Introduction

The current trend reports that conventional oil supply will reach its peak and decline due to the never-ending demand and the fact that few new sedimentary basins remain to be exploited (Oldroyd, 2003). Report from International Energy Agency (IEA) showed that a large share of the remaining oil resources was classified as unconventional heavy and extra heavy oil but only a small fraction of total daily oil production came from heavy and extra heavy crude oil (Oil market outlook, 2016). This is why heavy crude oil will play such crucial role in contributing to the world energy source in the future.

Heavy oil production is based primarily on thermal techniques, which revolve around the reduction of oil viscosity. In thermal recovery method, the reservoir is heated by steam or hot water, which result in reduction of viscosity and subsequently improves the mobility of trapped oil (Speight, 2013). During the heat propagation within the oil-bearing matrix, fine particles are leached from the formation rock and dissolved thereafter into the oil. This causes an alteration of physico-chemical properties of the stranded oil (Patel et al., 2018). The presence of fine resident particles has been covered in previous researches, with a main focus given to various types of clays containing silica (SiO₂), alumina (Al₂O₃) and iron oxide, Fe₂O₃ (Pu et al., 2015). Other studies were conducted with the present of limestone, CaCO₃ (Verşan Kök et al., 2017). Yet, specific types of particle have not been focused in the study.

In this study, sandstone reservoir where silica (SiO₂), alumina (Al₂O₃), zinc oxide (ZnO) and ferric oxide (Fe₂O₃) are commonly found (El-Taher et al., 2004) was taken into account. The purpose of this study is to understand the effects of the of those minerals in form of very fine particle that have the possibility to have direct contact with crude via dissolution during thermal process on the physical properties of crude oil. Changes in physical properties in crude oil are crucial to the efficiency of thermal process on oil recovery.

Experimental method

In this study, a dead Japanese heavy oil, HO, was used for the experiments. HO has a density of 0.955 g/cm³ (measured at 15°C), a viscosity of 50 cP (measured at 30 °C) and an API of 16.6°. SiO₂, Al₂O₃, ZnO and Fe₂O₃ nanoparticles (NP) were modeled as fine particles.

The weights of oil and nanoparticles were weighed accordingly to achieve the wanted weight percent of NP in the mixture. The concentration was initially 0.1 wt.% when studying the effect of different types of particle and then varied later up to 1.0 wt.% when studying the effect of the particle amount in the crude oil. The oil was mixed with nanoparticles using a homogenizer (AS ONE Homogenizer AHG-160A Series) to make sure that the mixture is homogeneously well-mixed for the experimental study.

TG/DTA7300 (Hitachi EXSTAR7000 Series) was used in this analysis. The equipment consists of two balance beams; one for experimental sample and another one for referential sample, with which we can detect the smallest change in sample’s weight to the scale of micrograms and the change in temperature of the sample. In thermos-gravimetric (TG) analysis, weight of the sample is measured as the temperature changes in the oven from room temperature to 300 °C under inert nitrogen atmosphere at constant heating rate of 15 °C/minute. At the same time, differential thermal analysis gives the differential temperature between the sample and the reference material \( \Delta T = T_s - T_r \), where \( \Delta T \) is the differential temperature (in °C), \( T_s \) is temperature of the sample (in °C) and \( T_r \) is temperature of the reference material, which is the temperature of the oven in this study (in °C). At the same time, Derivative Thermogravimetry (DTG), which is the rate of sample’s weight change per period of time, can also be derived to show change upon the heating process.

Physical properties of interest were viscosity and density. To more accurately represent reservoir conditions, the samples were put in pressure cell and then heated in the oven at 150 °C for different periods of time, namely 2h, 4h and 6h respectively in order to study the effect of heat as well as the time the crude oil exposed to the heat. The samples were later kept to cool down back to room
temperature so that the properties could be measured. Viscosity were measured by Brookfield Programmable Rheometer (DV-I Prime Series). Density was measured using a pycnometer (10 mL).

**TG/DTA of Blank HO and HO-NP Mixtures**

TG/DTA analyses were carried out for blank HO and several HO-NP mixtures including SiO$_2$, Al$_2$O$_3$, ZnO and Fe$_2$O$_3$. The results are shown in Figure 1.

