Review

In-Situ Heavy Oil Aquathermolysis in the Presence of Nanodispersed Catalysts Based on Transition Metals

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Abstract: The aquathermolysis process is widely considered to be one of the most promising approaches of in-situ upgrading of heavy oil. It is well known that introduction of metal ions speeds up the aquathermolysis reactions. There are several types of catalysts such as dispersed (heterogeneous), water-soluble and oil soluble catalysts, among which oil-soluble catalysts are attracting considerable interest in terms of efficiency and industrial scale implementation. However, the rock minerals of reservoir rocks behave like catalysts; their influence is small in contrast to the introduced metal ions. It is believed that catalytic aquathermolysis process initiates with the destruction of C-S bonds, which are very heat-sensitive and behave like a trigger for the following reactions such as ring opening, hydrogenation, reforming, water–gas shift and desulfurization reactions. Hence, the asphaltenes are hydrocracked and the viscosity of heavy oil is reduced significantly. Application of different hydrogen donors in combination with catalysts (catalytic complexes) provides a synergetic effect on viscosity reduction. The use of catalytic complexes in pilot and field tests showed the heavy oil viscosity reduction, increase in the content of light hydrocarbons and decrease in heavy fractions, as well as sulfur content. Hence, the catalytic aquathermolysis process as a distinct process can be applied as a successful method to enhance oil recovery. The objective of this study is to review all previously published lab scale and pilot experimental data, various reaction schemes and field observations on the in-situ catalytic aquathermolysis process.

Keywords: heavy oil; in-situ upgrading; transition metals; aquathermolysis; catalyst

1. Introduction

Heavy oil stands for one-third of global hydrocarbon resources. Only in Russia, the reserves of heavy oil are estimated at 6–7 billion tons [1]. The depletion of traditional hydrocarbon resources and the increasing demand of energy makes the enhancement of heavy oil recovery methods relevant and crucial. However, the high viscosity, significant content of heavy molecular mass fractions and high heteroatom-containing compounds with complex structures and compositions make the production, transportation and refinery of heavy oil very difficult and challenging. Currently, steam-assisted gravity drainage (SAGD), steam and hot water flooding, cyclic steam stimulation (CSS), and in-situ combustion (ISC) heavy oil recovery techniques are widely applied and very attractive due to their physical consequences. However, the feasibility of these techniques can be improved by accelerating the overall chemical reactions occurring between the steam, heavy oil and rock minerals, which were termed by Hyne et al. as “Aquathermolysis” [2]. The authors proposed the catalytic role of metal ions in the aquathermolysis process. Since then, substantial advances in catalysis have made the catalytic aquathermolysis a distinct
process, and catalytic steam-based heavy oil recovery techniques has been investigated as a promising technology to recover heavy oil resources [3–16]. More importantly, this process occurs in the cheapest high-pressure reactor of all, petroleum formations [3–6]. Thus, the catalytic aquathermolysis process provides not only feasible enhancement of heavy oil recovery, but also contributes to its further transportation and refinery by changing the quality of difficult-to refine feedstock in-place. This paper sheds new light on the process of upstream heavy oil aquathermolysis in the presence of transition metal-based catalysts.

2. Catalytic Aquathermolysis

An increasing number of studies have found that steam flooding of heavy oil and oil-saturated rocks results in the destruction of the weakest carbon–heteroatom bonds with detachment of peripheral fragments from resins and asphaltenes and formation of lighter hydrocarbons [1–11]. The destruction of asphaltenes under the steam treatment occurs primarily through the weak aliphatic sulfide bonds (Figure 1) that are destabilized by electron-withdrawing functional groups. Such a process initiates already at 120 °C [13]. The destruction products of resins and asphaltenes joins other fractions, which determines reduction in heavy oil viscosity and increase in heavy oil recovery [3,4,7]. The schematics of the main chemical reactions that describe the catalytic aquathermolysis process are illustrated in Figure 1. The attempt was done to interrelate the products of one chemical reaction to the feed of another one. According to the proposed mechanism, we believe that the weak C–S bonds in heavy oil are very sensitive and under the steam exposure act like a trigger to initiate the overall chemical reactions, which make up the aquathermolysis process. Moreover, the transition metal species can accelerate certain chemical reactions as illustrated in Figure 1.

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RCH_2CH_2SCH_3 + 2H_2O = RCH_3 + CO_2 + H_2 + H_2S + CH_4
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*Figure 1.* The schematics of main chemical reactions during the aquathermolysis process in the presence of nickel sulfide catalyst.

Lin et al. reported that catalyst particles are retained on the surface of silicate particles and accelerate the chemical rupture of carbon–heteroatom bonds [14]. They draw our attention to the significant amount of \(\text{H}_2\text{S} \) generation after catalytic aquathermolysis of
tetra-hydro-thiophene, as a model compound [14]. The authors consider C-S bond cleavage and ring opening reactions, which lead to the formation of low-molecular alkanes and alkenes (Figure 2).

Figure 2. Reaction pathways for tetrahydrothiophene aquathermolysis.

Decarbonylation of aldehydes and other organic compounds leads to the formation of CO, hydrocarbons and other related compounds. The high-temperature water plays a key role during the aquathermolysis of tetra-hydro-thiophene and is directly involved in the main reactions such as hydrolysis and water–gas shift (WGS). These simple reactions will eventually lead to the transfer of hydrogen from water into gaseous or liquid phase products. In addition, the kinetic model of H₂S formation after aquathermolysis of tetrahydro-thiophene was established, the activation energy of which was 54.55 kJ/mole [14].

