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The Effect of Nanoparticles on Heavy Oil Viscosity and Production: Review Article

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Abstract

The effective and inexpensive modification and advancement of heavy crude oil are key to enhancing the discrepancy between the energy source and energy required because of the ongoing exhaustion of easily producible oil resources. Although the abundance of heavy polar components like resins and asphaltenes substantially increases oil's viscosity and makes it difficult for it to flow through pipelines, hence, oil viscosity reduction is crucial going forward. In recent decades, the oil and gas sector has paid special attention to nanoparticles (NPs); now known to be efficient viscosity reducers. The potential roles of NPs as pour point dispersants, emulsifiers, catalysts, and inhibitors of asphaltene precipitation, as well as influencing parameters and limitations, are reviewed in this work. A review of studies on highly stable NPs manufacturing and NPs migration regulations is done. The major goal of this exertion is to present a thorough assessment, identify the shortcomings of previous investigations, and provide some suggestions to clarify the development studies.

Keywords: Nanoparticles, heavy oil production, crude oil viscosity reduction, nano-emulsifiers, nano-surfactants, nano-catalysts

1. Introduction

Due to population growth, economic development, and limited fuel supply, there is a growing and urgent need for energy, which has prompted researchers to explore practical and innovative routes to enhance energy supply [1], develop renewable sources of energy such as biodiesel [2][4], biogas [5], and bioethanol [6][8], and improve energy usage [1]. Above two-thirds of the world's geological oil assets, or roughly 6 billion barrels (bbl.), are thought to be in the form of crude heavy oil, according to the International Energy Agency (IEA). Saturates, aromatics, resins, and asphaltenes make up heavy oils. Individually, saturated and aromatic compounds typically have low heteroatom concentrations and carbon numbers of (38-50) and (41-53) [9]. Asphaltenes are amorphous, non-volatile carbon compounds that exist in colloidal forms, in contrast to resins, which are viscous, sticky, and easily evaporated carbon compounds. According to the American Petroleum Institute (API), the presence of resins and asphaltenes greatly lowers oil API gravity (10-20 API for standard heavy oil and 10 API for extra-heavy oil) and significantly increases oil viscosity (typically 100 mPas at reservoir conditions)[10]. Pipelines cannot transport oils with an API gravity > 19 and a viscosity of 350 cSt at room temperature, according to empirical data [11][113] Therefore, it is difficult to produce heavy oil at all times, especially at low temperatures [12]. To lessen the resistance of heavy/extra-heavy oil flow and their mobility, viscosity must be reduced [13][14]. Nanotechnology has recently sparked a revolution in engineering and research across several sectors. in particular, they characterize, produce, design, and use materials and devices with nano meter-scale construction, ranging from around 1 to 100 nm [15]. Utilizing nanotechnology in oil/gas business offers unmatched opportunities for developing more efficient, environmentally friendly, and cost-effective oil/gas extraction technologies [16-18]. Although NPs are effective emulsifiers [19], efficient pour point depressants and wax deposition agents [20][22], wetting agents[23][24], catalysts[25][26], adsorbents [27][30], interfacial tension reducers [31][33], improvers for diesel engine performance and emissions [34], adsorbents displacing fluid thickeners[35], polyolefin improvers [36], etc., their efficiency and potential for heavy oil exploitation have been covered in various research. The main goal of this work is to discuss the possibilities and difficulties of employing NPs to emulsify heavy crude oil and catalyze oil upgrading based on recent achievements.

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Figure 1 Methods to increase the flow of heavy oil through pipelines.

Paper elements:

1. Title page with author name(s) and affiliation(s)
2. Abstract
3. Keywords
4. Introduction
5. Experimental
6. Results and discussion
7. Conclusion
8. Conflicts of interest
9. Formatting of funding sources
10. Acknowledgment
11. References

2. Production of Heavy Oil

The most cost-effective way to produce heavy oil is to reduce pipeline pressure drop, which reduces the amount of pump power needed to propel the crude oil over long distances [37]. As shown in Fig. 1, there are three ways to carry heavy oil: (1) lowering of viscosity [ex. blending and dilution using light hydrocarbons or solvents, emulsification (oil-in-water emulsion), heavy oil preheating and subsequent pipeline heating, blending and diluting by pour point depressants (PPD)]; (2) reduction of drag/friction (e.g., pipeline lubrication using core-annular flow, or addition of drag-reducing), and (3) in situ partial upgrading of heavy crude yields Syncrude with improved viscosity, (API) gravity, and reduced asphaltenes, heavy metals, and sulphur content[38][41].

3. The Role of Emulsification in Viscosity Reduction of Heavy Crude Oil

Heavy crude oil poses challenges in extraction and transportation due to its high viscosity, which hinders flow through pipelines and reservoirs. Viscosity reduction through emulsification has emerged as a promising solution to enhance the mobility of heavy oil during production processes. This article explores the significance of emulsification in reducing the viscosity of heavy crude oil and the role of various factors, including emulsifiers and nanoparticles, in this process [42][43]. Viscosity reduction through emulsification plays a crucial role in improving the flow properties of heavy crude oil, making it easier to extract and transport. By transforming high-viscosity water-in-oil (W/O) emulsions into low-viscosity oil-in-water (O/W) emulsions, the mobility of heavy oil can be significantly enhanced. This article delves into the mechanisms behind emulsification and its impact on the viscosity of heavy crude oil. Heavy oils contain natural surface-active compounds such as asphaltenes and resins, which promote the formation of high-viscosity W/O emulsions. These emulsions create challenges in oil production due to their resistance to

