Supplemental Material: Energy and cost-saving potential of combined carbon capture and conversion: a pioneering design of a process intensification concept harnessing CeO_2 as a dual-functional material

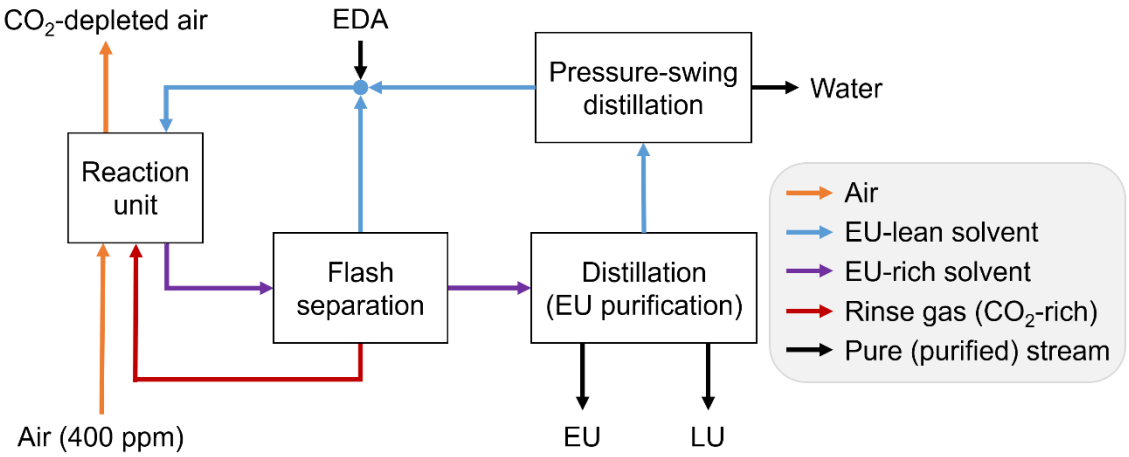

Figure 1 Schematic of the quad-C EU production process

S1. Specifications of unit models in Aspen simulations

S1.1. Reaction unit without air-drying

The reaction unit was simulated using two Rstoic unit models in Aspen Plus because an Rstoic reaction unit can define chemical reactions under one specific set of operating conditions.

The first one was used for the CO_2 adsorption and rinse gas injection, solvent inflow for the ethyleneurea (EU) retrieval using lean-EU ethylenediamine (EDA) liquid due to their identical operating conditions (298 K and 1 atm). This unit model features one input stream for ambient CO_2 and three recycle streams: lean-EU EDA solvent, rich-EU solvent (an internal

recycle stream as described in **Figure 3**), and a rinse gas stream. It has a single outlet stream where the EDA-CA/EDA ratio is measured, which then feeds into the second Rstoic model.

The synthesis of EU and linear urea (LU) was simulated at 363 K and 1 atm [1] in the second unit model, which has two outlet streams: an internal recycle stream to concentrate EU and rich-EU solvent for chemical separation.

Figure S1 shows the process flow diagram (PFD) of the entire reaction unit as simulated in Aspen Plus.

