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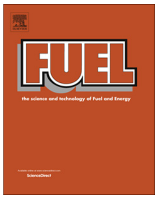

Review article

Aquathermolysis of heavy oil: A review and perspective on catalyst development

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HIGHLIGHTS

- Aquathermolysis has many advantages over other heavy oil upgrading methods.
- Progress made and issues on catalysts development were adequately reviewed.
- Minerals and organic systems of transition metals were the early catalysts.
- Nanometals, hydrophobic solid acids and carbides are potential catalysts.
- Catalyst design, operational conditions and mechanisms need further studies.

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ABSTRACT

Aquathermolysis process is one of the key and economical viscosity reduction technologies being considered for the successful exploitation of huge heavy oil deposits across the world. The paper substantially reviewed the progress made and the fundamental issues related to catalysts development. The most appropriate catalysts are those containing strong, active sites that can actively break the C—C, C—S, C—O and related bonds in resins and asphaltenes, with a net increase in the concentration of saturates and lighter aromatic hydrocarbons. Solid catalysts based on natural zeolites, heteropoly acids and modified zirconia oxides have so far demonstrated excellent activities. Catalysts such as alloys of Mo, W, C and Ni, nano oxides of Cu and Fe, Ni-chelates, supported nano-Fe particles and Cu^{2+} and Fe^{3+} complexes of toluene sulfonic acid were also recently reported as good candidates for the aquathermolysis reactions. Hydrophobic zeolites prepared in the fluoride or organic silane routes, carbides of W and Mo are prospective catalysts for the future due to their excellent performance in related reactions. In all cases, further studies are required to explore the optimal catalyst synthesis procedures, operation conditions and actual reaction mechanisms.

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1. Introduction

Consequent to the increasing global energy demand and the declining nature of the conventional oil reserves, heavy oil production will increase around the world. Heavy oil accounts for at least 25% of the world oil reserves, a large portion of the total known hydrocarbon reserves. In region like Middle East, large deposits that could be correlated to abundant light oil fields have been proven. In fact, there are thirty global countries identified with huge heavy oil reserves, with USA, Canada and Venezuela accounting for the largest deposits [1,2]. Accordingly, the respective possible supplies from Venuzuela and Canada are 1.5 and 2.5 trillion barrels, and the total global reserves at 5.6 trillions (more than five times the 1.02 trillions for the conventional light oil). However, the technically recoverable oil reserves based on available technologies have been estimated at 434.3 and 650.7 billion barrels (BBO) for heavy oil and bitumen, respectively [3]. Figs. 1a and 1b depict the global distribution of recoverable reserves for heavy oil and bitumen, respectively [4]. The major deposits are found in the countries within the North and South American regions. Countries in Europe have the lowest deposits (i.e. <100 billion barrels of both bitumen and heavy oil). Huge reserves of heavy oil are also available in the Middle East with no reported reserves of bitumen.

Heavy oil is known to be rich in heavier organic compounds such as resins and asphaltenes. The portion of heavier compounds (i.e. aromatics and naphthalenes) and light linear alkanes are significantly low. In fact, common heavy oil deposits are richer in compounds with at least sixty carbon atoms, in addition to heterocyclic derivatives. These mixtures resulted to high physico-chemical characteristics such as viscosity, boiling points and molecular weight [5,6]. The properties also in return posed serious recovery difficulties. The mobility of the oil is seriously restricted, and therefore displacement by simple fluids like water or gas became inefficient [7]. For these reasons, recovery factors for all the global regions are within the range of 0.1–0.2 only [3].

A number of interesting options are being considered for enhancing the recovery efficiency [8,9]. The common processes include thermal, microbial and chemical recovery. Common alternatives are *in situ* combustion and gravity drainage by steam (SAGD) [10]. Among the thermal options, steam stimulation is the most popular. The method encompasses the used of steam to increase the temperature of heavy oil and therefore lower its viscosity. This consequently reduces the flow resistance and enhances oil mobility. However, the process is expensive. Similarly, application of steam generates new free radicals that initiate polymerization reactions, producing larger molecules, which are more viscous than the heavy oil [11,12]. *In situ* combustion method, on the other hand, proceeds by the oxidation of the oil. The heat generated from this exothermic process causes bond breakage of heavy molecules and therefore partially upgrade the heavy oil. However, problems like the formation of sulfated compounds (e.g. sulfones) and carboxylic acid derivatives, with potentials to increase viscosity and consequently reduce mobility ratio have been reported [13–15]. The microbial recovery process involved the application of microorganisms and possibly metabolic products, under low temperature conditions, to enhance the extraction of oil. Several bacteria species were evaluated and additional recovery of 12% had been recorded [16,17]. The action of micro-organisms alters the pH and viscosity of the oil, thereby promoting its mobility [18]. One major issue is that, the microorganisms may be destroyed by the action of chemicals or heat at the temperature of reservoir. Similarly, is not yet clear, which microbial species provide the best activity, considering variation in reservoir properties. Other recovery options under consideration include water flooding, micellar solution, miscible displacement and solution-gas drive methods. Recovery by water flooding method involved the direct injection of water into the oil reservoir with the aid of water pumps or by the influence of gravity [19,20]. For the light oil reservoirs, the process can recover between 5% and 50% of the remaining reservoir oil, but achieving this with heavy oil reservoirs is very difficult [21]. Other problems commonly encountered include corrosion, pores clogging and growth of bacteria [22]. Micellar flooding otherwise called microemulsion recovery method involved the application of micellar solution into the reservoir with the aid of flooding water. The solution comprised of 10–15% of a surfactant, hydrocarbon and water. Low concentrations of alcohol and metal salt solution are usually incorporated to ensure adequate control of phase

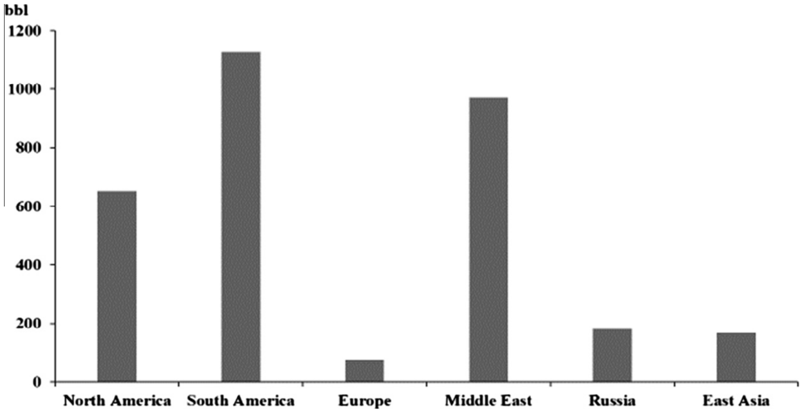

Fig. 1a. Distribution of heavy oil in billion barrels (bbl) for key global regions. Data source: Ref. [4].