In [10] the authors studied the group composition and elemental analysis after the thermolysis of asphaltenes, which were previously extracted from the heavy oil of the Usinskoye reservoir [10]. The temperature range of the carried out thermolysis process was 120–750 °C [10]. Gas Chromatography–Mass Spectrometry (GC-MS) was used to reveal the main thermolysis products such as alkylbenzenes (AB) and saturated aliphatic hydrocarbons (SAH), while aromatic structures obtained at higher temperatures were mainly separate aggregates [10]. The authors claim that the temperature of thermolysis is directly proportional with the ratio of AB/SAH + Alkenes and inversely proportional with phenanthrene/alkylbenzenes (PN/AB) and polycyclic aromatic hydrocarbons/alkylbenzenes (PAH/AB) ratios [10].

Wren Montgomery and his co-workers carried out an aquathermolysis process under various thermobaric conditions (up to 325 °C and 13.8 MPa) [16]. The authors affirm the generation of aliphatic hydrocarbons from polar resins and asphaltenes. The analysis of maturity parameters in the destruction products showed the lower temperatures than the feed material. According to the FTIR Spectroscopy results, the amount of methane gas gradually increased with temperature and pressure [16]. More importantly, FT-IR data justified the defunctionalization of polar components. The significant amount of methane and CO₂ were detected in high temperature and pressure experiments, which is probably due to the cracking of C-C bonds.

2.1. Use of Hydrogen Donors

As heavy oils suffer from hydrogen deficiency and often have a high content of sulfur, nitrogen and oxygen, many attempts have been made to supply the source of hydrogen in reservoir. Hydrogen participates in hydrogenation (inhibits polymerization reactions) and hydrocracking reactions. During the aquathermolysis process thermally unstable bonds,
which are mostly found in resins and asphaltenes, break down to generate free radicals. The hydrogen attacks the free radicals to make them stable. Thus, the role of hydrogen in in-reservoir processes is very significant. However, the injection of molecular hydrogen is not considered for industrial scale applications due to safety and technical implementation. The ability of naphthenoaromatic compounds to give hydrogen atoms is used in hydrogen donor solvent cracking [17]. A considerable amount of the literature on in-situ upgrading of heavy oil suggests the application of tetralin (tetrahydronaphthalene) as hydrogen donor source in downhole processes. The steam treatment of heavy oil in the presence of tetralin provides a higher reduction degree in viscosity, density and asphaltene content due to saturation of free radicals by hydrogen and inhibition of polymerization reactions. The latter fact is confirmed by a decrease in the rate constant of the thermal cracking reaction in the presence of hydrogen donors [18–20]. The main limitation of using tetralin as a hydrogen donor is its inaccessibility and considerable cost. Therefore, the relevant task is to find the more cost-effective alternative hydrogen donor source with high content of naphthene-aromatic compounds. In [20] the authors showed that the main distinction of heavy oil transformation in the presence of catalyst and hydrogen donors is in activation of destructive reactions of C–C, C–N, C–O, C–S bonds and inhibiting polymerization reactions that reduce the formation of coke-like compounds.

The heavy oil and natural bitumen containing aliphatic hydrogen or compounds that contain active C-H bonds (for example heteroatom-containing bonds) decompose during steam reforming [21,22]. The general process may be presented as:

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C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2
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CO + H_2O \rightarrow CO_2 + H_2
\]

Thus, the hydrogen closes radicals formed after the thermolysis of asphaltenes and other components of heavy oil, preventing coke formation. Catalysts based on iron and ruthenium are well known for steam reforming processes [23,24]. Moreover, they accelerate the desulphurization processes [25,26]. Desulphurization catalysts were thoroughly discussed in a review article [27]. According to the proposed mechanism, the yield of hydrogen justifies conduction of cyclization reactions and aromatization of hydrocarbons and this path was justified in another scientific paper [28].

The first systematic study on the application of water as a hydrogen source in both catalytic and non-catalytic aquathermolysis was carried out by Al-Muntaser et al. via a deuterium tracing study [29]. The authors used deuterium oxide (D_2O) instead of normal water (H_2O) to reveal the hydrogen donating ability of water in aquathermolysis reactions. The results justified the chemical impact of water as a hydrogen source in aquathermolysis processes (Figure 3), particularly significant substitution of deuterium (deuteration) in both heavy oil and its fractions according to the results of isotope analysis. The results are additionally confirmed by significant deuterium exchange of aliphatic and aromatic components in the initial and deuterated extra-heavy oil samples and their individual SARA (Saturates, Aromatics, Resins, Asphaltenes) fractions in FT-IR spectra. The authors concluded that addition of nickel carboxylates as oil-soluble catalyst leads to the increase in the hydrogen donating capacity of water. Alemán-Vázquez and co-workers [30] studied polycyclic naphtene and aromatic compounds, which can be reversibly hydrogenated and dehydrogenated in reaction mixture. They noted that such hydrogen donors significantly reduce the formation of coke after thermal treatment of heavy oil. Thermodynamics and quantum chemistry methods were applied to study the relative hydrogen donating capacity of hydroderivatives of aromatic compounds: benzene, naphthalene, anthracene and phenanthrene depending on temperature and pressure [30,31].
Figure 3. Deuterium generation in the presence of Ni<sub>n</sub>S<sub>m</sub> nanoparticles during thermal cracking of heavy oil molecules.

Fujimoto et al. studied hydrogenolysis of thiophene using decalin as a hydrogen donor and in the presence of carbon catalysts [32]. The results of their experiments revealed the relation between the dehydrogenation degree of decalin and hydrogenolysis degree of thiophene. The authors concluded that decalin can be adsorbed and desorbed on/from the surface of active carbon. The hydrogen atoms migrate to the surface of carbon and react with thiophene (Figure 4).

Figure 4. Reaction model of transfer hydrodesulfurization.

