Molecular Dynamics Simulation of Water Demulsification from Crude Oil Using Cellulose

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ABSTRACT

In this study, the process of water demulsification from crude oil using cellulose as a demulsifier has been investigated through molecular dynamics simulations. The behavior of water molecules in the emulsion was analyzed both in the presence and absence of the demulsifier. The results revealed that the aggregation of water molecules increased in the presence of the demulsifier, and the intermolecular distances between water molecules decreased. Considering the demulsification mechanism, which involves coalescence and subsequent separation of water from crude oil, the findings of this study indicate that the presence of cellulose as a demulsifier enhances the efficiency of the water demulsification process in crude oil systems.

Keywords: *Molecular Dynamics, Demulsification, Crude Oil, Demulsifier*

1. INTRODUCTION

During the production and extraction of crude oil, the extracted oil is typically accompanied by significant amounts of water, sludge, and other compounds. Natural emulsifying agents present in crude oil, such as resins and asphaltenes, contribute to the formation of highly stable water-in-oil emulsions. Millions of tons of such emulsions are generated annually as a result of oil extraction processes. These emulsions pose numerous challenges across various sectors, making their removal of great importance. In recent years, the separation of emulsified water from crude oil has become one of the major challenges in the petroleum industry, thereby emphasizing the need to understand the structure of these emulsions and the factors affecting their stability [1–3].

Various methods have been developed for the demulsification of crude oil, including magnetic, thermal, and chemical techniques. Among these, the chemical method is one of the most commonly employed approaches, wherein a surface-active chemical compound—known as a demulsifier—is used to facilitate the separation of water. Selecting a suitable demulsifier based on the chemical composition of the crude oil remains a significant challenge in the oil industry [4].

Due to environmental concerns, recent studies have focused on the application of biodegradable demulsifiers [5–10]. Cellulose has emerged as a promising candidate due to its biodegradability, ease of preparation from waste materials, and the possibility of modifying its properties through functionalization [11].

Molecular dynamics (MD) simulation is a computational method that has been employed in several studies to investigate the molecular behavior of emulsions and the demulsification process at the atomic level. By analyzing MD simulation data, valuable insights can be gained into the spatial and temporal behavior of various molecules involved [12–14].

In this study, considering the advantages of cellulose and the importance of exploring demulsification mechanisms at the molecular scale, a molecular dynamics simulation was conducted to investigate a model emulsion containing heptane, asphaltenes, and water in the presence and absence of cellulose. By analyzing the behavior of water molecules, the influence of cellulose as a demulsifier in enhancing water separation from the emulsion was demonstrated.

2. SIMULATION METHODOLOGY AND DETAILS

In this study, the molecular structures of the components present in the emulsion, including water, heptane, asphaltene, and cellulose, were first constructed. Subsequently, a simulation box containing the emulsion system was built. Following the molecular dynamics simulation, the results were analyzed and interpreted.

2.1. Construction of Molecular Structures

As is well known, crude oil contains a wide range of molecules, including various hydrocarbons and asphaltenes. Among them, asphaltenes are recognized as one of the key contributors to the formation of stable water-in-oil emulsions. Therefore, to accurately represent the emulsion system and investigate the demulsification process, it is essential to include asphaltene, a representative hydrocarbon (in this case, heptane), water, and cellulose molecules in the simulation.
For molecular dynamics simulations to be conducted, the molecular structures of all components must be defined, visualized, and optimized. Accordingly, the molecular structures of asphaltene, heptane, cellulose, and water were constructed and structurally optimized. Figure 1 presents the optimized structures of the molecules.