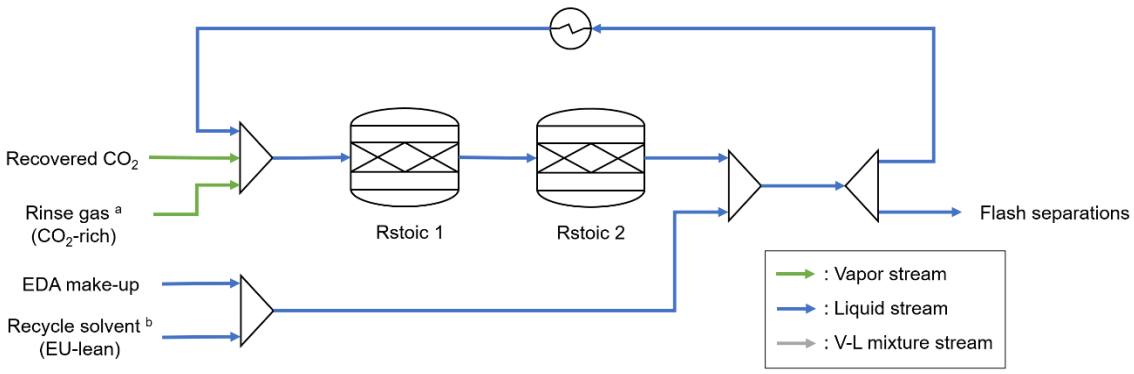

Figure S1 PFD of the entire reaction unit in Aspen Plus

S1.2. Flash separation system

The flash separation system consists of one Rstoic unit and three flash separators (**Figure 4**). The operating conditions for the flash separation system is shown in **Table S1**. According to the literature [2, 3], it is imperative to carefully control the EDA-CA content and temperature of the EDA liquid for reliable process operations, as EDA-CA facilitates EU formation under

high-temperature conditions. Considering that EU and LU had high boiling points and subsequent distillation systems operated at high temperatures, this study assumed that the EDA-CA discharged from the reaction unit would readily decompose in Flash 1. The operating pressure for Flash 4 was set to maintain a consistent temperature of 130°C.

Table S1 Operating conditions for the flash separation system

Equipment	Temperature [°C]	Pressure [atm]
Flash 1	160	2.50
Flash 2	140	1.50
Flash 3	25	1.00
Flash 4	130	Varying

S1.3. Distillation system for EU purification

The EU purification system has two distillation columns which have been modelled using Radfrac units. The first distillation column separates EU and LU from other chemical substances, and the second column separates EU from LU at a high purity. The operating conditions for the EU purification were determined to obtain 99 wt% EU and 97 wt% LU, as shown in **Table S2**, depending on the recycled EU-rich solvent ratio (SR) in the reaction unit.

Table S2 Operating conditions for the EU purification system

Equipment	Number of stages [-]	Feed stage [-]	Pressure [atm]	Reflux ratio (mole-basis) [-]	Distillate rate [mol/h]
COL 1	40	37	1.0	0.7	180.1 ~ 242.2
COL 2	20	5	0.1	3.0	97.3

S1.4. Pressure-swing distillation system

The pressure-swing distillation system comprises two distillation columns, and both columns are modelled using Radfrac units, as shown in **Figure 6**. The system has a recycle stream, transferring water-EDA mixture from the bottom stream of the second column back to the feed stream of the first one. **Table S3** represents the specifications of the pressure-swing distillation, as the distillate rate changes depending on the SR values.

Table S3 Operating conditions for the pressure-swing distillation

Equipment	Number of stages [-]	Feed stage [-]	Pressure [atm]	Reflux ratio (mole-basis) [-]	Distillate rate [mol/h]
COL 3	35	10	0.2	5.5 ~ 7.5	111.4 ~ 180.1
COL 4	30	10	5.0	15 ~ 20	96.8 ~ 97.5

166 The vapour-liquid equilibria between water and EDA at 0.2, 1.0, and 5.0 atms are depicted
167 in **Figure S2**. Comparing these results with those from a previous study [4], the vapor-liquid
168 equilibria at 0.2 and 1.0 atms simulated in Aspen Plus show good agreement. However, the
169 case at 5.0 atmospheres exhibits a slight deviation in the molar fraction at the azeotrope. For
170 detailed modelling, corrections to the vapor-liquid equilibria may be necessary for high-
171 pressure operations.

