Molecular dynamics simulation of nanocellulose-oil-water interaction in enhanced oil recovery application

M Ledyastuti* and J Jason
Inorganic and Physical Chemistry Division, Chemistry Department, Institut Teknologi Bandung, Jalan Ganesa no. 10 Bandung 40132
Email: mia@chem.itb.ac.id

Abstract. Enhanced Oil Recovery (EOR) is a way to obtain long hydrocarbon-structured oil by flooding oil reservoirs using water with certain materials. Hydrolyzed polyacrylamides (HPAM) and xanthan gum are commonly used in the EOR process. Both of these materials have several disadvantages, including unstable at high salinity and leave debris in the environment. One alternative to substitute HPAM and xanthan gum is nanocellulose, which is an abundant amount of natural polymer. Molecular dynamics simulations investigate the potential of nanocellulose as an EOR agent. A mixture of decane and naphthalene is used as an oil model, while the SPC/E model is used as a water model. By analyzing the simulation trajectory, the interfacial tension and viscosity values were obtained. The simulation results showed the value of the water-oil interfacial tension increased with the addition of nanocellulose. This was caused by the position of nanocellulose that was always in the aqueous phase during the simulation. The water-oil interfacial tension also increased from 46.94 dyne/cm to 47.96 dyne/cm with the presence of two nanocellulose molecules at 353 K. Water viscosity increased from $3.10 \times 10^{-4}$ kg/m.s to $3.80 \times 10^{-4}$ kg/m.s after the addition of one cellulose molecule at 353 K. Nanocellulose can be an EOR agent by increasing the water viscosity but unfortunately the water-oil interfacial tension also increasing. Due to the change of these two opposing properties, nanocellulose cannot optimally improve oil recovery as shown by previous research.

1. Introduction
Enhanced Oil Recovery (EOR) is a way to obtain long hydrocarbon-structured oil by flooding oil reservoirs using water with certain materials. Injected fluids generally can reduce interfacial tension, increase crude oil mobility, or form microemulsions [1]. The ability to reduce interfacial tension is possessed by surfactants such as alcohol propoxy sulfate (APS), C$_{20-24}$ alpha olefin sulfonate (AOS), and C$_{15-18}$ internal olefin sulfonate (IOS) [2]. Adding polymers to the water that caused the viscosity increases can do the increase of crude oil mobility. Increased viscosity is expected to have greater thrust to facilitate crude oil mobility to the production well area. Commonly used polymers to increase viscosity are hydrolyzed polyacrylamides (HPAM) and xanthan gum. Unfortunately, these polymers exhibit some disadvantages. HPAM decreases its performance under conditions of high salinity [3]. Meanwhile, xanthan gum can leave debris that will reduce reservoir permeability [4].

Recently, nanocellulose is predicted to be an EOR agent replacing HPAM and xanthan gum. Nanocellulose is cellulose that has a nanometer size in one of its dimensions. It has unique properties including low density, high strength, and stiffness [5-8]. Nanocellulose has emulsifying properties, but it can also be a thickener [5, 9]. Aadland et al have reported that adding nanocellulose to the water...
flooding process can increase oil recovery by 1.2% [1]. This oil recovery is not very effective for an EOR agent [1]. The ineffectiveness can be caused by several factors, including changes in interfacial tension and viscosity that are not significant. The previous research did not discuss in depth how nanocellulose interactions in the water-oil system.

This study aims to look at the interactions that occur when nanocellulose is in the water-oil system. Our study was carried out using a molecular dynamics simulation approach, which allows revealing the position and movement of molecules in detail. Molecular dynamics simulations can be used to complement the explanation of the data obtained from experiments such as how the orientation of molecules on a surface [10-11]. Molecular dynamics simulations can also be used to predict the dissolving energy of a solute in a particular solvent [12-13].

2. Computational methods

The nanocellulose-water-oil interaction was investigated with the GROMACS-2018 software [14]. The force field for all components in the system was using CHARMM36 [15]. In this calculation, three types of water molecules were used, namely SPC, SPC/E, and TIP3P [16]. Preliminary calculations were carried out to determine the water model that was close to the real water molecule. The results of our preliminary calculation were consistent with previous calculations conducted by Vega and de Miguel [17]. They choose that the best model for water is SPC/E based on the surface tension value at 298 K. In this case, we also chose the SPC/E model as the best water model. Our calculation had resulted in 56.69 dyne/cm for the surface tension of the SPC/E model. This study also had proven the number of water molecules did not significantly affect the value of surface tension. In addition, the surface tension values were calculated at 4000, 6000 and 8000 water molecules can be seen in table 1. Based on these results, the next simulation was using 4000 water molecules.

| Table 1. Surface tension values using SPC/E model in different number of water molecules at 298 K. |
|-----------------|------------------|
| Number of water molecules | Surface tension (dyne/cm) |
| 4000            | 56.69            |
| 6000            | 56.32            |
| 8000            | 56.27            |

A mixture of decane and naphtalene was used as an oil model in this study. This mixture was representative of aliphatic and aromatic compounds commonly found in crude oil [18]. The composition of decane and naphtalene used was 1:1. The oil model was then mixed with water, as shown in figure 1. In the water-oil system that was formed then nanocellulose molecules were added. The selected nanocellulose molecule was glucose dodecamer. Based on previous research, dodecamer glucose was thermodynamically soluble in water [13]. The number of nanocellulose molecules added varies to see how they affected the water-oil system.

