate to be applied to 2-PA in terms of both ΔG_f° and ΔH_f°.

Based on the variety of the estimated ΔG_f°, the equilibrium of the 2-CP regeneration reaction was differently simulated as shown in Figure S1. In the lowest ΔG_r° in GCM choices (i.e., both Joback's for 2-CP and 2-PA), the reaction proceeds regardless of the condition. As ΔG_r° becomes larger, the reactivity becomes lower. When we chose Benson's GCM for both 2-CP and 2-PA, the reaction hardly proceeds at the normal pressure. To obtain 2-CP by dehydrating 2-PA under the harder estimation of the parameter, low pressure is required.

Table S1. Standard Gibbs free energy of formation and standard enthalpy of formation of 2-cyanopyridine (2-CP), 2-picolinamide (2-PA), and Water included in ASPEN Plus database and estimated by group contribution methods

Parameter	Source	2-CP kJ/kmol	2-PA kJ/kmol	H2O kJ/kmol
DGFORM: ΔG_f°	Included	X	X	-228572
	Joback	322280	126630	-
	Benson	326358	45961	-
	Gani	X	48388	-
DHFORM: ΔH_f°	Included	280674	-65302	-241818
	Joback	267030	23360	-
	Benson	264194	-69915	-
	Gani	X	-58291	-

-: Not estimated, X: Not available

Table S2. Patterns of the change of Gibbs free energy and enthalpy in the reaction of 2-CP regeneration (i.e., 2-PA dehydration) in various combination of values estimated by GCMs

Choice of GCM		Calculated changes in the reaction kJ/kmol	
2-CP	2-PA	Gibbs free energy	Enthalpy
Included	Included	X	104158
Joback	Joback	-32922	1852
Joback	Benson	47747	95127
Joback	Gani	45320	83503
Benson	Joback	-28844	-984
Benson	Benson	51825	92291
Benson	Gani	49398	80667

The duty of the reaction converges around 1100 MJ/hr in every choice of GCM because ΔH_r° is calculated based on the originally included ΔH_f° in ASPEN database.