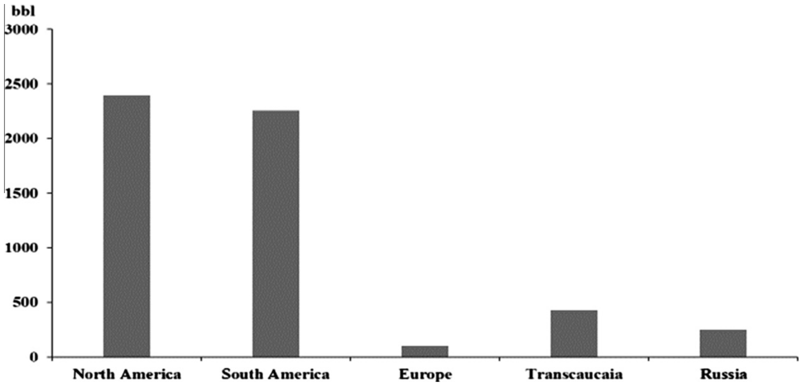

Fig. 1b. Distribution of bitumen in billion barrels (bbl) for key global regions. Data source: Ref. [4].

behavior [12]. The major challenges with this method are that, it requires expensive background work and does not yield good viscosity reduction for heavy oils of very high viscosity (i.e. super-heavy oils). The miscible displacement (i.e. miscible drive) method involved the injection of gases like CO_2 or light hydrocarbons (i.e. methane, ethane and propane) into the heavy oil reservoir at high pressure [23]. The process ensures the retention of reservoir pressure and improved oil recovery due to the associated reduction in interfacial tension between heavy oil and water. The CO_2 gas being cheaper than the light hydrocarbons is commonly employed for this application. However, problems such as low sweep efficiency associated with the large viscosity difference between CO_2 and heavy oil and the difficulty in achieving miscible front in the reservoir have seriously limited the success of the method [24]. Solution-gas drive is another recovery method being considered by the petroleum companies. The required energy for heavy oil production is provided by the dissolved gas [25,26]. It involved the expansion of the dissolved gas and oil in response to drop in reservoir pressure. This change in volume increases the recovery of oil from the reservoir. However, the method is more applicable for light oil reservoirs and can be associated with serious reservoir damage [27]. Generally, these recovery methods are associated with problems that limited their reliability.

An important alternative being considered is the process called "aquathermolysis", which involved the application of specific temperature and pressure conditions to break bonds (like C—S bond) in heavy oils and improve the concentration of saturated hydrocarbons and lighter aromatics. In the present day, scientist realized that, the application of catalyst improved the extent of the bond breakage and viscosity reduction. Therefore the "catalytic aquathermolysis" involved the introduction of appropriate catalyst (s) to efficiently achieve the viscosity reduction.

The previous viscosity reduction methods, that are associated with technical and economic challenges, gave emphasis to the role of temperature on viscosity reduction. However, in 1986, Hyne indicated temperature as not the only parameter to be considered [28]. The physical properties of the oil changed as a results of chemical reactions involving the oil components, steam and in some cases catalysts. These catalytic materials are responsible for the cleavage of various bonds in resins and asphaltenes, with net increase in the concentrations of lighter species of low viscosities. Earlier studies on catalytic aquathermolysis gave emphasis to the evaluation of Ni and Fe based catalyst systems These metal species can interact with the oil components and produce good conversion. However, efficiency and recyclability problems are common. In the recent years metal complexes, salts of heteropoly acids, hydrogen donor solvents (with catalysts), zeolites and associated acid catalysts are being considered [17,18].

Studies by Clark et al. [29] and some other authors showed the presence of catalysts in aqueous phase to significantly lower the viscosity of oil. The net increase in the oil mobility could therefore be attributed to the reduction of resins and high viscous asphalthenes. Apart from the importance of the method, literature in aquathermolysis is limited. The latest review on the subject was the work by Maity et al. [30] in 2010. We are therefore presenting a critical review on the progress made, especially with respect to catalysts development. The paper would lay emphasis on the catalysts already evaluated, their modes of action and the prospects of solid acid catalysts for the aquathermolysis process. Understanding of the aquathermolysis process, especially with respect to catalyst development is very essential. It is inevitable that, the huge global heavy oil reserves would be appropriately extracted for sustainable energy supply in future. The details presented in this paper will therefore provide useful guides on the selection of most appropriate catalysts, their modes of action and associated challenges. Laboratory studies could similarly be carried out based on the key findings of the paper and later escalated to oil field for development. The paper have critically examined the action of hydrogen donors. The details will provide a clue on the choice of most appropriate donor material(s) with respect to viscosity reduction.

2. Historical background

In the introduction part, we have explained the various challenges associated with other heavy oil viscosity reduction options like *in situ* combustion, thermal, microbial and chemical recovery methods. With the catalytic aquathermolysis process, an appropriate quantity of a catalytic system or catalyst mixture is introduced into the oil reservoir simultaneously with a steam at high temperature [31]. There are some vital steps to be observed with this technology. The thermolysis process and the effect of steam at high temperature (i.e. aquathermolysis) are responsible for deriving the overall process energetically. Thus, the key role of the aquathermolysis aspect is to break down the heavy molecules in the oil to smaller molecules by the combined effect of steam and heat. The recovery method termed "Huff and Puff" process was the main commercial aquathermolysis process employed for fields in Canada and America since 1960s [30]. It proceeds by the injection of superheated water into the reservoir well. This trigger the cracking of large asphaltenes compounds, lower the oil viscosity and consequently enhance recovery by improving flow properties. The addition of catalytic material provides an additional opportunity for improving the pyrolysis of the heavy oil by initiating more C—S, C—N, C—O and C—C bond fissions. It could therefore be viewed that, a combination of the aquathermolysis process and catalysis gave rise to the term "catalytic aquathermolysis", which is the main subject of the paper.

Early studies in this research area could be traced to the work of Hyne and co-workers [32] around 1982. Their initial investigations reported the aquathermolysis process to involve the chemical interaction between the oil, steam at high temperature and the reservoir minerals. Therefore, reservoir minerals also facilitate the viscosity reduction and compositional changes associated with action of the steam at elevated temperatures. These fundamental observations were further confirmed in their subsequent studies [33,34]. An important challenge observed from these subsequent studies was the viscosity reversal with time. The bond cleavages usually produce radical species of heteroatoms (i.e. radical species of S, N and O). These compounds trigger polymerization reactions and reproduce giant molecules of very high viscosity, making the process very complex. Similarly, the viscosity reversal could be more severe when the oil under consideration is an extra-heavy oil. The viscosity reversal process via radical-assisted polymerization was subsequently reported by other authors [35–39], who employed different heavy oil brands and aquathermolysis conditions. It has been established that, addition of suitable catalyst can provide a non-reversible mechanism for catalyzing the hydrodeoxygenation, hydrodesulfurization and hydrodenitrogenation by the breakage and removal of O, S and N derivatives in the oil, thus given a prospective way to the catalytic aquathermolysis. The catalytic material should also have exceptional capabilities for breaking the S-compounds, being the more susceptible to polymerization [31]. Different catalyst systems based on solid acids, transition metals and hydrogen donors are therefore been evaluated for the catalytic aquathermolysis process [30,38,40–43].

2.1. An overview of main mechanism

The major components of the heavy oil are resins, asphaltenes and associated derivatives. The main viscosity reduction mechanism is therefore one that targeted direct decomposition of these species irreversibly. It has been established that, hydrocarbon compounds in the heavy oil could be ruptured even without the influence of water when the temperature exceeds 300 °C [30]. However, complexities are associated with the S-bearing compounds, whose decomposition by C—S bond fission is very critical for the overall process. A common chemical reaction (Eq. (1)) believed to occur with these species involved their reaction with steam to produce methane, hydrogen sulfide, carbon dioxide, hydrogen and possibly low molecular weight hydrocarbons that are heavier than methane [30,44].

$$RCH_2CH_2SCH_3 + 2H_2O \leftrightarrow RCH_3 + CO_2 + H_2 + H_2S + CH_4 \quad (1)$$

Some of the produced gases such as hydrogen and carbon dioxide are also very important in reducing the viscosity. Since the hydrogen comes from water, it can initiate viscosity reduction by attacking the oil in a manner similar to the hydrogen donor compounds (see Section 5). Similarly, olefinic compounds from bond fissions could be hydrogenated in the presence of catalyst, thus improving the oil properties. On the other hand, since carbon dioxide can be produced from hydrodeoxygenation of heavy oxygenated molecules in the oil, its evolution revealed a positive effect towards viscosity reduction. It can also modify the pH of the reaction medium.

