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Preventing Wax Gelation and Deposition Using Zinc Oxide Nanoparticles

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Abstract

The global population growth and increasing energy demand pose challenges to the Oil and Gas industry, leading to increased exploration and production in offshore and deep-sea areas. Offshore oilfields in colder regions produce crude oils with higher wax content, causing wax deposition and flow assurance issues in pipelines. Nanoparticle inhibitors can mitigate wax deposition in pipelines. In this study, the performance of zinc oxide nanoparticle is evaluated by measurement of degree of viscosity reduction and wax deposition of a Niger Delta crude oil sample. Wax deposition is determined by cold finger technique. 10g of zinc oxide (ZnO) nanoparticle is mixed in 500mL of crude oil sample. From this experiment, it was observed that at 2rpm (revolutions per minute), the degree of viscosity reduction (DVR) was 31% at 10°C and 3% at 15%. Increase in crude oil temperature enhanced the viscosity of the blank sample and the sample blended with ZnO nanoparticle. However, at lower temperatures of 10 and 15C, the viscosity of the blank crude increased. higher, indicating a poor performance of ZnO on the viscosity of the crude oil sample. The addition of 10g of ZnO nanoparticle had more cumulative wax deposit of 16.76g than the blank crude having a cumulative wax deposit in the cold finger as 14.32g. This implies that 10g nano ZnO did not prevent or reduce the wax deposition in the cold finger, but it was efficient at improving the viscosity and flowability of the Niger Delta crude sample.

Keywords: *Viscosity; ZnO; Nanoparticle; Shear stress; Shear rate; Wax deposition.*

1. Introduction

The increasing global population has led to a surge in energy demand, particularly crude oil, which has prompted the oil and gas industry to explore unconventional oil reserves like offshore sub-sea. These reserves face extreme conditions, including high pressure, low temperatures, and corrosive salt water. Pipelines are ideal for transporting crude oil from offshore drilling platforms to processing facilities and refineries. However, high wax content in crude oil, particularly from the Niger Delta basin, poses a challenge to flow assurance in pipelines [1]. The Nigerian oil and gas industry faces challenges like decreased flow rates, pipeline blockages, pressure drop, increased costs, shutdowns, and equipment failure due to wax deposits in Niger delta crude oil, emphasizing the need to prevent wax deposits.

The Niger Delta region is the oil rich region in Nigeria. It covers 7.5% of the country's land area and is the third-largest wetland in the world [2]. The country has a significant reserve of paraffinic crude oils, valued for their high API gravity, low sulphur content, and moderate to high paraffinic wax content [3]. However, these oils have high pour points, making them difficult to work with in low-temperature conditions [4]. This poses a threat to the pipeline system, which transports crude oil from production wells to refineries. Waxiness in Nigeria's crude oil has led to billions of dollars in lost prevention and remediation costs, resulting in decreased production, well closures, pipeline replacements, and abandonment [5].

The production of wax crystals is a key factor in crude oil's poor fluidity at low temperatures [6]. Crystallization, a process that creates a solid system from a chaotic phase, is common in unstable situations [7]. Crude oil molecules move slower at lower temperatures, allowing them to align, cluster, and bind to one another. The wax crystallization process is divided into three steps: nucleation, crystal formation, and aggregation [8]. Nucleation leads to the formation of microscopic solid aggregates, responsible for the supersaturation of paraffin waxes in the oil phase. Crystal growth occurs when wax molecules travel from the bulk to the nuclei, forming an orthorhombic lattice with zigzag patterns. Aggregation occurs when many wax nuclei consolidate to produce wax crystal particles, trapping leftover oil in cage-like structures and clogging the pipeline. Deposition functions as a heat retention mechanism for the system when it forms on the pipeline surface.

To improve production and ensure optimal flow, lots of research has been done to combat the deposition of wax. Recent research has focused on preventing wax problems in waxy crude oil by using chemicals or additives. Some studies have been conducted to evaluate the performance of wax inhibitors, such as hexane, poly(maleic anhydride-alt-1-octadecane) (PMAO) and monoethanolamine (MEA). In research conducted by Maneeintr [9], hexane is shown to be able to lower pour-point temperatures by up to 19.55 percent and lower wax deposits by up to 92.56. For MEA, the percentage of wax deposit ranges from 39.19% to 83.19%, and for PMAO, it ranges from 58.54% to 88.51%.According to the findings, a 10% hexane concentration is preferred, and 5000 ppm of PMAO is needed at higher temperatures and 7500 ppm at lower ones [9].

