Review

Current Status and Future Trends of In Situ Catalytic Upgrading of Extra Heavy Oil

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Abstract: In situ catalytic upgrading of heavy oil decomposes viscous heavy oil underground through a series of complex chemical and physical reactions with the aid of an injected catalyst, and permits the resulting lighter components to flow to the producer under a normal pressure drive. By eliminating or substantially reducing the use of steam, which is prevalently used in current heavy oil productions worldwide and is a potent source of contamination concerns if not treated properly, in situ catalytic upgrading is intrinsically environmentally-friendly and widely regarded as one of the promising techniques routes to decarbonize the oil industry. The present review provides a state-of-the-art summarization of the technologies of in situ catalytic upgrading and viscosity reduction in heavy oil from the aspects of catalyst selections, catalytic mechanisms, catalytic methods, and applications. The various types of widely used catalysts are compared and discussed in detail. Factors that impact the efficacy of the in situ upgrading of heavy oil are presented. The challenges and recommendations for future development are also furnished. This in-depth review is intended to give a well-rounded introduction to critical aspects on which the in situ catalytic application can shed light in the development of the world’s extra heavy oil reservoirs.

Keywords: heavy oil; upgrading; viscosity reduction; catalysts; EOR

1. Introduction

The world’s energy consumption is on the rise, while fossil fuels are still the main source of energy. The increase in demand and consumption of light crude oil has led to a decline in global oil reserves and supply. Therefore, short-term and long-term demand needs to be supplemented by unconventional oil resources [1–8]. Heavy oil resources are widely spread around the world. The proven reserves are 9911.8 × 10⁸ t, and the recoverable resources are 1267.4 × 10⁸ t [9]. Thermal recovery techniques, such as steam huff and puff, steam flooding, SAGD (steam-assisted gravity drainage), in situ combustion (ISC) are the main methods for heavy oil resources [10,11].

1.1. Problems in Thermal Recovery for Heavy Oil

Serious formation pressure loss and interwell channeling after steam injection have become the main factors restricting the thermal recovery of heavy oil sources. In particular, several key issues must be addressed [12–18].

Interwell channeling.

Due to the condensate phase transformation characteristics of steam, when steam flows through porous media and reaches production wells, it generally appears in a hot water form in these wells; however, it can become steam channeling. The causes of
steam channeling include heterogeneity within or between layers, severe steam overlap in thick reservoirs, unreasonable steam injection parameters, high permeable lines between injection and production wells, and interwell thermal or pressure communications caused by continuous steam injection. Steam channeling is an extreme form of thermal connectivity between thermal recovery wells. Although a heat viscosity reduction and recovery of crude oil in a cyclic steam stimulation (CSS) process mainly occur near wellbores, injection, and production replacement exists between multiple wells and multiple cycles, and serious steam channeling between wells is also easy to occur [19–22].

Physical property changes during steam injection.

The mechanisms of reservoir petrophysical property changing under hot and humid conditions include mineral dissolution, transformation, wettability transformation, emulsion plugging, clay mineral dissolution, and particle migration. During a steam injection process, the injected steam interacts with reservoir rocks, which easily leads to rock particles falling off and migration with fluids in porous media. The formation of rock particles deteriorates the reservoir’s physical properties and is harmful to reservoir development. The solid particles migrate to pore throats and form “bridge blocks”, resulting in a decrease in permeability, and are easy to deposit on rock surfaces as heavy oil flows slowly, making the pores narrower. Steam condensates are usually characterized by low salinity and high alkalinity, which can easily accelerate the dissolution of quartz and induce mineral transformation. When a fluid containing silicate migrates to low-temperature pores, cementation will occur, and the pores will be plugged. The contact between steam condensate and reservoir minerals converts dolomite and kaolinite to analcite, calcite, montmorillonite, and chlorite, and the accumulation of these minerals significantly reduces the reservoir permeability. During a steam injection process, rapid changes in the fluid velocity, salinity, and temperature will also cause damage to reservoir permeability [23–26].

Variations of crude oil properties during thermal recovery.

Aquathermolysis exists both in CSS and steam flooding processes, and a series of chemical reactions such as acid polymerization and hydrodesulfurization occur between heavy oil and steam. The resin and asphaltene components in extra heavy oil will be converted to saturated and aromatic hydrocarbons, which can reduce the heavy oil viscosity. The distillation effect is obvious at 300 °C. On one hand, a variety of alkanes, cycloalkanes, and light aromatic hydrocarbons can be produced after cracking. On the other hand, thermal reactions of crude oil make macromolecules, highly condensed coking components, and carbon residues generated by polarization remain in porous media, which will block pores, and make reservoir rocks gradually transform to oleophilic [27–29].

1.2. In-Situ Upgrading of Heavy Oil

The composition of heavy oil is divided into saturated hydrocarbon, aromatic hydrocarbon, resin, and asphaltene (SARA) according to molecular polarity, and all kinds of substances contain O, N, S, and a small number of metal heteroatoms. Resin and asphaltene are the main reasons for the high viscosity of heavy oil. In essence, a viscosity reduction in heavy oil needs to break such macromolecules and molecular recombination, change the molecular composition and atomic arrangement, and destroy atomic bond interactions. The in situ upgrading of heavy oil can realize catalytic upgrading under reservoir conditions, thus irreversibly and greatly reducing crude oil viscosity. The recovery mechanism of the in situ upgrading technology is to transform heavy oil that has poor mobility under reservoir conditions into crude oil that can flow under a production pressure difference [30–33].

The viscosity reduction mechanisms of heavy oil include an irreversible chemical viscosity reduction after a catalytic reaction and a physical viscosity reduction in dilution and dissolution between the upgraded crude oil and the original heavy oil. Usually, upgrading catalysts are injected into a reservoir which is heated by steam or electromagnetic methods to provide the basic temperature for the upgrading chemical reactions. After a series of complex chemical and physical reactions, heavy oil can be exploited under normal
production pressure differences, and the quality of the oil is also significantly improved. The necessary conditions for the catalytic reactions of in situ upgrading are a catalyst, reactants, and reaction temperature [34–36]. The reactants include chemical agents such as hydrogen donors in an injection system and long-chain alkanes, aromatics, and resins in heavy oil. The injected upgrading catalyst must be in full contact with heavy oil and the ambient temperature reaches the threshold temperature of chemical reactions. Therefore, an efficient upgrading catalyst is the core of the reactions, and the injection process of catalyst dispersing sufficiently in a reservoir and the large-scale heating of the reservoir is the guarantee of a viscosity reduction effect of the upgrading reactions. The principle of catalytic upgrading is that the macromolecules in heavy oil break chemical bonds to become small molecules under the actions of high temperatures and catalysts. On one hand, by reducing the content of heavy components such as alkanes above C_{22}, resins, and asphaltenes and increasing the content of light components such as alkanes below C_{21} and aromatics, the average molecular weight of crude oil is reduced. On the other hand, the desulphurization and denitrification reactions can reduce the heteroatom content in crude oil and reduce intermolecular forces to achieve a substantial irreversible viscosity reduction in heavy oil [37–42].

1.3. Overview of Catalysts in In-Situ Upgrading

The key factor in the upgrading effect is a catalyst. The commonly used synthetic catalysts in an upgrading process can be divided into water-soluble catalysts, oil-soluble catalysts, amphiphilic catalysts, dispersed catalysts, and nanocatalysts [43–46]. Catalytic aquathermolysis and air injection catalytic oxidation are the widely adopted catalytic upgrading methods over the world. The water-soluble catalysts present a good upgrading property in the laboratory and are cheap. The oil-soluble catalysts can be fully mixed with crude oil, and more efficiently and accurately act on the macromolecules in heavy oil, thus promoting the macromolecules’ crack and obtaining good upgrading and viscosity reduction effects. The amphiphilic catalysts can have the advantages of both water-soluble and oil-soluble catalysts. The metal nanocatalysts can be highly dispersed in crude oil and promote hydrogen evaluation reactions in hydronitrogen compounds. For example, in the application of nanocatalysts for heavy oil viscosity reduction, downhole aquathermolysis plays a main role. During steam huff and puff, metal/bio nanoparticles (NPs) are injected into a reservoir together with steam, and metal NPs can catalyze the aquathermolysis reactions, making these reactions occur more easily [47–49].

Guo et al. [50] and Dong et al. [1] performed comprehensive reviews on EOR (enhanced oil recovery) techniques for heavy oil and bitumen, mainly focusing on thermal, chemical, and gas injection, as well as some typical hybrid processes. In this paper, the popular catalysts for heavy oil catalytic upgrading and viscosity reduction and their advantages and disadvantages are first reviewed. The status and application of catalytic upgrading methods are also introduced. Finally, the influence factors on an upgrading effect and the future trends of catalytic upgrading methods are discussed.