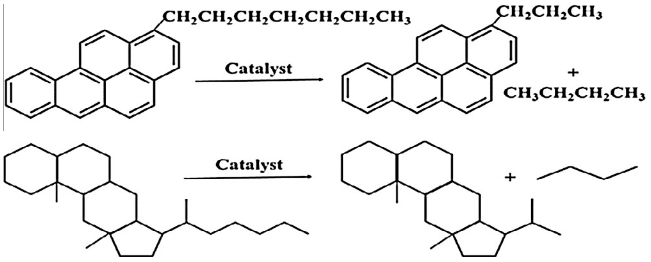

Fig. 2. Catalytic pyrolysis of saturated and unsaturated hydrocarbons in heavy oil. Adapted from Ref. [31].

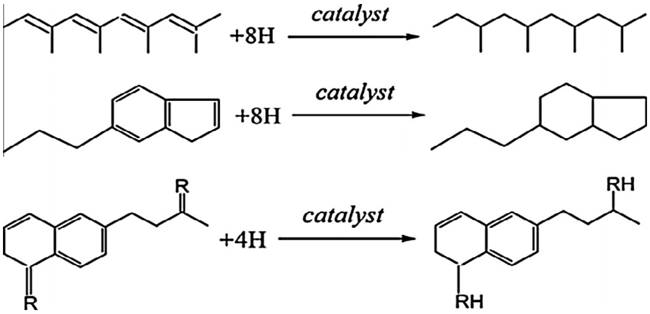

Fig. 3. Catalytic hydrogenation of olefinic and aromatic hydrocarbons in heavy oil. Adapted from Ref. [31].

The work of Wang and co-workers [31], indicated the addition of an acidic catalyst, like aromatic sulfonic iron, to catalyze a series of chemical reactions including the pyrolysis of side reaction chains of both saturated and unsaturated compounds (Fig. 2), hydrogenation of unsaturated compounds (with or without heteroatoms, Fig. 3) and isomerization. The other identified catalytic role includes polymerization on active metal sites, oxygenation of S-compounds, ring opening reactions of saturated and unsaturated cycles. However, appropriate selection of catalyst materials with good acidity, thermal stability and irreversible bond fission properties is necessary. Otherwise, reconstruction of ruptured species and polymerization reactions could be reversibly catalyzed.

The authors [31] demonstrated that, reactions of resins and asphaltenes involved the disintegration of the side chains to produce alkanes and/or olefin compounds with subsequent possibility of hydrogenation. Similarly, the derived polyaromatic species are subject to depolymerization into mono- or slightly heavier aromatic compounds. Therefore, the action of catalyst could be summed as the cleavages of C—C, C=C, conjugations, C—X (where X = heteroatoms) and promoting the dissolution of low molecular weight hydrocarbons produced, with a net reduction in the oil viscosity. Similar mechanisms have also been reported by other authors [40,45–48].

3. Solid catalysts in aquathermolysis

Solid catalysts represent a large group of heterogeneous materials that could be acidic or basic in nature, usually employed for catalyzing a range of industrial chemical processes (Fig. 4). Their ability to interact strongly with reactant molecules, at some important stages of the reactions, provides the opportunity for achieving varieties of reaction products. The choice of appropriate solid catalyst is much dependent on the reaction of interest. Similarly, the catalytic activity is dependent on the surface area, acidity–basicity (Brønsted/Lewis), shape selectivity, pore properties, stability, and availability and preparation routes. These factors are not different for solid catalysts suitable for the aquathermolysis process.

The major classification of various solid acid catalysts is presented in Fig. 4. They can be either acidic or basic in nature, and are already good candidates for many reactions in the petroleum industry. Materials such as zeolites and some oxides (e.g. zirconia and alumina based catalysts) have been studied for the aquathermolysis. Other reefing catalysts like unsupported oxides, carbides and structured materials have not been exploited so far.

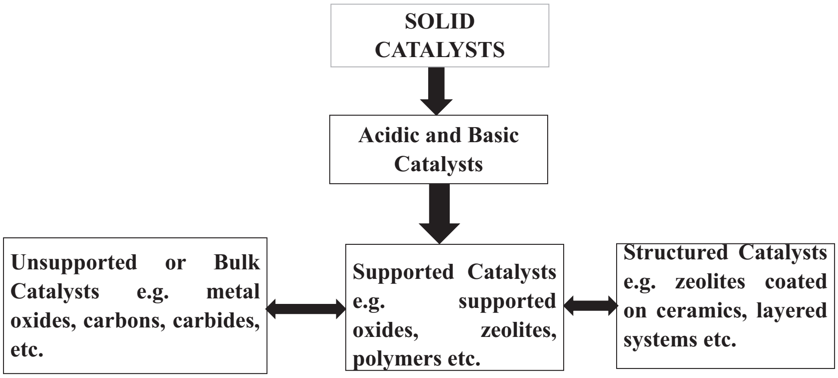

Fig. 4. Different types of solid catalysts with potentials for industrial applications such as aquathermolysis.

Therefore, their documented properties would be considered and reasonable details would be provided on their potential applications in the catalytic aquathermolysis reaction. Metal oxides and carbides are normally supported with alumina, silica or inert transition metal oxides like titania to obtain excellent activities. Structured catalysts based on zeolites can form good catalysts due to simplicity in designing materials with excellent structure-acidity or structure-basicity properties.

Catalysts play an important role during the aquathermolysis reaction. One major role is the catalytic hydrolysis of the aliphatic sulfur bonds of the heavy oil compounds. Hydrogen sulfide is produced and the concentration of lighter hydrocarbons increased [28]. These compounds are characterized by lower molecular weights and viscosities compared to resins and asphaltenes. Catalysts based on metal species like Ni and Fe attack bonds containing oxygen, sulfur and/or nitrogen and generate gases such as hydrogen, ammonia, hydrogen sulfide, carbon monoxide and carbon dioxide. Lighter hydrocarbons are similarly produced. The ability of the catalysts to break the complex structures of resins and asphaltenes formed the major deriving force for viscosity reduction. The catalysts also promote heat transfer and favor the effect of steam. Catalytic systems such as acidic zeolites, heteropoly acids and their salts and hydrogen donor catalysts produced H^+ species that attack the resins and asphaltenes and cause fission, rupture, cyclization and cleavages. Lighter aromatics and alkanes of low molecular weights are normally produced. Production of gaseous species is low compared to metal ion catalysts. Mechanistically, the action of the catalyst breaks C—S bond of many S-bearing compounds and yield saturates in addition to the H_2S gas. By the process of aeration, compounds of nitrogen such as pyridine, amides and derivatives of pyrrole are produced via C—N cleavages and rearrangements [46]. The mechanism also involved pyrolysis of the C—O or C—C in cyclic alkanes and bridging groups. The main reaction routes involved pyrolytic fission, cyclization and ring openings, desulphurization, denitrogenation and/or deoxygenation [46,49]. Availability of hydrogen or hydrogen donors in the reaction systems also promote hydrogenation process.