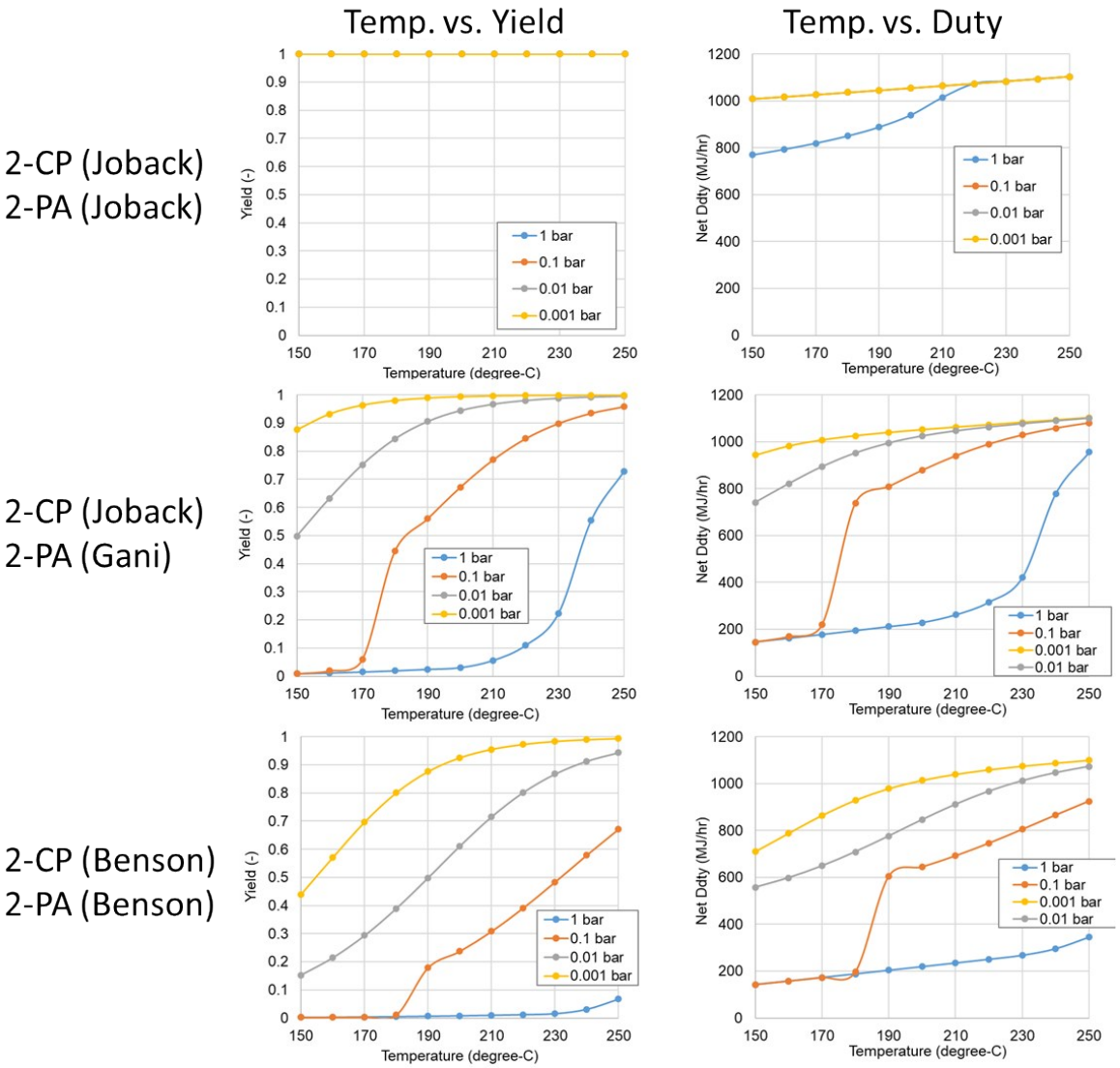

Fig. S1. Reactivity and duty of 2-CP regeneration in different GCM choices

S2. Data for lifecycle assessment

Table S3. Global warming potential of factors used in the lifecycle assessment in this study

Factors	GWP kg-CO_2-eq	GWP LCIA estimation method	Data Type	Data Category	Description	Reference
CO_2 Captured, per 1 kg	-1.0000	-	Assumption	Feedstock	Assumed 100% of the CO_2 is captured and used in the synthesis process. The emissions are regarded as credit emissions.	-
Methanol (CH3OH), per 1 kg	0.8780	CML 2001, GaBi (method version: Jan. 2016)	LCI database	Feedstock	Methanol from natural gas (integrated technologies)	Ecoinvent v3.5[4]
2-Cyanopyridine, per 1 kg	6.1980	CML 2001, GaBi (method version: Jan. 2016)	Estimation	Feedstock	Estimated by Finechem model.	Wernet et al. 2008[5], 2009[6]
Heat production from natural gas [1 MJ]	0.0652	CML 2001, GaBi (method version: Jan. 2016)	LCI database	Energy	heat production, natural gas, at boiler condensing modulating >100kW (DMC)	Ecoinvent v3.5[4]
Electricity Grid Mix, Japan, total [3.6 MJ capacity]	0.711	CML 2001, GaBi (method version: Jan. 2016)	LCI database [Modelled in GaBi]	Energy	Power sources (from high to low)==> Natural Gas: 38.26%, Coal: 33.81%, Hydro: 7.96%, Oil: 6.72%, Solar: 5.29%, Nuclear: 3.16%: Other sources, 2.04%, Biomass: 1.88%, Wind: 0.62%: Geothermal: 0.24%, and Biogas: 0.01%	Energy Statistics & Training Office, Asia Pacific Energy Research Centre (APERC). The Institute of Energy Economics, Japan, 2017[7]
Process steam from natural gas for wastewater treatment per 1 kg of wastewater	0.0711	CML 2001, GaBi (method version: Jan. 2016)	LCI database [Modelled in GaBi]	Waste treatment	GaBi Professional Database 2020 (SP 40)	Gabi Professional Database 2020[8]
Wastewater treatment process of chemicals	0.0366	CML 2001, GaBi (method version: Jan. 2016)	LCI database	Waste treatment	"EU-28, Waste water treatment, ts", GaBi Professional Database 2020 (SP 40)	Gabi Professional Database 2020[8]

Table S4. Input data used for Finechem model and GWP predictions for 2-cyanopyridine and alpha-picoline (reference for validation)

