

A Review of Water-Soluble Liquid Catalysts Application for *In-Situ* Enhanced Heavy Oil Recovery

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Abstract

Liquid Catalysts (LCs) have been used in surface upgrading of heavy oil for a long time, but their *in-situ* application in heavy oil reservoirs has been considered only recently. There are four main types of LCs for *in-situ* applications: water-soluble, oil-soluble, mineral, and dispersed. This paper reviews various types of water-soluble liquid catalysts applied for *in-situ* upgrading of heavy oil. These LCs have shown great potential in terms of reducing viscosity and *in-situ* upgradation of heavy oil, thus facilitating recovery and transport of heavy oil in experimental studies and in the field pilot implementation. These studies show that the water-soluble LCs have great potential in becoming an economically and environmentally competitive alternative enhanced oil recovery technique to the established conventional heavy oil recovery EOR techniques, such as thermal and solvent injection. However, further research is needed in studying and developing suitable LCs in terms of their behaviour under the heavy oil reservoir pressure and temperature conditions, and to develop efficient water-soluble LCs with desirable properties.

Keywords

Water-Soluble Liquid Catalyst, Enhanced Heavy Oil Recovery, *In-Situ* Heavy Oil Upgrading

1. Introduction

The forecast of increasing demand for crude oil in the long term has been based

on the rising world population and living standards, resulting in increasing world-wide transportation (land, air and sea) and petrochemicals requirements. The latest OPEC demand projection forecasts that oil demand will reach 123 million barrels per day (mb/d) by the year 2050, from the current level of 103.7 mb/d, with no peak in oil demand on the horizon [1]. This means that the oil demand will continue to rise in the foreseeable future. This requires a large investment in developing the known reserves of both conventional and unconventional oil. As heavy oil and bitumen constitute 70 percent of total crude oil reserves in the world, research and development in heavy oil is important to supplement the conventional oil resources. However, heavy oils have high density and viscosity, which makes it difficult to produce and transport. Therefore, further research and development of *in-situ* upgrading techniques of heavy oil becomes necessary.

Among the existing tertiary extraction methods, thermal oil recovery methods are the most commonly used methods for achieving reduced viscosity and high recovery factors. However, these methods are now facing economic and environmental challenges due to high energy consumption. While the chemical and miscible processes suffer from a lack of mobility control, viscous fingering, and high interfacial tension in field applications. *In-situ* catalytic upgrading of heavy oil is emerging as a viable alternative to these conventional EOR methods. It is therefore anticipated that Liquid Catalysts (LCs), due to their low energy requirement and environmental suitability, will emerge as a new EOR technology.

Liquid catalysts are either water-soluble or oil-soluble homogeneous catalysts (in which the catalysts and reactants are in the same phase, e.g., liquid-liquid), which lowers the activation energy without being consumed in the process. Examples of water-soluble liquid catalysts are transition-metal salts (nickel, copper, zinc acetates), ionic liquids, and amphiphilic metal complexes. *In-situ* upgrading of heavy oil involves the injection of liquid catalysts along with a carrier fluid, such as water or steam, into the underground oil formation for simultaneous upgrading and recovery. The objective of this paper is to review the status of the current application and experimental research on the various types of water-soluble liquid catalysts used for the *in-situ* upgrading of heavy oil.

2. Crude Oil Physical Properties and Composition

2.1. Definition

Heavy crude oil has been defined as liquid petroleum having an API gravity less than 20 or a viscosity higher than 100 cp under reservoir conditions of pressure and temperature. Heavy oil and bitumen are complex mixtures of about 10^5 - 10^6 different hydrocarbons.

2.2. Physical Properties of Crude Oils

The properties of heavy and extra-heavy oil are characterized by its high molecular weight, resulting in high viscosity, high C/H ratios and the presence of S, N, and O heteroatoms and heavy metals. Specific gravity and viscosity are used to

classify crude oil into light, heavy and extra-heavy oil [2]. Crude oil classification based on physical properties is shown in **Table 1**.

Table 1. Physical properties of various crude oils [2].

	API Gravity (° API)	Viscosity (cP)	Density (Kg/m ³)	Sulfur (wt.%)	Nitrogen (wt.%)	Metals (Ni + Va, ppm)	Asphaltenes (wt.%)	Resins (wt.%)
Light oil	>31	<10	<870	0.02 - 0.2	0.0 - 0.01	<10	0 to <2	0.05 - 3
Medium oil	22 - 31	<100	<934	0.05 - 4.0	0.02 - 0.5	10 - 200	<0.1 - 12	3 - 22
Heavy Oil	10 - 22	>100	934 - 1000	0.1 - 5.0	0.2 - 0.8	50 - 500	11 - 25	14 - 39
Extra-heavy oil (bitumen)	<10	>10,000	>1000	0.8 - 6.0	0.1 - 1.3	200 - 600	15 - 40	—

2.3. Crude Oil Composition

The main building blocks of the hydrocarbon are: 1) an alkyl, or paraffin chain, 2) the saturated ring (naphthene ring), and 3) the aromatic ring. Crude oil also contains compounds of sulfur, nitrogen, oxygen, and metals.

Paraffin or aliphatic HC are composed of straight or branched chains of carbon atoms with attached hydrogen atoms, having a formula C_nH_{2n+2} . Paraffin hydrocarbons are also called alkanes. An alkane with one hydrogen removed (so that the carbon atom involved can bond to another carbon) is called an alkyl group, and it is given the symbol R. For example, the methyl group, generally R, represents any organic group.

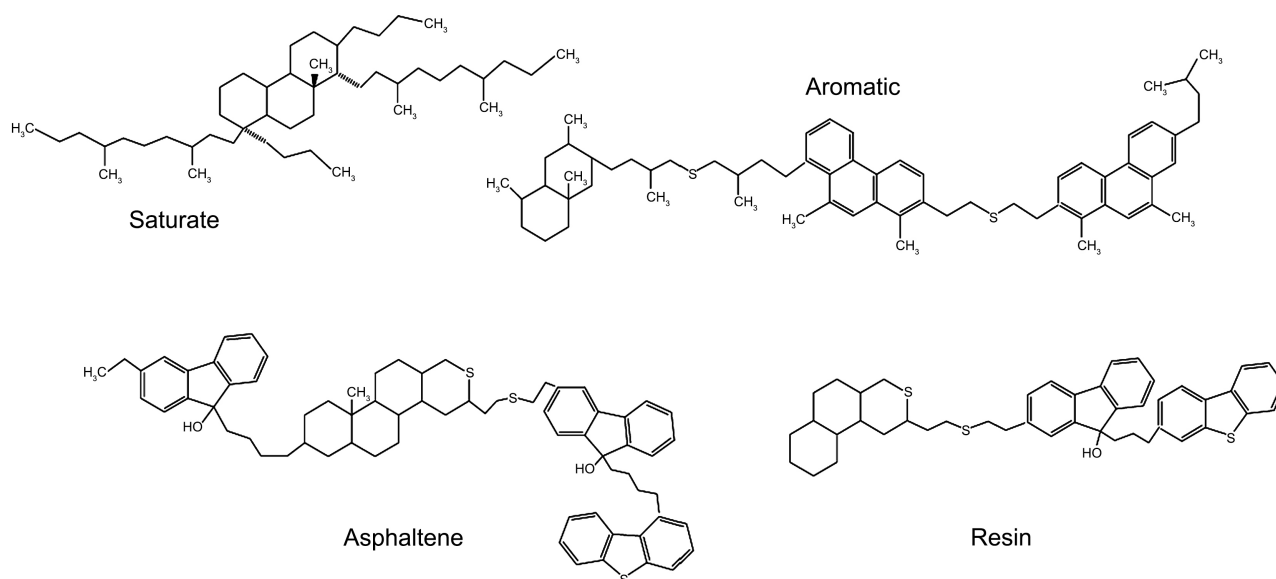


Figure 1. Molecular structures of SARA components of Heavy Oil [3].

