Recent Approaches, Catalysts and Formulations for Enhanced Recovery of Heavy Crude Oils

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Abstract

Crude oil deposits as light/heavy form all over the world. With the continued depletion of the conventional crude and reserves trending heavier, the interest to maximise heavy oil recovery continues to emerge in importance. Ordinarily, the traditional oil recovery stages leave behind a large amount of heavy oil trapped in porous reservoir structure, making the imperative of additional or enhanced oil recovery (EOR) technologies. Besides, the integration of downhole in-situ upgrading along with oil recovery techniques not only improves the efficiency of production but also the quality of the produced oil, avoiding several surface handling costs and processing challenges. In this review, we present an outline of chemical agents underpinning these enabling technologies with a focus on the current approaches, new formulations and future directions.

Keywords

in-situ upgrading, enhanced oil recovery, aquathermolysis, heavy oil, catalyst

1 Introduction

The world is caught up in the ever-increasing need for energy and reliance on fossil sources. In this scenario, the US accounted for 17.34 % of the world's 2015 total primary energy consumption [1], with projections of the continued predominance of petroleum and other liquids over other renewable energy resources. In 2019, petrol and distillate fuel oil's share of the total transportation energy consumption reached a record 84 % [2]. The predominance of proved heavy oil reserves, energy demand, and potential to yield as many hydrocarbons (HCs) as conventional oil resources ignite interest in heavy oil production [3].

Globally, oil reserves are mainly unconventional, in the form of heavy oil, extra-heavy oil, oil sand, tar sands, oil shale or bitumen [4], reaching up to six times the proven reserves of the conventional oil [5]. Basically, the term heavy oil has been variously defined by organisations such as the Alberta Energy Resources Conservation Board (AERCB), American Petroleum Institute (API), Canadian Centre for Energy (CCE), the United Nations Institute for Training and Research (UNITAR)/World Petroleum Congress (WPC), and the US Geological Survey (USGS) based on API gravity

Table 1 Selected definitions of heavy crude oil at 15 °C.

Source	API (°)	Viscosity (mPa.s)	References
CCE	> 10	< 10^5	[6]
AERCB	10 to 19	10^2 to 10^5	[7]
API	< 22.3	> 10	[6]
USGS	< 22	> 10^2	[8]
UNITAR/WPC	10 to 20	10^2 to 10^5	[9]

(which is specific gravity related) and viscosity, as displayed in Table 1. The UNITAR definition has been the most widely used over the decades. Even though sufficient for many purposes, this definition will not be complete without the mention of the high content of asphaltenes, waxes, carbon residue and an excessive amount of metals (V, Ni, Cu, Fe), and non-metals (N, and usually > 2 % S) in the heavy crude oil.

Various methods have been developed for the recovery and upgrading of such unconventional feedstocks [10]. The traditional primary recovery (which is based on the reservoir pressure) and the secondary (water or gas flooding) process (Fig. 1) can recover only 25–50 % of the original oil in place (OOIP) [11, 12]. A tertiary process called
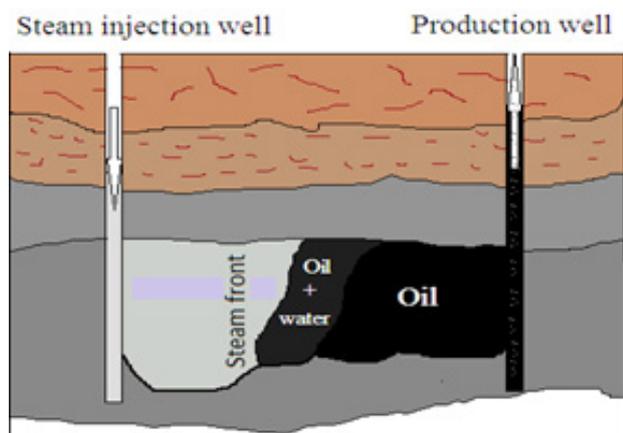
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Fig. 1 Schematic diagram showing steam flooding

the enhanced oil recovery (EOR) is necessary due to poor quality and production efficiency [13].

The EOR techniques (and their global usage) can be thermal (10 %), chemical (67 %), gaseous (10 %), and miscellaneous (3 %) [14]. In the chemical EOR, chemical agents are applied to improve sweep efficiency without any influence on the chemical properties of the oil, while in the thermal upgrading methods, catalysts have the potential to not only assist recovery but the overall quality of the oil for use. To overcome refining, logistical and cost challenges, interest has been geared towards combining heavy crude oil recovery with upgrading, and this has led to the emergence of new chemical formulations [15]. In this review, we undertake to present an update on the approaches to the exploitation of catalysts and chemical additives in chemical and thermal EOR and in-situ heavy oil upgrading.