3.1. Solid acid catalysts: zirconia, alumina, natural zeolites

Since the aquathermolysis process involved the reaction of heavy oil with steam in the presence of catalyst (i.e. catalytic aquathermolysis), the catalyst material must have evidently favor the reaction. Initially, salts and organic compounds of transition metals were the main catalysts [37,50,51]. Exploitation of solid acids and other super acids could be traced to the work of Strausz and co-workers [52]. The authors employed HF modified BF_3 super acid for thermolysis of heavy oil from Alberta, that is rich in bitumen, tar sand and asphaltenes. Reactions were carried out under mild conditions (i.e. $\leqslant$190 °C, 500 psi) for a period of 1 h. Their results suggested the reactions to proceed by depolymerization and hydrogenation, involving an ionic mechanism that was believed to be more favorable than the radically assisted mechanism known for transition metal catalysts. Up to 56% conversion was achieved, with the main products comprising of volatile organic compounds and alkylbenzenes. Results from this study triggered the exploitation of solid catalysts such as heteropoly acids, modified zirconia and zeolites for the aquathermolysis reaction. Because, although the HF-BF_3 catalyst formed very active system in terms of viscosity reduction and compositional modification, its water solubility poses removal difficulty after the reaction.

Wen et al. [53] studied the activity of $H_4SiW_{12}O_{40}$ on the viscosity reduction of heavy oil obtained from the Shengli reservoirs. Reactions over this catalyst proceeds by vis-breaking, involving the hydrocracking of heavier hydrocarbon fractions in the feed. A decrease in viscosity by more than 67% was observed after 36 h reaction time at 240 °C. They showed the co-presence of $H_4SiW_{12}O_{40}$ and reservoir minerals to further promote viscosity reduction to more than 73%. Chen et al. [40] showed the viscosities of a range of extra-heavy oils to reduce by up to 90% using $K_3PMo_{12}O_{40}$ with nano-Keggin structure as aquathermolysis catalyst at 280 °C. The action of this catalyst involved pyrolysis of the heavier compounds into lighter species. Degradation into ethers, phenols and similar molecules is associated with the breakage of C—C and C—O bonds, especially at the side chains. The overall activity was attributed to the nano-Keggin structure. This model was later supported by other authors [54]. Nano-Keggin structure permits the interaction of the catalyst with heavy compounds in the bulk of the oil, and consequently favor bonds fission. Heteropoly acid catalyst assisted bonds breakage (Fig. 5) during this reaction was also recently reported by Chen and co-workers [55]. The authors employed modified $H_3PMo_{12}O_{40}$ at 280 °C and 3 MPa for the thermolysis of heavy oil in 30% water. Reduction in compositional hydrocarbon chains from C19-30 to C12-16 was observed after the reaction. Lighter oxygenated compounds such as organic acids and alcohols with carbon numbers below 10 were also produced to significant concentrations. The net viscosity reduction was also favored by temperature and water effects. Similarly, the presence of aromatic sulfonic modifier promotes the interaction between catalyst and heavy oil. The mechanism of action involved the cleavage of C—C bonds and generation of new reaction products that are richer in saturates and lighter aromatics of low viscosity (Fig. 5). Reactions at the side C—C chains can produce much lighter alkanes. The complex C—O bonds in resins and asphaltenes can be attacked by the active sites (e.g. Brønsted acid sites) of the catalyst, producing lighter aromatic alcohols like phenols and carboxylic acids. The production of

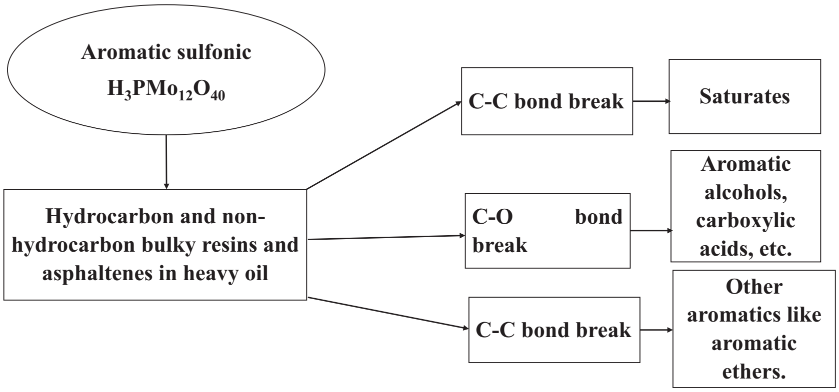

Fig. 5. Proposed schematic mechanism of catalytic aquathermolysis of heavy oil using modified heteropoly acids as catalyst. Adapted from Ref. [56].

certain lighter reaction products and net viscosity reduction are therefore much dependent on the initial composition of the heavy oil and catalyst nature. As shown in Fig. 5, the sulfonic acid interacts with hydrocarbon and non-hydrocarbon bulky resins and asphaltenes in heavy oil causing C—C and C—O bond fissions with the net production of saturated hydrocarbons, oxygenates (e.g. carboxylic acids, aromatic ethers and aromatic alcohols).

Heteropoly acids are known for their strong acidity, and therefore the materials were applied in many acidity-dependent reactions, including the aquathermolysis. However, to ensure stability and water tolerance, modification with metals such as Cs and Pt or the incorporation of SiO_2 or TiO_2 support is required [56]. A key advantage of these compounds is that they can be regenerated and reused as observed in some previous reactions.

Studies on the effects of sulfated zirconia catalysts was reported by Jing et al. [57]. SO_4^{2}-/ZrO_2 was modified with Ni^{2+} and Sn^{2+} precursors and evaluated as vis-breaking catalysts for Shengli reservoir oil. Reactions were carried out at 240 °C and under pressure from 3 to 4 MPa for a period of 24 h. Separate addition of both Ni^{2+} and Sn^{2+} particles modified the acidity-activity properties of the sulfated zirconia, with positive effects on oil cracking and viscosity reduction. Synergic effect of SO_4^{2}-/ZrO_2 acidity and metal ion modification caused a viscosity reduction by at least 50%, with best activity observed with the Ni^{2+} modified catalyst. While the amount of heavy resins and asphaltenes decreased, the production of fully saturated and lighter aromatic compounds increased. Reduction of sulfur and nitrogen species was also observed. A mechanism similar to that reported for heteropoly compounds (Fig. 5) was proposed, but water content should be low to achieve the desired activity. Previous infrared spectroscopic studies with probe compounds such as CO and pyridine showed the existence of both strong and weak Brønsted and Lewis acid sites in sulfated zirconia catalysts [58,59]. Their availability could be promoted by the selection of appropriate calcination temperatures. The values employed by Jin et al. [57] are within the optimal range of 500–650 °C recommended by authors [60,61]. It should be noted that, these acid sites enhance the activity of most oxide catalysts during aquathermolysis as reported by Maity et al. [30]. Therefore, this can provide further explanation on the activity established by Jin et al. [57]. Recently, Wang et al. [62] studied the effect of synthesis method on the viscosity reduction activity of WO_3/ZrO_2. Catalyst systems were prepared by either impregnation or hydrothermal treatment of precursor materials. Their characterization data showed the hydrothermal method to be more favorable. Highly dispersed phase that was also richer in acid sites was obtained. This resulted from stronger interaction between zirconia and tungsten via this synthetic route. Catalysts were evaluated for viscosity reduction at 220 °C and 2 MPa for a period of 6 h. The results indicated the degree of viscosity reduction to be acidity dependent. Hydrothermally prepared catalyst formed the best system, showing 82.2% viscosity reduction with no regression. Evidences of improving acid sites density in zirconia catalysts by hydrothermal synthesis has been previously documented by other authors [63,64]. The route also promotes crystallinity and generation of stabilized pore structure. These features could therefore also be attributed to the activity established by Wang et al. [62].