Naphthenes are similar to paraffins except that the chain is joined at the ends to form five -or six-membered rings, e.g., cyclopentane and cyclohexane. Naph-

thenes are also called cycloalkanes. In aromatics, carbon atoms are connected by double bonds. Benzene, C_6H_6 , is the simplest aromatic component. Aromatics have high octane numbers but can cause health and environmental problems. Benzene is a documented carcinogen. Asphaltenes are considered the highest molecular weight component of crude oil and are defined as that portion of the crude oil that is soluble in toluene and insoluble in n-heptane. Collectively, these are referred to as Saturates, Aromatic, Resins and Asphaltenes (SARA), and molecular structures are shown in **Figure 1**.

Two groups of metal compounds occur in crude oil. The first are light metals that are cations in the brine that accompanies crude oil production; these are mainly sodium, with lesser amounts of calcium and magnesium. The second group of metals includes vanadium, nickel, cobalt, and iron, which occur in the higher boiling point fractions of crude oils. Two types of oxygen compounds that occur in crude petroleum are acidic and non-acidic. Most of the oxygen compounds are organic acids. Naphthenic acids occur in appreciable amounts and are important feedstocks to produce surface-active agents (surfactants). Non-acidic oxygen compounds include Esters, Amides, and Ketones.

2.4. Heteroatoms in Crude Oils

Sulfur compounds in crude oils are sulfides (inorganic) or organosulfur compounds. Two typical model compounds for organosulfur molecular types in heavy oils are thiophene and tetrahydrothiophene [2]. Sulfur and nitrogen compounds tend to concentrate in the higher boiling fractions of crude oil [4].

Compounds of oxygen present in crude oil are classified as acidic compounds and non-acidic compounds. Acidic oxygen compounds are: Aliphatic Carboxylic acid, Branched Aliphatic Carboxylic acid, Monocyclic Naphthenic Acids, Bicyclic Naphthenic Acids, Polynuclear Naphthenic Acids, Aromatic Acids, Binuclear Aromatic Acids, Polynuclear Aromatic Acids, Phenols and Cresols. Non-acidic oxygen compounds include Esters, Amides, Ketones, Benzofurans, and Dibenzofurans [4].

Although nitrogen compounds occur in relatively small amounts in crude oil, they tend to poison noble metal and nickel catalysts in the refining process [4]. Basic nitrogen compounds present in crude oil are Pyridine, Quinoline, Isoquinoline and Acridine, while non-basic nitrogen compounds are Pyrrole, Indole, Carbazole and Porphyrin [5].

3. Surface Treatment of Heavy Oil

Hydrotreatment (HDT) is a refinery process in which crude oils are upgraded using an appropriate type of reactor depending on crude oil density. Hydrotreating includes many processes such as removal of heteroatoms S, N and O by hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), in which cleavage of C-S, C-N, and C-O bonds occurs concurrently. In hydrodemetalization (HDM), the cleavage of metal bonds, such as Ni, V, Fe, etc., occurs. Other

important reactions in heavy oil upgrading are hydrogenation (hydrogen transfer) and ring opening (opening of aromatic rings).

The catalysts in surface upgrading of heavy oil have been classified as supported or unsupported catalysts. Supported catalysts have an active component dispersed on a porous support, as used in fixed-bed and ebullated-bed reactors. Whereas unsupported catalysts include water-soluble, oil-soluble, and dispersed catalysts used in slurry-bed reactors. The unsupported catalysts are well dispersed in heavy oil and directly catalyze the hydrogenation of macromolecules in heavy oil [6].

The predominant catalysts used in refinery HDT upgrading of heavy oils are oxides of the Group VIb metals, mostly molybdenum (Mo) and Tungsten (W), with promoters as support from Group VIII, such as Nickel (Ni), Cobalt, and Alumina (Al_2O_3) (Bello *et al.*). Pore diameter and surface area of these catalysts are important properties because heavy oil contains large molecules of asphaltenes and metal compounds. During the treatment, these molecules diffuse into catalyst pores, and their metal atoms are removed from the ring structure. Thus, the catalyst's pore size controls the diffusion process while a high surface area provides high dispersion of active sites [7].

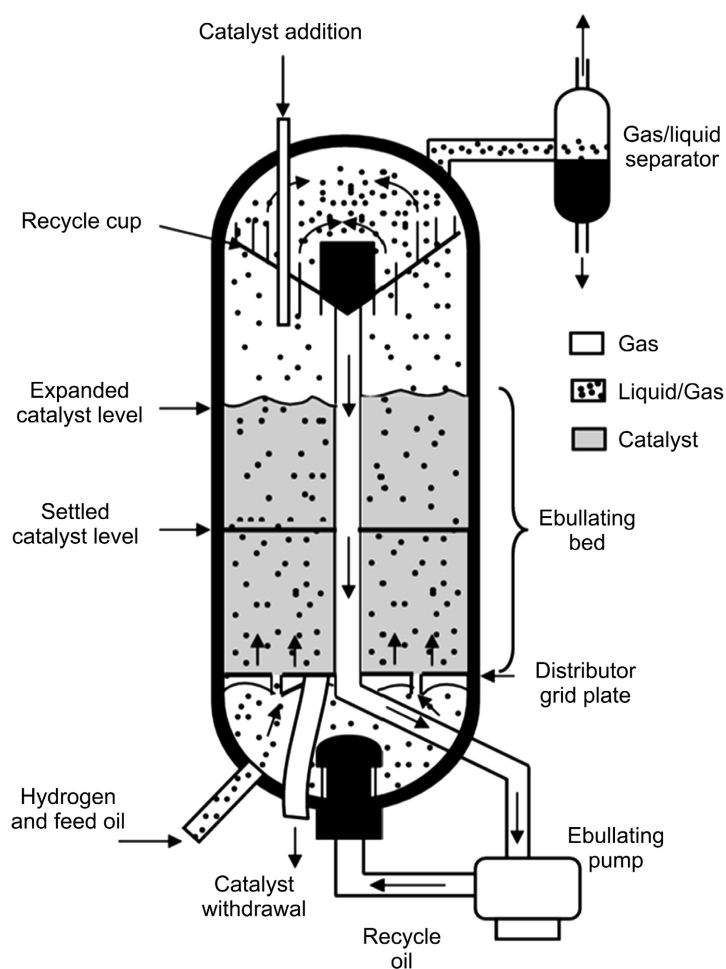


Figure 2. Schematic representation of the H-Oil reactor [7].

Hydrodesulfurization (HDS) is used in refineries for achieving deep desulfurization of heavy oils with low API gravity. In refinery operation, when there is no constraint on H₂ supply, such as in continuous flow reactors, NiMo and NiW catalysts are preferred for achieving deep HDS. However, tungsten is expensive, and high pressure and temperature requirements make the process energy-intensive and less environmentally sustainable [5].

