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PERSPECTIVE

Role of Model Compounds in Advancing Aquathermolysis-Based Technologies for Heavy Oil Upgrading

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Abstract

Using model compounds to study the aquathermolysis reaction mechanism has been a cornerstone in understanding the complex chemistry underlying in-reservoir upgrading of unconventional oil resources, including oil shale, bitumen, and heavy and extra-heavy crude oils. These compounds, often selected to represent key structural features such as alkyl or polyaromatic hydrocarbons and heteroatom-containing molecules, act as simplified analogs of the chemically complex constituents present in real oil systems. Their use in controlled experimental setups enables the isolation and analysis of specific reaction pathways, providing mechanistic insights that are difficult to extract from real oil resources due to their compositional heterogeneity. This strategy has played a crucial role in advancing heavy oil upgrading technologies, particularly by enhancing the understanding of water-oil interactions, reaction mechanisms, and the impact of various catalyst systems under aquathermolysis conditions. However, several challenges remain in achieving a complete comprehension of the reaction mechanism that could lead to a considerable increase in the efficiency of steam injection technologies and the upgrading of unconventional oil reserves through the development of novel strategies and technologies, such as specialized catalysts for the hydrogenation and heteroatom removal of these complex oil systems.

Keywords: aquathermolysis, model compounds, heavy oil upgrading.

1 Introduction

The production and upgrading of unconventional oil resources, including heavy crude oil, bitumen, and shale oil, present significant technical challenges. Steam-injection processes are the most effective method used for in-situ upgrading of these reservoirs through aquathermolysis reactions. A key step involves breaking down complex macromolecules into smaller, lower-molecular-weight compounds. This process generates highly reactive free radical fragments, which, if not effectively saturated, lead to polyaddition, forming high-condensed structures

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that substantially increase the system viscosity. Under adequate conditions (temperature and pressure), water has been shown to play multiple roles, including heat transfer medium, hydrogen-donor, and catalytic species, facilitating viscosity reduction, heteroatom removal, and conversion to lighter fractions with higher hydrogen-to-carbon (H/C) ratios. Nonetheless, the molecular structure of these complex oil systems is highly diverse, consisting of intricate macromolecular networks and a wide range of functional groups [1–3].

To better understand the chemical behavior of these complex systems, simplified model compounds are analyzed. Although they do not capture all interactions within real oil systems, they allow for targeted investigation of specific functional group transformations and structural motifs, providing invaluable information for elucidating the fundamental reaction mechanisms governing heavy oil upgrading [4, 5]. This perspective analyzes the insights gained using these model molecules, as well as the challenges in elucidating the mechanism of aquathermolysis to develop new technologies capable of improving the performance of steam injection processes.

2 The Role of Model Compounds in Understanding the Reaction Mechanism

Studies involving various model compounds, such as thiophene, cyclohexyl phenyl sulfide, tetrahydrothiophene, and dibenzyl sulfide, have shown that superheated water promotes hydrolysis reactions that lead to desirable products by secondary reactions. Due to their well-defined structures and predictable reaction pathways, these model compounds are ideal for isolating key mechanisms in aquathermolysis, such as the cleavage of C-S, C-N, and C-O bonds. Experiments using organosulfur model compounds representative of heavy oils have demonstrated that their hydrolysis yields products including H_2S, CO_2, and hydrocarbon gases. The formation of CO_2, in particular, indicates that water participates directly in chemical reactions with the organosulfur species. The reactivity of these compounds is influenced by their molecular structure as well as operating parameters, including temperature, water-to-oil ratio, pH, and the presence of catalysts [6–11].

Mechanistic studies provide valuable insight into the transformation pathways of heavy oil constituents, suggesting that desulfurization is initiated by the cleavage of organosulfur species, leading to the release of H_2S, making it a central process under hydrothermal conditions. The water-gas shift reaction $CO + H_2O \longrightarrow CO_2 + H_2$ also plays a significant role in aquathermolysis, generating hydrogen that can participate in upgrading reactions, including hydrocracking and hydrodesulfurization. Investigations using deuterium-tracer techniques have provided both qualitative and quantitative evidence of hydrogen incorporation from water in preferential molecular sites of various compounds, including alkanes, aromatics, and light gases such as methane [12]. For instance, benzyl groups and α-carbons adjacent to aromatic or heteroaromatic rings exhibit high reactivity. These studies offer crucial insights into the underlying reaction mechanisms, which can support the development of targeted catalysts for breaking down complex molecules, removing heteroatoms, and facilitating hydrogenation during heavy oil upgrading. The catalytic role of metal ions in enhancing the conversion of organosulfur compounds has been attributed to their strong interaction with heteroatoms. Density Functional Theory calculation confirmed that the cleavage pathway of C-S bonds in cyclohexyl phenyl sulfide is most favorable by heterolytic (ionic) mechanism due to a substantially lower kinetic barrier compared to homolytic (free-radical) cleavage or hydrolysis [13]. In addition, theoretical studies have shown that transition metal cations (Fe^{2+}, Cu^{2+}, Ni^{2+}, and Co^{2+}) can significantly lower the activation energy for C-S bond cleavage, thereby accelerating the upgrading process. The presence of reservoir minerals further promotes CO conversion to CO_2 and hydrogen, enhancing the hydrogen supply for in situ upgrading [14, 15].