Natural zeolite catalysts are also among the materials been evaluated for the aquathermolysis reaction due to their abundance and structure-acidity properties. Merissa et al. [65] studied the activities of two natural zeolites (heulandite and clinoptilolite). The materials were initially pre-milled and activated at 300 °C. Although the milling process have negative effect on catalyst crystallinity, it was very beneficial for viscosity reduction. As low as 0.5 wt.% of catalyst employed at 200 °C for 6 h caused viscosity reduction of 65%. Junaid et al. [66] reported natural Ca-chabazite and clinoptilolite as good systems for viscosity reduction of oilsand bitumen under aquathermolysis conditions. They found 81% conversion with 96% production of liquid hydrocarbons. There was also significant decreased in the amount of nitrogen and sulfur compounds. Resulting liquids were low viscous with low boiling points and molecular weights. Therefore, the activity could be applicable to heavy oil of comparable compositions. In a related development, Kuznicki et al. [67] modified Na and Ca rich chabazite from Arizona into their acidic forms by NH_4^+ exchange at 400 °C. The resulted catalysts were very active for viscosity reduction of bitumen at the same temperature. The superior adsorption properties also favored the removal of metals and derivatives of sulfur and nitrogen. Similarly, Junaid et al. [68] demonstrated clinoptilolite to yield comparable activity under similar conditions. Unlike heteropoly acids and soli oxides, natural zeolites are abundantly distributed in many parts of the world. Their exploitation is considered economically feasible [69,70]. They are environmentally friendly with low processing difficulties. These factors can therefore eclipse their prospects as aquathermolysis catalysts.

3.2. Hydrophilic and soluble catalysts

Soluble catalysts for aquathermolysis can be viewed from two perspectives. The hydrophilic materials are those systems with good affinity for water, whereas the other category comprised of oil soluble catalysts. Clark et al. [37] were among the first authors to show water soluble catalysts based on transition metals like ruthenium and iron as good materials for aquathermolysis. They can attack the C—O, C—S or C—N bonds of most heavy oil compounds and produce low molecular/viscous counterparts irreversibly. Recently, Chao et al. [71] prepared an aromatic sulfonic copper complex catalyst from the reaction of aromatic sulfonic acid with copper sulfate at neutral pH and 100 °C. The FT-IR data showed features consistent with the presence of acidic groups, which are the main active sites required for the aquathermolysis process. The evidence of chelation was also observed. As low as 0.2 wt.% of catalyst sufficiently causes a viscosity reduction of 95.5% for a super heavy oil containing 25 wt.% of water for 24 h at a temperature of 280 °C. Its mode of action was mainly by pyrolysis, with the removal of O, N and S species at some important reaction stages. An interesting issues here is that, the water soluble catalyst can easily be prepared using simple procedures, at low cost compared to many other catalysts. Similarly, most other reported catalysts employed by other authors [57,72,73], are less active for super heavy oil due to its complex compositions. Therefore, it is highly prospective for this application.

On the other hand, the early used of oil soluble catalysts could be traced to the work of Wen et al. [72]. The authors synthesized molybdenum oleate from precursor MoO_3 and oleic acid in water at 100 °C for 30 min. The catalyst was tested for viscosity reduction of Liaohe oil at 240 °C for 24 h. The results indicated that, 0.5 wt.% of catalyst is adequate to achieve 90% viscosity reduction for 75 g oil and 25 g water mixture. Similarly, molybdenum oleate formed a better catalyst than some inorganic catalysts. The authors have also carried out a field test, adopting puff-and-huff operation method in Qi-40 and Qi-108 blocks of the Liaohe oilfield. An overall decrease in viscosity and improved production consistent the laboratory results were observed. Youngjian et al. [74] showed modification with emulsifier to enhance the activity of the molybdenum oleate catalyst. Incorporation of 0.1 wt.% emulsifier produces more than 90% reduction in viscosity at lower temperature of 200 °C. Lowering the temperature favors catalyst stability and enhances the interaction of its active sites with molecules in the heavy oil. Zhao et al. [75] also reported emulsification with petroleum sulfonate to promote the activity of Co and Ni based oil soluble catalysts. The catalysts yield 90% viscosity reduction at 180 °C. They were very stable after repeated applications, producing promising activity.

3.3. Other potential catalysts

One of the important aspects of viscosity reduction during aqauathermolysis is the removal of heteroatoms such as O, N and S. Similarly, the catalyst materials must have excellent water stability to avoid sudden activity decay and/or viscosity reversal. An important category of catalysts with prospects for the catalytic aquathermolysis reaction are the hydrated molybdenum oxides. These materials could be designed with enough Brønsted acidity to catalyze hydrocracking and/or transfer of hydrogen, an important property required for heavy oil upgrading. Raman studies by Williams et al. [76] showed the hydration of a range of molybdenum oxide loadings over Al_2O_3 to improve the acidity properties. Similarly, new structures could be developed depending on the molybdena loadings. Lower loadings (i.e. 1–5 wt.%) formed mainly tetragonal structures whereas higher loadings (i.e. >5 wt.%) corresponding to monolayer coverage produced mainly polymeric molybdate species. Interestingly, both structures were previously reported to show good activities in acidity dependent reactions [77–79]. Sotani et al. [80] prepared hydrated MoO_3 from nitric acid treatment of ammonium heptamolybdate precursor at 110 °C. The material was very active (80% conversion) for thiophene HDS at moderate temperatures around 350 °C. But structural and compositional changes were observed when the temperature reached 375 °C and beyond. The mild-temperature activity implies that the material may form a better catalyst for aquathermolysis reactions that are usually carried out at lower temperatures (i.e. 200–315 °C). Similarly, presence of water in the aquathermolysis feed can stabilize the $MoO_3.n\ H_2O$ and/or $MoO_2(OH)_2$ species by retarding dehydration. Mathew et al. [81] reported hydration of support instead of the active molybdena species to also generates new acid sites with good dehydration performance. Hydrated alumina supported molybdena catalyst exhibited more acidity, as observed from pyridine adsorption experiments, than pure molybdena catalyst. Similarly, the supported molybdena catalyst was more acidic than supported vanadium or chromium oxide. The trend was consistent with the benzyl alcohol dehydration activity. Supported molybdena being the most acidic produced the highest activity of 82% conversion and 80% selectivity to dibenzyl ether. The catalyst was also stable throughout the reaction period. In fact, hydrated and analogue oxides of molybdena have been evaluated in other acidity dependent reactions like isomerization and hydrocracking, yielding excellent activities [82,83]. They are therefore prospective materials for the aquathermolysis reactions.

Hydrophobic zeolites are also promising catalysts, particularly due to their aqueous stability. However, careful and mild preparation conditions are necessary. The hydrophobicity may be achieved by increasing the Si/Al ratio of zeolite materials [84,85]. This factor decrease catalyst acidity and consequently lower its activity in acidity dependent reaction. To handle this problem catalyst preparation via the fluoride routes or modification with organic silane compounds would be very beneficial [86,87]. These options increase catalyst hydrophobicity without destruction to the structure-acidity properties.

Designing any of these prospective catalysts must be carried out with an utmost care. Incipient wetness impregnation is a good method for preparing supported tungsten and molybdenum catalysts. The loading of active components should be selected based on previous history of the materials in related reactions stated above. Hydration of molybdena to form molybdenum hydroxide must be performed completely to avoid the existence of unreactive layers that can hinder the accessibility of the active sites by the reactants in heavy oil. In addition to hydrophobicity, zeolite structures that preferentially favor carbon to heteroatom bond cleavages are very necessary for the aquathermolysis reaction.

4. Stability of catalysts in aqueous medium (hot water)

Catalysts stability entails its ability to be utilized for long period of time without activity decay, disproportionation, structural collapse, sintering due to high temperatures, active sites deactivation and/or compositional changes due to interaction with the reaction feed. In aquathermolysis, the reaction is normally carried out at low to mild temperatures (200–400 °C). Therefore catalyst instability due to sintering or rapid structural collapse is basically very challenging problem. However, the presence of hot water in the reaction feed may create stability difficulties depending on the catalyst system, and consequently retards its viscosity reduction efficiency. Catalysts that have good water tolerance should therefore be more preferable for this application.