2 Chemical enhanced recovery methods

Chemical enhanced oil recovery (CEOR) can improve recoveries from thin or deep oil reserves injection, especially where thermal methods cannot be applied. Based on the use of a single chemical agent, a mono-chemical CEOR may be alkaline (A), surfactant (S), polymer (P), solvent, CO_2-based method, but a combination of two or more versions of these methods (AS, ASP etc.) have been commercially more successful. One important feature of all CEOR methods is that increase in oil is caused only via physical mechanism, necessitating the need for costlier handling and refining in order to produce lighter fractions.

2.1 Alkaline flooding

Alkaline flooding (A) is a relatively simple, cheaper, and more readily understood of all EOR processes. Lye/

NaOH and/or sodium salts (Na_2CO_3, $NaBO_2$, and sodium orthosilicate), injected into the reservoir, react with naphthenic acids to form a natural surfactant which drastically reduces the interfacial tension (IFT) at the oil-water interface. The efficiency of the process depends on concentration, alkali type, and whether it was used singly or with other substances. Polyphosphate, NH_4OH, and Na_2CO_3 are less efficient than NaOH, whereas $Ca(OH)_2$ and $Mg(OH)_2$ do not significantly lower IFT [16]. Naphthenic acids are the major components of the total acid content of crude oil. Although they are popular corrodents in oil refineries, the water-soluble, low molecular weight-naphthenic acids (C8-C12) can readily form industrially-desirable sodium naphthenate as shown in chemical Scheme 1.

2.2 Surfactant flooding

Surfactant composes of lipophobic site to which a lipophilic site is attached. It may be anionic, cationic, nonionic or zwitterionic, depending upon the charge of its polar group. It is water-soluble if containing < C12 hydrocarbon (HC) chains attached to the lipophilic site. The anionic ones account for more than 70 % of the surfactant market and can be used mostly with the cationic ones as wettability agents [17]. They work by generating form or emulsion in water which reduces surface tension. However, at neutral pH these reservoirs tend to be negatively charged, favouring the adsorption of anionic surfactants. Variants with large hydrophobes, low retention, and compatibility with specific crude and conditions are therefore desirable [18]. A list of selected surfactants used in CEOR is given in Table 2.

A prominent disadvantage of surfactant flooding (S) is that it is capital intensive, requires laborious operation test cycles [24] and uses mostly environmentally unfriendly surfactants [25]. These reasons caused a decline in surfactant injection from nearly 10 % (in the 1970s and the 80s) to 0.5 % in the 90s [26], and renewed interest in environmentally benign EOR chemicals [27].

2.3 Polymer flooding

Polymer flooding (P) is the most widely applied EOR for more than five decades. The first successful application on heavy-oil was the Canadian Pelikan Lake reservoir [28].
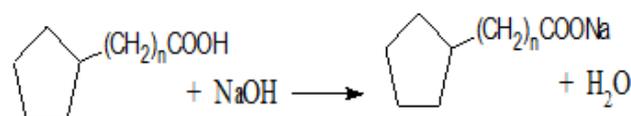

Scheme 1 Esterification of crude oil-based naphthenic acids to useful naphthenates

Table 2 Selected surfactant groups used in the oil recovery fields.

Surfactant family	Description	Advantage	Disadvantage	References
1. Alkyl aryl sulphonates	A C_9-C_{30} alkyl benzene sulphonate.	1. Stability and ability to be tailored based on reservoir conditions. 2. Availability of raw materials.	1. Unstable at high salinity. 2. Non-biodegradable. 3. Only the unconventional types (such as those derived from alpha-olefin) can recover highly waxy heavy oil.	[19, 20]
2. Sodium alkyl sulphate (SDS)	Anionic surfactants with formula $ROSO3Na$, where R = hydrocarbon chain such as dodecyl, octyl or lauryl	1. One of the most commonly manufactured surfactant. 2. Synergy with hydrophobic modified silica for increased temperature tolerance.	1. Toxic and non-biodegradable. 2. Insoluble in water at high temperature.	[21]
3. Alkyl-olefin sulphonates (AOS)	$R-CH=CH(CH_2)nSO_3Na$, where R = C_{10} to C_{20}, usually C_{14}-C_{20} alkene, alkane or substituted alkane.	1. One of the most commonly manufactured surfactant. 2. Used as foaming agent. 3. Stability at steam temperatures.		
4. Linear alkyl benzene (LAB) sulphonates	Organic compounds with the formula PhC_nH_{2n+1}, where n = 10 to 16.		1. Perform better with crudes having C_7 to C_{10} 2. Ecotoxicity	
5. Alkyl propoxy sulphates	Usually in the form of $R(PO)OSO3Na$, where PO = propylene oxide and R is an etheryl moiety with > C_{12}.	1. Show good performance. 2. Have large hydrophobes. 3. Suitable for tight carbonate reservoirs Up to 40 % additional recovery.	1. Commercial product not adequately available. 2. Not suitable for high temperature application	[22]
6. Alpha olefin sulphates	$ROSO_3Na$, where R is an olefinic chain within the range of C_{14}-C_{16}.	1. Superior over many surfactants including LAB sulphonates. 2. Industrial products are available. 3. Readily biodegradable.	Not suitable for high-temperature application	[23]
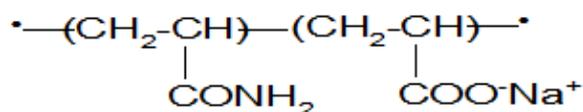
Scheme 2 Structural formula of traditional Xanthan

