Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary data for

Mechanism of asphaltene aggregation induced by supercritical CO_2: insight from the molecular dynamics simulation

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1. The process of asphaltene aggregation

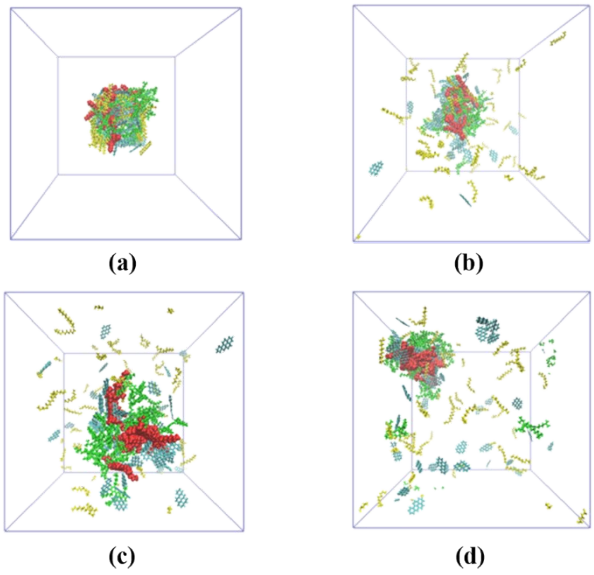

Fig.S1. Perspective view of oil-$scCO_2$ system. Snapshots are taken at (a) 0ns (b) 1.2 ns (c) 3.5 ns and (d) 10 ns. Color scheme: red, asphaltene; green, resin; blue, aromatic; yellow, saturate; $ScCO_2$ is not shown for clarity.

To visualize the process of selective extraction and asphaltene aggregation, perspective view of oil-$scCO_2$ system were reported in Fig. S1. It can be seen that saturate and aromatic are extracted firstly, as shown in Fig. S1(b). During the extraction of resin, the distance among asphaltenes increases significantly, as shown in Fig. S1(c). Finally, asphaltenes aggregate and form a compact nanoaggregate after other components are extracted, as shown in Fig. S1(d). The formation of asphaltene aggregate coincides with experimental results [1,2].

2. The potential and temperature of system

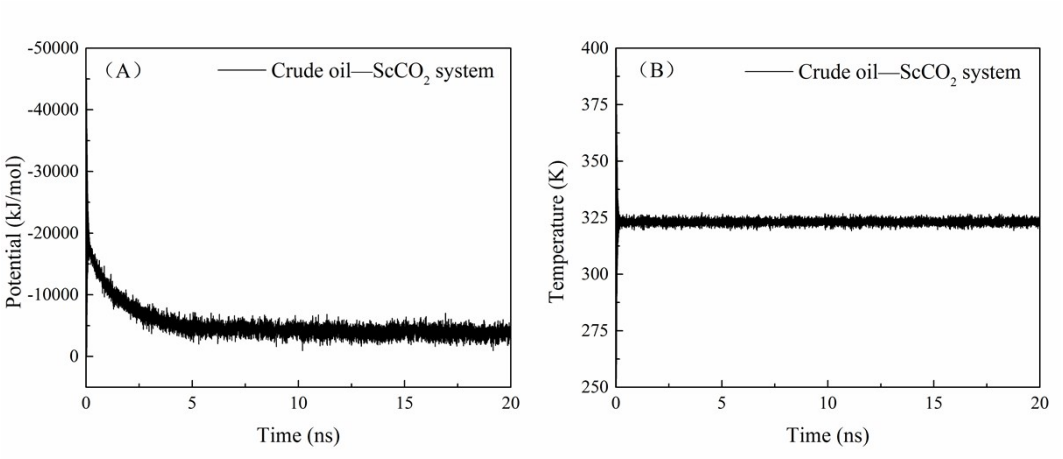

Fig.S2. The time evolution of the system's (A) potential energy and (B) temperature.

