Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Insight into effective denitrification and desulfurization of liquid fuel with deep eutectic solvents: an innovative evaluationcriterion to filtrate extractants using compatibility index

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1. Calculation details

(1) Oxidation of DBT

Standby oil with only DBT (6000 μg/g) was used as the model oil. Equal mass of DESs and model oil were mixed in a round-bottom flask, followed by addition of H_2O_2 with the mass ratio of $m(H_2O_2)$: m(DBT)= 10: 1. The mixture was agitated vigorously at 50 °C for 60min in water bath, and then settled for another 60min at the same temperature. The DESs with sulfides (bottom phase) was taken out and diluted with equal mass of deionized water. The solution was filtered by using ultrafiltration membrane (Φ= 0.45 μm) to obtain the oxidative product of DBT. After drying in a vacuum oven at 60 °C for 24h, the oxidative product was collected in a sample bottle.

(2) Calculation of electronic static potential (ESP) difference

Gaussian 09 revision D.01 was applied to optimize the molecular geometries of HBDs and heterocycles with DFT-D3 method at M062X/6-311+G** level, and then followed by investigation of ESP mapped on an isosurface of electronic density of 0.001 a.u. as shown in Fig. S4. Considering the acidity or alkalinity, the electronic static potential difference of HBDs and heterocycles was calculated by:

$$\left|\Delta E_i\right| = \left|E_i^H - E_\infty\right| \tag{S1}$$

$$\left|\Delta E_j\right| = \left|E_j^{HA} - E_\infty\right| \tag{S2}$$

where E_i^H donates the ESP upon hydroxyl hydrogen atom in HBDs, $E_i^{S/N}$ is the ESP of heteroatom (sulfur or nitrogen) in heterocycles, and E_∞ represents the ESP at infinity. Theoretically, the value of E_∞ should be zero.

For heterocycles without acidity or alkalinity, the electronic static potential difference of HBDs and heterocycles was obtained by:

$$\left|\Delta E_i\right|' = \left|E_i^A - E_i^B\right| \tag{S3}$$

$$\left|\Delta E_j\right|' = \left|E_j^A - E_j^B\right| \tag{S4}$$

where E_i^A (or E_j^A) and E_i^B (or E_j^B) are the ESP of A and B atoms upon HBDs (or heterocycles), respectively.

(3) Calculation of intermolecular interaction energy

The di-molecular structures of HBDs and heterocycles were optimized with DFT-D3 method at M062X/6-311+G** level to obtain the total energy. By the way, the individual energy of optimized HBDs and heterocycles was also calculated by Gaussian. The interaction energy between HBDs and heterocycles was therefore determined from:

$$Interaction\ energy = E(Hh) - E(H) - E(h) \tag{S5}$$

where $E(Hh)$ means the total energy of the di-molecules, $E(H)$ and $E(h)$ represent the individual energy of HBDs and heterocycles, respectively.

(4) Calculation of proton dissociation enthalpy (⊿H)

The geometries of the HBDs molecules and their anions were optimized at first, and then followed by vibrational frequency calculation with DFT-D3 method at B3LYP/6-31+G (d, p) level. The ⊿H values of HBDs could be obtained from:

$$\Delta H = E(M^-) - E(M) + E(H^+) \tag{S6}$$

where $E(M^-)$ was the enthalpy of the anion, $E(M)$ represented the enthalpy of the molecule, and $E(H^+)$ was the enthalpy of H^+ (6.19 kJ/mol) [1].

(5) Regeneration of DESs

The recycled DESs was diluted with qual mass of deionized water, followed by a filtration for the solution using ultrafiltration membrane (Φ= 0.45 μm). The rotary evaporation would be conducted to eliminate most of water in the solution. Finally, the sticky liquid was throughly dried in a vacuum oven at 60 °C for 24h to obtain regenerated DESs.

2. Tables

Table S1 Calculation results of $\left|\Delta E_i\right|$ and $\left|\Delta E_j\right|$ for various HBDs and heterocycles

Classification	Components	$\left\|\Delta E_i\right\|$ (kJ·mol^{-1})	$\left\|\Delta E_j\right\|$ (kJ·mol^{-1})
HBDs	p-Methylphenylacetic acid	197.9	
	Mandelic acid	201.9	
	p-Toluenesulfonic acid	232.2	
	1, 3-Propylene glycol	179.4	
	Malonic acid	217.8	
	Urea	150.5	
	L-(+)-Tartaric acid	237.8	
Heterocycles	Quinoline		147.7
	Carbazole		33.73
	DBT		54.25
	$DBTO_2$		148.8

Table S2 Calculation results of $\left|\Delta E_i\right|'$ and $\left|\Delta E_j\right|'$ for various HBDs and heterocycles

Classification	Components	$\left\|\Delta E_i\right\|'$ (kJ·mol^{-1})	$\left\|\Delta E_j\right\|'$ (kJ·mol^{-1})
HBDs	p-Methylphenylacetic acid	15.37	
	Mandelic acid	18.96	
	p-Toluenesulfonic acid	25.1	
	1, 3-Propylene glycol	58.76	
	Malonic acid	79.84	
	Urea	83.28	
	L-(+)-Tartaric acid	104.9	
Heterocycles	Carbazole		19.82
	DBT		3.544
	DBTO$_2$		24.78