Basically, it involves the improvement of water injection profile, and reducing viscous fingering and water permeability relative to oil [29]. The traditional Xanthan (Scheme 2) is not as popular as the more soluble and cheaper, partially hydrolysed polyacrylamide (HPAM) (Scheme 3) [30]. Even though the HPAM is less tolerant to salinity, susceptible
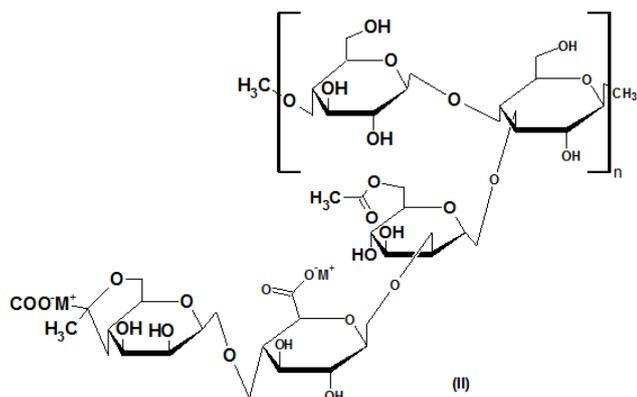
Scheme 3 Structural formula of partially hydrolysed polyacrylamide

to alkaline hydrolysis and degradation at > 70 °C, unlike Xanthan, it does not require a stabiliser against microbial degradation [31].

Polymer flooding produces lower additional oil, and due to cost and mechanical consideration of injection pressure, they are of little benefit for heavy oils with higher viscosities. The modification of the hydrophobicity of HPAM is among potential solutions to these problems [32]. A hydrophobically-modified terpolymer for example, can reduce viscosity at high salinity and temperature conditions, with the ability to dry up within 2 h [33].

2.4 Combined methods
Combined chemical flooding methods gives the beneficial effect of two or more classes of chemicals in CEOR. Whereas the technical feasibility of alkaline-surfactant flooding (AS) is still being assessed in laboratories and results are promising [34], surfactant-polymer flooding (SP) has demonstrated outstanding performance at low temperatures (70 to 120 °C) [35]. However, one of the disadvantages of SP flooding is rapid sediment accumulation, forming multi-modal pores in conglomerate reservoirs [36]. Alkaline-surfactant-polymer flooding (ASP) will reduce the adsorption of expensive surfactants and

expand the sweep efficiency [37] but as the concentration of Ca^{2+} and Mg^{2+} exceeds 10ths of mg/L, scaling takes place as shown in chemical Eq. (1). This problem can be mitigated by prior water-treatment, or by adopting surfactant-polymer flooding (SP), which in addition can prevent strong emulsification, and alkali corrosion [38]. For all surfactant-based methods however, the scarcity of highly-performing industrial surfactants, unsound pilot tests, and high technical risk has been a limiting factor [39].

$$Na_2CO_3 + Ca^{2+} \rightarrow 2Na^+ + CaCO_3 \qquad (1)$$

In the organic alkali-surfactant-polymer flooding (OASP), an organic alkali (OA) is applied to enhance sweep efficiency. A coreflooding study showed that a combination of ethanolamine as OA and SLPS can achieve > 20 % increase in recovery [40], which is as a result of increased oil-in-water emulsification [41]. Recovery depends upon the properties of the oil, fluids, and formation interfaces such as wettability, contact angle, capillary forces, viscosity, and interfacial tension (IFT) [42]. Basically, interactions between reservoir minerals and surfactant/polymer may occur depending on the geology of the reservoir rocks, and this can affect interfacial properties such as surface charge and wettability. For certain additives, these interactions are not fully understood [43]. Consequently, the criteria for the application of a particular EOR is formation-dependent. On the whole, due to the high chemical consumption of the fractured carbonates at majority of the world's largest reservoirs [44] the application of AP and ASP is limited to sandstone reservoirs [45].

