**Jurnal Kimia Valensi, Vol 9(1), May 2023, 53-58**
Available online at Website: http://journal.uinjkt.ac.id/index.php/valensi

# Synthesis of Iron Oxide ($Fe_2O_3$)-Xanthan Gum Nanoparticle Composites Its Potential as a Chemical Flooding Media in Enhanced Oil Recovery (EOR)

**Yong Richard Sriwijaya[1], Paramita Jaya Ratri[1*], Tirta Rona Mayangsari[1], Azis Adharis[1], Shabrina Sri Riswati[2]**

[1] Department Chemistry, Faculty Science and Computer, Universitas Pertamina
[2]Department of Petroleum Engineering, Universitas Trisakti

**Corresponding author: paramita.jr@universitaspertamina.ac.id; 0813-1517-1773*

Received: December 2022; Revision: March 2023; Accepted: May 2023; Available online: May 2023

**Abstract**

Increasing oil consumption in Indonesia encourages an improvement of production using chemical flooding of Enhanced Oil Recovery (EOR) technology. Chemical flooding is an injection method of materials based on polymer and nanoparticles such as α-$Fe_2O_3$-xanthan gum nanocomposite into the reservoir. In this study, α-$Fe_2O_3$ nanoparticles were synthesised and then blended to xanthan gum by sonochemical method through an ex-situ process. The α-$Fe_2O_3$-xanthan gum nanocomposite X-ray diffraction (XRD) shows that there are no additional peaks. Only the α-$Fe_2O_3$ and the xanthan gum peaks are detected with the crystallite size of around 16-20 nm. The particle size of α-$Fe_2O_3$-xanthan gum (1:1) nanocomposite as measured by Particle Size Analyzer (PSA) was 228.43 nm with the type of polydisperse. The functional group of the nanocomposite is a combination of the α-$Fe_2O_3$ and xanthan gum functional groups which shows there are no other compounds detected in IR spectra. The EOR test showed that xanthan gum had a significant effect on increasing the viscosity of the α-$Fe_2O_3$-xanthan gum nanofluid to 1.964 cP at a 1:2 composition. Based on these results, α-$Fe_2O_3$-xanthan gum nanofluid is the potential material used in the chemical flooding process in the reservoir.

***Keywords:*** EOR; nanocomposite; xanthan gum; viscosity

***DOI:*** *10.15408/jkv.v9i1.29468*

## 1. INTRODUCTION

Demands for crude oil in Indonesia will increase with total population growth. However, from 2018 until 2021 there was a decline in crude oil production in Indonesia. This contrasts with an increase in the number of crude oil imports from 2020 to 2021. Indonesia has imported crude oil by 20.14% in 2021 to meet domestic needs (ESDM, 2022). Although, this oil production can still be increased with the Enhanced Oil Recovery (EOR) technology. In oil fields in the United States, EOR technology can increase oil production by 30-60 % more than the total conventional methods (Gov, 2022).

Chemical injection is one type of EOR method by inserting a fluid containing chemical substances into the reservoir. These chemicals include polymers such as xanthan gum or hydrolyzed polyacrylamide (HPAM) and nanoparticles such as $Fe_2O_3$, $Fe_3O_4$, $TiO_2$, and $SiO_2$ (Jiang et al., 2014: Ali et al., 2015). Polymer addition will increase the viscosity of working fluid to reduce water permeability due to mechanical entrapment. This will make a good mobility ratio to move the oil from the reservoir to the production well (Kamal et al., 2015). The addition of nanoparticles based on metal catalysts in a working fluid can significantly reduce oil viscosity (Zhao et al., 2021). Nanoparticles also have changed the wettability of the reservoir rock, decreased interfacial tension (IFT) between water and oil, and increased the viscosity of working fluid from previous research (Cheraghian, Rostami, & Afrand, 2020).