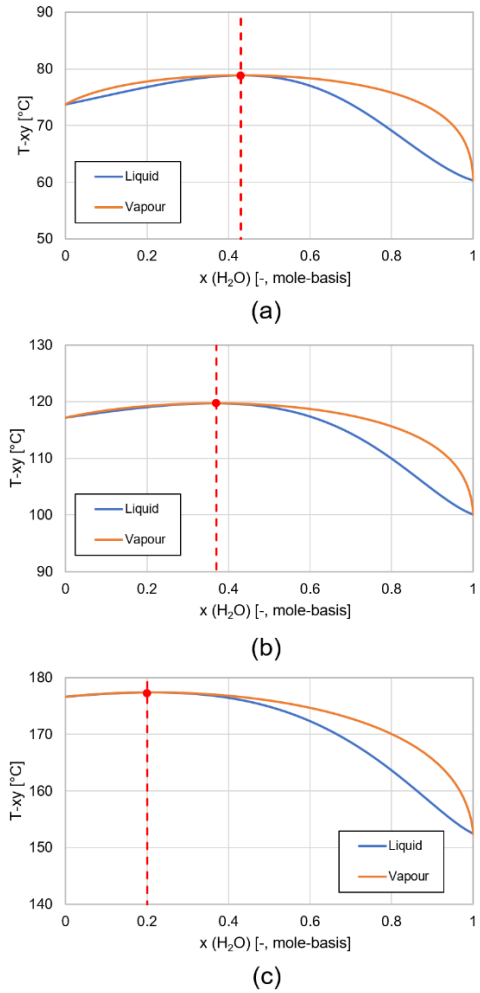

Figure S2 Vapour-liquid equilibria between water and EDA at (a) 0.2, (b) 1.0, and (c) 5.0 atms

S2. Details of sensitivity analysis on energy requirements for air-loading

S2.1. Example of input data for Python programming execution

Table S4 Input data on equation coefficients (v = 1 m/s, l = 1 m)

ep^3	ep^2	ep^1	ep^0
119.969	-2713.31	7479.552	-4766.25
179.992	-2713.31	7479.552	-4766.25
240.04	-2713.31	7479.552	-4766.25
300.114	-2713.31	7479.552	-4766.25
361.879	-2713.31	7479.552	-4766.25
421.396	-2713.31	7479.552	-4766.25
480.734	-2713.31	7479.552	-4766.25
540.819	-2713.31	7479.552	-4766.25
600.935	-2713.31	7479.552	-4766.25
661.088	-2713.31	7479.552	-4766.25
721.43	-2713.31	7479.552	-4766.25
781.699	-2713.31	7479.552	-4766.25
841.999	-2713.31	7479.552	-4766.25
902.324	-2713.31	7479.552	-4766.25
962.674	-2713.31	7479.552	-4766.25
1023.051	-2713.31	7479.552	-4766.25
1083.573	-2713.31	7479.552	-4766.25
1143.992	-2713.31	7479.552	-4766.25
1204.437	-2713.31	7479.552	-4766.25

Note: ep^3 = a, ep^2 = -b, ep^1 = 2b + c, ep^0 = - (b + c)

S2.2. Python programming code for the sensitivity analysis

```python
import numpy as np
import pandas as pd

df = pd.read_csv('Air-L_input.csv')

PD_input = df.values.tolist()
PD_output = [0]*len(PD_input)
cnt = 0


for i in range(len(PD_input)):
    sol_row = np.roots(PD_input[i])

    for j in range(len(sol_row)):
        if np.isreal(sol_row[j]) and 0 < sol_row[j] < 1:
            PD_output[i] = np.real(sol_row[j])

out_df = pd.DataFrame(PD_output)

out_df.to_csv("out.csv", float_format='%.5f')
```

Figure S3 Python code for the sensitivity analysis

S3. Analysis of the cost of raw materials and energy for EU production

S3.1. Conventional EU production

The commercial process for EU production converts EDA and urea into EU with the ethylene glycol solvent. The schematic diagram of this process is shown in **Figure S4** [5]. The source of the process scheme for commercial EU production was provided by Hebei Kangzhuang (China), which is the second largest EU producer in the world.

