A heuristic process prediction model for screening the optimal green entrainer with TAC and LCA impacts based on PSE concepts

Electronic Supplementary Information

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Table S1: The optimization operation parameters and objective function of TAC evaluation following the Luyben model[49].

Parameters	Unit	Content
condensers		
heat transfer coefficient	$kW \cdot m^{-2} \cdot K^{-1}$	0.852

capital cost		$7296 \times (Ac)^{0.65}$
heat transfer area: A	m^2	$A_C = \frac{Q_C}{K_C \Delta T_C}$
reboilers		
heat transfer coefficient	$kW \cdot m^{-2} \cdot K^{-1}$	0.568
capital cost		$7296 \times (A_R)^{0.65}$
heat transfer area: A	m^2	$A_R = \frac{Q_R}{K_R \Delta T_C}$
Q is the duty of the heat exchanger (kW), Δt is the temperature difference (K), and K is the heat transfer coefficient		
column vessel		
capital cost		$17640 \times D^{1.066} \times H^{0.802}$
length: H	m	$H = 1.2 \times 0.61 \times (NT-2)$
diameter: D	m	Calculated by Aspen tray sizing

Table S2: Comply with the optimization operation parameters of the Douglas model and the objective function of TAC evaluation[50].

Project	Content	Unit
ID	Aspen tray sizing	m
H	0.61×(NT/0.75-3) +6	m
Column shell cost	$C_1 = \left(\frac{M\&S}{280}\right) \times 937.636 \times D^{1.066} \times H^{0.802} \times (2.18 + F_C)$	$
	F_C=Fm·Fp, Fm=3.67, Fp = 1.05, P≤ 6.8atm; Fp = 1.00, P≤ 3.4atm	
A_C	$A_C = \frac{Q_C}{K_C \Delta T_C}$	m^2
Kc	0.852	kW·m^{-2}·K^{-1}
EH cost	$C_2 = \left(\frac{M\&S}{280}\right) \times 474.668 \times A^{0.65} \times (2.29 + F_C)$	$
F_C=(F_d+F_p) ·F_m, F_m=3.75, F_d=1.35(kettle reboiler), F_d= (fixed tube sheet heat exchangers), F_p=0		
A_R	$A_R = \frac{Q_R}{K_R \Delta T_C}$	m^2
K_R	0.568	kW·m^{-2}·K^{-1}
Energy costs		
LP steam /433 K	7.78	$·GJ^{-1}
MP steam /457 K	8.22	$·GJ^{-1}
HP steam /537 K	9.88	$·GJ^{-1}
M&S	1431.7	
Membrane Cost	327.62 × A_M	$
Vacuum Pump Cost	$C_3 = 4200 \times \left(\frac{60 \times F_P \times 8.314 \times 273.15}{3600 \times 101.325}\right)^{0.55}$	$
Fp	Aspen simulation results	kmol·h^{-1}
TAC	$TAC = \frac{capital\ cost}{paybackperiod} + energy\ cost$	$·y^{-1}
Payback period	3	years
Operation time	8000	h·year^{-1}

Table S3: The thermodynamic data of Methanol+Toluene azeotropes[44].

Azeotrope	Methanol-toluene	
	$x_{methanol}$ /mol	Temperature /K
Experimental data	0.8820-0.8860	336.41-336.95
NRTL model	0.887	337.02
UNIQUAC model	0.8843	336.91

