Effect of Titanium Oxide (TiO2) Nanoparticles on Reduced Crude Oil Residue

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Abstract. Over the last decade, Nanotechnology has been developed and enter in many fields especially in the oil and gas industries such as gas mobility control, sensing or imaging, enhanced oil recovery and other applications. Nanotechnology research and development in the oil and gas industries are very active and this is because of special properties of nanoparticles. The purpose of this paper is to review recent research into the effect of nanoparticles of titanium oxide (TiO2) on reduce crude oil viscosity that produce from atmospheric distillation. RCR has high viscosity and transport of it is very difficult through pipes caused many problems and financial loses so that many treatments are needed to overcome these problems. This research investigated many parameters through three pipes with different diameters (0.0127, 0.01905 and 0.0254 m) I.D., different concentrations (0.00625, 0.0125, 0.01875, 0.025 and 0.0375 (gm/L) w/v) at 50 oC and flow rate is about 50% of maximum. The results of this research: are display below:

- The drag reduction performance is much better in larger pipes diameter than smaller, TiO2 NP's effect on RCR viscosity and the maximum percentage of viscosity deviation is about 1.6% and addition of TiO2 NP's to RCR is reduced pressure drop, %Dr and shear stress.

Keywords: Viscosity Reduction, Drag Reduction, Reduced crude oil Residue, Titanium oxide Nanoparticles.

1. Introduction
The product that is existed from the bottom of atmospheric distillation is a heavy product and has a boiling point above 425oC and it is called reduced crude oil (RCR) (black oil). RCR is the feed of vacuum distillation and the purpose of this process is to fractionate RCR to derivatives so that used it as base oil. The transport of RCR caused many problems through pipes and that because of its high viscosity which waste a large amount of it. The Chemical composition of RCR are Paraffin Hydrocarbons compounds, Naphthenic hydrocarbons compounds, Aromatic Hydrocarbons, Glues, Asphalt and minerals that be existent in crude oil [1].

Many methods are used to decrease viscosity of heavy crude oil to avoid many problems and high costs. The science that improve the flow of fluid through reducing the frictional pressure drop across a pipe or channel is called Drag reduction (DR). The main method used to achieve drag reduction is through adding drag-reducing agents (DRAs) and are usually high molecular mass like surfactants, polymers, or suspended solids which have been known for reducing drag up to 80% [2, 3].
There are many advantages to use Drag Reducers in pipeline systems such as power optimization, throughput improvement, batch management, scheduled maintenance, by passing intermediate pump stations, peak shaving, shortening barge download time and operating pressure reduction [4]. Recently nanotechnology science has involved in many applications one of them is the oil & gas industry application like imaging or sensing, gas mobility control, enhanced oil recovery and other applications [5]. Nanoparticles are a particulate matter which have at least one dimensioned range from 1 to 100 nm. In addition, submicron particles (<1000 nm) possibly will be considered nanoparticles [6, 7]. NPs have a very high surface area proportionate to volume ratio [8].

2. Methods of preparation of titanium oxide

There are two methods are commonly used to prepare Titania (TiO2) flame pyrolysis and stabilized precipitation. The preparation TiO2 nanoparticles is including by oxidizing a solution of titanium tetrachloride (TiCl4) in a flame [9]. Basically the solution of metal-oxide forerunner is spraying into flame, and this led to form oxide particles during the process of burning. This is method does not permit for any in situ-tailored surface fractionalization, and additional reactions that occur because of suspension of material in solvent specifically water. Any charge stabilization of final particles will be a result of The other method that used to prepare TiO2 nanoparticles is hydrolysis of compounds like titanium alkoxides in presence of a capping agent [10, 11]. These methods are adding benefit of further surface fractionalization and size control [12].