An ebullating bed heavy oil residue treatment process is shown in **Figure 2** as a demonstration of surface treatment of heavy oil. This process uses hydrogen gas, oil feed, and a solid catalyst. It is a stirred reactor type operation using a fluidized catalyst. In this process, the catalyst is separated from the top and then recirculated from the bottom and mixed with new oil feed.

4. In-Situ Techniques for Recovery of Heavy Oils

Due to the high viscosity of heavy oils, only 10% - 20% of the oil originally in place, OOIP, can be recovered by primary and secondary recovery processes; therefore, extensive efforts are devoted to the third stage of recovery, which is called tertiary or enhanced oil recovery. The primary recovery mechanisms involve utilizing the natural energy of the reservoir by pressure depletion, solution gas drive, fluid and rock expansion, and gravity drainage. In heavy oil recovery, the terms used for primary oil recovery are foamy oil flow, when oil is produced from solution-gas-drive reservoirs, and gas evolves due to a decline in reservoir pressure, and Cold Heavy Oil Production with Sand (CHOPS).

The secondary oil recovery process involves oil production by using external sources of energy, such as water injection to drive the oil towards production wells, or pressure maintenance in the reservoir by water or immiscible gas injection. Due to high viscosity contrast between heavy oil and water, lower secondary recovery is achieved in unconventional heavy oil reservoirs as compared to waterflooding in conventional oil reservoirs.

The third stage of tertiary recovery includes enhanced oil recovery techniques such as thermal oil recovery, chemical injections, and miscible processes. The thermal oil recovery processes commonly employed in the field aim to lower oil viscosity, such as Cyclic Steam Stimulation (CSS), Steam Assisted Gravity Drainage (SAGD) or in situ combustion Toe-to-Heel Air Injection (THAI) [8].

Chemical enhanced oil recovery techniques comprise injecting polymers, surfactants, alkalis, alkaline-surfactant-polymers (ASP), and ionic liquids. The main aims of these methods are viscosity reduction, IFT reduction, and mobility control. The use of polymers has various limitations, such as polymer degradation, polymer loss in the reservoir pores and the presence of polymers with the produced heavy oil [9].

Oil upgrading involves thermal or thermocatalytic conversion of high molecular weight components of the crude oil to light distillates via cleavage of C-C and C-S bonds, and improvement of the H/C ratio of the distillate products and removal of heteroatoms to an acceptable level. Thermal enhanced oil recovery tech-

niques include Cyclic Steam Stimulation (CSS), which is usually applied as the primary production process and gives a low recovery of up to 30%. Attempts are made to improve the effectiveness of CSS by incorporating chemical additives such as solvents, surfactants, and gas along with the injected steam. However, extensive water and energy consumption in CSS increases the economic and environmental costs. In Toe-to-Heel Air injection (THAI), along with catalytic upgrading (THAI-CAPRI), a catalytic layer is fixed on the horizontal production well. As the heated oil from the vertical *in situ* combustion well moves towards the production well, thermal catalytic cracking occurs, which improves the heavy oil quality. The concept is to create an in-reservoir refinery that distills and mobilizes light fractions and converts heavy components to light components [11] as shown in **Figure 3** below.

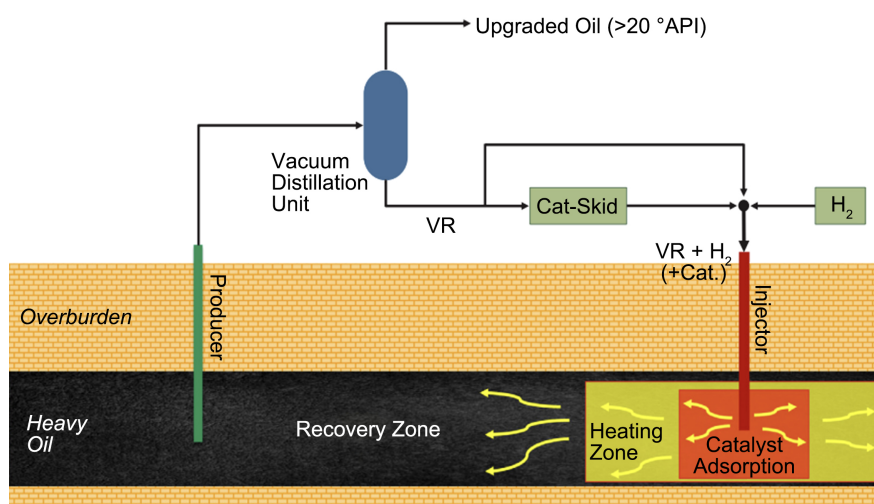
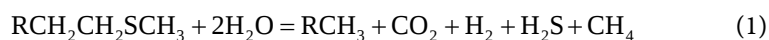


Figure 3. Schematic of *in-situ* upgrading technology [12].

5. Chemical Reactions in Catalytic Aquathermolysis

Hyne *et al.* [13] found that the injected stream not only physically reduces the viscosity of crude oil but also changes the chemical compositions of crude oil as a result of specific chemical reactions between the rock, water, and crude oil. This process is named hydrothermal cracking or “aquathermolysis”. A common chemical reaction with the fission of the C-S bond, which results in the reduction of heavy oil viscosity and hydrogen gas generation, is as follows:



Production of both hydrogen and carbon dioxide in the aquathermolysis process is beneficial for the upgrading of oil and viscosity reduction. Hydrogen helps in hydrocracking, and carbon dioxide improves oil recovery by reducing the heavy oil viscosity and adjusting the pH value of the reaction. A catalyst may enhance the reaction rates of the hydrothermal cracking reactions. Catalysts control the reaction rate without changing the selectivity and physical properties of the catalyst itself. The catalysts reduce the activation energy by providing adsorption sites

and reaction active sites, thus facilitating the reaction. Catalyst action is shown in **Figure 4** below can be generally described as follows:

- 1) The reactant molecules from the crude oil containing sulfur, such as thiophene, diffuse onto the catalyst's surface/pores.
- 2) The reactant forms a weak interaction with the metal atoms of the catalysts (Ni, Mo, Co, W etc.,).
- 3) The metal surface changes electron density around the C-S bond, which weakens the bond and reduces the activation energy.
- 4) The hydrogen atom migrates towards the surface of the catalysts and reacts with the polar component of heavy oil.
- 5) The C-S bond breaks with low activation energy.
- 6) Reactants leave the catalyst's surface, and the catalyst is regenerated.

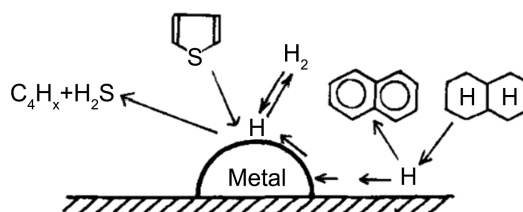


Figure 4. Reaction model of hydrosulfurization [14].

Various types of catalysts used in the upgrading of heavy oil are mineral catalysts, water-soluble catalysts, oil-soluble catalysts, solid acid catalysts, dispersed catalysts, and nano-catalysts [15]. Maity *et al.* [16] concluded that viscosity reduction achieved during catalytic aquathermolysis is in the order of mineral < water-soluble < oil-soluble < dispersed catalyst. The reactions occurring in chemical upgrading of heavy oil are homogeneous cracking of C-C bonds, ring growth, hydrogen transfer, aromatic hydrogenation, or dehydrogenation of cycloalkane, ring opening, and the removal of heteroatoms (S, N, and O) and heavy metals (Ni, V, Fe, etc).