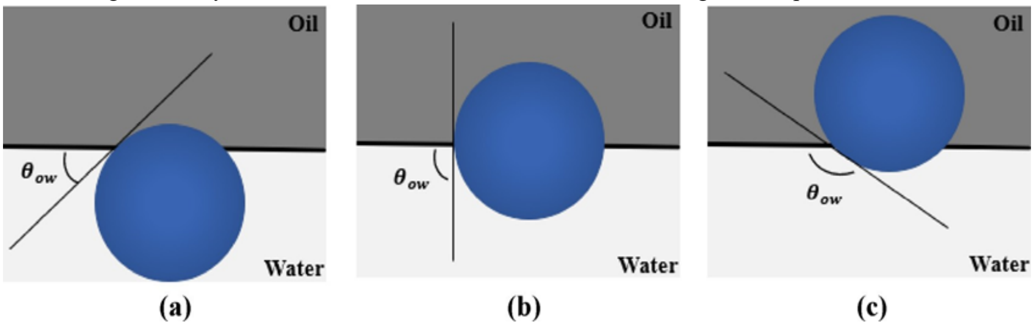

Figure.2 Different hydrophobicity of nanoparticles various how: (a) Hydrophilic, (b) intermediate hydrophobic, (c) hydrophobic.

flow. Understanding the role of surface-active compounds in emulsion formation is essential for devising effective viscosity reduction strategies [44][45]. By adding appropriate emulsifiers, high-viscosity W/O emulsions can be transformed into low-viscosity O/W emulsions. This transformation alters the structure of the emulsion, leading to improved mobility of heavy oil. The use of emulsifiers is critical in modifying the emulsion properties to enhance oil flow characteristics. Surface-active chemicals present in heavy crude oil can alter the wettability of rocks and pipelines, affecting the flow behavior of oil. By promoting water-wet conditions, the frictional resistance within the reservoir or pipeline can be reduced, facilitating the flow of oil. Understanding the adsorption mechanisms of surface-active chemicals is key to optimizing oil recovery processes [47][48]. Surface modification of nanoparticles is a key strategy for enhancing their emulsifying properties. By modifying the surface characteristics of NPs through ex-situ or in-situ approaches, their effectiveness as emulsion stabilizers can be improved. The impact of surface modification techniques, such as covalent grafting and surfactant/polymer physisorption, on emulsion stability is discussed in this section. Emulsions can be stabilized using different methods, with Pickering emulsions relying on solid particles for stabilization, while conventional emulsions use surfactants and polymers. The unique properties of Pickering emulsions, such as stability at high shear rates, make them ideal for viscosity reduction applications. The advantages of Pickering emulsions over conventional emulsions are discussed in this section. Nanoparticles with different degrees of hydrophilicity and hydrophobicity can act as stabilizers for emulsions. While hydrophilic NPs are suitable for O/W emulsions, hydrophobic NPs are commonly used for W/O emulsions. However, challenges arise when highly hydrophobic or hydrophilic NPs fail to reach the oil-water interface efficiently. Strategies for enhancing the emulsifying properties of NPs with intermediate hydrophobicity are explored in this section [56][57].

3.1. The Impact of Nano-Emulsifiers on Viscosity Reduction in Heavy Crude Oil

Nanoparticles (NPs) play a crucial role in stabilizing emulsions and enhancing their properties for various applications, including heavy crude oil production. Through ex-situ alteration, NPs can be tailored to absorb at oil-water interfaces, improving emulsion stability and flow characteristics. This article explores the impact of NP-assisted emulsification on viscosity reduction and oil recovery in heavy crude oil operations. Research by Zhongliang et al. [58] has led to the development of surface anchoring NPs coated with amphiphilic polymers, allowing for adjustable surface hydrophobicity. These hybrid NPs offer flexibility in switching between water-in-oil (W/O) and oil-in-water (O/W) emulsions, providing versatility in emulsion stabilization strategies. The role of surface anchoring NPs in enhancing emulsion stability is crucial for optimizing viscosity reduction processes. Studies by Wang et al. [59] have investigated the emulsification capacity of various NP types, including cellulose nanocrystals (CNCs), SiO2, Al2O3, Fe3O4, and ZrO2. The research findings indicate that increasing NP content results in smaller droplet size and improved emulsion stability. The selection of the right NP type is essential for achieving efficient viscosity reduction and enhancing the flow properties of heavy crude oil. Sulfated CNCs have been identified as efficient emulsifiers for heavy oils under optimal solution conditions, including PH and salinity levels. Careful consideration of the water/oil volume ratio is necessary to prevent the formation of undesired W/O emulsions, especially when dealing with high oil volume fractions. The application of sulfated CNCs highlights the importance of selecting emulsifiers that are compatible with the specific characteristics of heavy crude oil. In field applications, activating naturally existing particles such as clays or asphaltenes can offer acost-effective and advantageous approach to emulsion stabilization. Wang et al.'s research on clay swelling and delamination demonstrates the activation of in-situ nano-clay, leading to improved emulsion stability. This approach provides insights into leveraging existing resources for enhancing emulsification processes in heavy crude oil production [60]. The water/oil ratio plays a critical role in emulsion stability, with high ratios facilitating the stabilization of heavy oil using bentonite. Wang et al.'s findings indicate that at a high water/oil ratio, bentonite in water emulsions can effectively stabilize heavy oil, leading to enhanced flow properties. Understanding the influence of particle concentration and pH on emulsion stability is essential for optimizing the emulsification process. Adjusting PH levels can trigger the release of natural surfactants in heavy oil, enhancing emulsion stability through changes in particle wettability and interfacial tension. However, maintaining a balance between electrical repulsive force and Van der Waals attractive force is crucial to prevent oil coalescence as salinity increases. The interplay between PH, salinity, and emulsion properties is vital for achieving optimal viscosity reduction and oil recovery [61].NP-assisted emulsification not only improves emulsion stability but also enhances sweep efficiency and oil recovery in heavy crude oil applications. Wang et al.'s research highlights the potential for increased oil recovery and improved field performance through the utilization of NP stabilization techniques. The findings underscore the importance of NP-assisted emulsification in optimizing oil extraction processes and maximizing production efficiency [62].