Zhen *et al.* [10] studied the wax deposition patterns of Malaysian crude oil and the effectiveness of surfactants and their combinations with nanoparticles in inhibiting wax formation. The result showed that the silane-based surfactants significantly reduced wax deposition, by 53.9% and the treated wax deposited as a thin gel-like form, which didn't stick to the cold finger's surface. It was discovered that the concentration, load ratio, residence time, differential temperature, and rotation rate all affected the synergy between the surfactant and nanoparticles.

Nanoparticles (NPs) are tiny materials with size ranging from 1 to 100 nm. They can be classified into different classes based on their properties, shapes or sizes. The different groups include fullerenes, metal NPs, ceramic NPs, and polymeric NPs [11]. NPs possess unique physical and chemical properties due to their nanoscale size and high surface area to volume ratio, which means they have a lot of surface for interaction [12]. These properties make them suitable for application in the oil and gas industry.

Huang *et al.* [13] evaluated the effect of Polymer inhibitors such as nanocomposite pour point depressant (NPPD) created by melting together an organically modified montmorillonite and an ethylene/vinyl acetate (EVA) copolymer. It was found that NPPD exhibits dominated nucleation and a co-crystallization/adsorption mechanism combination, offering a basic and microscopic viewpoint for understanding the mechanism of modification of wax crystallization. Subramanie [14] evaluated the performance of wax inhibitor and nanoparticle, sodium cloisite Na^+, on crude oil viscosity using a Brookfield DV-III viscometer. The nanoparticle alone reduced crude oil viscosity to 92.5%, while EVA and MA reduced it to 88% and 86.4%, respectively. A blend of these substances significantly reduced crude oil viscosity.

At some point during the production and transportation of crude oil, the pour point of the oil has become a major source of concern for flow assurance. In order to keep the fluid from stopping while being transported at temperatures below their pour point, pour point depressants are used as chemical additives.

Solomon and Osokogwu [15] investigated the oil extracted from plant waste material such orange peel (OP) and soya bean husk (SBH) as pour point depressants for Nigerian waxy crude oil, and the pour point values of the following waxy crude oil samples were obtained: 86°F, 75.5°F, 64.48°F, and 75.5°F for the sample without pour point depressant; 80.6°F, 75.2°F, 59°F, and 80.6°F at 2800 ppm for the waxy crude oil samples A and B; and 80.6°F, 75.2°F, 64.48°F, and 80.6°F for the sample doped with toluene. The findings showed that the oils extracted from these agricultural waste products could significantly lower the crude oil's pour points, with orange peel oil (OPO) showing the greatest depression ability. OPO, however, outperformed soya bean husk oil (SBHO) and toluene, suggesting that it could be a good alternative to pour point depressants for waxy.

Alawode *et al*. [16] expanded their research scope by investigating the potentials of aluminium oxide and copper oxide nanoparticles in wax precipitation inhibition. It was found that a decrease in temperature increases wax precipitation, while an increase in nanoparticle concentrations reduces it. The optimal concentrations for aluminium oxide nanoparticles were 0.4,0.3,0.6 and 0.7g.

Subramanie *et. al.* [17] investigated the effect of wax inhibitor and sodium cloisite, Na^+ nanoparticle on wax deposition of Malaysian crude oil through cold finger analysis. This study evaluated the effectiveness of three wax inhibitors: sodium cloisite Na^+ nanoparticle (NP), poly (maleic anhydride-alt-1-octadecene) (MA), and poly (ethylene-co-vinyl acetate) (EVA) in relation to the wax deposition of Malaysian crude oil. Using cold finger analysis, the most effective inhibitor to stop the formation of wax was found. The optimal paraffin inhibition efficiency (PIE) was achieved at 80.91% after treating the crude oil with a 1000 ppm EVA/NP blend and 600 ppm NP. The least amount of wax that formed at 25°C indicates that a cold finger temperature is important in influencing the amount of wax that forms.