Other reactions are thermal and catalytic cracking of C-C, C-S, and C-N bonds, while the C-S bond has the lowest bond dissociation energy, as shown in **Table 2**, and therefore easily breaks at low temperatures, leading to viscosity reduction. During C-S bond cleavage, reactive intermediates are formed, which may lead to the formation of higher molecular weight molecules, thereby reversing the viscosity reduction in the heavy oil. Adequate hydrogen supply is required to stabilize these intermediates; therefore, different hydrogen donors such as formic acid and tetralin are used in the aquathermolysis process. Use of hydrogen donors such as tetralin in the aquathermolysis process increases hydrogen availability and suppresses coke formation. The produced hydrogen improves the H/C ratio of the upgraded oil and reduces the heavy oil viscosity [16].

Hydrogenation is the process of adding hydrogen to unsaturated organic compounds like alkenes in the presence of a catalyst, in which the double bond is converted to a single bond. Hydrogenation is widely used in refining to improve fuel

quality, hydrogenate olefins and aromatics and remove impurities like V, Ni, sulfur, nitrogen, and oxygen from crude oil fractions.

Table 2. Bond dissociation energies [16].

Bond	Kcal/mol
C-S	66
C-N	69 - 75
Ar-CH ₂ CH ₂ -Ar	71
S-H	82
C-C	83 - 85
C-O	85.5
N-H	93
C-H	96 - 99
H-H	103
O-H	110 - 111
Ar-H	111
C=S	132
C=C	146 - 151
C=N	147
C=O	191

6. Catalysts Used for *In-Situ* Heavy Oil Recovery

Catalyst reduces the activation energy by providing adsorption sites and reaction active sites to yield a product. Catalysts used for in situ heavy oil recovery have been broadly classified as homogeneous catalysts and heterogeneous catalysts. In homogeneous catalysis, both the reactants and catalysts are in the same state of matter, while in heterogeneous catalysis, the reactants and catalysts come from different states of matter. Solid acid catalysts, mineral catalysts, and nanoparticle-dispersed catalysts are placed in the heterogeneous catalysts category.

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 [17]. Hyne *et al.* [13] found that the natural minerals present in the reservoir formation aid in viscosity reduction in addition to the reduction by thermal process. However, such a reduction in viscosity was reversible due to the presence of heteroatoms (S, N, and O). Later researchers found that using suitable catalysts, non-reversible viscosity reduction could be achieved. In their paper, Muraza *et al.* [17] have presented a review of catalyst properties for the aquathermolysis process and the action of hydrogen donors in this process. In the aquathermolysis process,

catalysts are injected with steam to break down the heavy molecules in oil into smaller molecules. This process is called “catalytic aquathermolysis”. Use of appropriate catalysts prevents polymerization reactions, which can result in reversal of viscosity reduction in the aquathermolysis process, such as steam injection.

Desirable properties of an effective liquid catalyst include having good acidity, thermal stability, providing non-reversible (C-C, C-N, C-O, C-S) bond fission, and possessing excellent water stability. Catalyst stability enables it to be utilized for an extended period without activity decay and structural destruction.

When a water-soluble catalyst is used for enhanced oil recovery, the catalytic interaction takes place at the oil-water interface [18]. Water-soluble catalysts include transition metal salts, heteropoly acids and ionic liquids. Oil-soluble catalysts are miscible with oil and can interact easily with the heavy molecules present in the crude oil. Transition metal-based sulfonates (Fe, Co, Ni, Cu, Mo, etc.) and transition metal-based carboxylates are examples of oil-soluble catalysts. In dispersed catalysts, catalytic interaction takes place at the surfaces of the dispersed particles. Soluble catalysts have high activity because they form infinitesimally minute active metal sites *in situ* with their high surface-area-to-volume ratios. However, these catalysts are only effective within a certain dosage range [6]. Water-soluble liquid catalysts for heavy oil aquathermolysis encompass several chemical classes, each with distinct advantages and limitations as shown in Table 3. The most extensively studied systems include:

Transition-metal acetates: Hydrophilic metal acetates such as nickel acetate ($\text{Ni}(\text{CH}_3\text{COO})_2$), copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), and zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) have been widely investigated due to their water solubility, commercial availability, and demonstrated activity in hydrogenation and desulfurization reactions. Comparative studies show that nickel acetate typically outperforms zinc acetate under identical conditions (300°C, 24 h), achieving viscosity reductions of approximately 58% versus 48%, respectively. Bimetallic nickel-copper acetate mixtures have also been explored, with reported viscosity reductions of ~58% and evidence of *in-situ* decomposition to active metal nanoparticles [19] [20].

Ionic liquids: The ionic liquids (ILs) are liquids that are simply composed of anions and cations at room temperature. Ionic liquids (ILs) are typically liquid organic salts at room temperature and are generated from an organic cation and an organic or inorganic anion. Additionally, ILs are extremely conductive, polar, and heat-capable (thermally stable), which may make them resistant to harsh reservoir conditions. The ILs are water-soluble and are used as catalysts in the hydrothermal cracking reactions. Ionic liquids are considered low-temperature viscosity reducers and can be effective at the low temperatures found in shallow heavy oil reservoirs. Acidic ionic liquids (ILs) represent a newer class of water-soluble catalysts with activity at lower temperatures. The lower operating temperature for ILs is attractive for shallow or moderate-depth reservoirs, but the high cost of ionic liquids remains a significant barrier to field applications [21].

After ILs are injected into a formation, the polar components of heavy oil (as-

phaltenes and resins) can diffuse into ILs, resulting in a reduction of these polar components, inhibiting precipitation of asphaltenes and lowering the viscosity of crude oil [22]. However, a significant obstacle to field usage is the high expense of synthesizing these ILs [9].

Fan *et al.* [22] found that the use of nickel naphthenate with the ILs has a synergistic effect on the upgrading and viscosity reduction of heavy oil. When the heavy oil in Xinjiang was treated with 5% [BMIB] [AlCl₄] IL, the asphaltene content of heavy oil reduced, and the viscosity reduced by 60% at the low temperature range of 65°C - 85°C.

The ILs have been used as catalysts to catalyze the hydrothermal cracking reactions. Tunnish *et al.*, [23] conducted a screening study of various ILs for their EOR suitability. Laboratory results indicated that the main mechanisms behind IL-enhanced recovery include increased viscous force, interfacial tension (IFT) reduction, aromatic interactions, and wettability alteration. The screening highlighted acetate-based ILs, especially 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]), as strong candidates owing to their advantageous solubility and miscibility properties.

Amphiphilic metal complexes: Amphiphilic structures possess both hydrophilic (water-attracting) and hydrophobic (water-repelling) properties. This property enables these catalysts to function effectively at the oil-water interface, and their surface-active nature promotes catalytic activity [19]. Aluminum dodecylbenzenesulfonate (ABSA) and cobalt dodecylbenzenesulfonate are amphiphilic catalysts designed to improve oil-water interfacial contact. ABSA demonstrated >80% viscosity reduction at 250°C in stirred HPHT reactors, with high thermal stability (up to 400°C reported for cobalt analogs). These catalysts address the challenge of poor distribution in oil-saturated reservoir rocks by enhancing emulsification and catalyst-oil contact.