Billmers et al. [33] studied the mechanism and kinetics of hydrogen transfer between 9, 10-dihydroanthracene and substituted anthracene at 498–673 K. The results are consistent with the non-chain free radical mechanism and the reactions correspond to molecular disproportionation. However, such reaction types are the main source of free radicals in condensed phase in relatively lower temperatures that allow the use of the given compounds in reservoir conditions in order to upgrade heavy oil. Several studies, for instance [33,34] have been carried out on the influence of formic acid on the aquathermolysis processes, where significant increase in the content of paraffinic and naphthenic aromatic hydrocarbons with further decrease in fractions of resins and asphaltenes were observed. Other researchers [35] imply that cyclohexane is more effective in terms of decreasing coke content (45% vs. 41.3%) due to inhibition of polymerization reactions in the presence of hydrogen. The proposed reaction paths of hydrogen donating ability of cyclohexane are presented in . Such upgrading resulted to the viscosity reduction of heavy oil by 85% [35].
2.2. Use of Aquathermolysis Catalysts

The key factor in successful application of the aquathermolysis process is introduction of catalysts that promote the overall chemical reactions occurring down in the reservoir, such as hydrogenation, hydrodesulfurization, water–gas shift reaction, etc. The influence of catalysts on aquathermolysis reactions has been widely investigated [2,9,10,14]. The aquathermolysis catalysts can be roughly divided into four groups: nanocatalysts, water-soluble catalysts, oil-soluble catalysts and rock minerals.

2.2.1. Nanocatalysts

The most widely applied catalysts are heterogeneous catalysts based on transition metals, oxide, sulfide, carbide and phosphide nanoparticles, as well as metalized solid acids [36–38]. The possible approaches to apply the nanoparticles in various heavy oil production technologies were evaluated in a review article [39]. The main advantages of nanocatalysts over traditional ones is their huge surface area with the absence of a porous structure that can be clogged with coke-like compounds [40]. Pevnevo and co-workers studied the composition of hydrocarbons and heteroatoms after cracking of fuel oil fraction in the presence and absence of a tungsten carbide/nickel–chromium. The process was carried out in a high-pressure reactor at 500 °C for 30 min. The addition of catalysts promoted the destructive hydrogenation reactions of heavy weight molecules. Moreover, the contents of low-molecular n-alkanes (C9–C17) and alkylbenzenes (C9–C10) in the experimental products were increased after the catalytic treatment in contrast to the conventional cracking reactions. Alkyl- and naphthene-substituted aromatic hydrocarbons, naphthalene, phenanthrene, arenes, thiophenes were observed [41]. Other authors [42] synthesized and characterized MCM-41/γ-Al2O3, which was covered by La, W, Ni, W, Co, Mo and Zn compounds. The given additives in the mixtures of industrial catalysts revealed that 10% La/MCM-41/-Al2O3 lead to the reduction in organosulfur content in the products of vacuum gasoil cracking up to 40%. Kadieva et al. obtained nanoparticles of molybdenum oxides from “inverted” emulsion of aqueous paramolybdate ammonium solution in pentadecane and surfactant medium. The characteristics of dispersed phase particles and factors that influenced them were metal concentration, treatment temperature, water and surfactant content [43].

In [44], the effect of oil-soluble cobalt salt and formamide as hydrogen donor on aquathermolysis of heavy oil was tested in a high-pressure reactor. The authors imply that the given catalyst in combination with the hydrogen donor significantly affect the viscosity of heavy oil, group composition and heavy oil components. The structural changes of heavy oil under the influence of catalytic complex were identified in FT-IR spectra. Moreover, the reduction in resins and asphaltenes, which is a deterministic factor in viscosity reduction degree, and increase in saturated and aromatic fractions were dependent on the concentration of the hydrogen donor. The synergetic effect from the catalyst and hydrogen donor provided a decrease in the carbon content and increase in the hydrogen content leading to the increase in the H:C ratio and reduction in sulfur content. The infrared spectra of catalytic treatment products revealed reduction in the number of aromatic rings and decarboxylation path [44].

The destruction mechanism of C-S bonds is thoroughly discussed in [45]. It was revealed that non-conjugated C-S bonds in high-molecular compounds are more susceptible to aquathermolysis process in contrast to the conjugated C-S bonds (Figure 5) [45].
Figure 5. The destruction mechanism of C-S bonds.

SiO$_2$/H$_2$TiO$_3$ nanocomposite with 20 nm size particle was synthesized for in-situ aquathermolysis of Shengli heavy oil from China. The viscosity was reduced from 58,000 cP to 16,000 cP (72.4% reduction) in the presence of nano-catalyst with the mass concentration of 0.5%. The temperature of the carried out experiment was 150 °C and the duration of the experiment was 36 h [46]. Avbenake and co-workers synthesized Ni-Co/γ-alumina catalyst for upgrading heavy oil. In this paper, the role of the water gas shift reaction (WGSR) during the aquathermolysis process was discussed and the preliminary results suggested in-situ generation of hydrogen for the further reactions. The results of experiments, which were conducted at 380 °C, 32 bar and 2-h exposure with a catalyst/oil ratio of 0.01 revealed lower density and higher hydrogen-to-carbon ratio for the samples, which were pressurized by hydrogen rather than nitrogen. The experiment pressurized by hydrogen generated no coke in contrast to the catalytic aquathermolysis carried out in a nitrogen environment, where 0.2 wt % of coke was observed. Meanwhile, the sulfur content and viscosity of the samples, which were reacted in a nitrogen environment, were higher compared to that of hydrogen [47]. Moreover, the share of C7–C30 homologues in the products of catalytic upgrading of heavy oil was higher than non-catalytic thermal cracking process [47,48].