After 6-7 ns, system's potential energy essentially halted decline, as shown in Fig. S2(A). System's temperature was controlled around 372.15 K during simulation, as shown in Fig. S2(B). Base on that, equilibrium is considered has been attained.

3. RDF

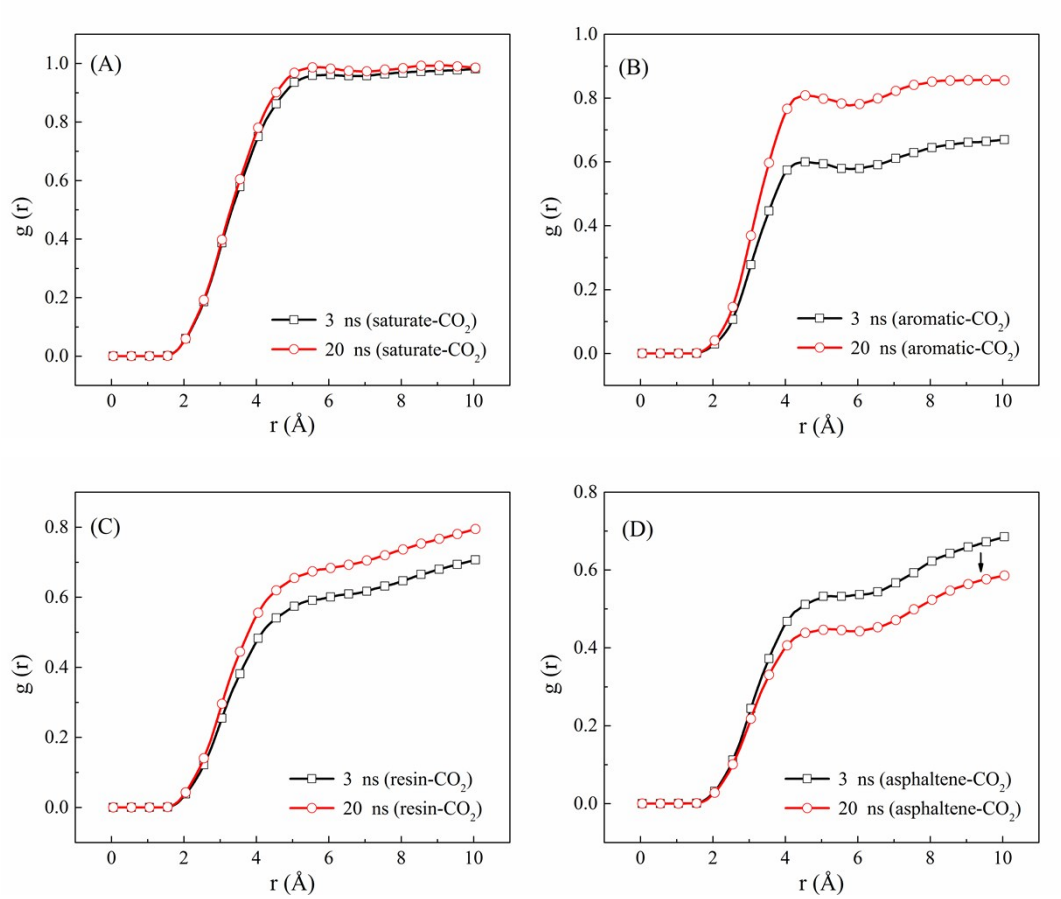

Fig. S3. Radial distribution functions between oil components and CO_2. (A): saturate-CO_2, (B): aromatic-CO_2, (C): resin-CO_2, and (D): asphaltene-CO_2. Radial distribution functions are taken from 3ns and 20ns.

2-D molecular number density maps do not include the information content in Z-direction, to assess quantify certainties the radial distribution functions between oil components and CO_2 are analyzed. It can be seen that saturate, aromatic and saturate components are more soluble in $scCO_2$ at 20 ns than 3 ns. By contrast, asphaltene is more insoluble at 20 ns than 3 ns, in other words, more compact in $scCO_2$.