3.2. Enhancing Emulsification Through Np-Surfactant Co-Assisted Stabilization.

The combination of nanoparticles (NPs) and surfactants offers a powerful approach to enhancing emulsion stability and improving oil recovery processes. Modifying the surface of nanoparticles in situ presents practical and cost-effective advantages, allowing for tailored interactions at the water-oil interface [63]. This article explores the synergistic effects of NP-surfactant co-assisted emulsification in optimizing emulsion properties for heavy crude oil applications. Systems that incorporate both nanoparticles and surfactants have been shown to produce superior emulsions, with surfactant molecules effectively interacting with the water-oil interface and nanoparticle surfaces. This interaction leads to the appropriate alteration of hydrophilic properties, enhancing emulsion stability and flow characteristics. Visual representations of these interactions, such as those involving silica nanoparticles (SiNPs) and surfactants, Figure 3 provide valuable insights into the mechanisms of NP-surfactant co-assisted emulsification [64].

Research by Rui Liu and colleagues [66] focused on the synthesis of hydrophilic amine-terminated nano silica particles (ATNPs) and nonionic surfactant laurel monoanolamide (LEMA) molecules. These complementary particles and molecules

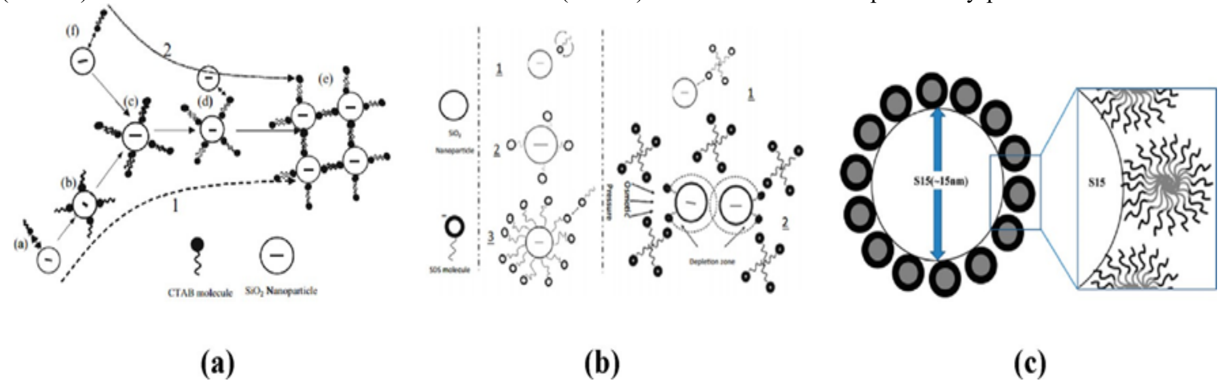

Figure.3 Schematic diagram of surfactant adsorption on hydrophilic SiNPs surface.
(a) cationic surfactant[64], (b) anionic surfactant[64], (c) nonionic surfactant[65].

with hydrogen bonding functionalities bind at the oil/water (O/W) interface, offering a method for in-situ preparation of O/W emulsions without phase inversion points. The study highlights the potential for tailored interactions between nanoparticles and surfactants to enhance emulsion stability and viscosity reduction.

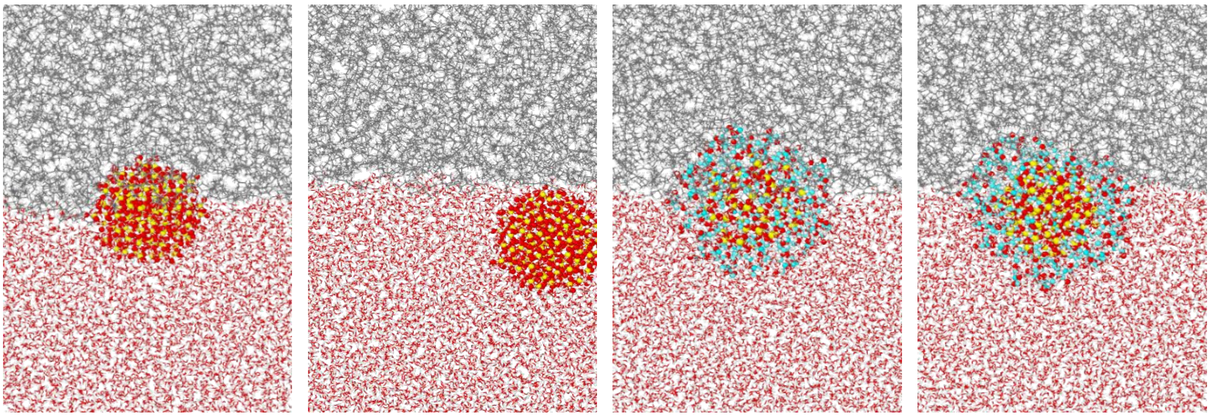

Figure.4 [68]. Snapshots of O/W interface with different SiO2 NPs oil (top layer), and water (dwon layer). (1) SiO2OH NPs, Initial state, (2) SiO2-OH NPs, Equilibrium state, (3) SiO2-GLYMO NPs, Initial state, and (4) SiO2-GLYMO NPs, Equilibrium state.

Studies by Raman et al. [67] investigated the effects of nonionic surfactant Span 80 on Pickering emulsions stabilized by hydrophobic fumed silica particles. The addition of surfactant molecules resulted in changes in droplet size and emulsion viscosity, with implications for emulsion stability. Understanding the interplay between surfactants and nanoparticles in Pickering emulsions is crucial for optimizing emulsion properties and enhancing oil recovery processes. Zhong et al. [68] examined the stabilization of SiNPs co-stabilized with zwitterionic surfactant CAPHS, leading to enhanced surface charge and improved emulsion stability. The adsorption of surfactant molecules on SiO2-GLYMO NPs altered the interaction between nanoparticles and cations, creating a more water-wet environment. These changes were beneficial for water imbibition and oil displacement processes, highlighting the potential of NP-surfactant co-assisted emulsification in enhancing oil recovery efficiency. Research by Bashir et al. [69] demonstrated the significant improvement in heavy oil recovery through the combination of hydrophilic silica with cationic surfactants such as dodecyl or cetyl trimethyl ammonium bromide (C12TAB/C16TAB). The synergistic effects of these combinations on emulsion stability and oil recovery underscore the potential of NP-surfactant co-assisted emulsification in optimizing heavy oil extraction processes.