The subfractions of resins and asphaltenes after catalytic and non-catalytic aquathermolysis processes will be discussed in order to shed new light on the group composition and structure of high-molecular components, as well as better understand the decrease in average molecular mass of asphaltene fractions after catalytic treatment. Previously, we have reported the chemical changes in the five subfractions of asphaltenes after catalytic and non-catalytic aquathermolysis [49]. It was observed that the content of sulfur was significantly reduced under the influence of cobalt metal in the subfraction with the highest molecular mass—A5. The NMR $^{13}$C spectra revealed reduction in mean chain length (MCL) by 15 times in subfraction A1, which is considered a solvate layer, and by almost 13 times in subfraction A2. The authors imply that destruction of C-O and C-S bonds mainly occurs in peripheral chains of aromatic and alicyclic hydrocarbons. The amount of primary, the sum of the secondary and quaternary carbons increased, while the content of tertiary and aromatic carbons decreased. Probably, the linear and branched aliphatic hydrocarbons were cracked from heavy polyaromatic and polyaromatic components that transformed into coke-like compounds such as carbene–carboids [49]. In paper [50], the comparison of catalytic effects from pure nickel with nano size and Raney nickel under steam injection was carried out. Nickel nanoparticles showed the best performance in contrast to the Raney nickel. It was shown that a nickel catalyst provides much higher efficiency in the presence of terrigenous rocks. The introduced suspension was stabilized with xanthan gum polymer under the ultrasound treatment (Figure 6). Three organic surfactants such as
sodium laurilsulfate (SDS), cetrimonium bromide and hypermer were used in combination with xanthan gum polymer to stabilize the nickel nano-catalyst particles [50].

Figure 6. The images of micromodel (a) before and (b) after the injection of 2 wt% nickel nano-catalyst suspension in the presence of 0.5 wt% sodium laurilsulfate (SDS) and 0.06 wt% xanthan.

The contribution of nano-catalysts to the energy efficiency of the steam recovery method was investigated in [51]. Nano-catalysts were selected through immersion experiments and further thermogravimetric analysis (TGA) was conducted to determine the temperature of steam gasification. The activity of nano-catalysts was improved by 1.0 wt% of NiO and PdO nanocrystals. A sandpack was used to carry out the aquathermolysis process in the presence and absence of 500 mg/L SiNi1Pd1 nano-fluids. Incremental heavy oil recovery after injection of nanoparticles was 56%. In addition, due to the destruction of asphaltene molecules and the decrease in their content after the catalytic treatment, the API (American Petroleum Institute) gravity of heavy oil increased from 7.2° to 12.1°. The viscosity reduction degree after catalytic treatment of heavy oil was 85% [52].

In recent years, there has been considerable interest in composite catalysts generated from the mixture of oil-soluble precursors based on two or three metal salts: iron, nickel and copper [53]. The composition of active form of catalyst particles after the steam treatment was investigated by X-ray Diffraction (XRD), Mossbauer spectroscopy, Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDX) analysis methods. The results revealed not only ferrite spinel MFe$_2$O$_4$ (where, M = Ni or Cu), but also individual oxides. However, three phases are formed in case of catalyst based on nickel: magnetite FeO–Fe$_2$O$_3$, ferrite spinel NiFe$_2$O$_4$ and probably nickel oxide. According to the result of X-ray diffraction analysis, the intermediate oxides under hydrothermal influence transform into non-stoichiometric ferrites—Cu$_{0.86}$Fe$_{2.14}$O$_4$ and Ni$_{1.43}$Fe$_{1.7}$O$_4$ spinels. This is due to the thermodynamically favorable transformation processes of this special phase composition [54]. Cu(OH)$_2$ was used in order to obtain CuO as an aquathermolysis catalyst [55]. Mukhamatdinov and co-workers investigated nanosized magnetite during aquathermolysis of Ashalcha heavy oil (Tatarstan, Russia) [56]. The catalyst addition led to the decrease in the content of resins and asphaltenes. The significant effect from heavy oil conversion is reached at 300 °C [57]. In Figure 7, a transformation mechanism of iron nitrate during catalytic steam cracking (CSC) is provided. The first step is the decomposition of Fe(NO$_3$)$_3$ solution, where iron nitrate decomposes to form the hematite suspension in heavy oil [57] followed by partial reduction to magnetite and sulfidation with heavy oil molecules and/or H$_2$S to form the Fe$_{0.91}$S phase.
Few studies have been published on the modification of nanocatalysts dispersed in ionic liquid in order to improve the catalytic aquathermolysis process. The magnetic multiwalled carbon nanotubes (Fe$_3$O$_4$/MWCNT) modified with 1-ethyl-3-(3-formyl-4-hydroxybenzyl)-1H-imidazol-3-ium acetate (EFHIA) showed an outstanding performance in the catalytic aquathermolysis of heavy asphaltic crude oil (Figure 8) [60].

The composition of magnetite is studied thoroughly by a Mossbauer spectroscopy method in [61]. The oil-soluble catalyst based on iron, intensified destructive processes in oil-saturated rocks from the Riphean–Vendian complex. The content of sulfuric compounds (-SO) in resins and asphaltenes sharply dropped due to the reduction of sulfoxide to sulfide and hydrogen sulfide. The efficiency of catalytic aquathermolysis even at low temperatures was enough to crack the most macromolecular components and increase the content of light fractions of heavy oil [62,63]. Application of biogenic magnetite in the Toe-to-Heel Air Injection and its add-on CAtylatic upgrading PRocess In-situ (THAI-CAPRI) process is described in article [64].