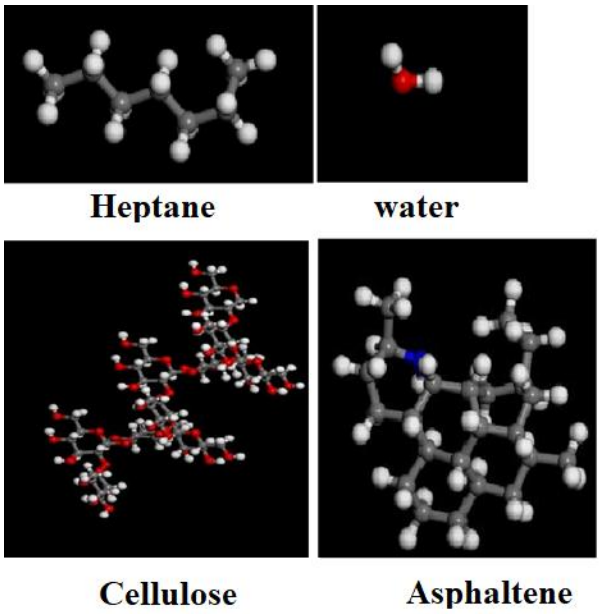

Fig. 1. Molecular structures of the compounds used in the simulation

2.2. Geometric Optimization

To minimize the energy and optimize the molecular structures used in the simulation, the Compass force field was employed using the Material Studio software. The energy minimization graphs for the geometric optimization of the molecular structures utilized in the simulation are presented in Figs. 2-1 through 2-4.

2.3. Simulation Box Construction

After the geometric optimization of the molecular structures, a simulation box containing the molecules is created to form a molecular-scale emulsion. For this purpose, a box containing water, heptane, asphaltene, and cellulose molecules is considered. The density of this emulsion is assumed to be approximate. The simulation box is illustrated in Figure 3.

3. RESULT AND DISSCUSION

After creating the simulation box, the system's density is initially calculated, followed by molecular dynamics simulation. The results from the movement of water molecules and their concentration are analyzed, along with the analysis of the system at the beginning and end of the simulation, focusing on the changes in the emulsion and the changes in the water molecules.

3.1. Calculation of Emulsion Density

To calculate the density and equilibrate the system, the NPT ensemble is used. The temperature is considered to be ambient, and the emulsion reaches equilibrium at ambient temperature after 100 picoseconds.

After the molecular dynamics simulation, the status and position of water molecules at the beginning and end of the simulation are examined based on the output frames. As shown in Figure 3, the water molecules are initially randomly and sparsely distributed within the simulation box, and by the end of the simulation, the clustering of water molecules is observed. As we know, in the process of demulsification, the approach of water molecules towards each other and their transformation into droplets, as well as the coalescence of droplets, leads to the separation of water from oil. Therefore, from figure 5, it can be inferred that over time, the distance between water molecules decreases, resulting in coalescence and the separation of water from oil.

$$g(r) = \frac{1}{\rho 4\pi^2 \delta r} \frac{\sum_{t=1}^{T} \sum_{j=1}^{N} \Delta N\ (r \to r + \delta r)}{N \times T}$$

In this relation, ρ represents the system density, N is the number of atoms, T is the total simulation time, r is the distance, and ΔN is the number of atoms within the distance between r and r+δr. This function and its analysis can provide important results regarding the self-aggregation of molecules, or in other words, the closer proximity of molecules to each other. The demulsification of water-in-oil emulsions results from the closer approach of water molecules to each other and their self-aggregation. Therefore, comparing this function for water molecules in the case where cellulose as an emulsion breaker is present, with the case where the emulsion does not contain cellulose, provides valuable insights into the demulsification process.