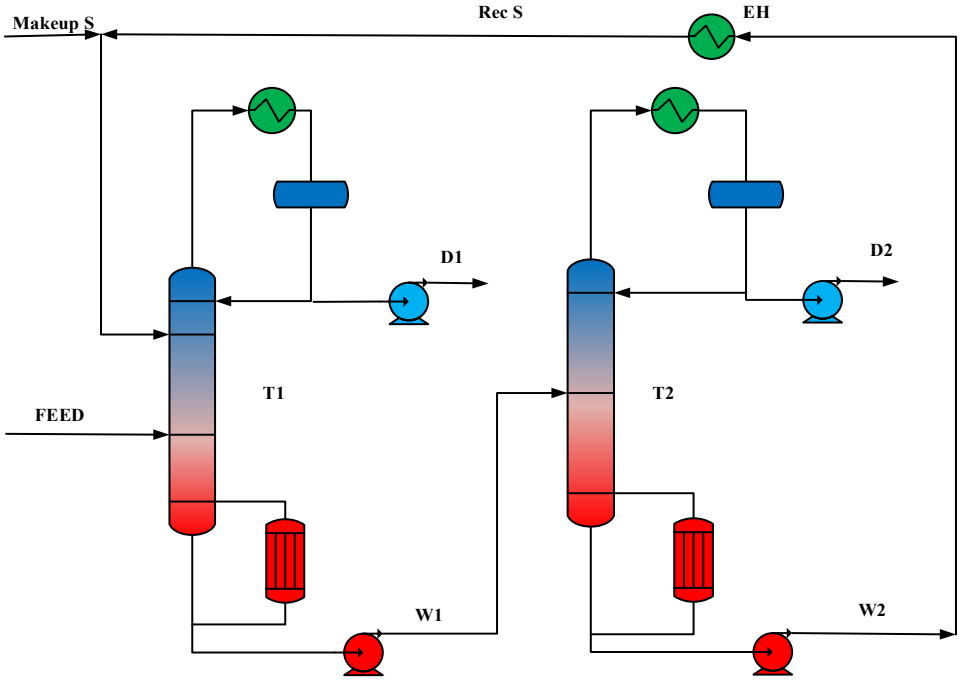


Fig. S1 The flowsheet of separating azeotropes by ED with different entrainer

Table S4: The relationship $between\ V_i, R_{i,min}, R_i, N_{i,min}$, and $N_i\ to\ \alpha_{i44}$.

Parameters	Content	Unit
Total steam load (*Vi*)	$Vi = Di + Li = Di \times (Ri+1) = \frac{C_1}{\lvert\alpha_i - 1\rvert}$	kg·h^{-1}
Ri,min	$R_{i,min} = \frac{1}{\lvert\alpha_i - 1\rvert} \times \left(\frac{x_{D,LK}}{x_{F,LK}} - \alpha_i \times \frac{x_{D,HK}}{x_{F,HK}}\right) = C_2 \times \frac{1}{\lvert\alpha_i - 1\rvert}$	
Ri	$R_i = (1.2\sim2) \times R_{i,min}$	
Ni,min	$N_{i,min} = \frac{\log_{10}\left(\frac{x_{D,LK}}{x_{D,HK}} \times \frac{x_{W,HK}}{x_{W,LK}}\right)}{\log_{10}\alpha_i} = C_4 \times \frac{1}{\log_{10}\alpha_i}$	
Ni	$N_i = (1.2\sim2) \times N_{i,min} = C_5 \times \frac{C_4}{\log_{10}\alpha_i}$	