Data	Value	
	2-cyanopyridine	Alpha-picoline
Molecular weight	104.112	93.129
Number of nitrogen atoms in the molecule	2	1
Number of halogen (Fluorine, Chlorine, Bromine) atoms in the molecule	0	0
Number of rings in the molecule, both aromatic and aliphatic	1	1
Number of tertiary or quaternary carbon atoms in the molecule	0	0
Number of heteroatoms within rings in the molecule	1	1
Number of unique substituents on aromatic ring systems in the molecule	1	1
Number of total functional groups in the molecule	1	1
Number of oxygen atoms in carbonyl groups	0	0
Number of oxygen atoms except those in carbonyl groups in the molecule	0	0
Estimated GWP (kg-CO_2-eq)	6.198	6.308

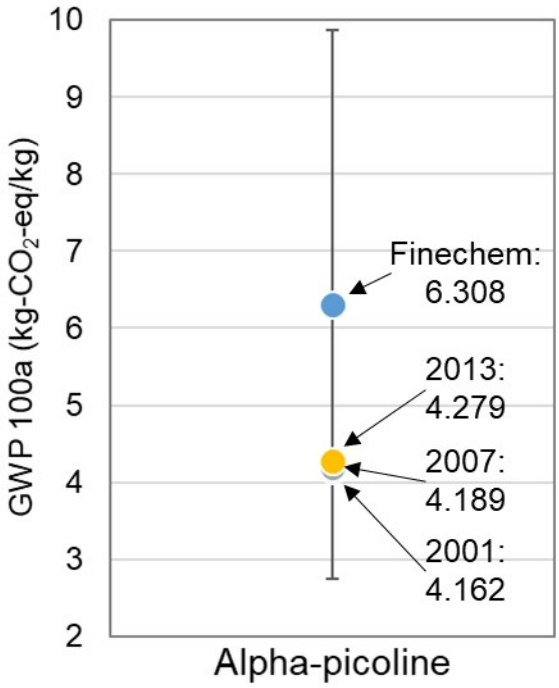

Fig. S2. Validation of the result of Finechem model with database. Alpha-picoline was used as a reference substance which is one of the precursors of 2-cyanopyridine because of the availability of lifecycle inventory in Ecoinvent database[4]. The standard deviation of the estimated value was 3.559.

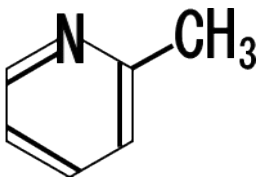

Fig. S3. Molecular structure of alpha-picoline

S3 Characterization of the reaction of the direct DMC synthesis

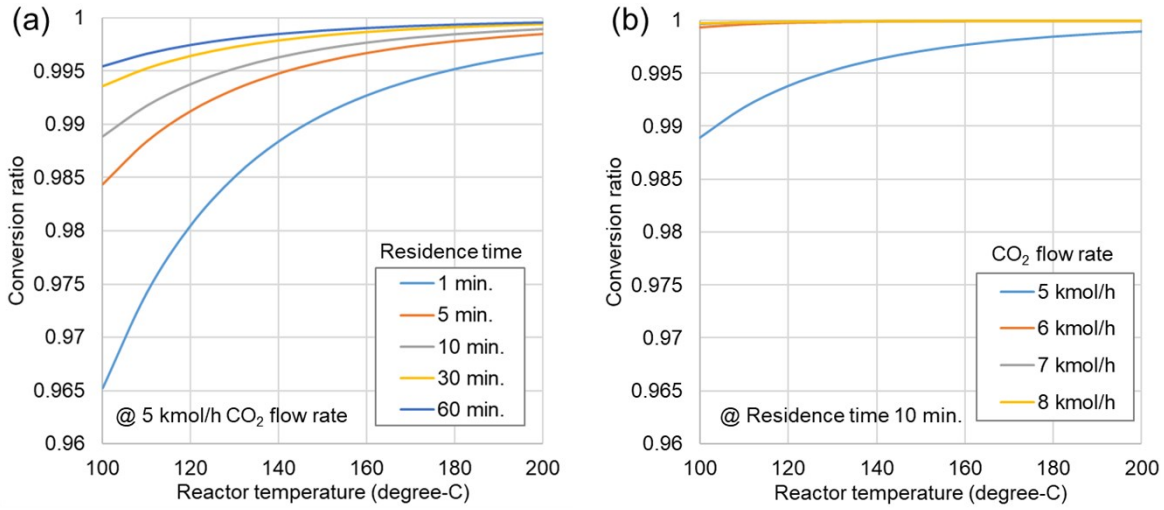

Fig. S4. Characteristics of the reaction: MeOH + CO2 + 2-CP => DMC + 2-PA. (a) Temperature dependence of the conversion ratio in various residence time at 5 kmol/h CO_2 flow rate; (b) Temperature dependence of the conversion ratio at various flow rate of CO_2 in 10 minutes residence time.