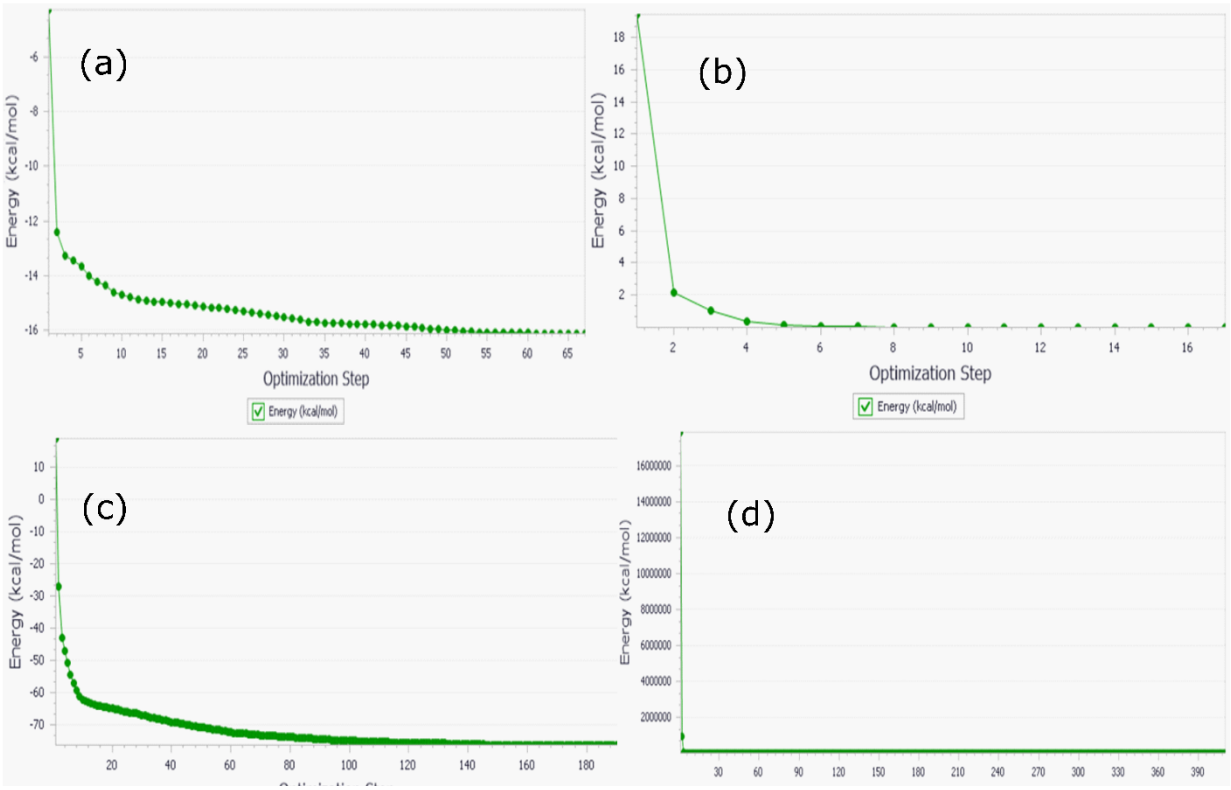

Fig. 2. Geometric optimization and energy minimization of the molecular structures: (a) Heptane, (b) Water, (c) Asphaltene, (d) Cellulose

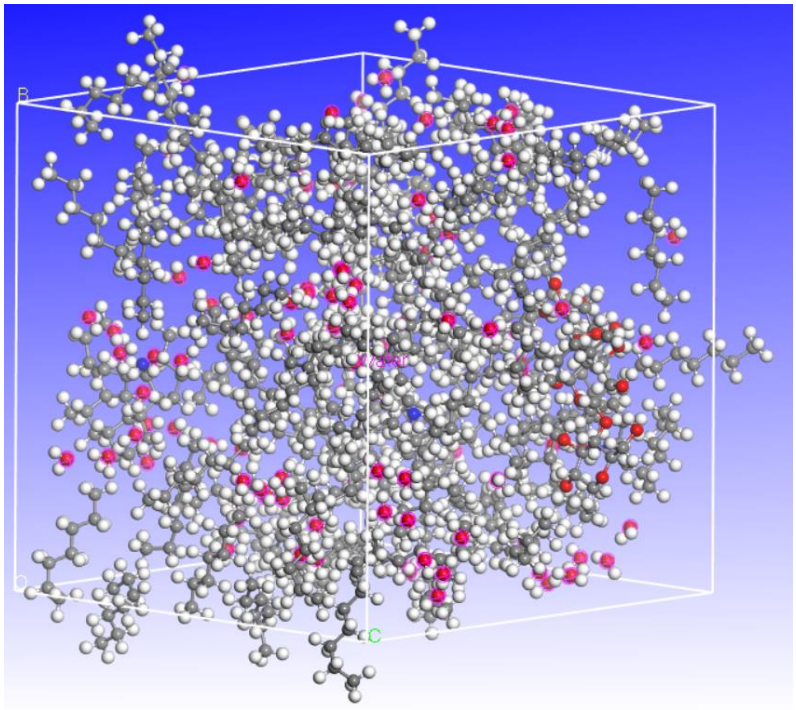

Fig. 3. Position of water molecules at the beginning of the simulation.