3.3. Advancing Emulsification Through Responsive Pickering Emulsions

Responsive Pickering emulsions play a crucial role in heavy oil production, offering stability benefits during the oil displacement process. However, the inherent stability of these emulsions can present challenges during demulsification stages. To address this issue, researchers have focused on developing Pickering emulsions that respond to specific stimuli, such as light oils, acid/alkali, CO2/N2, and oxidizer/deoxidizer.

Table 1 :An overview of current developments in responsive Pickering emulsions

Ref.	NP	Modifier	Stipulations	Stimulus	Rusalt
[70]	SiO2	FA-DMDA-Ox	Oil phase: paraffin oil, n-octane, or toluene Oil fraction: 50 %(v/v) C(NP): 0.5 wt%	Redox, pH	Stable when adding NaOH or H2O2 but phase separate when adding HCl or Na2SO3
[71]	SiO2	C14PAO	Oil phase: n-decane Oil fraction: 60 %(v/v) C(NP): 0.5 wt%	CO2	Stable when exposed to CO2 and phase separate when exposed to N2
[72]	SiO2	Lignin	Oil phase: soybean oil, n-decane or paraffin Oil fraction: 50 %(v/v) C(NP): 0.5 wt%	pH	Stable at pH = 3–4 but phase separate at pH > 4
[73]	Pd-SiO2	[C4AzoC2-8DMEA]Br	Oil phase: n-octane C(NP): 0.5 wt%	UV/vis light	Stable when exposed to UV-light and phase separate when exposed to vis-light
[74]	Fe3O4	Poly(PDMNC)	Oil phase: hexadecane Oil fraction: 30 %(v/v) C(NP): 0.05 wt%	Magnetic, pH	Stable at pH = 5–9 upon magnetic exposure
[75]	Starch	Poly(DMAEMA)	Oil phase: grape oil Oil fraction: 33.3 %(v/v) C(NP): 1.0 wt%	pH	Stable at pH > 6
[76]	Na- MMT	Alginate	Oil phase: liquid paraffin wax Oil fraction: 50 %(v/v) C(NP): 2.0 wt%	pH, salt	Stable at pH = 5–7 but phase separate when salt concentration > 10 mM
[77]	Graphene QDs	Alkyl groups	Oil phase: dodecane Oil fraction: 10 %(v/v) C(NP): 0.001 wt%	pH	Phase separate at pH < 2 or pH > 12

This article explores the advancements in responsive emulsification and the tailored structures of emulsifiers to meet the diverse needs of heavy oils. The development of stimuli-responsive Pickering emulsions has been a significant area of research, with a focus on controlling emulsion properties through external stimuli. Li et al. synthesized a dual-responsive Pickering emulsion stabilized by silica nanoparticles (SiNPs) and a redox and pH-responsive surfactant. This innovative emulsion could be reversibly controlled by alternating the addition of Na_2SO_3 and H_2O_2 or by alternating the addition of HCl or NaOH. The ability to respond to specific stimuli offers new possibilities for manipulating emulsion stability and demulsification processes in heavy oil production. Traditional emulsification methods face challenges in heavy oil applications, including limited adaptability for oils with diverse compositions, corrosion issues, and low stability in harsh environmental conditions. The development of cost-effective emulsifiers with excellent thermal stability is essential for overcoming these challenges and optimizing emulsion performance in heavy oil extraction processes. Addressing these challenges will pave the way for more efficient and sustainable oil recovery practices [70].

4. Pour Point Depressants function to improve the low-temperature operability of fuel oils.

A Pour Point Depressant (PPD) is an additive used in fuel oils to lower the temperature at which the oil stops flowing, known as the pour point. The pour point is an important characteristic of fuel oils, especially in cold climates, as it determines the lowest temperature at which the fuel can be pumped and used effectively.

Fuel oils can become viscous and even solidify at lower temperatures due to the presence of wax crystals that precipitate out of the oil and form a solid matrix. This can lead to operational issues in engines and fuel systems, such as clogged filters and poor fuel flow.

Pour Point Depressants work by interfering with the formation and growth of wax crystals. They are typically polymers or copolymers that absorb onto the surface of the wax crystals, altering their shape and preventing them from aligning and forming a solid network. This allows the fuel to remain fluid at lower temperatures, ensuring that it can be pumped and burned efficiently even in cold conditions.

The use of Pour Point Depressants is particularly important for diesel fuels, heating oils, and other fuel oils that are used in cold environments. By improving the low-temperature operability of these fuels, PPDs help to ensure reliable performance and reduce the risk of equipment failure due to fuel gelling or solidification.

Pour Point Depressants (PPDs) improve the low-temperature operability of fuel oils by inhibiting the formation and growth of wax crystals, which are responsible for the increase in fuel viscosity and eventual solidification at lower temperatures. Here’s a detailed look at how they function:

Adsorption onto Wax Crystals: PPDs are typically polymers or copolymers that adsorb onto the surface of wax crystals as they begin to form in the fuel oil. This adsorption process is driven by the affinity of the polymer chains for the wax molecules.

Alteration of Crystal Structure: Once adsorbed, the PPD molecules disrupt the natural alignment and growth of the wax crystals. They can alter the shape and size of the crystals, preventing them from forming the large, interlocking structures that contribute to the solidification of the fuel.

Formation of Smaller, Dispersed Crystals: Instead of large, networked crystals, the presence of PPDs leads to the formation of smaller, more dispersed wax crystals. These smaller crystals are less likely to aggregate and form a solid mass, which helps maintain the fluidity of the fuel oil at lower temperatures.

Reduction of Crystal Interaction: PPDs can also act as a physical barrier between wax crystals, reducing their ability to interact and coalesce. This further prevents the formation of a continuous solid phase within the fuel.