There are many researchers study the influence of NPs on viscosity of heavy crude oil by using nanoparticles of various material and with different methods. It observed that the reduction of heavy oil viscosity was for high temperature effect in addition to chemical reactions series known as aqua-thermolysis which change the physical properties [13]. Clark et al. (1990) revealed that heavy oil viscosity is further reduced when aqueous metal is added in comparison to Steam-only experiments [14]. Li et al. (2007) has been found that reduced viscosity, asphaltene content and resin of extra-heavy oil efficiently and this is because of effect of nano-nickel catalyst in reduction of viscosity of Liaohoextra-heavy oil as a result of aqua-thermolysis reaction [15].

Hascakir et al. (2008) examined the effect of micron sized iron particles on viscosity of heavy oil without steam treatment [16]. Chen et al. (2009) found that nano-keggin-K3PMo12O40 is effected on viscosity reduction in catalytic aqua-thermolysis of heavy oil and it changes in oxygen-containing groups basically through catalytic aqua-thermolysis [17].

Hamedi Shokrlu and Babadagli (2010) have been studied the effect of nano-sized metals on reduction of heavy oil/bitumen viscosity throughout thermal applications [18]. I. M. Mahbubul et.al (2011) investigate the frictional pressure drop characteristics of TiO2–R123 nano-refrigerants [19]. Ehsan-ollah Etefaghi et.al (2013) study the effect of CuO nanoparticles on the viscosity of engine oil and conclude that no appreciable change in it [20]. M. Mahbubul et.al (2013) investigated the Migration of TiO2 nanoparticles during the pool boiling of R141b refrigerant under various situations[21].Srinivasan and Shah (2014) discovered that nanoparticles display the ability to improve specific heat of reservoir and thermal conductivity, in addition their ability to enhance density and viscosity of treatment fluids[22]. S. Afzal et.al. (2015) found that TiO2 nanoparticles act as catalytic cracking and add it to heavy oil increased viscosity at different concentration but at 0.5wt% at different temperatures [23].

The objectives of this study is to investigate the effect of titanium oxide nanoparticles on viscosity of RCR, drag reduction and other parameters when transport it through pipeline.

3. Methodology

3.1 Description the system of flow

The system is containing three pipes with length of 6 m and 0.0127, 0.01905 and 0.0254 m inside diameter are arranged from bottom to top and made from carbon steel. As well it contains two tanks, two pumps, valves, flow meter, pressure gauges, digital thermometer, and digital screens. The pipes are
dividing to four sections of Pressure testing and distance between each other is equivalent to 0.5 m. These parts are shown in figure (1).

![Schematic diagram of the flow of system](image)

**Figure 1.** Schematic diagram the flow of system

### 3.2 Material used

**a. Titanium oxide nanoparticles**

The properties of TiO$_2$ nanoparticles are recorded below

| Physical Properties | Value          |
|---------------------|----------------|
| Chemical Formula    | TiO$_2$        |
| Appearance (Color)  | white          |
| Molecular Weight    | 79.866 g/mol   |
| Average particle size | 10-30 nm     |
| Appearance (Form)   | Powder         |
| Surface area (m$^2$/g) | >50 m$^2$/gm |

**b. Reduce crude oil**

RCR that be used in experiment is taken from Al-Samawah refinery. The physical properties are shown in table (2).
Table 2. The physical properties of RCR

| The Viscosity @ 50 °C (c.st) | Sp.gr. | API    |
|-------------------------------|--------|--------|
| 252                           | 0.93   | 20.65  |

3.3 Experiments Procedure
Firstly fill the open tank with RCR and run the system. Then pumping RCR through first, second and third pipe respectively and scored initial readings of pressure after that adding the amount of TiO\(_2\) nanoparticles to open tank and recycle it for 30 minutes to make sure that mixture is mixing very well. Later, repeat previous steps to recognize the improvement. Lastly receiving tank and second pump are used to recycle RCR to the first tank for continuation process.

4. Results and Discussion
4.1 Effect of Pipe Diameter and Reynolds Number
Figures (2-6) show the effect of pipe diameter and Reynolds number on % Dr at different concentrations of TiO\(_2\) nanoparticles at 50 °C. It noticed that %Dr is decreased then increased while shear stress decreased with increased pipe diameter, this occur because of increase in interaction area between RCR and TiO\(_2\) nanoparticles[24].