The development of chemical flooding materials in EOR technology continues to combine nanoparticles with polymer-surfactants. Previous research that has been reported by Pereira et al. using $Fe_3O_4$-CTAB (cetyltrimethylammonium bromide) showed an increase in oil recovery efficiency by 27% with the addition of $Fe_3O_4$ nanoparticles to fluids

Copyright©2023, Published by Jurnal Kimia Valensi
P-ISSN: 2460-6065, E-ISSN: 2548-3013

CTAB. This occurs due to changes in the wettability of the reservoir rock surface which was previously wet with oil to become wet with water. This change allows oil droplets trapped on the rock surface to be solvated by $Fe_3O_4$-CTAB material and can be carried out of the reservoir (Pereira, et al., 2020). This phenomenon also occurs in the study of Saha et al, the reetha-xanthan gum-Si material succeeded in increasing the oil recovery efficiency by 24.97% by reducing the wettability of contact angle and IFT, as well as the increasing viscosity of the working fluid (Saha et al., 2019). Furthermore, the study of PAM- grafted-$TiO_2$ material by Corredor et al., can increase oil recovery by 2% compared to using only HPAM as polymer flooding (Corredor et al., 2019). In addition, the incorporation of nanoparticles with surfactants or polymers can also prevent the occurrence of blocking in the pores of the reservoir rock by the aggregation of solid nanoparticles (Gbadamosi, et al., 2021; Rellegadla, et al., 2018).

$Fe_2O_3$ nanoparticles studied by Joonaki and Ghanaatian, showed that this material reduces the contact angle of the wettability of the rock by 32° and lowers the oil-water surface tension from 38.5 dyne/cm to 2.75 dyne/cm. Chemical injection with $Fe_2O_3$ nanoparticles can increase the oil recovery from 56.6% to 73.6% (Joonaki & Ghanaatian, 2014). Another material that is often used in chemical injections is xanthan gum. In the study of Jang, et al., xanthan gum can increase the viscosity of the working fluid at room temperature up to 27.8 cp. This figure is much higher than HPAM which is only 10.0 cp (Jang et al., 2014). This increase in viscosity can reduce the permeability of the rock in the reservoir. This reduces the mobility of the working fluid so that it can better push out the oil that is still trapped in the reservoir rock (Jang et al., 2014; (Jang, Zhang, Chon, & Choi, 2014; Rellegadla, et al., 2018). Xanthan gum polymers can also reduce the surface tension (IFT) between oil and water from 19.8 mN/m to 17.2 mN/m (Gbadamosi, et al., 2021).

Research on α-$Fe_2O_3$ nanoparticles modified by polymers, especially xanthan gum, has not been widely developed for EOR technology. Therefore, this research will focus on the synthesis of α-$Fe_2O_3$- xanthan gum nanocomposite. The stages of this research are divided into three, the first is to synthesize α-$Fe_2O_3$ nanoparticles. The second part is the mixing of α-$Fe_2O_3$ nanoparticles with xanthan gum in the form of composites and nanofluids. The third part is to analyze the effect of mass composition on α-$Fe_2O_3$-xanthan gum nanocomposite on changes in viscosity of working fluid and oil.

## 2. MATERIALS AND METHODS

### Materials and Instrumentations

Solids $FeCl_3.6H_2O$ for analysis (Merck, Germany), NaOH A-2052 (Smartlab, Indonesia), ethanol pure analysis (Supelco, Germany), synthesized biopolymer xanthan gum from xanthomonas campestris (Sigma-Aldrich), hexane pure analysis (Supelco, Germany).

Instrumentations were used in this research are Lindberg Blue M furnace, oven 20-300˚C (Memmert UN30), Nicolet™ iS50 FTIR Spectrometer with NIR Module, BTX III Benchtop XRD Analyzer, Nano Particle Analyzer Horiba SZ-100 (PSA), and NDJ-8S Viscometer.

### Procedure

### Synthesis of α-$Fe_2O_3$-Xanthan Gum Nanocomposite

The process of synthesizing α-$Fe_2O_3$-xanthan gum nanocomposite was carried out using a sonochemical that has been proposed by (Hassanjani-Roshan, Vaezi, Shokuhfar, & Rajabali, 2011) with reflux methods. The $FeCl_3.6H_2O$ (0.1 M) and NaOH (0.1 M) were dissolved in 50 mL of aquadest separately. The NaOH solution dripped slowly into the $FeCl_3$ solution. Then the analyte was sonicated for 30 minutes at 30 C. The solids formed were filtered and dried for 15 minutes at 105 C. Then annealed for 1 hour at 500 C to obtain α-$Fe_2O_3$. The ex-situ method was applied to synthesis nanocomposite by mixing the synthesized α-$Fe_2O_3$ nanoparticle with xanthan gum in 50 mL of ethanol (mass ratio α-$Fe_2O_3$: xanthan gum is 1:1, 2:1, and 1:2) (T. Hanemann and D. V. Szabó, 2010). The mixture was reflux at 65 C for 1 hour and filtered to form α-$Fe_2O_3$-xanthan gum nanocomposite.