Enhanced Cold Flow Properties: By inhibiting the formation of large wax crystals, PPDs effectively lower the pour point of the fuel oil. This means the fuel can remain fluid at lower temperatures, ensuring it can be pumped and used efficiently in cold conditions.

Improved Fuel Stability: Some PPDs also have antioxidant properties, which can help stabilize the fuel against oxidation. This can improve the overall stability and longevity of the fuel, reducing the risk of degradation over time.

5. Nanoparticle types and application

Nanoparticles are particles with at least one dimension sized from 1 to 100 nanometers (nm). They can be engineered for various applications due to their unique properties, which often differ significantly from those of their bulk materials. The applied nanoparticle types and their sizes can vary widely depending on the intended use. Here are some common types of nanoparticles and their typical size ranges:

Metal Nanoparticles: These include gold, silver, platinum, and iron nanoparticles. They are used in catalysis, electronics, and medical applications. Size can vary, but they are often in the range of 2-100 nm.

Metal Oxide Nanoparticles: Examples include titanium dioxide (TiO_2), zinc oxide (ZnO), and iron oxide (Fe_3O_4) nanoparticles. These are used in sunscreens, gas sensors, and magnetic storage devices. Their sizes typically range from 10 to 100 nm.

Quantum Dots: These are semiconductor nanocrystals, such as cadmium selenide (CdSe) or indium arsenide (InAs). They are used in biomedical imaging, solar cells, and LEDs. Quantum dots are usually 2-10 nm in size.

Carbon-based Nanoparticles: This category includes carbon nanotubes (CNTs), fullerenes, and graphene. CNTs are used in electronics and composite materials, fullerenes in drug delivery and cosmetics, and graphene in electronics and energy storage. Their sizes can vary; for example, CNTs can be a few nanometres in diameter and up to several micrometres in length.
Lipid Nanoparticles: These are used in drug delivery systems, including vaccines. They encapsulate drugs or genetic material to protect them from degradation and facilitate their entry into cells. Lipid nanoparticles can range from 50 to 200 nm.
Polymer Nanoparticles: These are made from natural or synthetic polymers and are used in drug delivery, coatings, and packaging. Their sizes typically range from 10 to 1000 nm.
Ceramic Nanoparticles: These include silica (SiO_2) and alumina (Al_2O_3) nanoparticles. They are used in abrasives, coatings, and biomedical implants. Their sizes usually range from 5 to 100 nm.
Dendrimers: These are highly branched, spherical polymeric nanoparticles used in drug delivery, catalysis, and imaging. They can range from 1 to 20 nm.
The specific applications for each type of nanoparticle can be quite diverse, depending on their unique properties. Here's a more detailed look at the applications for the types of nanoparticles mentioned:

5.1. Metal Nanoparticles:

Gold Nanoparticles: Used in biosensing, medical diagnostics, drug delivery, and cancer therapy due to their biocompatibility and ease of functionalization.
Silver Nanoparticles: Known for their antimicrobial properties, they are used in wound dressings, food packaging, and water purification.
Platinum Nanoparticles: Used as catalysts in chemical reactions, fuel cells, and in the treatment of cancer.
Iron Nanoparticles: Employed in magnetic storage devices, targeted drug delivery, and environmental remediation for the removal of pollutants.

5.2. Metal Oxide Nanoparticles:

Titanium Dioxide (TiO_2): Used in sunscreens and cosmetics for UV protection, in paints for self-cleaning surfaces, and as a photocatalyst for water and air purification.
Zinc Oxide (ZnO): Utilized in sunscreens, skin care products, and as an additive in rubber and plastics for its UV-blocking and antibacterial properties.
Iron Oxide (Fe_3O_4): Employed in magnetic resonance imaging (MRI) contrast agents, targeted drug delivery, and as a catalyst in various chemical reactions.

5.3. Quantum Dots:

Used in high-definition displays, solar cells, and biomedical imaging due to their ability to emit light in various colors based on their size and composition.

5.4. Carbon-Based Nanoparticles:

Carbon Nanotubes (CNTs): Used in electronics (e.g., transistors, sensors), energy storage (e.g., batteries, supercapacitors), and as reinforcement in composite materials for aerospace and automotive applications.
Fullerenes: Employed in drug delivery systems, cosmetics, and as antioxidants in various products.
Graphene: Used in electronics (e.g., transparent conductors, touch screens), energy storage (e.g., batteries, supercapacitors), and as a reinforcement material in composites.

5.5. Lipid Nanoparticles:

Used primarily in drug delivery systems, including vaccines (e.g., mRNA vaccines), to enhance the stability and efficacy of therapeutic agents.

5.6. Polymer Nanoparticles:

Employed in controlled drug release systems, coatings for sustained release, and in packaging to improve barrier properties and enhance product shelf life.

5.7. Ceramic Nanoparticles:

Silica (SiO_2): Used as a filler in composites, in chromatography for separation processes, and in personal care products for its flow and texture properties.
Alumina (Al_2O_3): Utilized in abrasives for sandpaper and grinding wheels, in ceramics for high-temperature applications, and in biomedical implants due to its biocompatibility.

5.8. Dendrimers:

Used in drug delivery to encapsulate and protect therapeutic agents, in gene therapy, and as catalysts in chemical reactions due to their well-defined structure and multifunctional surface.

