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Innovative Experimental Design for the Evaluation of Nanofluid-Based Solvent as a Hybrid Technology for Optimizing Cyclic Steam Stimulation Applications

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Abstract: Worldwide gas emissions are being strictly regulated, therefore processes to reduce steam injection for enhanced oil recovery (EOR) require a deeper analysis to identify the means to contribute to environmental impact reduction. Lately the usage of additives such as a solvent for steam injection processes has taken a new interest due to its positive impact on improving oil recovery and energy efficiency and reducing greenhouse gas emissions. In that sense, the use of nanoparticles in thermal EOR has been explored due to its impact on avoiding the volatilization of the solvent, offering greater contact with the oil in the reservoir. Nanoparticles have well-known effects on asphaltenes adsorption, aquathermolysis reactions, oil upgrading, and improving energy efficiencies. This article presents a summary and ranking of the nanoparticles evaluated in nanofluid-based solvent for steam processes, specifically in the catalysis of aquathermolysis reactions. A novel experimental design is proposed for the characterization, formulation (based on catalytic activity and dispersion), and evaluation of solvent improved with nanoparticles. This new approach will be used as a guideline for the evaluation of nanoparticles dispersed in hydrocarbon-type solvents as a hybrid technology to improve steam injection processes.

Keywords: nanomaterials; core-shell nanohybrid; solvents; naphtha; cyclic steam stimulation; enhanced oil recovery; heavy oil upgrading

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1. Introduction

Heavy oil has great potential for increasing reserves worldwide. In Colombia, it is estimated that 45% of current crude production corresponds to heavy oil [1,2]. However, due to the high content of heavy fractions such as asphaltenes and resins, its production represents a challenge. Among the difficulties are the precipitation and deposition of asphaltenes, which forms a viscoelastic network that reduces the flow of crude oil due to high viscosities. Following the above, it is necessary to use thermal methods for its extraction, among which partial upgrading of oil occurs depending on the type of recovery process used [3–13]. Additionally, the viscosity difference between steam and heavy oil results in viscous fingering problems and thus poor sweep and displacement efficiency [14]. It is proposed to incorporate additives to the steam to mitigate the disadvantages of the technique and thus improve its effectiveness. Some of these additives are chemicals, solvents, surfactants, and gases [15].

In general, the addition of hydrocarbon-type solvents improves the mobility ratio between steam and crude oil. Adding small amounts of solvent creates a mobility transition zone, which improves vapor sweep and reduces oil viscosity [16–19]. In addition, the hybrid technology reduces input energy per unit of recovered oil (a decrease in the steam/oil ratio—SOR) [20,21] and therefore a positive environmental impact is generated by reducing the carbon footprint [22]. Despite the benefits, there are some restrictions. At high oil saturation, the addition of solvent does not improve recovery, but close to residual oil saturation obtained better effects [23,24]. Moreover, there is an optimal injection quantity for each solvent based on the maximum recovery concerning the unrecovered solvent. It will depend on the expected incremental recovery, recovery time, efficiency, and cost of the solvent [17]. In addition, there is a synergistic effect in the recovery time (steam advance) when a light solvent is part of the solvent mixture. The success in the process will depend on the placement of the solvent and the movement of steam; its volatility in turn controls this.

The main challenges related to the cyclic steam injection and solvent are retention, loss of hydrocarbon solvents, and asphaltene deposition, especially from an economic point of view. Asphaltene's precipitation and consequent deposition strongly depend on the type of solvent, the asphaltenes concentration in the crude oil, and its saturation conditions at the pressure and temperature of the reservoir. Due to the constant pressure and temperature change during the process, asphaltene's deposition becomes a potential risk for the technology.

Nanotechnology can solve these problems due to the addition of particles to the solvent that increases the boiling point of the mixing. This allows for reducing the loss of solvent in the process [25] and improves the catalytic of aquathermolysis [5,6], thereby generating a substantial improvement in the crude oil present in the reservoir. However, the most used nanoparticles as catalysts are metallic ones for steam injection processes, and their application has only been studied in the aqueous phase as a carrier.

In that sense, a nanoparticle ranking was developed to identify the nanoparticles/nanocomposites with the better catalytic performance in aquathermolysis reactions. Then an evaluation of the key aspects affecting nanocatalysts in the EOR process, their environmental impact, and an identification of the tests required to evaluate CSS performance was developed. Based on the previous mentioned information, this article presents an innovative experimental design for evaluating nanoparticles dispersed in solvents as a hybrid technology to improve steam injection processes.

2. Methodology

The approach to developing the experimental design for nanofluid-based solvent as a hybrid technology for optimizing cyclic steam stimulation required a deep evaluation of the following concepts:

2.1. Nanotechnology for EOR Thermal Process

The use of nanotechnology in thermal processes emerges as an alternative to recover heavy and extra-heavy oil by upgrading, which allows low energy consumption, less impact on the environment, and a high recovery factor. The most frequent use of nanomaterials in thermal recovery is as nanocatalysts. These are mainly metal and metal oxide nanoparticles used in the adsorption of asphaltenes and catalytic decomposition. Its mechanism of action consists of [26,27]:

- Reducing the decomposition temperature of asphaltenes so that the aquathermolysis reaction can occur;
- Less effective activation energy is necessary for the reaction;
- Decomposition of large hydrocarbon chains into lighter fractions with lower molecular weight implies a reduction in viscosity and improvement in mobility in the production of extra-heavy oils.

This paper shows mainly nanoparticles studied in steam injection processes as an alternative to conventional steam injection. It makes an experimental design proposal for naphtha enhanced with nanofluids evaluation for cyclic steam injection processes.

2.2. Aquathermolysis in Cyclic Steam Injection Processes

The in situ upgrading process is called aquathermolysis. Aquathermolysis reactions begin, with the breaking of C–S bonds present in the molecular structure of n-C_7 asphaltenes, generating the production of H_2S since these bonds have lower dissociation energy [28]. Their reaction mechanism is shown in Equations (1)–(3).

$$\text{Asphaltenes} \rightarrow \text{Coke} + H_2S + H_2 + CH_4 + CO_2 + CO + C_2H_6 + \text{Hydrocarbons}_{3\leq C} + \text{HO} + \text{LO} \quad (1)$$

$$\text{HO} \rightarrow \text{Coke} + \text{LO} + CH_4 + C_2H_6 + C_{3+} \quad (2)$$

$$\text{LO} \rightarrow \text{Coke} + CH_4 + C_2H_6 + C_{3+} \quad (3)$$

where LO is light oil crude and HO is heavy oil crude.

The carbon monoxide (CO) produced reacts with water during the water-gas exchange reactions producing hydrogen. These reactions occur in a temperature range for EOR thermal processes of 200 to 300 °C. The hydrogen molecules attack the unstable and unsaturated crude oil molecules, producing lighter and more saturated molecules by hydrogenolysis [29]. Therefore, this generates the following effects:

- Decrease in the content of the heavy fraction in the crude oil matrix;
- Increase in the H/C ratio;
- Improvement of oil quality;
- Decrease in viscosity.

Since steam injection techniques do not have recovery factors greater than 50% [27,30], it is necessary to improve the process with catalysts. The main reactions in catalytic aquathermolysis [31] are pyrolysis, hydrogenation, and ring-opening reactions.

The catalytic aquathermolysis also generate an increase in the H/C ratio of the crude oil due to the hydrogenation reaction. Furthermore, the presence of a metallic catalyst improves the heat transfer capabilities during the steam injection process [32]. This thermal promoting effect occurs because metals have high thermal conductivity, which improves the thermal conductivity of the hydrocarbon or the porous medium in the reservoir.