Table S3 Desulfurization efficiency of real diesel with D2 and D3

Extractant	Oxidant	Classes (μg/g) with removal efficiencies (wt.%)				Total (μg/g)
		Thiophenes [a]	Thiols	Thioethers	Others	
None	None	2367.3 (-)	160.3 (-)	358.7 (-)	764.3 (-)	3650 (-)
D2	None	2206.4 (6.8)	97.32 (39.3)	336.4 (6.2)	627.2 (17.9)	3267 (10.5)
D3	None	2127.9 (10.1)	95.20 (40.6)	333.8 (6.9)	611.5 (20.0)	3168 (13.2)
D2	H_2O_2	933.8 (60.6)	84.29 (47.1)	120.1 (66.5)	198.4 (74.0)	1337 (63.4)
D3	H_2O_2	799.6 (62.2)	73.66 (54.0)	124.8 (65.2)	181.0 (76.3)	1179 (67.7)

[a] contains thiophenes, benzothiophene, dibenzothiophene and their derivates.

Table S4 Denitrification efficiency of real diesel with D2 and D3

Extractant	Oxidant	Classes (μg/g) with removal efficiencies (wt.%)				Total (μg/g)
		Amines [a]	Pyrroles [b]	Pyridines [c]	Others	
None	None	77.27 (-)	115.88 (-)	58.33 (-)	174.8 (-)	426.3 (-)
D2	None	30.60 (60.4)	47.60 (58.9)	16.04 (72.5)	96.30 (44.9)	190.5 (55.3)
D3	None	28.55 (63.1)	47.79 (58.7)	14.98 (74.3)	91.13 (47.9)	182.4 (57.2)
D2	H_2O_2	24.67 (68.1)	32.17 (72.2)	14.97 (74.3)	87.18 (50.1)	159.0 (62.7)
D3	H_2O_2	26.81 (65.3)	28.13 (75.7)	13.53 (76.8)	86.17 (50.7)	154.6 (63.7)

[a] contains amine, amide and their derivates; [b] contains pyrrole, indole, carbazole and their derivates; and [c] contains pyridine, quinoline and their derivates.

3. Figures

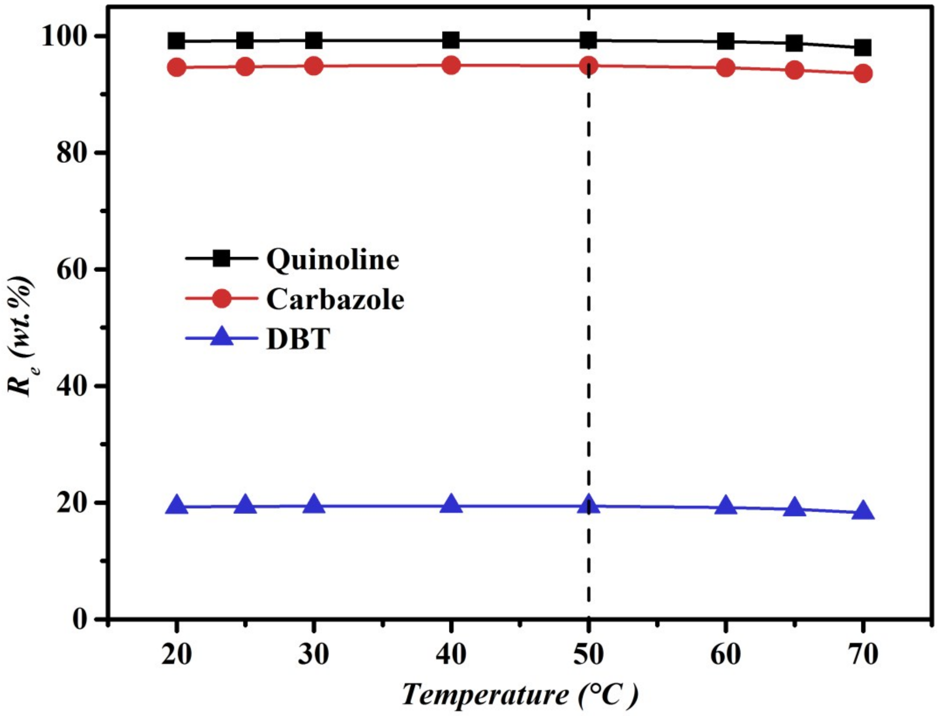

Fig. S1 Effect of extaction temperature on the removal efficiency (extraction time of 60min, m(DESs):m(model oil) ratio of 1:1)