Two different Fe$_3$O$_4$ nanoparticles with different morphology were prepared by a co-precipitation method. Figure 9h illustrates the mean size of Fe$_3$O$_4$ nanoparticles (15 nm) adsorbed on the surface of heulandite. Based on 150 nanoparticles, the average size of magnetite nanoparticles was calculated. It was reported that the mean porosity of Fe$_3$O$_4$ is crucial for cracking C-S bonds and decreasing the content of heavy fractions. The magnetite was combined with zeolite to intensify the process of aquathermolysis. It was reported that 85% viscosity reduction degree was achieved after using a Fe$_3$O$_4$/heulandite nano-catalyst. The designed catalyst has a potential of industrial-scale application [65]. The synergetic effect from magnetite and zeolite on aquathermolysis of heavy oil was justified [66]. In Figure 9, energy-dispersive X-ray spectroscopy elemental mapping and TEM images are presented.
The aquathermolysis catalysts based on Ni, W, Mo, and C with different dispersions were obtained by mechanical grinding [67]. However, in order to apply such catalysts in reservoir scale requires investigation of their flow through porous media and precipitation on the rock mineral surfaces. The precipitation of the catalysts on the reservoir rocks was investigated by Almao et al. The flow test of molybdenum oxide in vacuum gasoil through clean sandpack and oil-saturated sandpack revealed that the former retains 36% of catalysts, while the oil saturated sandpack—54% [68]. The retention degree of trimetallic catalyst Ni-Mo-W in oil saturated sandstones of Athabasca in case of high permeable sands (248 Darcy) was 30% and in case of low permeable sands (8.9 Darcy)—45% [68,69]. However, in [70] the influence of rock permeability on the amount of retained particles was not mentioned. A recent review of the literature on this matter analyzed the flow behavior of nanoparticles through porous media considering criteria necessary for application of them in Enhanced Oil Recovery (EOR) projects [71]. The various promising mechanisms for enhancing oil recovery are discussed. The influence of intermolecular forces along with other external forces on the stability of dispersion, agglomeration of nanoparticles
and subsequent precipitation were analyzed in order to prepare stable nanofluids for their further application in EOR.

2.2.2. Water-Soluble Catalysts

Preliminary studies of water-soluble salts of transition metals (FeSO$_4$, RuCl$_3$, NiSO$_4$, VOSO$_4$, etc.) corresponds to Hyne, Clark and others [72]. They proposed that water-soluble transition metal salts could accelerate cracking of sulfur-containing components of heavy oil into alkanes, carbon dioxide, hydrogen and hydrogen sulfide that reduces the viscosity of heavy oil. After that, water-soluble non-organic metal salts have been widely used as catalysts in the steam injection process. The contact of the catalysts’ surface with the oil phase is a crucial point to provide high efficiency of the reagents. In this regard, homogenous catalysts, which can be distributed in the interface of an oil–water system have been intensively being developed to improve the quality of heavy oil. The laboratory experiments of catalytic aquathermolysis of extra-heavy oil in case of the Liaohe field revealed decrease in the content of heavy components and increase in the share of light components. Moreover, the removal of S, N, O-containing compounds assisted in reduction of viscosity by 15–75% at 240 °C, 24 h. Fan, et al. suggested the combination of transition metal salts with alkali such as KOH/NaOH that reduced the viscosity of heavy oil samples from 10 various reservoirs by 75–93% [73]. Moreover, Zhong and co-workers compared efficiency of Fe (II) salts, tetralin and their combination in terms of viscosity reduction of Liaohe extra-heavy oil [74,75]. The viscosity reduction up to 90% was achieved after catalytic treatment at 240 °C and for 72 h. However, tetralin is a hydrogen donor; the main contribution to the aquathermolysis process was done by Fe (II) salts. The results of industrial scale application of the developed catalytic complex during injection of steam with a concentration of 0.02 kmol/ton and hydrogen donor 0.1 mol/ton revealed that such a combination was able to provide the total oil accumulation of 4139 tons per 14 days [76]. Despite the positive results of using inorganic catalyst precursors reported in many papers, it is not rational to apply such precursors in reservoir scale due to their insolubility in hydrocarbons and inability to penetrate the low-permeable reservoir rocks. Moreover, they can form big size particles downhole in the reservoirs. In this regard, a significant number of studies are devoted to the application of oil-soluble catalyst precursors.

2.2.3. Oil-Soluble Catalysts

In the following section of the given paper, the oil-soluble catalysts are thoroughly discussed. The colloid and molecular catalysts based on transition metals (Mo, Co, Ni, V, Fe, etc.) that form in-situ from precursors under the temperature of hydrogen sulfide are organometallic compounds or complexes [77–79]. Kadiev et al. used tools of thermodynamic and quantum chemistry to reveal the active form of catalysts. They imply that hydrogenation of molybdenum disulfide is formed by the interaction of molybdenum oxide with hydrogen sulfide rather than the sulfur element [80]. It was revealed that introduction of the sulfur element with further transformation into hydrogen sulfide provides conversion of molybdenum oxide into molybdenum disulfide. The hydrogen sulfide participates in reactions of disproportionation with hydrogen transfer.