Odutola and Idemili [18] conducted research on the effect of temperature on the viscosity of a crude oil sample and the degree of viscosity reduction (DVR) of the crude oil sample in the presence of poly (ethylene-butene) (PEB) and nano-aluminum oxide (Al_2O_3) blend at different temperatures. It was found that the blend with 2000 ppm of PEB with 100 ppm nano-Al_2O_3 is the best for offshore application as it gave the highest DVR of 77.9% and 73.7% at 10°C and 15°C, respectively, while the other blends gave a DVR of about 70% at 10°C and 15°C. The DVR of the PEB/ Al_2O_3 blend significantly decreased as the temperature of the crude sample got closer to the 29°C wax appearance temperature. Other research conducted by this group include studying the effect of aluminum oxide (Al_20_3) nanoparticle on the viscosity of Niger Delta waxy crude at varying temperatures [19], investigating the effect of polyethylene butene (PEB) and xylene on the shear stress of Niger delta crude oil [20], studying the synergistic effect of nano zinc oxide and polyethylene butene in improving rheology of waxy crude Oil [21]. Ofuoku and Odutola [22] applied xylene for crude oil viscosity reduction while Odutola and Oduola [23] conducted an experimental design approach for investigating the influence of various factors on wax deposition in production tubing and pipelines.

Although some works have been done on waxy crude oil gelation and prevention of wax deposition in the Niger Delta, this research investigates the efficacy of ZnO nanoparticle in preventing wax gelation and deposition in Niger Delta crude oil sample using a viscometer and a cold finger apparatus.

2. Methodology

2.1. Material

The materials used in this research include Nigerian Niger Delta crude oil sample and ZnO nanoparticle. ZnO powder has a hexagonal wurtzite structure with a molar mass of 81.38g/mol and size ranging from 20nm to 50nm, It is sublime and has a melting point of $1{,}975^{o}$ C, ZnO NPs are hydrophilic and have a wide energy band gap varying from 3.36 to 3.43 eV.

2.2. Characterization of the crude oil

Physiochemical characteristics of crude oil such as specific gravity and API gravity and total petroleum hydrocarbon (TPH) were determined. Using a hydrometer, the specific gravity and API density were determined empirically. The TPH showing the array of hydrocarbon components (Figure 1) by concentration in the crude was obtained through a gas chromatography (GC-FID) analysis. Gas chromatography with flame ionization detection (GC-FID) is the main technique for TPH analysis because it is quite simple and robust. The result shows a peak in the graph between C_{12} and C_{36} indicating a high presence of these components in the sample under review, with the highest peak points between C_{14} and C_{30}.