The whole system went through the processes of geometry optimization, equilibration, and production. The production stage trajectory was then analyzed to obtain the value of the interfacial tension and viscosity. The geometry optimization stage used the steepest descent algorithm with a maximum force of 100 kJ / mol / nm [19]. Equilibration used NVT and NPT ensembled with a time step of 1.0 fs and a total simulation of 1.0 ns. The Nose-Hoover thermostat was used to keep the temperature constant during the NVT ensemble [20]. Whereas for calculations with the NPT ensemble the Berendsen thermostat and barostat were used [21]. Simulations were carried out at 298 K and 353 K, while the pressure was maintained at 1 bar. The temperature of 353 K illustrated the temperature in the reservoir. The production phase was carried out with an NPT ensemble for 30.0 ns with a Nose-Hoover thermostat and a Parrinello-Rahman barostat [21-22].
3. Results and discussion

3.1. Interfacial tension

The oil model used in this study was a mixture of 1:1 decane and naphtalene, which had a density of 891.88 kg/m$^3$ at 298 K. The value was close to the density of crude oil that ranged around 900 kg/m$^3$ at room temperature [23]. The analysis of the oil density profile showed that decane and naphtalene were well mixed, as in figure 2. The oil was then mixed with water to form two separated phases. The density profile of this system showed that the water phase and the oil phase were perfectly separate. Based on the trajectory processing of this system simulation, an interfacial tension of 53.51 dyne/cm was obtained at 298 K. If the temperature was raised to 353 K, the interfacial tension decreased to 46.94 dyne/cm. This was caused by the interaction of water-oil, which was getting stronger with rising temperatures. Based on figure 3, naphtalene had a stronger interaction with water. This was consistent with previous research that revealed stronger aromatic compounds in their interactions with water [11].
The nanocellulose used in this study had good solubility in water as shown in figure 4. Based on the density profile, nanocellulose was spread evenly along the z-axis. The addition of nanocellulose molecule into the water had increased the surface tension as seen in table 2. The increase of surface tension was probably caused by a stronger interaction between nanocellulose and water. As the data shown in table 2, the surface tension was higher with the addition of nanocelluloses. This proved the presence of nanocellulose strengthened the interaction in the aqueous phase.

**Table 2.** Surface tension value with nanocellulose variation at 353 K.

| Number of Cellulose molecules | Density (kg/m³) | Surface tension (dyne/cm) |
|------------------------------|----------------|----------------------------|
| 0                            | 962.47         | 47.81                      |
| 1                            | 988.35         | 49.19                      |
| 2                            | 1012.66        | 49.93                      |
| 3                            | 1036.91        | 50.78                      |
The nanocellulose-water-oil system can be seen in figure 5. The addition of one nanocellulose molecule to the system causes the water-oil interfacial tension to decrease slightly to 46.38 dyne/cm (1.12%) at 353 K. The next addition of two and three molecules increased the interfacial tension to 47.96 dyne/cm (2.17%) and 47.27 dyne/cm (0.70%), respectively. This was likely due to increased interactions in the aqueous phase when the nanocellulose molecule was more than one molecule. Stronger interaction in the aqueous phase caused the weakening water-oil interaction that increased the interfacial tension.

![Figure 5. Nanocellulose in the oil-water system.](image)

The addition of nanocellulose, which caused an increase in the water-oil interfacial tension, could also be analyzed based on the position of the nanocellulose during the simulation. Figure 6 showed the position of the nanocellulose throughout the simulation time. In the figure, it appeared that nanocellulose tended to be in the middle of the water phase. This also reinforced the reason for the increased value of the water-oil interface tension. The nanocellulose molecules which tended to be in the water phase caused interactions in the water phase to get stronger and weakened the interaction of the water phase with oil. The hydroxyl groups of nanocelluloses were responsible for the strong interactions with water. This interaction could be reduced by modifying the hydroxyl group to a less polar group.

![Figure 6. Density profile all components in nanocellulose-water-oil system.](image)
3.2. **Viscosity**

In addition to the interfacial tension, molecular interaction in the system can also be investigated by viscosity value. Experimental measurements showed the value of water viscosity at 298 K at 1.0 cP, equivalent to $1 \times 10^{-3}$ kg/m.s [24]. At the same temperature, the results of calculations with the SPC/E water model produced a viscosity of $6.5 \times 10^{-4}$ kg/m.s. These results were similar to previous calculations [25]. At 353 K, the water viscosity decreased to $3.1 \times 10^{-4}$ kg/m.s (52.31%). This was because water molecules absorbed additional energy to increase mobility. Adding one nanocellulose molecule to water could increase the viscosity to $3.8 \times 10^{-4}$ kg/m.s (22.58%). The additions of two and three nanocellulose molecules were way more had the same effect, increasing the viscosity to $4.4 \times 10^{-4}$ kg/m.s (41.93%). Due to box size limitations, the addition of nanocellulose to the system was only up to three molecules. Higher viscosity had indicated stronger interaction in the presence of nanocellulose molecules in the aqueous phase. Stronger interaction in the aqueous phase could be reflected from the positions of these molecules as shown in figure 7. Distances among nanocellulose molecules were around 2 nm in average during the simulation.