2. Catalysts for Upgrading and Viscosity Reduction

2.1. Water-Soluble Catalysts

Clark et al. [51–57] first proposed that water-soluble transition metal salts can promote the decomposition of sulfur-containing compounds in heavy oil and generate hydrocarbons, CO_{2}, H_{2}, and H_{2}S in the process of aquathermolysis. Water-soluble transition metal inorganic salt catalysts such as Fe, Ni, Zn, and Mn have been widely used in upgrading and viscosity reduction experiments of heavy oil. Chen et al. [58] used water-soluble catalyst (NH_{4})_{6}Mo_{7}O_{24}·4H_{2}O to study a catalytic upgrading effect on heavy oil in the Huanxiling Oil Production Plant in the Liaohe Oilfield. It was found that (NH_{4})_{6}Mo_{7}O_{24}·4H_{2}O with a mass concentration of 0.3% can upgrade 40% of the resins in heavy oil. It was considered that the degradation of heavy oil was due to the cracking of C-S bonds and the cracking of bridge bonds between the polycyclic aromatic hydrocarbons in the resins and C-C bonds at
the β positions in branched chains. Wang et al. [59] studied the influence of water-soluble catalysts Fe$^{3+}$ and Mo$^{6+}$ on an improvement effect of heavy oil by TLC-FID, elemental analysis, $^1$H-NMR, and GC-MS. Under an experimental temperature of 200 °C and reaction time of 24 h, the viscosity reduction rate of heavy oil can reach 95.6% and 99.3% with a mass concentration of 0.7% Fe$^{3+}$ or Mo$^{6+}$, respectively. These two catalysts showed different mechanisms of action. Catalyst Fe$^{3+}$ mainly acted on resins, saturated hydrocarbon, and oxygen-containing groups, while catalyst Mo$^{6+}$ mainly acted on asphaltene, aromatic hydrocarbon, and sulfur-containing groups. Fan et al. [60] studied the influence of water-soluble dispersed catalysts NiSO$_4$, VOSO$_4$, FeSO$_4$, and a hydrogen donor agent on the catalytic effect on ultra-heavy oil in the Shengli Shanjiasi Oilfield. Under the experimental conditions of 250 °C and 24 h, it was found that the hydrogen donor tetrahydronaphthalene had the most significant effect on a catalytic modification. When the catalyst and hydrogen donor are combined in their experiments, the viscosity reduction rate of Shanjiasi ultra-heavy oil can reach more than 70% under a synergistic effect, and a composite application has a more significant improvement effect than only using a catalyst.

At present, water-soluble catalysts have shown strong performance in upgrading under laboratory conditions and good economic advantages with a low price. However, field tests of water-soluble catalysts are not very optimistic [50]. The water-soluble characteristics of such catalysts determine that they mostly act on an oil-water interface and cannot fully mix with the oil phase to play a role in promoting oil quality. In addition, limited by formation conditions, most water-soluble catalysts are still dissolved in the water phase after being injected into a reservoir, and the mixing degree with heavy oil is too low to achieve ideal quality improvement and a viscosity reduction effect.

2.2. Oil-Soluble Catalysts

Oil-soluble catalysts can improve their solubility in crude oil and ensure contact between a catalyst and crude oil, thus improving the catalytic viscosity reduction effect. After being added to heavy oil, a polar group in an oil-soluble viscosity reducer combines with the resins on a resin core in heavy oil, and a long chain alkyl group in the viscosity reducer inhibits the condensation of an aromatic layer. Thus, the viscosity agent enters the space between macromolecules. A solvation layer is formed by disassembling the assembled molecules, thus reducing the viscosity of heavy oil. Oil-soluble catalysts are mainly organic acid salt formed by organic acids and transition metal ions such as Fe, Ni, Co, and Va. Wang et al. [61] found that oil-soluble catalysts had higher catalytic efficiency than similar water-soluble catalysts. Feng et al. [62] studied the improvement and viscosity reduction effects of oil-soluble catalysts on crude oil. They performed experiments at 220 °C for 24 h, using sulfonated organic acid iron with a mass weight of 0.4% as the catalyst. Their result showed that the viscosity reduction rate reached 96.3%, and the content of asphaltene and resin was reduced by 10.7%.

An oil-soluble catalyst was better dissolved in crude oil and had good compatibility with oil layers, which greatly improved the catalytic efficiency. However, the dissolution of oil-soluble catalysts in crude oil will increase the difficulty of subsequent oil processing and refining, and such catalysts are difficult to be injected into a reservoir through the aqueous phase, which usually requires the addition of solution-aids and challenges a technological process. In view of these problems in the injection of oil-soluble catalysts, some scholars have made optimization in the molecular structure or injection system of catalysts. Tang et al. [63] synthesized a polymer bifunctional viscosity-reducing catalyst, which improved the solubility of this catalyst by loading transition metal ions on the polymer. The catalyst not only improved the quality and reduced viscosity but also qualified for good physical viscosity-reducing function. The molecular structure of a polymer catalyst can effectively disperse the aromatic lamellae in glia and asphaltenes and reduce their accumulation and aggregation. Wu et al. [64] synthesized an amphiphilic catalyst and comprehensively analyzed crude oil samples before and after their upgrading by various means such as nuclear magnetic resonance, and found that the amphiphilic catalyst promoted cracking
and inhibited polymerization at the same time, achieving a viscosity reduction effect of heavy oil. Huang et al. [65] used a combination of iron naphthenate, an oil-soluble catalyst, and iron nitrate, a water-soluble catalyst, to form an amphiphilic catalytic upgrading system. The amphiphilic system increased the solubility of the upgrading system, and the synergistic effect increased the viscosity reduction rate of the oil-soluble catalyst from 56.29% to 97%. However, it is difficult to control the stability of the amphiphilic structure of the catalyst, resulting in an imbalance of hydrophilicity and lipophilicity. The components of the amphiphilic complex system are prone to separate in a process of reservoir migration, and a concentration change between the oil-soluble and water-soluble catalysts in the system will affect the improvement effect.

Compared with water-soluble catalysts, the advantage of oil-soluble upgrading catalysts is that they can be fully mixed with oil, act on heavy oil macromolecules more efficiently and accurately, promote the chain breaking of macromolecules and other reactions, and obtain better catalytic upgrading and viscosity reduction effects. However, in field applications, the use of oil-soluble catalysts requires supporting carrier agents, which can be used to bring the catalysts into a reservoir for mixing and upgrading reactions with heavy oil. The carrier agents will lead to the rise of production costs and cause potential pollution to the reservoir environment [66–70].

2.3. Amphiphilic Catalysts

The catalytic aquathermolysis brings a new idea of heavy oil recovery, especially for ultra-heavy oil. The key to this technique is the development of an aquathermolysis catalyst. The current catalysts have problems such as high reaction temperature (>240 °C), insufficient contact with heavy oil, and low catalytic activity, which are difficult to meet field requirements. Therefore, it is very important to develop a kind of catalyst that is suitable for lower formation temperatures and can fully contact with crude oil, which determines a large-scale field application for this technique.

Wu et al. [71,72] studied the physical and chemical properties of ultra-heavy oil in Shengli Shanjiasi Oilfield systematically, and the main factors affecting the high viscosity of the ultra-heavy oil were put forward. Two kinds of catalysts, microemulsion nano-nickel and nickel sulfonic acid, were synthesized and their synthesis processes and properties, including salt resistance and universality, were presented. The laws of thermal cracking, aquathermolysis, and catalytic aquathermolysis of ultra-heavy oil were investigated with the use of a high-temperature-high-pressure reaction oven and a steam flooding system. They also investigated the mechanisms of upgrading, viscosity reduction and reaction kinetics of ultra-heavy oil by gas chromatograph, an elemental analyzer, a molecular weight analyzer, an infrared spectrometer, a nuclear magnetic resonance spectrometer, and chemical molecular simulation technology. The results showed that microemulsion nano-nickel and nickel sulfonic acid hydrothermal cracking catalysts had good viscosity reduction effects on Shengli ultra-heavy oil, and the synthesis of these two kinds of viscosity reduction catalysts had good salt resistance and universality. High-temperature water had a certain catalytic effect on the viscosity reduction in heavy oil aquathermolysis cracking, but the degree of catalytic viscosity reduction was limited. The synthesis of these two kinds of viscosity reduction catalysts effectively promoted the aquathermolysis reactions, and inhibited the polymerization reactions in the process, so that the heavy components of heavy oil were converted to light components.