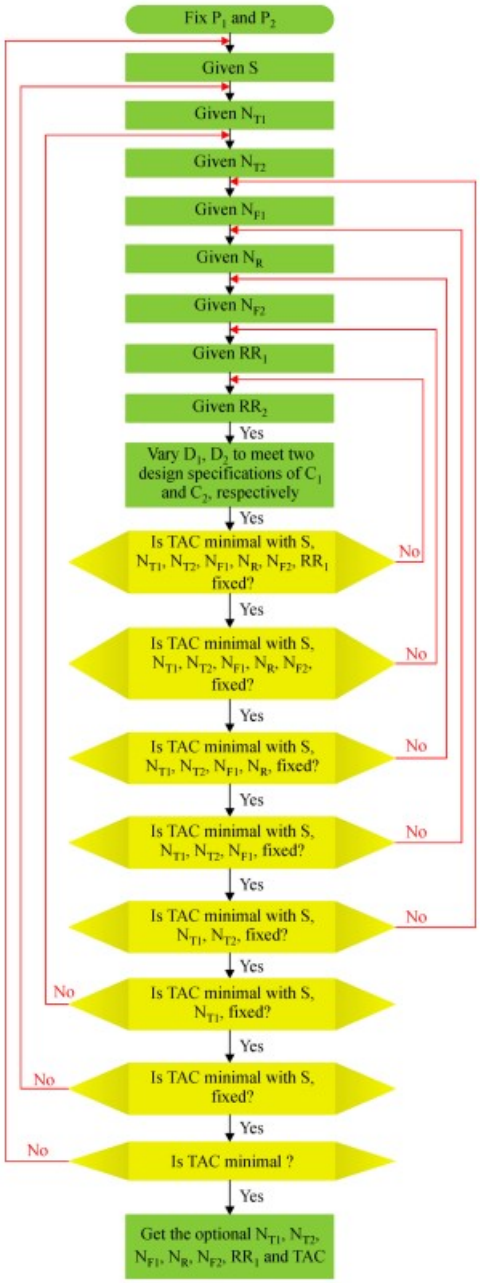


Fig. S2 The simulated and optimized procedure of the ED processes[44].

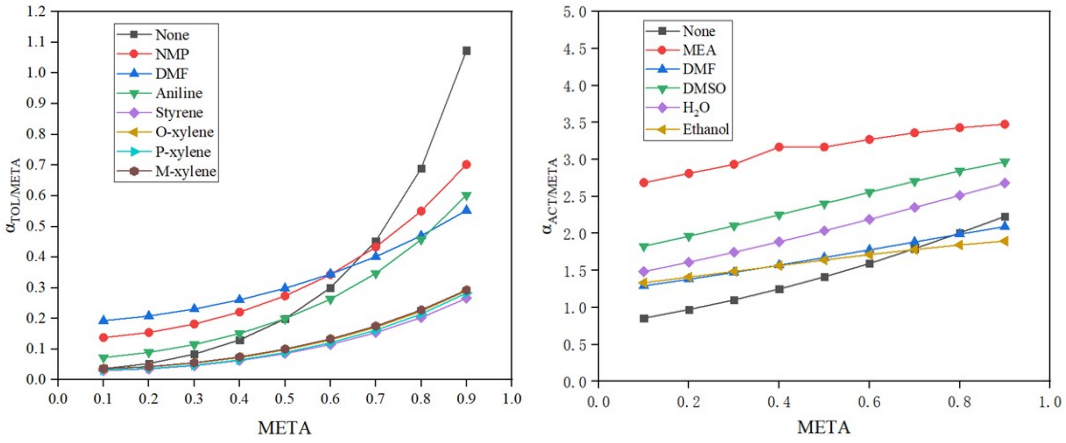


Fig. S3 The changed curves of a: $\alpha_{TOL\text{-}META}$ and b: $\alpha_{ACT\text{-}META}$ after non or adding entrainers[45].

Table S5: The detailed life cycle inventory of each entrainer for separating TOL+META azeotropes with the ED processes.

Project	Unit	**NMP**	Aniline	DMF	Styrene	o-xylene	p-xylene	m-xylene
GWP	$kg \cdot y^{-1} CO_2$ Eq.	289.703	281	285.973	335.708	345.655	407.781	494.128
AP	$kg \cdot y^{-1} SO_2$ Eq.	0.5176	0.5021	0.511	0.5998	0.6176	0.7287	0.8775
HTP	kg DCB Eq.	8.9837	8.7138	8.8681	10.4103	10.7188	12.6447	15.2299
FETP	kg DCB Eq.	0.1545	0.1499	0.1525	0.1791	0.1844	0.2175	0.262
TETP	kg DCB Eq.	0.1611	0.1563	0.159	0.1867	0.1922	0.2268	0.2731
TEDI		**0.56**	**0.58**	**0.79**	**1.62**	**1.74**	**2.75**	**2.81**
LTEDI		**0.3815**	**0.4156**	**0.5319**	**0.7431**	**0.7772**	**0.9981**	**1.0178**

Table S6: The detailed life cycle inventory of each entrainer for separating ACT+META azeotropes with the ED processes.