2.5 Synergy with new formulations
An array of chemical agents such as urea, terpolymers, binary mixtures, and monomers, has been examined for possible synergy with EOR chemicals [46–48]. Notably, the synergy between nano-sized crosslinked polymeric particles with low salinity water can lead to ultra-low interfacial tensions and huge (> 62 %) oil recovery [49]. In a study, the combination of poly(vinyl alcohol)-rhamonolipid and NaOH−rhamonolipid−PVA in saline EOR medium was found to significantly reduce the surface tension and IFT [50]. Similarly, a polyacrylates/amorphous carbon thin film composite recovered 19.2 % of residual oil saturation [51]. Some binary surfactant mixtures (such as polyoxyethylene ether carboxylate blended with a quaternary ammonium chloride) [52] as well as non-traditional CEOR chemical agents (such as nanopyroxenes) can also cooperatively and significantly improve oil recovery [53].

Experimental results showed that a binary mixture of cocamidopropyl hydroxysultaine and alcohol propoxy sulphate can outperform mixtures of zwitterionic, and anionic surfactants, with good oil displacement (63–75 %) and surfactant retention (0.08 mg/g) [54].

Certain ethoxylated nonionic surfactants (Scheme 4) have been proposed for limiting or even overcoming the retention of anionic sulphate or sulphonate surfactants, in carbonate and clayey reservoirs [55], where m is the number of propylene oxide units (0 to 20), n is the number of ethylene oxide units usually greater than 20. Moreover, nonionic amines (compound Scheme 5; "A" = is alkylene, R = either H or alkyl, and x can be zero) with good chemical stability, thermal stability, low adsorption, high salinity tolerance, and a wide pH range, have been described [56]. Lastly, an efficient ASP injection of an extended sulphate surfactant of alkoxyated, alkyl propoxylated, or their combination and a co-surfactant (alkyl benzene sulphonate, internal olefin sulphonate, or their combination) has been reported [57]. Much as in the ASP, silica nanoparticles having a hydrophobic chain can reduce adsorption and IFT, and recover up to 15.74 % oil [58, 59].
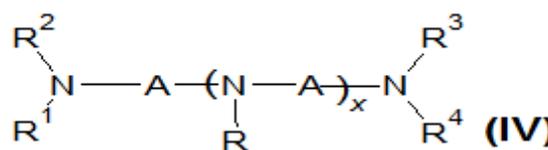
3 Thermal enhanced recovery methods
3.1 Overview of the methods
Over the past few decades, thermal methods accounted for nearly 70 % of the world's EOR [60, 61]. Five thermal EORs are widely recognised, namely, the cyclic steam stimulation (CSS), steam-assisted gradient drainage (SAGD), steam and hot water flooding, steam/solvent hybrid system which all involve fluid injection, and in-situ combustion (ISC) or fire flooding. A schematic display of EOR methods is shown in Fig. 2. Newer injection approaches include the high pressure air injection (HPAI) (for deep, high pressure light oil reservoirs) and the use of an in-situ generated syngas (H_2 and CO). The steam-assisted gradient drainage (SAGD) injects steam into the
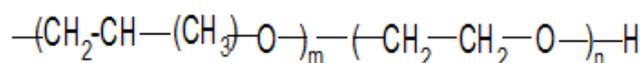
Scheme 4 Desorbing agents for enhanced oil recovery in carbonate or clayey reservoirs

Scheme 5 Potent nonionic amines for exploitation in ASP. Substituents A and R, and subscript x as described in the text
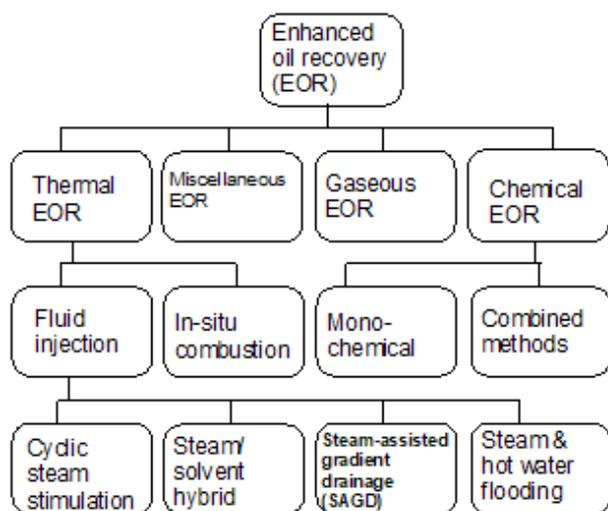
Fig. 2 Chemical and thermal enhanced recovery methods