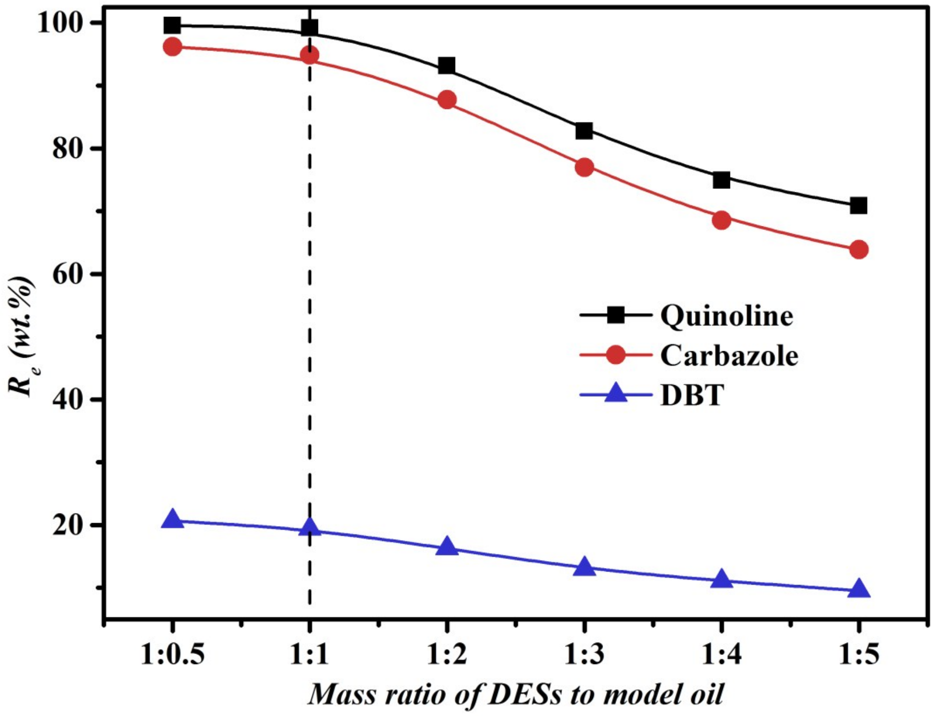

Fig. S2 Effect of DESs/model oil mass ratio on the removal efficiency (extraction temperature of 50 °C, extaction time of 60min)

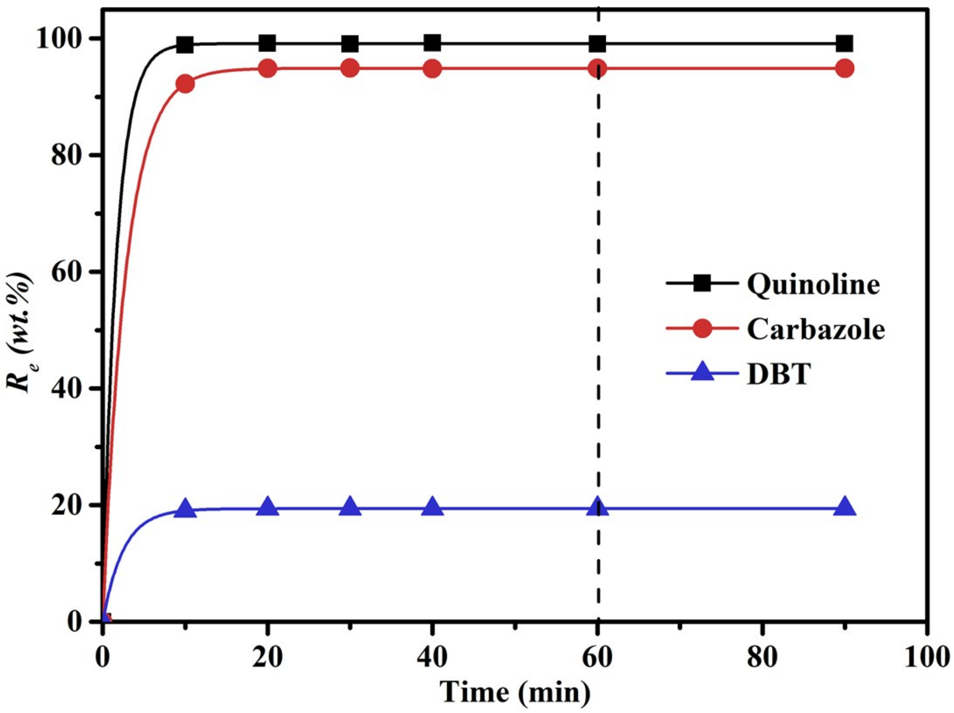

Fig. S3 Effect of extraction time on the removal efficiency (extraction temperature of 50 °C, m(DESs):m(model oil) ratio of 1:1)

