

# Solvation of asphaltenes in supercritical water: A molecular dynamics study



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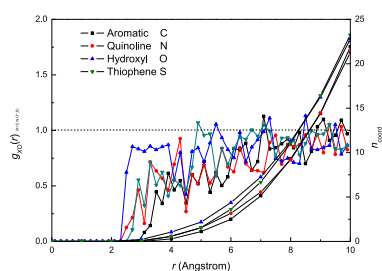
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## HIGHLIGHTS

- Solvation of asphaltenes in SCW was characterized by molecular dynamics simulation.
- The vdW interaction determines the repulsive nature between asphaltenes and SCW.
- Asphaltenes in SCW presents a cavity short-range solvent structure.
- Asphaltenes in SCW has a positive solvation free energy in most cases.
- A coke-like structure is formed by the spontaneous aggregation of asphaltenes in SCW.

## GRAPHICAL ABSTRACT

The van der Waals interaction plays a dominant role on the repulsive nature between asphaltenes and SCW. Accordingly, asphaltenes in SCW present a cavity short-range solvent structure, having a positive solvation free energy in most cases.



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## ABSTRACT

To improve the understanding of the condensation of asphaltenes in supercritical water (SCW), the solvation of asphaltenes under SCW environments was investigated with molecular dynamics simulation. The simulation results indicate that the repulsive van der Waals interaction has a primary influence on the nature and the magnitude of the interaction between asphaltenes and SCW. A cavity short-range solvent structure surrounding asphaltenes thus is formed, and the solvation free energy ( $G_{sol}$ ) of asphaltenes in SCW has a positive sign in most cases. The scale of cavities and the value of  $G_{sol}$  both are determined mainly by the bulk density of water. By the repulsive asphaltenes/SCW interaction and the attractive  $\pi$ - $\pi$  aromatic interaction, the aggregation of asphaltenes in SCW occurs spontaneously. The asphaltene clusters formed, containing asphaltene monomers and nanoaggregates, present a coke-like supramolecular structure. Benefiting from excellent diffusivity in SCW, the aggregation of asphaltenes in SCW can be accomplished rapidly.

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## 1. Introduction

With the increasing demand for fuel oil but the decreasing reserves of light crude oil, the processing of unconventional heavy oil becomes important for refineries. Water, a typical protic solvent for inorganics under ambient conditions, behaves like a non-polar solvent in its supercritical region with excellent diffusivity and solubility

for organics (Akiya and Savage, 2002). In recent years, the upgrading of heavy oil primarily with pyrolysis mechanism in environmentally benign supercritical water (SCW,  $T_c=647$  K,  $P_c=22.1$  MPa) has attracted growing attention in academia (Morimoto et al., 2010; Kokubo et al., 2008; Wahyudiono and Goto 2008; Meng et al., 2006; Luik and Luik 2001).

Earlier studies held the view that SCW could be an effective H-donor for the pyrolysis of hydrocarbons, a process dominated by free radical mechanism (Dente and Ranzi, 1983; Sato et al., 2003; Han et al., 2008; Henrikson et al., 2006). However, the experimental

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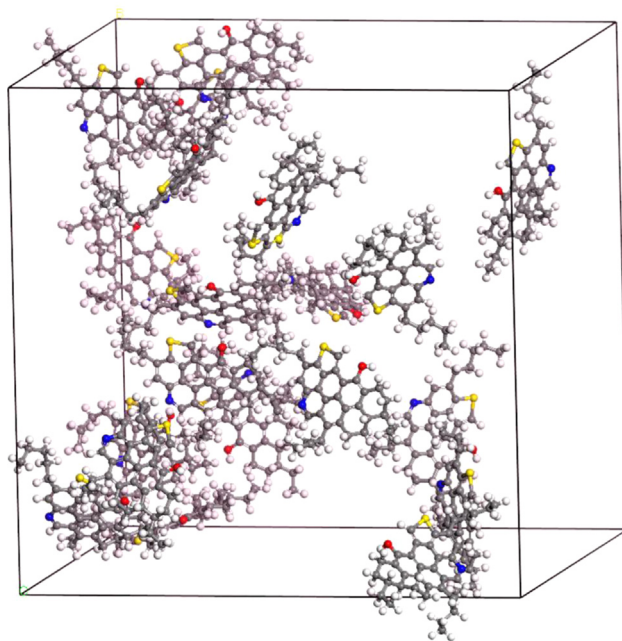
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characterization using D<sub>2</sub>O and H<sub>2</sub>O (Amani et al., 2014) as tracers and the theoretical calculation based on quantum mechanism both denied the possibility of the H-donation of SCW for the reactions involving hydrocarbon radicals (Moriya and Enomoto, 1999, 2001; Zhu et al., 2013). A growing number of researches now considered that the role of SCW in the pyrolysis of heavy oil basically is physical (Morimoto et al., 2010, 2014; Cheng et al., 2009).