![Figure 1 TG/DTA curves of blank HO and various HO-NP mixtures](image)

From Figure 1, the percentage of weight loss of the samples, the differential temperature and derivative thermogravimetry (decomposition rate per minute) during the heating process were plotted against the temperature. As the temperature increased, the weight of the samples started to decrease, resulting from evaporation process. It can be seen that among all the samples, HO-SiO$_2$ mixture exhibited both the highest decomposition and differential temperature and the earliest decomposition rate. While other mixtures did not exhibit much of noticeable changes, the temperatures shifted from 157.5 to 150 °C for HO-SiO$_2$ mixture compared to blank HO. The plausible reason behind this alteration could be attributed to the bonding between SiO$_2$ and the heavy fractions of crude oil (asphaltene and/or resins), leaving the lighter fractions more exposed and susceptible to the heat (Franco et al., 2016; Hashemi et al., 2014).

**TG/DTA of Blank HO and HO-SiO$_2$ Mixtures**

The concentrations of SiO$_2$ in oil mixture were varied for further insights. The concentrations were 0.1, 0.25, 0.5 and 1.0 wt.%. The results were shown in Figure 2. TG/DTA curves of blank HO and HO-SiO$_2$ mixture samples to observe the weight change and differential temperature. The increase in differential temperatures and the hastening of decomposition rates were also spotted along with the increase of SiO$_2$-NP concentration. This implies that SiO$_2$, by bonding with the heavy fraction of crude oil, can help fasten the evaporation process as we increased the load of SiO$_2$ in the mixtures. However, as the concentration approached 1.0 wt.%, the trend started to change its pattern.

HO-SiO$_2$ mixture with the concentration from 0.1 up to 0.5 wt.% showed that the decomposition temperatures kept decreasing from 157.4 to 137 °C. However, the number bounced back as the concentration of SiO$_2$-NP hit 1.0 wt.%. From 0.5 to 1.0 wt.%, decomposition temperature advanced back from 137 to 143 °C. The change can be attributed to the fact that the amount of SiO$_2$-NP became excessive in crude oil and the fact that SiO$_2$ has higher tolerance to heat.
Physical Property Measurement

As noticed from TG/DTA analysis, the initial decomposition temperatures of HO and HO-NP mixtures are at approximately 150 °C. Thus, physical properties were observed after heating up the samples in pressure cell to this temperature and let cool down back to room temperature.

Figure 3(a) shows the density of blank heavy crude oil and HO-SiO₂ mixture with various concentrations. As can be observed, the addition of NP seemed to have very little effect on the density of crude after being heated and cooled down back to room temperature. The densities of the mixtures ranged from 0.951 to 0.953 g/cm³ from difference concentrations of particle and different heating periods compared to 0.951 g/cm³ of the blank HO. These changes are still very minimal considering the obtained result. This is due to the fact that the heating of HO-NP mixture process was conducted in enclosed environment which prevented the evaporation process of the light components of crude oil from occurring.

Contrary to density, viscosity measurements, shown in Figure 3(b), showed an opposite trend. The effect of SiO₂-NP looked more prominent on the viscosity. At low concentration, additional particle created less viscous solutions. As the heating process is prolonged, the viscosity is reduced even further. This is can be due to the adsorption of the asphaltene content onto the nanoparticles dispersed in crude oil (Taborda et al., 2016). Furthermore, the increase in heating period also helped increase
the adsorption process, resulting in more reduction in viscosity. In the case of 0.1 wt.% of SiO$_2$-NP, the viscosity is down from 74.47 cP (original blank HO) to 66, 65 and 64.4 cP with the heating period of 2, 4 and 6 hours respectively. This implied that the presence of SiO$_2$-NP can create an in-site upgrade of crude during thermal recovery. However, adding more particles can also increase back the viscosity due to the formation of colloidal system of HO-NP. This can be evidenced in the cases of 0.25 and 0.5 wt.% of SiO$_2$-NP.

Conclusions

- Among the minerals commonly found in sandstone, silica (SiO$_2$) has the most prominent effect on thermal properties of oil as per TGA analysis due to the possible bonding between SiO$_2$ and heavy fractions of crude oil.
- By increasing the load in SiO$_2$-NP, it increases the interaction with heavy fraction of the oil, leaving behind lighter fractions. Thus, the evaporation of light fraction is hastened.
- When heated in the pressure cell, the density of the crude oil and the crude-NP mixture do not significant change, as the evaporation is restricted.
- Contradicted to density, viscosity reduction can be witnessed due to the separation of the heavy components of crude oil that interact with the particles and precipitate. This lead to the in-situ upgrade of heavy oil.

References


*Oil market outlook* (pp. 107–160). [2016]. OECD.