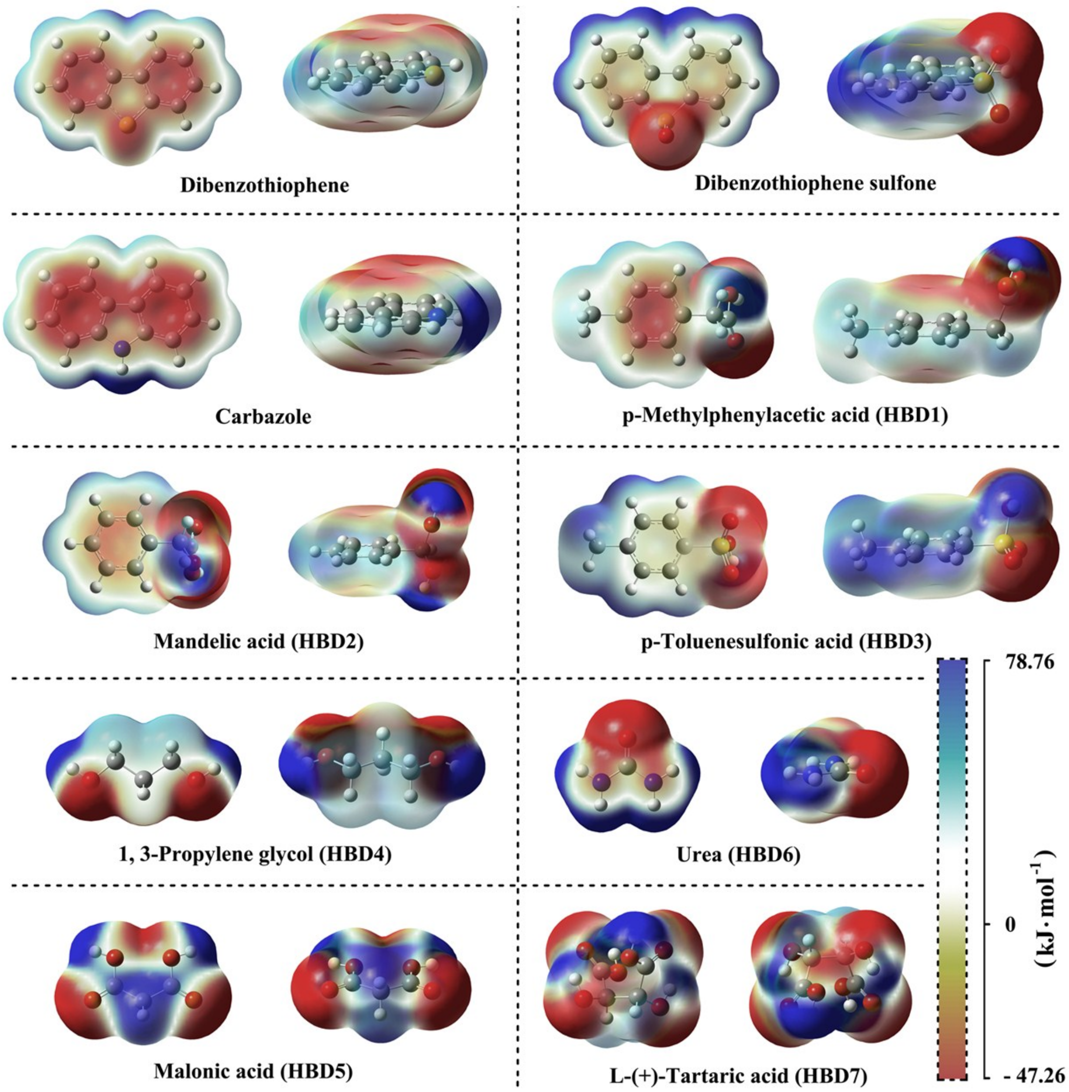

Fig. S4 Electronic static potential (ESP) of various HBDs and targeted heterocycles molecules

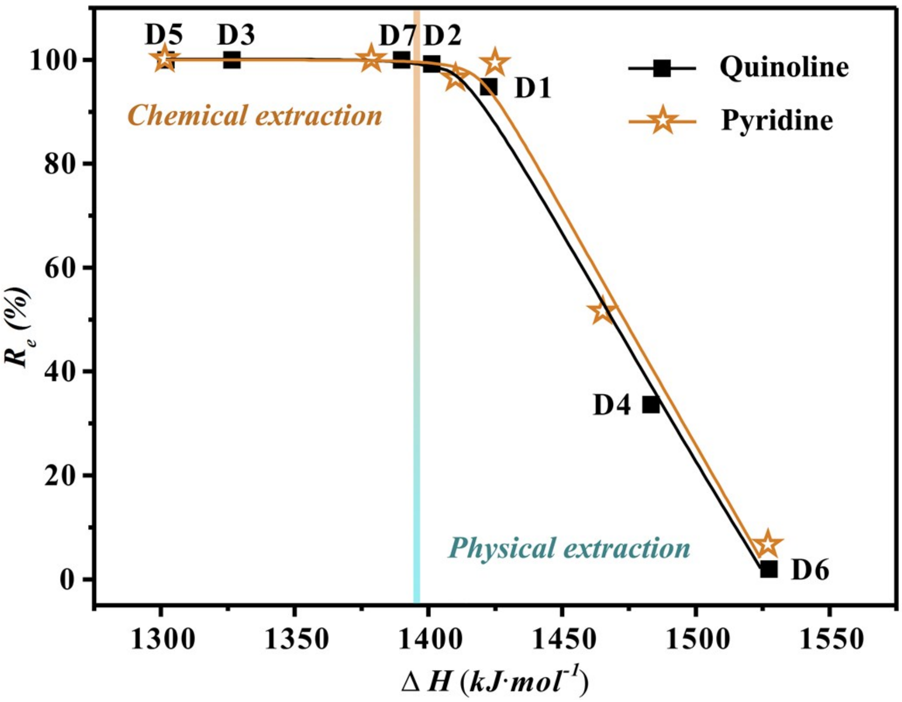

Fig. S5 Plots of R_e values for quinoline and pyridine as a function of proton dissociation enthalpy (⊿H) for HBDs. The calculation was conducted at B3LYP/6-31+G** level with DFT-D3 empirical dispersion corrections using Gaussian 09 D.01 software. (Quinoline: this work, pyridine: from Ali et al. [2])