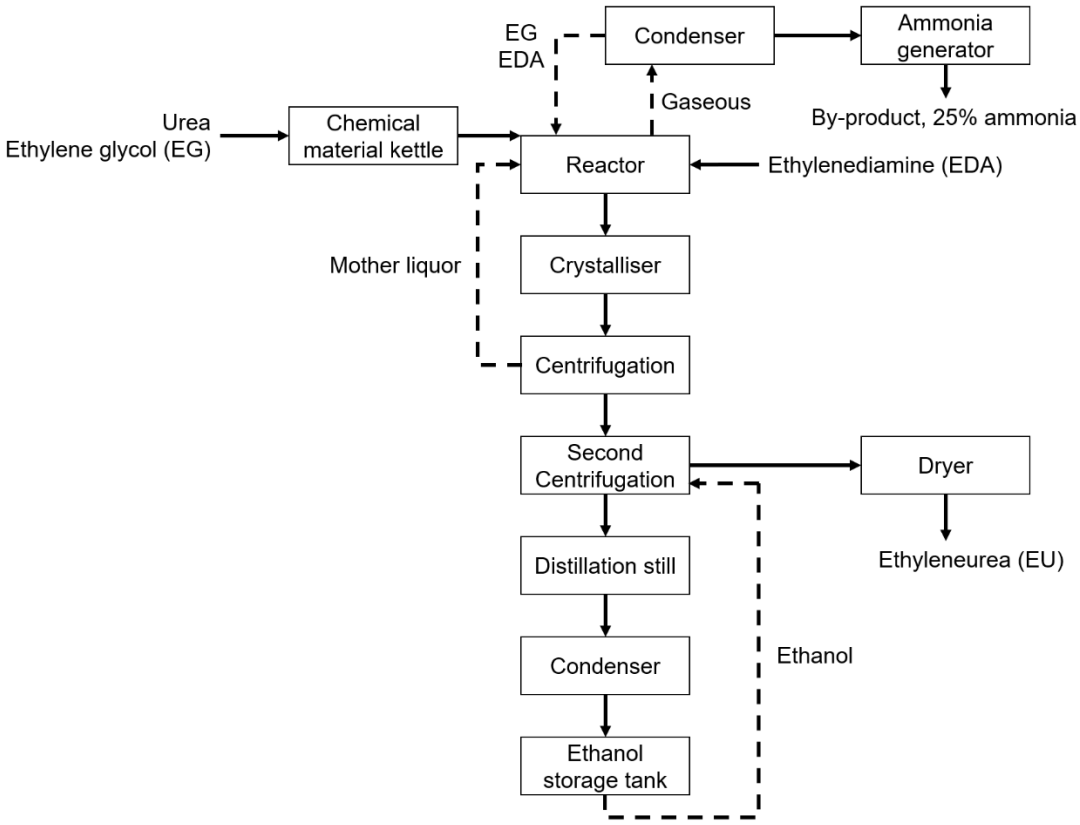

Figure S4 Schematic diagram of commercial EU production process

S3.2. The cost of raw materials and energy for EU production

Table --- indicates the cost of raw materials and energy for EU production report by the market analysis references [5, 6]. The Japan's market analysis report provides the EDA cost by the JPY, and the cost base year cost is fixed on the average currency exchange rate (110.5 JPY/USD). The base year cost in Table S5 was fixed on the 2023 fiscal year basis according to the Chemical Engineering Plant Cost Index (CEPCI) [7].