heavy oil or bitumen reservoir via two horizontal wells, except in the vapour extraction (VAPEX) variant, which injects vaporized solvents. Cyclic steam stimulation (CSS) is also commonly used steam injection for the recovery of high viscosity oils. A successful steam EOR needs at least 20 % porosity of the reservoir rock, at least 100 mD permeability, 40 % heavy oil saturation, at least 800 bbl per acre-ft of oil content, reservoir depth of < 3000 feet, and thickness of at least 30 ft [62].

The ISC method uses vertical producer wells except in the toe-to-heal air injection (THAI) variant which consists of a combination of direct or staggered vertical injection (into which air is injected at 600 to 700 °C) and horizontal producer wells [63]. Today, due to huge cost limitation and requirement of special operation conditions, only a few ISC operate. At present, a catalytic version of classical THAI known as the toe-to-heal air injection CAtalytic upgrading PRocess In-situ (THAI CAPRI) has been successfully performed [64].

3.2 In-situ catalytic upgrading
Heavy oil upgrading refers to the fractionation or chemical treatment of heavy oils that produces permanent changes in the physicochemical properties of these materials [9]. Considerable research interest has been geared into the use of catalysts and additives to upgrade heavy oil en route thermal recovery by the conventional SAGD, VAPEX, THAI, and CSS technologies. The THAI CAPRI was introduced in 1998 to avoid surface upgrading and mitigate the environmental impact of the heavy oil components. Primarily, the decision to upgrade depends partly on the physical properties of the oil and the cost of

upgrading [65]. Because the main essence of upgrading is to increase sulphur-free, nitrogen-free and metal-free distillates, as well as H/C ratio which typically stands at 1.5 [66], typical surface-based approaches for heavy oil upgrading involve carbon rejection (such as coking, thermal cracking, visbreaking), hydrogen addition (with slurry, fixed-bed, moving-bed, ebullated reactor), or their combination [5, 67]. The traditional thermal conversion of heavy oil involves either pyrolysis, cracking (which may be catalytic or thermal-only), or hydrocracking to yield valuable distillates components [68]. The key reactions in upgrading have been detailed previously [6, 69].

In subsurface upgrading (SSU) the reservoir is made to act as a refinery, to liberate lighter products. Revolutionary, non-catalytic SSUs such as the Shell's in-situ upgrading process (IUP) and the NSolv, widely referred to as game-changers, have been successfully pilot-tested in the last decade. Each of these technologies has the capacity to produce above 100,000 bbls of lighter oil. The NSolv is based on the downhole injection of alkanes into SAGD well while in the Shell's IUP downhole electric heaters initiate the conversion of heavy oils in subsurface [9]. Even though these methods outside the scope of this paper, being non-catalytic and metal-free, is a lofty beauty to reflect.

In-situ upgrading differs markedly from chemical EOR in that it causes structural changes in the crude, leading to the production of higher quality and recovery factor of the OOIP, and leaving behind coke in the subsurface. In addition, the reservoir mimics a gigantic refining vessel and the production may be carbon-neutral if upgrading is coupled with nuclear or renewable energy generation systems [6]. However, despite these advantages over CEOR, the in-situ upgrading technology is energy-demanding, relatively poorly controllable, has less mixing efficiency, poses more environmental challenge and has limitations on the use of metals [9].

3.3 Supports in surface upgrading
The most suitable catalysts for oil upgrading are those containing active sites that can effectively break the C–C, C–S, C–O, C-N, and other related bonds in resins and asphaltenes [70, 71]. Ultrafine particles of unsupported metals such as base (Mo, W, Ni, V, Co, Cr, Zn etc.) or noble (Pb, Rh, Pt, etc.) are good cracking catalysts due to their dispersibility and flow within the heavy oil, and interaction with large molecules. For example, submicronic NiWMo particles can enhance the hydrocracking of heavy oil and inhibit coke production and desulphurisation [72]. However, supports are crucial for

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effective hydrodesulpharisation (HDS), hydrodemetallisation (HDM), hydrodenitrogenation (HDN), and hydroconversion. In fact, ultradispersed, unsupported NiO (< 50 nm), MoO_3 (< 100 nm), and Fe_2O_3 (50 nm), can improve the viscosity, inhibit coking, and produce better upgraded oil (21° API, 108 mPa.s) than thermal cracking (24°, 53.5 mPa.s) when operated initially at 450 °C, 50 bar initial H_2 pressure for 50 min, then at 425 °C for 60 min [73]. This moderate level of upgrade is attributed to the lack of support.