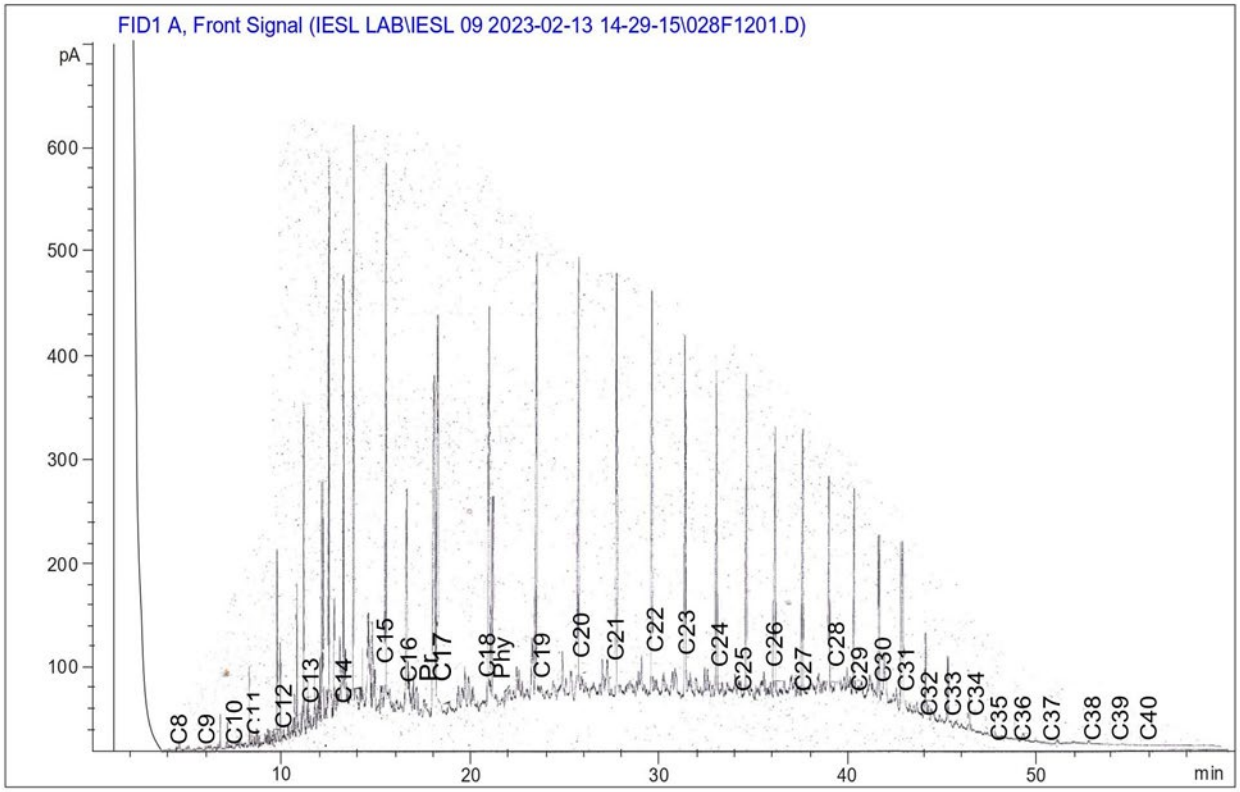

Figure 1. Total petroleum hydrocarbon (TPH) of the crude sample.

2.3. Preparation of nanoparticle sample

2% by weight (10grams) of ZnO nanoparticle sample was weighed and added to 500mL of blank crude oil, it was stirred for 5mins using a JJ-1 Accurate electric stirrer and this was used for viscosity and then wax deposition measurements.

2.4. Viscosity measurement

The apparent dynamic viscosity of crude oil was measured using a Znn-d12 12-speed rotary viscometer. Prior to the viscosity reading, the crude oil was conditioned using a chiller and electric water bath to the required temperature. The dial readings were taken and the viscosity of the blank crude sample (without inhibitor) and the viscosity of the crude oil mixed with the ZnO nanoparticle at different temperatures were obtained using the viscometer.

2.5. Degree of viscosity reduction (DVR)

There is a noticeable decrease in viscosity when nanoparticles are added to crude oil. At different shear rates and various temperatures, the viscosity was measured. A higher DVR denotes a more effective inhibitor. The DVR can be used to evaluate the inhibitors' efficacy. The DVR can be calculated using Eq. (1)

$$\text{DVR}\% = \frac{\mu_{ref} - \mu_{treat}}{\mu_{ref}} \times 100 \quad (1)$$

where μ_{ref} and μ_{treat} are the reference and the after-treatment viscosity values.

2.6. Wax deposition measurement

The mass of wax deposited by the blank crude sample (without inhibitor) and the mass of wax deposited by crude oil mixed with ZnO nanoparticle at different temperatures were obtained using the cold finger apparatus (Figure 2).