Likewise, some of the properties of nanoparticles, mainly their high surface area, are the reason for their high performance over other fixed-bed catalysts studied in this type of recovery [15]. Nanocatalysts can also permeate through sandstones and be recovered in the producing wells after adequate treatment to be reused and therefore improve their cost-effective ratio of the process [33,34]. Conversely, nanoparticles catalyze the breaking of carbon–sulfur bonds in asphaltenes, increasing the amount of saturates and aromatics in heavy oil as follows [35]:

$$R - S - R\ (\text{sulfur organic compound}) + H_2O \rightarrow CO + H_2S + \text{light organic compounds}$$

Similarly, in Figure 1 a summary of the main advantages of nanocatalysts concerning the conventional volumetric catalyst is presented.

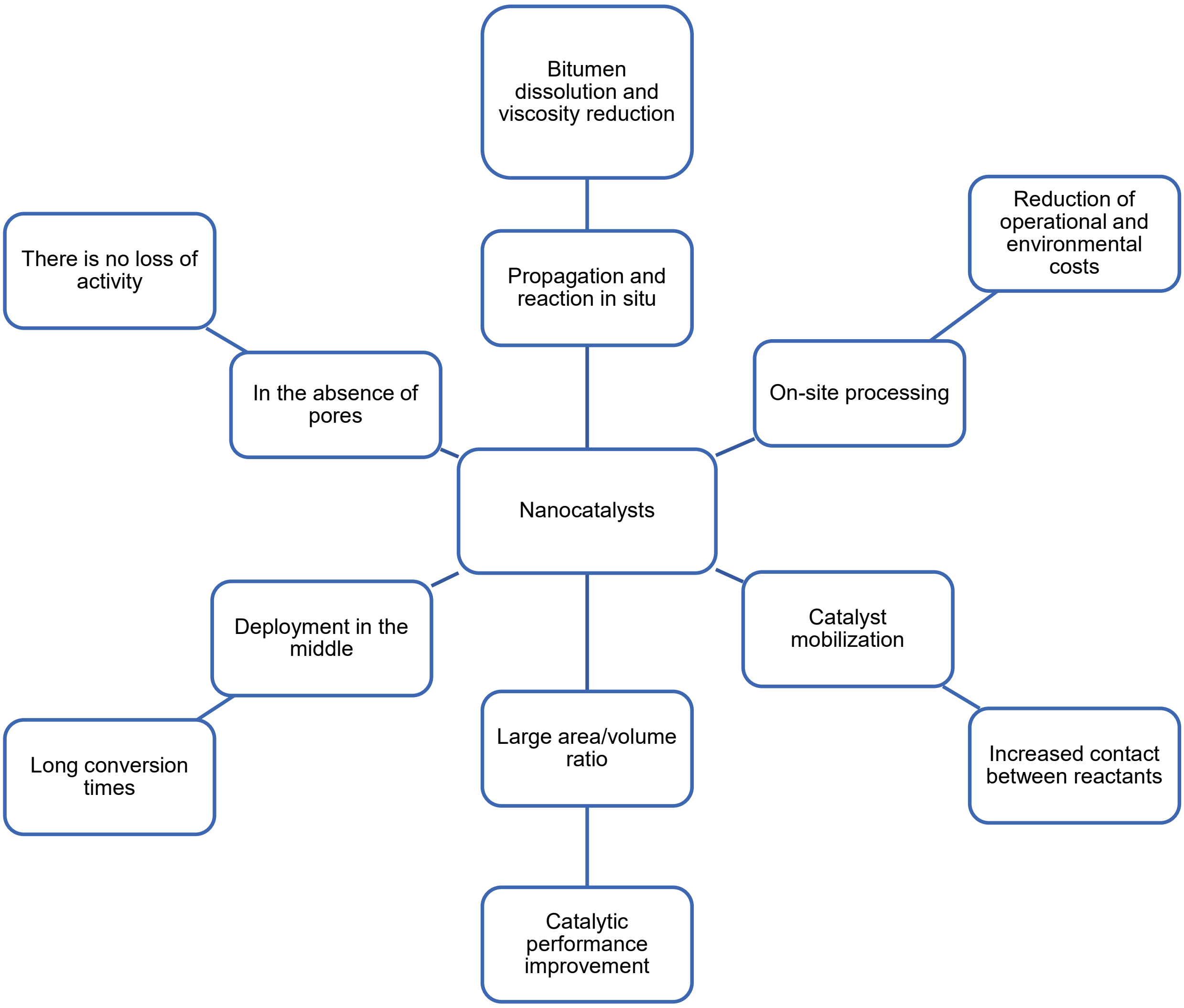

Figure 1. Advantages of using nanocatalysts compared to traditional catalysts, modified from Sun et al. (2017) [36].

2.3. Nanocatalizers for Cyclic Steam Injection

Similarly, in Figure 1, nanocatalizers are substances with catalytic properties and have at least one dimension on a nanometric scale [34,37]. They also have a high surface/volume ratio, which creates more exposition to the contact with oil, which may generate a complete chemical reaction influencing oil density and viscosity and breaking of C–S bonds due to its catalytic activity [38]. Nanocatalizers, depending on their phase, can be classified as homogeneous and heterogeneous. They also sort as minerals, water-soluble, oil-soluble, and dispersed; this last one is the most used form due to the greater contact area nanocatalizers have in the form of powder. Table 1 shows metallic nanoparticles used in the steam injection process.

Table 1. Summary of studies reported on nickel nanoparticles used in EOR steam processes.

Reference	Observed Catalytic Performance	Remarks
Y.H. Shokrlu & Babadagli (2011) [39]	Oil viscosity reduction: 29.63% C-S chain breaking, but with time this effect is reduced [5]	Sandstone core in CSS. Concentration used: 500 ppm.
Li, Zhu, & Qi (2007) [40]	Oil viscosity reduction: 98.2% H/C: 1.46	Particle size: 6.3 nm
Wu, Su, Zhang, Lei, & Cao (2013) [41]	Oil viscosity reduction: 90.36% H/C: 2.09	Particle size: 4.2 nm Asphaltenes molecular weight reduction: 28.06%

As shown in Table 1, the nickel nanoparticle's performance in aquathermolysis processes depends mainly on its size, obtaining a considerable asphaltenes molecular weight reduction and increased H/C ratio with a small size.

Table 2 presents the main results in terms of catalytic performance and sweep efficiency for metallic oxide nanoparticles that are widely used in EOR steam processes. As can be seen, nickel oxide reaches a lower temperature decomposition, with concentrations relatively low (0.2%).

Table 2. Summary of metallic oxide nanoparticles for EOR steam processes.

Nanoparticles	Observed Catalytic Performance	Remarks	Reference
NiO	Oil viscosity reduction: 22% Temperature decomposition reduction (TD): 37% in presence of steam	Nanoparticle size: 60–70 nm. Athabasca asphaltenes 12 nm (crystal size) Asphaltenes conversion: 37%	Noorlaily, Nugrah, Khairurrijala, Abdullah, & Iskandar (2013) [42] Nashaat Nassar, Hassan, & Pereira-Almao (2011) [43]
ZnO		Incremental sweep efficiency: 35.5% compared to conventional SAGD	Tajmiri & Ehsani (2016) [38]
CuO	Oil viscosity reduction: 85.75% at 350 °C for 40 min	Used concentration: 0.2% p/p % Asphaltenes reduction: 13.62%	Zhong, Tang, Zhou, & Deng (2020) [44]
Fe_2O_3	Oil viscosity reduction: less than 40%	Concentration 0.2% p/p	Afzal, Ehsani, Nikookar, & Roayaei (2018) [45]
α-Fe_2O_3	Oil viscosity reduction: 93.3% Oil viscosity reduction: 95.6%	Resins and asphaltenes reduction. Aromatics and saturated increase.	Chen, Wang, Wu, & Xia (2008) [46] Wang et al. (2010) [31]
Fe_3O_4	TD reduction: 24% Less catalytic activity compared to NiO and Co_3O_4. Oil viscosity reduction: 30%	Concentration: 0.2% p/p Crystal size: 22 nm Asphaltenes conversion: 21% Crystal size: 43 nm	Nashaat Nassar et al. (2011) [43] Nugraha, Noorlaily, Abdullah, Khairurrijal, & Iskandara (2013) [47]
Co_3O_4	TD reduction: 34%	Crystal size: 22 nm Asphaltenes conversion: 32%	Nashaat Nassar et al. (2011) [43]

Table 3 presents composed materials from metallic oxide mixes, which take advantage of internal transition metallic nanoparticles with other components or nanoparticles bringing additional properties.