Supported metal catalysts especially the transition metal oxides and sulphides have the capacity to suppress coking and yield high surface conversion of heavy oil and extraheavy oil (37–49 %) [74, 75]. Supports can contribute to the activity or selectivity of the catalysts. Silica or alumina supported Ni and Mo are usually (but not always) good upgrading catalysts [76]. For example, MgO-supported Ni and Cu can convert 90 % of mixed acid hydrocarbon solution, but SiO_2 and Al_2O_3 produced no conversion [77]. The catalysts may perform better in a mix with heated sand than the heated catalyst alone [78] and perform remarkably at lower steam-oil ratio [79], suitable catalyst concentration, acidity, and pore geometry [80]. Certain supported catalysts such as $NiMo/Al_2O_3$, are highly efficient for the upgrading of pretreated oil [81] while others such as supported haematite, can perform better when applied under supercritical water conditions [82] entailing challenges for large-scale operation.

Zeolites usually are popular active, sulphur-resistant hydrogenation and surface upgrading catalysts but they are susceptible to active site poisoning and coke deposition especially with feedstocks containing residues [83]. Different zeolite catalysts can give a different distribution of upgrade products [84]. In a preliminary study to upgrade Omani heavy oil under microwave heating at 250 °C and autogenous pressure, combinations of 500 µm, 5 wt% NiCoMo on zeolite supports (NH_4-Zeolite-Y, H-zeolite-Y, NH_4-Mordenite, NH_4-Zeolite-Y) converted decalin, a model light oil, to several lighter ring-opening products [85]. Commercial ternary and multi-element supported catalysts (such as MoCoP/Al_2O_3 or $MoWNiCoP/Al_2O_3$) have also been outstanding in upgrading heavy oil to useful distillates [86].

To avoid sulphur poisoning noble metals should be used in environments containing below 10 mgS/g [23]. Generally, Pd stands out among several noble metals for efficiency in hydrocracking (HC) and hydrodesulpharisation (HDS) [87]. Noble metals have also been successful when loaded on natural supports such as clay and metakaolin [75]. In fact, traces of Rh-Pd on high porous saponite containing exchangeable Co exhibit a significant enhancement of the catalytic activity over Rh alone [88].

3.4 Hydrogen donors
Practically, the traditional hydrogen addition and carbon rejection have limitations when used singly in heavy oil surface upgrading [89, 90]. Even though successful upgrading can be performed under an inert atmosphere (He or N_2), hydrogen donors are crucial to provide the needed H/C ratio and avoid coking. In actual fact, heavy crude oil reactivity and hydrogen availability (not catalyst activity), were found to be the primary factors limiting oil upgrading [78]. Basically, the hydrogenation of heavy cuts can be assisted by hydrogen donors such as cyclohexane, sodium borohydride, water, tetralin, ammonia, methanol, ethanol, citric acid, formic acid, hydrazine, methane, pentane, naphtha, and hydrogen [91, 92]. A laboratory-scale in-situ THAI-CAPRI study over alumina catalysts shows a higher potential of methane, ethane, and hydrogen to provide the highest H/C ratio and better upgrading [93]. In fact, the partial surface upgrading of bitumen for pipeline transportation with CH_4 over the zeolite-supported catalyst at moderate conditions, without diluent addition, has been established [94]. Among fused ring hydrogen donors such as naphthalene, decalin, tetralin, 1–methyl naphthalene, tetralin showed superiority for use in upgrading with < 4 % coke formation [95]. Methane and $Fe_3(CO)_{12}$ assisted HDS and heavy oil conversion efficiencies are equivalent, and are much lower than with H_2 [96]. This observation supports a prior evidence which showed no improvement in oil recovery under hydrogen partial pressures below 5.2 MPa (and 343.3 °C) and oil recoveries are higher from experiments carried out under higher H_2 partial pressures than under N_2 atmosphere [97]. Certain in-situ combustion can generate CO, from which H_2 can be produced via water-gas shift, but with implication of coking [98].

3.5 Modification of heterogeneous catalysts
The performance of catalysts can be dramatically increased by making key considerations regarding size, catalyst acidity and composition [99]. Carbon-loaded iron and Ni-Mo/Al_2O_3 materials having larger mesopore volume tend to give higher oil conversion and a very high hydrodemetallisation (HDM) and hydrodesulpharisation (HDS) [100]. Similarly, nanoparticles of NiO, SiO_2, and Fe_3O_4 can prevent the aggregation of asphaltenes in heptane solutions and increase the adsorption of large molecules [101]. A study with NiO shows that only certain nano range may be more catalytically effective for upgrading [102].