4. PMF calculation

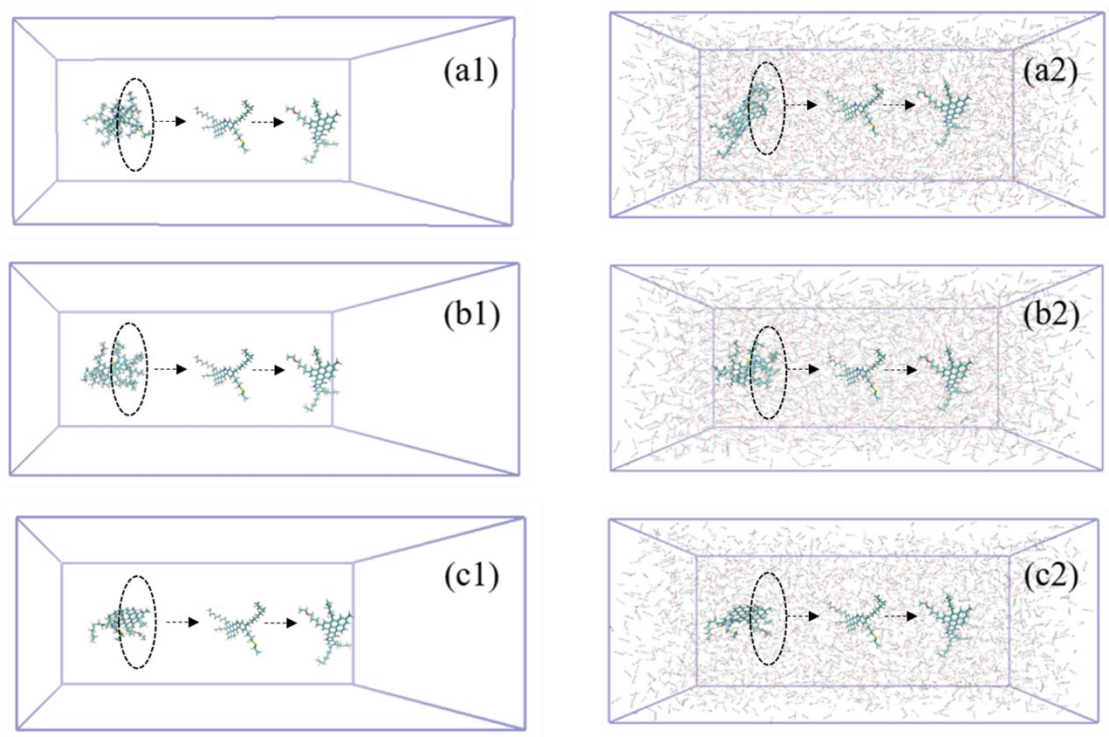

Fig.S4. Perspective view of simulation setup for PMF. Color scheme: cyan = carbon, white = hydrogen, red = oxygen, yellow = sulfur, blue = nitrogen.

In order to investigate the effective interaction among oil components using umbrella sampling method [3], 6 simulation boxes were established as shown in Fig. S4. The upper two boxes contain two asphaltene molecules; the middle two boxes contain one asphaltene molecule and one resin molecule; and the bottom two boxes contain one asphaltene molecule and on aromatic molecule. In addition, the right three boxes fill with CO_2 molecules. Then the COM of one molecule was pulled along Z-axis while the other one was restrained.

References

[1] R. Nguele, M. R. Ghulami, K. Sasaki, S. A. Salim, A. Widiatmojo, Y. Sugai, M. Nakano, Asphaltene aggregation in crude oils during supercritical gas injection, Energy Fuels, 30 (2016) 1266-1278.

[2] P. Zanganeh, H. Dashti, S. Ayatollahi, Visual investigation and modeling of asphaltene precipitation

and deposition during CO_2 miscible injection into oil reservoirs, Fuel 160 (2015) 132-139.

[3] J. Kästner, Umbrella sampling, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 1 (2011) 932-942.