An amphiphilic catalyst can fully contact with heavy components of heavy oil, and the particles or groups of the catalyst carrying active catalytic functions acted with high-temperature water on the bonds in molecules, resulting in series chain breaking, hydrogenation, ring opening, ring formation, desulfurization, denitrification, and other reactions [73,74]. After the reactions, the surface area, volume, hydrophobicity, refractive index, and polarity parameters of asphaltene and reins molecules in heavy oil were reduced, the intermolecular van der Waals, dispersion, and hydrogen bond forces were weakened, a system became more dispersed, the viscosity of heavy oil was greatly reduced, and the
quality of heavy oil was improved. On this basis, the mechanisms of upgrading and viscosity reduction by catalytic aquathermolysis of heavy oil were comprehensively discussed, including the mechanisms of high-temperature water cracking, hydrogenation, asphaltene cracking, light hydrocarbon dissolution, intermolecular force reduction, and catalytic viscosity reduction. Asphaltene cracking played a key role in decreasing the viscosity and average molecular weight of heavy oil.

Both oil-soluble catalysts and water-soluble catalysts have their own advantages and disadvantages. When the two catalysts are combined, the advantages of these two catalysts can be expanded, while their respective disadvantages can be weakened to a certain extent, so that the adaptability of the catalysts is higher and the viscosity reduction rate of heavy oil can be further improved. However, a combination of catalysts will lead to more complex reaction processes. Further studies are still needed to characterize the reaction processes of different combination catalysts, clarify the reaction mechanisms, and provide theoretical guidance for the application of amphiphilic catalysts [75–77].

2.4. Solid Catalysts

The common solid catalysts for aquathermolysis include immobilization catalysts, heteropoly acid catalysts, zeolites, molecular sieve catalysts, metal oxides, metal carbides, and metal nanoparticles. Among them, solid acids have been widely used in the petroleum industry, and many industrial heavy oil refining reactions use solid acids as a catalyst. The catalytic activity of solid acids is affected by many factors, such as a specific surface area, acidity, an acid type, shape selection, pore structure, stability, and a preparation route. The larger the specific surface area, the higher the acidity and the stronger the catalytic ability of solid acids. In particular, a molecular sieve catalyst has the property of a shape selection. The size of a channel in a crystal is different, which makes only a specific size or shape of molecules pass through a channel. In the catalytic cracking of heavy oil, many intermediates with high activity will be produced. The use of a suitable selective catalyst will make the catalytic reactions of heavy oil proceed in a favorable direction. Different molecular sieves have different pore structures so a study on the compatibility of the catalytic reactions between solid acids and heavy oil becomes very valuable. An immobilized catalyst is a combination of a catalytic active center with solid support by physical or chemical methods. The active components in the catalyst tend to have high activity and selectivity because of a large specific surface area. Heteropoly acids are known for their strong acidity, so they are used in many reactions that require catalyst acidity, including aquathermolysis of heavy oil [16]. Natural zeolites have also been studied as catalysts for aquathermolysis due to their high stratigraphic abundance and acidic structure. Because of their hydrothermal stability, hydrophobic zeolites are also a promising catalyst for underground upgrading of heavy oil. However, the synthesis conditions of hydrophobic zeolites are very harsh. The hydrophobic properties of a zeolite can be improved by increasing the Si/Al ratio of zeolite materials, but this will also reduce the acidity of a catalyst, thus reducing its catalytic activity in an aquathermolysis process of heavy oil. To solve this problem, it is very beneficial to prepare catalysts with fluoride or to modify them with organosilane compounds, which can increase the hydrophobicity of a catalyst without destroying its acidic structure. Nano-solid superacid catalysts have the advantages of easy preparation and high strength. However, they will be converted into bronsted acids with water [78]. Therefore, a solid acid catalyst should be applied for catalytic upgrading without water; otherwise, the corrosion of recovery equipment and pipelines will be caused. However, such application conditions have very strict requirements on the production process of heavy oil.

2.5. Dispersed Catalysts

The dispersed catalysts have a good effect on heavy oil upgrading and viscosity reduction. In addition, the use of different hydrogen donors such as cyclohexane, methylcyclohexane, and tetrahydronaphthalene during aquathermolysis improves the quality
of heavy crude oil [79,80]. The most common hydrogen donor is tetrahydronaphthalene. When the hydrogen donor is used in combination with a catalyst, the effect of a viscosity reduction is better than that of the catalyst alone. Based on the improved mobility of crude oil, the overall evaluation of the effectiveness of catalysts is as follows: dispersal catalyst > oil soluble catalyst > water-soluble catalyst > natural catalysts in reservoir minerals.

When a conventional catalyst is used in an aquathermolysis process, the oil viscosity was reduced by up to 98%. However, this reduction is not sufficient for the crude oil to be pumped into pipelines. Super-dispersed catalysts can be divided into heterogeneous and homogeneous ones. Homogeneous catalysts are classified as soluble compounds in aqueous or organic phases. Heterogeneous catalysts are introduced into solids in a treatment process by dispersing finely crushed catalytic solids or precursor dry states into crude oil [81–84]. The main disadvantages of heterogeneous solids are that they have lower activity and produce by-products that are difficult to handle. Soluble precursors are highly reactive, but they are used in large quantities and, therefore, expensive. Soluble compounds in the aqueous phase are injected as catalytic emulsions in a treatment process, whose advantage is that these precursors are cheaper than organometallic substances.

The mechanisms of an ultra-dispersed catalyst in a process of upgrading and viscosity reduction include activating a reactant, accelerating a hydrogenation reaction rate, and increasing a conversion rate of heavy oil hydrogen supply upgrading. The catalytic actions of the catalyst can form a chemisorption bond with hydrogen molecules, change a crack pathway of hydrogen molecules, and reduce the activation energy of a reaction between hydrogen molecules and free radicals, thus accelerating the hydrogenation cracking reactions of heavy oil organic molecules. Meanwhile, the catalyst also promotes the C-C bond cracking in the organic material of heavy oil dissolved in a hydrogen donor, which is conducive to the cracking reactions of the organic material of heavy oil and the initial pyrolysis products [85–88].

2.6. Ionic Liquid Catalysts

In recent years, ionic liquids (ILs), as a new type of green surfactant, have attracted wide attention in the catalytic upgrading of heavy oil. ILs belong to organic salts, are a kind of liquid at 100 °C or below 100 °C and are completely composed of ionic compounds. ILs achieve changes in their physical and chemical properties through changes in cations, substituents, and anions. Compared with the liquid phase of traditional solvents (mostly between 75 °C and 200 °C), ILs have no vapor pressure and present a liquid phase from room temperature to 400 °C, which has a very wide range of operations and applications [89–91]. ILs are green solvents in terms of applicability, environmental protection, and economy.

Fan et al. [92] synthesized an alkyl imidazole-type ionic liquid [Bmim][AlCl₄], and studied the effects of sulfur content, water content, transition metal salts, and temperature on the upgrading and viscosity reduction in Tarim heavy oil in Xinjiang, China. Their experimental results showed that a water content of less than 10% was a basic condition for an effective viscosity reduction. The catalytic activity of ILs is mainly on the hydrogen protons of an imidazole ring. When an IL encounters water, the hydrogen bonds between the water molecules and the hydrogen protons of the imidazole ring are easy to form, and an interaction between them is greater than that of ordinary hydrogen bonds, so the IL will be inactivated. Their study further confirmed the mechanisms of C-S bond cracking and hydrogen bond formation during an upgrading and viscosity reduction process and preliminarily discussed the applicable principle of ILs when the water content was greater than a certain value. Different heavy oils differ from each other due to geological conditions and later modification, and sulfur content is also different, so the dominant mechanisms can be different. In addition, the water content is also a dynamic parameter, which poses more challenges to the application of ILs for upgrading and viscosity reduction and needs further research.
2.7. Bio-Based Catalysts

At present, nanomaterials are increasingly used for catalytic reactions. Even substances without a catalytic activity will have catalytic performance when a particle size reaches the nanoscale. Due to their small nanostructure and large specific surface area, the use of nanocatalysts will have higher catalytic efficiency. With the development of nanotechnology, biosynthesis technology is more suitable for the sustainable development of the environment and has attracted more attention in recent years. Tang et al. [93] prepared a biomass-based catalyst for catalytic upgrading and viscosity reduction in Liaohe heavy oil. An optimal catalytic effect was achieved with a 0.2 wt% target catalyst at 320 °C for 30 min. They achieved a 95.63% reduction in oil viscosity from 508,800 to 22,230 mPa·s (@50 °C) and a 10.1% decrease in resin content after an optimal experiment. They also found that the non-acidic components in the target catalyst can act as dispersants or hydrogen donors to partially inhibit the reaggregation of a macromolecular structure, thereby weakening the π-π bonds in polycyclic aromatic systems and improving the heavy compositions in heavy oil, as shown in Figure 1 [93].