Project	Unit	**MEA**	DMSO	Water	DMF	Ethanol
GWP	$kg \cdot y^{-1} CO_2$ Eq.	273.415	353.737	516.617	487.398	1883.69
AP	$kg \cdot y^{-1} SO_2$ Eq.	0.488513	0.632023	0.923043	0.870837	3.36561
HTP	kg DCB Eq.	8.4786	10.9694	16.0203	15.1142	58.4134
FETP	kg DCB Eq.	0.1458	0.1887	0.2756	0.26	1.0048
TETP	kg DCB Eq.	0.152	0.1967	0.2873	0.271	1.0495
TEDI		**1.06**	**2.21**	**4.5**	**7.32**	**12.77**
LTEDI		**0.5209**	**0.7985**	**1.4536**	**1.6221**	**2.8898**

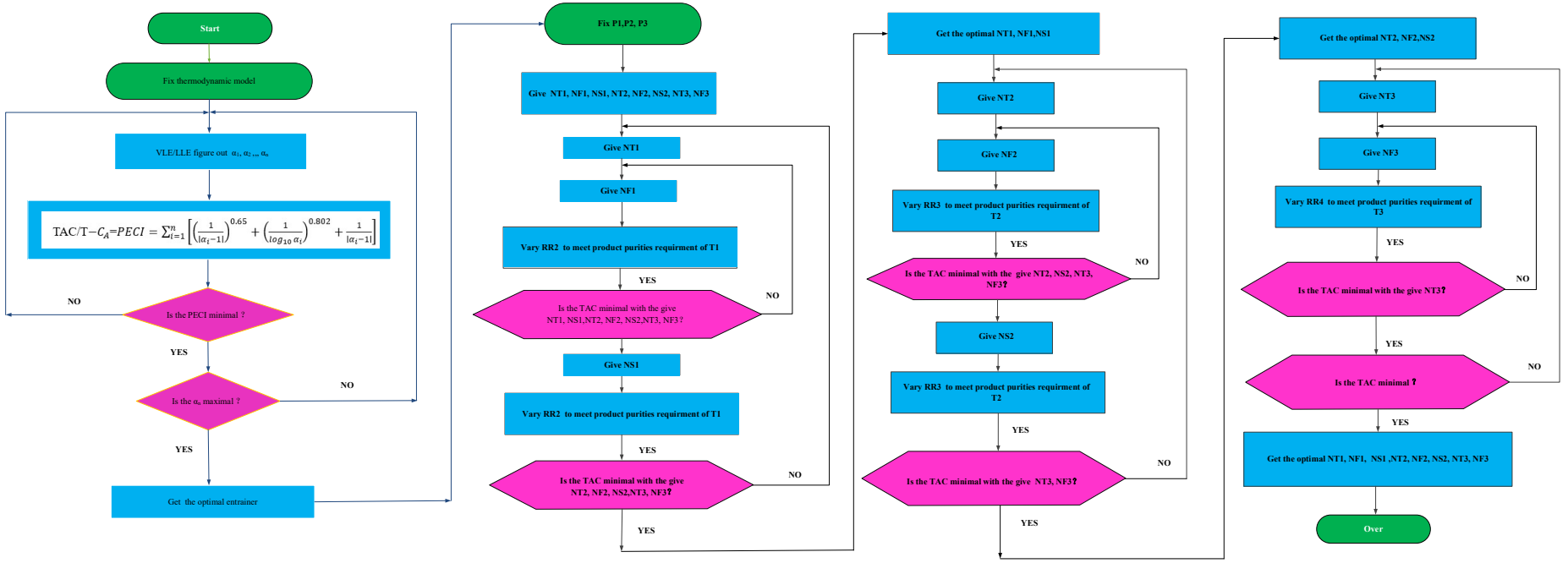


Fig. S4 The simulated and optimized procedure of combining with the heuristics process prediction model, Luyben model, and Douglas model.

Table S7. RMSD of thermodynamic models for DIPE/IPA/EG system.