Catalysts based on minerals, transition metal ions, their salts and derived complexes like those employed by Clark et al. [29], Chao et al. [71], Strausz et al. [52] and Clark et al. [37] were very active, yielding viscosity reduction as high as 80%, with significant production of saturates and lighter aromatics. However, their hot water solubility implies that catalyst recovery and subsequent reuse is fundamentally difficult. This can significantly limit industrial value due to cost and disposal implications. Similarly, transition metal ions with water affinity like Cu^{2+}, Fe^{3+}, Mo^{6+} and others are prone to form stable aqua-complexes with water in the reaction medium, thereby limiting their accessibility to resins and asphaltenes in the heavy oil. This factor will definitely reduce their viscosity reduction efficiency.

Solid acids and bases are known for their water tolerance and stability. For examples, materials such as natural zeolites (heulandite and clinoptilolite) employed by Merissa et al. [65] and Ca-chabazite by Junaid et al. [66], transition metal oxides and their composites such as WO_3/ZrO_2 by Wang et al. [62] and modified SO_4^{2}-/ZrO_2 by Jing et al. [57] have shown excellent viscosity reduction. Similar trend was also observed with heteropoly acids, especially the nano-compounds with Keggin structure, that were very active for extra-heavy oil [53,54]. Their hot water tolerance implies that, they could be removed and reused, producing comparable activities, and therefore more prospective for the industry.

Among the prospective catalysts such as nitrides and carbides of transition metals like W and Mo, hydrated molybdenum oxides and zeolites, the hydrophobic zeolites have already been evaluated for their water tolerance in other aqueous reactions like isomerization and acylation [88,89]. Their superior properties could be extended for the aquathermolysis reactions. However, the zeolite materials must be synthesized in the fluoride routes or modified with organic silane compounds to avoid destruction to acidity, which is the main requirement for catalyzing cracking reactions and pyrolysis during the aquathermolysis process. Catalysts based on W and Mo are also known for their good thermal stability. They have been employed for different reactions at temperatures similar or higher than those considered for the aquathermolysis process without encountering stability problems. Li et al. [90] used Fe–Mo catalysts for methanol upgrading at 600 °C for a period of 200 h. Both methanol conversion and formaldehyde selectivity were stable throughout the reaction time. Moene and co-workers [91] conducted stability studies for Mo catalysts supported with different supports (i.e. SiC, Al_2O_3 and SiO_2). The supported catalysts were heated in air at the temperatures of 500 and 1000 °C for 8 h. The characterization data showed complete retention of the physico-chemical properties of the various catalysts after the treatment. Qin et al. [92] evaluated the stability of Fe–Mo–W catalyst prepared by sol gel method during p-xylene oxidation. Post-synthesis thermal analysis demonstrated the catalyst as very stable in the temperature range of 200–650 °C. No any structural destruction was observed and the weight loss was <5%, which had been attributed to removal of moisture from the catalyst. Similarly, a stable p-xylene conversion was achieved at 300 °C for a period of 3 h. Badawi et al. [93] studied the effect of water treatment on stability of Mo–Co/Al_2O_3 catalyst during 2-ethylphenol hydrodeoxygenation at 350 °C for 14 h, using 0.25–0.73 MPa partial pressure of water. The catalyst was resistant to deactivation under these conditions. Therefore, introduction of water does not exert structural deterioration or active sites decay by poisoning. The various studies indicated that, the W and Mo based catalysts could be good candidates for the aquathermolysis process due to their hydrothermal stability properties.

5. Cracking and hydrogen donor

Cracking and hydrogen donor catalysts have the ability to retard or stabilize radical formation and promotes the hydrocracking of heavy oil fractions. For these reasons, the materials are now considered as aquathermolysis systems. Some of these materials are solvents like organic acids or functionalized cyclic hydrocarbons that could donate hydrogen at some important stages of the reaction. Evidence of their hydrogen donation, radical inhibition and cracking initiation during aquathermolysis have been reported by a number of researchers [94,95]. Ovalles et al. [96] employed tetralin for the upgrading of a heavy oil sample from Hamaca in Venezuela. The reaction mechanism involved the transfer of hydrogen from the solvent into the heavy oil, forming dihydronaphthalene, which consequently formed naphthalene. Both compounds are good indication of the viscosity reduction by this solvent. Particularly, the viscosity reduction doubled and API gravity reached 15° after 24 h at 315 °C. The same authors [97] combined steam injection process with hydrogen donation (using tetralin) mechanism to upgrade an extra heavy oil. For a period of 24–64 h at 315 °C, a threefold reduction in viscosity was achieved, that is higher than that observed with tetralin alone in the previous case. Interestingly, the mechanism was similar but the presence of steam favors the hydrogen donation process. Hydrocracking reactions were further activated, leading to 8% reduction in asphalthenes content with significant rise in API gravity. Ovalles et al. [95] reported the combination of three parameters; hydrogen donor (i.e. tetralin), methane (from natural gas) and steam injection conditions to have pronounced effect on the upgrading process. Their physic-chemical and simulation data showed an increased in API gravity to 12° from 3° for the original heavy oil. Although no details was available on the main mechanistic role of methane, its presence exerts a reduction in viscosity and heavier fractions. Liu et al. [98] have shown that, depending on the amount of solvent/hydrogen donor employed, the viscosity reduction could be reduced at milder conditions. They employed 0–1% of teralin to upgrade a heavy oil from Liaohe, employing milder conditions of 240 °C for 24 h period. Although the mechanism of action was the same to that proposed by Ovalles et al. [96,97], the reduction in viscosity was favored by higher solvent concentrations. Up to 80% decrease was observed when the solvent amount reached steady state amount of 0.8%, beyond which no further reduction in viscosity could be achieved. Similarly, the decrease in the compositions of resins and asphalthenes confirmed the existence of cracking process, at the intermediate stages. Heavier aromatics were also reduced to naphthalenes, as also reported by Ovalles et al. [96,97].

The used of formic acid as hydrogen donor was reported by Liu et al. [99]. They employed 80% Liahoe heavy oil in water and upgraded it with variable concentrations of formic acid (i.e. 0–7%) at 280 °C for a period of 24 h. Results from FTIR indicated the mechanism to involve decarboxylation, in addition to hydrogen attack. Hydrogen donated by formic acid was of high strength and therefore very active. Heavier aromatic rings were rapidly cleaved to lighter compounds. Increasing the amount of formic acid caused a decreased of all heavier compounds, with a net reduction in viscosity of the oil. The viscosity reduction reached 87.02% (i.e. higher than optimal values reported by

Table 1
Heavy oil upgrading behaviors of some hydrogen donors.

Heavy oil grade/source	Hydrogen donor	Aquathermolysis conditions	Activity/ viscosity reduction (%)	Refs.
Liahoe reservoir oil	Toluene	0.1 wt.% toluene, 0.2 wt.% Ni catalyst, 240 °C, 24 h	85	[102]
Asphalthenes and sulfur rich heavy oil from Shengli oilfield	Tetralin	Nickel sulfate catalyst, tetralin, steam injection conditions	More than 70	[38]
Liahoe extra heavy oil	Tetralin	Fe (II) catalyst, water, tetralin, 160–260 °C, 240 h	90	[103]
Super heavy oil from Shengli oilfield	Alkyl ester sulfonate copper	Alkyl ester sulfonate copper act as both hydrogen donor and catalyst, 0.3 wt.% at 240 °C for 24 h. 20% water	90.72	[48]
Liahoe heavy oil	Syngas ($CO + H_2$)	Finely Nickel powdered dispersed catalyst, syngas, 240 °C, 24 h	More than 80%	[104]

Ovalles et al. [95,96] for tetralin), with significant removal of S, N and O derivatives. Similarly, the formation of saturates and lighter aromatics was enhanced to 31% and 41% from less than 20%, respectively. Zhao et al. [100] reported that the reaction mechanism involved pyrolysis when the action of formic acid was promoted with steam injection at moderate temperatures. The combined effect yielded an enhanced viscosity reduction and production of lighter more volatile compounds. Recently, Zhao et al. [101] demonstrated that other hydrogen donor solvents such as methyl formate and dihydroanthracene produced comparable activity with formic acid for the Liahoe heavy oil. Both compounds caused a viscosity reduction from 11 Pa s to 3 Pa s, closer to 2 Pa s achieved for formic acid.