Table 3. Summary of composed nanoparticles used in EOR thermal processes.

Nanoparticles	Observed Catalytic Performance	Remarks	Reference
α-Fe_2O_3/zeolite	Oil viscosity reduction: 89%	Particle size: 135 nm Composition α-Fe_2O_3: zeolite of 1:3	Nurhayati, Iskandar, Abdullah, & Khairurrijal (2013) [48]
Fe_3O_4/zeolite	Oil viscosity reduction: 92%	Particle size: 96 nm Composition Fe_3O_4:zeolite of 1:4	Iskandar et al. (2014) [49]
Functionalized Ni		Tar reduction: Ni/Al_2O_3: 99% Ni/Olivina: 93.1% Ni/Fe_2O_3: 83.6%	Gao, Ghorbanian, Gargari, & Gao (2018) [50]
Functionalized Ni-Pd	Asphaltenes TD reduction: Ni-Pd/TiO_2: 37.25% Ni-Pd/Al_2O_3: 35.75%	Ni-Pd/CeO_2: 93% n-C_7 asphaltenes conversion in presence of steam in less than 90 min.	Nashaat N. Nassar et al. (2015) [12]
Functionalized SiO_2 with 1% NiO and 1% PdO	API increase: 40.5% Better asphaltenes thermal cracking compared to SiO_2 nanoparticles by itself.	CH_4 production increase Sweep efficiency increase: 56% compared to steam injection	Franco, Montoya, Nassar, & Cortés (2014) [51]
Functionalized Al_2O_3	Functionalized Al_2O_3 with 2%NiO: TD reduction of approx. 25%. API increasing of 5°.	Functionalized Al_2O_3 with 2%NiO: 20% increase in sweep efficiency Promote gas reduction like CH_4 y CO over others like CO_2, with a coke better performance of aprox 0.13%	Cardona Rojas (2017) [52]
Functionalized TiO_2 with 2% NiO	Reduce TD approx. 170 °C: 42.5%	Residual coke is higher with a mass fraction of 0.17%.	Nashaat Nassar et al. (2015) [12]; Nashaat Nassar, Hassan, & Vitale (2014) [53]
Functionalized CeO_2 with NiO and PdO	API increase: 50% Oil viscosity reduction: 78%	0.89% of PdO and 1.1% of NiO over CeO_2 Asphaltenes conversion: 100% in less than 80 min. Asphaltenes reduction: 15.8% Sweep efficiency improvement: 11.8%	Medina, Gallego, Arias-Madrid, Cortés, & Franco (2019) [54]
Janus nanoparticles	TD asphaltenes reduction at 200 °C: 50%	Interfacial tension decreased	Diez et al. (2018) [55]
NPs core (magnetite)—Shell (silica)	TD starts at 200 °C and max at 440 °C, 20 °C less than base case: 4.35%	Promote CH_4 and light HCs formation during heavy fractions decomposition.	Betancur, Franco, & Cortés (2016) [56]
Ni/W/Mo		Promote a decrease in sulfur and nitrogen-based gases.	Hashemi et al. (2013) [27]

According to the studies, composed nanoparticles generate sweep efficiency increase compared to the traditional technique (up to 56%), due mainly to the combination of recovery mechanisms of each nanoparticle present in the mixture. These bring additional benefits such as the decrease in the sulfur and nitrogen mixture gas production.

In summary, nanoparticles and nanomaterials presented good catalytic performance, sweep efficiency improvements, and high asphaltenes conversion. Likewise, the most relevant recovery mechanisms are viscosity reduction and oil upgrading. Another significant issue is the capacity of the carrier to keep the nanoparticles dispersed deep into the reservoir to contact most of the oil.

Figure 2 presents the ranking of nanoparticles/nanocomposites that show viscosity reduction and decomposition temperature reduction, which refer to catalytic performance.

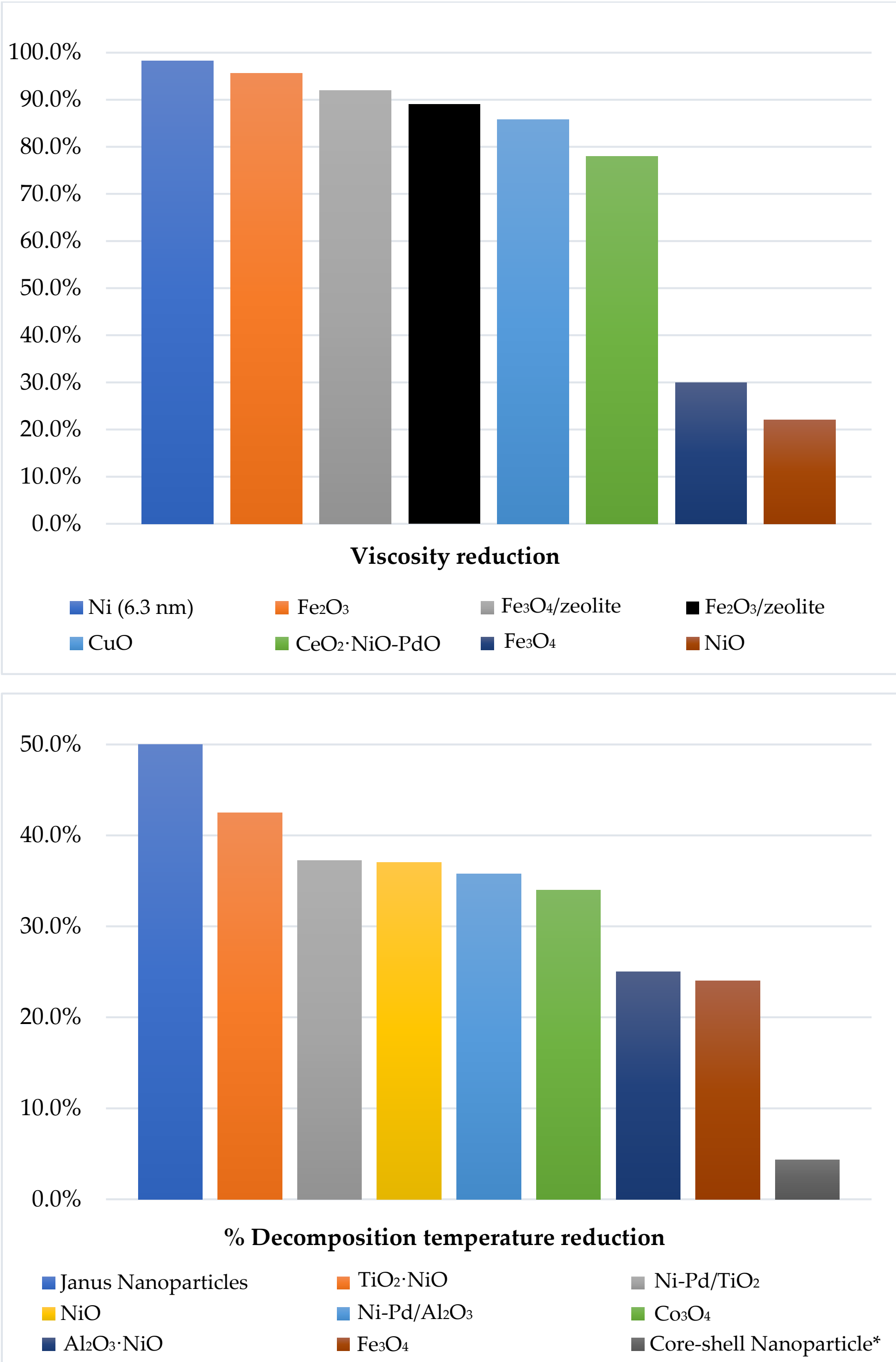

Figure 2. Ranking nanoparticles/nanocomposites according to catalytic performance. Note: * Core (magnetite)-shell (silica).