Zirconium-containing liquid catalysts: Zr-based water-soluble catalysts tested at 380°C and 10.8 MPa with hydrogen achieved dramatic viscosity reductions (kinematic viscosity from 1444 to 24 cSt at 37.5°C) and residue conversion of ~43%. These catalysts form sulfides and oxides with Lewis and Brønsted acidity during reaction, contributing to cracking activity [24].

Table 3. Various types of water-soluble catalysts are used for upgrading heavy oil, along with their advantages and disadvantages.

Water-Soluble Liquid Catalysts		
Type of Liquid Catalyst	Advantages	Disadvantages
Transition metal salts: Ruthenium (Re), iron (Fe ²⁺), Cobalt (Co ²⁺), Nickel (Ni ²⁺), Zinc (Zn ²⁺), Molybdenum (Mo ²⁺), Copper (Cu ²⁺), Aluminum (Al ³⁺), Tin, Mn ²⁺ , Sc ³⁺ . Zr-based water-soluble catalysts	Improvement in reservoir wettability. Reduce the activation energy. Inexpensive and easily available. Easily available	Greatly influenced by factors such as reservoir water, minerals, and adsorption on rock, which reduces efficiency. Cannot sufficiently contact the reservoir oil.

Continued

Transition-metal acetates:

Nickel acetate ($\text{Ni}(\text{CH}_3\text{COO})_2$), copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), and zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$)

Other water-soluble salts:

Ni(II) sulfate, Ru(III) chloride, Ruthenium Ru(II), Rhodium Rh(III), Iridium Ir(III), Osmium Os(III), Al(III) sulfate, Vanadyl VO(II) salts, Tungsten W(VI), Pt(IV)

Ionic Liquids:

[BMIM][FeCl₄], [EMIM][OAc]

Ionic liquids have high thermal stability, incombustibility, nonvolatility and high ionic conductivity. ILs are very effective for the desulfurization of heavy oil.

Heteropoly acids:

$\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$

Heteropoly acids have strong acidity and can be effectively used in aquathermolysis. It can be regenerated and reused. Effective with extra-heavy oils. The nano-Keggin structure of heteropoly acids permits interaction with heavy compounds of the oil.

Amphiphilic metal complexes:

Aluminum dodecylbenzenesulfonate (ABSA) and cobalt dodecylbenzenesulfonate are amphiphilic catalysts.

Possesses both hydrophilic and hydrophobic properties, which allow the catalyst to function effectively at the oil-water interface.

7. Experimental Studies

It has been concluded through various laboratory and field studies that incorporation of suitable catalysts and hydrogen donors actively interacts with heavy oil under variable conditions and triggers viscosity reduction as evidenced by an increase in contents of saturates and aromatics and a decrease in resins and asphaltene contents, thus resulting in upgrading of heavy crude oil [19]. The catalysts that could break C-C, C-S, C-O, and related bonds in resins and asphaltene and consequently enhance the concentration of saturates and aromatic hydrocarbons are the most effective [10].

Alarbah *et al.* [10] synthesized different water-soluble metallic liquid catalysts in the laboratory and studied the impact on heavy oil viscosity, density, molecular weight, IFT, and SARA compositions and their impact on the oil recovery factor in sand pack experiments using the catalysts in *in-situ* upgrading techniques at low temperatures. They synthesized an acidic Ni-Mo-based liquid catalyst (LC), a

self-synthesized Co-Mo liquid catalyst, and an organobimetallic LC as a heavy oil upgrading agent. SARA (Saturates, Aromatics, Resins, Asphaltenes) analysis allows useful characterization of different components of the crude oil and provides insights into the oil upgradation process and catalytic efficiency.

Ni-Mo bi-metallic acid catalyst was synthesized by mixing 5 g of Ammonium Molybdate and 10 g of Nickel sulfate hexahydrate in 50 ml of distilled water at a temperature of 50 °C. Then 1 g of sulfuric acid was added to dissolve the metals in the LC solution. Afterwards, 0.82 g of sodium hydroxide was added to adjust the solution acidity. The solution was allowed to settle for 24 hours at 25 °C, then the precipitation was removed by filtration paper to avoid formation damage. A similar procedure was followed for preparing the other Co-Mo bimetallic liquid catalyst.

The third Organometallic liquid catalyst, synthesized by Alarbah *et al.* [10], was prepared by dissolving 1230 mg Ammonium molybdate tetrahydrate together with 396 mg nickel (II) sulfate hexahydrate at room temperature in distilled dichloromethane. Then the solution was added to a 10 ml distilled dichloromethane solution containing 0.26 ml 1, 3-diethylbenzene and 160 mg NaOH and refluxed for 25 hours at 50 °C. The resultant solution turned yellow-green, which was purified by washing with diethyl ether. Drying and vacuuming resulted in the required catalyst powder. The powder was dissolved in 50 ml of distilled water to obtain the required solution for testing in the sand pack experiments.

For the acidic Ni-Mo catalysts, oil viscosity reduction of 18.5% was obtained. Density improved to 17.291 API, indicating slight upgrading of the heavy oil, which was further confirmed by SARA analysis, which showed that saturate and aromatic hydrocarbons increased by 3.3 wt.% and 2.05 wt.% respectively, while the resins and asphaltenes decreased by 2.73 wt.% and 1.34 wt.% after the reaction. It was suggested that the liquid catalysts can perform the hydrogenation function and cracking activity. It was observed that IFT reduced from 24.8 mN/m to 17.11 mN/m for the catalyst-treated brine and oil system, which can result in increased mobility and improved heavy oil recovery. Effects of LC slug size, initiation time, and fluid temperature on oil recovery were compared with the baseline regular water flooding. It was observed that all slug sizes of LCs recovered more oil than that of brine alone, and the total recovery factor improved significantly. The effect of LC injection timing showed that when the LC slug was injected at the beginning of the flooding process, the displacement efficiency was better than when injecting only brine. The effect of increasing the temperature of the LC has directly improved the heavy oil recovery. The flooding experiments demonstrated that acidic Ni-Mo-based LC may boost oil recovery at low reservoir energy conditions up to 60.50% of OOIP.

For the Co-Mo liquid catalyst [25] to assess its impact on improved heavy oil recovery, a total of eleven flooding tests were performed with Devon heavy oil samples. A numerical simulation model of a laboratory experiment was built to quantify the main process controlling parameters that affect LC flooding, history

matching of the lab results for predicting the behaviour of a specific LC EOR approach and perform a sensitivity study to optimize oil production.

For the acidic Co-Mo catalysts, oil viscosity reduction of 16.25% from the initial level was obtained. Density improved to 16.63 °API, indicating slight upgrading of the heavy oil, which was further confirmed by SARA analysis, showing that saturate and aromatic hydrocarbons increased by 0.31 wt.% and 0.19 wt.% respectively, while the resins and asphaltenes decreased by 0.31 wt.% and 0.54 wt.% respectively after the reaction. It was observed that IFT reduced from 24.8 mN/m to 18.78 mN/m for the catalyst-treated brine and oil system.

The impact of different Co-Mo LC slug sizes on oil recovery factor was evaluated, and 0.5 PV was concluded to be the optimum slug size. When injected 1 PV of slug size, recovered 6.92% additional oil recovery over the 26.83% OOIP recovery from simple waterflooding. The effect of increasing the temperature of the LC has directly improved the heavy oil recovery, with the highest recovery of 58.06% obtained at 50°C.