The surface modification of β-zeolite catalyst with triphenyl silane has the potential to reduce coke formation and generate 55.7 % C_7 to C_{13} cuts (petrol) from heavy oil in 2 h [103]. The significant reduction in coke formation

confirmed the stability of the catalyst. In aquathermolysis, the modification of the surface of heamatite nanoparticles with oleic acid was found to significantly reduce the viscosity and upgrade the quality of heavy crude oil [104]. Similarly, TiO_2 has served as a good modifying agent for alumina supporting CoMo, for HDM and HDS [105]. In addition, temperature tolerant ionic liquid-modified catalysts such as imidazolium tetracholoferrate BMIM [$FeCl_4$] when added to heavy crude (at 0.25, 0.5 and 1 % catalyst oil ratio) can achieve remarkable reduction in viscosity (52.2 %), and HDS (20 %) at 70 to 90 °C[106].

Molybdenum-doped akaganeite (*ca* 30 nm *β*-FeOOH) can form nanorods, which in presence of tetralin exhibit remarkable enhancement in the viscosity reduction rate of extra-heavy crude oil (viscosity 750,000 mPa.s at 50 °C) to 72.7 % [107]. A commonly used catalyst in heavy oil upgrading is the SO_4^{2-}-modified ZrO_2-based nanoparticle catalyst, but having fewer acid sites and poor hydrothermal stability limited its application [108]. However, modification of the zirconia catalysts by doping or compositing with oxides has proved beneficial. Kondoh et al. [109] found that a fifty-fifty TiO_2–ZrO_2 mixed catalyst possesses high BET surface area and acidity compared to either ZrO_2 or TiO_2, which can improve heavy oil upgrading reactions.

3.6 Homogeneous catalysts
The efficacy of homogeneous catalysts to improve oil upgrading. Heavy oil bound sulphur has been removed successfully as sulphide by continuous in-situ process exploiting NaOH (10–20 %) at 380 to 450 °C [110], with the regeneration of the alkali by stripping with in-situ metals. Instead of regeneration, the catalyst can be conveniently removed. A homogenous ammonium molybdate catalyst used in the upgrading was removed by calcining the residue followed by the addition of NH_4OH and ammonium carbonate and leaching at 60–80 °C for 1–5 h [111].

The acceleration of heavy oil recovery in presence the case of Fe($CH_3COCHCOCH_3$)$_3$ as a homogeneous catalyst is established. A coreflooding study has shown that the addition of 5wt% tetralin can increase oil recovery by 15 % while premixing tetralin-catalyst solution with sand mix yielded 20 % higher recovery [112]. Similarly, heavy crude oil can effectively be transformed into lighter oil by a liquid Ni-Mo catalyst from (NH_4)$_6Mo_7O_{24}$.$4H_2O$ and $NiSO_4$.$6H_2O$ [113].

3.7 Solvent effects and viscosity reduction
In surface upgrading, the viscosity of the heavy oil may rise due to the absence of hydrogen donors or the presence of oil-insoluble hydrogen donors [91, 114]. Fortunately,

the synergistic effect between the catalyst and ultrasonication (a physical process) can reduce up to 86 % of the original viscosity of heavy oil [115]. The synergy between carbon nano-catalysts and microwave heating great viscosity reduction ratio (over 96 %), short reaction time (less than 1 h), and low required temperature (about 150 °C) [116]. Nano-nickel catalysts have demonstrated higher ability than iron, Co nanoparticles, and iron(III) oxide to increase the efficiency of microwave heating for viscosity reduction [117, 118]. Under microwave electric heating, in-situ heavy oil recoveries with nano-Ni nanoparticles can rapidly reach high recovery factors (87 %) [119].

The in-situ upgrading of heavy oil has been studied using different solvents such as supercritical methanol (sc-MeOH) and supercritical water (sc-H_2O) due to their great diffusivity, mass transfer, and the ability to dissolve organic components and gases [119] and a source of hydrogen. In fact, the successful upgrading of bitumen, a semi-solid, in presence of sc-H_2O, to stable lighter components in the presence of a ZrO_2-Al_2O_3-FeO_x catalyst has been reported [120]. The sc-H_2O is believed to be a source of hydrogen and oxygen which can assist the upgrading process.