As can be seen in terms of viscosity reduction, the best performances in descending order were those of Ni nanoparticles (particle size: 6.3 nm), Fe_2O_3, and Fe_3O_4/zeolites with viscosity reductions of 98.2%, 95.6%, and 92.0% respectively. Likewise, Janus-type nanoparticles, TiO_2 functionalized with NiO and Ni-Pd functionalized with TiO_2 have the best percentages of decomposition temperature reduction with 50.0%, 42.5%, and 37.3%, respectively.

Conversely, Figure 3 shows the ranking of nanoparticles and nanocomposites according to the conversion of asphaltenes and an increase in oil recovery factor concerning steam injection.

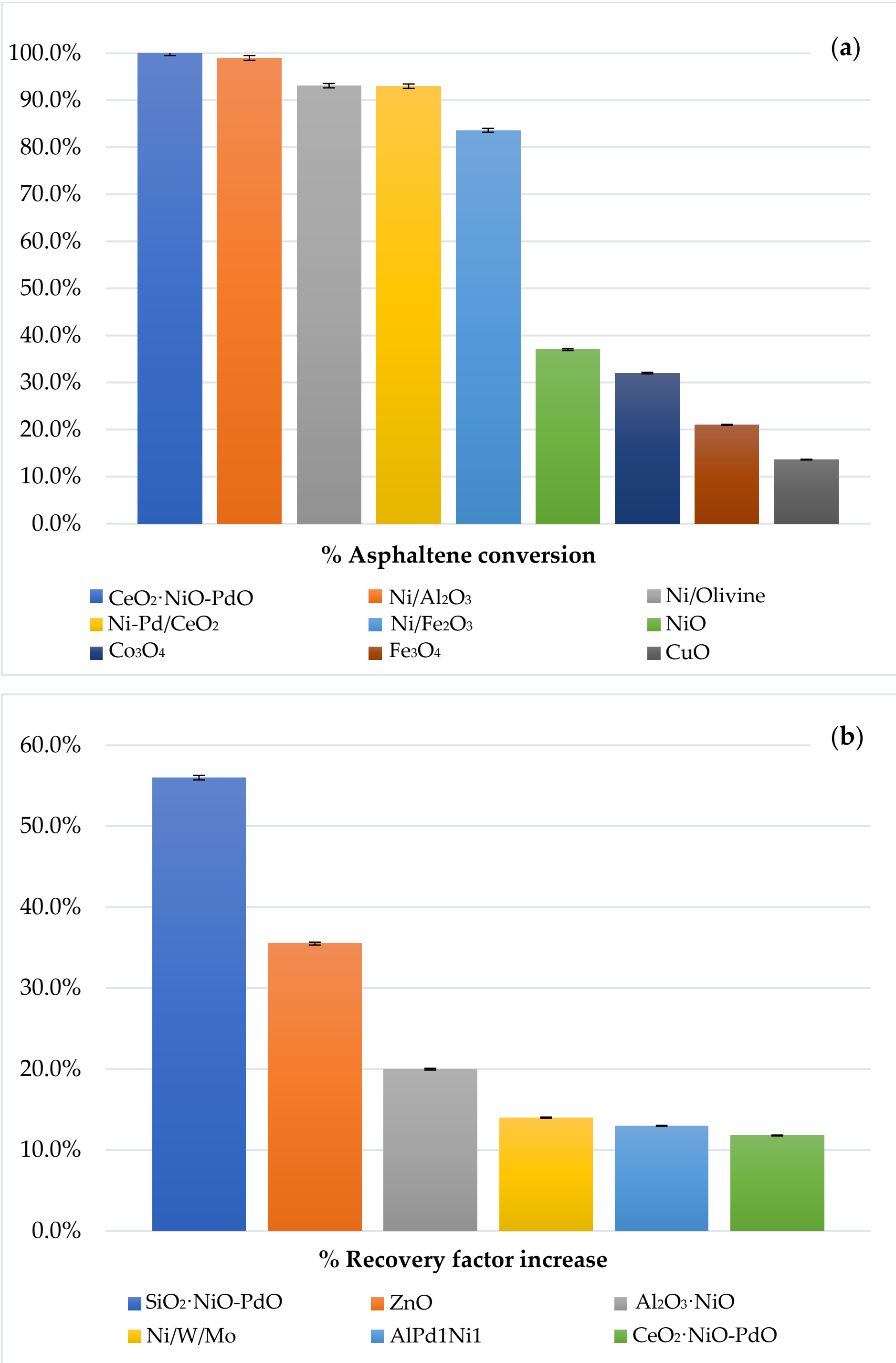

Figure 3. Ranking nanoparticles/nanocomposites according to the conversion of asphaltenes (**a**) and its increase in the oil recovery factor (**b**).

According to the results, CeO_2 nanoparticles functionalized with NiO; PdO, Ni/Al_2O_3, and Ni/Olivine have conversions of asphaltenes of 100%, 99%, and 93.1%, respectively. Likewise, the nanoparticles/nanocomposites with the highest recovery factor increases are SiO_2 nanoparticles functionalized with NiO and PdO, ZnO, and Al_2O_3 functionalized with

NiO, with an increase of oil displacement recovery factor concerning conventional steam injection of 56.0%, 35.5%, and 20.0%, respectively. Figure 4 presents a summary of factors reported for nanoparticles/nanocomposite and their relationship.

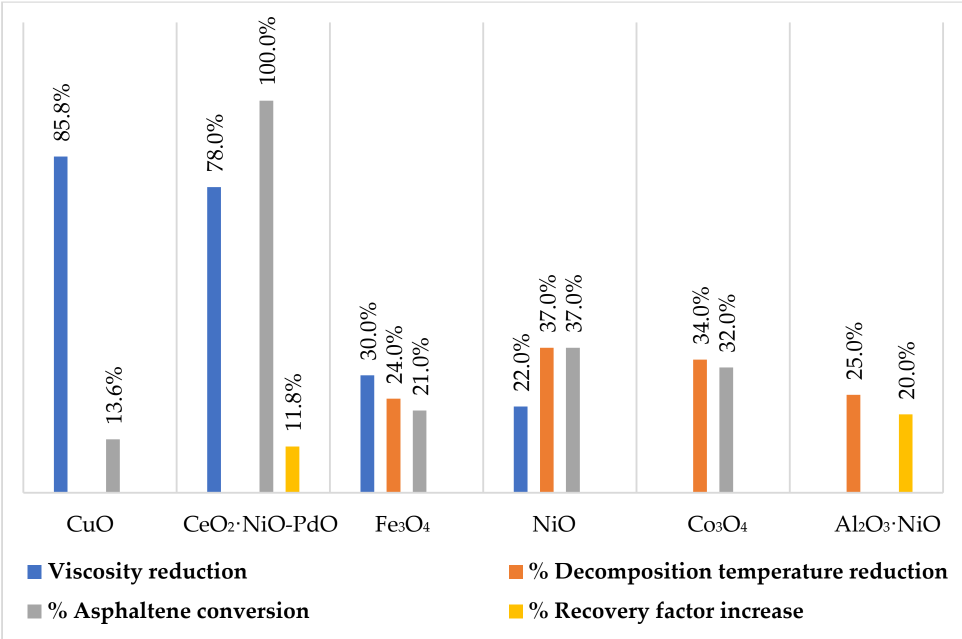

Figure 4. Nanoparticles/nanocomposites according to the different parameters reported in the literature.

The analyzed studies show an increase in the oil recovery factor and conversion of asphaltenes due to catalytic performance. The recovery mechanisms of great interest are the reduction in viscosity achieved and the increase in the oil recovery factor compared to the conventional steam injection technique.

