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PERSPECTIVE

Integrating Supercritical Water and Catalysts: A Synergistic Approach for Heavy Oil Upgrading

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Abstract

The depletion of conventional hydrocarbons has forced researchers to focus on unconventional petroleum, i.e., heavy crude oils. However, the typical methods to recover the former are not suitable for the latter. Therefore, new technologies, such as supercritical water (SCW) upgrading, commercial and novel catalytic compounds have been proposed individually and in combination to solve the difficulties in recovering these reserves. In this work, the advantages and disadvantages, mechanisms, reactions, and challenges when using SCW and catalysts for heavy oil upgrading are discussed, giving a perspective for new synergetic approaches.

Keywords: supercritical water, catalyst, heavy oil.

1 Introduction

Around 70% of the crude oil worldwide reserves correspond to unconventional hydrocarbons, for instance, extra-heavy and heavy crude oil (40%). This blend of heavy fractions is considered a promising source for future high-value fuels. However, its recovery and upgrading are challenging due to high-molecular-weight compounds, such as asphaltenes, and impurities (heteroatoms and metals) that increase viscosity and reduce the catalyst capability. These factors limit the applicability of many recovery and upgrading technologies [7, 9].

For heavy crude oil recovery, thermal methods are effective in decreasing viscosity and yielding a higher amount of oil. Among all the heat carriers, water increases the mobility of unconventional hydrocarbons and facilitates chemical reactions of large molecules. At the supercritical state (>374 °C), water enhances the cleavage of chemical bonds because of a change in the reaction mechanism, primarily through free radical production, during the upgrading of heavy crude oils. Although the hydrogen released by supercritical water (SCW) neutralizes the generated free radicals, the high temperature promotes coke formation, hindering the selectivity toward light fractions [4, 11].

Catalysts play a crucial role in various reactions, particularly in the hydrothermal process, promoting heat transfer and favoring the effect of water. Their effectiveness depends on several factors, such as stability, surface area, shape selectivity, and acidity. In supercritical water reactions, catalysts based on metal species facilitate the hydrolysis of bonds

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containing oxygen, sulfur, and nitrogen in heavy oil, producing gases and lighter hydrocarbons with lower viscosities [13]. Therefore, integrating SCW and suitable catalysts could overcome existing challenges in heavy oil upgrading through the synergistic enhancement of their qualities.

2 The role of supercritical water in heavy oil upgrading

The characteristics of water in its supercritical state (T > 374°C, P > 22.1 MPa) enhance its interaction with hydrocarbons found in heavy oil. The reactivity of water rises with increasing temperature (T), pressure (P), and density (ρ). Water reactivity becomes significant only when the density surpasses 150 $\mathrm{kg/m^3}$. A higher water-to-oil ratio promotes oil recovery and minimizes coke formation, but it does not impact the levels of heteroatoms or the viscosity of the oil. Consequently, raising this ratio does not enhance water reactivity; instead, it reduces the concentration of heavy oil in the water, limiting the redistribution of hydrogen among the various compounds present in heavy oil [2].

The breakage of carbon-heteroatom bonds is a key reaction in reducing viscosity during hydrothermal upgrading. Besides these reactions, water can donate hydrogen (through hydrocarbon reforming or water-gas shift reaction, WGSR) to aliphatic hydrocarbons in both subcritical and supercritical conditions, but only to aromatic hydrocarbons under subcritical conditions due to their solubility. However, hydrogen supply from water is insufficient for effective heavy-oil upgrading, as the demand for hydrogen in upgrading reactions exceeds what water can provide. The free-radical (H• and HO•) reaction is considered the dominant mechanism for thermal cracking at SCW conditions. These compounds are significantly unstable and react with adjacent molecules (well-dispersed aliphatic hydrocarbons). Consequently, the phase interface can significantly affect the upgrading reactions, influencing their rate, selectivity, and equilibrium [6].