6. Revolutionizing Heavy Oil Upgrading With Nano-Catalytic Technology

Heavy oil upgrading involves the continuous conversion of heavy substances into lighter hydrocarbons and gases, improving the quality of the oil and facilitating its flow. The conversion of asphaltene into saturated hydrocarbons plays a crucial role in enhancing oil properties and aiding in its transportation. Catalytic upgrading is a key process that utilizes suitable catalysts to prevent undesired reactions, leading to more environmentally friendly pathways for heavy oil upgrading. The use of catalysts in heavy oil upgrading processes is essential for promoting selective reactions that enhance oil quality while avoiding the formation of undesired by-products such as partially oxidized hydrocarbons, difficult-to-break emulsions, and cokes [78][79]. By employing suitable catalysts, the pathways of heavy oil upgrading can be tailored to be more environmentally friendly,

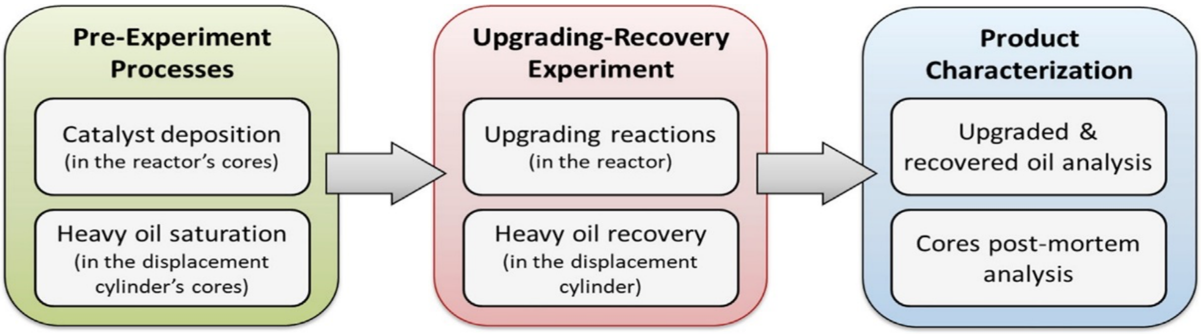

Figure.5 Flow chart of upgrading experiment with dispersed catalysts [78].

ensuring efficient conversion and improved oil properties. Nano-catalytic upgrading represents a novel approach to enhancing the quality of heavy and extra-heavy oil using nano-sized catalysts(fig.5). Transition metals such as Mo, Al, V, Cr, Mn, Fe, Co, Ni, Sc, Sn, and Cu are commonly employed as catalysts in various chemical processes. Nano-catalysts offer advantages in dispersibility, recyclability, and eco-friendliness, making them preferred over ionic solutions for catalytic applications in heavy oil upgrading [80][81]. Nano-catalysts possess an elevated surface-to-volume ratio, enhanced thermal properties, and increased capacity to absorb heavier components, promoting catalytic reactions more effectively. Their heightened mobility allows for greater contact with reactants, reducing the risks of coke formation, asphaltene precipitation, and catalyst deactivation. Additionally, nano-catalysts exhibit superior thermal conductivity, further enhancing their efficiency in catalytic processes for heavy oil upgrading [82]. Nanoparticles used as catalysts in heavy oil upgrading can be synthesized through top-down and bottom-up approaches, enabling precise control over particle shape, size, and surface functionality. Careful selection of process parameters allows for the creation of nanoparticles with tailored properties that optimize catalytic performance and enhance the efficiency of heavy oil upgrading processes. The utilization of nano-catalysts in heavy oil upgrading offers several advantages, including enhanced mobility for improved reactant contact, mitigation of undesirable reactions, and superior thermal conductivity. Nano-catalysts play a crucial role in promoting efficient catalytic reactions, reducing by-product formation, and enhancing the overall quality of upgraded heavy oil. Significant progress has been made in the application of diverse nano-sized heterogeneous catalysts in heavy oil upgrading. Transition metals, alloys, oxides, sulphides, carbides, and phosphides are among the materials utilized for catalytic processes, demonstrating the versatility and effectiveness of nano-catalysts in enhancing heavy oil properties and promoting sustainable oil extraction practices [78].

6.1. Transition Metal Nanoparticles For Efficient Heavy Oil Upgrading

The interactions between the d-orbitals in the catalytic center of transition metal catalysts and reactants play a pivotal role in catalytic processes. Transition metals such as iron (Fe), nickel (Ni), and molybdenum (Mo) are highly sought after as catalysts due to the abundance of electrons on their d-orbitals. Among these, Ni-based nanoparticles (NPs) have emerged as promising catalysts for the upgrading of heavy oil, offering cost-effectiveness and high catalytic activity [85]. Ni-based nanoparticles exhibit great potential in catalyzing the conversion of heavy oil into lighter components. Their low cost and high activity make them desirable catalysts for enhancing the efficiency of heavy oil upgrading processes. The unique properties of Ni-based nanoparticles make them effective in catalyzing the breakdown of complex hydrocarbons in heavy oil, leading to improved oil quality and flow characteristics. IN a study conducted by Aliev, Firdavs et al. [86], steam stimulations were performed on mixtures of heavy oil and distilled water with and without nano catalysts. The nano catalysts efficiently facilitated the breakdown of bonds between carbon, oxygen, and sulfur atoms in the heavy oil mixture. The addition of Ni NPs stabilized by xanthan gum resulted in the conversion of asphaltene into lighter components, leading to a significant decrease in oil viscosity and an increase in overall oil recovery. The incorporation of Ni NPs in heavy oil upgrading processes led to the conversion of asphaltene into lighter components, contributing to a notable decrease in oil viscosity. The application of Ni NPs resulted in a 5% increase in overall oil recovery, highlighting the effectiveness of these nanoparticles in enhancing oil extraction and processing efficiency. While Ni-based nanoparticles offer significant benefits in heavy oil upgrading, the performance of catalysts may deteriorate over time, necessitating adjustments in deployment strategies. Utilizing microwaves for the fragmentation of heavier components by nano-Fe and micro-Cu presents a solution to enhance catalytic efficiency and prolong catalyst lifespan in heavy oil upgrading processes.[87] Zero-valent transition metals have the potential to promote hydrocracking and prevent the deposition of coke in heavy oil upgrading processes. These metals play a crucial role in enhancing catalytic efficiency, improving oil quality, and facilitating the conversion of heavy substances into lighter hydrocarbons and gases [88].