### Nanofluids Preparation

The α-$Fe_2O_3$-xanthan gum nanocomposite, α-$Fe_2O_3$ nanoparticle, and xanthan gum were dissolved into 100 mL of aquadest with a concentration of 1000 ppm and sonicated for 90 minutes.

**Characterization of α-$Fe_2O_3$-Xanthan Gum Nanocomposite, α-$Fe_2O_3$ Nanoparticle, and Xanthan Gum**

Solid α-$Fe_2O_3$-xanthan gum nanocomposite, α-$Fe_2O_3$ nanoparticle, and xanthan gum were characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Particle Size Analyzer (PSA). In FTIR, characterization was carried out using a transmission method with the KBr plate (mass ratio sample:KBr is 1:9). Then the Cobalt K-α was used in XRD characterization with 2θ ranging from 5 to 45˚.

**Viscosity Measurements**

The rotor 0 of NDJ-8s Viscometer was inserted into nanofluids with angular velocity from 30 to 60 rpm. The values of viscosity that are detected by the instrument were recorded.

## 3. RESULTS AND DISCUSSION

**Identification of α-$Fe_2O_3$-Xanthan Gum Nanocomposite and Its Crystallite Size with X-Ray Diffraction (XRD).**

The results of α-$Fe_2O_3$-xanthan gum nanocomposite that was characterized by XRD can be seen in **Figure 1**. The pattern of XRD spectrum shows that α-$Fe_2O_3$-xanthan gum nanocomposite is a combination of peaks α-$Fe_2O_3$ and xanthan gum. The 2θ positions of α-$Fe_2O_3$ corresponded to previous research by (Hassanjani et al., 2011) and JCPDS no. 01-105. Indicates that the α-$Fe_2O_3$ nanoparticle was successfully synthesized before it is mixed with xanthan gum. However, xanthan gum just has one broad peak at 19.5° which means that xanthan gum is an amorphous polymer. The α-$Fe_2O_3$-xanthan gum nanocomposite main spectrum is at positions 24, 33, 35.5, dan 40.7°, describing α-$Fe_2O_3$ as a majority structure in nanocomposite for all composition mass. Furthermore, exceeding the mass of xanthan gum in the composite will increase amorphous phase in 1:2 composition (α-$Fe_2O_3$: xanthan gum) in the presence of a spectrum at 19,6˚. No other diffraction arises from the impurity compound other than α-$Fe_2O_3$ or xanthan gum as shown in **Figure 1**. Therefore, the crystallinity of the synthesized α-$Fe_2O_3$-xanthan gum nanocomposite has a high degree of purity (Ali, Manshad, Imani, Sajadi, & Keshavarz, 2020).

Based on the Scherrer equation, obtained the size of the crystallites in each solid as shown in **Table 1** (Mustapa et al., 2019). The crystallite size of α-$Fe_2O_3$ nanoparticle has decreased from 19.2 nm to 13.18 nm in α-$Fe_2O_3$-xanthan gum nanocomposite 1:1 composition due to presence of xanthan gum. Although the excess addition of xanthan gum has an opposite trend to the previous one. There was an increase in crystallite size of α-$Fe_2O_3$-xanthan gum nanocomposite becoming 16.86 nm in 1:2 composition.

**Table 1.** Crystallite Size (nm) of α-$Fe_2O_3$ and α-$Fe_2O_3$-xanthan gum

| Materials | Crystallite Size (nm) |
|---|---|
| α-$Fe_2O_3$ | 19.2 |
| α-$Fe_2O_3$-xanthan gum (2:1) | 14.64 |
| α-$Fe_2O_3$-xanthan gum (1:1) | 13.18 |
| α-$Fe_2O_3$-xanthan gum (1:2) | 16.68 |