S4 Detailed specification of heat exchange

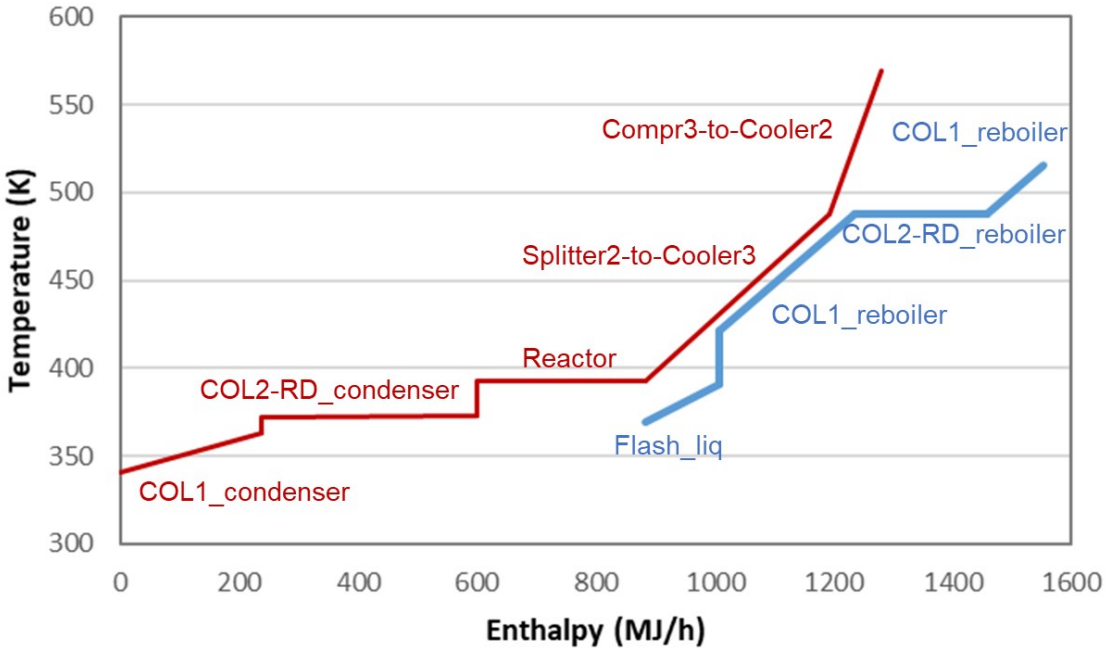

Fig. S5. Composite curve of the heat exchanging case

S5 Alternative 2-CP regeneration process under the parameters estimated by Benson's GCM

