

Supporting Information

Multi-Objective Optimization of TETA Blended Amines for Microwave-Regenerated CO₂ Capture via RSM and Entropy-Weighted TOPSIS

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This Supplementary Information provides the metrological inputs used in the uncertainty analysis, the complete Box–Behnken design (BBD) data set, ANOVA and model-fit statistics, model-diagnostic plots, validation of the microwave-reactor temperature reading, entropy-weighted TOPSIS calculations, CO₂-recovery uncertainty propagation, and the exact water/n-butanol formulations.

Instrument specifications are reported first in Table S1, followed by the BBD matrix and RSM results in Tables S2–S5 and Figures S1–S3. The entropy calculations are given in Tables S6 and S7, the water/n-butanol formulations in Table S8, and thermocouple validation in Table S9.

Table S1. Instrument specifications and metrological inputs used in the uncertainty analysis.

Measurement	Instrument/model	Range	Resolution/readability	Accuracy/uncertainty input
Mass	Mettler Toledo MS304TS/02	0-320g	0.1mg	Repeatability: 0.1 mg; linearity deviation: 0.2 mg
Gas pressure	DP-A(YWS) barometric pressure/temperature/humidity meter	71.3-131.3kPa	0.01kPa	Accuracy: ± 0.5 kPa
Gas-collection temperature	DP-A(YWS) barometric pressure/temperature/humidity meter	-20-100°C	0.1°C	Accuracy: ± 0.5 °C
Desorption liquid temperature	Built-in thermocouple of XH-100B microwave reactor	85–105 °C experimental setpoints	—	Validated against aqueous-MEA boiling points; relative deviations: 0.005%–0.182%; maximum absolute deviation: ≈ 0.18 °C (Table S9)
Displaced gas volume	Three identical 1000 mL graduated measuring jugs	0–1000 mL each	50 mL	Type-B reading standard uncertainty $u(V_i) = 50/(2\sqrt{3}) = 14.4$ mL; for n cumulative readings, $u(V) = 14.4\sqrt{n}$ mL
CO ₂ flow control	LZB-2 glass rotameter	160–1600 mL·min ⁻¹	—	Basic error limit: $\pm 4\%$; maximum working pressure: ≤ 1 MPa; used for inlet-flow control

Table S2. BBD experimental design and measured absorbed CO₂ mass, desorbed CO₂ mass, and CO₂ recovery.

Std	Run	A:TETA relative mass part (-)	B: DEA relative mass part (-)	C:AMP relative mass part (-)	Absorbed CO ₂ mass (g)	Desorbed CO ₂ mass (g)	CO ₂ Recovery (%)
4	1	6	5	2	2.39	1.779	74.44
10	2	4	5	1	2.45	1.981	80.86
17	3	4	3	2	2.48	1.894	76.37
16	4	4	3	2	2.52	1.796	71.25
2	5	6	1	2	2.86	2.676	93.56
7	6	2	3	3	2.18	1.922	88.15
8	7	6	3	3	2.57	1.893	73.67
5	8	2	3	1	2.12	1.873	88.33
13	9	4	3	2	2.6	2.054	78.99
14	10	4	3	2	2.43	1.913	78.72
12	11	4	5	3	2.28	1.744	76.47
6	12	6	3	1	2.74	2.321	84.72
15	13	4	3	2	2.39	1.717	71.86
3	14	2	5	2	2.06	1.866	90.56
1	15	2	1	2	2.43	1.913	78.72
11	16	4	1	3	2.54	1.777	69.97
9	17	4	1	1	2.88	1.999	69.41

Table S3. ANOVA for the reduced quadratic model of absorbed CO₂ mass.