194

195 **Table S5 Cost reported by market analysis references**

Process	Item	Base year cost [USD/kg-EU]	Notes
Commercial process (Case I)	EDA + Urea (+ EG)	6.11	2020 fiscal year basis,
	Energy	0.12	Ref. 5
CeO_2-based process (Case II and III)	EDA	3.88	2018 fiscal year basis, Ref. 6

196

197

198 **S4. Exploration of process intensification from conceptual process design**

199 *S4.1. Air drying in the reaction column*

200 By applying the air-drying to the process intensification approach, the cyclic operation of
201 the reaction unit changed as shown in **Figure S5**. To simulate the water removal from the
202 reaction unit, the simple separation unit model was employed after the two Rstoic models to
203 examine the effect of the water removal prior to a series of the chemical separation. The process
204 flow diagram for Aspen simulations is represented in **Figure S6**. The compressor-type
205 dehydration part was modelled independently from other simulation parts. It should be noted
206 that liquid-phase water discharged from the reaction unit was completely transformed in the

207 vapour phase by contacting the dry air due to a relative humidity of the wet air (10%).

208

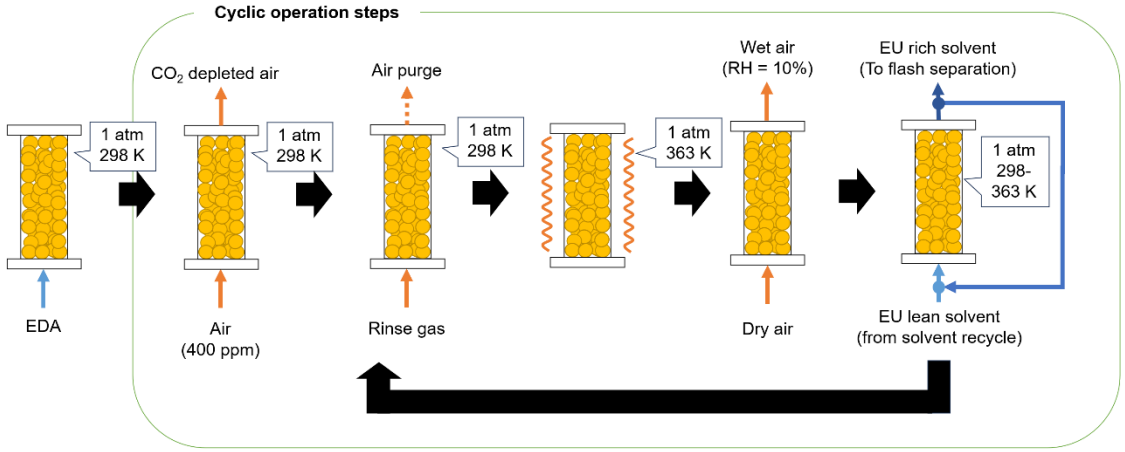

Figure S5 Operating procedures for the reaction unit with air-drying

Note: RH: relative humidity

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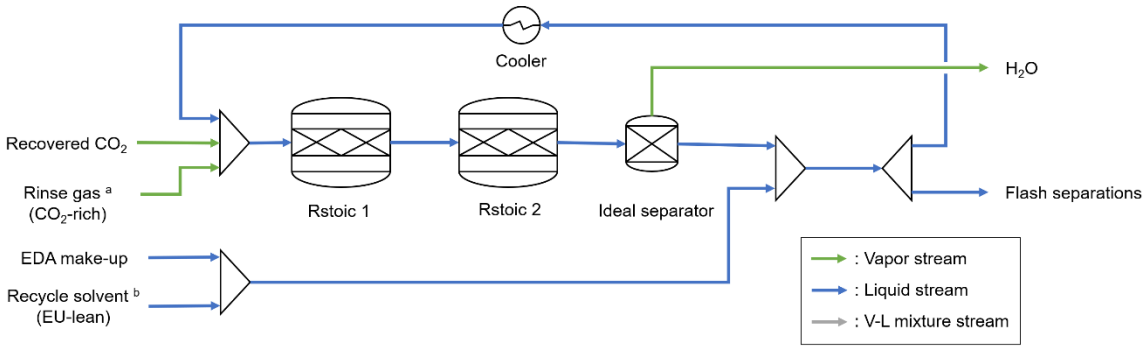

Figure S6 PFD of the entire reaction unit with air-drying as simulated in Aspen Plus

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References

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