![Figure 1. Schematic diagram of catalytic upgrading process, adapted from [93].](image)

Some microorganisms can convert heavy metals in the environment into elemental forms through redox reactions. The negatively charged groups in biomass include hydroxyl (-OH), amino (-NH2), and carboxyl groups(-COOH). When biomass and metal salt precursors are combined, metal ions, such as silver ions (Ag+) and gold ions (Au3+), are reduced to zero valences, whose process is enzymatically carried out either intracellularly or extracellularly [94–96]. The extracellular enzymes of microorganisms can reduce the heavy metals around cells, while the intracellular enzymes are targeted to reduce metal ions inside the microbial cells. The particles produced in this way have a larger specific surface area and a higher catalytic activity [97–99]. Furthermore, these nanoparticles (NPs) can be designed in various shapes and sizes. Since the 1990s, many microorganisms have been introduced to synthesize metal compound NPs or metal NPs in the form of oxides and sulfides. Microorganisms can obtain metal ions from the environment, and the reduction in metal ions and the formation of NPs involve the participation of microbial-secreted metabolites [100–103]. Another theory for microbial synthesis of nanoparticles is that bacteria synthesize metal NPs through a detoxification pathway because bacteria are continuously exposed to a toxic environment with high concentrations of heavy metal ions. Microbial cells are a complex system, so it is very difficult and needs time to study the specific mechanisms of NP synthesis by microorganisms [104,105]. The common microbial NPs include bacterial, fungal, and algae, and there are two main mechanisms for metal NPs in catalytic upgrading and viscosity reduction in heavy oil.
3. Catalytic Upgrading and Viscosity Reduction Methods

3.1. Catalytic Aquathermolysis for Heavy Oil

Aquathermolysis for heavy oil recovery is a technique based on steam injection or in situ combustion (ISC) with the injection of catalysts and other additives to promote the aquathermolysis reactions. The heavy components in crude oil are cracked and upgraded, thus reducing the heavy oil’s viscosity and increasing its mobility. The Canadian scientist Hyne first proposed the concept of aquathermolysis [106]. A series of reactions, including denitrification, desulfurization, and hydrogenation of heavy oil under the action of high-temperature steam are together called aquathermolysis. A catalyst addition in a process of the above reactions will promote asphaltene and resin molecules to crack at some weak bonds; that is, the aquathermolysis occurs. The molecular configurations of asphaltene and resin before and after the aquathermolysis reaction are shown in Figure 2.

![Molecular configuration of asphaltene before aquathermolysis reaction](image1)

![Molecular configuration of asphaltene after reaction with nanonickel](image2)

![Molecular configuration of asphaltene after reaction with amphiphilic nickel](image3)

![Molecular configuration of resin before aquathermolysis reaction](image4)

![Molecular configuration of resin after reaction with nanonickel](image5)

![Molecular configuration of resin after reaction with amphiphilic nickel](image6)

**Figure 2.** Molecular configurations of asphaltene and resin before and after aquathermolysis reaction, adapted from [72].

The aquathermolysis of heavy oil is largely determined by its specific molecular composition. Organic sulfides in heavy oil are the key substances in their reaction with high-temperature water, and C-S bond cracking is a key in an aquathermolysis process. Gases, such as CO₂, H₂S, CH₄, CO, and H₂ are produced during aquathermolysis, among which CO₂ and H₂ have higher production. The gas production may depend on the relative amounts of various types of organic sulfides, and a water-gas conversion reaction is important in the aquathermolysis of heavy oil. The most important characteristic of aquathermolysis is that the hydrogen transfer from water to oil phases leads to a hydrodesulfurization reaction of sulfur-containing organic compounds in a heavy oil recombination fraction so that heavy oil can be modified. The viscosity and average molecular weight of heavy oil decrease after aquathermolysis. For example, the Canadian heavy oil viscosity decreases by more than 50% and its average molecular weight decreases by 25% at a temperature between 200–300 °C as the reaction time is long enough. At the same time, the viscosity of
the Canadian heavy oil is increased at the early stage of aquathermolysis at a temperature between 200–240 °C [107].

The crack of organic sulfur compounds in heavy oil is not accomplished in one step but through a series of reactions, including acid polymerization, low-temperature oxidation, and water-gas conversion. Metals show a positive and catalytic effect on aquathermolysis [21,108–113]. Metal ions play a catalytic role in the crack of C-S bonds, WGSR (Water Gas Shift Reactions), hydrocracking, and hydrodesulfurization. Addition of metal ions, oxides, or sulfides breaks the C-S bonds in the heavy oil, reducing the content of asphaltene or the average molecular weight of asphaltene, resulting in a decrease in the viscosity of heavy oil. The thiols generated by the reactions are further hydrolyzed to release H₂S. In addition, the enols in the products can be changed into aldehydes, which are easily broken down to produce CO. Under the action of a catalyst, CO, and water undergo WGSR to produce hydrogen, making the hydrodesulfurization proceed smoothly. As a result, the asphaltene in the heavy oil is partially modified due to the aquathermolysis during steam huff-n-puff above 200 °C, which shows a decrease in the average molecular weight, viscosity, and sulfur content of the heavy oil. The cracking reaction and polymerization reaction in the aquathermolysis are competing. An increase in viscosity observed at the beginning of some experiments is probably due to the predominance of polymerization. However, the addition of a catalyst promotes the cracking reaction, but inhibits the polymerization, so that the aquathermolysis proceeds in the favorable direction of upgrading heavy oil.

For a field application of catalytic aquathermolysis, Liu et al. [114,115] first carried out a field application test of aquathermolysis for heavy oil recovery in the Liaohe Oilfield. Under the condition of steam huff and puff, they made ultra-heavy oil in situ aquathermolysis cracking by adding a catalyst and an auxiliary system with the method of slug injection. The experiments of aquathermolysis recovery in situ were carried out in the Du84 region in Liaohe Oilfield. At a temperature of cyclic steam stimulation (160–240 °C), the aquathermolysis of the extra heavy oil consequently took place in the formation with the addition of the catalyst and compounding chemicals. Additionally, the oil recovered by aquathermolysis was upgraded. The total carbon number and aromatic carbon number obviously decreased, and so did the ring number of aromatic and naphthenic hydrocarbons. These implied that some gases and light hydrocarbons were formed. In an early production period, the viscosity reduction ratio came to 80% and decreased to 50% in 30 days. The production for the eight experimental steam injection wells by aquathermolysis was significantly increased, and the accumulative oil production of these eight test wells was 5933.9 t, with an average oil production of 740 t. It was proved that the aquathermolysis recovery technique was feasible for the Liaohe heavy oil, and the obvious economic efficiency could be achieved.

Catalytic aquathermolysis is a promising method for viscosity reduction and heavy oil recovery, but some problems and challenges make it still have a long way to go before it can be used as an effective technique in fields. The R&D of catalysts for catalytic aquathermolysis is still in the initial stage in China and cannot meet the needs of heavy oil exploitation either in variety or quantity. In addition, there is a lack of in-depth and systematic research on the mechanisms of catalytic viscosity reduction by aquathermolysis. On one hand, heavy oil is a complex macromolecular compound, and its composition and structure are not determined. Thus, it is difficult to find a suitable model for simulation and understand its cracking kinetic mechanisms. On the other hand, it is not easy to capture the formation of some small molecules and fragments. All of these bring difficulties and challenges to the future study of the mechanisms. What’s more, the lack of simulation calculations before test and optimization research of an implementation process limits a field application of this technique. In general, there is a corresponding simulation program that can simulate the effect, production, and dynamic characteristics of steam injection. However, there is no such technology for catalytic aquathermolysis. Moreover, the steam temperature and quality in a field test are not high enough, resulting in low reservoir temperature. A catalytic viscosity reducer cannot shake the skeleton structure of heavy oil molecules, but
can only destroy part of its branch chains, so that a viscosity reduction effect is limited, and a recovery effect is greatly affected. In recent years, except for catalysts, hydrogen donors or emulsifiers are also added during an aquathermolysis process to improve the viscosity reduction effect of heavy oil.