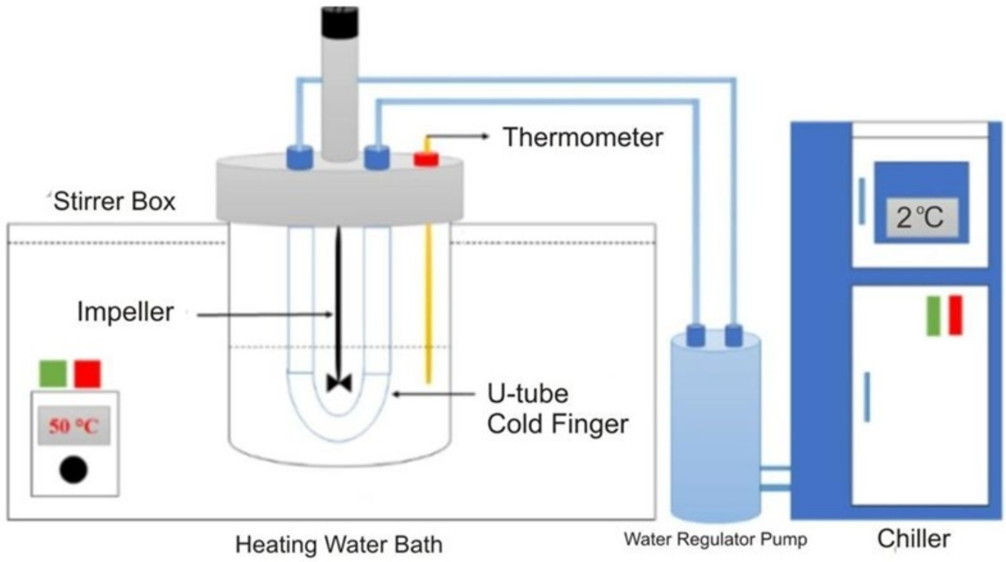

Figure 2. Schematic diagram of the cold finger apparatus.

Figure 3. Wax deposit on U-tube.

The cold finger crude chamber was heated or cooled using a water bath or chiller respectively as required. The duration of this analysis was 30mins per required temperature, 500mL of Niger delta crude oil was added into the cold finger chamber and 10g of ZnO nanoparticle was thoroughly stirred into the crude oil. This mixture was placed in the U-tube chamber and stirred continuously by the impeller for the 30mins time duration. The mass of wax deposited (Figure 3) at the end of the 30mins duration is scraped off and weighed, the temperature of the crude oil and the mass of wax deposit were measured and recorded.

3. Results

The physiochemical properties of the crude sample are as shown in Table 1. The API gravity is 17.45 indicating a heavy crude sample (Table 1). This implies that the crude oil will become viscous as the temperature reduces.

Table 1. Physiochemical properties of the Niger delta crude oil sample.

Parameter	Value
Density, g/cm^3	0.95
^oAPI	17.45

The shear stress against shear rate of the crude oil at temperature between 10°C to 35°C was plotted in Figure 4. Notice that the shear stress gradually increases with increasing shear rate for all temperatures considered in this study and there was a sharp increase in the shear stress at 10.218 s^{-1}. At shear rates lower than 10.218 s^{-1}, the shear stress did not rise significantly because there was little impediment to the flow of the crude oil due to the slow speed of the viscometer. However, as the shear rate is increased to 10.218 s^{-1}, the shear stress increased rapidly due to the wax particles in the crude oil, causing difficulty in flow of the crude oil. This trend continues as the shear rate is further increased to 51.09 s^{-1}, causing even higher shear stress. This is because the fluid experienced higher resistance to flow at elevated shear rate due to the presence of wax content in the fluid.

It was also observed that as the temperature increased, the shear stress reduced. This was the trend for all shear rates considered in this study (Figure 4) but can be seen clearly at shear rate of 51.09 $s^{-1.}$ Increasing the fluid temperature increases the kinetic energy of particles in the fluid, thereby increasing the fluid flow capabilities.

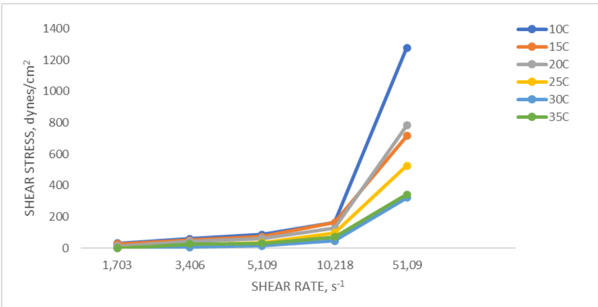

Figure 4. Plot of shear stress against shear rate of blank crude.

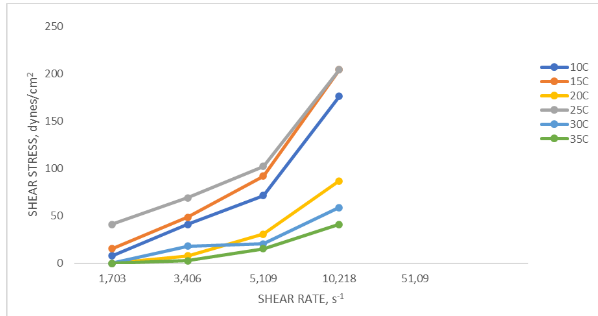

Figure 5: Plot of shear stress against shear rate of crude mixed with 10g zinc oxide.