2.4. Factors That Affect Nanocatalysts in EOR Processes

The main factors that affect the performance of nanocatalysts in thermal processes are show below:

2.4.1. Type, Size, and Concentration of Nanoparticles

The combination of viscosity and concentration of nanoparticles can significantly alter the rheology of the oil produced [57–59]; the above improves the efficiency of the EOR process. Physical and chemical processes carried out in the presence of the nanoparticles can be positive or negative depending on the reaction.

The decrease in particle size generates an increase in the surface-volume ratio of the nanoparticles, which causes an improvement in their physical and chemical properties [58]. Furthermore, another significant property is the increase in dispersion efficiency. However, at high concentrations, the viscosities of mixtures of nano-emulsions and micro-emulsions are very close, mainly due to the aggregation of particles [58,60].

2.4.2. Heat Transfer

The thermal properties of heavy oil/bitumen cause a limitation in energy-efficient thermal techniques. For this reason, it is necessary to use nanoparticles that show better thermal properties to generate a faster distribution of heat in EOR thermal processes. Mainly, nanoparticles with the best thermal performance are metallic particles [61]. However, different studies show atypical results, which indicates that more in-depth research on the thermal properties is necessary [62–64].

2.4.3. Crude Oil Composition

Nanocatalysts show a significant reduction in the viscosity of different crude oil [58,65,66]. This effect is due to chemical processes, rather than physical ones, mainly due to the reaction of breaking of the C–S bonds in asphaltenes/resin molecules. However, the sulfur content is negligible to generate environmental problems, and other chemical bonds with high dissociation energy can break to reduce the oil viscosity.

2.4.4. Porous Medium

The physical properties of the reservoir rock affect the catalyst performance, especially the permeability has a significant impact on retention. Likewise, the chemical composition of the porous medium affects the performance of the process. The presence of components such as calcite ($CaCO_3$) or siderite ($FeCO_3$) increases the production of carbon dioxide at the steam injection temperature [67].

Likewise, the catalyst injected has metal cations (such as VO^{2+} and Ni^{2+}) that are adsorbed on the surface due to electrostatic forces caused by the negative charge of clay mineral surfaces. These reactions generate products similar to amorphous silica-alumina catalysts used in catalytic cracking processes [66,67]. The core mineralogy also plays a significant role in the generation of CO_2 and the quantity of H_2S produced [68].

2.4.5. Formation Damage Inhibition

Asphaltenes in heavy oil cause adsorption and deposition in a matrix of the rock affecting reservoir properties such as porosity, permeability, and wettability [69,70]. Nanomaterials could inhibit the deposition of asphaltenes generating a reduction of damage to the reservoir rock and upgrading heavy oil by reducing oil viscosity [43,69]. The function of the nanoparticles is to adsorb the asphaltenes and then be adsorbed in the porous medium, delaying their precipitation [60,69,71].

2.5. Environmental Influences of Nanoparticles in Steam Injection Processes

The main advantages of using nanoparticles in situ upgrading processes are the following [72]:

2.5.1. Decrease in Heat Consumption

Nanoparticles in contact with the oil molecules accelerate cracking and hydrogenation, generating a large amount of heat and gaseous products that improve the release of oil from the rock. The decrease in heat consumption also allows a reduction in steam requirements.

2.5.2. Sulfur Removal

The use of nanocatalysts in aquathermolysis processes generates a significant decrease in the sulfur concentration. This is mainly due to the breaking of the C–S bond during the process, favoring the quality of the crude oil, and generating a positive effect on the environment by reducing the sulfur load in refining [72].

2.5.3. Greenhouse Gases

Nanoparticles generate other effects such as decreases in water consumption due that the reduction of steam requirements. Other effects include reduction of greenhouse gases such as CO_2 and toxic chemicals such as SO_x and NO_x between others.

In addition, use of hybrid steam technology reduces operating costs and transportation to the refinery due to oil upgrading.

It is necessary to evaluate the performance of the best nanoparticles in each aspect regarding their dispersion capacity in the proposed medium (naphtha) and their subsequent response in terms of an increase in the recovery factor and reduction in crude oil viscosity. Due to the above, the proposed experimental design allows evaluation of the technology of naphtha improved with nanoparticles in steam injection processes.

3. Results

Based on the methodology previously described, an experimental design of nanofluid-based solvent as a hybrid technology for optimizing cyclic steam stimulation is proposed. The experimental design begins with injection fluid and reservoir components characterization. Subsequently, the nanoparticle selection includes catalytic properties such as thermal conductivity, metal concentration, and dispersion in carrier naphtha. Later, evaluation includes compatibilities at a fluid-fluid level and rheological behavior of nanofluid-oil at different concentrations.

Once compatibility and dispersion are guaranteed, rheological, kinetic, and adsorptive tests are conducted to evaluate the impact of the nanoparticles on the oil's behavior, emphasizing the aquathermolysis reactions; this stage is named an experimental test at static conditions.

Finally, the experimental design includes a rock-fluid test using a core holder designed and fabricated for testing steam-based hybrid technologies for CSS. This stage aims to evaluate the injection strategy of the nanofluid and the environmental impact of the nanocatalyst in CSS, focusing on reducing of production of greenhouse gases and steam requirements. Figure 5 presents the five stages of the proposed experimental design for hybrid technology of CSS + naphtha improved with nanoparticles as an alternative to improve CSS performance.

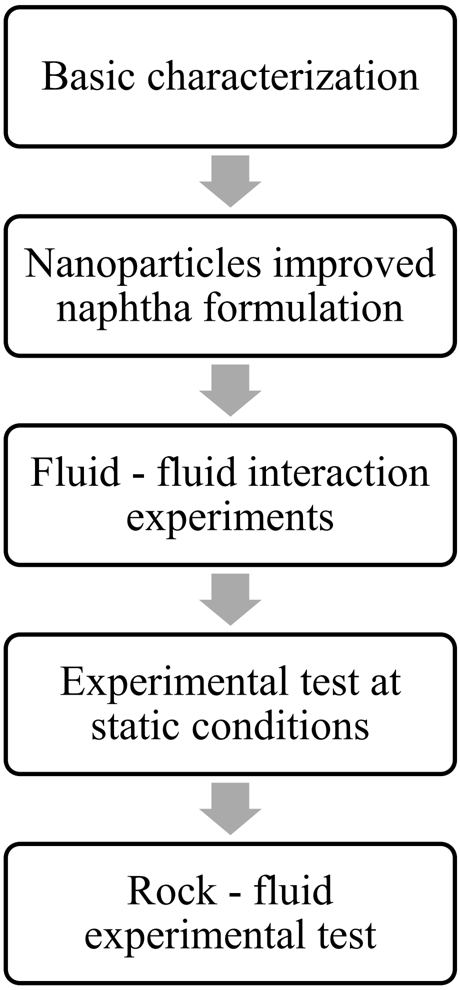

Figure 5. Proposed experimental design of nanofluid-based solvent as a hybrid technology for optimizing cyclic steam stimulation.

Subsequently, a numerical simulation should develop to evaluate injection strategies that help choose the optimal scheme. It will also allow determining of effluents' quality and detecting of potential rheological issues considering the effects of the aquathermolysis process. Each of the stages that make up the experimental design to evaluate the use of naphtha enhanced with nanofluids in cyclic steam injection processes is detailed below.

3.1. Basic Characterization

This characterization aims to evaluate the properties required to establish changes generated during the injection process using improved naphtha with nanoparticles (Figure 6).