3.2. Air Injection Catalytic Oxidation for Heavy Oil

Due to abundant and cheap gas resources, the air is widely used in oil reservoir exploitation. Air catalytic oxidation upgrading and viscosity reduction are a method that irreversibly reduces the viscosity of heavy oil by air injection to accelerate the cracking and lightening of heavy components and the emulsification and dispersion of heavy oil by oxidation products under the action of a catalyst. It not only has an effect on conventional flooding by increasing reservoir pressure but also generates oxidation reactions, which release a lot of heat that is beneficial to displace heavy oil [116–119]. Air injection for heavy oil refers to the technique of ISC. It mainly uses the reactions between crude oil and oxygen in the air, which burns to release large quantities of heat and makes heavy oil crack under high temperatures, thus irreversibly improving oil quality. The crude oil viscosity is decreased, and its mobility is increased. The in situ formed steam flooding and flue gas flooding also contribute to heavy oil recovery [120–123]. There are mainly three intervals for the oxidation reactions of most crude oils, namely a low-temperature range (LTR), a negative temperature gradient range (NTGR, a reaction rate decreases with an increase in temperature), and a high-temperature range (HTR), shown in Figure 3 [109]. For heavy oil and oil sands, a LTR reaction rate and a heat release rate are low, while a HTR oxidation rate is very obvious and its oxygen consumption rate and heat release rate are very large. Initially, the injected air is distributed in a near wellbore area in porous media and leads to the emergence of low-temperature oxidation (LTO) reactions. The reaction heat makes oxygen dissolve in crude oil at reservoir temperature and generates oxygen compounds, such as aldehydes, ketones, carboxylic acids, alcohol, and hydrogen peroxide, as shown in Equations (1)–(6) [110]. During the oxidation reactions, the viscosity, density, boiling point, and asphaltene content of crude oil increase, while the content of saturates and aromatics decreases. Therefore, LTO is undesirable in an ISC process, whereas its presence makes the high-temperature oxidation (HTO) reactions more likely to occur because they are the first exothermic reactions to occur. As the air volume and temperature in a reservoir rise significantly, the middle-temperature oxidation (MTO) or fuel deposition reactions occur. During this period, dehydrogenation, cracking, and condensation reactions occur. In the dehydrogenation reactions, hydrogen atoms are derived from hydrocarbon molecules, while the carbon atoms will not change. In the cracking reactions, the C-C bonds break, and finally, some of the carbon atoms gather to form carbon-rich compounds or cokes, which are the fuel of HTO reactions. During the HTO reactions, cokes react with oxygen to form carbon dioxide and water. The heat released is sufficient to sustain the propagation of a burning front.

![Figure 3. A schematic diagram of the oxidation reaction of heavy oil at different temperatures, adapted from [109].](image-url)
The oxidation process of hydrocarbons (hydrocarbons) in crude oil is described as follows [110]:

Complete combustion:

\[
R - C - R' + \frac{3}{2}O_2 \rightarrow RR' + CO_2 + H_2O \quad (1)
\]

Incomplete combustion:

\[
R - C - R' + O_2 \rightarrow RR' + CO + H_2O \quad (2)
\]

Oxidized to carboxylic acid:

\[
R - C - H + \frac{3}{2}O_2 \rightarrow R - C - OH + H_2O \quad (3)
\]

Oxidized to ketone:

\[
R - C - R' + O_2 \rightarrow R - C - R' + H_2O \quad (4)
\]

Oxidized to alcohol:

\[
R - C - R' + \frac{1}{2}O_2 \rightarrow R - C - O - H \quad (5)
\]

Oxidation to peroxides:

\[
R - C - R' + O_2 \rightarrow R - C - O - O - H \quad (6)
\]
The main constraint limiting the applicability of ISC is the amount of fuel prior to a combustion zone. The local fuel quantity and combustion front rate are controlled by the kinetics of oxidation and pyrolysis of crude oil in porous media. A catalytic compound affects the kinetics of reactions and, therefore, the amount of fuel formed. Catalysts can significantly change an oxidation process of SARA components at low temperatures, and promote the formation of hydroxyl oxides and CO$_2$, while they inhibit the formation of ethers. The addition of a catalyst makes the temperature range of each reaction stage move towards a low-temperature region. The temperature ranges of the LTO and HTO stages shrink, and the temperature range of thermal cracking expands. The heat release of an oil sample in a low-temperature oxidation stage increases. The crude oil is upgraded by the catalyst. After reactions, the content of saturates and aromatics is increased, while that of resin and asphaltenes is decreased. If appropriate catalysts can be introduced into a reservoir to modify the tendency of oil to deposit fuel, ISC can be made feasible for a wider range of crude oils and reservoirs [124–127].

Low-temperature catalytic oil with air injection (LTCOAI) is a new technique to improve the effect of steam injection. Tang et al. [128–133] have carried out a lot of work and concluded the EOR mechanisms as follows: (a) The injection of air can maintain and increase reservoir pressure, thus increasing reservoir elasticity, which is beneficial to liquid flow back and artificial lift in a wellbore. (b) A small amount of CO and CO$_2$ is generated during an LTO process, together with N$_2$ to form flue gas flooding, and N$_2$ can adjust a steam absorbing profile and inhibit steam override, thus increasing thermal efficiency. (c) A large quantity of polar hydrocarbons containing an oxygen compound is generated, which can form surfactant flooding with alkaline additives. It can decrease the interfacial tension between oil and water and increase oil displacement efficiency. (d) The injected steam and heat released by LTO will heat a reservoir, thus reducing oil viscosity and increasing oil mobility. (e) The injection of catalysts with catalytic oxidation and cracking activity can not only accelerate the consumption of oxygen in the air to ensure the safety of oil production but also promote crude oil upgrading. The oil molecular weight is reduced, and the oil quality is increased.

Xia et al. [134–139] have carried out a lot of research on CAPRI (the catalytic version of THAI) (as shown in Figure 4) on the basis of THAI (Toe-to-Heel Air Injection) for Wolf Lake heavy oil, Lloydminster heavy oil, and Athabasca Oil Sand bitumen. THAI and CAPRI are relatively new technologies for the upgrading and recovery of heavy oil and bitumen, which combine horizontal production wells, in situ combustion, and catalytic cracking to convert heavy components into light oils in situ. They found that compared with thermal upgrading alone (the THAI process), the crude oil viscosity is reduced sharply with the use of a catalyst (NiMo or CoMo) (the CAPRI process). Hart et al. [140–147] also studied the catalytic upgrading effects of heavy oil in the CAPRI process. They used Co-Mo/Al$_2$O$_3$ as a dispersed catalyst and performed the experiments at a temperature of 425 °C and a pressure of 20 bar. In their study, in addition to an increase of 5.6° in the API gravity of the crude oil, there was also a 38.6% reduction of sulfur content, which not only increases oil mobility but also improves oil quality.

The composition of reservoir rock, clay minerals, and mental salts play a very important role in the oxidation kinetics of crude oil. There are illite, montmorillonite, chlorite, and kaolinite in a reservoir, and different clay minerals have different catalytic capabilities. Vossoughi et al. [148] studied the influence of silica and kaolin on the pyrolysis of crude oil. They pointed out that kaolin and silica had an important influence on the shape of a DSC curve, and the addition of kaolin and silica changed the temperature interval from which a large amount of heat was generated to a lower temperature interval. The presence of kaolin changed an oxidation reaction process, catalyzed the oxidation reactions, and reduced the activation energy. Kaolin showed a very high catalytic effect in the pyrolysis stage of crude oil combustion, while silica had no catalytic effect. Kozlowski et al. [149] studied the catalytic effect of clay on ISC performance with oil samples from Mexico and Alberta, Canada. Their results showed that the catalytic effect of clay controls the combus-
tion front propagation, the fuel formation, and the produced oil quality. Clays visualized on postmortem samples in the shape of lumps indicated that clay alteration occurred at elevated temperatures due to an interaction of clay with crude oil and due to the thermal decomposition of clay. The lump formation was associated with mainly saturates and asphaltene contents of initial oil and an asphaltene-clay interaction during fuel formation. Yu et al. [150] studied the effects of montmorillonite, kaolinite, and chlorite on Liaohe heavy oil oxidation before ignition in an ISC process at different reservoir temperatures and air/oil ratios. Their results showed that clay improved a reaction rate, accelerated a heat release rate, and magnified the rate of oxygen consumption on crude oil in an LTO stage. Meanwhile, due to the catalytic action of clay proceeding in fuel deposition, after oxidation, the concentration of asphalt in crude oil increased as a side effect. The catalytic activities of all three types of clay minerals increased in crude oil LTO with the rising temperature and an increase in the air/oil ratio. Except for clay minerals, mental additives are also widely used as catalysts for heavy oil recovery with air injection.