3 Catalysts in SCW environments: Enhancing selectivity and efficiency

The outcomes of several studies concluded that metal oxide catalysts promote the capping of free radicals and unsaturated hydrocarbons produced by catalytic cracking. The investigations confirmed that the active hydrogen was formed primarily from the dissociation of water rather than from hydrocarbon reforming. Moreover, it was established that the metal phase influences hydrogen production since the oxide form induces a redox cycle with SCW. According to the metal type in the oxide compound, the catalytic performance increases in the following order: Cu < Zn < Co < Fe < Cr < Ni [8, 10].

The mineral catalysts exhibit various mechanisms depending on their composition, composition, with carbonates and clays presenting higher reactivity. For carbonates, the higher dolomite content facilitates the hydrothermal decomposition of large molecules into lighter compounds. This performance is attributed to Mg and Ca oxides, but it is insufficient for the coke fraction due to the hydrophilicity of dolomite surface. Regarding the clay minerals, calcium montmorillonite promotes oil production through ring-opening and cleavage reactions owing to its larger concentration of Bronsted-acid sites. Meanwhile, the higher acid site distribution and specific area of zeolites hinder aromatization reactions. However, these minerals contain a larger composition of active sites within the porous structure, limiting the conversion of big condensed aromatic cores, such as asphaltenes. Quartz and feldspar exhibit the lowest catalytic efficiency; only the latter marginally reacts with water through charge disproportion, enhancing the C-C breakage in the organic matter [14].

Different studies confirm that using multi-metallic catalysts exhibits higher catalytic effectiveness than using a single active metal. This performance is related to the combined influence of two or more active metals, which enhances interactions with water, produces a higher distribution of reactive hydrogen, and promotes hydrodesulfurization, hydrolysis, hydrogenation, and cracking reactions [3, 12].

Based on the results, the active sites of suitable catalysts interact mainly with C–S, C–O, and C–C bonds in heavy fractions and H–O in water. Then the radicals resulting from the catalytic cracking of large hydrocarbons become bonded with hydrogen produced from the dissociation of water on catalyst particles. This performance (see Figure 1) promotes selective cracking and free radical capping (with active hydrogen) to avoid excessive gas and coke formation.

The stability of the catalyst plays a significant role in maintaining its activity during the upgrading process. By comparing metal oxide and sulfide compounds, the latter has demonstrated an enhanced resistance to water compared to the former, while maintaining its structural parameters unchanged. Although the

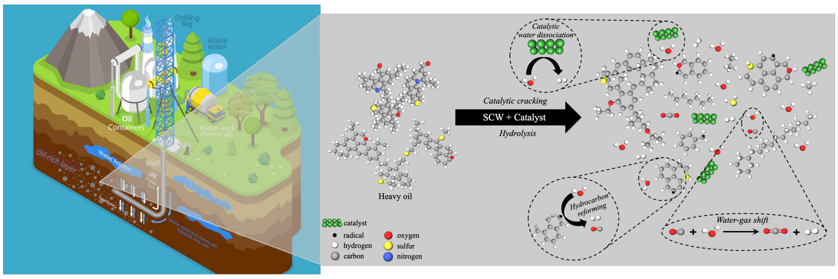

Figure 1. General enhanced mechanism for heavy oil upgrading by combining SCW and a suitable catalyst.

capability of SCW to hinder coke formation and prolong the catalyst life, this medium is very aggressive for some materials, particularly supported materials, which can sinter and dilute active metals or degrade the supports, such as alumina and silica [1].

Novel catalysts have shown outstanding performance during heavy oil upgrading, i.e., ionic liquids. These green organic salts are highly active due to the proton production capability from the imidazole ring. However, these hydrogen protons can be inhibited by the presence of SCW, which forms strong hydrogen bonds [5]. These results confirm that although the catalytic activity of a specific compound enhances the heavy oil upgrading under diverse conditions, its combination with SCW can produce negative consequences that are more severe than expected.