In their third series of experimental studies, Alarbah *et al.* [10] used self-synthesized Organobimetallic Catalysts OLC towards the enhanced oil recovery, *in-situ* upgrading of heavy oil and contaminants removal. The OLC was prepared using 1, 3-diethynylbenzene, Ammonium Molybdate Tetrahydrate and Nickel (II) sulfate hexahydrate. The heavy oil viscosity reduction of 16% was obtained after 24 hours of treatment with OLC. API gravity increased from 14.84 to 16.98. The oil recovery showed that 26.83% of the oil was recovered after brine flooding without OLC. An additional 34.08% of the oil was recovered when 0.5 PV OLC was injected at room temperature, while an additional 20.36% after 0.5 PV OLC at 50°C.

Heavy oil quality improvement data for the three catalysts are summarized in **Table 4**. Since the LCs used in Alarbah *et al.* [10] investigations were metal-based, they have the advantage of carrying temperature for longer, as compared to others, which helps to reduce viscosity. Metal-based LCs also have less adsorption on the rock surface, hence less loss of LCs.

Schacht-Hernandez *et al.* [24] conducted experimental studies by using liquid catalysts containing Cu, Fe, Ni and Zr for upgrading *in-situ* heavy oil in a bench-scale batch-stirred reactor operated at 380°C and 10.8 MPa in the presence of high-purity hydrogen. Water-soluble catalysts containing transition metals (e.g., Fe, Ru, Mo, Ni, Cu, Zn, Mn, Co, W) are mostly used because of availability, low cost, ease of preparation, low environmental impact, and safety. They observed a reduction in oil viscosity and an increase in oil API gravity for all four liquid catalysts used in the experiment. However, Zr displayed the best performance, and the LC containing Cu exhibited the poorest upgradation behaviour. The catalysts containing Zr or Ni led to the 54% and 35% sulfur reduction, respectively. The authors also noted that the denitrogenation capacity of the catalysts displaced the following decreasing order: Cat-Zr > Cat-Ni > Cat-Cu > Cat-Fe. The comparative performance of the four catalysts used in their study is shown in **Table 5**.

Table 4. Experimental results of heavy oil recovery and upgrading using various acidic liquid catalysts [10].

Liquid Catalysts	Viscosity Reduction	Density Improvement (° API)	IFT (mN/m) Improvement	Heavy Oil Composition- SARA Changes (Saturates and Aromatics) Before-After (wt.%)	Heavy Oil Composition- SARA Changes (Resins and Asphaltenes) Before-After (wt.%)	Oil Recovery % of OOIP at 50 °C
Acidic Ni-Mo	18.5%	Increased from 14.84 to 17.291	24.8 to 17.11	Saturates (24.40 - 27.70) Aromatics (26.00 - 28.05)	Resins (23.40 - 20.67) Asphaltenes (19.80 - 18.46)	60.50%
Acidic Co-Mo	16.25%	Increased from 14.84 to 16.63	24.8 to 18.78	Saturates (24.40 - 24.71) Aromatic (26.00 - 26.19)	Resins (23.40 - 23.09) Asphaltenes (19.80 - 19.26)	58.06%
Orgao-bimeta-llic OLC	16.0%	Increased from 14.84 to 16.98	24.8 to 18.22	Saturates (24.40 - 28.31) Aromatic (26.00 - 26.36)	Resins (23.40 - 21.52) Asphaltenes (19.80 - 18.01)	71.87%

Table 5. Experimental results of heavy oil recovery and upgrading using various liquid catalysts [24].

Liquid Catalyst Containing	Viscosity Reduction (%)	Density Improvement (° API)	Sulfur Reduction (%)	Heavy Oil Composition- SARA Changes Before-After (wt.%)	Heavy Oil Composition- SARA Changes Before-After (wt.%)
Fe	97.4	Increased from 12.6 to 18.0	25.5	Saturates (13.2 - 25.40) Aromatics (25.6 - 36.6)	Resins (24.40 - 15.3) Asphaltenes (36.7 - 22.7)
Cu	97.02	Increased from 12.6 to 16.5	27.45	Saturates (13.2 - 27.1) Aromatics (25.6 - 45.2)	Resins (24.40 - 13.1) Asphaltenes (36.7 - 18.6)
Ni	97.65	Increased from 12.6 to 19.6	35.3	Saturates (13.2 - 26) Aromatics (25.6 - 49.8)	Resins (24.40 - 13.13) Asphaltenes (36.7 - 11.0)
Zr	98.34	Increased from 12.6 to 21	45.1	Saturates (13.2 - 19.1) Aromatics (25.6 - 55.2)	Resins (24.40 - 16) Asphaltenes (36.7 - 9.3)

Nares *et al.* [26] experimentally studied the Gulf of Mexico heavy oil upgrading using transition metals. First thermal hydrocracking of the heavy oil was conducted in a batch reactor as a base case for comparison with cracking in the presence of catalysts. Upgrading of the heavy oil was conducted in a batch reactor with hydrogen (99.99%) at 10.8 MPa and 673 K. The oil was homogenized at 1000 rpm for 4 hours. Then, the hydrocracking of the heavy oil with two supported catalysts, a commercial catalyst MoCoP/Al₂O₃ and an experimental NiMoCoWP/Al₂O₃, under the same pressure and temperature conditions. Again, hydrocracking was conducted without supported catalysts under the same pressure and temperature conditions.

Table 6. Experimental results of heavy oil upgrading using various acidic liquid catalysts [25].

Liquid Catalysts Containing	Viscosity Reduction (%)	Density Improvement (* API)	Sulfur Reduction (%)	Heavy Oil Composition-SARA Changes Before-After (wt.%)	Heavy Oil Composition-SARA Changes Before-After (wt.%)
Commercial/ MoCoP/Al ₂ O ₃	8.17% @ 327.4 K	Increased from 12.5 to 21.2	69.4	Saturates (18.0 - 40.2) Aromatics (22.0 - 37.5)	Polar (34.0 - 15.1) (Resins + Asphaltenes)
Experimental NiMoCoWP/ Al ₂ O ₃	98.3% @ 327.4K	Increased from 12.5 to 23.5	67.6	Saturates (18.0 - 41.0) Aromatics (22.0 - 38.5)	Polar (34.0 - 14.1) (Resins + Asphaltenes)
MoO ₂ (acac) ₂	97.7% @1000 ppm wt. conc	Increased from 12.6 to 23.0 @ 1000 ppm wt. conc	46.0 @ 1000 ppm wt. conc	No data	No data
Fe(acac) ₃	98.0% @ 750 ppm wt. conc	Increased from 12.6 to 26.0 @ 750 ppm wt. conc	38.8 @ 750 ppm wt. conc	No data	No data
MoO ₂ (acac) ₂ - Fe(acac) ₃	97.9% @ 750 - 750 ppm wt. conc	Increased from 12.6 to 23.7 @ 750 - 750 ppm wt. conc	49.6@ 750 - 750 ppm wt. conc	No data	No data
Experiment # 4					
Commercial MoCoP/Al ₂ O ₃	99.5% @ 327.4 K	Increase from 12.5 to 21.1 @ 60 g (5 wt.%)	42.4 @ 60 g (5 wt.%)	Saturates (18.0 - 51.2) Aromatics (22.0 - 38.5)	Polar (34.0 - 13.6) (Resins + Asphaltenes)
Mo(II)alkylhexanoat e-Fe(acac) ₂	97.8% @ 327.4 K	Increased from 12.5 to 24.3 @ 500 - 1000 wt. ppm	46.0 @ 500 - 1000 wt. ppm	Saturates (18.0 - 46.6) Aromatics (22.0 - 38.5)	Polar (34.0 - 14.3) (Resins + Asphaltenes)

The higher hydrocracking activity observed for the experimental catalyst was due to an increase in its total acidity, a greater metal load and impregnation of Ni and W, which reduced the coke formation during the reaction. Another experiment, referred to here as experiment # 4 in **Table 6**, was conducted to compare a supported commercial versus an unsupported catalyst at the same operating conditions.