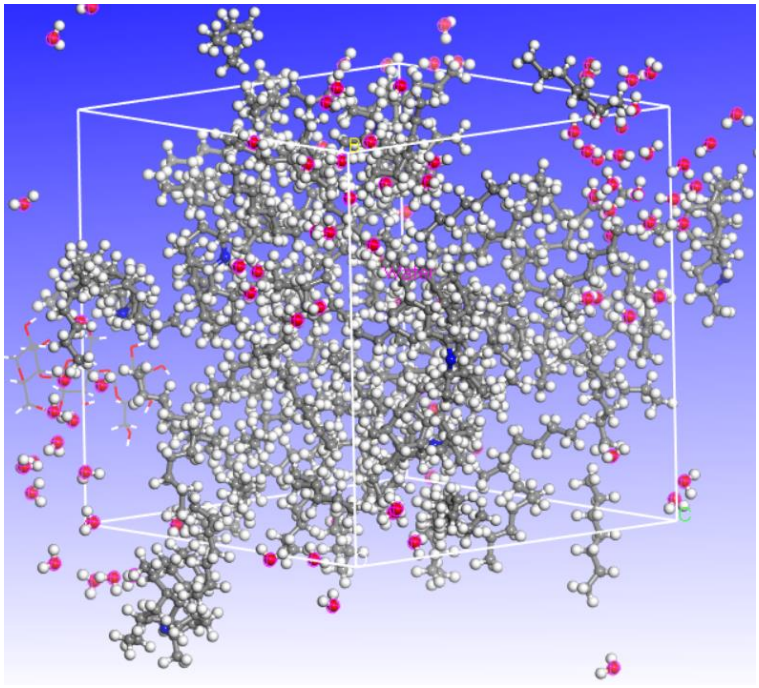

Fig. 4. End of the simulation at 30°C.

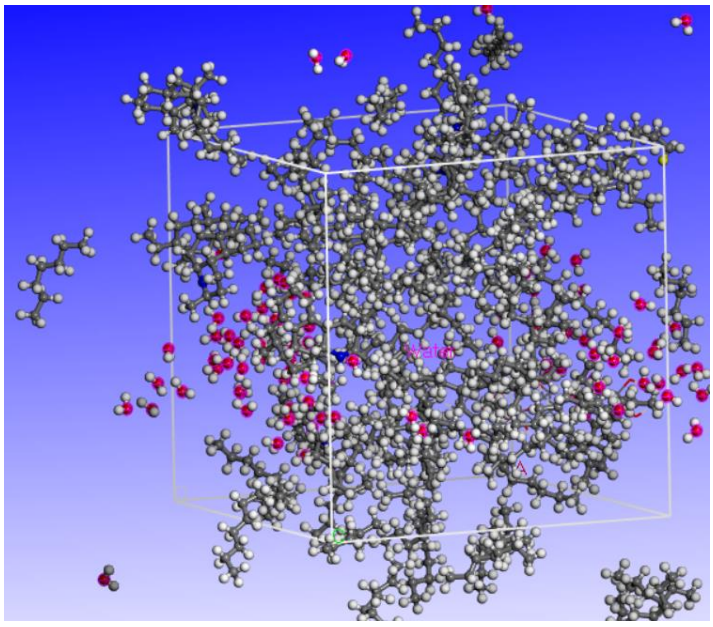

Fig. 5. End of the Simulation at 60°C.