In [81], the influence of ultradispersed iron oxide/hydroxide produced directly in the reaction zone with heavy oil was investigated. The procedure of catalyst synthesis was thoroughly described in [82]. In [83], the activity of redox catalysts based on ferrospheres in cracking of two heavy oil types (paraffinic and asphaltic), as well as fuel oil fraction of the paraffinic type of crude oil was investigated in reservoir conditions. Selectivity of generating liquid products for paraffinic crude was 95–96% at 450 °C in the presence of 10 wt% ferrospheres, while for asphaltic crude oil under the same conditions was 72%. The influence of ferrospheres was significant in cracking of paraffinic crude oil. During the cracking process, the phase composition and structural characteristics of ferrospheres change. The precipitation of carbonaceous formations, which were characterized by different reactivity in combustion reactions and concentrating sulfurous compounds from
crude oil, were observed on their surfaces. Under good solubility of the in-situ catalyst precursor, the hydrophobic part of heavy oil stabilizes the formed catalyst particles. Hence, it prevents the agglomeration of them in in-reservoir conditions. For instance, particles or molecules of polar (hydrophilic) metal sulfide catalysts are associated with hydrophilic resinous and asphaltene molecules of oil due to the significant amount of oxygen, sulfur and nitrogen containing functional groups, as well as associated metals in them such as nickel and vanadium, improving the efficiency of the catalytic process.

In work [84], spherical polymer brush nanocatalysts were synthesized, in which nano-TiO$_2$ is the core and poly(vinyl imidazole) (PVI)-loading nickel cations are polymer brushes. A group of scientists generated MoWNi-sulfides in-situ by thermal decomposition of metal–polymer precursors based on a co-polymer of polymaleic anhydrides in hydrocarbons [85]. Petrukhina et al. obtained nickel-molybdenum sulfide catalysts by decomposition of water-soluble bimetallic precursors (complexes with citric, oxalic, succinic, glutaric and tartaric acids) [86]. It was revealed that, after 1 h, the activity of catalysts in hydrogenation of bicyclic aromatic hydrocarbons and hydrodesulfurization of dibenzothiophene reaches higher values. It was reported that catalyst activity after recycling does not decrease due to the removal of negative influences of water in emulsion, causing oxidation of catalyst surface. The total oxygen content on the surface of catalyst is reduced and the proportion of metals in the sulfide environment and sulfur in the sulfide state increases.

In [87], Ni-W sulfide catalysts for in-situ hydrogenation of aromatic hydrocarbons of crude oil were obtained by decomposition of oil-soluble tungsten hexacarbonyl. The oil-soluble C$_{16}$H$_{30}$NiO$_4$ salt was used as the nickel source. The Ni/W/S catalyst showed high performance in hydrogenation reactions of aromatic hydrocarbons in case of hydro-upgrading crude with a high content of sulfur at temperature of 350 $^\circ$C and hydrogen pressure of 5 MPa. Ni-W-S particles in ion liquid had a plate form with 0.5 nm thickness combined into agglomerates with diameters of 100–150 nm [88]. Several studies have been carried out on the efficiency of aquathermolysis catalysts based on metal (Fe, Co, Ni, Cu) tallates for extra-heavy oil samples of Boca de Jaruco with the viscosity of 270 Pa·s [89–91]. The content of asphaltenes in the given object was very high—20%. Under the catalytic hydrothermal treatment, a redistribution in the group composition of extra-heavy oil was observed. The significant changes were observed in the resin content. Under the impact of catalysts, the mean reduction in the content of resins was 25 wt%. According to GC-MS data (Figure 10), the high-molecular molecules such as 2-methylphenanthrene, tetrahydrophenanthrene, 4-methylphenanthrene in aromatic fraction were observed after the catalytic aquathermolysis (Figure 9). Due to reduction in the content of resins and increase in the content of aromatics fraction of extra-heavy oil, it was proposed by authors that the heavy molecules are the destruction products of resins. The content of asphaltenes under the given experimental conditions was almost constant. However, the catalytic hydrothermal treatment provides a decrease in the molecular mass of asphaltenes [92,93]. The nickel-based catalyst showed the best performance in terms of affecting asphaltene molecules. The conversion degree of resins and asphaltenes was higher in rock extracts of the Boca de Jaruco field after the catalytic treatment. In general, the catalytic conversion of asphaltenes increased with the time of the aquathermolysis process. For the given extra-heavy oil sample, the content of asphaltenes was reduced at low temperatures independent from the presence of catalysts due to the thermal destruction. The significant performance of the catalyst based on nickel metal was clearly observed at 300 $^\circ$C [94].
Phenanthrene and fluorenone were used as tracing compounds to evaluate the hydroconversion of carbonate rock extracts in the presence of catalysts (Figure 11) [95]. The different hydrogenation degrees during catalytic aquathermolysis lead to hydrogenation of some rings in phenanthrene. Moreover, the transformation of fluorenone into fluorine and methyl fluorine was an indication of total deoxygenation. The authors imply fluorenone was absolutely transformed, while phenanthrene only by 25%.

The hot water and steam extraction are used for upgrading oil-saturated sandstones. A technology has been developed where water in bitumen emulsion is used as a feed in the water gas shift reaction (WGSR) to generate hydrogen (from CO) in reservoir conditions. The produced hydrogen is spent in further reactions of hydrodesulfurization (HDS) and bitumen upgrading. The applied catalyst precursor was phosphomolybdic acid, transformed into nano-dispersed molybdenum sulfide in-situ. This catalyst is effective for desulfurization processes. Other cations were investigated along with molybdenum—nickel, iron, vanadium and potassium. The gas phase is used as a model for bitumen emulsion treatment. The significant effects were observed at 391 °C from nickel and a mixture of nickel...
and molybdenum. The iron catalyst showed the weakest performance. The efficiency of catalysts was evaluated by the reduction degree of sulfur content in the treated gas [96]. The aquathermolysis of extra-heavy oil from the Liaohé (China) field led to the viscosity reduction of 80%, but early viscosity regression was observed. However, the application of tetralin inhibited the viscosity regression of heavy oil after aquathermolysis [97]. Gould et al. proposed an approach to evaluate reactivity of hydrogen donors with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ)—a strong hydrogen acceptor [98]. A hydrogen donor scale was proposed for a number of naphthenic and aromatic compounds. It was stated that the highest scaled hydrogen donors were tetralin,1,2,3,4-tetrahydroquinoline and 9,10-dihydro anthracene. However, there is no comparison study of the given compounds during the thermal upgrading of heavy oil. Thus, the efficiency and feasibility of the hydrogen donor is crucial for heavy oil field development. However, there is still a need for investigating alternative hydrogen sources for effective thermal upgrading of heavy oil in-situ.