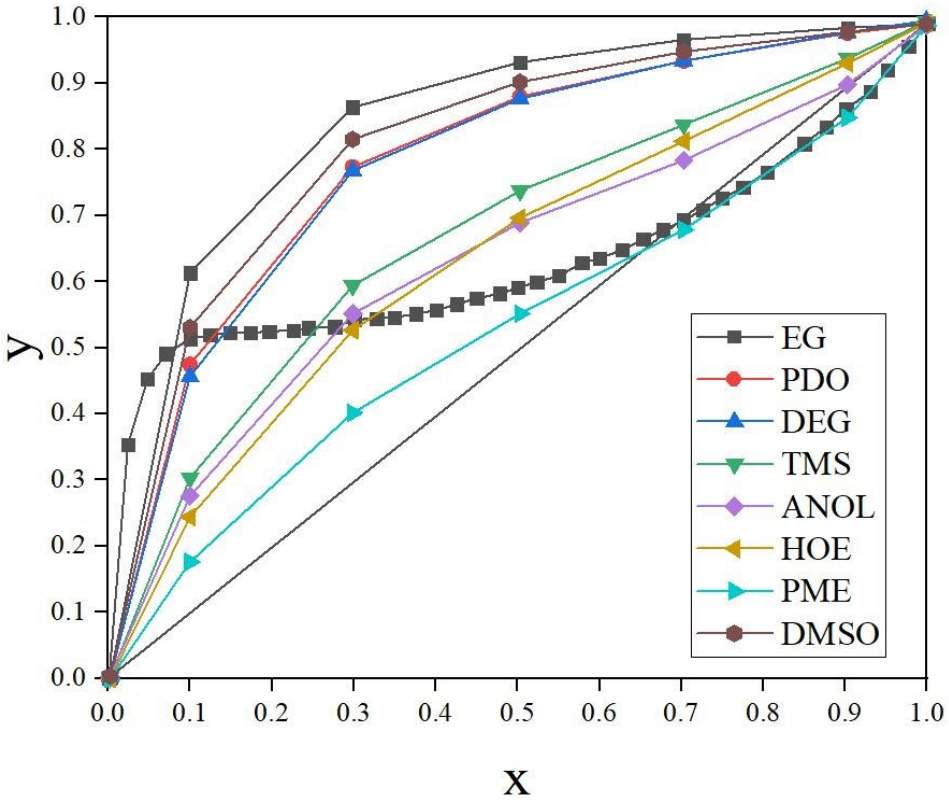
Model	T/K	RMSD
NRTL	303.2	0.96%
	323.2	1.00%
UNIQUAC	303.2	0.88%
	323.2	0.93%

Table S8. The binary interaction parameters of EG experimental data and the UNIFIAC model.

Project	Experimental data	UNIFIAC model
A_{ij}	-32.6817072	0
A_{ji}	8.07455844	0
B_{ij}	9753.87956	-605.303
B_{ji}	-2648.31753	-96.11

Table S9. The binary interaction parameters of components on the UNIQUAC model.

Component *i*	Component *j*	A_{ij}	A_{ji}	B_{ij}	B_{ji}
DIPE	IPA	0	0	-353.6478	129.0989
IPA	EG	4.4078	-4.9486	-1828.0739	1906.1646
DIPE	EG	-32.6817072	8.07455844	9753.87956	-2648.31753
DIPE	H_2O	0	0	-774.7116	-29.592
IPA	H_2O	2.9234	-3.3127	-1111.674	1045.5786
EG	H_2O	0.6018	-0.6018	-18.6714	120.7787
DIPE	PDO	0	0	-632.111535	67.2706956
IPA	PDO	-0.888692	1.46548	525.204	-925.082
H_2O	PDO	-0.624216	0.317496	-295.272	228.528