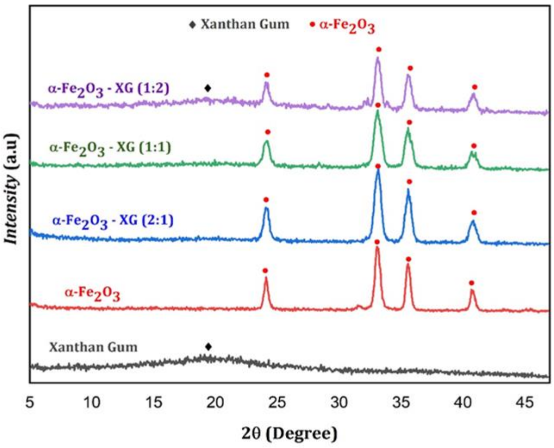


**Figure 1.** XRD patterns of α-$Fe_2O_3$ and α-$Fe_2O_3$-xanthan gum

**Identification of particles size in α-$Fe_2O_3$-xanthan gum nanocomposite with particle size analyzer (PSA).**

The particle size of α-$Fe_2O_3$ and α-$Fe_2O_3$-xanthan gum (1:1) is 177.56 and 228.43 nm, respectively (**Table 2**). This size classifies that materials synthesis is a type of nanoparticle due to it being in the range of 1-1000 nm (Mahato, 2017). Generally, many researchers categorized material sizes as nanoparticles with sizes under 100 nm. However, particle size analysers (PSA) have a weakness that could not measure particle size. The result of PSA often tends to be larger. Since, it measures sample particle size depending on their diffusion properties in a solvent from the hydrodynamic diameter. The sample tested must be a dispersion so that the measurement of composite solids is only carried out at a 1:1 composition, due to xanthan gum dissolving in water which makes the measurement only determined by α-$Fe_2O_3$ (Jindal & Khattar, 2018). Moreover, α-$Fe_2O_3$ and α-$Fe_2O_3$-xanthan gum (1:1) have a variety in particle size and distribution is polydispersion with a polydispersity index by 0.14 and 0.387, respectively.

**Table 2.** Particle size of α-$Fe_2O_3$ and α-$Fe_2O_3$-xanthan gum with particle size analyzer (PSA)

| Materials | Particle Size (nm) | Polydispersity Index |
|---|---|---|
| α-$Fe_2O_3$ | 177.56 | 0.14 |
| α-$Fe_2O_3$-xanthan gum (1:1) | 228.43 | 0.387 |

**Analysis of functional groups in α-$Fe_2O_3$-xanthan gum nanocomposite with fourier transform infrared spectroscopy (FTIR).**

**Figure 2** shows the spectrum of α-$Fe_2O_3$-xanthan gum nanocomposite, α-$Fe_2O_3$ nanoparticle, and xanthan gum. The absorption peaks in α-$Fe_2O_3$-xanthan gum nanocomposite have a functional group such as, O-H, C-H $sp^3$, C=O, C-O, dan Fe-O in all composition (Faria et al., 2011; Darezereshki et al., 2012). Those functional groups are a combination between α-$Fe_2O_3$ and xanthan gum but with different percentage of transmittance that indicate the interaction was occur.

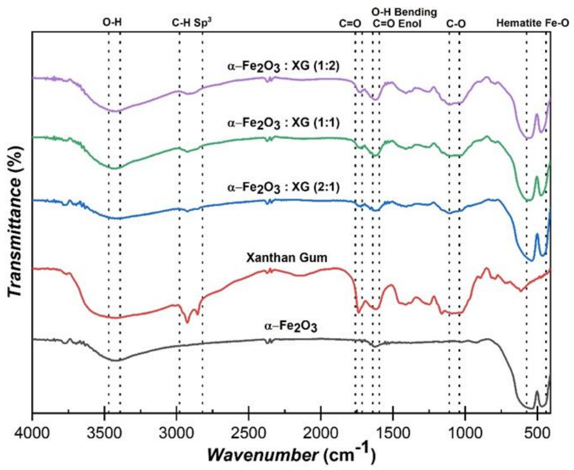


**Figure 2.** FT-infrared spectra of α-$Fe_2O_3$ and α-$Fe_2O_3$-xanthan gum

In 1727 $cm^{-1}$, the transmittance of C=O dropped moderate in α-$Fe_2O_3$-xanthan gum nanocomposite when mass of xanthan gum increase and the opposite mass trend of α-$Fe_2O_3$. In other regions, the transmittance of Fe-O has a slight shift to the high wavenumber from composition 2:1, 1:1, and 1:2. It represents that the interaction takes place between Fe in α-$Fe_2O_3$ with C=O in xanthan gum which the Fe-O bond will be stronger due to this new interaction.