In patents [99,100], the efficiency of carbon monoxide with steam injection for in-situ viscosity reduction is presented. The presence of hydrogenolysis catalysts (Ni, Mn, Co, Fe and other salts) increases the reduction degree of heavy oil viscosity. The application of formic acid provides redistribution in the group composition of heavy oil, increasing the content of paraffinic–naphthenic and aromatic hydrocarbons. Inhibition of alkene production indicates for hydrogenation reaction [101]. Inorganic and organic salts of formic acids, formamides, which can be injected together with steam, are proposed in patent [102] as an alternative hydrogen donor. Morozov and his colleagues developed a wolfram-carbide-based catalyst that was resistant to coking and poisoning [103]. According to the results of SEM, XRD, elemental analysis, TG-DSC and gas chromatography, the given catalyst has catalytic activity in cracking of heavy oil and allows increasing the yield of light fractions up to 70% even after three cycles of steam injection. It is well known that the morphology of the catalyst (size, shape, porosity) plays an important role during the hydrocracking process, like in all other catalytic processes [103–105]. For instance, it was reported that the light yield of hydrocracking products of heavy oil depends on the morphology of nanostructured molybdenum sulfide (MoS$_2$). In the case of MoS$_2$ nanoparticles, the yield of light hydrocarbons after hydrocracking was the highest. The authors imply that this is due to the significant surface area of MoS$_2$ nanoparticles in contrast to other nanostructured forms. This is confirmed by the results published in the work [106], where MoS$_2$ particles with diameter 20–70 nm were formed from the emulsion catalyst precursor (molybdenum ammonia) in hydro conversion conditions. Moreover, the catalyst positively effects kinetic characteristics of the hydroconversion processes of paraffinic–naphthenic and aromatic hydrocarbons, resins and asphaltenes. The hydrocracking products have the smallest content of aromatics in the presence of MoS$_2$ nanoparticles [107]. Another example on the influence of catalyst size on its activity is the research of Canadian scientists [108]. The authors showed that MoS$_2$ nanoparticles with the size of 13 nm had twice as good activity on desulphurization of vacuum gasoil in contrast to the catalyst with the particle size of 10,000 nm. The influence of catalyst (MoO$_3$/Al$_2$O$_3$) porosity on hydrocracking of heavy oil residues was thoroughly studied. For Al$_2$O$_3$ with the same acidity, the highest conversion and maximum yield of light cracking products are observed when using catalysts with a large pore size [109]. Korean scientists synthesized mesaporous iron oxide α-Fe$_2$O$_3$ with various shapes and porosities. The yield of light hydrocarbon fractions after hydrocracking of heavy oil residues is higher in case of a cylindrical crystalline form, rather than the spherical form of α-Fe$_2$O$_3$ nanoparticles [110]. Hur and co-workers synthesized a nanosheet-structured WS$_2$ catalyst and demonstrated its influence on hydrocracking of heavy oil residue. The yield of naphtha, medium distillates and gasoil were increased in the presence of the given catalyst compared to the available commercial catalysts [111]. The cracking of heavy oil in the presence of cerium oxide (CeO$_2$) with cubic and octahedral morphology was studied. It was revealed that both types of CeO$_2$ provided a sharp increase in the conversion
degree, while the yield of coke decreased. However, the conversion of asphaltenes was higher in case of cubic CeO$_2$ nanoparticle in contrast to the octahedral ones. The authors revealed that cubic CeO$_2$ nanoparticles have much higher specific surface area and hence provide high performance [112]. The dispersed nanosized spherical MoS$_2$ particles in liquid hydrocarbon medium is a very efficient catalyst for hydrogenation of coals and hydroconversion of heavy oil processes [113]. Thus, the influence of catalysts morphology (size, shape, porosity) is significant on the thermal upgrading of heavy oil processes. Identification of the elemental-phase composition of the catalyst at different stages of its formation is very crucial in order to define the catalytic influence mechanism. In this regard, X-ray fluorescence analysis, the X-ray diffraction method and Mössbauer spectroscopy techniques are used [114]. Mossbauer studies combined with electron microscopy and Auger spectroscopy methods provide a detailed insight into the morphology of ferrite nanoparticles and information about elemental composition and structural state of the core nanoparticles and their surface/interface [115].