Re, %Dr and τ have been calculated by equations below:

For laminar flow and fully developed in pipes (Re <2300) for various sections area[25]:-

\[
Re = \frac{ud}{v}
\]

\[
%Dr = \frac{\Delta Pb - \Delta Pa}{\Delta Pb} \times 100
\]

\[
\tau_W = \frac{D\Delta P}{4L}
\]

Figure 2. Effect of pipe diameter on Re at different concentration at 50 °C.
In the same way, %Dr increased with increased Re besides at specific points decreased at different concentration and pipe diameter, which it is predictable as a result of increasing the degree of turbulence inside pipes as Re increases which lead to provide effectively better media drag reducing [13, 26].

**Figure 3.** Effect of pipe diameter on shear stress at different concentration and 50 °C.

**Figure 4.** Effect of Re on %Dr at different concentration at 0.0127 m I.D. and 50 °C.
Figure 5. Effect of Re on %Dr at different concentration at 0.01905 m I.D. and 50 °C.

Figure 6. Effect of Re on %Dr at different concentration at 0.0254 m I.D. and 50 °C.

Figure 7. Effect of conc. on viscosity at different pipes and 50 °C.
4.2 Effect of concentration

Figures (7 and 8) evidence that viscosity and pressure drop are decreased with increased concentration of TiO2 nanoparticles and this is due to breakage C-S bonds in asphaltene which is unstable and this occurs because of exothermic chemical reactions between metal particles and oil phase [16].

![Figure 8](image1.png)

**Figure 8.** Effect of conc. on pressure drop at different s pipes and 50 °C.

4.3 Friction factor

Figures from (9 to 11) display the effect of Re on friction factor. It can be seen that the friction factor was calculated through two equations. The \( f \) which is calculated by equation (2) was smaller than \( f \) in eq.(1)[25]

\[
f = \left(\frac{64}{Re}\right) \quad \text{Poisuell's equation} \quad (4)
\]

\[
f = \frac{\Delta p \cdot d}{4L\left(\rho \cdot u^2 / 2\right)} \quad \text{Fanning equation} \quad (5)
\]

![Figure 9](image2.png)

**Figure 9.** Effect of Re on friction factor at 0.0127 m I.D. and 50 °C.
Figure 10. Effect of Re on friction factor at 0.0127 m I.D. and 50 °C.

Figure 11. Effect of Re on friction factor at 0.0254 m I.D. and 50 °C.

5. Conclusions
The studies have been conducted in the following terms, based on the analytics discussed above:

- Maximum% Dr of 11.3207% at 0.0375(gm/L), 8.696% at all used concentrations except at 0.01875(gm/L) and 31.579% at 0.0375 (gm/L) of TiO2 were obtained flowing in pipes of 0.0127 m, 0.01905 m and 0.0254 m I.D. at 50°C respectively.

- Minimum viscosity values of 249 cSt. at concentration 0.075 (gm/L), 249 cSt. at 0.075 (gm/L) and 248 cSt. at concentrations (0.0375, 0.0625 and 0.075) of TiO2 were obtained flowing in pipes of 0.0127 m, 0.01905 m and 0.0254 m I.D. at 50°C respectively.

- The best addition of NP's at 0.0375 (gm/L) at 0.0254 m I.D., which viscosity equal to 248 cSt.
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Nomenclature

| RCR       | Reduce crude oil Residue | %Dr   | Percentage drag reduction |
|-----------|--------------------------|-------|---------------------------|
| NPs       | Nanoparticles            | Sp.gr | Specific gravity          |
| τ         | Shear stress             | τw    | wall shear stress (bar).   |
| ΔP        | Pressure drop            | P     | The density of RCR         |
| u         | velocity of RCR inside the pipe. | Re     | Reynold number            |
| f         | Friction factor          | ΔPb, ΔPa | pressure drop before and after adding nano- additives. |
| D         | diameter of pipe (m).    | L     | length of pipe (m)        |

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