**Analysis of viscosity in nanofluids.**

**Figure 3** describes the effect of xanthan gum on the viscosity of nanofluids. Xanthan gum steeply improved viscosity of fluids to 16.58 cP which is bigger than other nanofluids. This trend has the same impact on nanofluids that dissolved from α-$Fe_2O_3$-xanthan gum nanocomposite, in which the viscosity in composition 1:2 is 1.964 and it is greater than others. This is because xanthan gum has a long and large molecular structure due to repeated bonds of the monomer (Patel et al., 2020) When the interaction between molecules or London force is large, it will result in a significant increase in the viscosity value (Khan et al., 2018). The anomaly condition occurred in composition 2:1 and 1:1, where nanofluids 2:1 have a viscosity more than nanofluids 1:1 by 1.334 cP and 1.182 cP, respectively. It can happen, because nanoparticles also can increase the viscosity of fluids with interactions between molecules α-$Fe_2O_3$ (Rudyak & Krasnolutskii, 2014). Therefore, it can be concluded that α-$Fe_2O_3$-xanthan gum has potential result to in EOR technology based on increasing of the viscosity when compared to $Fe_2O_3$ fluid.

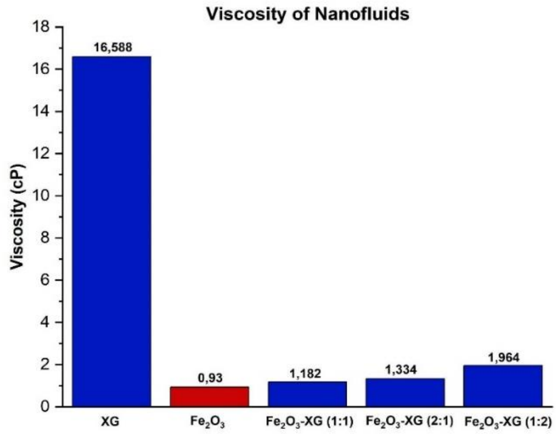


**Figure 3.** Viscosity of nanofluids α-$Fe_2O_3$, α-$Fe_2O_3$-xanthan gum, and xanthan gum

## 4. CONCLUSIONS

The α-$Fe_2O_3$-xanthan gum nanocomposite was successfully synthesized by sonochemical and ex situ methods, respectively. The spectrum of XRD shows that nanocomposite has the main structure as α-$Fe_2O_3$ and an additional peak of xanthan gum at 19.6, 24, 33, 35.5, dan 40.7°. This material belongs to the category of nanoparticles with a size of 228.43 nm (PSA). The functional group that has in α-$Fe_2O_3$-xanthan gum nanocomposite is O-H, C-H $sp^3$, C=O, C-O, and Fe-O, which interaction occurs between Fe from α-$Fe_2O_3$ and C=O from xanthan gum. EOR test in this research presents that xanthan gum is a material that has the function to increase the viscosity of fluids. Gumthermore, α-$Fe_2O_3$-xanthan gum nanofluid is the potential material used in the chemical flooding process in the reservoir.

## ACKNOWLEDGMENTS

This study was financially supported by the UPSKILLING Grant 2021 Universitas Pertamina.

## REFERENCES

Ali, J. A., Kolo, K., Manshad, A. K., Mohammadi, A. H. (2015). Recent advances in application of nanotechnology in chemical enhanced oil recovery: Effects of nanoparticles on wettability alteration, interfacial tension reduction, and flooding. *Egyptian Journal of Petroleum*, 27: 1371-1783.

Ali, J., Manshad, A. K., Imani, I., Sajadi, S. M., Keshavarz, A. (2020). Greenly synthesized magnetite@$SiO_2$@xanthan nanocomposites and its application in enhanced oil recovery: IFT reduction and wettability alteration. *Arabian Journal for Science and Engineering*, 45: 7751-7761.

Cheraghian, G., Rostami, S., Afrand, M. (2020). Nanotechnology in enhanced oil recovery. *Journal of Processes*, 8: 1-17.

Corredor, L. M., Husein, M. M., Maini, B. B. (2019). Impact of PAM-grafted nanoparticles on the performance of hydrolyzed polyacrylamide solutions for heavy oil recovery at different salinities. *Industrial and Chemical Engineering Chemistry Research* , 9888-9899.

Darezereshki, E., Bakhtiari, F., Alizadeh, M., Vakylabad, A. B., M. Ranjbar. (2012). Direct thermal decomposition synthesis and characterization of hematite (α$Fe_2O_3$) nanoparticles. *Materials Science in Semiconductor Processing*, 15: 91-97.

ESDM, K. (2022). *Handbook of Energy & Economic Statistics of Indonesia.* Jakarta: Kementrian ESDM Indonesia.