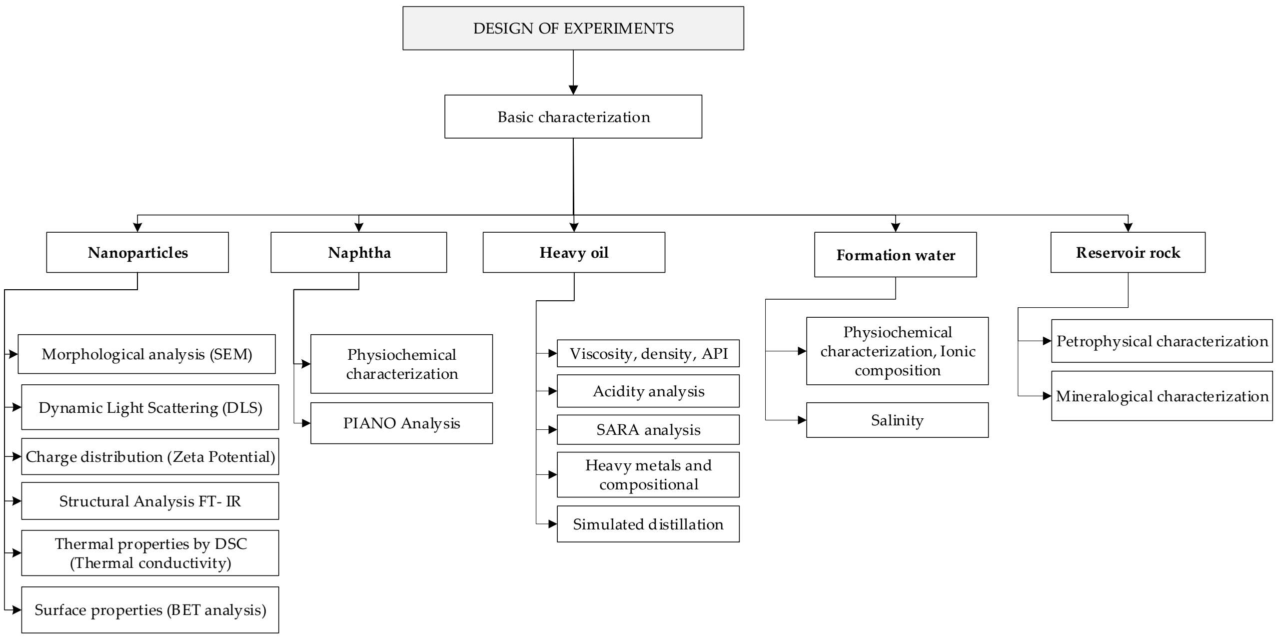

Figure 6. Basic characterization.

Each experimental technical will deliver the components properties required to understand the interaction with each other during the fluid-fluid and rock-fluid tests. The following tables (Tables 4–6) contain each technique to be applied and its purpose.

Table 4. Nanoparticle's characterization techniques.

Lab Technique	Technique Description
SEM-EDS (Scanning electron microscopy) or TEM	Particle morphology and size
Dynamic Light Scattering (DLS)	Particle size (ideal for monodispersed samples)
ζ-Potential	Z potential determination
Infrared spectroscopy through Fourier transform (FTIR-ATR)	Structural analysis of the nanoparticles
Thermal Property Analyzer	Thermal conductivity determination
BET (Brunauer, Emmett and Teller)	Superficial area determination

Table 5. Naphtha characterization techniques.

Property	Technique Description
API Gravity	At 60 °F, a specific gravity function
Density	Digital densimeter: through frequency measurement
Viscosity	Capillary viscosimeter: measure through Hagen–Poiseuille equation
Paraffins, Isoparaffins, Olefins, Naphthene, Aromatics determination (PIANO)	Polar column separates paraffins and naphthene from aromatics, while heavy aromatics and alcohols are kept in the pre-column.

Table 6. Oil characterization techniques.

Property	Technique Description
API Gravity	At 60 °F, a specific gravity function
Density	Digital densimeter: through frequency measurement
Viscosity	Flow through two parallel plates, the superior plate turns creating a shear.
Total Acid Number	Titration (neutralization) with potassium hydroxide (KOH)
SARA Analysis	Separation using solvents (heptane-toluene)
Compositional analysis	CHNO analysis based on sample combustion.
Heavy metals	ICP: an atomized liquid sample is injected into an argon plasma. The sample ionize into the plasma and the ions emit different wavelengths.
Simulated distillation	Samples are analyzed in a nonpolar chromatographic capillary column that separates hydrocarbons according to their boiling point. It allows identification of the type of crude: aromatic, paraffinic, or naphthenic.

3.2. Naphtha Improved with Nanoparticles Formulation

Nanofluid preparation is fundamental for the process's success. The nanofluid will prepare by mixing the carrier (naphtha) while adding the nanoparticles until a homogeneous dispersion is achieved. For this purpose, a cosolvent might be needed, and that will be part of the experimental process. Another significant property will be the dispersion effectiveness, which will depend, among others, on the nanoparticle's concentration, which could vary in viscosity depending on the particle's aggregation [58]. The proposed preparation consists of adding nanoparticles to the naphtha using a magnetic agitator at 300 rpm for one hour at 25 °C, then sonicated for 30 min to guarantee a correct dispersion in the liquid medium [73–77].

According to Mortazavi-Manesh & Shaw (2016) [78], the aromatic and polar diluents such as naphtha reduce viscosity better than non-polar alkanes. Conversely, according to Taborda et al. (2017) [25], surfactant micelles inhibit nanoparticle dispersion in a liquid carrier because it is not recommendable to use as a cosolvent. Likewise, nanoparticles dispersed in a liquid carrier have a better performance in oil viscosity reduction due to the uniform distribution of the nanoparticles in the nanofluid, which increases the contact between them and the hydrocarbons. However, laboratory tests allow obtaining a better understanding of the nanoparticle's dispersion by analyzing variables, such as agitation time and sonication [79] as can show in Figure 7.

The above could help identify the best conditions for nanoparticle dispersion. These formulation evaluations include morphologic analysis (SEM) and particle size distribution (DLS) to control the particle size expected. In addition, it is possible to evaluate the improved naphtha with nanoparticle formulation quality dispersion with Zeta potential and turbidity measurements. Finally, for evaluating the stability over time, required equipment such as a TURBISCAN for UV absorption is needed.

3.3. Fluid-Fluid Interaction

This stage is a continuous process that is a function of the formulation stability, in its interaction with each component, will be adjusted or will continue to the next step (Figure 8). The last is due to the nanoparticle's aggregation tendency because of the large surface area and the influences of other parameters such as temperature, pressure, and salinity [80]. These represent the most critical variables evaluated during fluid-fluid interaction.