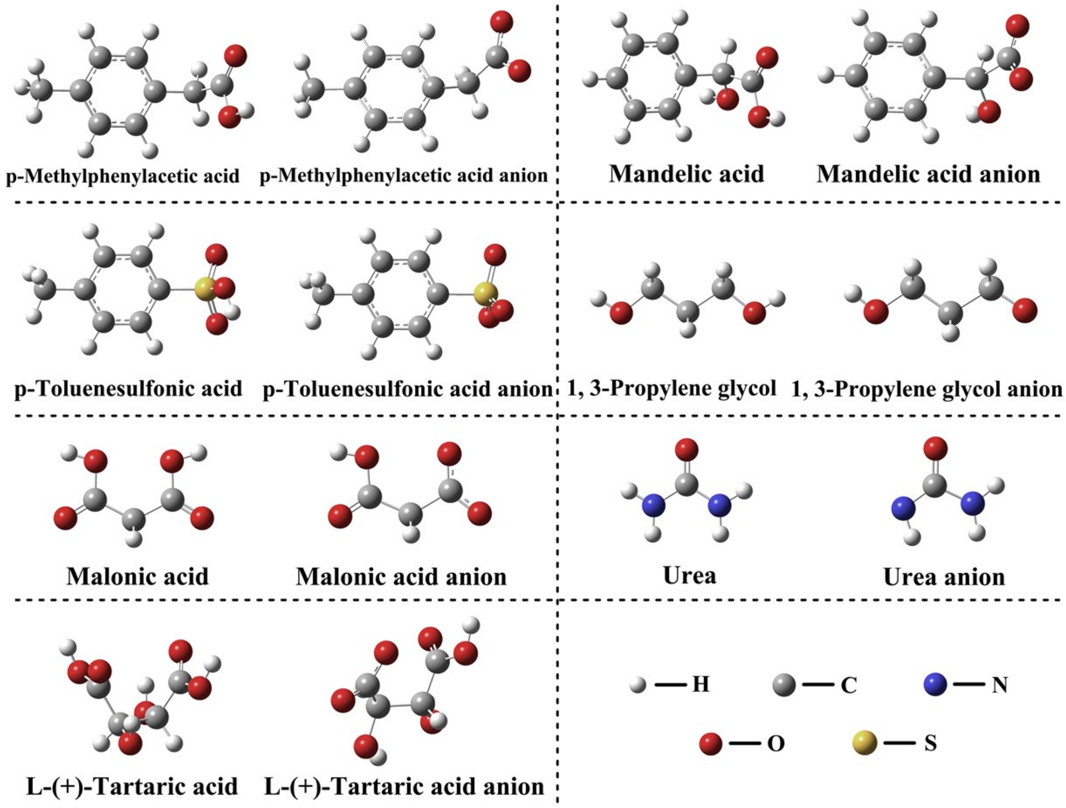

Fig. S6 Optimized geometries of various HBDs molecules and anions using Gaussian 09 software

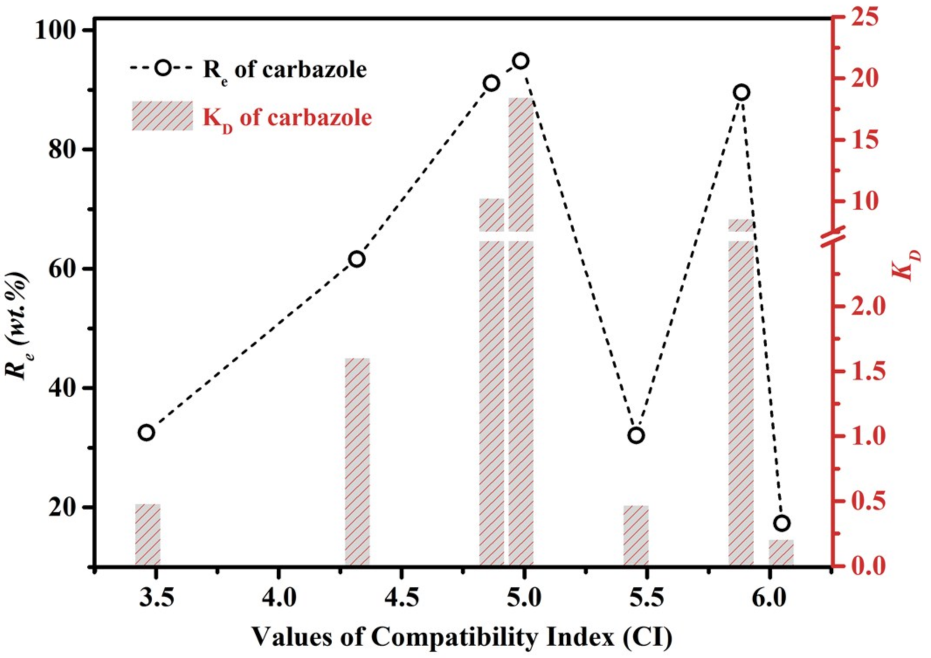

Fig. S7 Influence of parameter CI on the R_e and K_D values for removing carbazole