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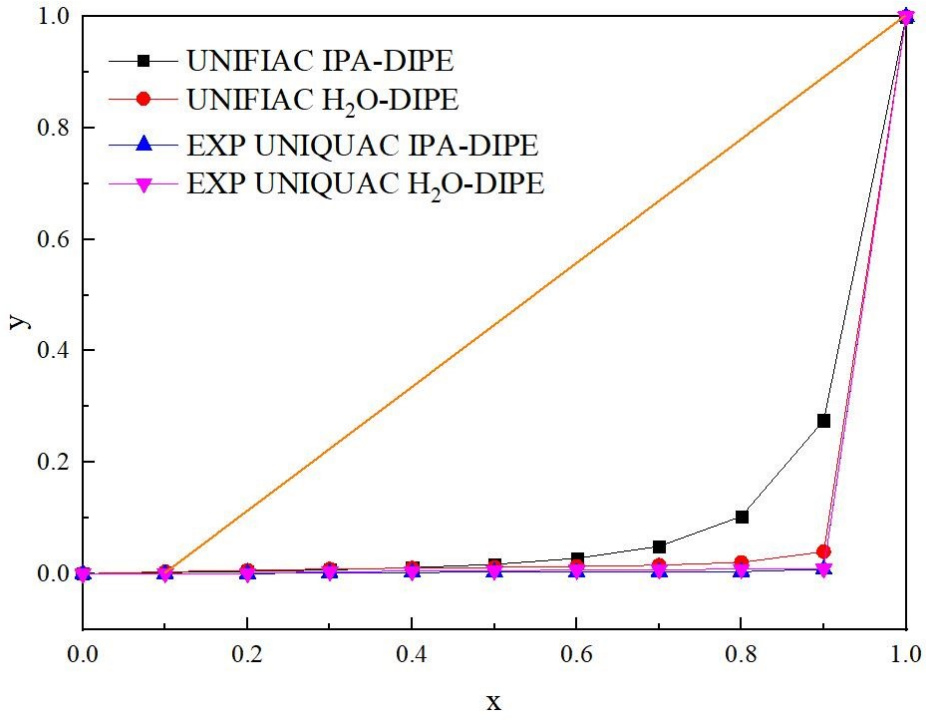

b

Fig. S5. The y-x diagram of relative volatility changes with extractant molar ratio is 0.5. *(a: The y--x diagram of $\alpha_{DIPE\text{-}IPA}$; b: the $\alpha_{IPA\text{-}DIPE}$ changes show the UNIQUAC model is superior to the UNIFAC model; EXP means experiment.)*