With the aid of visual observation, it has been confirmed that the mixture of heavy oil and SCW follows the type IIIb phase behavior defined by van Konynenburg and Scott (Amani et al., 2013; 2014). Under commonly applied pyrolysis conditions, the heavy oil/SCW system may exist in a water/oil two-phase structure or a pseudo-single phase structure (Watanabe et al. (2010)). As a result, non-polar maltenes originally in the oil phase are partly or completely extracted into the SCW phase, condensing further into asphaltenes and coke. At a high water density and a high water to oil ratio, the condensation occurring in the SCW phase may dominate the pyrolysis of heavy oil under SCW environments (Tan et al. (2015)).

In the presence of SCW, the sequential condensation of maltenes and asphaltenes, originally occurring in the oil phase, can be transferred into the novel SCW phase. By the consideration that SCW is inert for pyrolysis, the condensation of asphaltenes occurring in the oil and SCW phases should share the same reaction mechanism. However, the measurement on the reaction kinetics of the pyrolysis of heavy oil under SCW environments suggested that the condensation of asphaltenes in the SCW phase is much faster

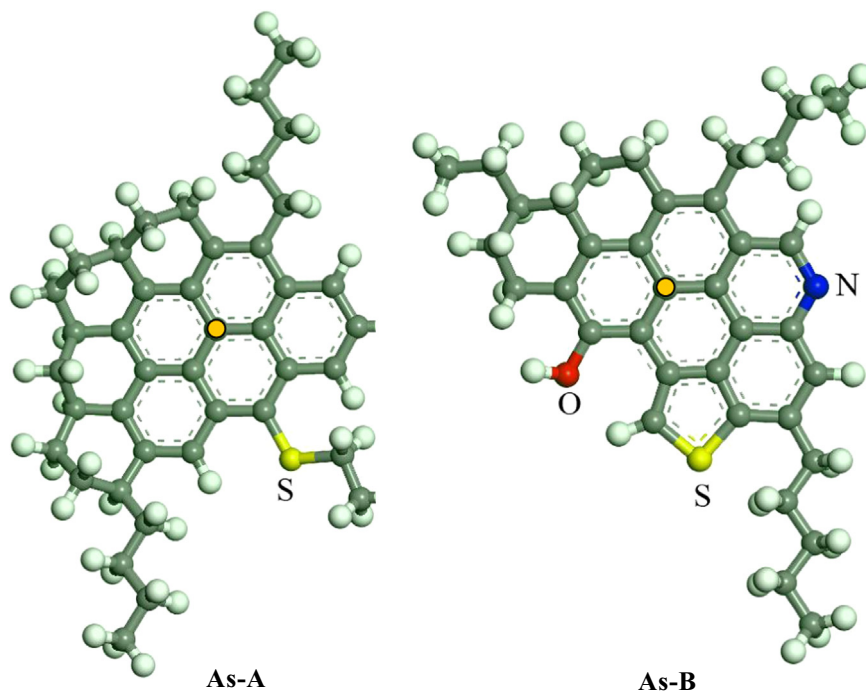
than that in the oil phase (Liu et al. (2016)). According to preliminary study, it has been confirmed that asphaltenes resulted from the condensation of maltenes in SCW have higher aromaticity and lower alkyl and naphthenic fractions than those of asphaltenes formed in the oil phase (Zhu et al. (2015)). In light of the huge difference in chemical environments between the oil and SCW phases, the authors deduced that the solvation of asphaltenes in SCW should be responsible partly for the accelerated condensation of asphaltenes to coke in the SCW phase.



**Fig. 2.** Schematic of cubic solvent box with periodic boundaries applied in MD simulations on solvation of asphaltenes in SCW, toluene or heptane. For clarity, solvent molecules in the box are removed.

**Table 1**  
Some properties of SCW at temperatures from 648 to 703 K.

Water density (g/cm <sup>3</sup> )	Pressure (MPa)	Viscosity (μPa s)	Static dielectric constant
0.10	18.0–20.8	24.7–26.6	1.8
0.20	20.8–28.1	26.6–31.8	1.8–2.9
0.30	22.3–31.4	40.2–39.2	5.0–4.6
0.40	22.5–34.8	47.8–48.4	7.5–6.8



**Fig. 1.** Asphaltene molecules based on average structure model; the aromatic C atoms labeled with orange circles are used in the calculation on the radial distribution function between aromatic C atoms and water molecules. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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