4 Challenges and Future Directions

Several remaining barriers must be addressed before achieving a suitable technology that combines SCW and an efficient catalyst to recover unconventional hydrocarbons. The chemically active SCW can affect equipment (corrosion or salt deposition) and catalytic agents (sintering, deactivation, and degradation), hindering the heavy oil upgrading process. Therefore, it is beneficial to find a suitable catalytic compound that suitably interacts with water and can be regenerated to increase its catalytic life. Moreover, the catalyst-water interplay within the reservoir must be efficiently dispersed in oil-rich zones and enhance heavy oil recovery.

Currently, using water for in-situ enhanced oil recovery demands a high cost. Additionally, the heating system is inefficient due to heat dispersion within the reservoir, which reduces its capability to preserve high temperatures during prolonged periods. Therefore, future work can address these challenges by using complementary methods that have exhibited suitable results for other technologies. Alternative heating equipment (microwave, ultrasonic, and electromagnetic) can be combined with the conventional approaches to supply the required energy for SCW upgrading conditions.

The addition of a blend of gases is a suitable alternative to diminish water feed and manage the disadvantages of this compound. Syngas ($CO+H_2$) is an outstanding option to address this issue due to the presence of CO and water, which can enhance the selectivity of WGSR to produce a higher number of active hydrogen. Another option for increasing the amount of in-situ-produced hydrogen during the hydrothermal upgrading are hydrogen donors. These organic compounds not only suppress coke formation by releasing hydrogen to neutralize free radicals but also elevate the quality of upgraded oils.

5 Conclusion

Heavy oil recovery and upgrading are complicated due to the high-viscosity compounds and impurities that limit the effectiveness of many technologies. SCW improves reactivity, facilitates the breakdown of heavy oil compounds, and provides active hydrogen to suppress coke formation. In addition, combining suitable catalysts with SCW enhance individual capabilities of both compounds. Metal oxide catalysts enhance the capping of free radicals and contribute to hydrogen production primarily through water dissociation. Their efficiency varies by metal type, with performance increasing in the order: Cu $<$ Zn $<$ Co $<$ Fe $<$ Cr $<$ Ni. Furthermore, mineral catalysts have different reactivities, with specific compositions influencing the effectiveness of reactions in heavy oil upgrading. With higher cracking efficiencies for carbonates and clays, while lower activity for quartz and feldspar. Using multi-metallic compounds increases the efficiency of heavy fraction conversion.

All these outcomes confirm the suitable synergy of SCW and most catalysts since few of them can achieve negative performance, i.e., ionic liquids. Therefore, the catalytic compounds (Ni-oxides, Mo-sulfides, dolomite, calcium montmorillonite, among others) showing a positive performance (lower coke formation and viscosity, and higher hydrogen production) in SCW environments need to be selected. However, scaling up for new technologies based on this combination requires managing challenges, such as the insufficient active hydrogen to suppress free radicals and the inefficient heating methods to maintain high temperatures. For this, the addition of syngas and hydrogen donors to the upgrading process represents an appropriate alternative to optimize these technologies.

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.

References

[1] Ates, A., Azimi, G., Choi, K. H., Green, W. H., & Timko, M. T. (2014). The role of catalyst in supercritical water desulfurization. *Applied Catalysis B: Environmental, 147*, 144–155. [CrossRef]

[2] Chen, Z. (2024). New insight into subcritical and supercritical water reactivity during non-catalytic hydrothermal upgrading of heavy oil. *Fuel, 366*, 131380. [CrossRef]

[3] Djimasbe, R., Ilyasov, I. R., Kwofie, M., Khelkhal, M. A., Emelianov, D. A., Al-Muntaser, A. A., Suwaid, M. A., & Varfolomeev, M. A. (2022). Direct Hydrogen Production from Extra-Heavy Crude Oil under Supercritical Water Conditions Using a Catalytic (Ni-Co/Al2O3) Upgrading Process. *Catalysts, 12*(10), 1183. [CrossRef]