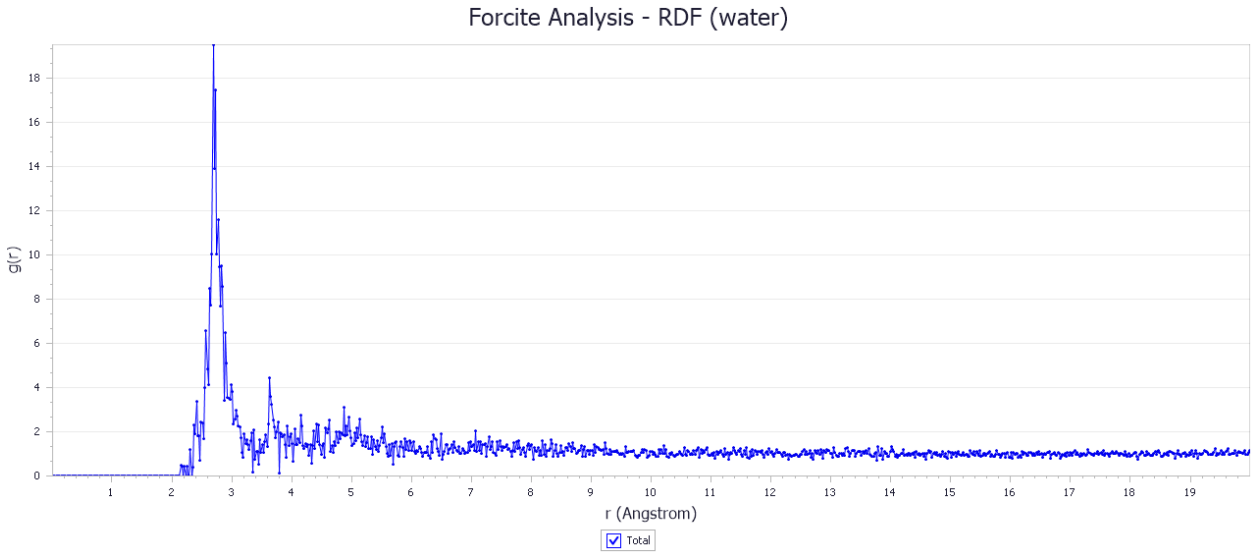

Fig. 6. Radial distribution function for water molecules in the presence of cellulose.

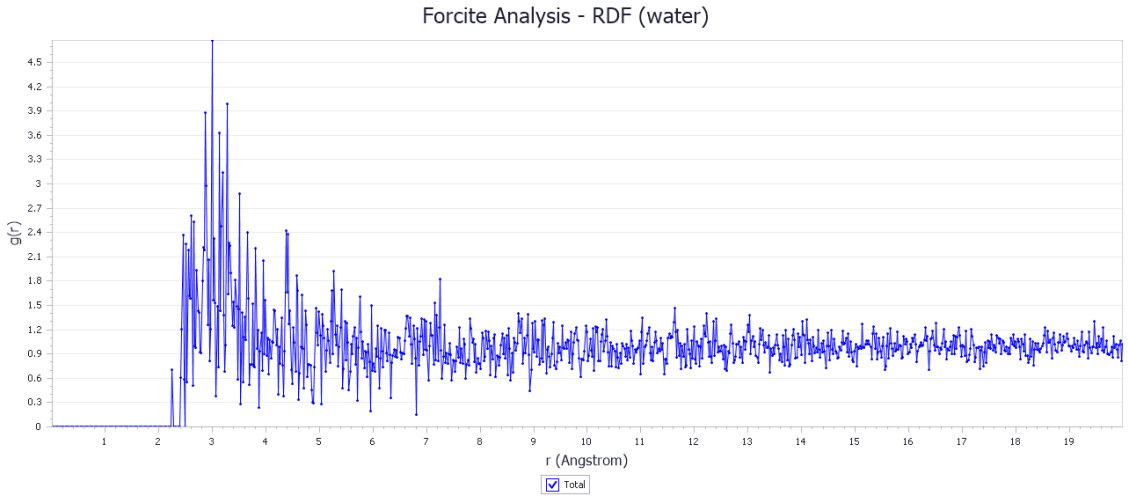

Fig. 7. Radial distribution function of water molecules in the blank sample.

By comparing the results in Figs. 6 and 7, it can be observed that the radial distribution function in the case without cellulose in the system has a lower peak intensity. Additionally, the reduction in the radius at which the maximum value of the radial distribution function occurs indicates greater aggregation of water molecules next to each other. This function represents the aggregation of water molecules; therefore, by adding cellulose, the aggregation of water molecules increases.

Conclusion

A sharp peak in the radial distribution function, especially in the presence of cellulose, indicates a significant aggregation of water molecules. This means that the water molecules are more likely to be found at a specific distance from one another, suggesting that they are not randomly distributed, but rather tend to cluster together.

In the case of an emulsion, this clustering behavior is critical. When cellulose is added to the system, it appears to promote the self-assembly or aggregation of water molecules, causing them to come closer and

form droplets. This process is a key step in demulsification, as the coalescence of water molecules leads to the separation of water from oil.

Therefore, the presence of a sharper and higher peak in the g(r)g(r)g(r) curve, compared to the system without cellulose, confirms that cellulose facilitates the approach and accumulation of water molecules. This structural information reflects a higher degree of order and interaction among water molecules, which is directly related to more effective demulsification.

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