![Figure 4. Schematic diagram of the CAPRI process, adapted from [138].](image)

For applications, from 2008 to 2010, low-temperature catalytic oxidation air injection was applied for eight heavy oil wells in Du 84 Block, Liaohe Oilfield, China. The liquid production and oil production both increased obviously after stimulation, as shown in Table 1. Since October 2008, Shuguang Oil Production Plant has implemented low-temperature catalytic oxidation-assisted steam huff-n-puff for heavy oil recovery. By the end of 2013, 511 wells have been implemented in total, with an oil increment of $22.8 \times 10^4$ t. At present, this technology has become the key technology of stable production in the Liaohe oilfield. Well C4-8 in Block Caoqiao in Shengli Oilfield started steam huff-n-puff in 2006. After six cycles of development, the oil-steam ratio (OSR) dropped to 0.38, showing a poor effect. In 2010, a field experiment was carried out on Well C4-8 by air injection with a catalyst. After the measurement, the periodic oil production and liquid production of Well C4-8 increased obviously, and the periodic water production rate decreased from 77.7% to 57%, while the OSR increased from 0.38 to 0.91 [132]. Qi40 Block in the Liaohe oilfield started steam flooding in 2006, and the oil production of some wells declined quickly in a late period of flooding. Field tests of air-assisted steam flooding were carried out for three well groups in 2010. Among them, the oil production of well group Qi40-17 increased obviously from 70.3 t/d to 97.8 t/d [151]. The results showed that the LTCOAI can effectively improve the oil recovery in a late stage of steam injection with the use of cheap air. There are several advantages of this technique. Air is adopted as an injection medium, which is not limited
by regions and has the oil displacement effects of \( \text{N}_2 \) and \( \text{CO}_2 \), while the cost can be saved by 40%~50%. Meanwhile, the requirement of gas injection pressure during this technique is obviously lower than that of ISC, so a suitable air compressor can be adopted, having obvious economic benefits. LTCOAI can be implemented at 80~200 °C, which breaks the temperature limit of heavy oil production by air injection. For example, the temperature required for fire flooding is more than 500 °C. Oxygen is consumed by LTO reactions, which are easy to be controlled and safe. During an LTO process, the heavy crude oil is thermally cracked and catalytically cracked under the actions of steam and a catalyst. The content of light components (saturates and aromatics) is increased while the heavy components (asphaltenes and resins) are decreased. The average molecular weight is also decreased. The oil is upgraded, and the oil quality is improved. In addition, the laboratory experimental results show that LTCOAI has strong reservoir adaptability and is suitable for the recovery of common heavy oil, extra heavy oil, super heavy oil, onshore heavy oil, and offshore heavy oil. In recent years, air foam flooding has been adopted in Baise, Zhongyuan, Liaohe, Yanchang, and Xinjiang oilfields in China to block high permeability reservoirs and effectively improve the recovery of light oil reservoirs [152,153]. For heavy oil reservoirs in the middle and late stages of steam injection development, the steam channeling and intra-layer and inter-layer contradictions become more and more obvious. It will be an important research direction to apply air foam flooding in heavy oil reservoirs to block high permeability layers, expand steam sweep efficiency and improve heavy oil recovery in the future.

### Table 1. Field applications of low temperature catalytic oxidation air injection in Liaohe Oilfield, adapted from [154].

<table>
<thead>
<tr>
<th>Well Group</th>
<th>Before Measurement</th>
<th>After Measurement</th>
<th>Increment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid Production/(t/d)</td>
<td>Oil Production/(t/d)</td>
<td>Water Cut/%</td>
</tr>
<tr>
<td>S1-42-039</td>
<td>0</td>
<td>0</td>
<td>/</td>
</tr>
<tr>
<td>S1-42-041</td>
<td>3</td>
<td>0.4</td>
<td>86.7</td>
</tr>
<tr>
<td>S1-38-38C</td>
<td>1.6</td>
<td>0.5</td>
<td>68.8</td>
</tr>
<tr>
<td>S1-45-23</td>
<td>3.5</td>
<td>1.6</td>
<td>54.3</td>
</tr>
<tr>
<td>D80-26-68</td>
<td>8.4</td>
<td>2.5</td>
<td>70.2</td>
</tr>
<tr>
<td>D48-DH1</td>
<td>3.1</td>
<td>0.6</td>
<td>80.6</td>
</tr>
<tr>
<td>D212-DH13</td>
<td>0</td>
<td>0</td>
<td>/</td>
</tr>
<tr>
<td>D212-DH16</td>
<td>1.3</td>
<td>0.6</td>
<td>53.8</td>
</tr>
</tbody>
</table>

#### 3.3. Microwave-Assisted Catalytic Upgrading

Microwave heating is a selective and volumetric heating technique, which features very high frequencies of about 300~300,000 MHz and shorter wavelengths [154,155]. Microwave is expressed in the form of heat after interacting with medium or material, and has the characteristics of fast heating speed, selective heating, volumetric heating, and low energy loss. As an efficient, fast, and clean new oil recovery method, microwave oil recovery is mainly used for deep, thin, and offshore heavy oil, super heavy oil, and other unconventional reservoirs. Microwave heating has the advantages of high heating efficiency and environmental protection [155–162]. Jiang et al. [163] selected crude oil from Liaohe and Tuha oilfields in China to perform microwave heating experiments. They tested the rheological properties before and after microwave heating and found that the colloid and asphaltene of the oil samples decreased, alkane and aromatic increased, and the oil viscosity and solidifying point decreased obviously. They also established a thermodynamic model of microwave and crude oil based on the theory of electromagnetic field and thermodynamics. A temperature distribution indicated that selective heating of microwave heating made heavy components in heavy oil cracks. Microwave heating-assisted catalytic upgrading and viscosity reduction are new techniques in recent years. Many transition metal nanoparticles that are applied in the study...
of microwave heating viscosity reduction can promote microwave absorption, enhance the heat conduction of oil samples, and thus play a better effect on viscosity reduction. Wan et al. [164] described an application of microwave on catalysis for crude oil. Copper or nickel was used as a microwave activation catalyst to treat oil sands and asphalts. The asphalt was hydrocracked to generate C1–C5 and desulfurized to generate H2S. Taheri-Shakib et al. [160] used iron, titanium oxide, and superactive carbon nanomaterials as catalysts to process Iran’s heavy oil under the condition of microwave. They found that the addition of nanoparticles makes the crack of heavy components more than the loss of light components in heavy oil. Their results showed that in terms of viscosity reduction, the super-activated carbon has the highest viscosity reduction within six min, which can reach 882.37 mP·s. In terms of asphaltenes removal, the iron nanoparticles have the best effect in reducing the asphaltenes content from 12.75% to 9.13% by weight within four min. Iskandar et al. [165] synthesized a zeolite-supported Fe3O4 catalyst. After a microwave treatment, Fe3O4 and zeolite showed synergism, which can play a catalytic role in heavy oil cracking. The viscosity reduction rate reached 92% at 200 °C for 6 h. Greff et al. [166] studied the effect of microwave radiation at 2.45 GHz on viscosity reduction, using Fe, Fe2O3, and Cu nano-metal particles as catalysts with concentrations between 0.1% and 1%. The viscosity of oil samples was measured at 55 °C, 75 °C and 95 °C, respectively, by continuous heating with microwave at 200 °C for two hours. No hydrogen donor was added to the experiments, and only a pyrolysis reaction was performed. It was found that the use of a small amount of nanocatalyst can reduce the viscosity of heavy oil, but with an increase in temperature, the volatilization of light components also led to an increase in viscosity. Li et al. [167] utilized the microwave with 800 W power and 2450 MHz frequency to heat heavy oil at 150 °C and used carbon particles with diameters of 21 nm, 70–80 nm, 5.7–7.1 μm and 40–50.1 μm, respectively. The reaction time was less than one hour, but the viscosity of the heavy oil was reduced by 96%. The oil samples could still flow after 20 days. It was found that the C-S bonds in the heavy oil were broken, and the macromolecules were cracked. Compared with a mental nanocatalyst, a carbon nanocatalyst was cheaper, and the pollution in the oil samples was less.