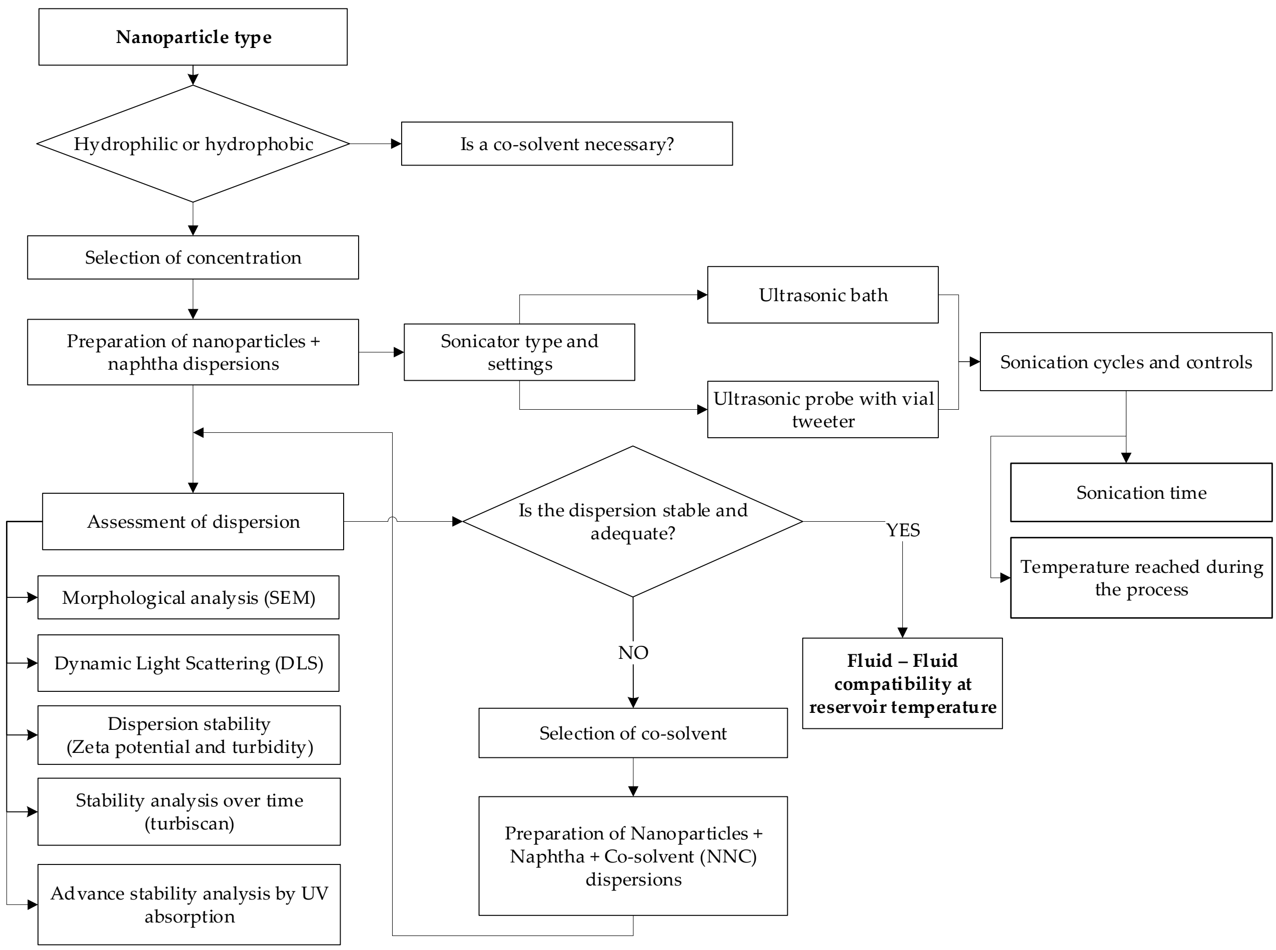

Figure 7. Experimental design for the nanoparticles improved naphtha formulation.

Oil rheological behavior is another factor to be evaluated at reservoir conditions and after each formulation component addition (naphtha and nanoparticles). It is necessary to assess the influence of viscosity nanoparticles concentration in the produced oil rheology and hence the influence on the EOR process [57–59]. Rheology analysis should include viscosity evaluation as a function of temperature through a range from room temperature to steam temperature at reservoir pressure. The purpose of the rheological evaluation of nanofluid oil is to determine the impact of the addition of the nanoparticles to the oil crude-naphtha system and its response to different shear and temperatures.

3.4. Experimental Test at Static Conditions

The most critical variables for the hybrid technology evaluated are reaction time, steam temperature, hydrogen donor presence, and naphtha concentration to assess them at reservoir conditions between others. The technology application response includes the evaluation of oil viscosity behavior through time, sulfur content determination, adsorption measurement, SARA analysis for the oil produced, produced gas chromatography, and heavy metals concentration (Figure 9). All these variables allow determining the influence of nanoparticles in the performance of cyclic steam injection by reducing environmental impact and oil recovery improvement.

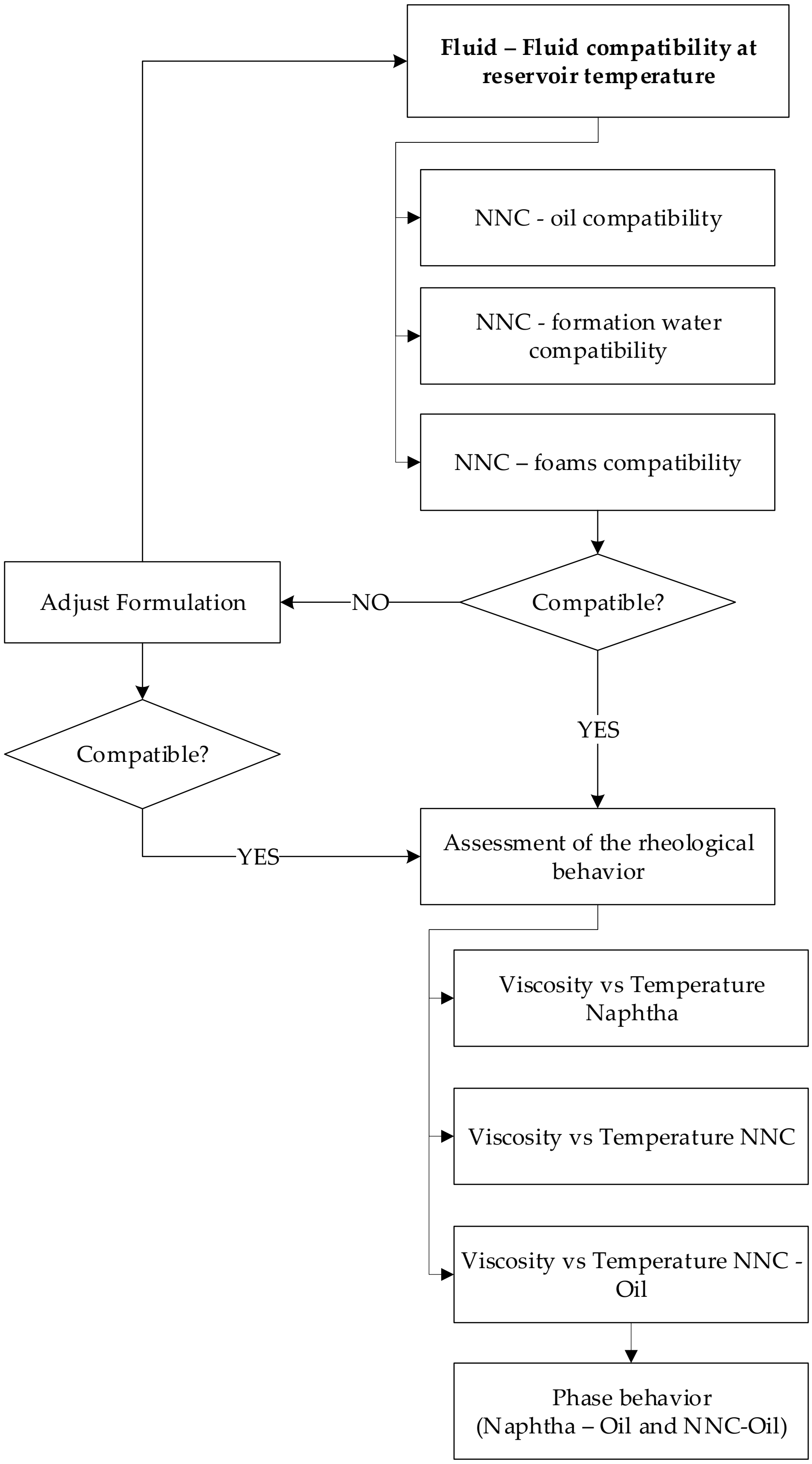

Figure 8. Experimental design for fluid-fluid interaction.

3.5. Rock-Fluid Experimental Test

This stage aims to determine the reduction in energy consumption of the process due to the nanocatalizers in contact with the oil, which contribute to accelerating cracking and hydrogenation. This generates a considerable amount of energy and gases that eventually improve the separation of the oil from the rock. The breaking of C-S chains during the process contributes to the sulfur remotion, generating upgrading oil crude quality [72], among other effects, such as a CO_2 production decrease. The scheme presented in Figure 10 shows the experimental design proposed for the Rock-Fluid evaluation of the technology.