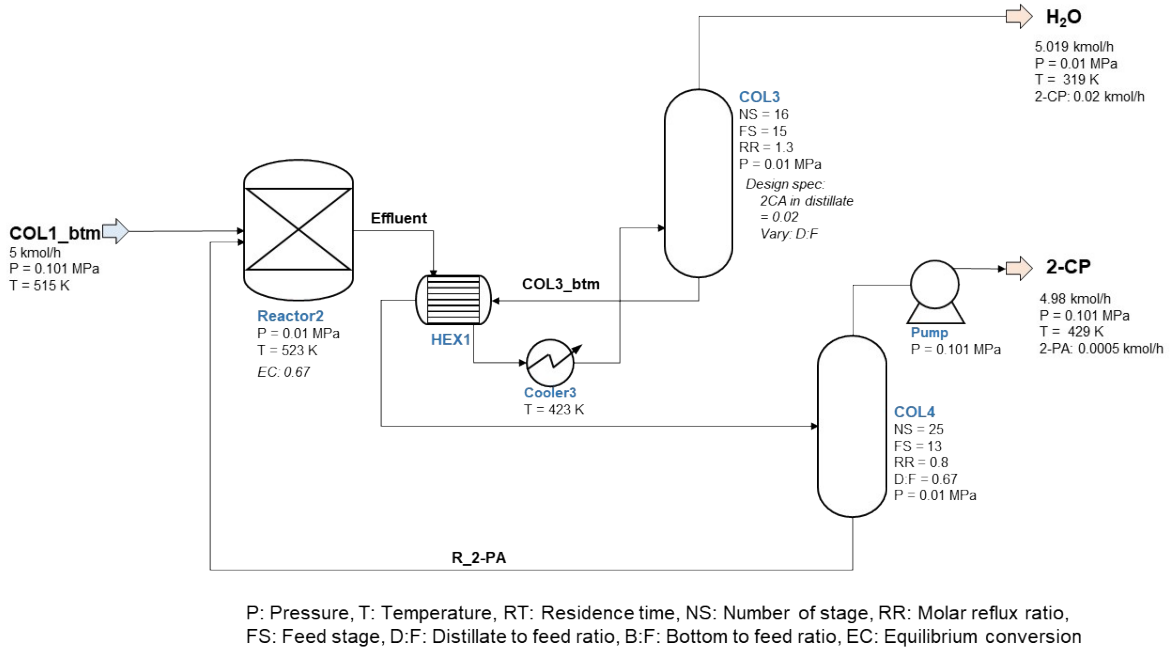

Fig. S6. Process flow diagram of the alternative 2-CP regeneration process for thermodynamically harder parameters estimated by Benson's GCM.

Table S5. Stream data of the alternative 2-CP regeneration process

Stream name	COL1_btm	Effluent	COL3_btm	R_2-PA	H_2O	2-CP
From		Reactor2	COL3	COL4	COL3	Pump
To	Reactor2	HEX1	HEX1	Reactor2		
Phase	Liquid	Vapor	Liquid	Liquid	Liquid	Liquid
Temperature (C)	242	250	165	197	46	156
Pressure (bar)	1.000	0.100	0.100	0.100	0.100	1.000
Mole Flow (kmol/h)	5.000	12.452	7.433	2.454	5.019	4.979
2-PA	0.000	5.000	4.980	0.001	0.020	4.979
2-CP	5.000	2.453	2.453	2.453	0.000	0.000
WATER	0.000	4.999	0.000	0.000	4.999	0.000

Table S6. Simulated energy demand of the alternative 2-CP regeneration process

Block	Energy demand	Unit
Reactor	996.25	MJ/h
COL3_reboiler	54.90	MJ/h
COL4_reboiler	361.70	MJ/h
COL3_condenser	-498.31	MJ/h
COL4_condenser	-448.30	MJ/h
Cooler	-215.65	MJ/h
Pump	0.06	kW

Table S7. Contribution to GHG emission by factors per 1 kg-DMC production.

		GHG (kg-CO_2-eq/kg-DMC)	
Category	Factor	Without heat utilization	With heat utilization
Feedstock	MeOH	0.63	0.63
	CO_2	-0.49	-0.49
	2-CP	0.03	0.03
Process	COL1_reboiler	0.07	0.04
	2-CP regeneration	0.21	0.21
	Electricity	0.07	0.07
Waste	Wastewater treatment	0.01	0.01
	Total	0.51	0.48

Reference

1. K. G. Joback and R. C. Reid, *Chem. Eng. Commun.*, 1987, **57**, 233-243.
2. S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.*, 1969, **69**, 279-324.
3. R. Gani, B. Nielsen and A. Fredenslund, *AIChE J.*, 1991, **37**, 1318-1332.
4. G. Wernet, C. Bauer, B. Steubing, J. Reinhard, E. Moreno-Ruiz and B. Weidema, *Int. J. Life Cycle Assess.*, 2016, **21**, 1218-1230.
5. G. Wernet, S. Hellweg, U. Fischer, S. Papadokonstantakis and K. Hungerbuhler, *Environ. Sci. Technol.*, 2008, **42**, 6717-6722.
6. G. Wernet, S. Papadokonstantakis, S. Hellweg and K. Hungerbühler, *Green Chem.*, 2009, **11**, 1826-1831.
7. APEC Energy Working Group: Expert Group on Energy Data and Analysis, Electricity Power Generation Table, https://www.egeda.ewg.apec.org/egeda/database_info/electricity_select_form2.html, (accessed July 10th, 2020).
8. Sphera, Professional Database 2020, http://www.gabi-software.com/support/gabi/gabi-6-lci-documentation/professional-database/, (accessed August 19th, 2020).