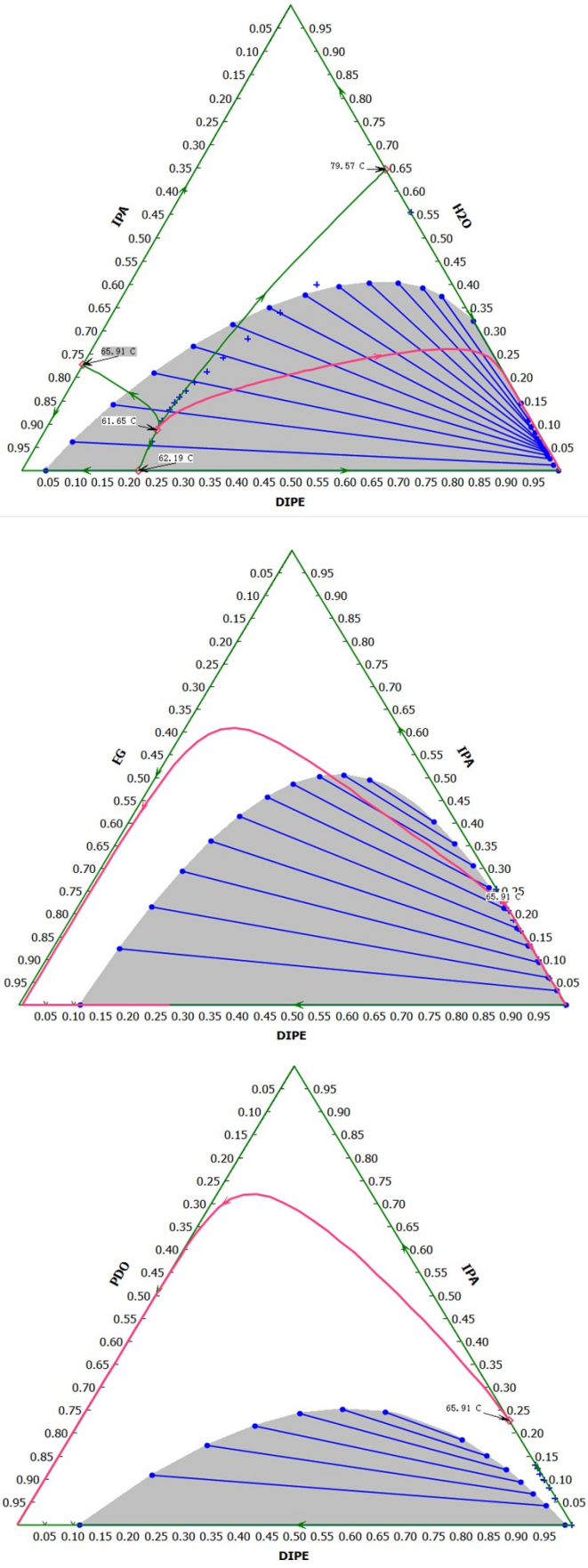

Fig. S6. The ternary phase diagram of DIPE/IPA/H_2O, DIPE/IPA/EG and DIPE/IPA/PDO.

Table S10. The calculation results are based on the model index for separating DIPE/IPA/H_2O (30 wt%: 10 wt%: 60 wt%) ternary azeotropes.

Project	Unit	DMSO	EG
T_{BP}	°C	189	197.3
$\alpha_{DIPE-IPA+H_2O}$		22.354	108.240
α_{IPA-H_2O}		***10.722***	***8.558***
α_{H_2O-SOL}		40.884	43.548
PECI1		0.970	0.623
PECI2		1.307	1.459
PECI3		0.798	0.784
PECI		3.075	2.866
LTEDI		0.175	0.165

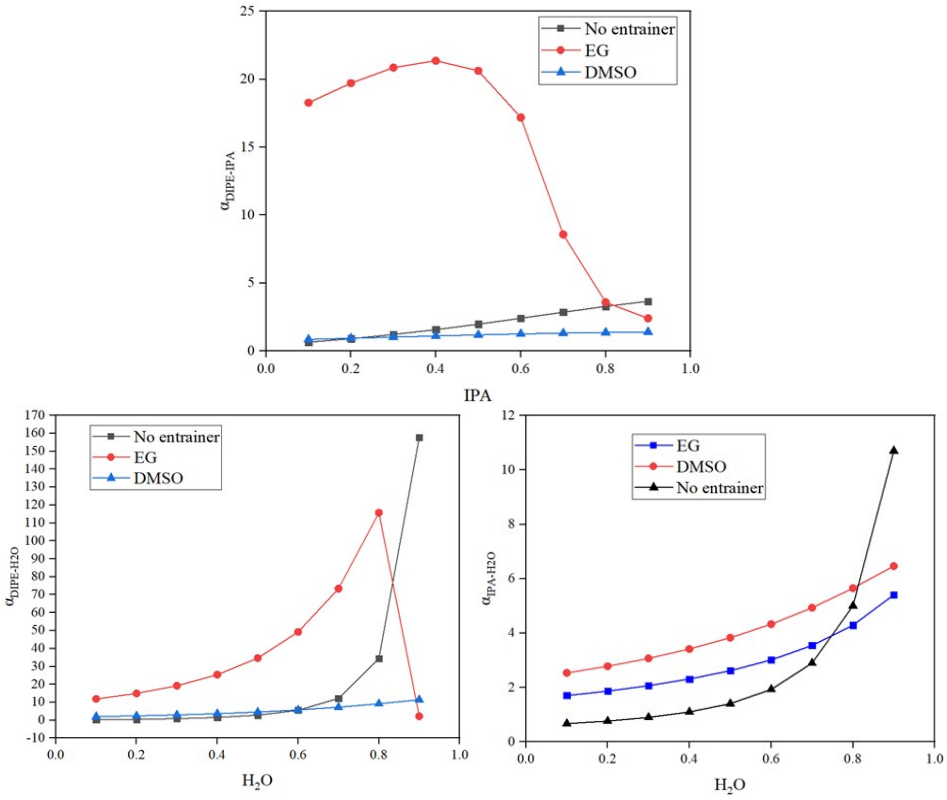

Fig. S7. The changes of relative volatility for DIPE/IPA/H_2O azeotropes with EG, DMSO, and no entrainer.