Faria, S., Petkowicz, C. L., Morais, S. A., Terrones, M. G., Resende, M. M., França, F. P., Cardoso, V. L. (2011). Characterization of xanthan gum produced from sugar cane broth. *Carbohydrate Polymers*, 86: 469-476.

Gbadamosi, A., Yusuff, A., Agi, A., Muruga, P., Junin, R., Jeffrey, O. (2021). Mechanistic study of nanoparticles-assisted xanthan gum polymer flooding for enhanced oil recovery: a comparative study. *Journal of Petroleum Exploration and Production Technology*, 12: 1-7.

Gov, U. S. (2022, March 03). *Enhanced Oil Recovery*. Retrieved from Energy: https://www.energy.gov/fecm/science-innovation/oil-gas-research/enhanced-oil-recovery.

Hassanjani-Roshan, A., Vaezi, M. R., Shokuhfar, A., Rajabali, Z. (2011). Synthesis of iron oxide nanoparticles via sonochemical method and their characterization. *Particuology*, 9: 95-99.

Jang, H. Y., Zhang, K., Chon, B. H., Choi, H. J. (2014). Enhanced oil recovery performance and viscosity characteristics of polysaccharide xanthan gum solution. *Journal of Industrial and Engineering Chemistry*, 21: 1-5.

Jindal, N., Khattar, J. S. (2018). Microbial Polysaccharides in Food Industry. In *Biopolymers for Food Design* (pp. 95-123). Amsterdam: Elsevier Inc.

Joonaki, E., Ghanaatian, S. (2014). The application of nanofluids for enhanced oil recovery: Effects on interfacial tension and coreflooding process. *Petroleum Science and Technology*, 31: 2599-2607.

Kamal, M. S., Sultan, A. S., Al-Mubaiyedh, U. A., Hussein, I. A. (2015). Review on polymer flooding: Rheology, adsorption, stability, and field applications of various polymer system. *Polymer Reviews*, 55: 1-40.

Khan, S., Yusuf, M., Sardar, N. (2018). Studies on rheological behavior of xanthan gum solutions in presence of additives. *Petroleum & Petrochemical Engineering Journal*, 2: 1-7.

Mahato, R. (2017). Chapter 2 - Multifunctional Micro- and Nanoparticles. In *Emerging Nanotechnologies for Diagnostics, Drug Delivery and Medical Devices* (pp. 21-43). Amsterdam: Elsevier Inc.

Mustapha, S., Ndamitso, N. N., Abdulkareem, A. S., Tijani, J. O., Shuaib, T., Mohammed, A. K., Sumaila, A. (2019). Comparative study of crystallite size using Williamson-Hall and Debye-Scherrer plots for ZnO nanoparticles. *Adv. Nat. Sci: Nanosci. Nanotechnol.* , 10: 1-8.

Patel, J., Maji, B., Moorthy, N. S., Maiti, S. (2020). Xanthan gum derivatives: review of synthesis, properties and diverse applications. *RSC Adv.*, 27103–27136.

Pereira, M. L., Maria, K. C., Silva, W. C., Leite, A. C., Francisco, A. D., Vasconcelos, T. L., Nascimento, R. S. (2020). $Fe_3O_4$ nanoparticles as surfactant carriers for enhanced oil recovery and scale prevention. *ACS Applied Nano Materials*, 3: 1-35.

Rellegadla, S., Bairwa, H. K., Kumari, M. R., Prajapat, G., Nimesh, S., N. Pareek, S. J., Agrawal, A. (2018). An effective approach for enhanced oil recovery using nickel nanopaticle assisted polymer flooding. *Energy and Fuels*, 32: 11212-11220.

Rudyak, V. Y., Krasnolutskii, S. L. (2014). Dependence of the viscosity of nanofluids on nanoparticle size and material. *Physics Letters A*, 378: 1845-1849.

Saha, R., Uppaluri, R. V., Tiwari, P. (2019). Impact of natural surfactant (Reetha), polymer (xanthan gum), and silica nanoparticles to enhance heavy crude oil recovery. *Energy and Fuels*, 33: 4225-4236.

Hanemann, T., Szabó, D. V. (2010). Polymer-nanoparticle composites: From synthesis to modern applications, Materials, 3(6): 3468-3517. doi:10.3390/ma3063468

Zhao, F., Liu, Y., Lu, N., Xu, T., Zhu, G., Wang, K. (2021). A review on upgrading and viscosity reduction of heavy oil and bitumen by underground catalytic cracking. *Energy Reports*, 7: 4249-4272.