2.2.4. Rock Minerals

Scientists have always seen rock minerals as an effective, green and natural catalyst for many chemical processes. Particularly, the role of rock minerals on the aquathermolysis processes was among the first studies of Hyne and his colleagues [116]. Dobrynkin and others [117] studied the performance of catalytic systems based on iron oxide and inorganic matrices of reservoir rocks such as basalt, sandstones and clays in the reactions of ammonium nitrate decomposition, methane oxidation and asphaltenes hydrotreatment. Catalytic systems were composed of iron oxide, attached on the matrices via co-hydrolysis of carbamide and iron chloride under hydrothermal conditions of $T = 433–473$ K and $P = 0.6–1.6$ MPa. The authors imply that the catalytic complex showed the performance in terms of hydrotreatment of asphaltenes in the following order Fe$_2$O$_3$/basalt > Fe$_2$O$_3$/clay > Fe$_2$O$_3$/sandstone and the iron oxide catalysts on clay being the most selective one. The catalytic role of rock-forming minerals was studied in transformation of heavy oil samples from Ashal’cha reservoir [118]. Kayukova et al. carried out laboratory physical stimulation of catalytic aquathermolysis processes of heavy oil samples with different chemical compositions (Ekaterinovskoe crude oil corresponding to the B2 type and Olympiadov crude oil corresponding to the A1 type) from the reservoirs located in Tatarstan Republic, Russia. The catalytic aquathermolysis processes were carried out at temperature of 300 °C in the presence of kaolin (with 44% montmorillonite content) and catalysts based on transition metal carboxylates (Fe, Co, Cu). The process medium was a mixture of carbon dioxide and water vapor. The distinguishing features of catalytic hydrothermal conversion of various oil types were evaluated according to the results of fractionation, structural group analysis, micro elemental composition and H:C ratio. The observed variations were due to the initial properties of crude oil and activation energy of destructive reactions mainly on C-C, C-N, C-O and C-S bonds that resulted in the increase in saturates content and reduction in the contents of resins and asphaltenes. Thermal analysis was used to evaluate the potential of oil content before and after the experiments. The high molecular weight components of naphthenic and aromatic oil corresponding to B2 type revealed a higher adsorption capacity to the rocks compared to the A1 oil type. Consequently, the adsorption of catalyst components on the reservoir rocks is also higher [119]. The adsorption of NiMo catalyst particles on carbonate rocks was studied in [120]. The SEM image of adsorbed NiMo catalyst particles on carbonate rock minerals is presented in Figure 12. The experiments were carried out within the temperature ranges of 320–360 °C. Another author studied the adsorption of NiMo/SiO$_2$ nano-catalysts on carbonate rock at 425 °C [121]. The size of catalyst particles is shown in Figure 13.
Hong-Fu and his colleagues studied the synergetic effects of minerals such as montmorillonite, kaolinite, quartz, calcite, etc. on the changes in molecular mass of asphaltenes of different heavy oils during aquathermolysis [122]. The catalytic effect of clay minerals was discussed in [123]. Unconventional oil resources such as shale oil may also be subjected to the aquathermolysis exposure. In our previous works, we have studied the aquathermolysis of kerogen of Domanic rocks. The kerogen fragments were identified in a fraction of aromatic hydrocarbons. The thermal treatment led to the changes in relative content of ortho-, para-, and meta-isomers of alkyl toluene. The content of heavy aromatic hydrocarbons increased along with the temperature increase. The changes in the ratio of kerogen microelements under thermal treatment indicates the maturity of organic matters [124].

2.3. Field Tests of Catalytic Aquathermolysis

The results of industrial-scale projects of Chinese colleagues that describe the results of in-reservoir catalytic treatment in heavy oil fields of China are very interesting [124,125]. The viscosity of the produced heavy oil was significantly decreased (four times), as well as the content of sulfur, oxygen, resins and asphaltenes. On the contrary, the ratio of H/C was increased. The main significant result was the increase in recovery factor. Chao et al. reported the field test results of catalytic aquathermolysis of the Xinjiang extra-heavy oilfield of China (in F10223 oil well). The viscosity of extra-heavy oil was 85,000 mPa·s at
50 °C. A difunctional catalyst–alkyl ester sulfonate copper was injected in the third cycle of CSS to maintain the declining oil production rate. The viscosity of extra-heavy oil was reduced by 84.82% reaching 12,900 mPa·s at 50 °C in 30 days after injection. The content of asphaltenes after the catalytic aquathermolysis was reduced from 13.61% to 7.39% [126]. Similarly, the oil-soluble catalysts synthesized in Kazan Federal University (Russia) have passed the field applications in the Boca de Jaruco extra-heavy oil field (Cuba), which has been developed by JSC «Zarubechneft» (Russia) and «Cuba Oil Union» (CUPET, Cuba). The successful application of nickel-based catalyst was reported in [127], which reduced the steam-to-oil ratio (SOR) by almost half.

Mohammad et al. propose oleates, naphthenates, molybdenum acetylacetonates, iron, nickel, copper, iron and surfactant complex compounds for field implementations [128]. The reduction in density, molecular mass, sulfur content, high molecular components and the viscosity reduction degree, which approaches 97%, were observed in all the given studies. Some studies propose the application of catalyst precursors in conjunction with hydrogen donors, where a synergetic effect on heavy oil recovery was observed [129–131]. Thus, a growing body of the literature on the field application of catalysts proposes the following order of procedures: injection of steam—catalyst precursor—steam—soaking period for several days—production cycle. In such a reservoir development regime, the heavy oil recovery factor has increased and the SOR (steam-to-oil ratio) has decreased in comparison to the tests without catalyst injection.

3. Concluding Remarks

In this review paper, we thoroughly discussed the application of the catalytic aquathermolysis process for in-situ upgrading of heavy oil. We have highlighted the importance of various aquathermolysis catalysts, which improve the efficiency of heavy oil recovery. The steam injection into the reservoir formation provides in-situ chemical transformation of hydrocarbons, while introduction of catalysts promotes the overall reactions that lead to the reduction of molecular mass of resins and asphaltenes. The injection of catalysts into the formations is challenging depending on the solubility of catalyst precursors: water soluble or oil-soluble. The in-reservoir decomposition of precursors generate nanoparticles. A stabilizing suspension is an alternative method for delivering the nanoparticles into the pay zone. This study is the first step towards enhancing our understanding of catalytic mechanism in the in-situ aquathermolysis process. However, for the wide industrial-scale application of catalytic aquathermolysis, further experimental investigations are needed to better understand the distribution behavior of catalyst particles in porous reservoir formations and adsorption of catalyst particles on the reservoir rock surfaces.

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