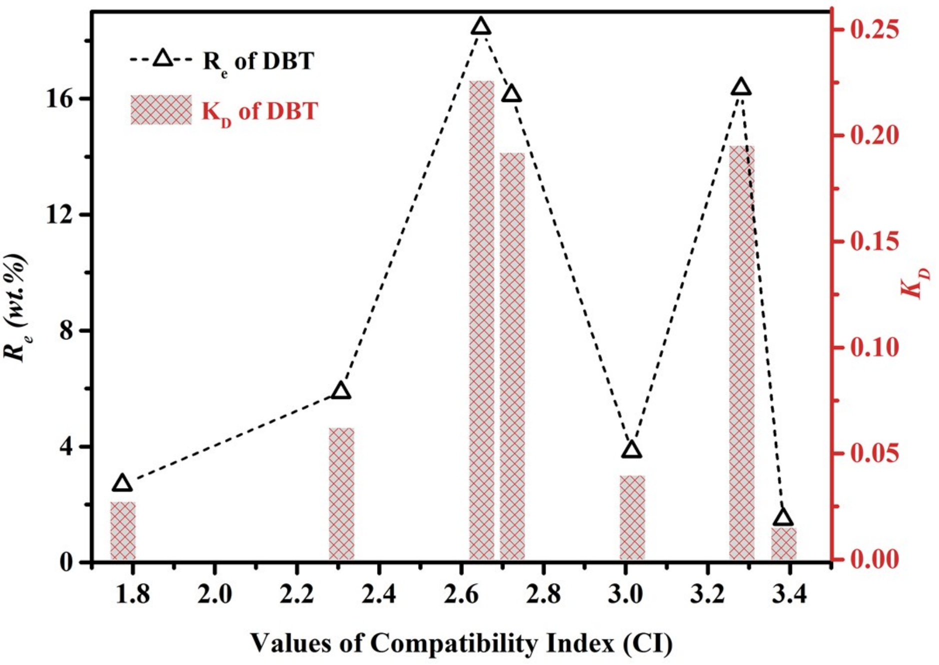

Fig. S8 Influence of parameter CI on the R_e and K_D values for removing DBT

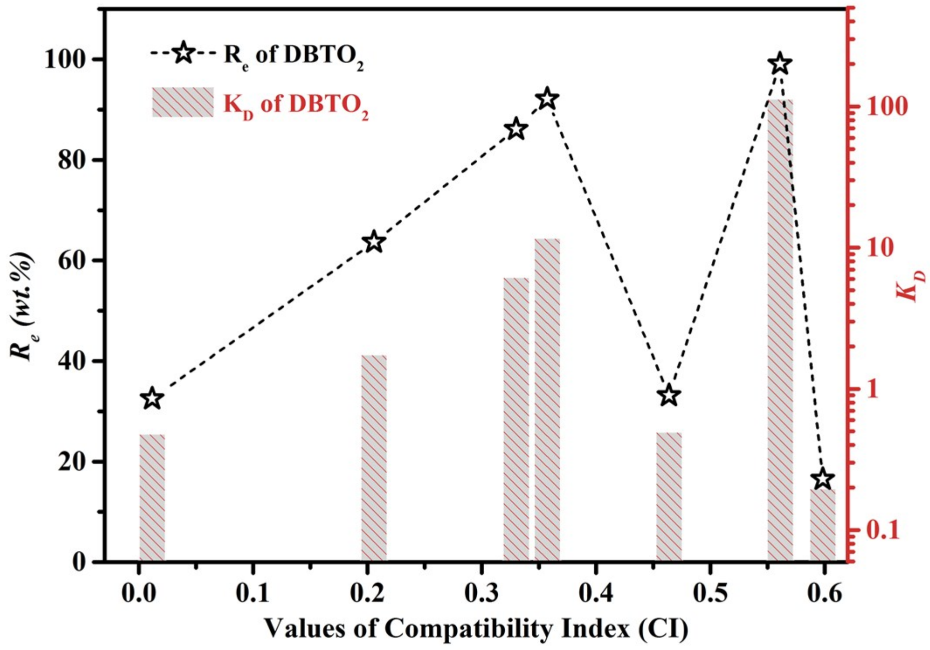

Fig. S9 Influence of parameter CI on the R_e and K_D values for removing $DBTO_2$

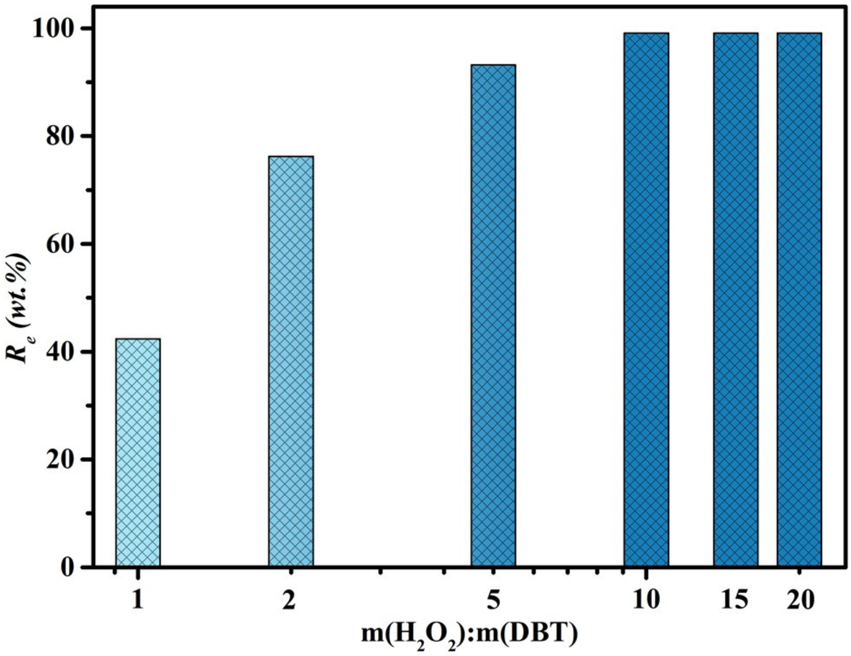

Fig. S10 Influence of $m(H_2O_2)$:m(DBT) ratio on the removal efficiency of sulfides (extraction temperature of 50 °C, extraction time of 60 min)