3.4. Ultrasonic-Assisted Catalytic Upgrading

When an ultrasonic wave propagates in a liquid medium, it will produce mechanical, thermal, optical, electrical, chemical, and other effects. The ultrasonic wave has three basic functions, namely a mechanical vibration effect, a thermal effect, and a cavitation effect. An ultrasonic viscosity reduction technology of crude oil belongs to an application of the ultrasonic cavitation effect, which has the advantages of an obvious effect, no pollution, good safety, and low costs. By introducing ultrasonic wave into a process of catalytic upgrading and viscosity reduction for heavy oil, a chemical reaction rate and the production of the target substance can be further increased and the conditions of a catalytic reaction can be reduced [168]. A lot of studies have shown that the promotion of ultrasonic waves on the catalytic reaction is due to an extremely high temperature and high-pressure physical and chemical environment generated when ultrasonic cavitation bubbles collapse. Especially in liquid-liquid reactions, the cavitation phenomenon is significant, which can obviously facilitate the degradation of reactants and the formation of free radicals to accelerate a reaction rate [169–171]. In addition, the collapse of the cavitation bubbles will produce an extreme micro jet, which has a good impact on a chemical reaction system. On one hand, this impact can effectively remove the reactants and impurities adsorbed and retained on the surface of a catalyst, which is helpful to restore the activity of the catalyst. On the other hand, the impact effect can lead to intense collision and aggregation between the reactants, which can significantly change the structure and composition of the catalyst and improve the reactivity of the catalyst [172–175]. Moreover, the impact effect can strengthen a chemical mass transfer process and increase the surface area of a catalytic reaction interface, thus accelerating the chemical reactions and improving the reaction efficiency.
Heterogeneous reactions between liquid and liquid (such as water and heavy oil) require high temperatures and strong mixing. The reaction conditions are extremely harsh, while their reaction rates and production are low. It usually needs the help of a phase transfer catalyst to make the reactions proceed smoothly. Ultrasonic waves can promote the phase transfer catalytic reaction. Ultrasonic waves and a phase transfer catalyst have complementary advantages, which can greatly improve the reaction rate, reduce the reaction conditions, increase the production of target products, and even make some reactions occur at room temperature without stirring. Xu et al. [175] studied an additional reaction of dichlorocarbene with styrene. Their experimental results showed that the production of the target product was only 15%, while the production was greatly increased, and the required catalyst was reduced under ultrasonic irradiation. The extreme conditions of ultrasonic cavitation promoted the reaction, and the ultrasonic emulsification increased the phase interface of the reaction, thus reducing the amount of the phase transfer catalyst. An application of ultrasonic wave in catalyst synthesis can increase the dispersion uniformity and a specific surface area of the active components in the catalyst, in order to improve the activity of the catalyst. Bianchi et al. [176] prepared PdCl$_2$ catalyst PdCl$_2$ with ultrasonic action and found it had a higher activity. The reason is that the shock wave and ultra-fast microjet generated in a process of ultrasonic cavitation can carry the active components deep into the pores of a carrier, thus forming the so-called “protein” type catalyst. A combination of ultrasound and aquathermolysis makes full use of a synergistic effect of an ultrasound treatment and catalytic aquathermolysis, which can not only provide energy for chemical reactions but also improve the activity of catalysts, thus facilitating the catalytic cracking for heavy oil and accelerate the cracking rate [177–179].

4. Current Research Challenges and Future Directions

Researchers have completed a lot of work on the development of catalysts (as shown in Table 2) and field tests preliminarily show the feasibility of an application of in situ upgrading for extra-heavy oil and have achieved viscosity reduction and stimulation effects. However, there is still a long way before industrial applications. At present, the key factors to restrict the industrial application of in situ upgrading technology lie in its high production cost and the relatively low scale of catalytic upgrading reactions, which directly determine economic benefits.

Table 2. The typical research on catalysts in recently 5 years.

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Catalyst</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xiong et al. [21]</td>
<td>Dispersed nickel-loaded nitrogen-doped carbon catalysts</td>
<td>Through a series of reactions, the catalyst can decrease 82.21% of viscosity and 13.04% of heavy component.</td>
</tr>
<tr>
<td>Mehrabi-Kalajahi et al. [22]</td>
<td>CoFe$_2$O$_4$ nanoparticles</td>
<td>The CoFe$_2$O$_4$ nanoparticles were used in ISC process, which slightly promoted LTO and significantly facilitated HTO.</td>
</tr>
<tr>
<td>Mehrabi-Kalajahi et al. [24]</td>
<td>Oil-dispersed $\alpha$-Fe$_2$O$_3$ nanoparticles</td>
<td>The $\alpha$-Fe$_2$O$_3$ nanoparticles were used in ISC process, which decreased the activation energy significantly from 537 kJ/mol to 246 kJ/mol.</td>
</tr>
<tr>
<td>Babapour Golafshani et al. [25]</td>
<td>Oil-dispersed transition metal acetylacetonate (Ni, Cu, and Fe) catalysts</td>
<td>The catalysts slightly promoted LTO and significantly facilitated HTO.</td>
</tr>
<tr>
<td>Sviridenko and Akimov [26]</td>
<td>Dispersed NiCrWC catalyst</td>
<td>The pre-oxidation of the dispersed catalyst showed an optimal performance at a temperature of 450 °C and a duration of 2 h in the air, at which condition the macromolecular components, sulfur, by-products were decreased.</td>
</tr>
<tr>
<td>Researchers</td>
<td>Catalyst</td>
<td>Remarks</td>
</tr>
<tr>
<td>------------------------------</td>
<td>---------------------------------------------</td>
<td>-------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Yeletsky et al. [28]</td>
<td>Nanodispersed catalysts based on K, Fe, Ni, Mo</td>
<td>The use of Mo-based catalysts achieved highest upgrading efficiency, which got lowest sulphur content and H:C ratio.</td>
</tr>
<tr>
<td>Djimasbe et al. [29]</td>
<td>Oil dispersed nickel-based catalyst</td>
<td>The Ni-based catalyst decreases the production of gases and coke from 14.92% and 3.09% to 8% and 2.27%, while increases oil production from 81.99% to 89.73%.</td>
</tr>
<tr>
<td>Yuan et al. [39]</td>
<td>Oil-soluble catalysts based on copper (II) stearate</td>
<td>The catalysts largely reduced the activation energy of LTO, FD, and HTO.</td>
</tr>
<tr>
<td>Khelkhal et al. [43]</td>
<td>Copper tallates</td>
<td>The copper tallates promoted the combustion front, thus facilitated the LTO and HTO processes.</td>
</tr>
<tr>
<td>Cui et al. [46]</td>
<td>Nano-Ni catalyst and ultrasonic wave</td>
<td>The asphaltene molecules were destroyed and decomposed into small molecular hydrocarbons.</td>
</tr>
<tr>
<td>Tajik et al. [67]</td>
<td>Oil soluble catalysts</td>
<td>Sunflower oil is an ideal resource to synthesize and prepare Fe, Ni, Co and Cu-based oil soluble catalysts used for ISC. The synthesized catalysts showed excellent activity on decreasing the activation energy of high-temperature oxidation.</td>
</tr>
<tr>
<td>Aliev et al. [75]</td>
<td>Amphiphilic catalytic</td>
<td>A novel amphiphilic catalyst was synthesized based on nickel and aluminum. The use of the amphiphilic catalyst can improve the oil mobility.</td>
</tr>
<tr>
<td>Al-Attas et al. [88]</td>
<td>Ni-TBC[4] as dispersed catalyst</td>
<td>It decreases the activation energy from 65.39 to 57.32 kcal/mol.</td>
</tr>
<tr>
<td>Tang et al. [94]</td>
<td>Biomass-based catalyst</td>
<td>The oil viscosity was reduced significantly from 508,800 to 22,230 mPa·s at 50 °C with a 0.2 wt% addition of the catalyst.</td>
</tr>
<tr>
<td>Sitnov et al. [112]</td>
<td>Fe₃O₄ nanoparticles and hydrogen donor</td>
<td>The resins and asphaltenes decrease from 19.6 wt% and 5.1 wt% to 8.9 wt% and 1.5 wt%.</td>
</tr>
<tr>
<td>Al-Ghefeili et al. [113]</td>
<td>Magnetite nanoparticles</td>
<td>A more than 50% reduction in viscosity and API gravity increase to 21° was observed.</td>
</tr>
<tr>
<td>Tang et al. [131]</td>
<td>Oil solubility organozinc</td>
<td>Physical experiments were performed to select high-efficiency in-situ reforming catalysts. Oil viscosity was reduced from 145,000 mPa·s to 54,260 mPa·s. The density and acid value of the heavy oil reformed by physical model experiment were decreased, the content of heavy components (colloid and asphaltene) was decreased by 10.85%, and the fractions before 300 °C and 500 °C were increased by 6.75% and 17.29%, respectively.</td>
</tr>
<tr>
<td>Hart et al. [147]</td>
<td>Tetralin and decalin as H-donor</td>
<td>The induction heat in CAPRI increases the activity of catalyst, thus improving the produced oil quality.</td>
</tr>
<tr>
<td>Taheri-Shakib [160]</td>
<td>Electromagnetic and nanoparticles (Fe, TO, CA)</td>
<td>Nanoparticles together with microwave decreased the content of heavy components, such as OH, S-H, alkyl groups, carbonyl, carboxylic acid, etc.</td>
</tr>
<tr>
<td>Li et al. [161]</td>
<td>Microwave and nano-catalyst</td>
<td>Under the synergistic effect of nano-catalyst and microwave, significant increase in tricyclic aromatic Hydrocarbons and hopanidanes, and decrease in bicyclic aromatic hydrocarbons was observed.</td>
</tr>
</tbody>
</table>
4.1. Costs

At present, the cost of a single well test of upgrading is about 2~3 times that of single well steam stimulation, and it is difficult to carry out an industrial application in the short term under the condition of low oil prices. Most of the existing field tests still use steam heating to provide the basic temperature required by reactions, which cannot avoid the shortcomings of low efficiency and high energy consumption of a traditional steam thermal recovery method. Under the requirements of the base temperature of the in situ upgrading reaction and the complex geological conditions, it is a very big problem to maximize the scale of the upgrading reaction deep in a reservoir. It is necessary to combine multiple disciplines and technologies to form a reservoir heating method suitable for reservoir upgrading reactions [180].