The plot of sear stress against shear rate for the crude oil mixed with 10g ZnO nanoparticle (Figure 5) shows significant increase in shear stress as shear rate increases from 1.703s^{-1} to 5.109s^{-1} and a maximum increase in shear stress at shear rate of 10.218s^{-1}, this increase in shear stress indicates a the resistance to flow due to the wax components in the crude oil. Like the blank crude, increasing temperatures in the crude/nanoparticle mixture, caused decrease in the shear stress (Figure 5).

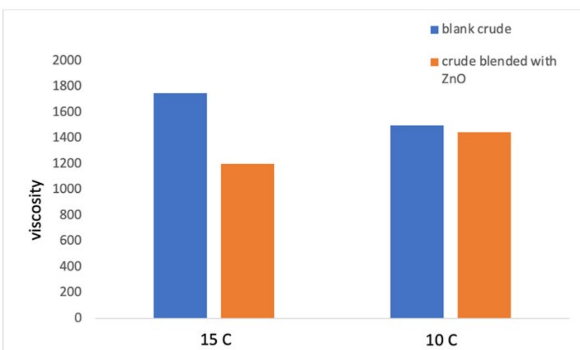

Figure 6. Viscosity of blank crude and viscosity of crude oil blended with zinc oxide against temperature (10 and 15°C).

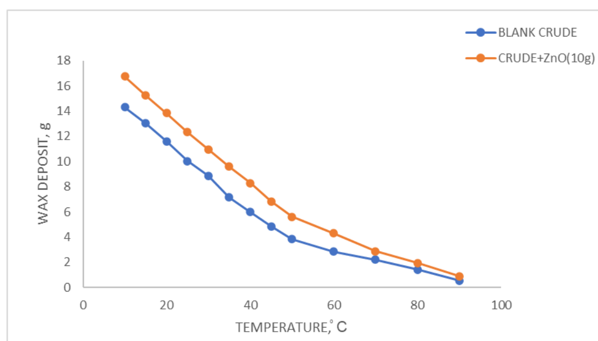

Figure 7. Cumulative wax deposit against temperature.

The effect of the viscosity changes is more evident at cold temperatures of 10°Cand 15°C due to the formation of wax crystals and decreased kinetic energy in the fluid. Hence comparing the effect of ZnO nanoparticle on the viscosity of the crude at 10 and 15°C showed that ZnO reduced the crude oil viscosity at both 10and 15°C (Figure 6), increasing the flowability of the Niger delta crude oil sample.

The degree of viscosity reduction effected by the addition of 10g of ZnO nanoparticles was computed using equation (1) as 31% and 3% respectively at 10°C and 15°C.

3.1. Wax deposition in the cold finger apparatus

The effect of ZnO on the wax deposition tendency of the Niger delta crude sample was analyzed using the cold finger apparatus. The plot of cumulative wax deposit against Temperature (Figure 7) compares the cumulative wax deposition of blank crude oil and crude oil with 10g of ZnO nanoparticle against temperature. This was obtained by summing up the wax deposited as the temperature was stepped down from 35°C to 10°C. The graph shows that at low temperature of 10°C, the crude oil with nanoparticle had more cumulative wax deposit of 16.76g and the blank crude had a cumulative deposit of 14.32g.

Although the ZnO lowered crude oil viscosity at low temperature of 15°C and 10°C, it could not prevent wax deposition in the cold finger apparatus.

4. Conclusion

The effect of ZnO nanoparticle on viscosity and wax deposition was investigated at varying temperature through experimental procedures using a viscometer and a cold finger apparatus. It was observed that increasing the crude oil temperature reduced the crude oil viscosity for the blank crude and the crude oil sample blended with ZnO nanoparticle. Also, the addition of 10g of ZnO nanoparticle to the Niger Delta crude oil sample reduced the crude oil viscosity at temperatures of 10°C and 15°C with a degree of viscosity reduction of 3% and 31% respectively. ZnO did not significantly reduced the wax deposition in the cold finger apparatus. It is therefore recommended that ZnO nanoparticles should be used to enhance the crude oil viscosity and ensure easy flow of crude oil at low temperatures of 10°C and 15°C.

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