Supplementary Information

Molecular dynamics simulation of heavy oil dissolution in supercritical water and multi-component thermal fluid

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S1.1. Model Verification

In order to verify the accuracy of the solubility parameter calculation method, the solubility parameters of supercritical water (SCW) were calculated at different temperatures, pressures, and molecular numbers, and the results were presented in Table S1. The calculated results were quite similar to the simulation and experimental results reported in the literature, with errors within 3% of simulation results and 15% of experimental results. In addition, the calculated results of CED and SP were confirmed to be independent of the number of model molecules. Therefore, to save computational resources, the supercritical water SP calculation models were all calculated using a water molecule number of 2000. As for the dissolution process of heavy oil, the applicability and accuracy of the simulation method and COMPASS force field in the supercritical state have been verified in our previous work by calculating the density of SCW, for details please refer to the report of Zheng et al. [S1]. Furthermore, Qu et al. [S2], Xin et al. [S3], Wang et al. [S4], and Zhang et al. [S5] in their work, also proved that the COMPASS force field could accurately predict the dissolution process in SCW properties by analyzing the radial distribution function (RDF) of SCW. All the above indicated that the selected force field and simulation method can correctly reflect the physical properties of SCW. On the other hand, the multi-component thermal fluid (MCTF) can be regarded as a mixed solution of carbon dioxide and nitrogen dissolved in SCW. Therefore, it can be believed that the COMPASS force field can also accurately describe the physical properties of the MCTF.

Table S1. Solubility parameters of supercritical water

	T, ρ	N	CED	Calculated SP	SP from simulation results	SP from experimental results
SCW	673.2, 0.523	500	6.30E+08	25.09±0.015	24.5 [S6]	22.6 [S7]
SCW	673.2, 0.523	2000	6.29E+08	25.07±0.008		
SCW	673.2, 0.523	4000	6.29E+08	25.09±0.006		

SCW	776.8, 0.316	500	2.53E+08	15.91±0.016	16.1 [S8]	13.7 [S9]
SCW	776.8, 0.316	2000	2.56E+08	15.99±0.007		
SCW	776.8, 0.316	4000	2.55E+08	15.98±0.005		

S1.2. Dissolution rate results

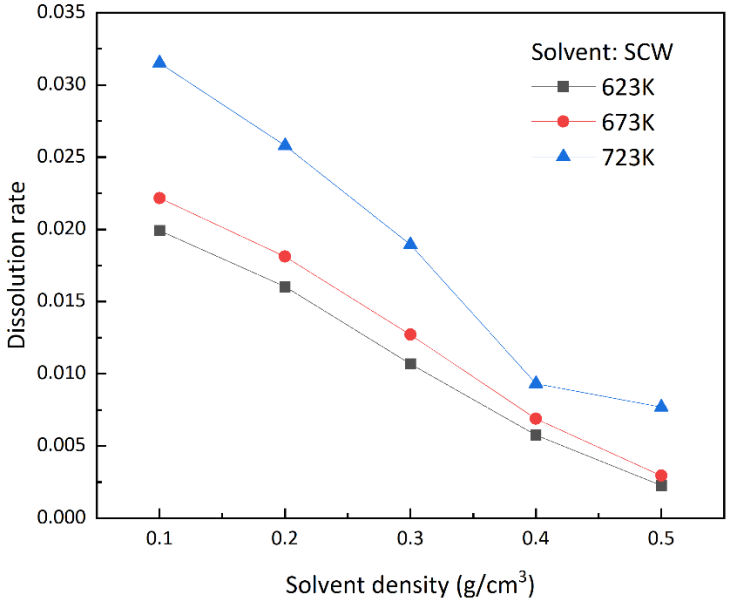

Fig. S1. Dissolution rate of heavy oil in SCW at 623-723 K and 0.1-0.5 g/cm^3.