3.8 Downsizing effects
Nanocatalysts and other nanomaterials have shown superior applicability in in-situ heavy oil upgrading [121, 122] because they eliminate internal and external mass transfer limitations, and contribute to the formation of high gas fractions and high conversion [123]. Ultradispersed metallic nickel nanoparticles can promote hydrogenation and 50 % conversion of asphaltenes and a 70 % reduction in resins, with improved aromatics and saturates fractions [124]. Oxide nano-catalysts such as NiO, SiO_2, ZnO, Fe_3O_4, Co_3O_4 are currently gaining interest [125–128]. Zirconia based nano-catalysts are particularly appealing due to their high acidity and stability in sub- and supercritical water [127] while ZnO has an unparalleled activity for supercritical water upgrading [128]. Silica-supported iron oxide nano-catalyst is effective in the supercritical water-based hydrogenation of the unsaturated fragments in vacuum residue cracking [129]. Moreover, fumed silica nanoparticles functionalised with 1 wt% nickel and palladium oxides have shown potentials for use as catalysts in the continuous steam flooding process [130]. The optimisation and integration of oil recovery with in-situ upgrading could be achieved through a Dense Hot Fluid Injection (DHFI) method in which nano-catalyst is injected into the reservoir [131]. Lastly, even though the applicability of supercritical water-oxygen fluid in

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heavy oil conversion has been widely demonstrated, with nanoparticles, the possibility of its use at large scale operation is slim [132]. Similarly, despite the numerous advantages, the use of nanocatalysts in large-scale upgrading application remains a challenge [133].

3.9 Aquathermolysis

Aquathermolysis involves metal complex-assisted degradation of large organic molecules in the presence of water as hydrogen donor. When catalyst is applied in the thermal cracking of the heavy oils, it is referred to as catalytic. It is called thermal if the thermal cracking is performed thermal-only, devoid of catalyst. Laboratory and field catalytic aquathermolysis tests have been conducted on various heavy crude oils, especially from China Liaohe fields [66, 134]. The applicable catalysts are divided into oil-soluble catalysts and water-soluble [135]. An array of transition metal-based oil-soluble catalysts has been reported in the literature [61, 136]. Instrumental evidence has shown that, during the aquathermolysis, iron(III) tris(acetylacetonate) can form in-situ magnetic nanoparticles (MNPs) which can exhibit synergy with organic solvents to give high conversion of resins into lighter components [137]. With Ni nanoparticles, the recovery of the steam-stimulation technique increased by 22 %, while the viscosity of the original oil reduced by 40 % [138].

By the aquathermolysis, resins and asphaltenes can be converted to lighter components on organic acid-derived complexes. For instance, the saturates, aromatics, resins and asphaltenes (SARA) composition of a sand-free Tazhong heavy oil 42.31 %, 19.70 %, 13.70 %, 24.47 % was transformed at 180 °C for 24 h by only 0.5 % of this complex to 45.20 %, 22.74 %, 1.78 % and 19.28 %, respectively, indicating a depolymerisation of resin and asphaltenes to aromatics and saturated hydrocarbons [139]. The viscosity of the Tazhong heavy oil reduced to 920 mPa.s from 4,080 mPa.s. Some successful aquathermolysis catalysts include Fe(III) complexes of citrate, lactate,

and tartrate ligands [140], nano-Keggin heteropoly acid salt, $K_3PMo_{12}O_{40}$ [141] and $[(CH_3(CH_2)_3CH(CH_2CH_3)COO]_2Co$ [142]. Initially, the term "aquathermolysis" was applied to systems consisting of transitional metal ion salts, transitional metal compounds, and some solid superacids which usually form homogeneous phase systems. Nowadays, the term has been extended to heterogeneous systems such as nano-Ni catalyst [143] and oleic acid-modified $NiFe_2O_4$ nanocatalyst [144], which have been successfully used in upgrading.

4 Conlusion, future directions and challenges

Various chemical formulations for exploitation in CEOR and thermal EOR have been reviewed. Despite attempts to push the current limits of chemical usage for successful operation, only a few surfactant formulations can be said to work under high salinity (> 200 g/L) and poorly permeable (5 mD) reservoirs [145], hence the thirst for new formulations with integrity under contemporary reservoir conditions. On the other hand, there is a constant need to further study the mechanisms of alkali flooding and mitigate saponification [125, 146].

In spite of the proposition of supercritical fluids, future breakthroughs are necessary for their application in field operations. Similarly, works involving nano-materials require serious collaborations to actualize the potential of applying nanotechnology to oil recovery projects to actualize the potential of applying nanotechnology to oil recovery projects, notwithstanding the existing one between academics and oil development companies [147]. Generally, the future of EOR depends on advancements in cost-effective technologies and chemicals.

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