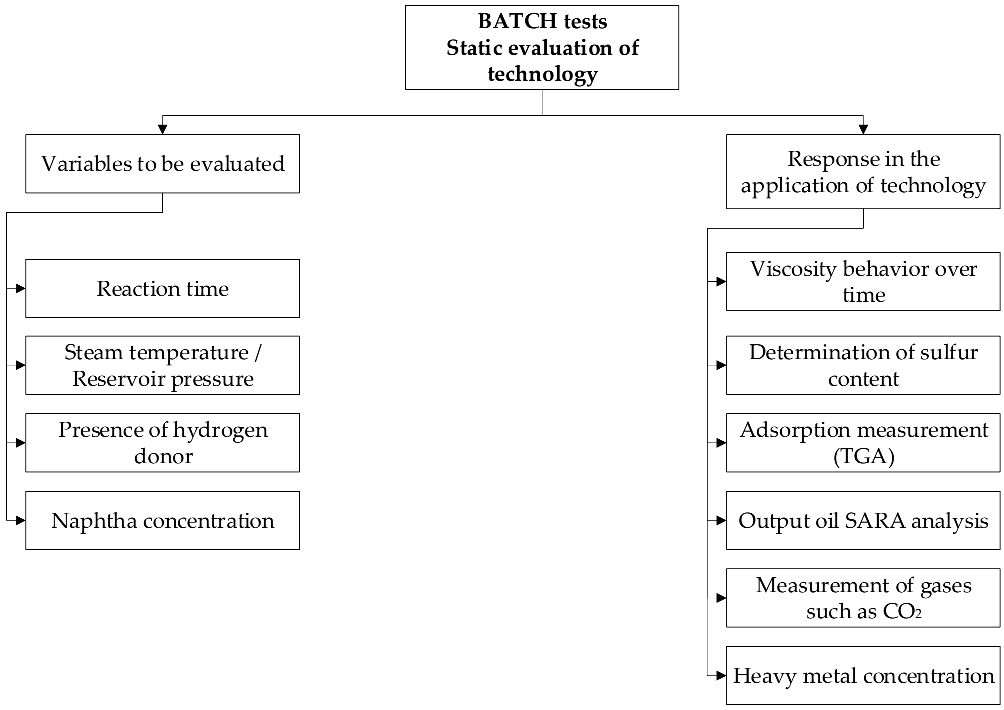

Figure 9. Experimental design for the static condition's evaluation.

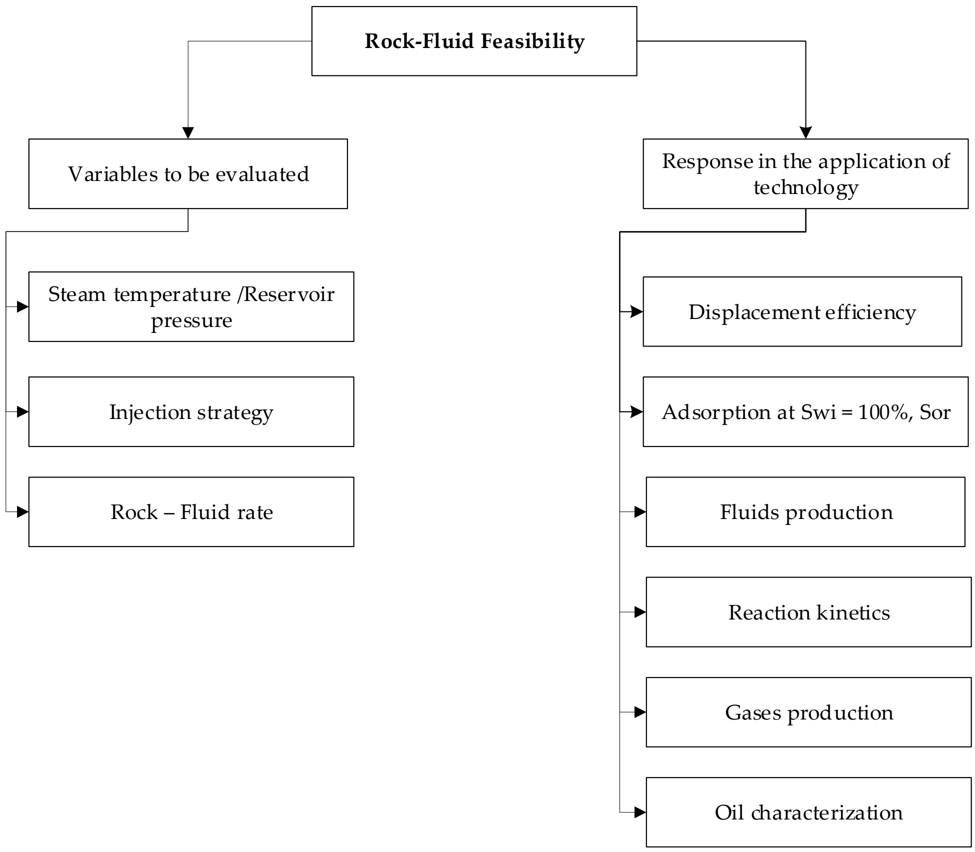

Figure 10. Experimental design for rock-fluid evaluation.

Conversely, the variables to control during the process are:

- Steam temperature: can decrease with increasing depth, obtaining less energy than required for the reaction;
- Residence time: can affect the interaction between nanoparticles and heavy oil;
- Rock adsorption of the nanocatalyst: is a benefit that allows increasing the catalyst time over the cycles.

4. Conclusions and Recommendations

Research shows that it is possible to use nanoparticles to catalyze aquathermolysis reactions in steam injection processes, making them occur at lower temperatures generating reduced decomposition temperature and activation energy. The reactions catalyzed by nanoparticles allow the reduction of the oil viscosity up to 99% of the initial value, a decrease of the molecular weight, removal of sulfur, and reduction of the fraction of asphaltenes and resins, among other effects that generate a permanent improvement in the crude oil evaluated. The above allows for reducing greenhouse gas production due to reducing steam requirement and avoiding the production of high amounts of sulfur in oil refining.

Moreover, the nanoparticles with great potential for application are those based on internal transition element metals and their oxides, mainly those based on nickel and palladium supported on materials such as silica, alumina, or zeolites.

It is noteworthy that the use of nanocatalysts in hybrid technology generates reactions that reduce the production of greenhouse and toxic gases such as sulfur oxide, carbon oxide, and carbon monoxide. Due to that, nanocatalysts have the potential for thermal recovery in the improvement (upgrading) of heavy crude oils and bitumen. However, a more in-depth study of the catalytic activity of nanocatalysts and how nanoparticles can be transported through the porous medium while maintaining their stability is necessary, with the aim to obtain the highest possible recovery while limiting the damage to the formation. Other challenges and limitations of the use of nanoparticles in steam injection processes include:

- The percentage of viscosity reduction in laboratory experiments in static tests is high compared to dynamic in situ experiments;
- Adequate dispersion of the nanocatalyst;
- Short time for nanoparticles to interact with heavy oil;
- The nanocatalyst must withstand the temperature gradient as the steam moves away from the injector well (temperature losses) to avoid losing the heat required for the reaction;
- Nanoparticle aggregation is a problem mainly due to its large surface area and destabilizing conditions such as temperature, pressure, salinity, oil, or other chemical species in the reservoir [80].

In conclusion, the hybrid technology of cyclic steam injection + solvents improved nanoparticles. This allowed the improvement of thermal efficiency of cyclic steam injection generating a reduction in steam consumption. The above generates a positive environmental impact due to less use of the steam generator and less combustion gas production.

5. Future Work

This work shows an exploratory and novel hybrid technology in thermal EOR from an experimental perspective. The future research should focus on numerical modeling to support a pilot test design and implementation in the field.

It is worth noting that in cyclic steam projects, the quantities required are low amounts of nanofluids. However, obtaining enough nanoparticles on an industrial scale for this thermal method would be a challenge. To face this issue, it is necessary that an evaluation of the optimal method for synthesis of nanoparticles that allows obtaining the volumes required for field massive applications [81,82]. Additionally, for the optimization of the process, it is important to develop nanofluid in the field based on solvents used in downstream processes as carriers of nanoparticles. Considering that the target fields in Colombia are in mature stages of cyclic steam stimulation, where there is implemented conformance technology such as preformed foams, experimental work for evaluating compatibility with the nanofluid developed is recommended [83].

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