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-value	P-value	Significance
Model	0.7836	7	0.1119	14.22	0.0003	***
A	0.3916	1	0.3916	49.76	<0.0001	***
B	0.2926	1	0.2926	37.18	0.0002	***
C	0.0480	1	0.0480	6.11	0.0355	*
AB	0.0025	1	0.0025	0.32	0.5868	
BC	0.0072	1	0.0072	0.92	0.3630	
A ²	0.0353	1	0.0353	4.49	0.0632	
B ²	0.0080	1	0.0080	1.02	0.3394	
Residual	0.0708	9	0.0079			
Lack-of-fit	0.0443	5	0.0089	1.34	0.4007	
Pure error	0.0265	4	0.0066			

Based on Tables S2 and S3, the empirical second-order polynomial for absorbed CO₂ mass (Y_1) is given by Equation (S1):

$$\begin{aligned}
 Y_1 = & 2.48842. + 0.22125 \times A - 0.19125 \times B \\
 & - 0.07750 \times C - 0.02500 \times AB + 0.04250 \times BC \\
 & - 0.09145 \times A^2 + 0.04355 \times B^2
 \end{aligned}
 \tag{S1}$$

Table S4. ANOVA for the quadratic regression model of CO₂ recovery.

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-value	P-value	Significance
Model	718.67	7	102.67	5.12	0.0135	*
A	46.9	1	46.90	2.34	0.1607	
B	14.23	1	14.23	0.7092	0.4215	
C	28.35	1	28.35	1.41	0.265	
AB	239.63	1	239.63	11.94	0.0072	**
AC	29.54	1	29.54	1.47	0.2559	
BC	6.13	1	6.13	0.3053	0.594	
A ²	353.89	1	353.89	17.64	0.0023	**
Residual	180.59	9	20.07			
Lack-of-fit	125.99	5	25.2	1.85	0.2862	
Pure error	54.5983	4	13.6496			

The corresponding regression equation for CO₂ recovery (Y₂) is given by Equation (S2):

$$Y_2 = 74.8778 - 2.42125 \times A + 1.33375 \times B - 1.88250 \times C - 7.74000 \times AB - 2.71750 \times AC - 1.23750 \times BC + 9.14097 \times A^2 \quad (S2)$$

Table S5. Fit statistics for the RSM models from Design-Expert 13.

Metric	Absorption-mass model	CO ₂ recovery model
Model p	0.0003	0.0135
Lack-of-fit p	0.4007	0.2862
R ²	0.9171	0.7992
Adjusted R ²	0.8526	0.6430
Predicted R ²	0.7573	0.6079
PRESS	0.2928	933.34
SD	0.0887	4.4795
CV (%)	3.60	5.66

The absorbed-mass model shows good fit and useful predictive ability within the investigated design space. The CO₂-recovery model is statistically significant and has non-significant lack of fit; however, its predicted R² of 0.6079 indicates that the model has moderate predictive capability within the investigated design space. It is therefore mainly used for screening and trend interpretation rather than precise prediction of new observations.