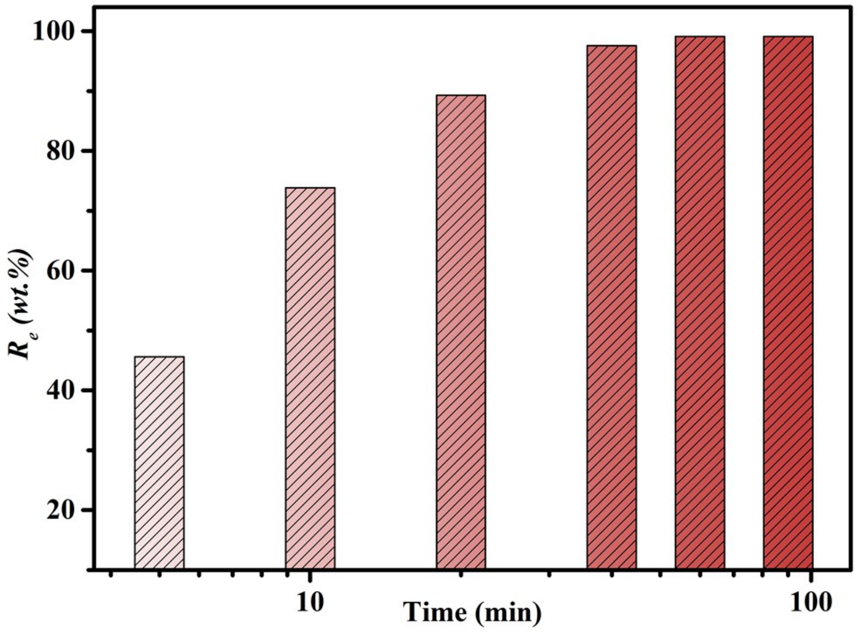

Fig. S11 Influence of reaction time on the removal efficiency of sulfides (extraction temperature of 50 °C, $m(H_2O_2)$:m(DBT) ratio of 10:1)

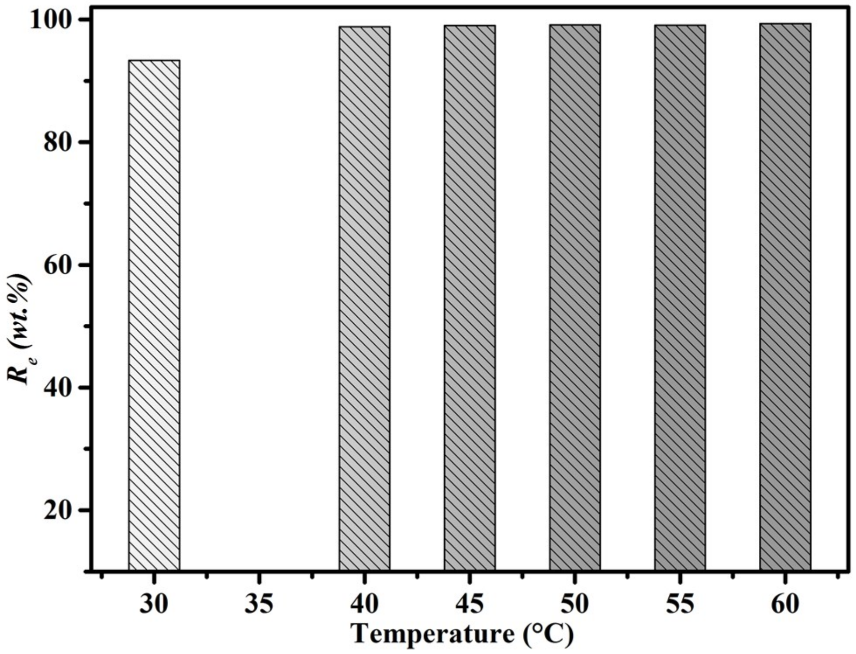

Fig. S12 Influence of reaction temperature on the removal efficiency of sulfides (extraction time of 60 min, $m(H_2O_2)$:m(DBT) ratio of 10:1)

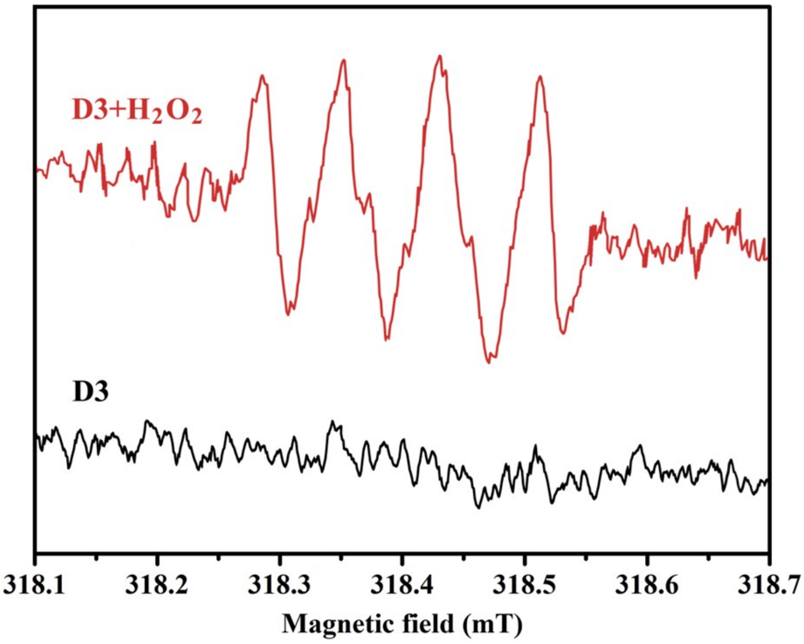

Fig. S13 Electron spin resonance (ESR) spectra of DMPO-$O_2^{\bullet -}$ in D3 systems with or without H_2O_2. The characteristic peaks suggest the generation of $O_2^{\bullet -}$ radical in D3 extraction system, which is responsible for the oxidation of DBT into $DBTO_2$.