Table 1 summarizes the behaviors of some hydrogen donor/cracking systems during aquathermolysis. According to the various groups [38,48,102,103], the synergic effect between a catalyst material and hydrogen donor mediates the reaction to involve hydrogen transfer with subsequent cleavage and cracking on the catalyst particles. Therefore reactions such as C—C bonds pyrolysis, opening of aromatic rings and subsequent cleavage, rupture of bridge bonds as well as breakage of C—O, C—S and C—N bonds were responsible for viscosity reduction, increased in the concentration of lighter compounds and significant reduction in the amount of heavier derivatives. The used of synthetic gas ($CO + H_2$) as hydrogen donor reportedly yielded comparable hydrogen transfer and viscosity reduction effect like other solvent donors [104].

6. Recent developments

Owing to its industrial relevance, more studies are underway to evaluate the most active, stable and economical catalytic systems for the aquathermolysis reaction. Mode of actions of the reported catalysts are also being evaluated. Recently, Olvera et al. [105] prepared different alloys from mechanical mixing and milling of Mo, W, C and Ni precursors. The X-ray diffraction data identified the presence of nanocrystalline carbides with different nanometer sizes (10–125 nm). The carbides were employed for the upgrading of a heavy oil sample with 1.13 Pa s viscosity, treated with equivalent quantity of sea water at 200 °C. Increasing the milling time favored catalyst activity. All the materials were very active and caused viscosity reduction between 80% and 97% for the 240 h milling period. The post-activity FTIR studies showed the catalysts to significantly decrease the concentrations of resins and asphaltenes, with increase in the amount of saturates and lighter aromatics. Shokrlu and Babadagli [106] reported the improvement of reduction in viscosity with increase in the concentration and sizes of nanoparticles for the oxides of Fe and Cu. It was also dependent on the oxide nature. CuO produced the highest reduction in viscosity under constant conditions. In all cases the activity was also attributed to the degree of interaction between catalyst particles and resins or asphaltenes, reaction temperature and the extent of bond cleavages. In a related approach using nanomaterials, Hendaningrat et al. [107] used nanoparticles of copper, zinc, nickel and iron metals as catalysts. Their study showed that, the nanosize metals are good for the aquathermolysis due to tremendous reduction in viscosity. The mechanism of action involved heat transfer, associated pyrolysis and catalytic bonds fission. Yang [108] showed that a naphthenate nickel catalyst can successfully crack most of the asphaltene derivatives in heavy oil at 300 °C for a period 24 h. Yang et al. [109] developed an ultrasonic-based reactor for vacuum residue upgrading using tetralin as the hydrogen donor. Without tetralin, the viscosity was reduced by 10.98%. However, incorporation of tetralin into the reactor further reduced the viscosity by 39.27%. Although this route produces good viscosity properties, it should be noted that its efficiency is much lower than 80–95% reduction in viscosity reported by other authors cited in this paper, who employed catalytic routes. Wu et al. [110] synthesized a nickel chelate (i.e. aromatic sulfonic nickel) with amphiphilic properties. The catalyst was very active at 200 °C, because it yielded a decrease in viscosity of over 96%. Results from mechanistic studies showed that the combined hydrophobic-hydrophilic characteristics of the catalyst enhanced reactions involving pyrolysis and heteroatoms removal. Evidences of ring opening and closure were similarly observed. Yang et al. [111] developed a new catalyst based on nano-Fe particles of various sizes supported over 10 nm SiO_2 from the interaction of ferric chloride precursor with silica, using conventional $NaBH_4$ reduction in the liquid phase. The catalyst was very active, with only 1.0 wt.% reducing the viscosity of Shengli heavy oil from 184 to less than 45 Pa s. Its reaction mechanism include oxidation inhibition and C—S bonds cleavage in resins and asphaltenes. Liu et al. [45] used Cu^{2+} and Fe^{3+} complexes of toluene sulfonic acid, prepared from reactions with precursor compounds (CuO, Fe_2O_3) in aqueous media under mild conditions, for the aquathermolysis of extra-heavy Shengli oil. Although both catalysts attacked asphaltenes in the oil, their mechanism of action was different. Cu^{2+} complexes causes depolymerization and bridging bond cracking whereas Fe^{3+} complex was more active to heterocyclic ring ruptures and isomerization of the side chains. Therefore, the former catalyst should be more attractive for upgrading asphaltenes-rich heavy oil. Some recent studies [108,112,28,113] proposed that these catalysts could be employed under reservoir conditions to yield good viscosity reduction. However, catalyst materials must be resistance to variation in pressure and temperature.

Table 2 presents an update on further studies conducted after 2010. Most of these studies employed chelates based on transition metals (Ni, Cu, Co) as catalysts. The results generally indicated the viscosity reduction to be dependent on the catalyst nature and/or reaction conditions. A highest activity of 98% viscosity reduction at 300 °C, was reported by Petrukhina and co-workers [114]. The authors employed carboxylates of Ni and Co and promoted the activity with teralin as hydrogen donor. This specific study indicated the combined effect of hydrogen donation and catalyst a better potential option for oilfield evaluation. However, a study by Wu et al. [115] indicated that, 96% reduction in viscosity could be achieved with Ni sulfonic acid at lower temperature of 200 °C even without the addition of a hydrogen donor. According to Li et al. [116], nickel oleate is a better catalyst for the upgrading of Niujuan heavy oil than either nickel sulfate or naphthenate under the operational temperatures of 100–200 °C. With the former catalyst, the optimal viscosity reduction reached 65% whereas 56% and 53% for the other catalysts, respectively. However, the activity is clearly much lower than the activities of 79–98% reported by other authors (Table 2). Xu et al. [117] and Xu and Pu [49] reported the incorporation of ultrasonic/vibrational treatment to yield a good viscosity reduction (86–88%) for the Shengli heavy oil. However, these values are still lower than the 98% obtained when tetralin was employed as hydrogen donor. Shaban et al. [118] showed ionic liquids as potential catalysts, yielding 79% viscosity reduction. However, the 70–90 °C employed as the optimal temperatures are unlikely to fit the operational conditions in oilfield, therefore extensive studies on these types of catalysts are critical. Degradation of resins and asphaltenes is the main role of catalyst, heat and steam during the aquthermolysis as described in Section 2 above. These observations are consistent with the work of Yang [108], who reported >31% degradation of asphaltenes in a given heavy oil at 300 °C, using a nickel naphthenate as catalyst for 24 h.

7. Application in oil fields

The various works presented in the previous subsections clearly demonstrated the incorporation of suitable catalysts or hydrogen

Table 2
Some more recent studies (after 2010) on catalytic aquathermolysis of heavy oils.