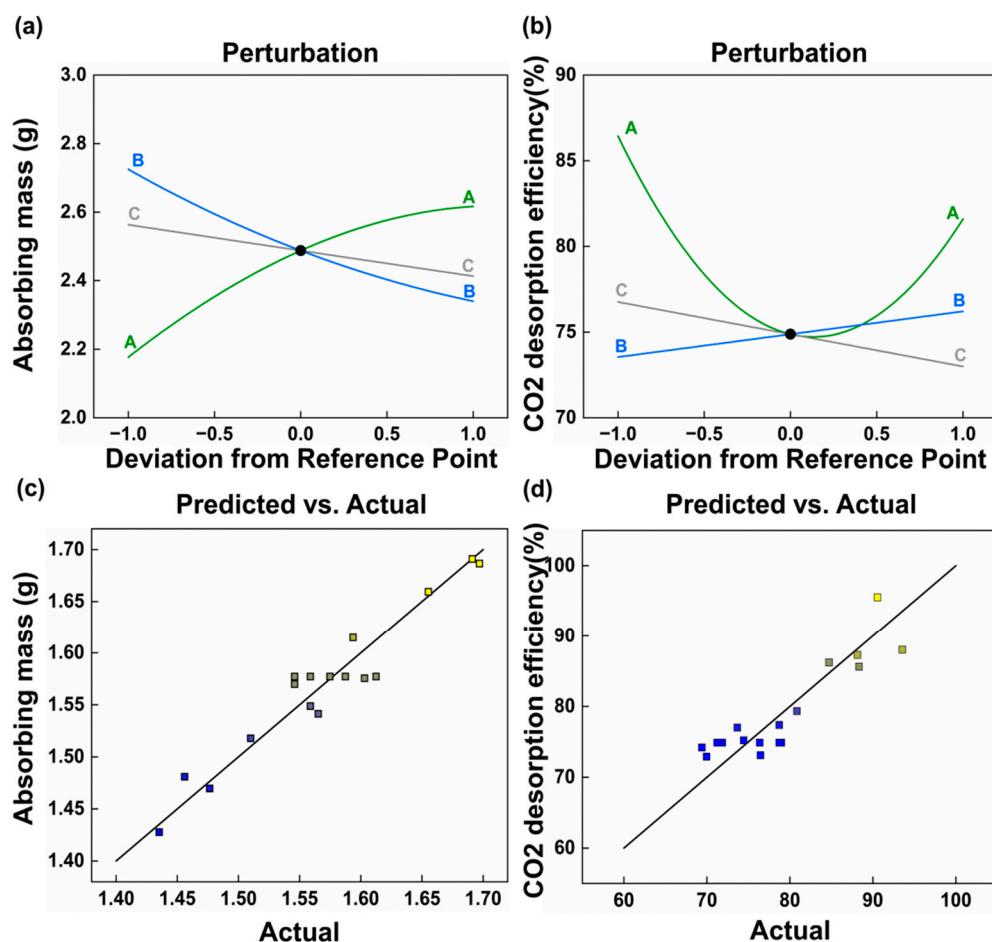


Figure S1. Perturbation plots for (a) absorbed CO₂ mass. (b) CO₂ recovery and predicted value vs. actual value for (c) absorption capacity. (d) CO₂ recovery.

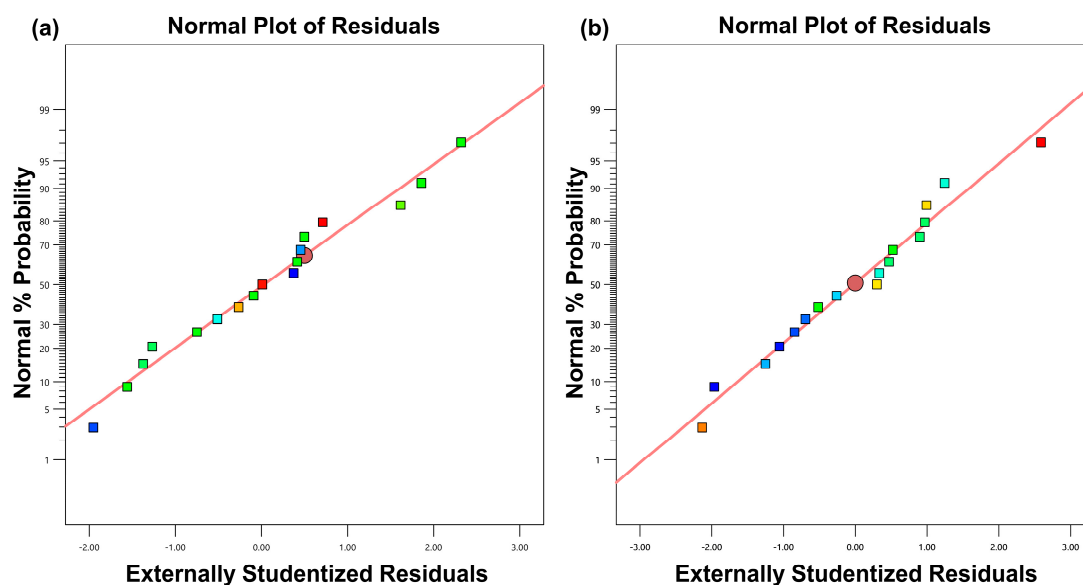


Figure S2. Normal probability plots for (a) absorbed CO₂ mass. (b) CO₂ recovery.