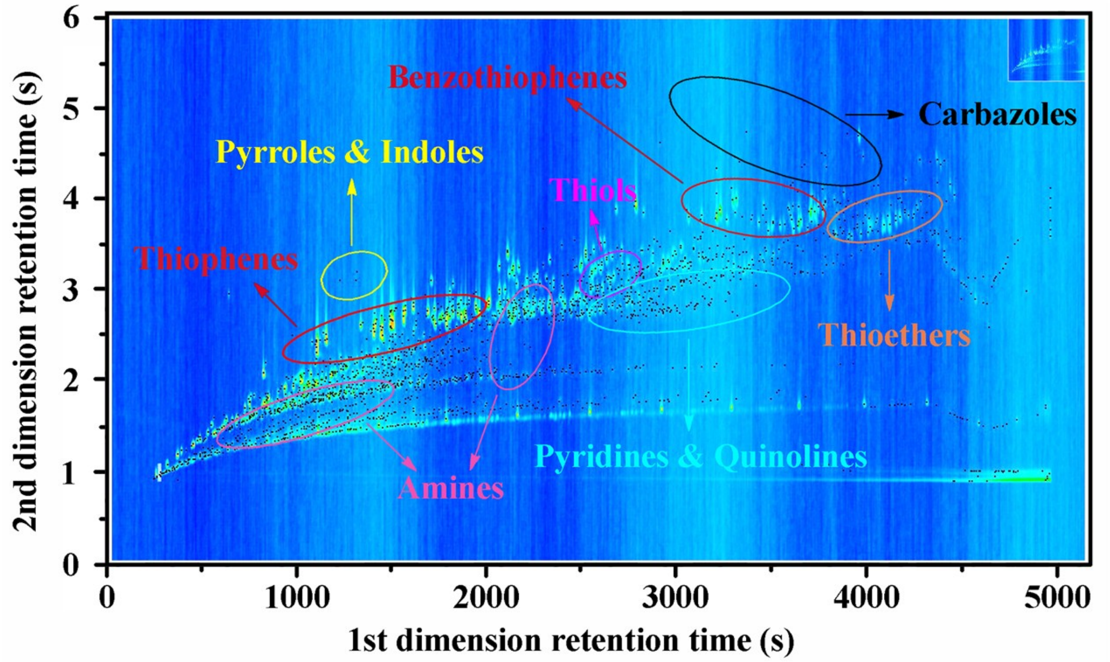

Fig. S13 Two-dimensional contour plot of raw catalytic cracking diesel

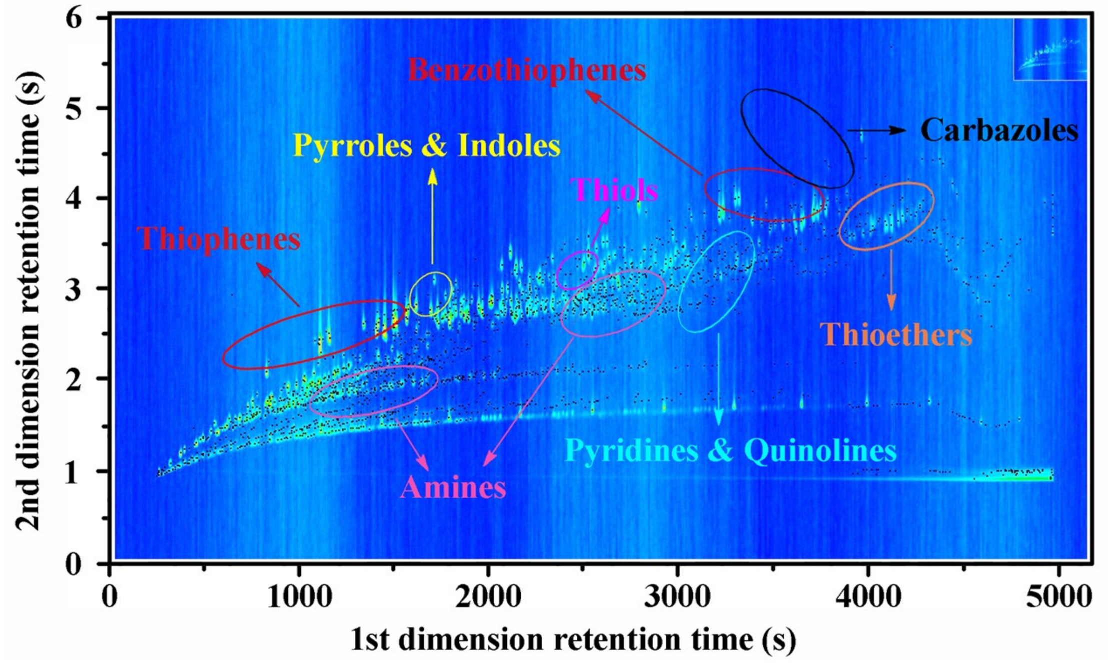

Fig. S14 Two-dimensional contour plot of catalytic cracking diesel after oxide-assisted extraction in D3

Reference:

[1] R. Vessecchi and S. E. Galembeck, *J. Phys. Chem. A*, 2008, **112**, 4060.

[2] M. C. Ali, Q. Yang, A. A. Fine, W. Jin, Z. Zhang, H. Xing and Q. Ren, *Green Chem.*, 2016, **18**, 157