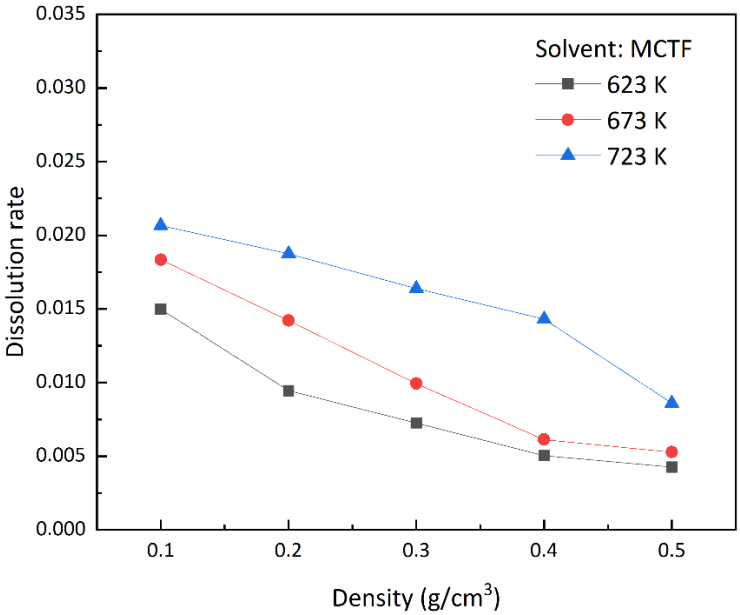

Fig. S2. Dissolution rate of heavy oil in MCTF at 623-723 K and 0.1-0.5 g/cm^3.

S1.3. Heavy oil model construction

Heavy oil sample from the Sinopec Shengli Oilfield (Dongying, China) was used in this study. The SARA fractions were separated by hexane, dichloromethane and isoamyl alcohol and tested with thin layer chromatography-flame ionization detection (ATROSCAN MK-6S TLC-FID) according to the petroleum and natural gas industry standard of China (SY/T 5119-2016). The heavy oil was also characterized by elemental analyzer (Elementar Vario Macro cube on CHNS mode). The SARA compositions and ultimate analysis of the heavy oil were shown in Table S2. The heavy oil molecular model was established based on the SARA component distribution data and compared with the ultimate analysis results. The percentages of C and H in the model were 88.08% and 10.11%, respectively, which were similar to the ultimate analysis results, and the percentages of N and S were 0.41% and 0.93%, respectively, which were slightly lower than the ultimate analysis results.

Table S2 Characteristics of the heavy oil sample

SARA compositions (wt.%)				Ultimate analysis (wt.%)			
Saturates	Aromatics	Resins	Asphaltenes	C	H	N	S
31.44	39.62	25.38	3.55	85.33	11.14	1.98	1.45

Reference of Supplementary Information

[S1] L.C. Zheng, Q.Y. Zhao, Y. Dong, H. Jin, B. Bawaa, L.J. Guo, Molecular dynamics simulation of sub- and supercritical water extraction shale oil in slit nanopores, Journal of Supercritical Fluids, 195 (2023) https://doi.org/11. 10.1016/j.supflu.2023.105862

[S2] H. Qu, J.H. Gong, X.C. Tan, P.Q. Yuan, Z.M. Cheng, W.K. Yuan, Dissolution of polycyclic aromatic hydrocarbons in subcritical and supercritical Water: A molecular dynamics simulation study, Chem. Eng. Sci., 195 (2019) 958-967. https://doi.org/10.1016/j.ces.2018.10.042

[S3] S.M. Xin, Q.K. Liu, K. Wang, Y. Chen, P.Q. Yuan, Z.M. Cheng, W.K. Yuan, Solvation of asphaltenes in supercritical water: A molecular dynamics study, Chem. Eng. Sci., 146 (2016) 115-125. https://doi.org/10.1016/j.ces.2016.02.032

[S4] Q. Wang, S. Pan, J.R. Bai, M.S. Chi, D. Cui, Z.C. Wang, Q. Liu, F. Xu, Experimental and dynamics simulation studies of the molecular modeling and reactivity of the Yaojie oil shale kerogen, Fuel, 230 (2018) 319-330. https://doi.org/10.1016/j.fuel.2018.05.031

[S5] W. Zhang, M. He, H.B. Wei, X.C. Zhu, X.F. You, X.J. Lyu, L. Li, Molecular dynamics simulations of interaction between sub-bituminous coal and water, Molecular Simulation, 44 (2018) 769-773. https://doi.org/10.1080/08927022.2018.1450981

[S6] H. Alasiri, A Molecular Dynamics Simulation Probe of the Solubility Parameters of Supercritical Water and Methanol, Arab. J. Sci. Eng., 44 (2019) 9911-9917. https://doi.org/10.1007/s13369-019-03957-w

[S7] Y. Marcus, Hansen solubility parameters for supercritical water, Journal of Supercritical Fluids, 62 (2012) 60-64. https://doi.org/10.1016/j.supflu.2011.10.018

[S8] J. Ma, X.Q. Dong, M.H. Zhang, A molecular dynamics study of solvent properties

of water, Computers and Applied Chemistry, 24 (2007) 004. https://doi.org/10.16866/j.com.app.chem2007.07.004
[S9] Y. Marcus, Are solubility parameters relevant to supercritical fluids?, Journal of Supercritical Fluids, 38 (2006) 7-12. https://doi.org/10.1016/j.supflu.2005.11.008