Heavy oil grade/source	Catalyst	Aquathermolysis conditions	Activity/viscosity reduction (%)	Refs.
Super heavy oil, Ashal'cha Field, Tastartan	Ni, Co carboxylates + tetralin as hydrogen donor	0.3 wt.% catalyst, 300 °C, 5 h	98	[114]
Extra heavy oil (San56-13-19)	Aromatic sulfonic Ni	200 °C	96	[115]
Niujuan heavy oil	Ni oleate	100–220 °C	65	[116]
Niujuan heavy oil	Ni naphthenate	100–220 °C	53	[116]
Niujuan heavy oil	Ni sulfate	100–220 °C	56	[116]
Asphaltene of Shengli heavy oil origin	Ni naphthenate	300 °C, 0.6 wt.% catalyst, 24 h	31% degradation	[108]
Shengli heavy oil	Commercial grade XAGD-2, Ultrasonic treatment	200 °C, 0.3 wt.% catalyst, 24 h	86	[49]
Shengli heavy oil	Aromatic sulfonic Cu, vibration assisted (3 ms^{-2}, 20 Hz, 90 min)	0.3 g catalyst, 3 MPa, 220 °C, 24 h	88	[117]
GPC heavy oil	Ionic liquid; [BMIM][$FeCl_4$]	70–90 °C, 1.0 wt.% catalyst, 72 h, 3–3.5 MPa	79	[118]

donor compounds, as an active way of viscosity reduction. Because they can actively interact with heavy oil under variable conditions and trigger viscosity reduction up to 90%. A key complication is whether or not the exact laboratory scale conditions adopted could successfully be employed in real oilfield applications [30]. Subject to this observation, some oil field studies were also carefully reviewed. A study by Chen and co-workers [119] reported ~91% decreased in viscosity of an EX35 heavy oil under the laboratory conditions of 200 °C and 6–7 MPa. The composition of light hydrocarbons and derivative species also reached ~15%. For appropriate comparison, field studies were carried out in the Henan oilfield with the same catalyst (i.e. aromatic sulfonic iron, a chelating compound). After steam injection at high temperature and pressure conditions, pH adjustments were carried out using NaOH to homogenize the experimental conditions with the laboratory parameters. Approximately, 998 and 1120 m^3 of steam were introduced into the two (G61012 and G6606) oil wells before subsequent closure for 3 and 14 days, respectively. The respective viscosity reduction of ~80% and 82% observed with these wells were reasonably high, but lower than the 91% observed from the laboratory tests. Interestingly, the wells production also risen by ~189 and 217 t, respectively during the 14 days period. Recently, Zhao et al. [120] conducted s study under closer reservoir conditions (280 °C, 8–10 MPa and 4:1 ratio of oil to water), using a combination of oil soluble catalyst and formic acid as hydrogen donor compound. The reaction was believed to involve the mechanisms reported in Section 2.1 above. Without the donor, the viscosity reduced by ~65%, with further linear reductions when the donor compound was added. Approximately, 69% and 87% viscosity reductions were observed when 1% and 7% of the formic acid were added, respectively. Similarly, the quantity of saturates increased by 7%, whereas resins and asphaltenes decreased by 5–6%. The results indicated that, the incorporation of a hydrogen donor that is stable under field conditions, in addition to the catalyst can significantly enhanced the process.

Xu et al. [121] performed some field investigations for some Shengli oilfield wells (K92N6 and KD192P2) at respective temperatures of 325 and 344 °C and pressures of 14.7 and 15.7 MPa. Similarly, 2203 and 2193 m^3 of steam were injected, respectively. They found respective viscosity reduction of 72% and 80% with increment in oil production by 376 and 694 t, respectively, with evidence of reasonable stability for 14 weeks. The authors also attributed the catalytic activity to comprise of a series of mechanistic steps similar to those explained in Section 2.1 above. Chao and co-workers [48], employed a multi-functional catalyst (alkyl ester sulfonate copper), comprising of both catalytic and hydrogen donor sites for upgrading super heavy oil of Shenli oilfiled origin. Laboratory experiments were first performed at 240 °C and 3 MPa, using 0.3 wt.% of the catalyst for a period of 24 h. The initial viscosity (181,000 mPa s) of the oil decreased by 91% under these conditions. Similarly, the content of light species (i.e. saturates and aromatics) improved by 10% in terms of oil conversion. On the other hand, a field study was conducted for an oil well (i.e. F10223, Xinjiang oilfield) with 73.3% oil saturation. Catalyst was simultaneously introduced into the reservoir with 1200 m^3 of superheated steam, before closing the well for six days. It was found that, the viscosity of the oil decreased by from 85,000 to 129,000 mPa s (i.e. about 85% reduction). The compositions of saturated and aromatic hydrocarbons increased from 31.21% and 20.85% to 49.29% and 24.50%, respectively. Conversely, the amount of resins and asphaltenes reduced from 34.33% and 13.61% to 18.82% and 7.39%, respectively. Their characterization data revealed the evidence of evolution of carbon dioxide and hydrogen sulfide associated with C—O and C—S bonds fission of the heavy molecules. The increased in the yields of saturates and aromatics was similarly attributed to C—C bond cleavages of the side chains and the hydrogenation of the derived olefins.

The various field studies indicated that, certain adjustments of the laboratory conditions are required to achieve a high degree of viscosity reduction under field operations, at usually longer reaction time due to the volume and composition of the heavy oil reservoirs. It could also be established that, most comparative results reported higher viscosity reduction values for the laboratory trials. Therefore, an extensive research is required toward improving the efficiency of the catalytic aquathermolysis process during oilfield applications.

8. Conclusions

There is no doubt, aquathermolysis is a promising technology with great potentials for enhancing the recovery of worldwide abundant heavy oil reserves. The process is associated with a number of interesting advantages over other upgrading technologies. There is no generation of free radicals with potentials to trigger polymerization reactions and subsequent viscosity reversal. Heavy oil mobility retarding compounds such as sulfones and bulky organic acids are not produced. Similarly, the process is economically cheaper than other processes such as *in situ* combustion and gravity drainage by steam (SAGD). However, full realization of these benefits requires an appropriate design of catalysts and selection of operational parameters. Hot water stability should also be emphasized.

Minerals, salts and organic compounds of transition metals were the main catalyst systems initially considered. However, catalyst recovery and reusability difficulties coupled with environmental disposal and implicative cost difficulties may limit their exploitations in the recent times. Solid catalysts such as nano-Keggin heteropoly acids, zirconias and natural zeolites have so far shown excellent viscosity reduction efficiencies due to their hot water tolerance, recovery nature and possession of strong active sites with potentials to break C—O, C—S and C—C bonds in resins and asphaltenes in the heavy oil. However, further studies are still required to identify the most optimal conditions and mechanisms of reaction. Hydrogen donor compounds like formic acid and tetralin work better when incorporated with catalysts. Therefore coupling them with the solid acids may yield better results.

There are recent reports that, alloys of Mo, W, C and Ni, nano oxides of Cu and Fe, Ni-chelates, nano-Fe particles supported over SiO_2 and Cu^{2+} and Fe^{3+} complexes of toluene sulfonic acid are promising candidates for the aquathermolysis reaction. However, optimal catalyst synthesis and operational conditions and the actual reaction mechanisms are still being soughted. Further studies are therefore very important. Catalysts such as hydrated molybdenum oxides and hydrophobic zeolites designed via the fluoride routes or modified with silanes are considerable for the future. Their activities in related reactions have so far been superior, therefore full evaluation for the aquathermolysis reactions is much likely to yield the best results.

Although many authors unanimously agreed to the main role of catalysts and associated reaction mechanisms, irrespective of whether the process was executed under laboratory or oilfield conditions, useful alterations to the laboratory parameters are necessary to achieve optimal performance during field operations. Further investigations are also required with the view of improving catalysts efficiency under field conditions at possibly shorter operational time. Another important issue to be explored is the possibility of catalyst regeneration and reuse.

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