6.2. Advancing Heavy Oil Upgrading With Transition Metal Oxide Catalysts

Transition metal oxide catalysts offer numerous advantages over traditional transition metal catalysts, including cost-effectiveness, stability, and ease of production. In heavy oil upgrading processes, transition metal oxide catalysts play a crucial role in reducing viscosity and improving oil quality. The utilization of transition metal oxides presents a promising approach to enhancing the efficiency and sustainability of heavy oil extraction and processing. In aqua thermolysis, green FexOy catalysts, including a-Fe2O3, c-Fe2O3, and Fe3O4, are commonly used for reducing viscosity in heavy oil. Studies on the catalytic performance of Fe2O3 nanoparticles (NPs) on Canadian heavy oil have shown significant improvements, with increased API gravity and reduced viscosity. However, challenges such as particle aggregation at high temperatures have been observed, necessitating innovative solutions to enhance catalytic effectiveness [89]. To address issues of particle aggregation and loss of active sites in Fe2O3 NPs, Chernozem grafted an oleic acid layer onto the surfaces of the nanoparticles. This modification led to improved dispersibility, stability of the oil phase, and overall catalytic effectiveness. The oleic acid layer played a crucial role in mitigating aggregation tendencies and enhancing the performance of Fe2O3 NPs in heavy oil upgrading processes [91]. Apart from FexOy catalysts, transition metal oxides such as Co3O4, NiO, CuO, and MoO3 show promise as catalysts for heavy oil upgrading. Studies have demonstrated the effectiveness of NiO NPs in reducing viscosity during oil cracking reactions and the successful application of MoO3 catalysts in decreasing oil viscosity and sulfur concentration. Additionally, CuO NPs have been utilized to convert asphaltene into lighter components, leading to a significant reduction in oil viscosity [92]. Researchers have developed innovative molybdenum oxide (MoO3) and copper oxide (CuO) catalysts for heavy oil upgrading. The application of MoO3 catalysts resulted in a substantial decrease in oil viscosity and sulfur concentration, showcasing the potential of MoO3 in enhancing oil quality. Similarly, the in-situ preparation of well-dispersed CuO NPs using Cu (OH)2 microemulsion led to significant asphaltene conversion and viscosity reduction, highlighting the effectiveness of CuO NPs in catalyzing heavy oil upgrading processes [94]. CuO NPs have demonstrated remarkable efficiency in converting asphaltene into lighter components, resulting in a substantial reduction in oil viscosity. The catalytic properties of CuO NPs, coupled with their ability to promote asphaltene conversion, make them valuable catalysts for improving heavy oil quality and flow characteristics. The significant reduction in oil viscosity achieved through CuO NPs catalysis underscores their potential in enhancing heavy oil upgrading processes.

6.3. Enhancing Heavy Oil Upgrading With Multi-Metal And Multi-Metal Oxide Nano Catalysts

The utilization of Nano catalysts composed of multi-metals, such as NiWMo, NiMo, NiW, CoMo, and others, has shown synergistic effects in improving outcomes in heavy oil upgrading processes. These multi-metal compositions offer enhanced efficiency and catalytic performance, leading to significant improvements in oil quality and flow characteristics. In a study conducted by Elahi et al., NiMo ultra dispersed nano-catalysts were introduced into vacuum residue (VR), and the co-injection of hydrogen and VR under optimal conditions resulted in a remarkable decrease in oil viscosity and API gravity.
Table 2: An overview of recent developments in improving heavy oil with conventional Nano catalysts.
The application of NiMo Nano catalysts showcased the effectiveness of multi-metal compositions in catalyzing heavy oil conversion and enhancing oil properties. Nano catalysts containing multi-metals like NiWMo, NiMo, and NiWCo have demonstrated advantages in catalyzing hydrocarbon oxidation and improving catalyst dispersity in the oil phase. The synergistic effects of multi-metal compositions contribute to enhanced catalytic activity, leading to more efficient and effective heavy oil upgrading processes. CoFe2O4 bimetallic oxide nanoparticles were synthesized hydrothermally and coated with oleic acid to ensure full contact with heavy hydrocarbons. The study revealed a significant increase in total heat release when applying

CoFe2O4 and CoFe2O4@oleic acid nanoparticles, indicating the enhanced catalytic performance and efficiency of bimetallic oxide Nano catalysts in heavy oil upgrading [95][96][97].

7. Tables And Figures Understanding Nanoparticles Retention And Transfer In Porous Media

Table 2: An overview of recent developments in improving heavy oil with conventional Nano catalysts.

Ref.	Nano-catalyst	Properties of feedstock	Conditions	Rusalts
[94]	CuO NP	l = 24,150 ± 100 mPas	Aqua thermolysis 180–260°C, 2.5 MPa (N2)	Viscosity reduced by 94.6 % Asp. conversion = 22.4 %
[97]	Ultra dispersed NiMo	l = 37,333 mPas at 100 C API gravity = 1.1 C(sulfur) = 5.02 wt%	350°C, 48 h 10 MPa	Viscosity reduced by 99.8 % API gravity increase by 8 API
[99]	NiFe NP (Spherical 1–20 nm)	API gravity = 13.1 C(C5-Asp.) = 32.5 wt%	372°C, 1 h 9.8 MPa (H2, Initial)	API gravity increased by 40.0 % Asp. conversion = 37.2–43.7%
[100]	Ni3Fe NP (Octagon-like, 120 nm)	l = 18.5 cSt at 25°C q = 1015 kg/m3 C(C5-Asp.) = 32.5 wt%	250°C, 2 h 10 bar (H2)	Viscosity reduced by 74.6 % TOC reduced by 19.6 %
[101]	NiO–PdO/CeO2±d	l = 6 106 mPas at 20°C API gravity = 6.4 C(sulfur) = 5.31 wt%	Steam flooding 210°C, 12 h	Asphaltene reduced by up to 71 % Viscosity reduced by up to 85 %
[102]	Nickel NP	l = 539.8 mPas at 50°C API gravity = 15.86 at 15.56 ◦C	Microwave-assist 68–90°C	Viscosity reduced by up to 96.81 % Resin/Asp. reduced by 17.3 wt%
[103]	Iron oxide NPs (Rivet-like)	l = 244520 mPa·s at 50°C	200°C, 24 h	Viscosity reduced by 37.8 %

Nanoparticles play a crucial role in reducing heavy oil viscosity, altering wax crystallization, preventing asphaltene precipitation, and catalyzing heavy oil upgrading. However, the behavior of NPs in complex subsurface porous materials remains a challenge. Understanding how NPs interact and move within porous media is essential for optimizing their effectiveness in oil recovery processes. The mobility of NPs in porous media is influenced by factors such as particle aggregation and their distribution within the porous structure.