Researchers have used transition metal ion salt, transition metal compounds, and organometallic compounds in catalytic aquathermolysis for upgrading of heavy oil. Originally, it was believed that cleavage of the C-S bond was the main reason for viscosity reduction of heavy oil, but later research proved that cleavage of the C-O bond in phenolic and ethereal molecules in heavy oils resulted in viscosity reduction.

Wen *et al.* [27] have reported a viscosity reduction of 73.2% at 240°C of heavy oil from Shengli reservoirs by using $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ in coordination with reservoir minerals. Chen Q. *et al.* [28] experimentally evaluated a water-soluble heteropoly acid $\text{K}_3\text{PMo}_{12}\text{O}_{40}$ in an aquathermolysis reaction at 200°C - 280°C temperature. They used a mixture of 100 g of extra-heavy oil, 43 g of water, and 0.3 g of the catalysts in a high-pressure reactor. The viscosity reduction of the heavy oil was 92.3% at 280°C and 80% at 200°C as given in **Table 7** below. The results indicated that this Keggin heteropoly acid salt has the capability of acidity, redox, and pseudo-liquid phase reaction.

Table 7. Experimental results of upgrading heavy oil [28].

Liquid Catalyst	Viscosity Reduction (%)	Heavy Oil Composition-SARA Changes Before-After (wt.%)	Heavy Oil Composition-SARA Changes Before-After (wt.%)
Heteropoly acid $\text{K}_3\text{PMo}_{12}\text{O}_{40}$	92.3% at 280°C 80% at 200°C	Saturates (14.65 - 19.02)	Resins (27.01 - 25.22)
		Aromatics (5.48 - 12.8)	Asphaltenes (52.86 - 42.96)

Suwaid M. A., *et al.*, [29] tested two water-soluble transition metal salts: nickel acetate and iron oxalate in an autoclave under reservoir conditions for 24 hours at 300°C for catalytic upgrading of Boca de Jaruco high-sulfur extra-heavy oil and compared the performance of the catalysts with upgrading with only water/steam. Significant reduction in oil viscosity was observed, with 80% reduction achieved by nickel acetate and 69% reduction by iron oxalate. SARA analysis also indicated a significant reduction in asphaltenes and resins. Nickel sulphide/nickel oxide was formed by the presence of sulphur in heavy oil and by reaction with water, indicating better desulfurization due to the more reactive nickel acetate catalyst.

Bondarenko, A. A., *et al.*, [30] conducted a series of laboratory experiments under high-pressure and high-temperature conditions in an autoclave using ammonium molybdate, a water-soluble liquid catalyst precursor for upgrading super-viscous heavy oil. The authors compared the upgrading of heavy oil with a non-catalytic cyclic steam stimulation (CSS) versus a catalytic aquathermolysis process. Oil viscosity reduction of 46.6% during catalytic aquathermolysis was observed, which was 24% more than the case of the non-catalytic aquathermolysis process. Furthermore, SARA analysis results showed 15.9% reduction in asphaltenes was observed in catalytic aquathermolysis as compared to 20.4% increase with the non-catalytic process, while the resin contents remain virtually unchanged.

In another study with a water-soluble catalytic precursor, ammonium tetrathiomolybdate, Wang J., *et al.*, [31] conducted experimental tests in an autoclave and successful field tests in the Shengli oil field (China). In one of the selected wells, 1 ton of catalytic precursor was injected, then 2500 tons of steam was injected at a rate of 10 ton/hour. The soaking period was 7 days, and trial production from the well was conducted for 4 months. The viscosity reduction was 85% for the first month and remained at 70% for the next three months. The SARA composition analysis showed that asphaltenes and aromatic contents decreased while resin contents increased as compared to the original oil. The long-term field experiment showed that the catalytic precursor could be *in-situ* converted in an active catalyst.

Aliev F., *et al.*, [14] conducted an experimental study using water-soluble amphiphilic pre-catalysts of metal acetate in an autoclave at high temperature and pressure. Of the various metal acetates tested, nickel and copper acetate demonstrated superior viscosity reduction effects, with nickel acetate showing 58% reduction from the initial oil viscosity. SARA analysis indicated that with nickel acetate, the high molecular weight components decreased from 38.3 to 23.5 wt.%, and the lighter saturates, and aromatic components increased from 61.7 to 76.5 wt.%. The authors concluded that the experiments showed the excellent potential of water-soluble metal acetates for *in-situ* heavy oil upgrading.

8. Catalyst Transport in Porous Media

Understanding water-soluble catalyst transport, adsorption in porous media, hydrothermal stability, regeneration/reuse and compatibility with reservoir brine and rock is important for successful field applications.

Water-soluble liquid catalysts are easier to inject into the reservoir during waterflooding or steam-injection recovery processes than oil-soluble catalysts. However, obtaining good oil contact and wider distribution inside the reservoir rock is a complex phenomenon governed by the interplay of convection, diffusion, dispersion, and adsorption processes. Understanding these coupled phenomena is critical for predicting catalyst distribution, optimizing catalyst delivery, and designing efficient catalytic enhanced oil recovery schemes.

The general transport equation for a dissolved species in porous media com-

bines convective transport due to fluid flow, dispersive/diffusive transport due to concentration gradients, and reactive terms, including adsorption and chemical reactions. The classical advection-dispersion-reaction (ADR) framework provides the foundation for modeling solute transport in porous media. The coupling between transport and adsorption is particularly important because adsorption not only removes the catalyst from the mobile phase but also creates concentration gradients.

The Advection-Dispersion-Reaction (ADR) equation, which gives the contribution of these different mechanisms on the overall change in reactant concentration with time at a fixed location, can be described as follows by Chen Q. *et al.* [28]:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} - \sum_i \left(\frac{\partial C}{\partial t} \right)_i + D_L \frac{\partial^2 C}{\partial x^2} \quad (2)$$

where:

C is the reactant concentration in water mol/Kg

t is the time (s)

v is the velocity of water transport or flow through the porous media m/s

x is the distance in meters

i represents the chemical reaction.

D_L is the longitudinal dispersion coefficient in the direction of flow.

The characteristics of porous media structure, such as pore size distribution, connectivity, tortuosity, and surface area, significantly influence both transport and adsorption processes. Porosity, the fraction of void space in the porous medium, directly influences both flow velocity and the available surface area. Pores connectivity and tortuosity determine the efficiency of transport through a porous medium. The multiscale nature of porous media, with pore sizes ranging from nanometers to millimetres, creates hierarchical transport and adsorption behavior. Small pores contribute disproportionately to surface area and adsorption capacity, while large pores dominate flow and advective transport.

The relative importance of convection versus diffusion depends on the Peclet number (Pe), which characterizes the ratio of advective to diffusive transport rates. At low Pe (<1), diffusion dominates, and concentration profiles are relatively uniform. At high Pe (>10), advection dominates and sharp concentration profiles develop. The transition between these regimes significantly affects the distribution and the efficiency of catalyst delivery to adsorption sites.