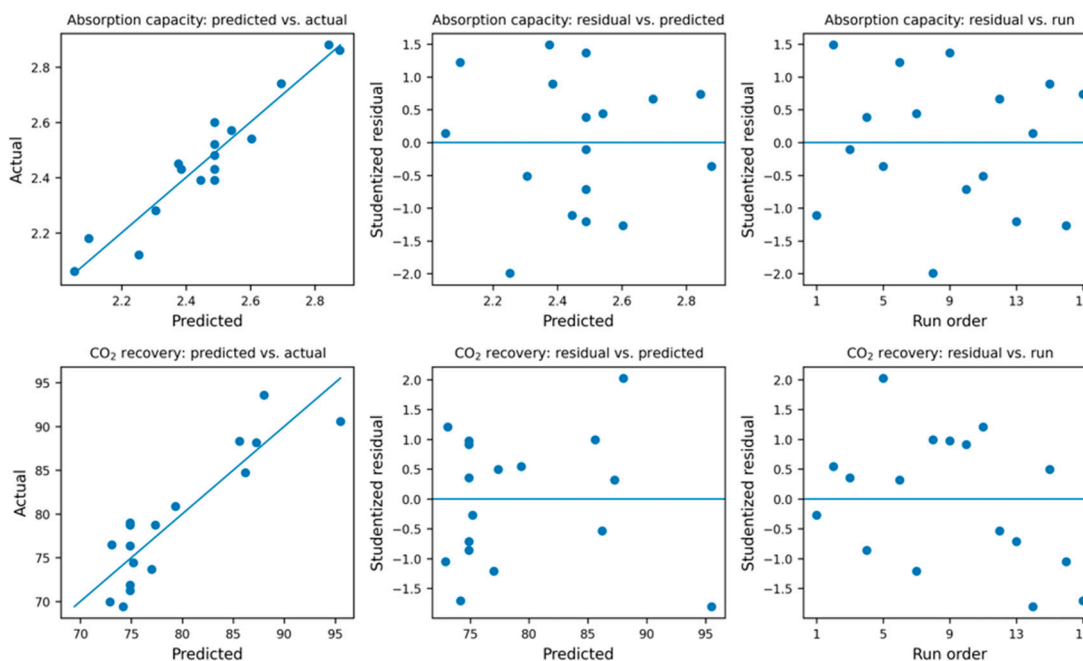


Figure S3. Diagnostic plots for the BBD models based on all 17 runs, including predicted versus actual values, studentized residuals versus predicted values, and studentized residuals versus run order for absorbed CO₂ mass and CO₂ recovery.

$$Z_{ij} = \frac{X_{ij} - \min(X_j)}{\max(X_j) - \min(X_j)} \quad (S3)$$

Here, X_{ij} is the original value of response j for experiment i , and $\min(X_j)$ and $\max(X_j)$ are the corresponding minimum and maximum values. For absorbed CO₂ mass, $\min = 2.06$ g and $\max = 2.88$ g; for CO₂ recovery, $\min = 69.41\%$ and $\max = 93.56\%$. The normalized values are listed in Table S6.

Table S6. Normalized values for absorbed CO₂ mass and CO₂ recovery in the seven-point TOPSIS decision matrix.

Expt. No.	Absorbed CO ₂ mass, Y_1 (g)	Normalized Z_1	CO ₂ Recovery, Y_2 (%)	Normalized Z_2
1	2.86	0.9756	93.56	1.0000
2	2.88	1.0000	69.41	0.0000
3	2.06	0.0000	90.56	0.8761
4	2.74	0.9268	84.72	0.6732
5	2.18	0.1463	88.15	0.7895
6	2.48	0.5122	76.37	0.3696
7	2.52	0.5610	71.25	0.2083

Table S7. Entropy-method weight calculation for the seven-point TOPSIS decision matrix.

Indicator	Entropy (e_j)	Divergence ($g_j=1-e_j$)	Weight (w_j)
Absorption (Y_1)	0.9802	0.0198	0.373
Recovery (Y_2)	0.9695	0.0305	0.627

CO₂ recovery uncertainty propagation

Equations (3a)–(3e) in the main text define the gravimetric absorbed mass, water-vapor correction, ideal-gas conversion, desorbed mass, and CO₂ recovery. Based on these equations, the propagation of measurement uncertainty is described below.