![Figure 7. Snapshot of nanocellulose molecules in the aqueous phase.](image)

4. **Conclusion**

Based on the analysis of our calculation, interaction in aqueous phase was stronger in the presence of nanocellulose molecules. Although the stronger interaction increased and had a good effect on water viscosity, it was not for interfacial tension. By analyzing the molecular dynamics simulation trajectory, the nanocellulose position that always in the aqueous phase makes interactions in the aqueous phase to strengthen while the water-oil interaction weakens. Nanocellulose can be an EOR agent by increasing the water viscosity but unfortunately the water-oil interfacial tension also increasing. Due to the change of these two opposing properties, nanocellulose cannot optimally improve oil recovery as shown by previous research.

**References**

[1] Aadland R C, Jakobsen T R, Heggset E B, Long-Sanouiller H, Simon S, Paso K G, Syverud K and Torsaeter O 2019 *Nanomaterials* 9 665

[2] Levitt D, Jackson A, Heinson C, Britton L N, Malik T, Dwarakanath V and Pope G A 2006 Identification and evaluation of high-performance EOR Surfactants, SPE/DOE Symposium on Improved Oil Recovery

[3] Abdel-Azeim S and Kanj M Y 2018 *Energy Fuels* 32 pp 3335-3343
[4] Sandvik E I and Maerker J M 1977 Application of xanthan gum for enhanced oil recovery in Extracellular Microbial Polysaccharides chapter 19 pp 242-264
[5] Salas C, Nypelo T, Rodriguez-Abreu C, Carrillo C and Rojas O J 2004 Current Opinion in Colloid & Interface Science 19 pp 383-396
[6] Edgar C D and Gray D G 2001 Cellulose 8 pp 5–12
[7] Sir i and Plackett D 2010 Cellulose 17 pp 459–94
[8] Oza K P and Frank S G 1986 J. Dispers. Sci. Technol. 7 pp 543–561
[9] Ioelovich M 2016 Fabrication and self-assembly of nanobiomaterials, applications of nanobiomaterials Nanocellulose-fabrication, structure, properties, and application in the area of care and cure Volume 1 chapter 9 pp 243-288
[10] Ledyastuti M, Liang Y, Kunieda M and Matsuoka T 2012 The Journal of Chemical Physics 137 p 064703
[11] Kunieda M, Nakaoka K, Liang Y, Miranda C R, Ueda A, Takahashi S, Okabe H and Matsuoka T 2010 J. Am. Chem. Soc. 132 pp 18281–18286
[12] Shivakumar D, Williams J, Wu Y, Damm W, Shelley J and Sherman W 2010 J. Chem. Theory Comput. 6 pp 1509-1519
[13] Santoso A 2019 Pengaruh Derajat Polimerisasi terhadap Energi Bebas Pelarutan Oligomer Glukosa melalui Simulasi Dinamika Molekul Skripsi ITB
[14] Lemkul J 2019 Living J. Comp. Mol. Sci. 1 p 5068
[15] Lee J, Cheng X, Swails J M, Yeom M S, Eastman P K, Lemkul J A, Wei S, Buckner J, Jeong J C, Qi Y, Jo S, Pande V S, Case D A, Brooks C L, MacKerrel A D, Klauda J B and Im W 2016 J. Chem. Theory Comput. 12 pp 405-413
[16] Zielkiewicz J 2005 J. Chem. Phys. 123 p 104501
[17] Vega C and De Miguel E 2007 J. Chem. Phys. 126 p 154707
[18] Sugiyama S, Liang Y, Murata S, Matsuoka T, Morimoto M, Ohata T, Nakano M and Boek E S 2017 SPE Journal SPE-189465-PA
[19] Petrova S S and Solov’ev A D 1997 Historia Mathematica 24 pp 361-375
[20] Evans D J and Holi an B L 1985 J. Chem. Phys. 83 p 4069
[21] Berendsen H J C, Postma J P M, van Gunsteren W F, DiNola A and Haak J R, 1984 J. Chem. Phys. 81 pp 3684–3690
[22] Parrinello M and Rahman A 1981 J. Appl. Phys. 52 p 7182
[23] Wei Q F, Mather R R, Fotheringham A F, Yang R D 2003 Marine Pollution Bulletin 46 pp 780-783
[24] Information on http://www.resources.saylor.org
[25] Markestijn A, Hartkamp R, Luding S and Werterweel J 2012 J. Chem. Phys. 136 p 134104