The Damkohler number (Da) is a key parameter describing the dynamic adsorption behaviour. The Da compares reaction (adsorption) rates to transport rates. At a low Da (fast transport relative to adsorption), the system approaches local equilibrium, while at high values (slow transport relative to adsorption), concentration gradients develop near adsorption sites.

The physicochemical properties of the catalysts, such as molecular size, charge, polarity, and functional groups, determine interactions with pore surfaces and transport characteristics. Restricted diffusion becomes significant when the mo-

lecular diameter approaches 10% - 20% of the pore diameter. For water-soluble catalysts, which may have hydrodynamic diameters of 1 - 10 nm, restriction effects are important in mesopores and micropores. Surface chemistry of the porous medium determines the nature and strength of catalyst-surface interactions. Hydrophilic surfaces with hydroxyl groups or charged sites interact strongly with polar water-soluble catalysts, leading to high adsorption capacity.

9. Field Screening Criteria and Practical Limitations

Water-soluble liquid catalysts - including transition-metal salts (e.g., nickel, copper, zinc acetate), ionic liquids, and amphiphilic metal complexes - have attracted attention because they can be co-injected with steam/aqueous phase and potentially avoid the coking and pore-plugging issues associated with oil-soluble or solid catalysts. Laboratory studies have indicated viscosity reduction ranging from 50% to 94%. However, translating these laboratory successes to field deployment requires rigorous screening for hydrothermal stability, adsorption loss, regeneration feasibility, and compatibility with brine and rock mineralogy.

Successful field deployment of water-soluble liquid catalysts requires integration of multiple screening criteria: thermal performance, hydrothermal stability, adsorption loss, regeneration feasibility, and brine/rock compatibility. No single metric is sufficient; catalysts must meet minimum thresholds across all criteria. For example, ionic liquids demonstrate excellent low-temperature activity (89% - 94% viscosity reduction at 175°C) and low catalyst loading (0.09 wt.%). Still, their high cost and lack of demonstrated regeneration methods raise economic concerns [14] [22]. Transition-metal acetates are less expensive and widely studied. Still, they undergo extensive transformation to solid phases and suffer from adsorption losses on clays. Amphiphilic catalysts address distribution challenges but require careful formulation to balance activity, stability, and cost [14].

An integrated screening workflow for successful field deployment should include the following screening criteria:

Catalyst distribution and sweep efficiency: In laboratory tests, catalysts are intimately mixed with oil and water in stirred reactors. In the field, catalysts must propagate through heterogeneous porous media, competing with gravity segregation, viscous fingering, and preferential flow through high-permeability zones. Core-flood or sand-pack experiments should be designed to evaluate catalyst propagation, oil displacement and upgrading under practical flow conditions.

Residence time and contact time: Laboratory tests typically employ 1 - 24 hour reaction times with continuous mixing. In the field, contact time between catalyst and oil depends on injection rate, soak period, and production strategy. Insufficient contact time may limit upgrading, while excessive soak periods increase cycle time and reduce economic returns [21]. Extended-duration tests (24 - 72 hours) may be planned to characterize catalyst transformation, phase changes, and time-dependent activity.

Temperature distribution: Steam injection creates complex temperature pro-

files in the reservoir, with peak temperatures near the injection well and lower temperatures at the steam front. Catalyst activity and transformation will vary spatially, complicating performance prediction [14].

Catalyst loss and consumption: Adsorption, precipitation, and transformation to immobile solid phases will reduce catalyst concentration as it propagates through the reservoir. Continuous or periodic catalyst injection may be required to maintain effective concentrations, increasing operating costs [32].

Formation damage and pore plugging: Transformation of water-soluble catalysts to solid nanoparticles or precipitated sulfides/oxides raises the risk of pore plugging and permeability reduction, particularly in low-permeability zones or near wellbores. Nanoparticle bridging and formation damage must be carefully monitored in pilot trials.

Salinity Tolerance and Water Content Effects: Reservoir brines vary widely in salinity. Reservoir brines vary widely in salinity (from a few thousand to >200,000 mg/L total dissolved solids) and ionic composition (dominated by Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-}). Catalyst compatibility with high-salinity brines is essential for field deployment, yet systematic data are limited. Water content is a key operational parameter for aqueous catalyst systems. Ionic liquids and many aqueous catalysts were tested with specified water cuts (e.g., 30% water) and showed strong viscosity reduction, indicating that the water fraction must be optimized for each catalyst-reservoir system [16]. Insufficient water content may limit catalyst dissolution and distribution, while excessive water reduces thermal efficiency and oil production rates. The presence of divalent ions (Ca^{2+} , Mg^{2+}) in brine can cause precipitation of surface-active compounds and may affect catalyst speciation and activity.

Hydrothermal stability: In the *in-situ* aquathermolysis, moderate to high temperatures of 200°C - 400°C are encountered due to hot water or steam injection. Catalytic thermal stability in terms of structural collapse and maintaining catalytic activity becomes important. Transition metal oxides such as WO_3/ZrO_2 used by Wang *et al.*, and Fe-Mo-W catalysts prepared by Qin *et al.*, have demonstrated good hydrothermal stability [18]. Studies have indicated that tungsten (W) and Mo-based catalysts could prove to be good candidates for the aquathermolysis due to their hydrothermal stability properties and resistance to degradation.

10. Conclusions and Recommendations

Water-soluble liquid catalysts have great potential for application in the *in-situ* upgradation and recovery of heavy oil when used in the catalytic aquathermolysis process. Transition metals (such as Fe, Cu, Ni, Cr, Mo, Co, and W) salts, ionic liquids, and heteropoly acids are the main catalysts that can be effectively used due to their high thermal stability and desulfurization potential. Metal-based LCs also have less adsorption on the rock surface, hence less loss of LCs. The catalytic aquathermolysis process has technical and economic advantages over other processes in terms of being environmentally more beneficial than oil-soluble catalysts, in which difficult-to-remove hazardous/toxic organic solvents are often

used.

It can be concluded from the literature review that all types of water-soluble catalysts reviewed in this paper were effective in crude oil viscosity reduction, density improvement and sulfur reduction from medium to high degrees. Viscosity reduction up to 90% was achieved by using a nickel sulphate metal ion liquid catalyst. These conclusions are substantiated by the SARA analysis, which shows a reduction in Asphaltenes and Resins and a gain in Saturates and Aromatic fractions in the treated crude oil composition. Furthermore, increasing acidity can accelerate the catalytic reaction rate; therefore, heteropoly acids can be effectively used in aquathermolysis. However, the catalyst's efficiency can be adversely affected by reservoir water chemistry and the adsorption on the rock surface during catalytic transport in porous media.

The process of using water-soluble catalysts for *in-situ* catalytic upgrading of heavy oil should prove to be economically cheaper in terms of lower maintenance requirements of field facilities and convenient availability of these chemicals. Water-soluble catalysts are easier to inject into the reservoir by utilizing the existing water-injection systems in oil fields. Various experiments conducted under reservoir pressure and temperature have indicated a significant reduction in asphaltenes and resins compared to the conventional heavy oil recovery processes.

However, further research is needed to develop better water-soluble catalysts to meet the requirements of greater catalytic efficiency, hydrothermal stability, wider catalyst distribution in reservoirs, lower-cost regeneration and higher reuse capability for oil field applications.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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