The gravimetric and volumetric measurement routes were treated separately. For the gravimetric measurement, the combined standard uncertainty of absorbed CO₂ mass is:

$$u_c(m_{abs}) = \sqrt{u(m_{rich})^2 + u(m_{lean})^2} \quad (S4)$$

For the water-displacement measurement, uncertainty in the corrected dry CO₂ pressure and the ideal-gas conversion is propagated as follows:

$$u_c(p_{CO_2}) = \sqrt{u(p_{total})^2 + u(p_{H_2O})^2} \quad (S5)$$

$$\frac{u_c(n_{des})}{n_{des}} = \sqrt{\frac{u(p_{CO_2})^2}{p_{CO_2}^2} + \frac{u(V)^2}{V^2} + \frac{u(T_K)^2}{T_K^2}} \quad (S6)$$

$$\frac{u_c(m_{des})}{m_{des}} = \frac{u_c(n_{des})}{n_{des}} \quad (S7)$$

$$\frac{u_c(\eta)}{\eta} = \sqrt{\frac{u_c(m_{des})^2}{m_{des}^2} + \frac{u_c(m_{abs})^2}{m_{abs}^2}} \quad (S8)$$

Table S1 summarizes the Type-B metrological inputs. For the DP-A(YWS) meter, the pressure and temperature accuracy limits of ± 0.5 kPa and ± 0.5 °C were treated as rectangular distributions, giving standard uncertainties of 0.289 kPa and 0.289 °C. The displaced gas volume was measured cumulatively using identical 1000 mL graduated jugs with 50 mL divisions. Each 50 mL graduation gives a Type-B reading standard uncertainty of $50/(2\sqrt{3}) = 14.4$ mL, and segmented readings were combined by root-sum-of-squares. The LZB-2 rotameter controlled inlet flow but did not enter the recovery equation. At 95 °C, absorbed and desorbed amounts were obtained from three independent replicates; using the approximately 3% relative SD of each mean as independent Type-A inputs gives:

$$u_{r,A}(\eta) = \sqrt{\left(\frac{0.03}{\sqrt{3}}\right)^2 + \left(\frac{0.03}{\sqrt{3}}\right)^2} = 0.0245 = 2.45\% \quad (S9)$$

$$u_A(\eta) = 93.56\% \times 0.0245 \approx 2.29 \text{ percentage points} \quad (S10)$$

For the representative 95 °C case, the absorbed and desorbed CO₂ masses were 2.86 and 2.676 g, the cumulative displaced volume was 1500 mL, the dry CO₂ pressure was 100.60 kPa, and the gas-collection

temperature was 25.3 °C. The Type-A relative standard uncertainty was 2.45%, equivalent to 2.29 percentage points at 93.56% recovery. Two jug readings were required for 1500 mL, giving $u(V) = 14.4\sqrt{2} = 20.4$ mL (1.36%). The pressure-accuracy input gives $u(p_{\text{total}}) = 0.289$ kPa; propagation of the ± 0.5 °C temperature limit through the local saturated-water-vapor-pressure slope gives $u[p_{\text{H}_2\text{O}}(T)] \approx 0.055$ kPa, so $u(p_{\text{CO}_2}) \approx 0.294$ kPa (0.292%). The gas-temperature contribution is approximately 0.097%, and the balance contribution is below 0.02%. Equations (S4)–(S8) therefore give a Type-B relative standard uncertainty of approximately 1.39%, dominated by volume reading. Combining the Type-A and Type-B terms gives approximately 2.82%, or 2.64 percentage points at 93.56% recovery.

Table S8. Exact compositions used in the water/n-butanol comparison (total solution mass 40.0 g; total amine mass 8.0 g; TETA:DEA:AMP = 6:1:2 by mass).

System	TETA(g)	DEA(g)	AMP(g)	Water(g)	n-Butanol (g)
Fully aqueous	5.333	0.889	1.778	32.0	0
10 wt% water	5.333	0.889	1.778	4.0	28.0
20 wt% water	5.333	0.889	1.778	8.0	24.0
Non-aqueous	5.333	0.889	1.778	0	32.0

Table S9. Validation of the XH-100B built-in thermocouple using atmospheric boiling points of aqueous MEA solutions.

MEA concentration (wt%)	Measured boiling temperature (°C)	PRO/II-calculated bubble-point temperature (°C)	Relative deviation (%)
0	100.2	100.0178	0.182
10	101.1	100.9619	0.137
20	102.2	102.2167	0.016
30	103.9	103.8945	0.005
40	106.3	106.1600	0.132
50	109.3	109.2647	0.132
60	113.7	113.6088	0.080

Note: The validation experiment was conducted using the XH-100B microwave reactor temperature-monitoring configuration. Bubble-point temperatures were calculated in PRO/II using the NRTL thermodynamic model.