Kinetic studies enable the establishment of quantitative reaction rates, identification of key reaction pathways, and prediction of product distributions under different conditions [16, 17]. The kinetics of H_2S formation during the tetrahydrothiophene aquathermolysis reaction established a reaction order (0.9), activation energy (54.55 kJ/mol), and frequency factor (166.47 day-1) [18]. This information is practically useful as initial estimates for reaction parameters when combined with scaling, calibration, and systems modeling, acting as a bridge between chemistry and engineering in the quantitative predictions of H_2S production of heavy oil upgrading under reservoir conditions.

3 Opportunities and Challenges

Although studies with model compounds have significantly advanced the understanding of aquathermolysis reactions relevant to heavy oil upgrading, significant challenges remain when extending these findings to real reservoir systems. A primary limitation lies in the lack of chemical representativeness. Since their are simplified nature, model compounds do not encompass the full molecular diversity, colloidal properties, or synergistic effects present in real oil systems, such as asphaltene aggregation and the complex behavior of multi-component mixtures. Consequently, reaction pathways observed in model systems may not accurately reflect those occurring in heavy crude under reservoir conditions, where pressure, temperature, mineral surfaces, and fluid-rock interactions introduce additional variables.

Another complicating factor is the divergence in time and temperature scales. Laboratory experiments are typically performed over short durations (hours or days) at elevated temperatures (200-320°C) and high pressures, whereas steam injection processes occur over larger periods. This disparity hinders the direct extrapolation of laboratory results to predict long-term in-situ upgrading behavior. Additionally, while often considered negligible, the potential catalytic effects of reactor materials such as quartz or Hastelloy may influence outcomes in specific setups. Translating laboratory-optimized parameters to field-scale operations introduces further complexity. In porous reservoir media, factors such as mass transport limitations, catalyst deactivation, and phase behavior under pressure can significantly alter reaction dynamics. Moreover, while model compounds are invaluable for isolating reaction mechanisms, they may not capture critical engineering considerations such as emulsion stability, solubility influences, or coke formation during aquathermolysis.

Catalysts based on transition metals and metal salts have shown considerable promise in enhancing desulfurization and hydrogenation upgrading. However, a complete understanding of their behavior under reservoir conditions remains elusive. In particular, the interaction between injected catalysts and native mineral phases is highly variable, depending on the specific geological formation. Furthermore, while sulfur removal reactions are often observed, demetallation and denitrogenation reactions remain poorly characterized.

In-depth molecular-level characterization of reaction products during aquathermolysis is still limited, thus further studies focusing on broad compositional changes in isolated SARA fractions are required. Similarly, despite water's active role in the aquathermolysis reaction, the precise quantification of water consumption has not been established, making it difficult to fully assess the influence of operating variables and catalyst formulations on system performance.

Finally, while kinetic studies using model systems have yielded quantitative parameters, such as activation energies and reaction orders, that are valuable for process modeling and scale-up, research in this area remains scarce. There is a pressing need for more kinetic investigations at the molecular level, which would improve our understanding of competing pathways, reaction rate magnitudes, and the thermodynamic and catalytic constraints that govern heavy oil upgrading under steam injection conditions.

4 Conclusion

Aquathermolysis-based technologies primarily aim to reduce the viscosity of heavy crude oils by favoring hydrogenation mechanisms. However, in the absence of catalysts or hydrogen-donor solvents, polyaddition and condensation reactions can lead to the formation of heavier, more complex molecular structures, ultimately raising the oil system viscosity.

Overall, this perspective suggests that advancing the understanding of the aquathermolysis mechanism requires hybrid approaches that integrate model compound studies with investigations on real crude oil systems supported by sophisticated modeling simulations.

The combination of experimental studies, kinetics modeling, and quantum chemical simulations provides a comprehensive and synergistic understanding of aquathermolysis, which is critical for the development of more efficient technologies for in-situ heavy oil upgrading under aquathermolysis conditions. Studies with model compounds can lead to the design and selection of novel catalysts that focus on breaking and hydrogenating the most complicated structures in oil molecules, such as aromatic cores and heteroatomic groups. Then, the experimentation with more representative model mixtures, such as oil fractions (resins, aromatics, and asphaltenes), alongside advanced characterization techniques, offers a promising route to narrow the gap between simplified model compounds and complex real systems.

Data Availability Statement

Not applicable.

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Conflicts of Interest

The author declares no conflicts of interest.

Ethical Approval and Consent to Participate

Not applicable.

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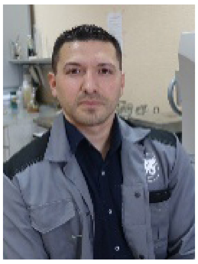

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