We must actively seek solutions to achieve industrial applications to make the technique of in situ upgrading become the next-generation replacement technology for heavy oil recovery. On one hand, we need to promote the research and development of catalysts. The first is to develop catalytic upgrading systems of high activity and low dosage. Then, the industrial production of related chemical agents is promoted through the increasing technological transformation demand of heavy oil reservoirs. In addition, injectivity improved sulfonate oil-soluble catalytic systems and recycling nano transition metal oxide catalysts are also the research and development directions of catalysts. On the other hand, the reservoir heating method should be transformed. The traditional steam heating method has low thermal energy efficiency, which inevitably leads to a high cost of subsequent water treatment. For example, electric pulse, ultrasonic, microwave, and electromagnetic wave can be combined with the in situ upgrading and viscosity reduction technology to provide the temperature required for extra-heavy oil upgrading reactions. Heating a reservoir through physical methods can truly achieve efficient and green production [181].

4.2. Catalytic Upgrading Scale

The complex geological conditions and the high development degree of a reservoir determine that a directly injected upgrading system usually passes through the reservoir quickly along high permeability channels. How to expand the spread volume of a catalytic upgrading agent, in order to efficiently contact and disperse it in an oil-rich area, is a bottleneck problem encountered in a field application of in situ upgrading technology. While improving the performance of the catalyst, it is necessary to develop stable injection systems and targeted injection methods, so that the injection agent can be fully integrated into the oil reservoir. A viscosity reduction rate of greater than 90% is defined as the limit of an efficient viscosity reduction. At present, a lower limit of reaction temperature for an efficient viscosity reduction is about 260 °C. However, the existing reservoir heating technology is difficult to maintain the high-temperature environment above 200 °C in a reservoir for a long time, so the action range of catalytic upgrading agents in the reservoir is limited to a large extent.

On one hand, the contact efficiency between an upgrading system and crude oil should be improved. The problem of ineffective injection cycle or accumulation caused by reservoir heterogeneity and high recovery degree can be solved by improving an injection method and technology. The method of deep profile control and infill wells in a late stage of water flooding can be used for reference so that an injected agent can avoid the dominant seepage channels and spread to an oil-enriched area. On the other hand, the scale of in situ catalytic upgrading reactions should be expanded. The long horizontal sections of horizontal wells can be used to create a large in situ upgrading reaction temperature chamber in a reservoir, which is a production mode to maximize the scale of upgrading reactions and the future application direction of the technology. Moreover, the temperature threshold of a catalytic upgrading reaction can be reduced, because under the same heating conditions, the lower the reaction temperature, the larger the in situ upgrading reaction temperature chamber, the more obvious the oil-increasing effect, and the higher the success rate of upgrading.
4.3. Novel Wellbore Configurations

4.3.1. Inflow Control Devices

Horizontal wells have the advantages of a strong reservoir control ability and a high oil production rate and are widely adopted for oilfield development in China and over the world. China National Petroleum Corporation (CNPC) has more than 10,000 horizontal wells. Affected by reservoir heterogeneity, drilling trajectories, start-up modes, and operation strategies, unsatisfactory results have been obtained, indicated by uneven downhole temperature, local steam channeling, low oil drainage rates, and low oil-steam ratios. Inflow control devices (ICDs) refer to a kind of completion hardware that acts as equalizers to balance or equalize a wellbore pressure drop to achieve an evenly distributed inflow profile along a horizontal section. They are in the form of channels, nozzles, or orifices, and provide great potential in profile adjustment and water control [182–187]. Figure 5 is a schematic diagram of a nozzl-type ICDs completed horizontal well [182]. Currently, the ICDs have been used in Kuwait, Malaysia, Russia, Ecuador, and China for production enhancement [188–192].

![Figure 5. Structural schematic diagram of three flow paths in ICDs, adapted from [182].](image)

4.3.2. Concentric/Parallel Dual Tubing Wellbore Configurations

When the reservoir heterogeneity is strong or a horizontal section is long, the local steam inrush and unequal reservoir utilization are more likely to occur under the condition of traditional single-pipe steam injection. A parallel dual-tube steam injection method is put forward to realize multi-stage steam injection. Two parallel pipes are used for steam injection in different parts of a reservoir, respectively. Compared with the single-point steam injection method, this method can realize the double-point steam injection with a main and secondary pipe. The main pipe goes down to the toe of a horizontal well while the second one goes down to the heel, and the steam injection parameters are adjusted at both ends at the wellhead according to the specific steam suction conditions, in order to improve the degree of uniform steam suction in the horizontal section. A concentric double-tube structure is often used in SAGD and steam huff-n-puff processes; that is, steam is injected simultaneously in the unconnected tubing and the annular to improve the heating effect at both the heel end and toe ends of a horizontal section [193–196]. The typical steam injection wellbore structures are shown in Figure 6.

Currently, an in situ upgrading technology for heavy oil is in an early stage of development and has the potential to become the next generation of main recovery technologies. Demand and innovation drive the development of this technology. It is believed that under the pressing pressure of heavy oil reservoir development and with the joint efforts of scholars, this technology is expected to achieve revolutionary breakthroughs in the future.
water phases, but the stability of its molecular structure is poor. A nanocatalyst has high water-soluble catalyst is convenient for mixed injection and has a relatively low cost, but water-soluble catalysts, oil-soluble catalysts, amphiphilic catalysts, and nanocatalysts. A price, there is a promising prospect for the combination of physical heating and catalytic viscosity reduction in heavy oil. Reducing application costs and improving the scale of and crude oil and the steam chamber size of the upgrading reactions. In addition to catalytic dual-string tube, and (c) parallel dual-string tube, adapted from [197].

5. Conclusions

EOR in the late stage of steam injection and efficient development of hard-to-use reserves are the two main difficulties in the development of heavy oil resources at present. The proposal of catalytic upgrading and viscosity reduction provides a new idea for overcoming these two main difficulties.

The core of in situ upgrading and viscosity reduction in heavy oil is the catalytic reactions, and the key is a selection of catalysts. The catalyst types are mainly divided into water-soluble catalysts, oil-soluble catalysts, amphiphilic catalysts, and nanocatalysts. A water-soluble catalyst is convenient for mixed injection and has a relatively low cost, but the catalytic effect is relatively poor. An oil-soluble catalyst has relatively high catalytic efficiency, but it has higher requirements on an injection process and will increase the cost of oil follow-up treatments. An amphiphilic catalyst has good solubility in both oil and water phases, but the stability of its molecular structure is poor. A nanocatalyst has high reaction efficiency, but its cost is relatively high.

There is a broad application for catalytic aquathermolysis in the Liaohe oilfield, Shengli Oilfield, and Henan oilfield, etc. in China. The addition of a hydrogen donor or emulsifier during the catalytic aquathermolysis will promote upgrading and viscosity reduction for heavy oil. Air injection catalytic oxidation is also widely applied in oilfields in China, Canada, Mexico, etc. Low-temperature catalytic oil with air injection is a tendency because the low requirement of work conditions. Microwave and ultrasonic are physical heating methods that assist catalytic upgrading, which not only improve crude oil quality but also excite the activity of catalysts. Under the political and economic environment of a low oil price, there is a promising prospect for the combination of physical heating and catalytic methods for heavy oil recovery.

The scale of upgrading reactions depends on the contact efficiency between catalysts and crude oil and the steam chamber size of the upgrading reactions. In addition to catalysts, hydrogen donors, reaction time and temperature have a great influence on the viscosity reduction in heavy oil. Reducing application costs and improving the scale of catalytic upgrading are the major challenges to realizing the industrial application of heavy oil underground upgrading technology. The key to reducing production costs is to control the price of upgrading catalysts. The main solution is to develop cheap catalysts and reuse catalysts. In addition, the application cost can be further reduced by using relatively green and efficient physical heating of a reservoir (e.g., electromagnetic heating, ultrasonic wave heating, and solar heating). To greatly improve the efficiency of in situ upgrading reactions, it is necessary to maximize the reaction scale, which can be achieved by establishing the corresponding injection and production methods to increase the contact efficiency between an injection system and crude oil, expanding the temperature chambers of reactions and reducing the reaction temperature threshold of a catalyst.
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