NPs that are well-dispersed and connected to solid surfaces are expected to move smoothly in porous media, impacting their availability and contact with hydrocarbon molecules. The adsorption of NPs on rock surfaces is influenced by particle size, mass density, and the formation of monolayers on solid surfaces [104]. The adsorption of NPs on rock surfaces is crucial for their retention and mobility in porous media. The adsorption behavior of NPs is affected by factors such as particle size, mass density, and the presence of monolayers on rock surfaces. Understanding the adsorption characteristics of NPs is essential for predicting their behavior in subsurface environments [105]. The recovery of NPs from porous media is influenced by the concentration of ions such as Ca2+ and Mg2+. The formation of salt bridges can impact the efficiency of NPs recovery, with higher ionic concentrations leading to reduced NPs recovery. The interaction between NPs and ions plays a significant role in determining the fate of NPs in porous media. The deposition and migration of NPs in porous media, such as TiO2 NPs, exhibit specific patterns and behaviors. Factors like surface roughness, temperature, and formation heterogeneity influence the retention of NPs in porous media. Understanding the deposition and migration patterns of NPs is crucial for predicting their movement and behavior in subsurface environments [107]. Increased retention of NPs in porous media can lead to enhanced wettability alteration and catalytic efficiency in heavy oil recovery processes. The retention of NPs plays a significant role in altering the surface properties of porous media and enhancing the catalytic activity of NPs in oil recovery operations. In reservoirs with ultra-low permeability, the retention of NPs can pose challenges such as pore plugging and irreversible permeability degradation. Understanding the impact of NPs retention on reservoir performance is essential for optimizing oil recovery strategies and mitigating potential risks associated with NPs mobility in subsurface environments [108].

8. Enhancing Nps Stability

Nanoparticles face challenges such as collision, agglomeration, and precipitation at elevated temperatures and salinities, impacting their stability and efficiency. Developing stable NPs that can withstand harsh conditions is crucial for ensuring optimal performance in various applications. To enhance NPs stability, the synthesis of hydrophilic or partially hydrophobic

NPs is recommended, as they exhibit better tolerance to harsh environments. Employing electrostatic, steric, and electrostatic stabilization techniques can help prevent NPs collisions, agglomeration, and precipitation, thereby increasing their stability and longevity. A study by Dandamudi et al. [109] demonstrated the development of a dispersion of Fe_3O_4 using poly (AMPS) as a steric stabilizer, showcasing remarkable stability for seven days at high temperatures in artificial seawater. This approach highlights the effectiveness of steric stabilization in maintaining NPs stability in challenging environments. Silica nanoparticles are widely utilized in engineering applications due to their cost-effectiveness and surface-modification potential. While SiO_2 may not directly catalyze heavy oil cracking, it has been confirmed to be effective as a catalyst supporter, showcasing its versatility and utility in various engineering applications.[110] The "H^+ protection" theory suggests that reducing the pH can prevent the aggregation of SiNPs, ensuring their stability in saline environments. Lowering the solution's pH to 2 has been shown to maintain SiNPs stability in synthetic brine, even at high temperatures, preventing aggregation and ensuring efficient performance [111]. Lan et al. [112] successfully grafted zwitterionic monomers onto SiNPs to enhance their thermal and salt tolerance, inspired using polyelectrolytes as NP stabilizers. This modification resulted in long-term colloidal stability, even in high-salt concentrations at elevated temperatures, demonstrating the effectiveness of surface modification in enhancing NPs stability.

9. Conclusions

The exploration of nanoparticles (NPs) as heavy oil viscosity reducers has revealed their potential in various functional mechanisms, including emulsification and accelerating heavy oil cracking. The effectiveness of NPs as emulsion stabilizers and their interactions with surfactants have been analyzed. Different types of nano-catalysts, such as supported nano-catalysts, multi-metal and multi-metal oxide nano-catalysts, zero-valent transition metals, and transition metal oxides, have been compared. Experiments on NPs transit and retention in porous media have been highlighted to guide the development and selection of appropriate NPs. Several strategies for improving NPs stability have been proposed, along with discussions on encountered challenges. Despite challenges in large-scale NPs applications, nanotechnology shows promise in the upstream oil sector. The principal findings from the reviewed publications are as follows:

1) NPs, either alone or in combination with surfactants, show promise as effective O/W stabilizers for heavy oil applications. Responsive Pickering emulsions offer a rapid method for wastewater treatment, emphasizing the importance of balancing the NPs to surface modifiers ratio for industrial use.
2) Heavy oil upgrading can be catalyzed by transition metals and their oxides, with a recent focus on multi-metal and multi-metal oxides to create synergistic effects. Supported nano-catalysts, utilizing less expensive materials like SiO_2, zeolite, or Al_2O_3, can help reduce costs while maintaining catalytic efficiency.
3) The complex behaviors of NPs in porous media, influenced by various factors, have been identified. NPs aggregation reduces active sites and increases retention rates, impacting efficiency. Providing steric hindrance to NPs is a valuable technique to enhance their resistance to high salinity and temperature conditions.

In conclusion, the study underscores the potential of NPs in heavy oil applications, highlighting the importance of tailored approaches for stability, catalytic efficiency, and effective deployment in porous media. The findings suggest promising avenues for further research and development in utilizing nanotechnology for enhanced performance in the oil and gas industry.

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