[4] Dong, X., Liu, H., Chen, Z., Wu, K., Lu, N., & Zhang, Q. (2019). Enhanced oil recovery techniques for heavy oil and oilsands reservoirs after steam injection. *Applied Energy, 239*, 1190–1211. [CrossRef]

[5] Fan, Z. X., Wang, T. F., & He, Y. H. (2009). Upgrading and viscosity reducing of heavy oils by [BMIM][AlCl4] ionic liquid. *Journal of Fuel Chemistry and Technology, 37*(6), 690–693. [CrossRef]

[6] Félix, G., Djimasbe, R., Tirado, A., Varfolomeev, M. A., & Ancheyta, J. (2025). Kinetic study for the Ashalcha heavy crude oil upgrading at supercritical water conditions. *Fuel, 380*, 133145. [CrossRef]

[7] Gomaa, S., Salem, K. G., & El-hoshoudy, A. N. (2024). Enhanced heavy and extra heavy oil recovery: Current status and new trends. *Petroleum, 10*(3), 399-410. [CrossRef]

[8] Hosseinpour, M., Fatemi, S., & Ahmadi, S. J. (2016). Deuterium tracing study of unsaturated aliphatics hydrogenation by supercritical water in upgrading heavy oil. Part II: Hydrogen donating capacity of water in the presence of iron(III) oxide nanocatalyst. *The Journal of Supercritical Fluids, 110*, 75–82. [CrossRef]

[9] Kornienko, V., & Avtonomov, P. (2015). Application of Neutron Activation Analysis for Heavy Oil Production Control. *Procedia - Social and Behavioral Sciences, 195*, 2451–2456. [CrossRef]

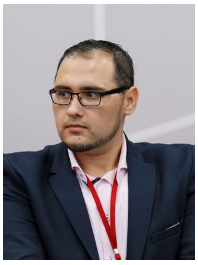
[10] Kosari, M., Golmohammadi, M., Ahmadi, S. J., Towfighi, J., & Chenari, A. H. (2017). On the catalysis capability of transition metal oxide nanoparticles in upgrading of heavy petroleum residue by supercritical water. *The Journal of Supercritical Fluids, 126*, 14–24. [CrossRef]

[11] Li, N., Yan, B., & Xiao, X. M. (2015). A review of laboratory-scale research on upgrading heavy oil in supercritical water. *Energies, 8*(8), 8962–8989. [CrossRef]

[12] Liu, R., Zhang, L., Han, X., Wang, Y., Li, J., Huang, C., ... & Lin, R. (2024). Viscosity reduction of heavy oil based on rice husk char-based nanocatalysts of NiO/Fe2O3. Journal of Analytical and Applied Pyrolysis, 183, 106788. [CrossRef]

[13] Muraza, O., & Galadima, A. (2015). Aquathermolysis of heavy oil: A review and perspective on catalyst development. *Fuel, 157*, 219–231. [CrossRef]

[14] Zheng, L., Zhao, Q., Dong, Y., Wang, X., Jin, H., & Guo, L. (2024). Supercritical water upgrading of heavy oil: Effects of reservoir minerals on pyrolysis product distribution. *Journal of Analytical and Applied Pyrolysis, 181*, 106616. [CrossRef]



Guillermo Felix obtained his PhD degree in advanced technology (2019) from the National Polytechnic Institute (IPN) and was awarded various national recognitions in Mexico. He is the author and co-author of several scientific papers and book chapters, and has participated in different international conferences. Furthermore, he has served as a reviewer for worldwide journals. Dr. Felix has participated in diverse international studies on crude oil compatibility, the upgrade of heavy crude oil, and the development of novel kinetic and thermodynamic models. Currently, his research is focused on the catalytic in-situ upgrading of unconventional hydrocarbons (heavy crude oil, oil shale, and bitumen) by different technologies (steam injection, hydrocracking, pyrolysis). (Email: jose.fl@mochis.tecnm.mx, KFeliks.Lugo@kpfu.ru)